

**IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE**

MIDWEST ENERGY EMISSIONS CORP.
and MES INC.,

Plaintiff,

v.

VISTRA ENERGY CORP., IPH, LLC,
DYNEGY INC., ILLINOIS POWER
RESOURCES GENERATING, LLC,
DYNEGY MIDWEST GENERATION LLC,
DYNEGY MIAMI FORT, LLC, AEP
GENERATION RESOURCES INC.,
SOUTHWESTERN ELECTRIC POWER CO.,
CARDINAL OPERATING COMPANY, LLC,
AEP TEXAS INC., NRG ENERGY, INC.,
NRG TEXAS POWER LLC, MIDWEST
GENERATION EME, LLC, MIDWEST
GENERATION, LLC, TALEN ENERGY
CORPORATION, TALEN ENERGY
HOLDINGS, INC., BRANDON SHORES
LLC, TALEN GENERATION LLC, AND H.
A. WAGNER LLC, ARTHUR J.
GALLAGHER & CO., GALLAGHER CLEAN
ENERGY, LLC, AND AJG COAL, LLC, DTE
REF HOLDINGS, LLC, DTE REF
HOLDINGS II LLC, CERT COAL
HOLDINGS LLC, CERT HOLDINGS LLC,
CERT HOLDINGS 2018, LLC, CERT
OPERATIONS LLC, CERT OPERATIONS II
LLC, CERT OPERATIONS III LLC, CERT
OPERATIONS IV LLC, CERT OPERATIONS
V LLC, CERT OPERATIONS RCB LLC,
CHEM-MOD LLC, AJG IOWA REFINED
COAL LLC, JOPPA REFINED COAL LLC,
THOMAS HILL REFINED COAL LLC,
WAGNER COALTECH LLC, WALTER
SCOTT REFINED COAL LLC, LOUISA
REFINED COAL, LLC, BELLE RIVER
FUELS COMPANY, LLC, ARBOR FUELS
COMPANY, LLC, PORTAGE FUELS
COMPANY, LLC, AND JOHN DOE LLCS

Defendants.

CIVIL ACTION NO. 19-1334-RGA-
CJB

**FIRST AMENDED COMPLAINT FOR
PATENT INFRINGEMENT**

JURY TRIAL DEMANDED

Plaintiff Midwest Energy Emissions Corp. and MES Inc. (collectively, “ME2C”) files this Original Complaint against Defendants Illinois Power Resources Generating, LLC, Dynegy Midwest Generation LLC, Electric Energy, Inc.; Illinois Power Generating Company; Coletto Creek Power, LCC; Oak Grove Management Company LLC; and Luminant Generation Company LLC (collectively, “Vistra”); AEP Generation Resources Inc., Southwestern Electric Power Co., and AEP Texas Inc. (collectively, “AEP”); NRG Energy, Inc., NRG Texas Power LLC, Midwest Generation EME, LLC, Midwest Generation, LLC (collectively, “NRG”); Talen Energy Corporation, Brandon Shores LLC, Talen Generation LLC, and H. A. Wagner LLC (collectively, “Talen”), (Vistra, AEP, NRG, and Talen, are referred to collectively as “Coal Plant Defendants”); Arthur J. Gallagher & Co., Gallagher Clean Energy, LLC, and AJG Coal, LLC (“AJG”); DTE REF Holdings, LLC, DTE REF Holdings II LLC (“DTE”); CERT Coal Holdings LLC, CERT Holdings LLC, CERT Holdings 2018, LLC, CERT Operations LLC, CERT Operations II LLC, CERT Operations III LLC, CERT Operations IV LLC, CERT Operations V LLC, CERT Operations RCB LLC (“CERT”); Chem-Mod LLC (“Chem-Mod”); and the additional named and unnamed entities referred to below as the “RC Defendants”: AJG Iowa Refined Coal LLC, Joppa Refined Coal LLC, Thomas Hill Refined Coal LLC, Wagner Coaltech LLC, Walter Scott Refined Coal LLC, Louisa Refined Coal, LLC, Belle River Fuels Company, LLC, Arbor Fuels Company, LLC, Portage Fuels Company, LLC, and John Doe LLCs (all of these entities are referred to collectively as “Defendants”) for patent infringement under 35 U.S.C. § 271. Plaintiff alleges, based on its own personal knowledge with respect to its own actions and based upon information and belief with respect to all others’ actions, as follows:

THE PARTIES

1. Midwest Energy Emissions Corp. is a Delaware corporation with its principal place of business at 670 D Enterprise Drive, Lewis Center, Ohio 43035.
2. MES Inc. is a North Dakota corporation with its principal place of business at 311 S. 4th St. STE 118, Grand Forks, ND 58201.
3. Defendant Illinois Power Resources Generating, LLC is a Delaware limited

liability company with its principal place of business at 601 Travis St., Suite 1400, Houston, TX 77002. Illinois Power Resources Generating, LLC has designated Capitol Services, Inc., 1675 S. State St., Ste. B, Dover, DE 19901 as its agent for service of process.

4. Defendant Dynegy Midwest Generation LLC is a Delaware limited liability company with its principal place of business at 2828 North Monroe St., Decatur, IL 62526. Dynegy Midwest Generation LLC has designated Capitol Services, Inc., 1675 S. State St., Ste. B, Dover, DE 19901 as its agent for service of process.

5. Defendant Electric Energy, Inc. is a Illinois corporation with its principal place of business at 6555 Sierra Drive, Irving, TX 75039. Electric Energy, Inc. has designated Capitol Corporate Services, Inc., 1315 W. Lawrence Ave., Springfield, IL 62704 as its agent for service of process. Vistra has identified this entity for inclusion in this case as an entity that owns/operates at least one of the Accused Coal Plants.

6. Defendant Illinois Power Generating Company is an Illinois corporation with its principal place of business at 6555 Sierra Drive, Irving, TX 75039. Illinois Power Generating Company has designated Capitol Corporate Services, Inc., 1315 W. Lawrence Ave., Springfield, IL 62704 as its agent for service of process. Vistra has identified this entity for inclusion in this case as an entity that owns/operates at least one of the Accused Coal Plants.

7. Defendant Coletto Creek Power, LLC is a Delaware limited liability company with its principal place of business at 45 FM 2987, Fannin, TX 77960. Coletto Creek Power, LLC has designated Capitol Services, Inc., 1675 S. State St., Ste. B, Dover, DE 19901 as its agent for service of process. Vistra has identified this entity for inclusion in this case as an entity that owns/operates at least one of the Accused Coal Plants.

8. Defendant Oak Grove Management Company LLC is a Delaware limited liability company with its principal place of business at 1601 Bryan St., Dallas, TX 75201. Oak Grove Management Company LLC has designated Capitol Services, Inc., 1675 S. State St., Ste. B, Dover, DE 19901 as its agent for service of process. Vistra has identified this entity for inclusion in this case as an entity that owns/operates at least one of the Accused Coal Plants.

9. Defendant Luminant Generation Company LLC is a Texas limited liability company with its principal place of business at 6555 Sierra Drive, Irving, TX 75039. Luminant Generation Company LLC has designated Capitol Corporate Services, Inc., 206 E. 9th St., Ste. 1300, Austin, TX 78701 as its agent for service of process. Vistra has identified this entity for inclusion in this case as an entity that owns/operates at least one of the Accused Coal Plants.

10. Defendant AEP Generation Resources Inc. is a Delaware corporation with its principal place of business at 1 Riverside Plaza, Columbus, OH 43215. AEP Generation Resources has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

11. Defendant Southwestern Electric Power Company is a Delaware corporation with its principal place of business at 1 Riverside Plaza, Columbus, OH 43215. Southwestern Electric Power Co. has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

12. Defendant AEP Texas Inc. is a Delaware corporation with its principal place of business at 1616 Woodall Rodgers Freeway, Dallas, TX 75202. AEP Texas Inc. has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

13. Defendant NRG Energy, Inc. is a Delaware corporation with its principal place of business at 804 Carnegie Center, Princeton, NJ 08540. NRG Energy, Inc. has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

14. Defendant NRG Texas Power LLC is a Delaware limited liability company with its principal place of business at 1301 McKinney St., Ste. 2300, Houston, TX 77010. NRG Texas Power LLC has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

15. Defendant Midwest Generation EME, LLC is a Delaware limited liability company with its principal place of business at 440 South La Salle St., One Financial Place,

Suite 3500, Chicago, IL 60605. Midwest Generation EME, LLC has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

16. Defendant Midwest Generation, LLC is a Delaware limited liability company with its principal place of business at 440 South La Salle St., One Financial Place, Suite 3500, Chicago, IL 60605. Midwest Generation, LLC has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

17. Defendant Talen Energy Corporation is a Delaware corporation with its principal place of business at 835 Hamilton St., Allentown, PA 18101. Talen Energy Corporation has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

18. Defendant Brandon Shores LLC is a Delaware limited liability company with its principal place of business at 2030 Brandon Shores Rd., Curtis Bay, MD 21226. Brandon Shores LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

19. Defendant Talen Generation LLC is a Delaware limited liability company with its principal place of business at Two North Ninth St., Allentown, PA 18101. Talen Generation LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

20. Defendant H. A. Wagner LLC is a Delaware limited liability company with its principal place of business at 3000 Brandon Shores Rd., Baltimore. MD 21226. H. A. Wagner LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

21. Defendant Arthur J. Gallagher & Co. is a Delaware corporation with its principal place of business at 2850 Gold Road, Rolling Meadows, IL 60008. Arthur J. Gallagher & Co. has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as

its agent for service of process.

22. Defendant Gallagher Clean Energy, LLC is a Delaware limited liability company with its principal place of business at Two Pierce Place, Itasca, IL 60143. Gallagher Clean Energy, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

23. Defendant AJG Coal, LLC is a Delaware limited liability company with its principal place of business at Two Pierce Place, Itasca, IL 60143. AJG Coal, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

24. Defendant DTE REF Holdings, LLC is a Delaware limited liability company with its principal place of business at One Energy Plaza, Detroit, MI 48226. DTE REF Holdings, LLC has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

25. Defendant DTE REF Holdings II LLC is a Delaware limited liability company with its principal place of business at One Energy Plaza, Detroit, MI 48226. DTE REF Holdings II LLC has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

26. Defendant CERT Coal Holdings, LLC is a Delaware limited liability company with its principal place of business at 2100 Southbridge Parkway, Suite 585, Birmingham, AL 35209. CERT Coal Holdings, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

27. Defendant CERT Holdings, LLC is a Delaware limited liability company with its principal place of business at 2100 Southbridge Parkway, Suite 585, Birmingham, AL 35209. CERT Holdings, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

28. Defendant CERT Holdings 2018, LLC is a Delaware limited liability company with its principal place of business at 2100 Southbridge Parkway, Suite 585, Birmingham, AL 35209.

CERT Holdings 2018, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

29. Defendant CERT Operations, LLC is a Delaware limited liability company with its principal place of business at 2100 Southbridge Parkway, Suite 585, Birmingham, AL 35209. CERT Operations LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

30. Defendant CERT Operations II, LLC is a Delaware limited liability company with its principal place of business at 2100 Southbridge Parkway, Suite 585, Birmingham, AL 35209. CERT Operations II, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

31. Defendant CERT Operations III, LLC is a Delaware limited liability company with its principal place of business at 2100 Southbridge Parkway, Suite 585, Birmingham, AL 35209. CERT Operations III, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

32. Defendant CERT Operations IV, LLC is a Delaware limited liability company with its principal place of business at 2100 Southbridge Parkway, Suite 585, Birmingham, AL 35209. CERT Operations IV, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

33. Defendant CERT Operations V, LLC is a Delaware limited liability company with its principal place of business at 2100 Southbridge Parkway, Suite 585, Birmingham, AL 35209. CERT Operations V, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

34. Defendant CERT Operations RCB, LLC is a Delaware limited liability company with its principal place of business at 2100 Southbridge Parkway, Suite 585, Birmingham, AL 35209. CERT Operations RCB, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

35. Defendant Chem-Mod LLC is a Delaware limited liability company with its

principal place of business at Two Pierce Place, Itasca, Illinois 60143. Chem-Mod LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process. On information and belief, Defendant A.J. Gallagher holds a controlling interest in Chem-Mod, and has controlled and directed the actions and infringement of Chem-Mod alleged herein.

36. Defendant AJG Iowa Refined Coal LLC is a Delaware limited liability company with its principal place of business at Two Pierce Place, Itasca, IL 60143. AJG Iowa Refined Coal LLC has designated Cogency Global Inc., 850 New Burton Road, Suite 201, Dover DE 19904 as its agent for service of process.

37. Defendant Joppa Refined Coal LLC is a Delaware limited liability company with its principal place of business at or near the Joppa Power Station near Joppa, IL. Joppa Refined Coal LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

38. Defendant Thomas Hill Refined Coal LLC is a Delaware limited liability company with its principal place of business at or near the Thomas Hill Energy Center near Clifton Hill, MO. Thomas Hill Refined Coal LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

39. Defendant Wagner Coaltech LLC is a Delaware limited liability company with its principal place of business at or near the Herbert A. Wagner Generating Station in Anne Arundel County, MD. Wagner Coaltech LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

40. Defendant Walter Scott Refined Coal LLC is a Delaware limited liability company with its principal place of business at or near the Council Bluffs Energy Center (also known as the Walter Scott Energy Center) near Council Bluffs, IA. Walter Scott Refined Coal LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

41. Defendant Louisa Refined Coal, LLC is a Delaware limited liability company

with its principal place of business at 6901 Dodge St., Suite 201, Omaha, NE 68132. Louisa Refined Coal, LLC has designated Corporation Service Company, 251 Little Falls Drive, Wilmington, DE 19808 as its agent for service of process.

42. Defendant Belle River Fuels Company, LLC is a Delaware limited liability company with its principal place of business at or near the Belle River Power Plant in Saint Claire County, MI. Belle River Fuels Company, LLC has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

43. Defendant Arbor Fuels Company, LLC is a Delaware limited liability company with its principal place of business at 414 S. Main St, Suite 600, Ann Arbor, MI 48104. Arbor Fuels Company, LLC has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

44. Defendant Portage Fuels Company, LLC is a Delaware limited liability company with its principal place of business 414 S. Main St, Suite 600, Ann Arbor, MI 48104. Portage Fuels Company, LLC has designated The Corporation Trust Company, Corporation Trust Center, 1209 Orange Street, Wilmington, Delaware 19801 as its agent for service of process.

45. On information and belief, AJG, DTE, CERT, and/or Chem-Mod have used additional Delaware John Doe LLCs to collect Section 45 Tax Credits and to provide refined coal to additional coal-fired power plants in a manner that induces and or contributes to infringement of the patents-in-suit.

JURISDICTION AND VENUE

46. This action includes a claim of patent infringement arising under the patent laws of the United States, 35 U.S.C. §§ 1 *et seq.* This Court has jurisdiction over this action pursuant to 28 U.S.C. §§ 1331 and 1338(a).

47. This Court has personal jurisdiction over Defendants, because each is incorporated in and/or a limited liability company formed in Delaware. In addition, Defendants have conducted business in this district by taking advantage of the laws of this district and by

forming and controlling affiliated entities involved in the acts of infringement described below.

48. Venue is proper in this district pursuant to 28 U.S.C. § 1400(b) with respect to each Defendant that resides in this District.

ASSERTED PATENTS

49. On July 9, 2019, the United States Patent and Trademark Office duly and legally issued U.S. Patent No. 10,343,114 (the “‘114 patent”) entitled “Sorbents for the Oxidation and Removal of Mercury.” A copy of the ‘114 patent is attached as Exhibit A.

50. On May 1, 2012, the United States Patent and Trademark Office duly and legally issued U.S. Patent No. 8,168,147 (the “‘147 patent”) entitled “Sorbents for the Oxidation and Removal of Mercury.” A copy of the ‘147 patent is attached as Exhibit B.

51. On March 17, 2020, the United States Patent and Trademark Office duly and legally issued U.S. Patent No. 10,589,225 (the “‘225 patent”) entitled “Sorbents for the Oxidation and Removal of Mercury.” A copy of the ‘225 patent is attached as Exhibit C.

52. On March 24, 2020, the United States Patent and Trademark Office duly and legally issued U.S. Patent No. 10,596,517 (the “‘517 patent”) entitled “Sorbents for the Oxidation and Removal of Mercury.” A copy of the ‘517 patent is attached as Exhibit D.

53. On June 2, 2020, the United States Patent and Trademark Office duly and legally issued U.S. Patent No. 10,668,430 (the “‘430 patent”) entitled “Sorbents for the Oxidation and Removal of Mercury.” A copy of the ‘430 patent is attached as Exhibit E.

FACTUAL ALLEGATIONS

The Federal Government Resolves to Regulate Mercury Emissions from Power Plants

54. In 1990, Congress passed the Clean Air Act Amendments of 1990.

55. That law required the U.S. Environmental Protection Agency (EPA) to study the impact of various air pollutants, including mercury.

56. To assist in the research, in 1992, the EPA established a National Center for Excellence at the Energy & Environmental Research Center (EERC) referred to as the Center for Air Toxic Metals (CATM).

57. In 1997 and 1998, the EPA issued two reports to Congress: Mercury Study Report to Congress (issued December 1997) and Study of Hazardous Air Pollutant Emissions from Electric Utility Steam (issued February 1998). As an outcome of these studies, the EPA found a pressing need for regulation of mercury pollution from coal-fired power plants. Unfortunately, it also found that no existing technologies were up to the task of significantly reducing the mercury pollution from those plants.

58. In the wake of these reports, various governmental and industry organizations injected millions of dollars into basic scientific research and experimental studies in the search for new mercury capture technologies.

The Inventors of the Patents-in-Suit Develop Mercury Capture Solutions

59. Researchers at the EERC were instrumental in developing new techniques for studying this problem and ultimately solving it.

60. In 2002, the EPA surveyed the state of research in this field and produced a follow-up report: Control of Mercury Emissions from Coal-Fired Electric Utility Boilers: Interim Report. This report identified some promising areas of research, and it noted that some technologies were available for reducing mercury emissions. However, the EPA recognized that there was no universal solution to this problem and that more work remained to be done.

61. During this time, the inventors of the patents-in-suit were researching the issue of mercury capture at the EERC. Through their work, they uncovered some of the complex chemistry that occurs in a coal-fired boiler.

62. They further discovered a number of methods for improving mercury capture. In particular, they found that applying a halogen additive such as bromine and bromide compounds onto coal or into a combustion chamber, when combined with sorbent injection, could dramatically reduce the mercury content of coal-fired power plant emissions.

63. By 2004, the inventors filed a provisional application that would lead to the patents in suit. This application, and the subsequently issued patents, cover some of their discoveries and various applications of their discoveries. In particular, the inventors discovered, and ultimately

proved, the benefits of combining halogen treatments (e.g., bromine containing materials) in-flight with backend sorbents (e.g., activated carbon).

64. In 2011, the EPA finalized the first national standards to reduce mercury and other toxic air pollution from coal-fired plants (the Mercury and Air Toxics Standards or “MATS”). Most coal-fired power plants were required to comply with this rule by 2016.

Congress Creates the Section 45 Refined Coal Tax Credit

65. While the EPA was working on addressing the issue of mercury emissions, Congress also took action. In 2004, Congress passed the American Jobs Act, which created a new tax credit related to the production of refined coal (referred to as “Section 45 tax credits”).

66. Under this law, a refined coal producer can receive an inflation-adjusted tax credit for each ton (\$/ton) of refined coal sold to a power plant that results in a 40% reduction in mercury emissions and a 20% reduction in NOx emissions. This law has resulted in companies receiving hundreds of millions of dollars in tax credits each year.

67. Because of this highly lucrative law, financial services companies such as AJG jumped at the chance to collect the tax credits.

AJG, DTE, CERT, Chem-Mod, and the RC Defendants Reap Staggering Profits from Section 45 Tax Credits

68. AJG is an insurance brokerage and risk management services firm.

69. AJG Chief Financial Officer Douglas Howell has claimed credit for designing a business model to maximize profits based on Section 45 tax credits.

70. “Our return on investment is staggering,” Mr. Howell told analysts in a March 14, 2018 call. “Oh, 200 percent, 300 percent, 400 percent, 500 percent. I mean, just because it costs so little to develop” facilities.

71. As a result, Mr. Howell has explained that AJG will not be paying much, if any, U.S. federal income tax for many years to come.

72. According to the AJG business model, AJG does not build standalone facilities to refine coal that is then shipped around the country for use at coal plants.

73. Instead, AJG uses shell companies that are designed to lose money each year, but that ultimately result in AJG profiting from Section 45 tax credits.

74. Specifically, AJG forms a limited liability company (“LLC”) to be associated with a particular coal-fired power plant (the “Refined Coal LLC”). The paragraphs below refer to actions taken by a Refined Coal LLC, but AJG maintains control throughout this process. For example, AJG maintains majority control, or, if it lacks majority control, AJG requires that all major decisions obtain approval from AJG.

75. Through its controlling interests in Refined Coal LLCs and Chem-Mod, AJG causes Chem-Mod to contract with the Refined Coal LLC to provide Chem-Mod chemicals, and technical, regulatory, and/or operational support to the Refined Coal LLC.

76. The Refined Coal LLC rents space on-site at a power plant where it can briefly take possession of coal from the power plant. It purchases coal from the plant, treats it with Chem-Mod chemicals, and then sells the coal—now considered “refined coal”—back to the coal-fired power plant at the same price or for a loss.

77. For example, the Refined Coal LLC can take possession of coal as it moves along a conveyor belt toward a combustion chamber. It can then add chemicals to the coal and return it to a conveyor belt leading to the combustion chamber.

78. The Chem-Mod chemicals applied to the coal include Br₂, HBr, a bromide compound such as CaBr₂, or a combination thereof.

79. One important aspect of this plan is that an LLC is a pass-through entity for tax purposes. That is, the benefits of the Section 45 tax credits pass through to AJG and other owners of the Refined Coal LLC.

80. AJG sells ownership in the LLC based at least in part on the value of those tax credits.

81. By using the Refined Coal LLCs as shell companies, AJG is able to operate companies that are designed to lose money, but that ultimately benefit AJG because they allow it to obtain hundreds of millions of dollars in federal tax credits.

82. This model has been emulated by others, such as DTE and CERT.

83. DTE and CERT both use Chem-Mod supplied chemicals and provide refined coal through Refined Coal LLCs in order to obtain Section 45 Tax Credits.

84. In order to obtain the benefits of Section 45 Tax Credits, AJG, DTE, CERT, Chem-Mod, and the RC Defendants must comply with 26 U.S.C. § 45 by demonstrating that the alleged refined coal is “a liquid, gaseous, or solid fuel produced from coal (including lignite) or high carbon fly ash, including such fuel used as a feedstock,” “is sold by the taxpayer with the reasonable expectation that it will be used for the purpose of producing steam,” and “is certified by the taxpayer as resulting (when used in the production of steam) in a qualified emission reduction.” To demonstrate “qualified emission reduction,” these parties must demonstrate “a reduction of at least 20 percent of the emissions of nitrogen oxide and at least 40 percent of the emissions of either sulfur dioxide or mercury released when burning the refined coal (excluding any dilution caused by materials combined or added during the production process), as compared to the emissions released when burning the feedstock coal or comparable coal predominantly available in the marketplace as of January 1, 2003.”

85. While the parties could qualify for this credit by demonstrating a reduction in either sulfur dioxide or mercury, on information and belief, they have elected to focus on a reduction in mercury rather than sulfur dioxide.

86. On information and belief, AJG, DTE, CERT, Chem-Mod, and the RC Defendants provide the required certification for qualified emission reduction by performing pilot scale testing that simulates the conditions of a particular coal-fired power plant or by performing testing at a particular coal-fired power plant. In either case, AJG, DTE, CERT, Chem-Mod, and the RC Defendants must prepare a specific refined coal designed to work for that plant, and they will be aware of a plant’s use of activated carbon injection.

87. On information and belief, when AJG, DTE, CERT, Chem-Mod, and the RC Defendants perform certification testing for a particular plant, they must be aware of the other mercury control equipment at the plant, including activated carbon injection. Because AJG, DTE,

CERT, Chem-Mod, and the RC Defendants make refined coal by adding chemicals to the coal, not by removing atoms of mercury, the mercury present in the coal will also be present in the gas emitted from the combustion chamber. Indeed, according to Chem-Mod, the additives applied to the coal do not destroy or remove the mercury atoms, they merely result in the mercury being converted into a different form of mercury (e.g., molecular mercury to oxidized mercury). Thus, if these Defendants attempted to perform a certification test by merely combusting refined coal and measuring the amount of emitted mercury leaving the combustion chamber (i.e., disregarding the plant's activated carbon injection and other mercury control equipment), they would be unable to demonstrate the required reduction in mercury.

88. On information and belief, for coal-fired power plants that use activated carbon injection, AJG, DTE, CERT, Chem-Mod, and the RC Defendants demonstrate qualified emission reduction for those plants by adding activated carbon sorbent downstream of the combustion chamber during the certification testing. For example, these Defendants can establish a baseline mercury capture rate by combusting non-refined coal in a combustion chamber and then using the mercury control equipment employed at the plant under test (e.g., activated carbon injection and electrostatic precipitator). This could be a test at the plant, or a test at a pilot scale facility that simulates the plant's equipment. In either case, mercury in the coal will be emitted from the combustion chamber, mix with the activated carbon, and at least some will be captured in the electrostatic precipitator. The gas downstream of the electrostatic precipitator can then be measured for mercury content to establish a baseline for mercury emissions. When the Defendants switch to using refined coal (which has been formulated to react with the plant's use of activated carbon and other mercury controls in a manner will meet the qualified emission reduction requirement and that meets the plant's regulatory obligations), the bromine added to the coal boosts the performance of the activated carbon sorbent such that additional mercury is captured in the electrostatic precipitator. The Defendants can then measure the gas downstream of the electrostatic precipitator and rely on the reduced level of mercury in that measurement to certify that they achieve the required emissions reduction. Thus, AJG, DTE, CERT, Chem-Mod, and the

RC Defendants are aware of a plant's use of activated carbon either by obtaining that information so that they can simulate this step during pilot scale testing, or by observing the use of activated carbon on-site at the plant.

89. On information and belief, for each coal-fired power plant using activated carbon injection, AJG, DTE, CERT, Chem-Mod, and the RC Defendants perform certification testing at least every six months in order to maintain their eligibility for section 45 tax credits.

90. Even if it were possible for AJG, DTE, CERT, Chem-Mod, and the RC Defendants to avoid learning of a plant's use of activated carbon for purposes of certification testing, on information and belief, these Defendants would learn of the plant's use of activated carbon by working with the plant. These Defendants must have access to coal-fired power plants to determine logistics for installing refined coal equipment, storing and supplying chemicals, and operating and maintaining equipment. As part of that process, they would be able to witness activated carbon injection equipment and on-site activated carbon, as this material is readily recognizable to persons familiar with mercury control equipment and procedures. Moreover, individuals on-site would be required to comply with safety protocols at the plant. For example, AJG, DTE, CERT, Chem-Mod, and the RC Defendants would be instructed as to plant operations and protocols for interfering with aspects of plant operation that are not under the control of AJG, DTE, CERT, Chem-Mod, and the RC Defendants. In addition, they would be aware of warnings and safety information regarding the hazards of activated carbon. As a result, those individuals would be aware of the plant's use of activated carbon injection.

91. Even if it were possible for AJG, DTE, CERT, Chem-Mod, and the RC Defendants to supply, maintain, and operate mercury control equipment on-site at a coal-fired power plant without learning of the other mercury control equipment on-site at the plant, on information and belief, they would learn of the plant's use of sorbent containing activated carbon through routine conversation and communications with individuals at the coal-fired power plant that are necessary to ensure coordination and smooth operation of the plant. For example, if the plant were to unilaterally reduce its activated carbon injection rate, or AJG, DTE, CERT, Chem-Mod, and the

RC Defendants were to unilaterally reduce the amount of bromine added to the coal, this could hinder the plant's ability to comply with state and federal mercury regulations and/or the certification process for section 45 tax credits. Thus, AJG, DTE, CERT, Chem-Mod, and the RC Defendants coordinate with coal-fired power plants by keeping each other aware of their respective bromine and activated carbon usage rates.

92. On information and belief, AJG, DTE, CERT, Chem-Mod, and the RC Defendants discuss with owners and operators of coal-fired power plants at least the following: how they will create the refined coal onsite, the equipment that would be installed, the location and integration of their equipment into the coal conveyance system, how the certification tests would be performed, how the plant operates, the plant layout and equipment, the emissions control equipment, and the mercury control system, such as the activated carbon injection equipment and the effect that the sorbent comprising activated carbon would have on the test results (emissions reductions), the impact and benefits the refined coal would have on the plant's mercury control strategy, and how best to combine and integrate refined coal into the plant's approach for an optimum solution for compliance (e.g., how best to set the quantities for bromine and activated carbon so as to minimize overall cost and balance of plant effects).

93. Moreover, one of the benefits of using coal with added bromine and/or bromide at a coal-fired power plant with an activated carbon injection system is that the bromine and/or bromide enhances the performance of the activated carbon. This results in a reduced need for emission controls (e.g., reducing the quantity of activated carbon that would otherwise be required). It is reasonable to infer that AJG, DTE, CERT, Chem-Mod, and the RC Defendants are aware of this fact and take it into consideration when marketing their offerings to coal-fired power plants and when negotiating contracts with coal-fired power plants.

94. For example, AJG CFO Doug Howell has stated: "people have asked what does it really cost to produce this and where does it go? You can see that the materials that we use are \$0.80 working from the bottom left, labor and other plant operating costs cost about \$0.72 a ton, the utility gets—we pay them rent for putting these plants on their property, or we give them a

discount on the coal they produce of about \$0.45, and then there's a license fee that goes to Chem-Mod – about \$0.30. Now, it's important to also know that not only does the utility—the reason why they participate in these projects is that they've got a financial incentive to participate in it, but they also receive the improved environmental results basically for free and they get a better ash and favorable operating results. So the utility is part of this process and they have a financial incentive and an environment incentive. It's very important for everybody to understand that this technology works to help the utilities solve new emissions standards.”

95. As another example, a refined coal contract between Belle River Fuels LLC (an AJG and Chem-Mod affiliated Refined Coal LLC) and DTE specifically references the reduced quantity of activated carbon sorbent (not elimination) as a benefit of the arrangement. (Attached as Exhibit F). At a minimum, this demonstrates that AJG and Belle River Fuels LLC are aware of activated carbon use at coal-fired power plants to which they supply refined coal. It is further reasonable to infer that these parties are not outliers, but rather that DTE, CERT, Chem-Mod, and the other RC Defendants have similar knowledge and require similar contractual provisions.

96. In addition, the use of high quantities of activated carbon injection can discolor the fly ash produced by a coal-fired power plant. This may prevent the plant from selling the fly ash to cement producers, and instead require it to take on the cost of disposing of the fly ash. Providing bromine and/or bromide additives onto the coal combusted at a coal-fired power plant can reduce, the quantity of activated carbon required for mercury capture and thus preserve the plant's ability to sell fly ash.

97. Chem-Mod advertises that its bromine-containing coal additives improve fly ash saleability. Thus, Chem-Mod specifically markets its bromine-containing additives to coal-fired power plants that use sorbents comprising activated carbon. Similarly, the contract between DTE and Belle River Fuels LLC also describes this fly ash benefit. Because AJG, DTE, CERT, and the RC Defendants work with Chem-Mod and use Chem-Mod, it is reasonable to infer that they are aware of this purported benefit and Chem-Mod's marketing. It is also reasonable to infer that AJG, DTE, CERT, and the RC Defendants also rely on this knowledge and Chem-Mod's marketing

materials when negotiating contracts with coal-fired power plants, and that they similarly target their efforts toward coal-fired power plants that they know use, and will continue to use, activated carbon injection systems.

98. An activated carbon injection system for mercury control requires an upfront cost and ongoing costs for operation. Plants with such systems installed operate the systems in order to comply with state and federal regulations regarding mercury emissions. Were a plant to stop operating its activated carbon injection system, it could face fines that would destroy the economic incentives for dealing with a refined coal provider, or be shut down.

99. AJG, DTE, CERT, Chem-Mod, and the RC Defendants are aware of state and federal mercury regulations and the economic incentives of coal-fired power plants with activated carbon injection systems.

100. Thus, AJG, DTE, CERT, Chem-Mod, and the RC Defendants must necessarily know and intend that the coal plants will go on to perform the step of injecting activated carbon.

101. Alternatively, if AJG, DTE, CERT, Chem-Mod, and/or one of the RC Defendants contend that they somehow avoid learning of a plant's use of sorbent comprising activated carbon, they are acting with willful blindness.

102. Once AJG, DTE, CERT, Chem-Mod, and/or one of the RC Defendants has provided section 45 certification of qualified emissions reductions for a plant, the amount of bromine and/or bromide applied to the coal will need to be tailored (chemically adjusted) depending on the ongoing needs of the plant (e.g., when considering a new coal supply that has different chemical properties or is mined from a different location, or operations of the plant change).

103. When such tailoring occurs, the coal-fired power plant must ensure that it does not cause the plant to emit mercury (or other emissions such as SO₂, NO_x, and PM)) in excess of state or federal mercury regulations. The refined coal provider (AJG, DTE, CERT, Chem-Mod, and/or one of the RC Defendants) must ensure that the tailoring will not interfere with its ability to provide section 45 certification. On information and belief, the parties must keep each other apprised of

the bromine, bromide, and activated carbon in use to ensure that they are able to comply with regulatory requirements. For example, plant personnel have requested (communicated to at least some of the refined coal provider Defendants) that the bromine concentration in the refined coal be altered during testing and evaluation of alternative carbon suppliers.

104. Thus, AJG, DTE, CERT, Chem-Mod, and the RC Defendants must know and intend that the coal plants will go on to perform the step of providing sorbent comprising activated carbon after the refined coal with added HBr, Br₂, and/or bromide has been tailored to account for changing circumstances.

105. Alternatively, if AJG, DTE, CERT, Chem-Mod, and/or one of the RC Defendants contend that they somehow avoid learning of a plant's use of sorbent comprising activated carbon, they are acting with willful blindness.

106. When AJG, DTE, CERT, Chem-Mod, and/or one of the RC Defendants provides refined coal to a coal plant with an activated carbon injection system, they intend for the plant to continue to operate that system by injecting sorbent comprising activated carbon so that these Defendants may continue to receive the benefits of Section 45 tax credits.

107. Thus, when AJG, DTE, CERT, Chem-Mod, and/or one of the RC Defendants provides refined coal on the conveyance leading to the combustion chamber of a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod, and the RC Defendants know that this refined coal has been specifically tailored and certified for that plant, and that the provided refined coal has no substantial non-infringing use (i.e., it cannot reasonably be used for purposes other than to be combusted at the plant where sorbent comprising activated carbon will later be injected).

108. In addition, even if the provided refined coal could have had some non-infringing use, because AJG, DTE, CERT, Chem-Mod, and one of the RC Defendants must sell the refined coal "with the reasonable expectation that it will be used for the purpose of producing steam," and as explained above, the refined coal is only certified for a particular plant (i.e., a plant that uses activated carbon), it is reasonable to infer that they require the coal plant to combust the provided

refined coal or at least some significant portion of it in accordance with those expectations, i.e., not in some non-infringing way.

ME2C Attempts to Compete in the Market for Mercury Capture Technologies

109. ME2C is the commercial extension of the patented technology.

110. MES, Inc. obtained an exclusive license to the '147 patent and pending related applications from the EERC. Midwest Energy Emissions Corp. later obtained an assignment of the patents-in-suit from the EERC including any rights retained by the EERC to receive past damages, and MES, Inc. agreed to terminate its exclusive license at that time. Thus, during the time period of alleged infringement, MES, Inc. and/or Midwest Energy Emissions Corp. held all substantial rights in the patents-in-suit.

111. ME2C develops, markets, and sells products and services that practice the patented technology.

112. ME2C's product development efforts have been led by named inventor and Chief Technology Officer John Pavlish. ME2C has developed both sorbent enhancement additives and activated carbon sorbents for practicing the technology described in the patents-in-suit and for practicing other patented methods owned by ME2C.

113. ME2C has also publicized its patent portfolio and explained the scope of the patented technology through its website, its interactions with customers and potential customers, and through presentations at industry events such as the MEGA Symposium, the Energy, Utility & Environment Conference, Lignite Energy Conference, and the Air Quality Conference. Representatives of Defendants have attended these conferences and received materials from such conferences.

114. ME2C has attempted to compete in the market for mercury capture technologies. In particular it attempted to negotiate supply contracts with coal-fired power plants in anticipation of MATS regulations that became effective in 2015 and 2016, and also periodically afterwards as plants re-evaluate their MATS compliance strategies.

115. However, ME2C it is at an unfair disadvantage with respect to the RC Defendants

that encourage power plants to use ME2C's patented technology instead of developing new technologies for refined coal. These RC Defendants induce power plants to infringe the patents-in-suit by offering the technology at no or artificially low costs to the plant.

116. AJG CFO Douglas Howell has explained, "the reason why [coal-fired power plants] participate in these [Section 45 Tax Credit] projects is that they've got a financial incentive to participate in it, but they also receive the improved environmental results basically for free and they get a better ash and favorable operating results."

117. In addition, because the Coal Plant Defendants have decided to infringe ME2C's patents, they now purchase various materials from different suppliers at artificially deflated prices and employ them in a manner that infringes ME2C's patents.

118. Despite these difficulties, ME2C has sold its products and services to various power plants throughout the country.

ME2C's Interactions with Defendant Vistra

119. In 2012, ME2C contracted with Luminant Generation Company LLC ("Luminant") to perform testing of the patented methods at various Luminant power plants.

120. At least as early as 2012, ME2C informed Luminant of its patent portfolio, including the '147 patent and parent applications to the '114 patent.

121. By 2012, ME2C had also explained that its patents cover the use of halogen-based sorbent enhancement additives and backend carbon-based sorbents.

122. After successfully testing its patented technology at Luminant plants, Luminant signed a Master Supply Agreement with ME2C.

123. Luminant is now a subsidiary of Vistra.

124. Through Luminant, ME2C has informed Vistra of the patents-in-suit and also explained that its patents cover the use of halogen-based sorbent enhancement additives and backend carbon-based sorbents.

125. ME2C also attempted to develop business with other affiliates of Vistra. For example, ME2C has had various interactions with Vistra subsidiary Dynegy Inc. and its

subsidiaries (“Dynergy”).

126. Beginning in 2011, ME2C and Dynergy evaluated the ME2C process for use at the Joppa Steam Plant in Massac county Illinois.

127. As part of that process, ME2C informed Dynergy of its patent portfolio, including the ’147 patent and parent applications to the ’114 patent.

128. ME2C has informed Dynergy that its patents cover the use of halogen-based sorbent enhancement additives and backend carbon-based sorbents.

129. Although the test results were favorable, Dynergy ultimately determined not to sign a supply agreement with ME2C.

130. Throughout 2014 and 2015, ME2C had further interactions with Dynergy and conducted a further demonstration at the Edwards Power Station in Peoria county Illinois.

131. Again, Dynergy declined to sign a supply agreement with ME2C.

132. In 2018, Vistra acquired Dynergy.

133. That same year, Vistra requested that ME2C again perform a demonstration at the Joppa Steam Plant.

134. ME2C informed Vistra of its patent portfolio and also explained that its patents cover the use of halogen-based sorbent enhancement additives and backend carbon-based sorbents.

135. ME2C also attempted to negotiate a supply agreement with Vistra for the Joppa Steam Plant.

136. However, the Joppa Steam Plant was receiving refined coal treated with halogen from a refined coal producer.

137. Joppa Refined Coal LLC, has and continues to provide refined coal to the Joppa Steam Plant. AJG, Chem-Mod and Joppa Refined Coal LLC provide financial, technical, and contractual incentives to Vistra to burn refined coal as part of their scheme to collect Section 45 Tax Credits.

138. The Joppa Steam Plant is owned and/or operated by Vistra in the United States.

139. Vistra negotiates and/or procures products and/or services related to mercury

control for use at the Joppa Steam Plant.

140. The Joppa Steam Plant has burned and/or burns coal that has added bromine and/or bromide.

141. The Joppa Steam Plant combusts coal along with added bromine and/or bromide.

142. The Joppa Steam Plant injects sorbent material comprising activated carbon downstream of the combustion chamber.

143. The Joppa Steam Plant contracts with Joppa Refined Coal LLC to obtain coal with added bromine and/or bromide.

144. The Joppa Steam Plant uses added bromine and/or bromide and activated carbon to ensure compliance with federal and state MATS regulations.

145. In addition to the foregoing, on July 17, 2019, ME2C provided notice to Vistra of the '114 and '147 patents and of the acts constituting infringement by filing the original complaint in this case.

146. It is reasonable to infer that Vistra would have reviewed the prosecution history for the '114 and '147 patents and would be generally aware of other patents in the same family.

147. On June 29, 2020, ME2C provided notice to Vistra of the '225, '517, and '430 patents and of the acts constituting infringement by providing Vistra with a draft amended complaint.

148. Despite being aware of ME2C's patents, and recognizing the benefits of the technology through its subsidiary Luminant, Vistra has elected to infringe the patents-in-suit at its coal-fired power plants, including at the Joppa Steam Plant.

ME2C's Interactions with Defendant AEP

149. In 2011, ME2C met with officials at AEP to discuss ME2C's mercury capture products and services.

150. In or around that meeting, ME2C informed AEP of its patent portfolio.

151. The parties did not enter into a commercial agreement at that time.

152. In 2013, representatives of AEP attended the Air Quality 9 conference and received

a presentation on the patented technology which identified the '147 patent and parent applications to the '114 patent.

153. In 2016, ME2C and AEP discussed potential work related to AEP's H.W. Pirkey Power Plant.

154. ME2C and AEP, including its subsidiary Southwestern Electric Power Co. contracted for ME2C to provide demonstration testing at the H.W. Pirkey Power Plant.

155. Through those interactions, ME2C again reminded AEP of its patent portfolio and explained that its patents covered the use of halogen-based sorbent enhancement additives and backend carbon-based sorbents.

156. ME2C specifically identified the '147 patent and parent applications to the '114 patent to AEP.

157. Between 2016 and 2018, ME2C explained its technology to AEP, provided technical and economic presentations, and performed demonstration testing at AEP's H.W. Pirkey Power Plant in Harrison county, Texas.

158. The H.W. Pirkey Power Plant is owned and/or operated by AEP in the United States.

159. AEP negotiates for and/or procures products and/or services related to mercury control for use at the H.W. Pirkey Power Plant.

160. The H.W. Pirkey Power Plant combusts coal along with added bromine and/or bromide.

161. The H.W. Pirkey Power Plant injects sorbent material comprising activated carbon downstream of the combustion chamber.

162. The H.W. Pirkey Power Plant employs halogenated PAC (Powdered Activated Carbon) sorbent injection as a form of mercury control.

163. The H.W. Pirkey Power Plant uses added bromine and/or bromide and activated carbon to ensure compliance with federal MATS regulations.

164. In addition to the foregoing, on July 17, 2019, ME2C provided notice to AEP of

the '114 and '147 patents and of the acts constituting infringement by filing the original complaint in this case.

165. It is reasonable to infer that AEP would have reviewed the prosecution history for the '114 and '147 patents and would be generally aware of other patents in the same family.

166. On June 29, 2020, ME2C provided notice to AEP of the '225, '517, and '430 patents and of the acts constituting infringement by providing AEP with a draft amended complaint.

167. Despite knowledge of ME2C's patents, AEP has elected to infringe ME2C's patents at its coal-fired power plants including at the H.W. Pirkey Power Plant.

ME2C's Interactions with NRG

168. In 2012, ME2C had various interactions with NRG to discuss ME2C's patented technology.

169. Over the next few years, NRG evaluated its options for coming into compliance with upcoming MATS regulations.

170. During that time, ME2C identified its patents to NRG and explained the operation of its patented technology.

171. The parties also considered having ME2C perform various demonstrations of the technology at NRG power plants.

172. In addition to the foregoing, on July 17, 2019, ME2C provided notice to NRG of the '114 and '147 patents and of the acts constituting infringement by filing the original complaint in this case.

173. It is reasonable to infer that NRG would have reviewed the prosecution history for the '114 and '147 patents and would be generally aware of other patents in the same family.

174. On June 29, 2020, ME2C provided notice to NRG of the '225, '517, and '430 patents and of the acts constituting infringement by providing NRG with a draft amended complaint. Nonetheless, NRG elected to infringe ME2C's patents.

ME2C's Interactions with Defendant Talen

175. Talen owns and/or operates the Colstrip and other power plants.

176. Prior to 2015 those plants were owned and/or operated by PPL.

177. In 2013, representatives of PPL attended the Air Quality 9 conference and received a presentation on the patented technology which identified the '147 patent and parent applications to the '114 patent.

178. In 2013, ME2C met with PPL employees tasked with understanding and designing mercury control procedures, including Jon Boucher, Bill Neumiller, and Steve Craig, to discuss the use of ME2C's patented technology at power plants in the PPL fleet, including Colstrip and other plants.

179. ME2C specifically identified the '147 patent and the parent patent to the '114 patent to at least Jon Boucher, and explained that these patents covered the use of halogen-based sorbent enhancement additives and backend carbon-based sorbents.

180. In 2015, PPL spun off a portion of its business to form Talen.

181. At least Jon Boucher has remained with Talen.

182. In addition, operation of a coal-fired power plant can be dangerous and complicated, requiring a team of qualified engineers. Similarly, ensuring compliance with mercury capture regulations requires managing complex chemical reactions occurring at the plant. Accordingly, it is reasonable to infer that even when Talen took over control of the plants at issue, it would have retained additional individuals knowledgeable of plant operations and mercury control processes at the plants. Thus, it is likely that at least some of those additional individuals that met with and/or received information about ME2C's patented technology would have remained with Talen as of 2015, or would have shared information related to mercury control at the plants with other Talen personnel and management as Talen is now responsible for complying with state and federal mercury regulations..

183. In addition to the foregoing, on July 17, 2019, ME2C provided notice to Talen of the '114 and '147 patents and of the acts constituting infringement by filing the original complaint in this case.

184. It is reasonable to infer that Talen would have reviewed the prosecution history for

the '114 and '147 patents and would be generally aware of other patents in the same family.

185. On June 29, 2020, ME2C provided notice to Talen of the '225, '517, and '430 patents and of the acts constituting infringement by providing Talen with a draft amended complaint.

186. Despite being aware of ME2C's patents, Talen has elected to infringe those patents.

ME2C's Interactions with Defendant AJG, DTE, CERT, Chem-Mod, and RC Defendants

187. AJG, DTE, CERT, Chem-Mod, and RC Defendants have worked with the EERC to conduct testing related to their coal treatment processes. For example, they have relied on the EERC to demonstrate that the processes employed by refined coal facilities qualify for Section 45 Tax Credits. Through those interactions, it is likely that they became aware of the patents-in-suit and/or related applications as they were initially developed by the inventors while they were at the EERC.

188. In addition, at least Chem-Mod participates in conferences where ME2C describes its patented technology. For example, Chem-Mod president Murray F. Abbott attended the 2018 MEGA conference where ME2C described the technology at issue in this case and explained that it was covered by its patents. ME2C also referred attendees to its website which has additional information regarding its patents.

189. Given the close relationship between Chem-Mod, AJG, DTE, CERT, and the RC Defendants, those Defendants know of ME2C's patented technology and patent portfolio and/or are willfully blind to ME2C's patents.

190. In addition, ME2C is one of a small number of companies that competes with Chem-Mod, AJG, DTE, CERT, and the RC Defendants to provide bromine-containing additives for mercury control. It is reasonable to infer that these companies have done at least some due diligence on potential competitors. During that process, it is likely that they would have discovered the patents-in-suit from the U.S. Patent Office, Google Patents, ME2C publications and product literature, and/or ME2C's website.

191. For example, prior to filing this lawsuit, AJG acknowledged that it could face

claims of patent infringement for its refined coal activities. This indicates that it has performed some due diligence to identify patents potentially relevant to its business. It has advertised to investors and/or potential investors that the risk of a patent infringement finding is mitigated by the fact that Chem-Mod has patent infringement insurance. This indicates that Chem-Mod has also performed some due diligence to identify patents potentially relevant to its business. Given the limited number of participants in the relevant market, it is reasonable to infer that Chem-Mod's decision to purchase patent infringement insurance, and AJG's reliance on that insurance, were motivated at least in part by their awareness of ME2C's patents and the risk of infringing those patents.

192. Because CERT, DTE, and the RC Defendants have emulated AJG's business model and also use Chem-Mod as a supplier, it is reasonable to infer that these parties would have also been aware of ME2C's patents either as a result of their own due diligence, or as part of their interactions with Chem-Mod and/or AJG.

193. Given that a company's internal knowledge and motivation for purchasing liability insurance is often not publicly available, further evidence regarding these Defendants' pre-suit knowledge of the patents-in-suit is likely solely within their possession and available to ME2C only through discovery.

194. In addition to the foregoing, on July 17, 2019, ME2C provided notice to AJG, DTE, CERT, Chem-Mod, and RC Defendants of the '114 and '147 patents and of the acts constituting infringement by filing the original complaint in this case.

195. It is reasonable to infer that AJG, DTE, CERT, Chem-Mod, and RC Defendants would have reviewed the prosecution history for the '114 and '147 patents and would be generally aware of other patents in the same family.

196. On June 29, 2020, ME2C provided notice to AJG, DTE, CERT, Chem-Mod, and RC Defendants of the '225, '517, and '430 patents and of the acts constituting infringement by providing Vistra with a draft amended complaint.

197. Despite being aware of ME2C's patents, AJG, DTE, CERT, Chem-Mod, and RC

Defendants have continued to infringe.

Defendants' Acts of Infringement

198. The Coal Plant Defendants each operate at least one coal-fired power plant where they combust coal in a combustion chamber with bromine and/or bromide that has been added to the coal and/or that has been provided to the combustion chamber, and where they inject a sorbent material comprising activated carbon downstream of the combustion chamber (the "Accused Coal Plants"). The Accused Coal Plants are not limited to the specifically named, exemplary coal plants named above.

199. In doing so, the Coal Plant Defendants perform the methods claimed by the patents-in-suit, and thus directly infringe the patents-in-suit.

200. As the parent of the other Vistra entities, Vistra Energy Corp. induces the other Vistra entities to perform the steps of the patented methods.

201. On information and belief and based on ME2C's past business encounters with Vistra, Vistra Energy Corp. does so by exercising control over subsidiaries, providing technical, administrative, logistical and financial services to subsidiaries, and/or negotiating standard form or bulk agreements for products and services related to mercury control. For example, Vistra Energy Corp. negotiates or exercises veto power over decisions to sign supply contracts for activated carbon and bromine-containing additives. In so doing, Vistra Energy Corp. takes part in the decisions regarding supply contracts and influences the other Vistra entities to select suppliers for the plant, including those that provide bromine-containing additives and activated carbon.

202. As the parent of the other NRG entities, NRG Energy Inc. induces the other NRG entities to perform the steps of the patented methods.

203. On information and belief and based on ME2C's past business encounters with NRG, NRG Energy Inc. does so by exercising control over subsidiaries, providing technical, administrative, logistical and financial services to subsidiaries, and/or negotiating standard form or bulk agreements for products and services related to mercury control. For example, NRG Energy Inc. negotiates or exercises veto power over decisions to sign supply contracts for activated

carbon and bromine-containing additives. In so doing, NRG Energy Inc. takes part in the decisions regarding supply contracts and influences the other NRG entities to select suppliers for the plant, including those that provide bromine-containing additives and activated carbon.

204. As the parent of the other Talen entities, Talen Energy Corporation induces the other Talen entities to perform the steps of the patented methods.

205. On information and belief and based on ME2C's business encounters with PPL and the fact that Talen retained at least some PPL employees, Talen Energy Corporation does so by exercising control over subsidiaries, providing technical, administrative, logistical and financial services to subsidiaries, and/or negotiating standard form or bulk agreements for products and services related to mercury control. For example, Talen Energy Corporation negotiates or exercises veto power over decisions to sign supply contracts for activated carbon and bromine-containing additives. In so doing, Talen Energy Corporation takes part in the decisions regarding supply contracts and influences the other Talen entities to select suppliers for the plant, including those that provide bromine-containing additives and activated carbon.

206. AJG, DTE, CERT, Chem-Mod, and the RC Defendants operate RC facilities that receive coal, add bromine and/or bromide such as CaBr_2 to the coal, and then provide that "refined" coal to a coal-fired power plant that injects a sorbent material comprising activated carbon downstream of the combustion chamber (the "Accused RC Facilities").

207. Chem-Mod provides chemicals and/or refined coal to at least some of the Accused Coal Plants and Accused RC Facilities.

208. Chem-Mod also assists in operating the Accused Coal Plants and Accused RC Facilities in connection with administering the chemicals supplied by Chem-Mod.

209. Given the location and operation of the Accused RC Facilities and the contractual relationships between Accused RC Facilities and associated coal-fired power plants, the refined coal provided by each Accused RC Facility has no substantial non-infringing use.

210. In addition, AJG, DTE, CERT, Chem-Mod, and the RC Defendants provide financial incentives to operators of coal-fired power plants to participate in a Section 45 Tax Credit

scheme.

211. AJG, DTE, CERT, Chem-Mod, and the RC Defendants condition participation in an activity or receipt of a benefit, i.e., the financial benefits of participating in the Section 45 Tax Credit scheme and the technical and environmental benefits of using refined coal, upon performance of a step or steps of a patented method, i.e., the combusting of coal with added bromine and/or bromide, and they establish the manner or timing of that performance by requiring the power plant to use the refined coal and by providing the refined coal directly onto conveyances leading to the combustor.

212. AJG, DTE, and CERT, directly and in concert with their subsidiaries including Chem-Mod and the RC Defendants, have engaged in a pattern of conduct intended to induce and/or contribute to the infringement of others, including the Coal Plant Defendants and the operators of coal-fired power plants connected to an Accused RC Facility. These actions have included:

- a. forming several of the RC Defendants specifically for the purpose of using Chem-Mod products in the manner described below as infringing;
- b. providing several of the RC Defendants and operators of coal-fired power plants with chemicals used to directly infringe the patents-in-suit;
- c. Building the core components of the RC facilities to use Chem-Mod chemicals;
- d. Connecting the RC facilities to coal-fired power plants;
- e. Placing the RC Facilities into service;
- f. Providing the RC Defendants with operational support, regulatory, and technical support necessary to use Chem-Mod chemicals at the Accused RC Facilities and Accused Coal Plants;
- g. Testing the performance of the RC Facilities for regulatory reasons and to obtain Section 45 Tax Credits;
- h. Conditioning participation in the Section 45 Tax Credits program on use

of Chem-Mod chemicals at the Accused RC Facilities;

- i. Limiting the amount of capital and/or supplies of the RC Defendants;
- j. Using the RC Defendants to claim Section 45 Tax Credits;
- k. Tailoring the treatments applied to coal for each individual power plant; and
- l. Modifying the amount of bromine and/or bromide added to coal sold to Coal Plant Defendants and/or operators of coal-fired power plants connected to an RC Facility in connection with plants' MATS obligations.

213. AJG, Chem-Mod, their associated RC Defendants, and the operators of coal-fired power plants connected to an RC Facility that is owned by AJG and/or its subsidiaries are involved in a joint enterprise to infringe the patents-in-suit.

214. AJG, Chem-Mod, their associated RC Defendants, and the operators of coal-fired power plants connected to an RC Facility that is owned by AJG contract to provide refined coal at the coal-fired power plant for the common purpose of obtaining the benefits of Section 45 tax credits. AJG, Chem-Mod, their associated RC Defendants and the operator of a coal-fired power plant have a community of pecuniary interest in that purpose because they share in the benefits of those tax credits either by receiving the tax credits or by relying on the value of the tax credits to provide discounted refined coal and/or pay rent to the coal-fired power plant.

215. AJG, Chem-Mod, their associated RC Defendants, and the operators of coal-fired power plants connected to an RC Facility that is owned by AJG have an equal right of control in the joint enterprise because each controls a necessary aspect of the endeavor. AJG, Chem-Mod, their associated RC Defendants control the certification process for obtaining the benefits of section 45 tax credits and the provision of chemicals onto the coal. AJG can exercise its controlling interest in the RC Defendants to cease providing refined coal, and it can exercise its controlling interest in Chem-Mod to cease providing the coal additives. The coal-fired power plant controls the process of combusting the coal and providing sorbent comprising activated carbon.

216. DTE, Chem-Mod, their associated RC Defendants, and the operators of coal-fired power plants connected to an RC Facility that is owned by DTE and/or its subsidiaries are involved in a joint enterprise to infringe the patents-in-suit.

217. DTE, Chem-Mod, their associated RC Defendants, and the operators of coal-fired power plants connected to an RC Facility that is owned by DTE contract to provide refined coal at the coal-fired power plant for the common purpose of obtaining the benefits of Section 45 tax credits. DTE, Chem-Mod, their associated RC Defendants and the operator of a coal-fired power plant have a community of pecuniary interest in that purpose because they share in the benefits of those tax credits either by receiving the tax credits or by relying on the value of the tax credits to provide discounted refined coal and/or pay rent to the coal-fired power plant.

218. DTE, Chem-Mod, their associated RC Defendants, and the operators of coal-fired power plants connected to an RC Facility that is owned by DTE have an equal right of control in the joint enterprise because each controls a necessary aspect of the endeavor. DTE, Chem-Mod, their associated RC Defendants control the certification process for obtaining the benefits of section 45 tax credits and the provision of chemicals onto the coal. DTE can exercise its controlling interest in the RC Defendants to cease providing refined coal. Chem-Mod can exercise control by ceasing to provide the coal additives. The coal-fired power plant controls the process of combusting the coal and providing sorbent comprising activated carbon.

219. CERT, Chem-Mod, their associated RC Defendants, and the operators of coal-fired power plants connected to an RC Facility that is owned by CERT and/or its subsidiaries are involved in a joint enterprise to infringe the patents-in-suit.

220. CERT, Chem-Mod, their associated RC Defendants, and the operators of coal-fired power plants connected to an RC Facility that is owned by CERT contract to provide refined coal at the coal-fired power plant for the common purpose of obtaining the benefits of Section 45 tax credits. CERT, Chem-Mod, their associated RC Defendants and the operator of a coal-fired power plant have a community of pecuniary interest in that purpose because they share in the benefits of those tax credits either by receiving the tax credits or by relying on the value of

the tax credits to provide discounted refined coal and/or pay rent to the coal-fired power plant.

221. CERT, Chem-Mod, their associated RC Defendants, and the operators of coal-fired power plants connected to an RC Facility that is owned by CERT have an equal right of control in the joint enterprise because each controls a necessary aspect of the endeavor. CERT, Chem-Mod, their associated RC Defendants control the certification process for obtaining the benefits of section 45 tax credits and the provision of chemicals onto the coal. CERT can exercise its controlling interest in the RC Defendants to cease providing refined coal. Chem-Mod can exercise control by ceasing to provide the coal additives. The coal-fired power plant controls the process of combusting the coal and providing sorbent comprising activated carbon.

222. Thus, AJG, DTE, CERT, Chem-Mod, and the RC Defendants induce and/or contribute to direct infringement of the patents-in-suit by coal-fired power plant operators, and thus indirectly infringe the patents-in-suit.

223. Defendants' infringement of the Patents-in-Suit is willful. Defendants continue to commit acts of infringement despite a high likelihood that its actions constitute infringement, and Defendants knew or should have known that their actions constituted an unjustifiably high risk of infringement.

224. In addition to the allegations provided above, Defendants have had notice of the '114 and '147 patents and ME2C's allegations of infringement at least as of the filing of the original complaint in this case on July 17, 2019, and Defendants have had notice of the '225, '517, and '430 patents and ME2C's allegations of infringement at least as of June 29, 2020, when ME2C provided Defendants with a draft amended complaint.

225. In accordance with 35 U.S.C. § 287, Defendants have actual notice and knowledge of all of the Patents-in-Suit as described above and no later than the filing of this Complaint and/or the date this Complaint was served upon each Defendant. In any event, Defendants may not avail themselves of 35 U.S.C. § 287 as a defense because ME2C is under no obligation to mark performance of the patented methods.

226. Defendants acts of infringement have been willful as of the date they became

aware of the patented technology and the patents-in-suit, and in any event no later than the filing of this Complaint and/or the date this Complaint was served upon each Defendant.

Defendants' Interactions With Each Other Related to Infringement

227. Each Coal Plant Defendant consists of a parent company and various subsidiaries. These various entities work together to procure materials and manage Accused Power Plants.

228. Each of AJG, DTE, and CERT own and operate Refined Coal LLCs (including the other named RC Defendants) that use Chem-Mod materials at the Accused Coal Plants and coal plants with associated Accused RC Facilities.

229. Vistra's Joppa Coal plant, and Talen's Brandon Shores, Herbert Wagner, and Montour coal plants obtain refined coal from AJG, Chem-Mod, and their associated Refined Coal LLCs.

230. Vistra's Duck Creek and Newton coal plants obtain refined coal from DTE, Chem-Mod, and their associated Refined Coal LLCs.

231. The Conesville power plant in Ohio has been/is owned and/or operated by Vistra and AEP.

232. At least Defendants Vistra, NRG, and Talen have owned and/or operated Accused Coal Plants using Chem-Mod products to directly infringe the patents-in-suit and thus Vistra is jointly and severally liable with Chem-Mod, NRG is jointly and severally liable with Chem-Mod, and Talen is jointly and severally liable with Chem-Mod with respect to those plants.

233. At least Defendants AJG, DTE, Chem-Mod and their associated Refined Coal LLCs have induced and/or contributed to infringement at Vistra and Talen Accused Coal Plants and coal plants associated with Accused RC Facilities, and thus those parties are jointly, severally, and/or in the alternative liable with respect to those plants.

234. Each of the RC Defendants is owned and/or operated by AJG, DTE, and/or CERT, and each uses Chem-Mod to induce and/or contribute to infringement. Thus, each RC Defendant is jointly, severally, and/or in the alternative liable with respect to Chem-Mod and the Defendant that is its associated owner/operator.

235. Defendants AEP and Vistra have owned and/or operated some of the same Accused Coal Plants, and thus are jointly, severally, and/or in the alternative liable with respect to those plants.

COUNT ONE: INFRINGEMENT OF THE '114 PATENT

236. ME2C incorporates by reference the preceding paragraphs as if fully set forth herein.

237. U.S. Patent No. 10,343,114 (the "'114 patent"), entitled "Sorbents for the Oxidation and Removal of Mercury", was issued on July 9, 2019, naming Edwin S. Olson, Michael J. Holmes and John H. Pavlish as the inventors. Exhibit A ('114 Patent).

238. ME2C owns all rights, title, and interest in the '114 Patent, and holds all substantial rights pertinent to this suit, including the right to sue and recover for all past, current, and future infringement.

239. The '114 Patent is valid and enforceable and directed to patentable subject matter.

240. Defendants infringe claims 1-30 of the '114 patent.

241. ME2C provides the following explanation of infringement with regard to an exemplary claim.

242. Claim 25 of the '114 patent recites: A method of separating mercury from a mercury-containing gas.

243. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this method in order to comply with federal and/or state mercury regulations.

244. Claim 25 of the '114 patent recites: combusting coal in a combustion chamber to provide the mercury-containing gas, wherein the coal comprises added Br₂, HBr, a bromide compound, or a combination thereof, added to the coal upstream of the combustion chamber, or the combustion chamber comprises added Br₂, HBr, a bromide compound, or a combination thereof, or a combination thereof.

245. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step by burning coal with an added Br₂, HBr, a bromide compound, or a

combination thereof and/or by adding Br₂, HBr, a bromide compound, or a combination thereof to the combustion chamber.

246. Claim 25 of the '114 patent recites: injecting a sorbent material comprising activated carbon into the mercury containing gas downstream of the combustion chamber.

247. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step by injecting activated carbon sorbent downstream of the combustion chamber.

248. Claim 25 of the '114 patent recites: contacting mercury in the mercury-containing gas with the sorbent, to form a mercury/sorbent composition.

249. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step because mercury contained in the gas exiting the combustion chamber contacts the sorbent as all of this material is contained in the same gas.

250. Claim 25 of the '114 patent recites: separating the mercury/sorbent composition from the mercury-containing gas, to form a cleaned gas.

251. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step using equipment to collect the mercury captured by the sorbent in order to comply with mercury regulations.

252. The Coal Plant Defendants have and continue to directly infringe, literally and/or under the doctrine of equivalents, the '114 patent under 35 U.S.C. § 271(a).

253. In addition, Vistra Energy Corp., NRG Energy Inc., and Talen Energy Corporation induce their respective subsidiary Defendants to infringe under 35 U.S.C. § 271(b). Vistra Energy Corp., NRG Energy Inc., and Talen Energy Corporation are each aware of the patents-in-suit, but nonetheless encourage their subsidiaries to infringe by, on information and belief, taking part in the supply contract process for activated carbon and bromine-containing additives at coal-fired power plants that directly infringe and signing, or encouraging their subsidiaries to sign, contracts with suppliers that provide the activated carbon and bromine-containing additives that lead to infringement.

254. AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to coal-fired power plants connected to an Accused RC Facility.

255. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

256. Alternatively, when AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants are willfully blind to the fact that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

257. The coal with added Br₂, HBr, a bromide compound, or a combination thereof provided by AJG, DTE, CERT, Chem-Mod and the RC Defendants is not a staple article or commodity of commerce suitable for substantial non-infringing use. This coal is supplied to a conveyance that moves the coal toward the combustion chamber of a power plant that directly infringes the '114 patent. In addition, AJG, DTE, CERT, Chem-Mod and the RC Defendants tailor the amount of Br₂, HBr, a bromide compound, or a combination thereof added to the coal for the specific needs of the power plant.

258. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the provided coal has no substantial use other than to be combusted at the plant that will perform the step of injecting sorbent comprising activated carbon.

259. AJG, DTE, CERT, Chem-Mod and the RC Defendants took the above-described actions intending to cause infringing acts by others.

260. AJG, DTE, CERT, Chem-Mod and the RC Defendants have actual knowledge of the '114 patent and know that actions described above, if taken, would constitute infringement of that patent. Alternatively, AJG, DTE, CERT, Chem-Mod and the RC Defendants believe there is a high probability that others would infringe the '114 patent but have remained willfully blind to the infringing nature of those actions. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '114 patent under 35 U.S.C. § 271(b) with respect to each coal-fired power plant connected to an Accused RC Facility.

261. AJG, DTE, CERT, Chem-Mod and the RC Defendants indirectly infringe the '114 patent by contributing to infringement by others, such as its customers and end-users by offering to sell and/or selling within the United States coal with added Br₂, HBr, a bromide compound, or a combination thereof used to practice one or more processes/methods covered by the claims of the '114 patent and that constitute a material part of the inventions claimed in the '114 patent. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '114 patent under 35 U.S.C. § 271(c) with respect to each coal-fired power plant connected to an Accused RC Facility.

262. AJG, Chem-Mod, and their associated RC Defendants, directly infringe the '114 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

263. DTE, Chem-Mod, and their associated RC Defendants, directly infringe the '114 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

264. CERT, Chem-Mod, and their associated RC Defendants, directly infringe the '114 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

265. AJG, DTE, CERT, Chem-Mod, and their associated RC Defendants also directly infringe when performing certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They perform each step of the '114 patent claims, or they engage a third party agent on their behalf to perform each step of the '114 patent claims that acts under their control.

266. Alternatively, AJG, DTE, CERT, Chem-Mod, and their associated RC Defendants also directly infringe by directing and controlling a third party to perform certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '114 patent claims.

267. Alternatively, AJG, DTE, CERT, Chem-Mod, and their associated RC Defendants also indirectly infringe by engaging a third party to perform certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '114 patent claims.

268. Defendants' acts of infringement have caused damage to ME2C. ME2C is entitled to recover from Defendants the damages sustained by ME2C as a result of Defendants' wrongful acts in an amount subject to proof at trial. In addition, the infringing acts and practices of Defendants have caused, are causing, and, unless such acts and practices are enjoined by the Court, will continue to cause immediate and irreparable harm to ME2C for which there is no adequate remedy at law, and for which ME2C is entitled to injunctive relief under 35 U.S.C. §

283.

COUNT TWO: INFRINGEMENT OF THE '147 PATENT

269. ME2C incorporates by reference the preceding paragraphs as if fully set forth herein.

270. U.S. Patent No. 8,168,147 (the "'147 patent"), entitled "Sorbents for the Oxidation and Removal of Mercury", was issued on May 1, 2012, naming Edwin S. Olson, Michael J. Holmes and John H. Pavlish as the inventors. Exhibit B ('147 Patent).

271. ME2C owns by assignment all rights, title, and interest in the '147 Patent, and holds all substantial rights pertinent to this suit, including the right to sue and recover for all past, current, and future infringement.

272. The '147 Patent is valid and enforceable and directed to patentable subject matter.

273. Defendants infringe claims 17-20 of the '147 patent.

274. ME2C provides the following explanation of infringement with regard to an exemplary claim.

275. Claim 17 of the '147 patent recites: "A method for separating mercury from a mercury containing gas."

276. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this method in order to comply with federal and/or state mercury regulations.

277. Claim 17 of the '147 patent recites: "promoting at least a portion of a particulate sorbent material comprising activated carbon by chemically reacting the sorbent material with a bromine containing promoter to form a promoted brominated sorbent, wherein the bromine containing promoter is in gaseous form, vapor form, or non-aqueous liquid form, and wherein the activated carbon contains graphene sheets having carbene species edge sites which react with the bromine containing promoter to form a carbocation paired with a bromide anion in the promoted brominated sorbent for oxidation of the mercury."

278. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step because they burn coal with added Br₂, HBr, a bromide compound, or a

combination thereof and/or they provide Br₂, HBr, a bromide compound, or a combination thereof into the combustion zone with the coal. The bromine containing promoter is in gaseous form when it comes into contact with activated carbon added by the Coal Plant Defendants and/or power plants connected to an Accused RC Facility. This contact causes the recited chemical reaction to occur.

279. Claim 17 of the '147 patent recites: "chemically reacting elemental mercury in the mercury containing gas with the promoted brominated sorbent to form a mercury/sorbent chemical composition."

280. As noted above, the Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step such that the recited chemical reaction occurs.

281. Claim 17 of the '147 patent recites: "separating particulates from the mercury containing gas, the particulates including ash and the mercury/sorbent chemical composition."

282. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this method in order to comply with federal and/or state mercury regulations.

283. Claim 17 of the '147 patent recites: "A method according to claim 1, further comprising injecting the particulate sorbent material at a sorbent material injection rate and injecting separately the bromine containing promoter into a gas stream whereby in-flight reaction produces the promoted brominated sorbent, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of the sorbent material."

284. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step because they burn coal with added Br₂, HBr, a bromide compound, or a combination thereof and/or they provide Br₂, HBr, a bromide compound, or a combination thereof into the combustion zone with the coal. In either case, the bromine containing promoter is injected into a gas stream, and it later comes into contact with activated carbon sorbent added by the Coal Plant Defendants and/or power plants connected to an Accused RC Facility. This contact causes in-flight promotion of the sorbent.

285. The bromine containing promoter is added at from about 1 to 30 grams per 100 grams of the sorbent material.

286. The Coal Plant Defendants have and continue to directly infringe, literally and/or under the doctrine of equivalents, the '147 patent under 35 U.S.C. § 271(a).

287. In addition, Vistra Energy Corp., NRG Energy Inc., and Talen Energy Corporation induce their respective subsidiary Defendants to infringe under 35 U.S.C. § 271(b). Vistra Energy Corp., NRG Energy Inc., and Talen Energy Corporation are each aware of the patents-in-suit, but nonetheless encourage their subsidiaries to infringe by, on information and belief, taking part in the supply contract process for activated carbon and bromine-containing additives at coal-fired power plants that directly infringe and signing, or encouraging their subsidiaries to sign, contracts with suppliers that provide the activated carbon and bromine-containing additives that lead to infringement.

288. AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to coal-fired power plants connected to an Accused RC Facility.

289. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

290. Alternatively, when AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants are willfully blind to the fact that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

291. The coal with added Br₂, HBr, a bromide compound, or a combination thereof provided by AJG, DTE, CERT, Chem-Mod and the RC Defendants is not a staple article or

commodity of commerce suitable for substantial non-infringing use. This coal is supplied to a conveyance that moves the coal toward the combustion chamber of a power plant that directly infringes the '147 patent. In addition, AJG, DTE, CERT, Chem-Mod and the RC Defendants tailor the amount of Br₂, HBr, a bromide compound, or a combination thereof added to the coal for the specific needs of the power plant.

292. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the provided coal has no substantial use other than to be combusted at the plant that will perform the step of injecting sorbent comprising activated carbon.

293. AJG, DTE, CERT, Chem-Mod and the RC Defendants took the above-described actions intending to cause infringing acts by others.

294. AJG, DTE, CERT, Chem-Mod and the RC Defendants have actual knowledge of the '147 patent and know that actions described above, if taken, would constitute infringement of that patent. Alternatively, AJG, DTE, CERT, Chem-Mod and the RC Defendants believe there is a high probability that others would infringe the '147 patent but have remained willfully blind to the infringing nature of those actions. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '147 patent under 35 U.S.C. § 271(b) with respect to each coal-fired power plant connected to an Accused RC Facility.

295. AJG, DTE, CERT, Chem-Mod and the RC Defendants indirectly infringes the '147 patent by contributing to infringement by others, such as its customers and end-users by offering to sell and/or selling within the United coal with added BR₂, HBR, a bromide compound, or a combination thereof used to practice one or more processes/methods covered by the claims of the '147 patent and that constitute a material part of the inventions claimed in the '147 patent. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '147 patent under 35 U.S.C. § 271(c) with respect to each coal-fired power plant connected to an Accused RC Facility.

296. AJG, Chem-Mod, and their associated RC Defendants, directly infringe the '147 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

297. DTE, Chem-Mod, and their associated RC Defendants, directly infringe the '147 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

298. CERT, Chem-Mod, and their associated RC Defendants, directly infringe the '114 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

299. AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also directly infringe when performing certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They perform each step of the '147 patent claims, or they engage a third party agent on their behalf to perform each step of the '147 patent claims that acts under their control.

300. Alternatively, AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also directly infringe by directing and controlling a third party to perform certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '147 patent claims.

301. Alternatively, AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also indirectly infringe by engaging a third party to perform certification testing of refined coal

designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '147 patent claims.

302. Defendants' acts of infringement have caused damage to ME2C. ME2C is entitled to recover from Defendants the damages sustained by ME2C as a result of Defendants' wrongful acts in an amount subject to proof at trial. In addition, the infringing acts and practices of Defendants have caused, are causing, and, unless such acts and practices are enjoined by the Court, will continue to cause immediate and irreparable harm to ME2C for which there is no adequate remedy at law, and for which ME2C is entitled to injunctive relief under 35 U.S.C. § 283.

COUNT THREE: INFRINGEMENT OF THE '225 PATENT

303. ME2C incorporates by reference the preceding paragraphs as if fully set forth herein.

304. U.S. Patent No. 10,589,225 (the "'225 patent"), entitled "Sorbents for the Oxidation and Removal of Mercury", was issued on March 17, 2020, naming Edwin S. Olson, Michael J. Holmes and John H. Pavlish as the inventors. Exhibit C ('225 Patent).

305. ME2C owns by assignment all rights, title, and interest in the '225 Patent, and holds all substantial rights pertinent to this suit, including the right to sue and recover for all past, current, and future infringement.

306. The '225 Patent is valid and enforceable and directed to patentable subject matter.

307. Defendants infringe claims 1-29 of the '225 patent.

308. ME2C provides the following explanation of infringement with regard to an exemplary claim.

309. Claim 1 of the '225 patent recites: "A method for treating a mercury-containing

gas.”

310. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this method in order to comply with federal and/or state mercury regulations.

311. Claim 1 of the '225 patent recites: “combusting a mixture comprising coal, pyrolysis char, and an additive comprising HBr, a bromide compound, or a combination thereof, to form the mercury-containing, gas.”

312. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step because they combust coal, pyrolysis char, and an additive comprising HBr, a bromide compound, or a combination thereof.

313. Claim 1 of the '225 patent recites: “adding a particulate sorbent material comprising activated carbon into the mercury-containing gas.”

314. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step by adding sorbent containing activated carbon to the gas that exits the combustion chamber.

315. The Coal Plant Defendants have and continue to directly infringe, literally and/or under the doctrine of equivalents, the '225 patent under 35 U.S.C. § 271(a).

316. In addition, Vistra Energy Corp., NRG Energy Inc., and Talen Energy Corporation induce their respective subsidiary Defendants to infringe under 35 U.S.C. § 271(b). Vistra Energy Corp., NRG Energy Inc., and Talen Energy Corporation are each aware of the patents-in-suit, but nonetheless encourage their subsidiaries to infringe by, on information and belief, taking part in the supply contract process for activated carbon and bromine-containing additives at coal-fired power plants that directly infringe and signing, or encouraging their subsidiaries to sign, contracts with suppliers that provide the activated carbon and bromine-containing additives that lead to infringement.

317. AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to coal-fired power plants connected to an Accused RC Facility.

318. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

319. Alternatively, when AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants are willfully blind to the fact that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

320. The coal with added Br₂, HBr, a bromide compound, or a combination thereof provided by AJG, DTE, CERT, Chem-Mod and the RC Defendants is not a staple article or commodity of commerce suitable for substantial non-infringing use. This coal is supplied to a conveyance that moves the coal toward the combustion chamber of a power plant that directly infringes the '225 patent. In addition, AJG, DTE, CERT, Chem-Mod and the RC Defendants tailor the amount of Br₂, HBr, a bromide compound, or a combination thereof added to the coal for the specific needs of the power plant.

321. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the provided coal has no substantial use other than to be combusted at the plant that will perform the step of injecting sorbent comprising activated carbon.

322. AJG, DTE, CERT, Chem-Mod and the RC Defendants took the above-described actions intending to cause infringing acts by others.

323. AJG, DTE, CERT, Chem-Mod and the RC Defendants have actual knowledge of the '225 patent and know that actions described above, if taken, would constitute infringement of that patent. Alternatively, AJG, DTE, CERT, Chem-Mod and the RC Defendants believe there is

a high probability that others would infringe the '225 patent but have remained willfully blind to the infringing nature of those actions. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '225 patent under 35 U.S.C. § 271(b) with respect to each coal-fired power plant connected to an Accused RC Facility.

324. AJG, DTE, CERT, Chem-Mod and the RC Defendants indirectly infringes the '225 patent by contributing to infringement by others, such as its customers and end-users by offering to sell and/or selling within the United coal with added Br₂, HBr, a bromide compound, or a combination thereof used to practice one or more processes/methods covered by the claims of the '225 patent and that constitute a material part of the inventions claimed in the '225 patent. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '225 patent under 35 U.S.C. § 271(c) with respect to each coal-fired power plant connected to an Accused RC Facility.

325. AJG, Chem-Mod, and their associated RC Defendants, directly infringe the '225 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

326. DTE, Chem-Mod, and their associated RC Defendants, directly infringe the '225 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

327. CERT, Chem-Mod, and their associated RC Defendants, directly infringe the '114 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

328. AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also directly infringe when performing certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They perform each step of the '225 patent

claims, or they engage a third party agent on their behalf to perform each step of the '225 patent claims that acts under their control.

329. Alternatively, AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also directly infringe by directing and controlling a third party to perform certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '225 patent claims.

330. Alternatively, AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also indirectly infringe by engaging a third party to perform certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '225 patent claims.

331. Defendants' acts of infringement have caused damage to ME2C. ME2C is entitled to recover from Defendants the damages sustained by ME2C as a result of Defendants' wrongful acts in an amount subject to proof at trial. In addition, the infringing acts and practices of Defendants have caused, are causing, and, unless such acts and practices are enjoined by the Court, will continue to cause immediate and irreparable harm to ME2C for which there is no adequate remedy at law, and for which ME2C is entitled to injunctive relief under 35 U.S.C. § 283.

COUNT FOUR: INFRINGEMENT OF THE '517 PATENT

332. ME2C incorporates by reference the preceding paragraphs as if fully set forth

herein.

333. U.S. Patent No. 10,596,517(the “’517 patent”), entitled “Sorbents for the Oxidation and Removal of Mercury”, was issued on March 24, 2020, naming Edwin S. Olson, Michael J. Holmes and John H. Pavlish as the inventors. Exhibit D (’517 Patent).

334. ME2C owns by assignment all rights, title, and interest in the ’517 Patent, and holds all substantial rights pertinent to this suit, including the right to sue and recover for all past, current, and future infringement.

335. The ’517 Patent is valid and enforceable and directed to patentable subject matter.

336. Defendants infringe claims 1-30 of the ’517 patent.

337. ME2C provides the following explanation of infringement with regard to an exemplary claim.

338. Claim 1 of the ’517 patent recites: “A method for reducing mercury in a mercury-containing gas.”

339. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this method in order to comply with federal and/or state mercury regulations.

340. Claim 1 of the ’517 patent recites: “combusting coal in a combustion chamber, the coal comprising an additive comprising Br₂, HBr, a bromide compound, or a combination thereof, to form the mercury-containing gas.”

341. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step because they combust coal with an additive comprising Br₂, HBr, a bromide compound, or a combination thereof to form mercury-containing gas.

342. Claim 1 of the ’517 patent recites: “collecting mercury in the mercury-containing gas with a sorbent added to the mercury-containing gas, the sorbent comprising activated carbon.”

343. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step by adding sorbent containing activated carbon to the gas that exits the combustion chamber. The mercury in the gas is then collected with the sorbent.

344. The Coal Plant Defendants have and continue to directly infringe, literally and/or

under the doctrine of equivalents, the '517 patent under 35 U.S.C. § 271(a).

345. In addition, Vistra Energy Corp., NRG Energy Inc., and Talen Energy Corporation induce their respective subsidiary Defendants to infringe under 35 U.S.C. § 271(b). Vistra Energy Corp., NRG Energy Inc., and Talen Energy Corporation are each aware of the patents-in-suit, but nonetheless encourage their subsidiaries to infringe by, on information and belief, taking part in the supply contract process for activated carbon and bromine-containing additives at coal-fired power plants that directly infringe and signing, or encouraging their subsidiaries to sign, contracts with suppliers that provide the activated carbon and bromine-containing additives that lead to infringement.

346. AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to coal-fired power plants connected to an Accused RC Facility.

347. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

348. Alternatively, when AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants are willfully blind to the fact that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

349. The coal with added Br₂, HBr, a bromide compound, or a combination thereof provided by AJG, DTE, CERT, Chem-Mod and the RC Defendants is not a staple article or commodity of commerce suitable for substantial non-infringing use. This coal is supplied to a conveyance that moves the coal toward the combustion chamber of a power plant that directly infringes the '517 patent. In addition, AJG, DTE, CERT, Chem-Mod and the RC Defendants

tailor the amount of Br₂, HBr, a bromide compound, or a combination thereof added to the coal for the specific needs of the power plant.

350. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the provided coal has no substantial use other than to be combusted at the plant that will perform the step of injecting sorbent comprising activated carbon.

351. AJG, DTE, CERT, Chem-Mod and the RC Defendants took the above-described actions intending to cause infringing acts by others.

352. AJG, DTE, CERT, Chem-Mod and the RC Defendants have actual knowledge of the '517 patent and know that actions described above, if taken, would constitute infringement of that patent. Alternatively, AJG, DTE, CERT, Chem-Mod and the RC Defendants believe there is a high probability that others would infringe the '517 patent but have remained willfully blind to the infringing nature of those actions. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '517 patent under 35 U.S.C. § 271(b) with respect to each coal-fired power plant connected to an Accused RC Facility.

353. AJG, DTE, CERT, Chem-Mod and the RC Defendants indirectly infringes the '517 patent by contributing to infringement by others, such as its customers and end-users by offering to sell and/or selling within the United coal with added BR₂, HBR, a bromide compound, or a combination thereof used to practice one or more processes/methods covered by the claims of the '517 patent and that constitute a material part of the inventions claimed in the '517 patent. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '517 patent under 35 U.S.C. § 271(c) with respect to each coal-fired power plant connected to an Accused RC Facility.

354. AJG, Chem-Mod, and their associated RC Defendants, directly infringe the '517 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal

comprising added Br₂, HBr, a bromide compound, or a combination thereof.

355. DTE, Chem-Mod, and their associated RC Defendants, directly infringe the '517 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

356. CERT, Chem-Mod, and their associated RC Defendants, directly infringe the '114 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

357. AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also directly infringe when performing certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They perform each step of the '517 patent claims, or they engage a third party agent on their behalf to perform each step of the '517 patent claims that acts under their control.

358. Alternatively, AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also directly infringe by directing and controlling a third party to perform certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '517 patent claims.

359. Alternatively, AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also indirectly infringe by engaging a third party to perform certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the

third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '517 patent claims.

360. Defendants' acts of infringement have caused damage to ME2C. ME2C is entitled to recover from Defendants the damages sustained by ME2C as a result of Defendants' wrongful acts in an amount subject to proof at trial. In addition, the infringing acts and practices of Defendants have caused, are causing, and, unless such acts and practices are enjoined by the Court, will continue to cause immediate and irreparable harm to ME2C for which there is no adequate remedy at law, and for which ME2C is entitled to injunctive relief under 35 U.S.C. § 283.

COUNT FIVE: INFRINGEMENT OF THE '430 PATENT

361. ME2C incorporates by reference the preceding paragraphs as if fully set forth herein.

362. U.S. Patent No. 10,668,430 (the "'430 patent"), entitled "Sorbents for the Oxidation and Removal of Mercury", was issued on March 24, 2020, naming Edwin S. Olson, Michael J. Holmes and John H. Pavlish as the inventors. Exhibit D ('430 Patent).

363. ME2C owns by assignment all rights, title, and interest in the '430 Patent, and holds all substantial rights pertinent to this suit, including the right to sue and recover for all past, current, and future infringement.

364. The '430 Patent is valid and enforceable and directed to patentable subject matter.

365. Defendants infringe claims 1-29 of the '430 patent.

366. ME2C provides the following explanation of infringement with regard to an exemplary claim.

367. Claim 1 of the '430 patent recites: "A method of separating mercury from a mercury-containing gas."

368. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this method in order to comply with federal and/or state mercury regulations.

369. Claim 1 of the '430 patent recites: “combusting coal in a combustion chamber, to provide the mercury-containing gas, wherein the coal comprises an additive comprising Br₂, HBr, a bromide compound, or a combination thereof, wherein the additive is added to the coal before the coal enters the combustion chamber, or the combustion chamber comprises an additive comprising Br₂, HBr, a bromide compound, or a combination thereof or a combination thereof.”

370. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step because they combust coal with an additive comprising Br₂, HBr, a bromide compound, or a combination thereof to form mercury-containing gas.

371. Claim 1 of the '430 patent recites: “injecting a sorbent comprising activated carbon into the mercury-containing gas downstream of the combustion chamber.”

372. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step by injecting sorbent containing activated carbon downstream of the combustion chamber.

373. Claim 1 of the '430 patent recites: “contacting mercury in the mercury-containing gas with the sorbent.”

374. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step because mercury contained in the gas exiting the combustion chamber contacts the sorbent as all of this material is contained in the same gas.

375. Claim 1 of the '430 patent recites: “separating the sorbent contacted with the mercury from the mercury-containing gas.”

376. The Coal Plant Defendants and power plants connected to an Accused RC Facility perform this step using equipment to collect the mercury captured by the sorbent in order to comply with mercury regulations.

377. The Coal Plant Defendants have and continue to directly infringe, literally and/or under the doctrine of equivalents, the '147 patent under 35 U.S.C. § 271(a).

378. In addition, Vistra Energy Corp., NRG Energy Inc., and Talen Energy Corporation induce their respective subsidiary Defendants to infringe under 35 U.S.C. § 271(b). Vistra Energy

Corp., NRG Energy Inc., and Talen Energy Corporation are each aware of the patents-in-suit, but nonetheless encourage their subsidiaries to infringe by, on information and belief, taking part in the supply contract process for activated carbon and bromine-containing additives at coal-fired power plants that directly infringe and signing, or encouraging their subsidiaries to sign, contracts with suppliers that provide the activated carbon and bromine-containing additives that lead to infringement.

379. AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to coal-fired power plants connected to an Accused RC Facility.

380. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

381. Alternatively, when AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants are willfully blind to the fact that the coal-fired power plant will perform the step of injecting sorbent comprising activated carbon.

382. The coal with added Br₂, HBr, a bromide compound, or a combination thereof provided by AJG, DTE, CERT, Chem-Mod and the RC Defendants is not a staple article or commodity of commerce suitable for substantial non-infringing use. This coal is supplied to a conveyance that moves the coal toward the combustion chamber of a power plant that directly infringes the '430 patent. In addition, AJG, DTE, CERT, Chem-Mod and the RC Defendants tailor the amount of Br₂, HBr, a bromide compound, or a combination thereof added to the coal for the specific needs of the power plant.

383. When AJG, DTE, CERT, Chem-Mod and the RC Defendants provide coal with

added Br₂, HBr, a bromide compound, or a combination thereof to a coal-fired power plant with an activated carbon injection system, AJG, DTE, CERT, Chem-Mod and the RC Defendants know that the provided coal has no substantial use other than to be combusted at the plant that will perform the step of injecting sorbent comprising activated carbon.

384. AJG, DTE, CERT, Chem-Mod and the RC Defendants took the above-described actions intending to cause infringing acts by others.

385. AJG, DTE, CERT, Chem-Mod and the RC Defendants have actual knowledge of the '430 patent and know that actions described above, if taken, would constitute infringement of that patent. Alternatively, AJG, DTE, CERT, Chem-Mod and the RC Defendants believe there is a high probability that others would infringe the '430 patent but have remained willfully blind to the infringing nature of those actions. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '430 patent under 35 U.S.C. § 271(b) with respect to each coal-fired power plant connected to an Accused RC Facility.

386. AJG, DTE, CERT, Chem-Mod and the RC Defendants indirectly infringes the '430 patent by contributing to infringement by others, such as its customers and end-users by offering to sell and/or selling within the United coal with added BR₂, HBR, a bromide compound, or a combination thereof used to practice one or more processes/methods covered by the claims of the '430 patent and that constitute a material part of the inventions claimed in the '430 patent. AJG, DTE, CERT, Chem-Mod and the RC Defendants therefore infringe the '430 patent under 35 U.S.C. § 271(c) with respect to each coal-fired power plant connected to an Accused RC Facility.

387. AJG, Chem-Mod, and their associated RC Defendants, directly infringe the '430 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

388. DTE, Chem-Mod, and their associated RC Defendants, directly infringe the '430 patent with respect to each joint enterprise formed between these Defendants and each coal-fired

power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

389. CERT, Chem-Mod, and their associated RC Defendants, directly infringe the '114 patent with respect to each joint enterprise formed between these Defendants and each coal-fired power plant with an activated carbon injection system to which they provide refined coal comprising added Br₂, HBr, a bromide compound, or a combination thereof.

390. AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also directly infringe when performing certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They perform each step of the '430 patent claims, or they engage a third party agent on their behalf to perform each step of the '430 patent claims that acts under their control.

391. Alternatively, AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also directly infringe by directing and controlling a third party to perform certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '430 patent claims.

392. Alternatively, AJG, DTE, CERT Chem-Mod, and their associated RC Defendants also indirectly infringe by engaging a third party to perform certification testing of refined coal designed for coal-fired power plants that use sorbent comprising activated carbon. They either instruct the third party to perform the test using coal with added bromine or bromide and using sorbent comprising activated carbon downstream of the combustion chamber, or they instruct the third party to simulate the operation of a particular plant that uses sorbent comprising activated carbon. In either case, they condition payment for the testing on the third party performing each step of the '430 patent claims.

393. Defendants' acts of infringement have caused damage to ME2C. ME2C is entitled to recover from Defendants the damages sustained by ME2C as a result of Defendants' wrongful acts in an amount subject to proof at trial. In addition, the infringing acts and practices of Defendants have caused, are causing, and, unless such acts and practices are enjoined by the Court, will continue to cause immediate and irreparable harm to ME2C for which there is no adequate remedy at law, and for which ME2C is entitled to injunctive relief under 35 U.S.C. § 283.

JURY DEMAND

Plaintiff hereby demands a trial by jury on all issues so triable.

PRAYER FOR RELIEF

WHEREFORE Plaintiff Midwest Energy Emissions Corp. asks this Court for an order granting the following relief:

- a. A judgment in favor of Plaintiff that Defendants have infringed, either literally and/or under the doctrine of equivalents, the '114, '147, '225, '517, and '430 patents;
- b. A judgment and order finding that Defendants' infringement has been willful;
- c. A permanent injunction prohibiting Defendants from further acts of infringement;
- d. A judgment and order requiring Defendants to pay Plaintiff its damages, costs, expenses, and any enhanced damages to which Plaintiff is entitled for Defendants' infringement;
- e. A judgment and order requiring Defendants to provide an accounting and to pay supplemental damages to Plaintiff, including without limitation, pre-judgment and post-judgment interest;
- f. A judgment and order finding that this is an exceptional case within the meaning of 35 U.S.C. § 285 and awarding Plaintiff its reasonable attorneys' fees against Defendants; and
- g. Any and all other relief as the Court may deem appropriate and just under the circumstances.

Dated: July 15, 2020

Respectfully submitted,

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***Midwest Energy Emissions Corp. and
MES Inc.***

EXHIBIT A

(12) **United States Patent**
Olson et al.(10) **Patent No.:** **US 10,343,114 B2**(45) **Date of Patent:** ***Jul. 9, 2019**(54) **SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY**(58) **Field of Classification Search**

None

See application file for complete search history.

(71) Applicant: **Midwest Energy Emissions Corp.**,
Lewis Center, OH (US)(56) **References Cited**(72) Inventors: **Edwin S. Olson**, Grand Forks, ND
(US); **Michael J. Holmes**, Thompson,
ND (US); **John H. Pavlish**, East Grand
Forks, MN (US)

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(73) Assignee: **Midwest Energy Emissions Corp.**,
Lewis Center, OH (US)

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(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
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This patent is subject to a terminal dis-
claimer.

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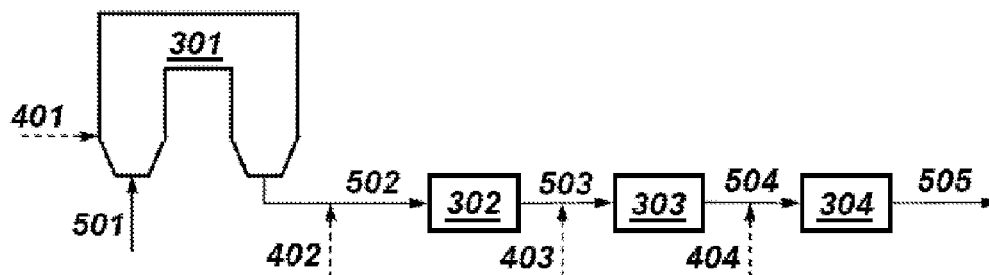
(21) Appl. No.: **15/978,760**(22) Filed: **May 14, 2018**(65) **Prior Publication Data**

US 2018/0257031 A1 Sep. 13, 2018

Primary Examiner — Amber R Orlando(74) *Attorney, Agent, or Firm* — Schwegman Lundberg &
Woessner, P.A.**Related U.S. Application Data**(60) Continuation-in-part of application No. 15/295,594,
filed on Oct. 17, 2016, which is a continuation of
(Continued)(51) **Int. Cl.**
B01D 53/64 (2006.01)
B01J 20/34 (2006.01)
(Continued)(52) **U.S. Cl.**
CPC **B01D 53/64** (2013.01); **B01D 53/10**
(2013.01); **B01D 53/346** (2013.01); **B01D**
53/83 (2013.01);
(Continued)(57) **ABSTRACT**

A promoted carbon and/or non-carbon base sorbent are described that are highly effective for the removal of mercury from flue gas streams. The promoted sorbent comprises a carbon and/or non-carbon base sorbent that has reacted with and contains forms of halogen and halides. Optional components may be added to increase and/or preserve reactivity and mercury capacity. These may be added directly with the base sorbent, or in-flight within a gas stream (air, flue gas, etc.), to enhance base sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The promoted sorbent can be regenerated and reused. Base sorbent treatment and preparation methods are also described. New

(Continued)



US 10,343,114 B2

Page 2

methods for in-flight preparation, introduction, and control of the active base sorbent into the mercury contaminated gas stream are described.

30 Claims, 6 Drawing Sheets

Related U.S. Application Data

application No. 14/102,896, filed on Dec. 11, 2013, now Pat. No. 9,468,886, which is a continuation of application No. 12/429,058, filed on Apr. 23, 2009, now Pat. No. 8,652,235, which is a continuation-in-part of application No. 12/201,595, filed on Aug. 29, 2008, which is a division of application No. 11/209,163, filed on Aug. 22, 2005, now Pat. No. 7,435,286.

(60) Provisional application No. 60/605,640, filed on Aug. 30, 2004.

(51) Int. Cl.

B01J 20/22 (2006.01)
B01J 20/28 (2006.01)
B01J 20/20 (2006.01)
B01J 20/12 (2006.01)
B01J 20/10 (2006.01)
B01J 20/04 (2006.01)
B01J 20/02 (2006.01)
B01D 53/34 (2006.01)
B01D 53/83 (2006.01)
B01D 53/96 (2006.01)
B01D 53/10 (2006.01)

(52) U.S. Cl.

CPC **B01D 53/96** (2013.01); **B01J 20/027** (2013.01); **B01J 20/0262** (2013.01); **B01J 20/04** (2013.01); **B01J 20/041** (2013.01); **B01J 20/043** (2013.01); **B01J 20/10** (2013.01); **B01J 20/106** (2013.01); **B01J 20/12** (2013.01); **B01J 20/20** (2013.01); **B01J 20/223** (2013.01); **B01J 20/28004** (2013.01); **B01J 20/3416** (2013.01); **B01D 2251/108** (2013.01); **B01D 2253/102** (2013.01); **B01D 2257/602** (2013.01); **B01D 2258/0283** (2013.01); **B01D 2259/128** (2013.01); **B01J 2220/42** (2013.01)

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US 10,343,114 B2

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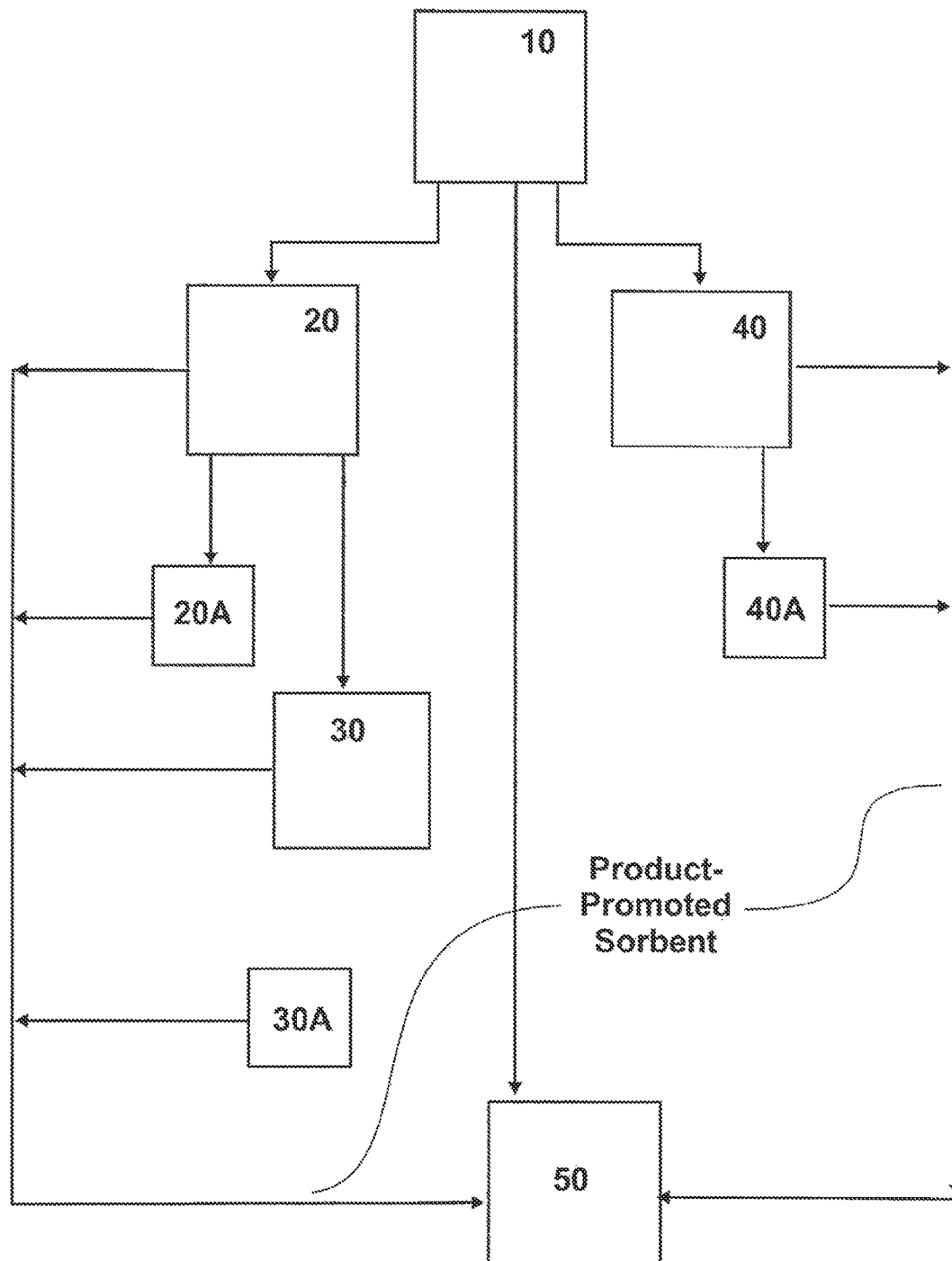
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Jul. 9, 2019

Sheet 1 of 6

US 10,343,114 B2**FIG. 1**

U.S. Patent

Jul. 9, 2019

Sheet 2 of 6

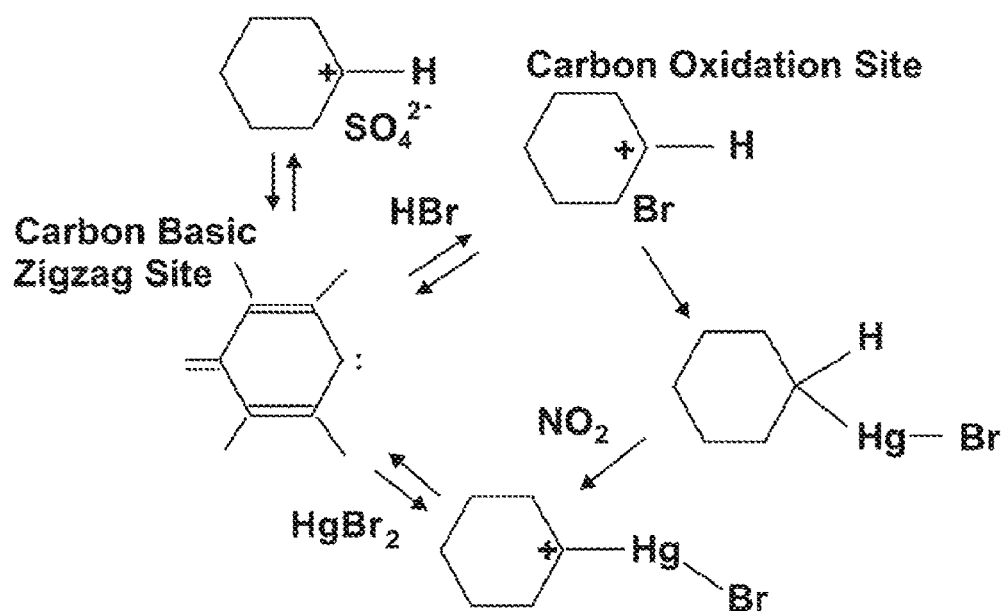
US 10,343,114 B2

FIG. 2

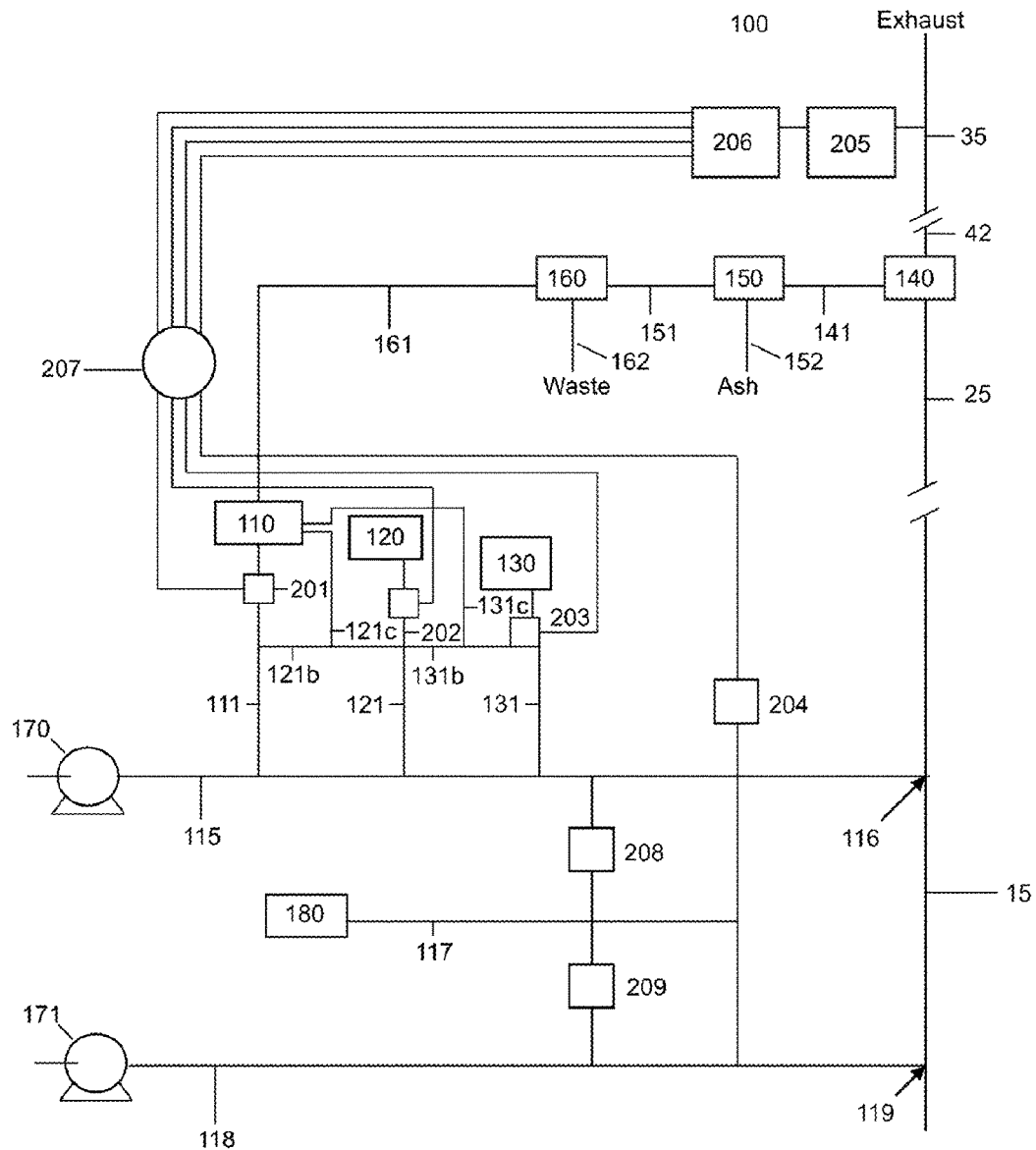


FIG. 3

U.S. Patent

Jul. 9, 2019

Sheet 4 of 6

US 10,343,114 B2

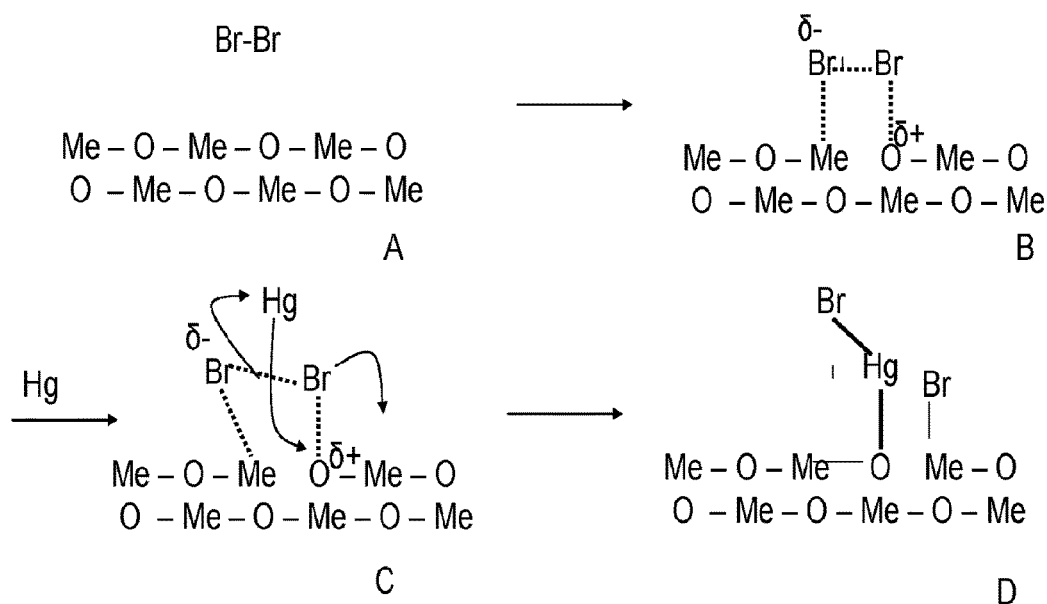


FIG. 4

U.S. Patent

Jul. 9, 2019

Sheet 5 of 6

US 10,343,114 B2

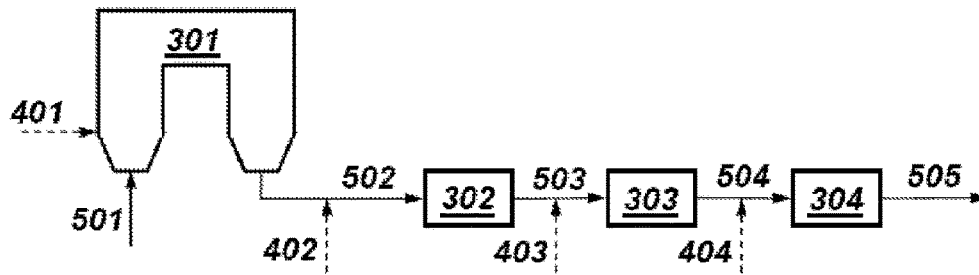


FIG. 5A

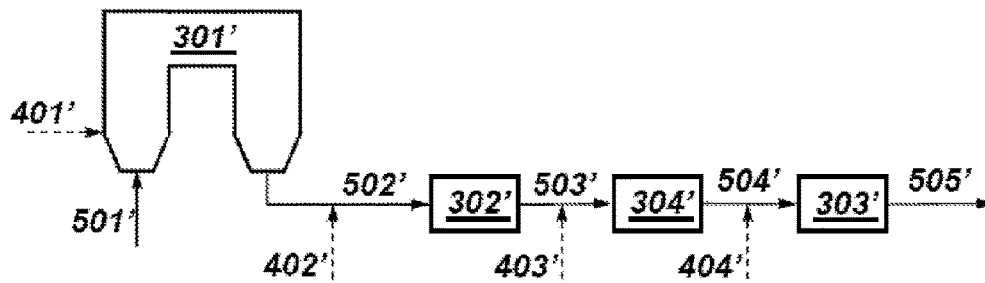


FIG. 5B

U.S. Patent

Jul. 9, 2019

Sheet 6 of 6

US 10,343,114 B2

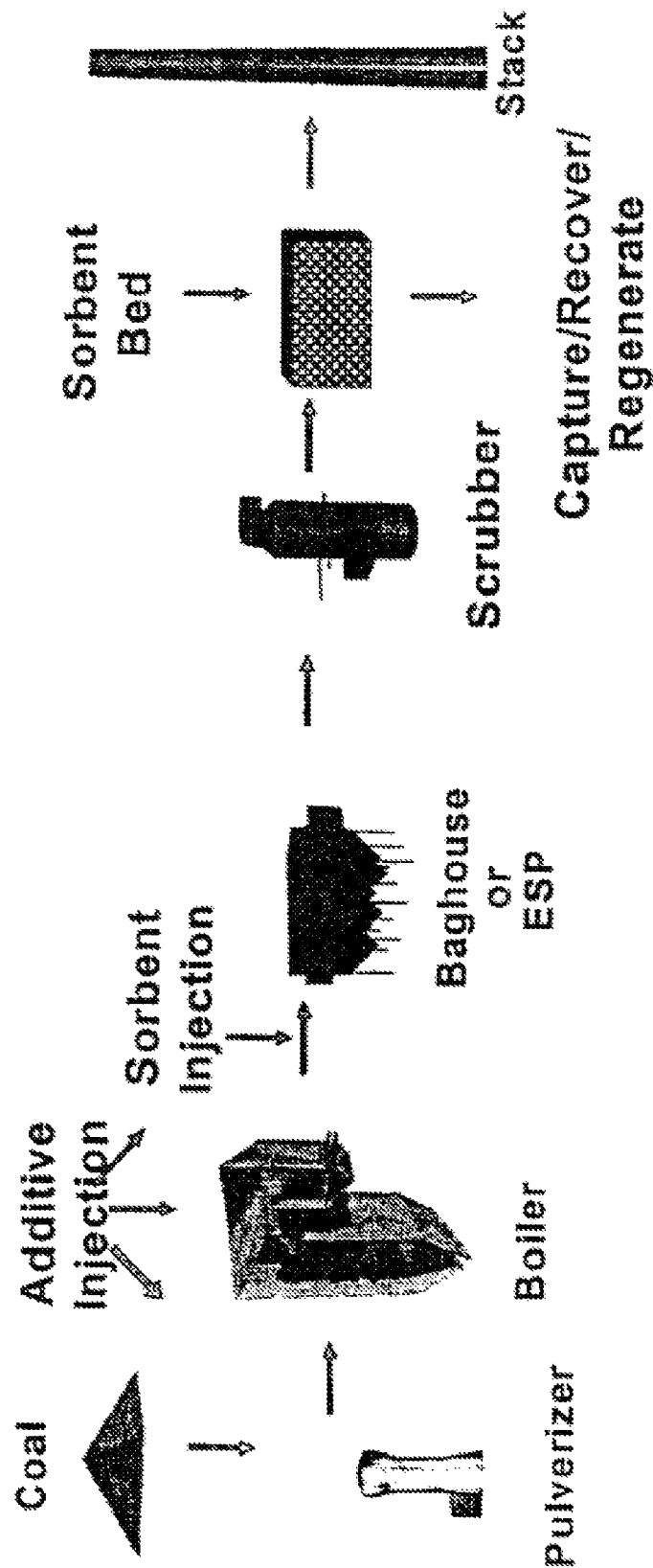


FIG. 6

US 10,343,114 B2

1

**SORBENTS FOR THE OXIDATION AND
REMOVAL OF MERCURY****CROSS-REFERENCE TO RELATED
APPLICATIONS**

This application is a continuation-in-part of U.S. patent application Ser. No. 15/295,594, filed Oct. 17, 2016, which is a continuation of U.S. patent application Ser. No. 14/102,896 filed on Dec. 11, 2013 (now U.S. Pat. No. 9,468,886), which is a continuation of U.S. patent application Ser. No. 12/429,058 filed on Apr. 23, 2009 (now U.S. Pat. No. 8,652,235), which is a continuation-in-part of U.S. patent application Ser. No. 12/201,595 filed on Aug. 29, 2008 (abandoned), which is a divisional of U.S. patent application Ser. No. 11/209,163 filed on Aug. 22, 2005 (now U.S. Pat. No. 7,435,286), which claims priority from provisional application Ser. No. 60/605,640 filed on Aug. 30, 2004. The disclosures of U.S. patent application Ser. Nos. 14/102,896; 12/429,058; 12/201,595; 11/209,163; and 60/605,640 are hereby incorporated herein by reference to the extent appropriate.

BACKGROUND OF THE INVENTION**Technical Field of the Invention**

The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

Background of the Invention

The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, a day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as off-gases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a particulate control device such as a baghouse or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit

2

slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when an ESP is used to collect the carbon because the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is relatively unreactive toward mercury. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

One solution has been to add an oxidative sorbent comprising an aluminosilicate material impregnated with a very heavy dosage of one or more oxidative metal halides plus activated carbon. For example, refer to Varma et al. (20070140940). However, the amounts of metal salts required for Hg oxidation are generally relatively large and expensive. Also, several of the salts that can be used in such a process are highly toxic. Although the metal salts are present for oxidation in this process, activated carbon is essential for getting adsorption of the Hg. As such, there is no synergistic role for the aluminosilicates as they appear to be only a support for the oxidizing salts.

Another approach has been the injection of aluminosilicate particulate such as bentonite, which contains neither oxidizing salts nor halogen complexes with a Lewis base site, and thus lacks the more powerful oxidizing capability of the said complexes as described in this application. For example, see U.S. Pat. No. 7,413,719. Additionally, the injection of an aluminosilicate (kaolin or metakaolin) containing calcium hypochlorite which thermally decomposes to form halogen is also known. For example, see U.S. Patent Application No. 20030103882. Thus these and similar impregnated aluminosilicate technologies require time in flight at appropriate high temperatures to heat the impregnated salt(s) to generate an oxidation site. This clearly represents a kinetic barrier to activation in contrast to the extremely fast complexing reaction of the Lewis acid on the surface of the appropriate Lewis base sorbent described in the present patent. The kinetic barrier is only for heating up the calcium hypochlorite to decompose it to Cl atoms or molecules. Halogen (bimolecular or atomic) would complex with carbon or noncarbon at any lower temperature to form reactive oxidation sites. Also, halide would require a very high temp or strong acid to form reactive halogen or halogen complex.

Yet another approach is the injection of bentonite plus a metal sulfide and a metal salt, none of which is oxidizing to elemental mercury and would require a slow thermal activation step. For example, see U.S. Patent Application No. 20070119300.

The injection of halogen or halogen precursors in a hot zone, followed by contact with an alkaline material in a wet or dry scrubber is another approach known in the art. With such an approach, elemental mercury is claimed to be oxidized by the halogen to Hg(II) which is collected by the alkaline material in the scrubber. For example, see U.S. Pat. No. 6,808,692 (Oehr), U.S. Pat. No. 3,849,267 (Hilgen), U.S. Pat. No. 5,435,980 (Felsvang), U.S. Pat. No. 6,375,909

US 10,343,114 B2

3

(Dangtran), U.S. Patent Application No. 20020114749 (Cole), U.S. Pat. No. 6,638,485 (Iida), U.S. Patent Application No. 20030185718 (Sellakumar), U.S. Patent Application No. 20030147793 (Breen), and U.S. Pat. No. 6,878,358 (Vosteen). However, even though it is known to inject halogen forms at some stage of the combustion process, such a process does not utilize a complexing method on a sorbent surface for conducting the oxidation and capture. Further, the alkaline material is rapidly surface-coated by the large concentrations of acid gases, lowering its capacity for adsorption of Hg(II). It is also recognized that the halogen forms initially introduced or generated are far more reactive to the large concentrations of SO₂ and moisture in the flue gas, and so gas-phase reactions of the halogens with Hg are hindered. In contrast, the present invention takes advantage of the Lewis acid complexes that rapidly form on the sorbent surface to effect the Hg oxidation, rather than rely on gas phase reactions for oxidation. Thus HCl, HBr, SO₂Br, and other gas-phase products all festoon the surface and promote the activity of the sorbent by forming complexes with the sorbent to form a promoted sorbent.

Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants, including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY

The various embodiments of the present invention overcome the various aspects of the deficiencies of the prior art and provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

A halogen/halide-promoted sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises any activated carbon and/or non-carbon compound, such as porous or vesicular felsic or basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, and/or bicarbonate compounds, or a combination thereof. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the promoted sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. Methods for in-flight preparation, introduction, and control of the sorbent, promoter and promoted sorbent into the mercury contaminated gas stream are described.

When a promoted or a non-promoted base sorbent reacts with elemental or oxidized mercury, a mercury/sorbent chemical composition is formed and, in the case of elemental mercury reacting with the promoted base sorbent, the mercury is oxidized. As discussed in further detail in other portions of the specification, the base sorbent may be either a carbon or a non-carbon material or a combination thereof. Additionally, the mercury/sorbent chemical composition may be comprised of covalent bonds, ionic bonds and/or chemical complexes between the promoted or non-promoted base sorbent and the oxidized mercury. The Lewis basic groups on the non-promoted base sorbent, or the non-promoted portions of a promoted base sorbent, are available for reaction with the Lewis acid groups of already existing oxidized mercury in the mercury containing gas. Thus,

4

mercury may be removed from the mercury containing gas stream through the formation of multiple and various mercury/sorbent chemical compositions even within the same process. For example, multiple sites on a sorbent particulate can form multiple and various mercury/sorbent chemical compositions in the case where only a portion of the sites on the base sorbent particulate are promoted.

In some embodiments, a carbon and/or non-carbon promoted sorbent and/or a combination thereof is provided comprising a sorbent structure that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream. The carbon sorbent comprises reactive Lewis acid groups/sites; the non-carbon sorbent comprises reactive Lewis basic groups/sites.

In an embodiment, a promoted carbon and/or non-carbon sorbent is provided wherein the base sorbent is selected from the group consisting of carbon, activated carbon, porous or vesicular felsic and basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, and/or bicarbonate compounds, or a combination thereof, with an average particle size similar to that of fly ash produced from a thermal process (combustion or gasification) or greater than that of fly ash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the promoted sorbent (carbon, non-carbon, or their combination) may have a mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base sorbent (carbon, non-carbon, or their combination) may have a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the promoted sorbent comprises from about 1 to about 30 grams of promoter per 100 grams of base sorbent. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the promoted sorbent are enhanced.

In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt % of the concentration of the promoter on the finished sorbent.

In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the base sorbent.

In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base sorbent. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base sorbent. In another embodiment, the promoter and optional secondary component are combined with the base sorbentsubstantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

In an embodiment, a method is provided comprising providing a granular base sorbent and reacting the base

US 10,343,114 B2

5

sorbent with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted sorbent effective for removal of mercury from a gas stream. In a further embodiment, the reaction product comprises from about 1 to about 30 grams of promoter per 100 grams of base sorbent. In another embodiment the reaction product has an average particle-size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment, the reaction product has a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the promoter is in the gas phase when contacting the base sorbent (carbon, non-carbon, or their combination). In another embodiment, the promoter is in an organic solvent when contacting the base sorbent (carbon, non-carbon, or their combination).

In another embodiment, the promoter is selected from the group consisting of Br_2 , a Group V bromide, a Group VI bromide, and combinations thereof.

In another embodiment, the method further comprises reacting the granular non-carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the promoted sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the non-carbon base sorbent. In another embodiment, the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S , SO_2 , H_2Se , SeO_2 , CS_2 , P_2S_5 , and combinations thereof. In an embodiment, a method is provided for control of mercury in a flue gas with substantially lower sorbent requirements. Through enhanced sorbent reactivity, mercury removal per gram of sorbent is increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

In an embodiment, the promoted sorbent is introduced by direct injection into the flue gas stream. In another embodiment, the base sorbent is promoted within the flue gas stream.

In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a base sorbent, either by injection or in situ creation, into a mercury-containing flue gas stream, collecting greater than 70 wt % of the mercury in the flue gas on the promoted sorbent to produce a cleaned flue gas, and substantially recovering the promoted sorbent from the cleaned flue gas. In embodiments where less than 70 wt % mercury removal is desired, the required removal is attained using less base sorbent as would be required with standard base sorbent. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered promoted sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of base sorbent and promoter. In another embodiment the injected promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination) and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodi-

6

ment, the promoter is added at from about 1 to about 30 grams per 100 grams of the base sorbent (carbon, non-carbon, or their combination).

In another embodiment, the injected promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination), a promoter, and an optional secondary component to enhance the reactivity and capacity of the promoted sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt % of the promoter content. In another embodiment, the method further comprises adding to the promoted sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S , SO_2 , H_2Se , SeO_2 , CS_2 , P_2S_5 , and combinations thereof.

In an embodiment, the method further comprises coinjecting an optional alkaline material, including without limitation alkaline and alkaline-earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce promoted sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the promoted sorbent. In another embodiment, the promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination) and a promoter within the flue gas stream or in a transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of the base sorbent (carbon, non-carbon, or their combination), wherein the rate at which the promoter is added and the rate of promoted sorbent injection are determined by a digital computer based, at least in part, on the monitored mercury content of the cleaned flue gas.

In an embodiment, a method for reducing the mercury content of a mercury and ash-containing gas stream is provided wherein particulate carbon and/or non-carbon promoted sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the promoted sorbent particles, the promoted sorbent particles are separated from the ash particles on the basis of size, and the promoted sorbent particles are reinjected to the gas stream. In another embodiment, the mercury-containing promoted sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is coinjecting into the gas stream. In another embodiment, the promoted sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

In an embodiment, a method for reducing mercury in a mercury-containing gas to a desired level is disclosed. The method comprises reacting a carbon base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to

US 10,343,114 B2

7

produce a promoted carbon sorbent; allowing said promoted carbon sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas. In some embodiments, the carbon base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the carbon base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In an embodiment, the rate at which the carbon base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

In a further embodiment, the method comprises reacting a non-carbon base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted non-carbon sorbent; allowing said promoted non-carbon sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas. In some embodiments, the non-carbon base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the non-carbon base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In an embodiment, the rate at which the non-carbon base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

In a further embodiment, a method for reducing mercury in a mercury-containing gas to a desired level is presented. The method comprises reacting a base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted sorbent, wherein said base sorbent is selected from the group consisting of a non-carbon material, a carbon material, and combination thereof; allowing said promoted sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas.

In some embodiments, the base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In some embodiments, introducing the base sorbent and the promoter comprises injecting the base sorbent and the promoter into the mercury-containing gas. In some embodiments, the promoter is introduced into the mercury-containing gas upstream of the introduction of the base sorbent. In some embodiments, the promoter is introduced upstream of a boiler or a combustion chamber. In an embodiment, the rate at which the base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

8

In an embodiment, the base sorbent for the promoted sorbent is selected from the group consisting of carbon, activated carbon, porous felsic materials, vesicular felsic materials, porous basaltic materials, vesicular basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, bicarbonate compounds, and combinations thereof. In embodiments, the non-carbon material comprises Lewis basic groups and the carbon material comprises Lewis acid groups. In some cases, the non-carbon material comprises amorphous forms of tectosilicates comprising nanoscale cavities lined with Lewis basic oxygen associated with alkaline-earth metals. The alkaline-earth metals comprise Group I and Group II alkaline-earth metals. In some other cases, the non-carbon material comprises amorphous forms of phyllosilicates comprising nanoscale cavities lined with Lewis basic oxygen.

In an embodiment, the promoted sorbent comprises metastable complexes formed between the promoter of this disclosure and inorganic species on the non-carbon base sorbent. In some embodiments, the inorganic species is selected from the group consisting of sodium compounds, calcium compounds, magnesium compounds, aluminum compounds, iron compounds, and combinations thereof. In an embodiment, the promoted sorbent comprises metastable complexes formed between the promoter of this disclosure and metal-oxygen-metal structures on the non-carbon base sorbent. In some embodiments, the promoter after being complexed with the metal-oxygen-metal structures is in the form selected from the group consisting of a dihalogen group, a halogen atom, a hydrohalogen group, a Group V halide, a Group VI halide, and combinations thereof. In an embodiment, the promoted sorbent comprises activated Lewis basic groups or activated Lewis acid groups or combination thereof. In some embodiments, the interaction between promoted sorbent and said mercury-containing gas stream comprises mercury diffusing from the gas phase onto said promoted sorbent surface; and reacting with the activated Lewis basic groups or activated Lewis acid groups or combination thereof to cause chemisorption on the promoted sorbent surface.

In an embodiment, the method for reducing mercury in a mercury-containing gas to a desired level further comprises pretreating the base sorbent to increase the number of Lewis basic groups or Lewis acid groups or combination thereof. In some cases, the pretreating methods comprise chemical treatment, thermal treatment, vacuum treatment, and combinations thereof. In some embodiments, chemical treatment comprises acid treatment and alkaline treatment. In an embodiment, the method for reducing mercury in a mercury-containing gas to a desired level further comprises introducing an alkali component into the mercury-containing gas.

As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from combustion and gasification systems.

The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the

US 10,343,114 B2

9

same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

FIG. 1 schematically illustrates methods for preparation of promoted carbon and/or non-carbon sorbents in accordance with the present invention.

FIG. 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

FIG. 3 schematically illustrates preparation of promoted carbon and/or non-carbon sorbents and processes for flue gas mercury reduction in flue gases and/or product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon and/or non-carbon sorbent.

FIG. 4 illustrates a mechanism for promotion of metal oxide base sorbent via formation of a reactive halogen complex sorbent and subsequent capture of elemental mercury on the promoted sorbent.

FIG. 5A schematically illustrates an exemplary process flow diagram for in-flight preparation of a promoted carbon and/or non-carbon sorbent.

FIG. 5B schematically illustrates an exemplary process flow diagram for in-flight preparation of a promoted carbon and/or non-carbon sorbent.

FIG. 6 is a block diagram illustrating the use of the invention in a coal fueled facility.

DETAILED DESCRIPTION

Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide-promoted sorbents using a bromide (or other halogen/halide) treatment of the promoted sorbent, that capture mercury via mercury-sorbent surface reactions, at very short contact times of seconds or less. The reactivity of the promoted sorbent toward the pollutants (i.e., mercury) is greatly enhanced, and the sorption capacity can be regenerated; i.e., the promoted sorbent may be regenerated, recycled and/or reused.

The treated base sorbents (carbon, non-carbon, or their combination), treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus it should be understood that the terms combus-

10

tion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

Hereinafter the disclosure may at times discuss the use of carbon base sorbents in further details; however the use of non-carbon base sorbents and a combination of carbon and non-carbon base sorbents is also contemplated to at least the same degree as carbon base sorbents.

Referring now to FIG. 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture in a mercury containing gas, such as a flue gas and/or product gas from gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base sorbent while block 20 illustrates adding a halogen or halide promoter that reacts with the base sorbent to produce a product-promoted sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A to produce a product-promoted sorbent suitable for injection.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base sorbent as shown by block 10, adding a halogen or halide promoter that reacts with the base sorbent, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product-promoted sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A to produce a product-promoted sorbent suitable for injection.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base sorbent as illustrated at block 10 and adding a halogen or halide promoter and a secondary component to the base sorbent together, with which they react to produce a product-promoted sorbent as illustrated by block 40. As above, in embodiments where vapor additions are made to the base sorbent, no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A to produce a product-promoted sorbent suitable for injection.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-50 in combination with path 20-50. In this embodiment, a base sorbent as illustrated by block 10 is introduced to the mercury containing gas as illustrated by block 50 while a halogen or halide promoter as illustrated by block 20 is introduced to the mercury containing gas stream. Thus the base sorbent and promoter react at block 50 to produce a product-promoted sorbent. In a similar manner, a secondary component as illustrated by block 30 may be added to the halogen or halide promoter as illustrated by block 20 and introduced into the mercury containing gas as illustrated by block 50. In embodiments where both the halogen or halide promoter and secondary component are added, for example, by vapor, no further steps may be taken. In embodiments where the halogen or halide and/or secondary component are

US 10,343,114 B2

11

added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A and/or block 30A.

Referring still to FIG. 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a mercury containing gas stream is treated with product-promoted carbon sorbent prepared as described above.

In some preferred embodiments, the carbon base sorbent provided may preferably be any of several types, as understood by those skilled in the art. For example, the carbon base sorbent may include powdered activated carbon, granular activated carbon, carbon black, unburned carbon, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product-promoted carbon sorbent, or other types as known in the art.

In some preferred embodiments, the carbon base sorbent provided may preferably have a mass mean particle size greater than the fly ash in a mercury containing gas, such as a flue gas stream, to be treated.

In some preferred embodiments, the carbon base sorbent provided may preferably have a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle-size distribution greater than that of the fly ash or entrained ash in a flue gas stream, or other mercury containing gas, to be treated, such that the activated carbon and ash can be separated by physical means.

In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the carbon base sorbent may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2 , respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2 , water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

Referring now to FIG. 4, a theory is illustrated developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in FIG. 4, a molecular bromine molecule forms a complex with the surface of the base sorbent comprising a high surface area form of a metal oxide. Complexing with bromine can occur at surface and defect sites on the surface of the glassy amorphous tectosilicates by association with the Lewis basic oxygen lining the interstitial cavities and the alkali actions on the surface. Molecular hydrogen bromide or an electrophilic or Lewis acid bromine compound react to form a similar structure. The precedence for this promotion of a metal oxide surface complex with an acidic species is described in a paper by Stark and Klabunde (Klabunde, K. J. Chem. Mater. 1996, 8, 1913-1918) who showed addition of acids, HCl , SO_3 , and NO , to a MgO surface to form a surface complex. In U.S. Pat. No. 6,517,423 to Koper et al. the described surface complexes were active for destroying biological agents and toxins. As shown in FIG. 4, addition of halogens to a metal oxide surface (A) can form a complex (B), in which electrophilic reactivity is maintained, owing to

12

the formation of positive charges on the surface. The electrophilic complex formed on the metal oxide base sorbent comprises an active site for oxidation of elemental mercury. Addition of mercury to the complex results in formation of a mercury oxygen bond and, simultaneously, a mercury bromine bond as shown in complex C in FIG. 4. Thus the final structure is a stable oxidized Hg form (D) described as a metaloxymercuric bromide.

In summary, it has now been found that the formation of the new bromide complex with the metal oxide surface increases the surface reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus as the mercury electrons are drawn toward the positive surface oxygen, the halide anion electrons are pushing in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus adding HBr or Br_2 to the appropriate metal oxide forms a similar surface bromide complex, in which the positive oxygen oxidizes the mercury with the assistance of the bromide ion.

In embodiments, a non-carbon base sorbent with Lewis basic sites/groups comprising metal-oxygen-metal structures is activated by a promoter of this disclosure, forming a promoted sorbent. The promoter and the metal-oxygen-metal structures of the non-carbon base sorbent form metastable complexes, which are responsible for mercury capture via chemisorption. For example, metastable complexes may form between a halogen promoter and inorganic species on a non-carbon base sorbent, wherein inorganic species include sodium (Na), calcium (Ca), magnesium (Mg), aluminum (Al), iron (Fe) compounds, and combinations thereof. In some embodiments, the metastable complexes comprise a dihalogen group, such as $\text{Br}-\text{Cl}$, $\text{Br}-\text{Br}$, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a halogen atom, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a hydrohalogen group, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a Group V or Group VI halide, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metal-oxygen-metal structures of the base sorbent are complexed with combinations of the functional groups disclosed herein. Without wishing to be limited by a theory, it is believed that mercury capture via chemisorption takes place through the action of mercury oxidation provided by these metastable complexes.

In embodiments, a carbon base sorbent with Lewis acid sites/groups comprising graphene sheets is activated by a promoter of this disclosure, forming a promoted sorbent. The promoter and the grapheme sheets of the carbon base sorbent form stable compounds, which are responsible for mercury capture via chemisorption. Without being limited by a theory, it is believed that mercury capture via chemisorption takes place through the action of mercury oxidation provided by these stable compounds. As one skilled in the art would appreciate, the versatility of chemistry associated with the base sorbent (carbon, non-carbon, or combination thereof) and the promoter of this disclosure

US 10,343,114 B2

13

enables versatile applications of the promoted sorbent system for mercury capture. This is especially advantageous because mercury content in flue gases varies from facility to facility, from operation to operation, and from day to day.

Examples of non-carbon base sorbents are amorphous forms of tectosilicates that comprise nanoscale cavities lined with Lewis basic oxygen associated with Group I alkali metals and Group II alkaline-earth metals. Such tectosilicates can be found in naturally occurring minerals, including, but not limited to, perlite and pumacite. Examples of non-carbon base sorbents also include amorphous forms of phyllosilicates. It is appreciated that other minerals may be used and also treated chemically and thermally to increase the activity of the base sorbent materials, such as phyllosilicates in the amorphous forms.

In some embodiments, bentonites are used as non-carbon base sorbents, including sodium bentonite and calcium bentonite. The use of other types of bentonites is contemplated as is known to one skilled in the art. The application of bentonite base sorbents is by introducing them into the flue gas at a location of the mercury capture system wherein the temperature of that location is below 800° C.

In some embodiments, the base sorbents are treated chemically and/or thermally to increase their activity. For example, perlite as a base sorbent may go through vacuum treatment and then thermal treatment so as to reduce the moisture contained therein, increase its activity, and potentially alter its morphology. Other treatment processes include chemical treatment, such acid treatment and alkaline treatment. These treatment methods may be combined to achieve desired effects as known to one skilled in the art. One of the desired effects is to increase the number of available Lewis acid sites/groups in the carbon base sorbent and/or the number of available Lewis basic sites/groups in the non-carbon base sorbent for subsequent activation via reaction with a promoter disclosed herein.

Referring now to FIG. 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted base sorbents and flue gas mercury reduction in accordance with preferred embodiments of the present invention. In the exemplary embodiment shown, there is provided a base sorbent reservoir 110, a halogen/halide promoter reservoir 120, a secondary component reservoir 130, and an alkali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the alkali component reservoir 180, flow control devices 208 and 209 can be used independently, together, or not at all. Further, reservoirs 110, 120, 130 and 180 are optional and can be used in any combination, or not at all, whereby the otherwise stored components can be introduced into the system by other means either together or independently. Further, the alkali and secondary components may not be used at all within the system, if so desired.

As shown, reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into contaminated flue gas stream 15. A source of air, nitrogen, or other transport gas(es) may be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such

14

materials, via injection point 119, into flue gas stream 15. Gas sources 170 and 171 may be the same or different, as desired. Alternatively, transport gas(es) may be provided to both transport lines 115 and 118 by gas source 170 (connection from source 170 to line 118 not shown). Although gas sources 170 and 171 are shown in FIG. 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

For clarity, single injection points 116 or 119 are shown in FIG. 3, although one skilled in the art will understand that multiple injection points and/or locations are within the scope of the present invention. In the embodiment shown, transport line 15 comprises multiple lines allowing for multiple injections and separate and/or combined injections of base sorbent 110 and promoter 120 and/or 130. One mode of operation, by example, comprises providing base sorbent 110 in a common line which is promoted inline “in-flight” using promoter 120 and/or 130 and injected at point 116. Another mode of operation, by example, comprises transport and injection of a base sorbent 110 in a separate line to a point downstream of the injection of promoter 120 and/or 130 in a line at point 116 which is upstream of injection of base sorbent 110, resulting in in-flight preparation at a promoted sorbent within stream 15.

In the exemplary embodiment shown, an optional optical density measuring device(s) 204 is connected to transport line 115 and/or 118 to provide signals representative of the optical density inside transport line 115 and/or 118 as a function of time.

Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 may comprise one or more fabric filters, one or more ESPs, or other particulate removal devices as are known in the art. It should be further noted that more than one particulate separator 140 may exist, sequentially or in parallel, and that injection point 116 and 119 may be at multiple locations upstream and/or downstream of 140 when parallel, sequential, or combinations thereof exist. Particulate separator 140 produces at least a predominantly gaseous (“clean”) stream 142 and a stream 141 comprising separated solid materials. A sorbent/ash separator 150 separates stream 141 into a largely ash stream 152 and a largely sorbent stream 151. Stream 151 may then preferably be passed to an optional sorbent regenerator 160, which yields a regenerated sorbent stream 161 and a waste stream 162.

An optional continuous emission monitor (hereinafter “CEM”) 205 for mercury is provided in exhaust gas stream 35 to provide electrical signals representative of the mercury concentration in exhaust stream 35 as a function of time. The optional mercury CEM 205 and flow controllers 201, 202, 203, 208, and 209 are electrically connected via optional lines 207 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream 15.

In operation, as example, promoted sorbent and/or an optional alkali component is injected into contaminated flue gas stream 15. After contacting the injected material with the contaminated flue gas stream 15, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, 25. The injected material is removed from the flue gas 25 by separator 140, disposed of or further separated by optional separator 150, and disposed of or regenerated by an optional regenerator 160, respectively. The reduced mercury clean

US 10,343,114 B2

15

flue gas stream **142** is then monitored for mercury content by an optional CEM **205**, which provides corresponding signals to an optional computer/controller **206**. Logic and optimization signals from **206** then adjust flow controllers **201**, **202**, **203**, **208**, and **209** to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art. Flow controllers **201**, **202**, **203**, **208**, and **209** can also be adjusted manually or by some other automated means to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art.

Referring still to FIG. 3, several embodiments are illustrated for preparation and injection of promoted sorbents and/or alkali components in accordance with the present invention. Stream **111** provides for introduction of base sorbent from reservoir **110**, as metered by flow controller **201** manually or under the direction of computer **206**. The halogen/halide may be combined and react with the base sorbent according to any of several provided methods. The halogen/halide may preferably be combined via line **121** directly into transport line **115**, within which it contacts and reacts with the base sorbent prior to injection point **116** or downstream at point **116**. This results in in-flight preparation of a promoted sorbent in accordance with the invention. Further, the halogen/halide may be combined via line **121b** with the base sorbent prior to entering transport line **115**. Still further, the halogen/halide may be contacted and react with the base sorbent by introduction via line **121c** into reservoir **110**. This option is preferably employed when, for example, reservoir **110** comprises an ebulliated or flueidized bed of base sorbent, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base sorbent in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in FIG. 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to FIG. 1.

Similarly, the optional secondary component may be contacted and react directly in transport line **115** via line **131**, or optionally as described above with respect to the halogen/halide, via lines **131b** and **131c**.

Similarly, the optional alkali component from **180** may either be added in transport line **115** directly, or may be injected separately by transport line **118**, combining downstream in flue gas **15** for synergistic effects with the base sorbent, promoted sorbent, or optional secondary components. Being able to vary on-site the amount of the optional alkali component relative to base sorbent, promoted sorbent, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base sorbent. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br₂, may be passed through an ebulliated or flueidized bed of granular or fibrous base sorbent, with the promoted sorbent so produced removed from the top of the bed via gas entrainment for injection.

16

In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl₂ and others. In some preferred embodiments, the promoted sorbent may comprise from about 1 to about 30 g of halogen/halide per 100 g of base sorbent. In some preferred embodiments, the promoted sorbent may comprise a secondary component in concentration of from about 1 to about 15 wt % of the concentration of the halogen/halide component.

In still other embodiments, the product-promoted sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof.

Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VITA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F₂, Cl₂, Br₂, and I₂, the reaction with hot flue gas components leaves little to react with elemental mercury. The atomic elemental halogen form, which includes the fluorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury, but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view, therefore, a halide salt-treated sorbent will not effectively oxidize elemental mercury and capture elemental mercury. Halogen-Promoted Sorbent Characteristics

The promoted sorbent described here has a very high initial reactivity for oxidizing mercury and therefore, can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the promoted sorbents produced using the inventive technology. The time interval required for the mercury and the promoted sorbents of the present invention to successfully interact in a flue gas duct, with subsequent collection of the mercury on the promoted sorbent and ash, is very short—less than seconds. Clearly, such collection times require the promoted sorbent to have both high capacity and high reactivity toward mercury. The promoted sorbent can be utilized in a

US 10,343,114 B2

17

very finely powdered form to minimize mass-transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the promoted sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a promoted sorbent containing a halide component formed on and/or within the base sorbent structure that provides a sorbent that is highly active on initial contact with the mercury-contaminated gas stream, which allows for very effective capture of the mercury.

The inventive sorbents chemically combine bromine species with Lewis acid/basic sites on the base sorbent. For example, x-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus the promoted sorbent produced from halogen and base sorbent does not represent a molecular halogen form, but rather a new chemically modified structure. This phenomenon may not occur with the less reactive iodine, where an I₂ molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of mercury. Thus an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury shown in FIG. 2. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the promoted sorbent, typically exceeding that of both the untreated base sorbent and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus the second component is an element with more polarized electrons (4p and 5p).

Optional Alkali Component

It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO₂, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio on-site in order to overcome and optimize for a given set of site conditions.

The synergy that can be gained when coinjecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e., sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and

18

react with these species/contaminants, thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury-binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (an order of magnitude less) than AC; thus more of it can be used, still resulting in overall lower costs.

In-Flight Sorbent Preparation

As stated previously, the halogen promoted sorbent can be readily produced in-flight. This is accomplished by, for example, contacting the vapors of any combination of halogens and, optionally, a second component, in-flight, with base sorbent particles. The particles may be dispersed in a stream of transport air (or other gas, such as the flue gas itself), which also conveys the halogen/halide-promoted sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

Referring to FIGS. 5A and 5B, process flow diagrams are shown as examples of the process for mercury removal from a mercury containing gas, such as a flue gas. In an embodiment shown at FIG. 5A, gas inlet stream 501 passes through chamber 301 and enters air heater 302 as stream 502; then it exits air heater 302 as stream 503 and passes through particulate control device 303 and enters scrubber 304 as stream 504; finally it exits scrubber 304 as stream 505. As shown, chamber 301 is a boiler, however, one skilled in the art will appreciate that chamber 301 can also be the combustion chamber of a coal fired boiler, a stand alone combustion chamber or any other chamber in which mercury containing gas is either generated or passed through. Injection streams 401, 402, 403 and 404, in addition to stream 501, are multiple locations wherein promoter, base sorbent, or a combination of promoter and base sorbent may be introduced.

FIG. 5B shows an embodiment similar to that of FIG. A, but with the position of the scrubber and particulate control device switched. Specifically, gas inlet stream 501' passes through chamber 301' and enters air heater 302' as stream 502'; then it exits air heater 302' as stream 503' and passes through scrubber 304' and enters particulate control device 303' as stream 504'; finally it exits particulate control device 303' as stream 505'. As shown, chamber 301 is a boiler, however, one skilled in the art will appreciate that chamber 301 can also be the combustion chamber of a coal fired boiler, a stand alone combustion chamber or any other chamber in which mercury containing gas is either generated or passed through. Injection stream locations 401', 402', 403' and 404', in addition to stream 501', represent multiple locations wherein promoter, base sorbent, or a combination of promoter and base sorbent may be introduced.

At each of the aforementioned injection stream locations 401, 401', 402, 402', 403, 403', 404 and 404', 501, 501' multiple injection points are contemplated so that promoter and base sorbent may be injected as a single injection stream or as separate injection streams, as further illustrated in the following exemplary embodiments.

In an embodiment, a promoter is introduced to chamber 301 at location 401. A base sorbent (carbon, non-carbon, or

US 10,343,114 B2

19

their combination) is introduced at location **402** upstream of air heater **302**. In a further embodiment, a promoter is introduced to at location **402** upstream of air heater **302**. A base sorbent (carbon, non-carbon, or their combination) is also introduced at location **402** either as a separate stream or as a mixed single stream with the promoter. In another embodiment, a promoter is introduced at locations **401** and **402**. A base sorbent (carbon, non-carbon, or their combination) is introduced at location **402** either as a separate stream or as a mixed single stream with the promoter.

With the aid of this disclosure, one of ordinary skill in the art will be able to configure the process in many different fashions for mercury removal using the promoted sorbent. All these configurations are considered equivalents of the disclosed process and therefore are within the scope of the claimed invention.

Advantages of On-Site Preparation

In-flight preparation of the halogen/halide-promoted sorbent on location produces certain advantages. For example, the treatment system can be combined with the base sorbent injection system at the end-use site. With this technique, the halogen/halide is introduced to the base sorbent air (or other gas, including to the flue gas or other mercury containing gas) mixture in a transport line (or flue gas duct part of the base sorbent storage and injection system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

Capital equipment costs at a treatment facility are eliminated.

Costs to operate the treatment facility are eliminated.

There are no costs for transporting carbon and additive to a treatment facility.

The inventive process uses existing hardware and operation procedures.

The inventive technology ensures that the sorbent is always fresh and, thus, more reactive.

No new handling concerns are introduced.

There are no costs for removing carbon from treatment system.

The inventive process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when fuels are changed or loads are reduced, thus further optimizing the economics.

The inventive technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide-promoted sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g., bromine) to the base sorbent structure.

Sorbent Injection Location

Some of the preferred embodiments contemplate the use of a halogen-promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen-promoted sorbent comprise a powdered modified AC prepared by adding Br₂ or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjunction with a base AC and/or with the use of a halogen-based sorbent and any other combinations of the sorbent technologies provided in this patent. Other embodiments allow for in-flight preparation of promoted sorbents by using and combining the promoters and base sorbents. Alternatively, embodiments include methods wherein the

20

base sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

Any of the above embodiments of the halogen/halide-promoted carbon and/or non-carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed, and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon and/or non-carbon itself contrasts with the earlier, more expensive, conventional methods of adding a reagent (such as peroxide, gold, triiodide, etc.) to a base sorbent. The halogen/halide-promoted carbon sorbent of the present invention, treated with bromine and/or optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in copending, commonly owned PCT Patent Application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT," which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

EXAMPLES

To more clearly illustrate the present invention, an example is presented below. This example is intended to be illustrative, and no limitations to the present invention should be drawn or inferred from the example presented herein.

Example 1

Non-carbon-Promoted Sorbent Tests at Full-Scale Plants

Full-scale commercial tests were conducted at several coal-burning facilities equipped with ESPs wherein three types of pre-cursors were injected upstream of an ESP at 325° F. In all, more than thirty tests were performed with variations in base sorbent material, base sorbent material injection rates and promoter injection rates. Promoters were halogen-based materials. Base sorbents were clay-based materials such as perlite and pumacite, which are vesicular forms of tectosilicates comprising silicates and aluminate tetrahedra with alkali metals in the interstitial spaces. Each base sorbent was injected upstream from the ESP.

The flue gas flow rate for the test was approximately 23 million dsft³/hr with a corresponding mercury flow rate of 0.0097 lbs Hg/hr. Initial mercury concentration in the flue gas prior to the introduction of the base sorbent or promoted sorbent was approximately 0.000417 lbs Hg/million dsft³.

As shown in Table 1, each base sorbent was injected at three different test rates: about 100 lb/hr ("Low"), about 150 lb/hr ("Ave.") and about 200 lb/hr ("High"). At each test

US 10,343,114 B2

21

rate, the mercury removal rate was measured both with and without the use of a promoter to show the relative benefit of introducing the promoter into the flue gas stream. For the tests where promoter was injected into the flue gas stream, promoter was injected at about 20 lb/hr for the "Low" tests, at about 25 lb/hr for the "Ave." tests and from about 30 to about 50 lb/hr for the "High" tests. The percent mercury removal for each test was calculated based on measurements taken from the inlet flue gas and the outlet flue gas. The results as shown in Table 1 clearly show a significant improvement in mercury capture when a promoter and base sorbent are injected, as compared to the injection of a base sorbent alone.

TABLE 1

Test Data for Non Carbon-Promoted Sorbents									
Base Sorbent	Base Sorbent Injection Rate (lb/hr)			Promoter Injection Rate (lb/hr)			Percent Removal of Mercury (%)		
Material	Low	Ave.	High	Low	Ave.	High	Low	Ave.	High
Perlite	100	150	200	0	0	0	37	40	43
	100	150	200	20	25	35	55	72	74
Pumacite	100	150	200	0	0	0	25	25	25
	100	150	200	20	25	50	52	60	65
Clay-	100	150	200	0	0	0	50	52	54
Based Mix	100	150	200	20	25	30	58	65	74
of Silica and Alumina									

PROVISIONAL APPLICATION

A reactive sorbent material is described for capture of mercury in a vapor stream. The vapor stream includes flue gas from coal combustion or incineration, synthesis gas from gasification, as well as offgases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories. The sorbent is especially suited to, but not limited to, use in low-chlorine flue or exhaust gases where the mercury is mainly elemental. The sorbent comprises a bromide-modified carbon form containing a reactive compound produced by the reaction of bromine with the carbon. Other additional promoting substances can be added in smaller amounts to increase the reactivity with and sorption of elemental mercury. This combination results in a carbon bromide structure in the carbon lattice that can oxidize the mercury to a species that is strongly bonded to the carbon structure and, therefore, easily retained on the sorbent at higher temperatures in the presence of flue gas constituents. In some examples, the sorbent consists of a fine or coarse powdered material for injection into the gas stream or a granular or fibrous material for use in a fixed or moving bed. In some examples, the sorbent does not require in situ activation (an induction period) in a flue gas stream as do conventional activated carbon sorbents. Other additives of base chemistry (Ca, Na, and others) may be added to flue gas as a sorbent mixture, or co-injected to selectively sorb acid gases or other flue gas constituents to keep available reactive sites for mercury oxidation and subsequent capture. The sorbent can be regenerated by washing off contaminating components derived from flue gas that poison the spent sorbent. Novel methods for introduction of the sorbent dispersion into the mercury contaminated gas stream are described.

22

Following is an outline of examples of the invention. The invention may also take on various other examples or embodiments, as a person skilled in the art would understand.

1. A modified carbon sorbent was prepared by reacting the carbon with molecular bromine by applying a solution of molecular bromine in an organic solvent to the carbon, followed by removal of the modified carbon from the bulk of solvent and further removal of solvent from the pores by drying the carbon in air or nitrogen. The solution may also contain an additional promoting substance in small amounts. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

1A. (Dependent)

Same as 1, carbon is powdered activated carbon.

Carbon is granular activated carbon.

Carbon is very fine carbon black.

Carbon is very fine carbon fiber.

Carbon is aerogel carbon film.

Carbon is char recovered from pyrolysis process.

Carbon is powdered activated carbon of size distribution larger than fly ash size distribution, so that it can be physically separated from the ash and regenerated for reuse.

Carbon is regenerated from previous usage cycle and recycled.

Other desired types of carbon may also be used.

1B. (Dependent)

Same as 1, Solvent is chlorinated hydrocarbon such as dichloromethane.

Same as 1, Solvent is hydrocarbon solvent such as petroleum ether or ligroin or pentane or hexane or toluene or benzene.

Same as 1, Solvent is water.

Same as 1, Solvent is carbon disulfide.

Same as 1, Solvent is a waste solvent.

Same as 1, Solvent is an ether.

Same as 1, Solvent is recycled from previous batch.

Same as 1, Solvent is supercritical solvent such as CO₂.

Other desired types of Solvents may also be used.

1C. (Dependent)

Same as 1, solution of bromine is applied by stirring the carbon in the bromine solution.

Same as 1, solution of bromine is applied by spraying a solution of molecular bromine in an organic solvent, followed by removal of solvent from the pores by drying the carbon in air or nitrogen.

The bromine may also be applied using other desired techniques.

1D. (Dependent)

Same as 1, removal of solvent is by filtration, centrifugation, settling, and decantation and drying in vacuum, air, or other gas.

Same as 1, when sprayed or minimal volume, removal of solvent is by drying in air, vacuum, or other gas.

The solvent may also be removed using other desired techniques.

1E. (Dependent)

Same as 1, additional substance is iodine, at 1%-10% of the bromine concentration added.

Same as 1, additional substance is hydrohalide (HI, HBr, HCl), etc, 1%-10% of bromine.

Same as 1, additional substance is a compound comprised of a Group V or VI element or combination of Group V or VI with Group VII element, such as SCl₂, 1-10 wt % of bromine.

US 10,343,114 B2

23

A modified carbon sorbent was prepared by reacting the carbon with molecular bromine by contacting the carbon with a gas containing molecular bromine. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Contacting is by passing the Br₂ gas through a bed of the carbon.

Bed is ebullated or fluidized.

Bed is moving bed of granules or fibers.

Contacting is by admitting Br₂ gas to a duct through which the carbon is transported from a reservoir to the flue gas duct via an air-driven entrainment method, thus promoting the activity of the carbon in-flight.

Same additives as 1E, except these are added in the gas phase, and added in-flight as in 2 above.

A modified activated carbon sorbent was prepared by reacting the carbon with hydrogen bromide (HBr) by stirring the carbon in a solution of HBr in an organic solvent or in water, followed by removal of the modified carbon from the bulk of solvent and further removal of solvent from the pores by drying the carbon in air or nitrogen. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon forms. Same solutions and treatment as 1B, 1C, 1D.

Same additives as 1E, added into the solution phase or later in the gas phase, and added in-flight as in 2 above.

An activated carbon sorbent was prepared by impregnating hydrogen bromide by passing a gas composition containing hydrogen bromide diluted with nitrogen or air through a fluidized bed or ebullated bed of the carbon. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon forms.

Contacting options are similar to 2.

Sequential treatment of activated carbon with bromine or HBr, followed by another mercury stabilizing reagent to generate a highly reactive bifunctional sorbent, the reagent to include sulfur and selenium species, such as H₂S, SO₂, H₂Se, Se, SeO₂, CS₂, P₂S₅.

6. Sequential treatment of activated carbon with mercury stabilizing reagent, followed by bromine or HBr to generate a highly reactive bifunctional sorbent, the reagent to include sulfur and selenium species, such as H₂S, SO₂, H₂Se, Se, SeO₂, CS₂, P₂S₅.

Treatment of a carbon with a Group V or VI element combined with Group VII element, such as PBr₃ or SCl₂. In one example, the amount of Group V or VI halide is 1-30 wt % of the carbon. The compound is added in vapor phase or in solution (solvent is hydrocarbon, chlorinated hydrocarbon, or other solvent as described in 1B, but not water, since the compound is destroyed in water solution).

The process for preparing the bromine-containing activated carbon sorbent as described in Examples 1-6 and coupled with the injection of the bromine-containing fine-particle sorbent into the contaminated gas stream and subsequent removal of the fine particles of sorbent from the gas stream in a collection device, such as bag filtration of electrostatic precipitator (ESP).

The process of using additives (1-8) in conjunction with sorbents to capture acid gases and other flue gas constituents that block oxidation reactions or consume sorbent sites that would otherwise capture mercury. The additive is a com-

24

pound comprised of Group I or II elements, such as Ca, Na, and others. These additives of base chemistry may be added to flue gas as a sorbent mixture or co-injected to selectively sorb acid gases or other gas constituents that compete for mercury reactive/sorption sites, thereby improving the effectiveness of activated carbon to capture mercury. In addition, the base additives can augment the treated activated carbon by helping to capture oxidized mercury forms in the flue gas, such as mercuric chloride, or that are produced on the carbon sorbent, such as mercuric bromide, but are released to the gas phase as the sorbent becomes saturated or capacity limited.

The process of preparing a larger-than-normal (>40 µm) sorbent particle size, promoting with the halogen treatment as described in 1-8, using the treated sorbent for capture of mercury by injecting in the flue gas, and finally separating and recovering the sorbent from the ash particles. The larger sorbent size thus will allow easy mechanical/physical separation so that sorbent can be regenerated, recycled, and reused, and the ash can be sold as a low-carbon cementitious byproduct for concrete. The separation can be effected by various methods, such as density (gravity), floatation, or sieving methods.

The process for preparing the bromine-containing activated carbon sorbent as described in Example 1-10, coupled with the direct injection of the slurry of the prepared fine-particle sorbent in the solvent or aqueous phase, so that the aerosol particles of the slurry achieve a high degree of dispersion in the gas stream and evaporation of the solvent in the hot gas occurs rapidly. The amount of slurry added is flow-controlled, and the concentration of particles in the slurry is monitored by optical density measurements prior to injection. Collection of particles is performed.

12. The process for preparing the bromine-containing activated carbon sorbent, as described in Examples 2 and 4, coupled where the fine-particle dispersion of brominated sorbent in the gas stream at the top of the ebullated bed is led to the flue gas or offgas duct where the said dispersion is contacted with mercury-contaminated flue gas or offgas stream. The amount of aerosol dispersion added is controlled by the gas flow to the ebullated bed, and the concentration of particles in the dispersion can be monitored by optical density measurements prior to injection. Collection of particles is performed by the existing particulate-collection equipment.

he process for preparing the bromine-containing activated carbon sorbent bed, coupled with contacting the bed with the mercury-contaminated flue gas or offgas.

The process for preparing the bromine-containing activated carbon sorbent, as described in Examples 2 and 4, or untreated activated carbon, coated on a substrate or as activated carbon material. This material is placed in a moving system that geometrically allows for control of rate of exposure, sorption, and exchange of material in a continuous or semicontinuous manner.

In the sorbent and mercury removal process outlined in paragraphs above, the bromine reagents promote metal oxidation activity by creating cationic or radical character on the carbon edge structure that attracts mercury atoms and extracts electrons from said mercury atoms, resulting in oxidized mercury, which is more easily captured on a sorbent. A similar mechanism applies to oxidation and capture of reduced arsenic and other pollutant species.

The invention relates to the process for the removal of mercury and other pollutant species from gas streams generated during the burning of fossil fuels, such as in a coal-fired utility or synthesis gas from gasification facilities.

US 10,343,114 B2

25

This removal process would utilize a sorbent and/or a combination of additives to remove pollutants from the gas stream, which are at the same time interacting with other gas components that result in poisoning or deactivating the sorbent and reducing its capacity or reaction rates with the targeted pollutant species. The present invention provides a cost-effective way to capture the pollutants by utilizing exceptionally active carbon sorbents and promoting mercury sorbent surface reactions, containing a bromide form of the carbon, that capture mercury with high kinetic chemisorption (oxidation) activity, so that capture can occur during contact times of seconds or less. The sorbent does not require in situ activation (induction period) in the gas stream to achieve high activity as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants and the sorption capacity can be regenerated, recycled, and reused.

Burning fossil fuels generates a flue gas that contains mercury (and other trace elements) that was in the coal, plus oxides of sulfur and nitrogen (acid gas emissions) and particulates whose release to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. While control of other elements and/or flue gas pollutants may apply, the discussion provided is focused on mercury. Initially, mercury is released in the elemental form during combustion/gasification, but downstream of the boiler, in the ducts and stack of the combustion system, part of the elemental mercury is oxidized. The amount oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the coal, but a typical concentration of mercury in the stream of combustion gas is about 5 parts per billion (ppb). A pound of mercury or more per day may be emitted in some utilities.

Discussion of Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles (for example, see U.S. Pat. No. 6,214,304), and basic silicate or oxide sorbents (for example, see the Ghorishi reference (Ghorishi, B.; Gullet, B. K. Waste Manage Res. 1993, 16, 582). and Lancia references). When particle injection is employed, the mercury chemisorbed to the sorbent particle is removed from the gas stream in a bag house or ESP and collected along with ash particulates (for example, see U.S. Pat. Nos. 4,889,698, 4,956,162, 5,672,323, 5,827,352, 6,027,551, and 5,505,766). The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of approximately 60% was attained with a baghouse to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon, since the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after exposure to the flue gas for about 20 minutes does the seasoned sorbent become effective and provide capture of 60% of the mercury in the gas. Consequently, these sorbents must be used in large amounts (high sorbent-to-mercury ratios) to effectively capture the mercury. These sorbents can be relatively expensive and cannot be easily separated from the

26

ash, regenerated and reused. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash for use in various applications.

5 Use of Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have not previously been effective. Halogen is defined as a member of the very active elements comprising Group VII-A of the periodic table. In the molecular elemental halogen form, including F₂, Cl₂, Br₂, and I₂, the reaction with elemental mercury is not fast enough to result in the formation of oxidized mercury in a coal combustion flue gas with conventional ash control technology. The atomic elemental halogen form, which includes F atom, Cl atom, Br atom, and I atom, is about a million times more reactive to mercury, but the concentrations of these forms are extremely low, and also, therefore, cannot result in oxidation of mercury in a utility flue gas.

A halide is a compound formed from reaction of a halogen with another element or radical. In general, the halide compounds are normally very much less reactive than the molecular halogens, having expended their high chemical potential in forming the low energy halide. The halide is considered a reduced form and cannot therefore oxidize anything by itself. It is for this reason that it is not obvious that a halide-halogen treated activated carbon would be effective at oxidizing elemental mercury and provide effective capture of elemental mercury. In fact, for tests with salts, analytical data show the addition of bromine to an activated carbon or carbon black or soot does form a compound by reacting with the unsaturated groups on the carbon. By applying x-ray photoelectron spectroscopy, it has been determined that bromine or HBr added to carbon black forms chemical compounds within a carbon structure.

A body of theory has been developed from scientific evidence to explain the nature of the promotion effect of the bromine compounds. This principle is illustrated in FIG. 2, which in step 1 shows the reaction of the hydrogen bromide with the unsaturated structure of the activated carbon. This may be a carbene species on the edge of the graphene sheets structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury.

We now teach that the formation of the new bromide compound with carbon increases the reactivity of the carbon forms toward mercury and other pollutants. The resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation results from the promotion effect of the halide exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, which stabilizes the positive charge developing on the mercury and lowers the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus, adding HBr or Br₂ to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion. Prior Art Publications

The earliest patents that relate to mercury capture on a sorbent are actually not for flue gas mercury control but for capture of mercury from air or other gas mixtures on a carbon or other sorbent. These patents were based on a model that recognized the affinity of halogens for mercury,

US 10,343,114 B2

27

rather than the formation of a reactive carbon. These patents are discussed below according to the type of halogen used for impregnation.

One patent that teaches a halogen impregnation (Stock, U.S. Pat. No. 1,984,164, issued in 1934) describes the use of activated carbon or other solid impregnated with a halogen for removing Hg from air. The impregnation method is not specified. This seems to be the most general claim with respect to halogen impregnation. All the statements and claims appear to refer to halogen or iodine, but the patent does not appear to address bromides or other halides or bromide compounds or even specifically iodide or an iodine compound. The only example in the description is iodine impregnation. The patent also is restricted to air systems and did not pertain to flue gas systems with reactive acid gases. The description did not assume that the iodine formed a reactive carbon species.

Japanese Patent JP 49-43197 describes the treatment of Hg-contaminated electrolysis cell gas using a metal iodide salt on a support. A similar treatment using a resin impregnated with a metal iodide is described in JP 50-6438. These patents do not appear to represent a carbon bromide compound as specified in this patent application.

Another early patent (Hilgen, U.S. Pat. No. 3,849,267, issued in 1974) describes a method for Hg removal from a gas which claims mixing molecular chlorine (Cl_2) with the gas to be cleaned and passing it through a nonporous sorbent such as glass wool and NaCl (not carbon). This was evidently not an obvious extension of the Stock patent, since a halogen was introduced as part of the gas phase being cleaned.

A later patent (deJong, et al., U.S. Pat. No. 4,196,173, issued in 1980) describes a method for Hg removal in air which claims using a bed of activated carbon impregnated with halogen-only Cl_2 is specified in the other claims and examples, and it is prepared by flowing the Cl_2 stream through a carbon bed.

An improved sorbent for mercury in air was patented by Revoir and Jones (U.S. Pat. No. 3,662,523, issued in 1972), in which ICl and ICl_3 vapors were impregnated into the activated carbon. No explanation of the increased activity was provided. Since these compounds are interhalogen compounds, the patent did not infringe Stock.

U.S. Pat. No. 5,891,324 describes an activated carbon containing an acid (HCl , H_2SO_4 , or H_3PO_4) for the removal of mercury contained in a liquid phase, such as would occur in a process stream in the oil industry. In this case, the model presented was that mercury is adsorbed from the liquid into the solid carbon phase at relatively low temperatures.

In U.S. Patent Application 2004/0003716, a method is described for removing mercury from a combustion gas. This method employs an exposure of a finely powdered activated carbon to a molecular bromine gas at an elevated temperature or to HBr to produce a sorbent with good mercury removal ability when injected into the flue gas duct. The model for the efficacy of the Nelson sorbent is not clearly stated, so it can be presumed that the reasoning for using bromine is the simple premise that some bromine form will help capture the mercury, as does iodine and chlorine. The methods for incorporation of the bromine in the Nelson application are not the same as with the present invention, and the Nelson method will not produce the identical carbon bromide species that are obtained in the art described in this application. The Nelson method lacks many of the features described in this application that impart exceptional activity to the sorbent in a convenient way, for example, the addition of smaller amount of a second more powerful promoting

28

agent, the use of facile solvent systems, including aqueous bromine, and the use of in-flight bromine treatment. Additionally, the patent application does not mention regeneration, recycling, or reuse, or the use of moving contactors or larger particle size to facilitate sorbent-ash separation.

Embodiments of the Invention

A sorbent that is initially very reactive in oxidizing mercury can be used in very small amounts to achieve high capture efficiencies, thus lowering operation costs and lessening the disposal problem. In addition, further disposal reduction is made possible by recycling and reusing the sorbent that is produced using this technology. The time interval for the mercury and sorbent to interact in a flue gas duct and the subsequent collection of the mercury on the sorbent and ash may be very short—only seconds. This requires the sorbent to have high capacity and be very reactive toward mercury. A sorbent can be utilized in a very finely powdered form (e.g., 1-10 μm) to minimize mass transfer limitations. But, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. One feature of this invention is the process to prepare a sorbent containing a bromide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for effective capture of the mercury.

One possible way to do this is to chemically combine molecular bromine from solution with activated carbon (edge sites). X-ray photoelectron spectroscopy established that the addition of bromine formed a chemical compound in the carbon structure. Thus, the sorbent does not represent a molecular bromine halogen form but a new chemically modified carbon structure. This may not occur with the less reactive iodine, where an I_2 —molecular complex can exist on the carbon basal plane. In the bromine case, it is actually the carbon that oxidizes the mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements as described herein. Chlorine treatment resulted in lower-activity carbons because the chloride anion was less effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, exceeding that of both the untreated carbon and the brominated carbon. The second component comprises either a second halogen or a compound from a second halogen, such as HBr . Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus the second component is an element with more polarized electrons (4p and 5p).

Furthermore, we demonstrated that the sorbent can be readily treated with any combination of bromine and the second component in-flight using vapors of these components contacting the very fine carbon particles dispersed in air or other gas stream that conveys the particles to the flue gas duct. There is no particular temperature requirement for this contact. This technology is very simple to implement, so it will result in a great cost savings to the utility using this technology for mercury capture.

A unique, nonobvious technique for preparation of the treated carbon is through combining the treatment system

US 10,343,114 B2

29

with the carbon injection system at the end-use site. With this technique, the halogen is introduced to the carbon-air mixture in the transport line (or other part of the sorbent storage and injection system). Benefits over current concepts to treat sorbents off-site include the following:

Capital equipment costs at a treatment facility are eliminated.

Costs to operate the treatment facility are eliminated.

There are no costs for transporting carbon and additive to a treatment facility.

This process uses existing hardware and operation procedures.

This technology ensures that the sorbent is always fresh, and thus, more reactive.

No new handling concerns are introduced.

There are no costs for removing carbon from treatment system.

This process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as needed when changing fuels or reducing loads, thus further optimizing the economics.

This technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the invention, a process for preparing and regenerating carbon sorbents whose activity for mercury capture is promoted by the addition of bromine to the carbon structure.

The invention applies to use of a sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Examples of the composition of the sorbent are a powdered modified activated carbon prepared by adding Br₂ or HBr plus a second optional component. Alternatively, the sorbent is on a moving contactor consisting of particles or fibers containing the compositions listed in the previous sentence. Either type can be regenerated; the poisoning contaminants from the flue gas are removed and an inexpensive promoting agent added to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive art of adding a reagent (such as peroxide, gold, triiodide, etc.) to the sorbent. The activated carbon sorbent treated with bromine and/or the other components is noncorrosive.

Detailed examples of sorbent regeneration techniques are described in co-pending, commonly-owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is incorporated by reference herein.

Although the invention is described herein as a sorbent material, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

The construction and method of operation of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of specific exemplary embodiments.

FIG. 6 is a block diagram illustrating the use of the invention in a coal fueled facility. Of course, the invention can also be used in any other desired type of facility. FIG. 6 shows a boiler for burning pulverized coal. The facility utilizes various devices to clean the exhaust of the boiler. In this example, a baghouse or ESP is used to collect particulates in the exhaust. A scrubber and sorbent bed are also used to remove undesired constituents from the flue gas stream,

30

before being fed to the stack. In the example shown, the sorbent is injected into the flue gas after the boiler. The additive can be injected where desired (e.g., before, after, or within the boiler).

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize the invention. Where possible, the mercury control technology of the present invention will utilize measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent levels in this way will ensure mercury removal requirements are met with the minimal sorbent requirements and therefore the associated costs will be minimized. In one example, the emissions are measured at the stack.

Carbon Sorbent

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a carbocation that accept electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine-containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several powdered carbon sorbents, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100° C. in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. Adding a second component to the solution was demonstrated to improve the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 µg/m³) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM. The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer.

A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it has been treated with 0.1 N HBr, collecting the powder by centrifugation and drying, revealed that the mercury capture activity is increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicates that it not only captures mercury at the same level as before

US 10,343,114 B2

31

(100% capture) but is enhanced such that its capacity is prolonged by several minutes. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed of ebullated bed of the carbon. The amount of bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 $\mu\text{g}/\text{m}^3$. The ash and injected carbons were collected in the baghouse at 350E to 375EF. Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/Macf resulted in mercury effluent concentrations of 3.8-4.2 $\mu\text{g}/\text{m}^3$ (representing 62%-58% removal of the mercury from the gas), and at 2.0 lb/Macf, gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/Macf resulted in 73%-69% removal and at 2.0 lb/Macf gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine-treated carbon.

Addendum: Other References to Hg Sorption Sorbent Beds with Particulate Removal

Carbon beds have also been utilized for mercury capture in flue gas. The German Patent 34 26 059 describes the use of a very thick carbon bed for treatment of flue gases containing polyhalogenated compounds. Although the system employed at Dusseldorf would also have the potential for Hg removal (for example, see the Streng reference), it is not very practical to use such a thick bed. Spent sorbent is burned and not regenerated. The carbons are not pretreated.

The GE-Mitsui-BF system (Tsuji, K.; Shiraishi, I.; Dague, R. F. Proceedings, Sixth International Symposium, Air & Water Management Assoc., New Orleans, La., Mar. 10-12, 1993) employs a recirculating carbon bed, where mercury is removed along with acid gases (as ammonium salts) and the carbon is regenerated at high temperatures where ammonium sulfate is decomposed to SO_2 and N_2 and mercury is converted to the elemental form, which desorbs from the sorbent. Attrition of the sorbent results in a significant sorbent cost. The carbons are not pretreated.

Sorbent Injection after Particulate Removal

A process of injecting manganese oxide sorbent particles is described in U.S. Patent Application 2002/0150516. Regeneration is claimed by removal of spent oxide particles from the reaction zone and rinsing with dilute aqueous acid.

Sorbent Beds after Particulate Removal

Of particular interest in designing a mercury control process is to use the sorbent downstream of a particulate control device so the sorbent is not highly diluted with the ash particles. The sorbent could then be more easily regenerated and recycled. The prior art teaches several examples of this type of configuration and sorbent processing.

U.S. Pat. No. 5,607,496 teaches the oxidation of mercury on a metal oxide sorbent bed and subsequent absorption to sorbent. The sorbent bed follows the particulate-removal equipment and, thus, the gas still contains the SO_x and NO_x , which react with the metal oxide sorbent to form the metal sulfates, which poison the bed. High temperatures are proposed to regenerate the bed. However, Hg is only partially removed from the sorbent at temperatures up to 500° C. The sorbents do not work effectively after regeneration using this

32

technique; the problem may be that manganese sulfate formed during the sorption cycle does not completely decompose back to an active manganese oxide form.

U.S. Pat. No. 6,383,981 describes a fixed MnO_2 or Fe_2O_3 bed for removal of Hg from a hydrocarbon stream. No regeneration method appears to be included.

A recent U.S. Patent application (2001/0003116) describes the regeneration of a plate or honeycomb material composed of transition metal oxides that was used for sorption of mercury in flue gas. The claimed process involves heating the sorbent in a reducing gas stream to remove poisons, followed by impregnation with a polyfunctional complex-forming reagent containing the catalyst active component to restore mercury capture capacity. The first of these steps can remove the mercury, but it is unclear whether it actually removes the sulfate poison. The second of these steps is rather expensive, because one is actually reconstituting the reagent on the sorbent.

Porous beds containing a mercury oxidizing reagent on a solid support are described in several patents for removal of mercury from gas streams. These include peroxomonosulfate (for example, see U.S. Pat. No. 4,786,483), triiodide or other mixed halogens (for example, see U.S. Pat. Nos. 3,194,629; 3,662,523), or sulfur (for example, see U.S. Pat. Nos. 3,194,629, 4,101,631, 4,708,853, 6,258,334). The reagent material is destroyed either by reaction with the flue gas during sorption or by attempts to regenerate the sorbent; there is no way to regenerate these sorbents, except by reimpregnation of the expensive reagent.

Amalgamating noble metals (gold, silver) on a suitable support can be regenerated by microwave heating (for example, see U.S. Pat. No. 6,136,072), but they are expensive and not especially active for sorption in flue gas.

Hg Sorbents for Air or Natural Gas Treatment

Melkersson (U.S. Pat. No. 3,786,619) described a Hg sorbent comprising SeO_2 or SeS_2 for air treatment. This method did not appear to employ a carbon support or halide.

Yan (U.S. Pat. No. 4,814,152) described a Hg sorbent comprising elemental sulfur and a metal catalyst on a carbon support. This method did not appear to employ a halide.

Attia (U.S. Patent 65/080,281) described a sorbent for mercury and a variety of other contaminants comprising an inorganic aerogel composition. This method did not appear to employ a carbon support or halide.

FOLLOWING IS A LIST OF VARIOUS BACKGROUND REFERENCES

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U.S. Pat. No. 6,258,334 Gadkaree

US 10,343,114 B2

33

U.S. Pat. No. 6,136,072 Sjostrom

U.S. Patent Application 2002/0150516

U.S. Patent Application 2001/0003116 Neufert

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

Although the invention is described herein as a promoted sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

What is claimed is:

1. A method of separating mercury from a mercury-containing gas, the method comprising:
combusting coal in a combustion chamber, to provide the mercury-containing gas, wherein the mercury-containing gas comprises a halogen or halide promoter comprising HBr, Br⁻, or a combination thereof, wherein the coal comprises added Br₂, HBr, Br⁻, or a combination thereof, added to the coal upstream of the combustion chamber, or
the combustion chamber comprises added Br₂, HBr, Br⁻, or a combination thereof, or
a combination thereof;
injecting a sorbent material comprising activated carbon into the mercury-containing gas downstream of the combustion chamber;
contacting mercury in the mercury-containing gas with the sorbent, to form a mercury/sorbent composition;
separating the mercury/sorbent composition from the mercury-containing gas, to form a cleaned gas;

34

monitoring the mercury content of the cleaned gas; and
controlling, in response to the monitored mercury content of the cleaned gas, an injection rate of injecting the sorbent into the mercury-containing gas, the sorbent composition, or a combination thereof, so that the mercury content of the cleaned gas is maintained at or below a desired level.

2. The method of claim 1, comprising removing greater than 70 wt % of the mercury in the mercury-containing gas.

3. The method of claim 1, comprising removing greater than 70 wt % of the mercury in the mercury-containing gas on the sorbent.

4. The method of claim 1, wherein the sorbent in the mercury-containing gas comprises about 1 g to about 30 g of the halogen or halide promoter per 100 g of the sorbent material.

5. The method of claim 1, wherein the combustion chamber comprises the halogen or halide promoter.

6. The method of claim 1, wherein the coal comprises added Br₂, HBr, Br⁻, or a combination thereof, added to the coal upstream of the combustion chamber.

7. The method of claim 1, wherein the promoter is contacted with the sorbent in vapor form, gaseous form, liquid form, or in an organic solvent.

8. The method of claim 1, further comprising injecting a secondary material into the mercury-containing gas downstream of the combustion chamber.

9. The method of claim 8, wherein the secondary material comprises a halogen, a compound derived from a halogen, a hydrohalide, a compound comprising a Group V or Group VI element and a molecular halogen, or a combination thereof.

10. The method of claim 1, wherein the sorbent material injected into the mercury-containing gas further comprises a non-carbon sorbent material.

11. The method of claim 10, wherein the non-carbon sorbent material comprises at least one of a porous felsic material, a vesicular felsic material, a porous basaltic material, a vesicular basaltic material, a clay-based compound, an alkaline compound, a calcium hydroxide compound, a sodium acetate compound, and a bicarbonate compound.

12. The method of claim 1, wherein the activated carbon comprises powdered activated carbon, granular activated carbon, or a combination thereof.

13. The method of claim 1, wherein the sorbent material injected into the mercury-containing gas is substantially free of halogen and halide promotion.

14. The method of claim 1, wherein the sorbent material injected into the mercury-containing gas is a promoted sorbent obtained by contacting a base sorbent with another halogen or halide promoter.

15. The method of claim 1, wherein the combustion chamber comprises a boiler.

16. The method of claim 1, wherein the mercury-containing gas is a flue gas.

17. The method of claim 1, wherein the injection of the sorbent material into the mercury-containing gas occurs upstream of an air pre-heater.

18. The method of claim 1, wherein the injection of the sorbent material into the mercury-containing gas occurs upstream of a particulate separator or a scrubber.

19. The method of claim 1, wherein the coal comprises added halide sorbent enhancement additive.

20. The method of claim 1, wherein the combustion chamber comprises added Br₂, HBr, Br⁻, or a combination thereof.

21. The method of claim 1, wherein the coal comprises added sorbent enhancement additive that comprises Br⁻.

US 10,343,114 B2

35

22. The method of claim 21, wherein the sorbent enhancement additive comprises a bromide compound.

23. A method of separating mercury from a mercury-containing gas, the method comprising:

combusting coal in a combustion chamber, to provide the mercury-containing gas, wherein the mercury-containing gas comprises a halogen or halide promoter comprising HBr, Br⁻, or a combination thereof, wherein the coal comprises added Br₂, HBr, Br⁻, or a combination thereof, added to the coal upstream of the combustion chamber, or

the combustion chamber comprises added Br₂, HBr, Br⁻, or a combination thereof, or a combination thereof;

injecting a sorbent material comprising activated carbon into the mercury-containing gas downstream of the combustion chamber;

contacting mercury in the mercury-containing gas with the sorbent, to form a mercury/sorbent composition; and

separating the mercury/sorbent composition from the mercury-containing gas, to form a cleaned gas.

24. A method of separating mercury from a mercury-containing gas, the method comprising:

combusting coal in a combustion chamber, to provide the mercury-containing gas, wherein the mercury-containing gas comprises a halogen or halide promoter comprising HBr, Br⁻, or a combination thereof, wherein the coal comprises added Br₂, HBr, Br⁻, or a combination thereof, added to the coal upstream of the combustion chamber, or

the combustion chamber comprises added Br₂, HBr, Br⁻, or a combination thereof, or a combination thereof;

injecting a sorbent material comprising activated carbon into the mercury-containing gas downstream of the combustion chamber such that the activated carbon reacts with the halogen or halide promoter in the mercury-containing gas to form a promoted sorbent;

contacting mercury in the mercury-containing gas with the promoted sorbent, to form a mercury/sorbent composition;

separating the mercury/sorbent composition from the mercury-containing gas, to form a cleaned gas;

monitoring the mercury content of the cleaned gas; and controlling, in response to the mercury content of the cleaned gas,

an injection rate of injecting the sorbent into the mercury-containing gas,

36

a rate of addition to the coal or the combustion chamber of the added Br₂, HBr, the bromide compound, or a combination thereof, or a combination thereof,

so that the mercury content of the cleaned gas is maintained at or below a desired level.

25. A method of separating mercury from a mercury-containing gas, the method comprising:

combusting coal in a combustion chamber, to provide the mercury-containing gas, wherein

the coal comprises added Br₂, HBr, a bromide compound, or a combination thereof, added to the coal upstream of the combustion chamber, or

the combustion chamber comprises added Br₂, HBr, a bromide compound, or a combination thereof, or a combination thereof,

injecting a sorbent material comprising activated carbon into the mercury-containing gas downstream of the combustion chamber;

contacting mercury in the mercury-containing gas with the sorbent, to form a mercury/sorbent composition; and

separating the mercury/sorbent composition from the mercury-containing gas, to form a cleaned gas.

26. The method of claim 25, wherein the coal comprises the added Br₂, HBr, the bromide compound, or a combination thereof, added to the coal upstream of the combustion chamber.

27. The method of claim 25, wherein the combustion chamber comprises the added Br₂, HBr, the bromide compound, or a combination thereof.

28. The method of claim 25, further comprising monitoring the mercury content of the cleaned gas; and controlling, in response to the mercury content of the cleaned gas,

an injection rate of injecting the sorbent into the mercury-containing gas,

a rate of addition to the coal or the combustion chamber of the added Br₂, HBr, the bromide compound, or a combination thereof, or a combination thereof,

so that the mercury content of the cleaned gas is maintained at or below a desired level.

29. The method of claim 25, wherein the mercury-containing gas comprises about 1 g to about 30 g of the element bromine per 100 g of the sorbent.

30. The method of claim 25, wherein the mercury/sorbent composition comprises the element bromine, the sorbent material, and mercury.

* * * * *

EXHIBIT B

US008168147B2

(12) **United States Patent**
Olson et al.

(10) **Patent No.:** **US 8,168,147 B2**
(45) **Date of Patent:** **May 1, 2012**

(54) **SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY**

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Michael J. Holmes, Thompson, ND (US); **John H. Pavlish**, East Grand Forks, MN (US)

(73) Assignee: **Energy & Environmental Research Center Foundation**, Grand Forks, ND (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **12/419,219**

(22) Filed: **Apr. 6, 2009**

(65) **Prior Publication Data**

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Related U.S. Application Data

(60) Continuation of application No. 12/201,595, filed on Aug. 29, 2008, which is a division of application No. 11/209,163, filed on Aug. 22, 2005, now Pat. No. 7,435,286.

(60) Provisional application No. 60/605,640, filed on Aug. 30, 2004.

(51) **Int. Cl.**
B01D 53/02 (2006.01)

(52) **U.S. Cl.** **423/210**; 95/134; 95/901; 423/103;
502/416; 502/417

(58) **Field of Classification Search** 110/345;
423/210; 95/134, 142

See application file for complete search history.

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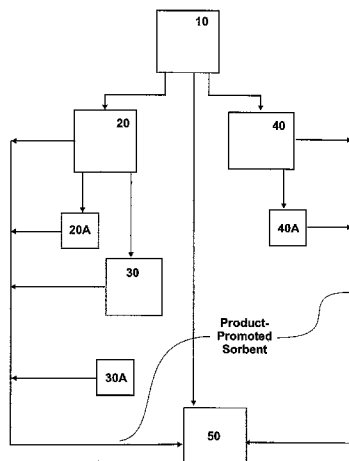
Assistant Examiner — Amber Orlando

(74) *Attorney, Agent, or Firm* — Schwegman, Lundberg & Woessner, P.A.

(57) **ABSTRACT**

A promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new modified carbon form containing reactive forms of halogen and halides. Optional components may be added to increase reactivity and mercury capacity. These may be added directly with the sorbent, or to the flue gas to enhance sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The sorbent can be regenerated and reused. Sorbent treatment and preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

25 Claims, 10 Drawing Sheets



US 8,168,147 B2

Page 2

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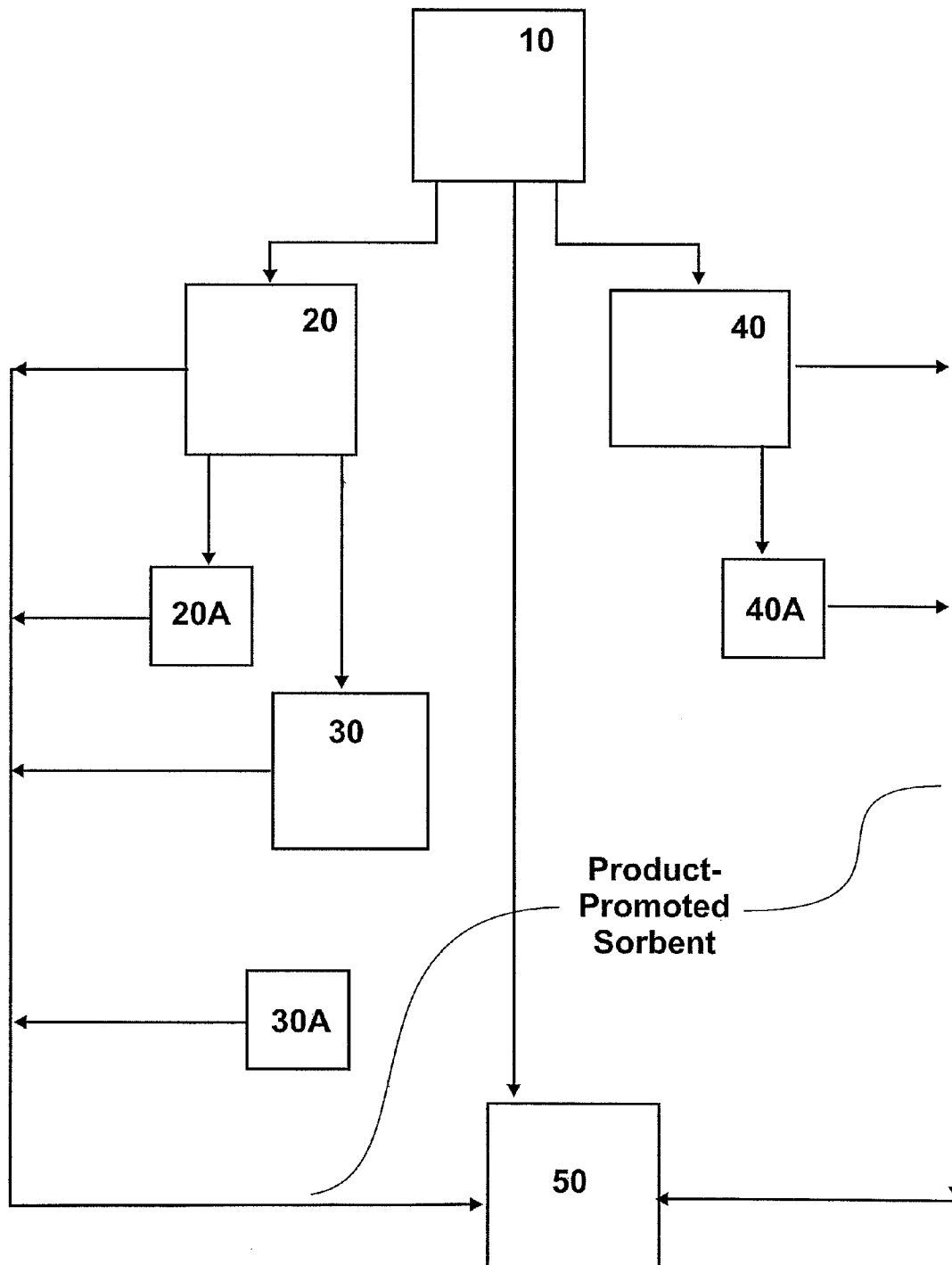


FIG. 1

U.S. Patent

May 1, 2012

Sheet 2 of 10

US 8,168,147 B2

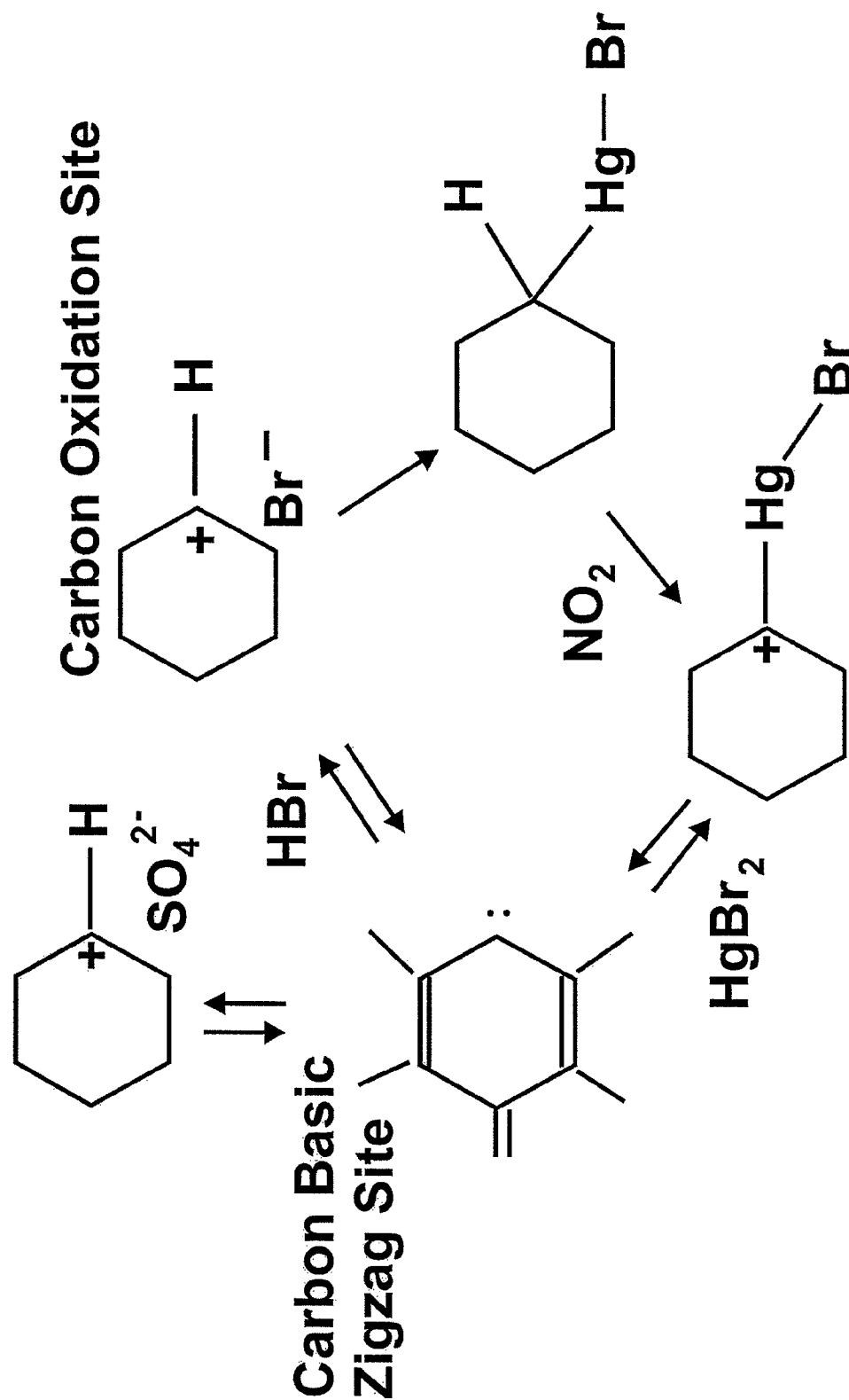


FIG. 2

U.S. Patent

May 1, 2012

Sheet 4 of 10

US 8,168,147 B2

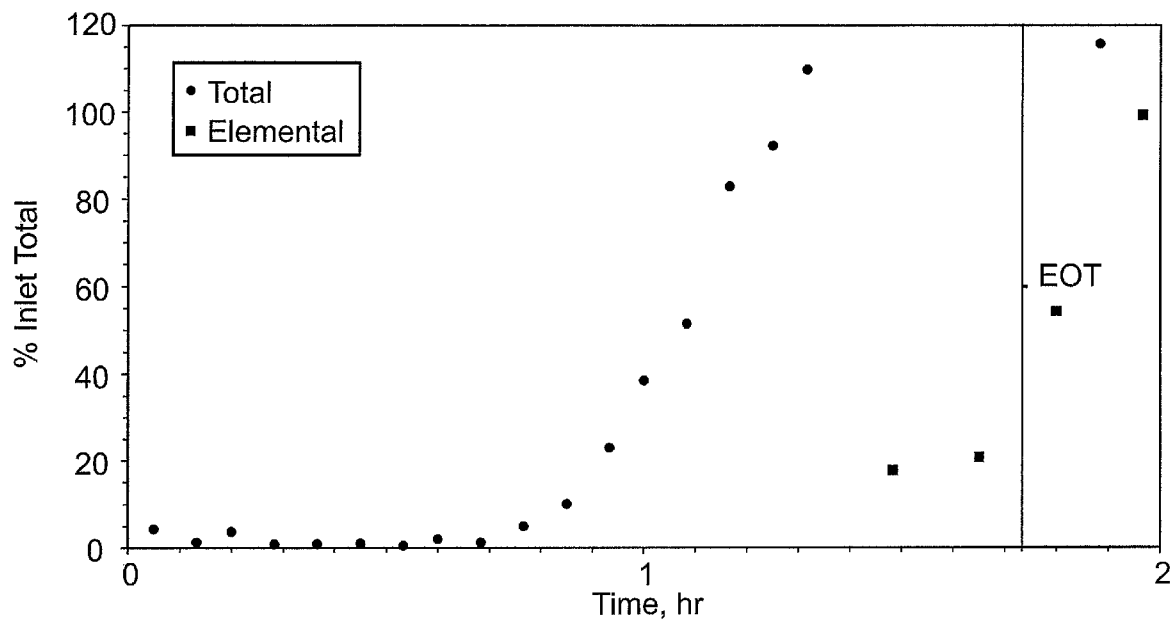


FIG. 4

U.S. Patent

May 1, 2012

Sheet 5 of 10

US 8,168,147 B2

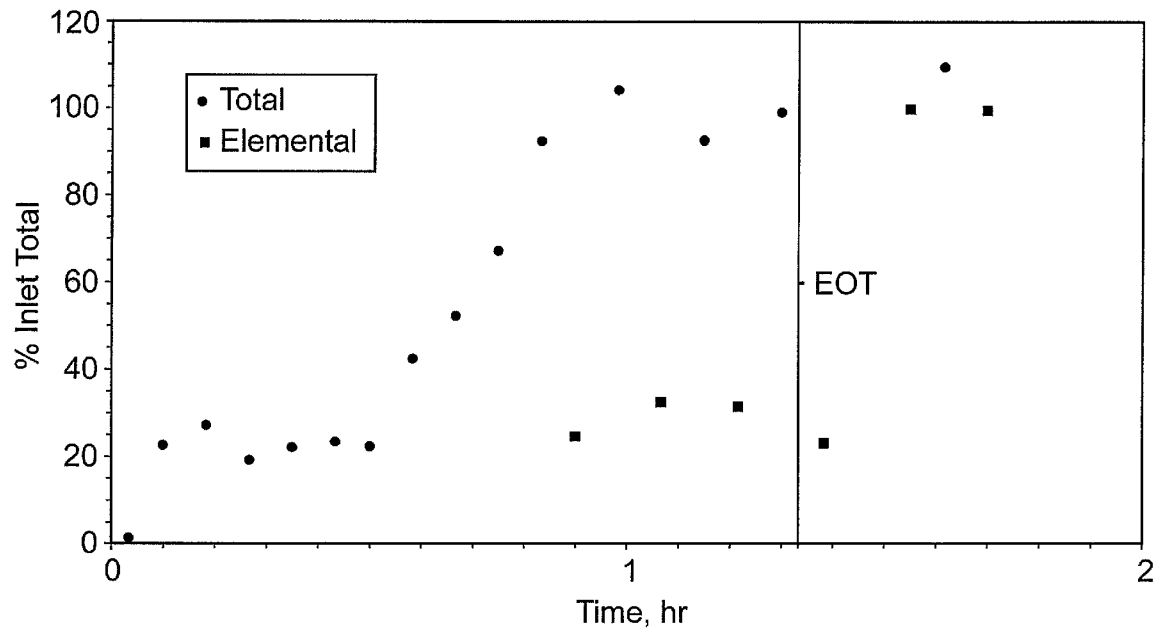


FIG. 5

U.S. Patent

May 1, 2012

Sheet 6 of 10

US 8,168,147 B2

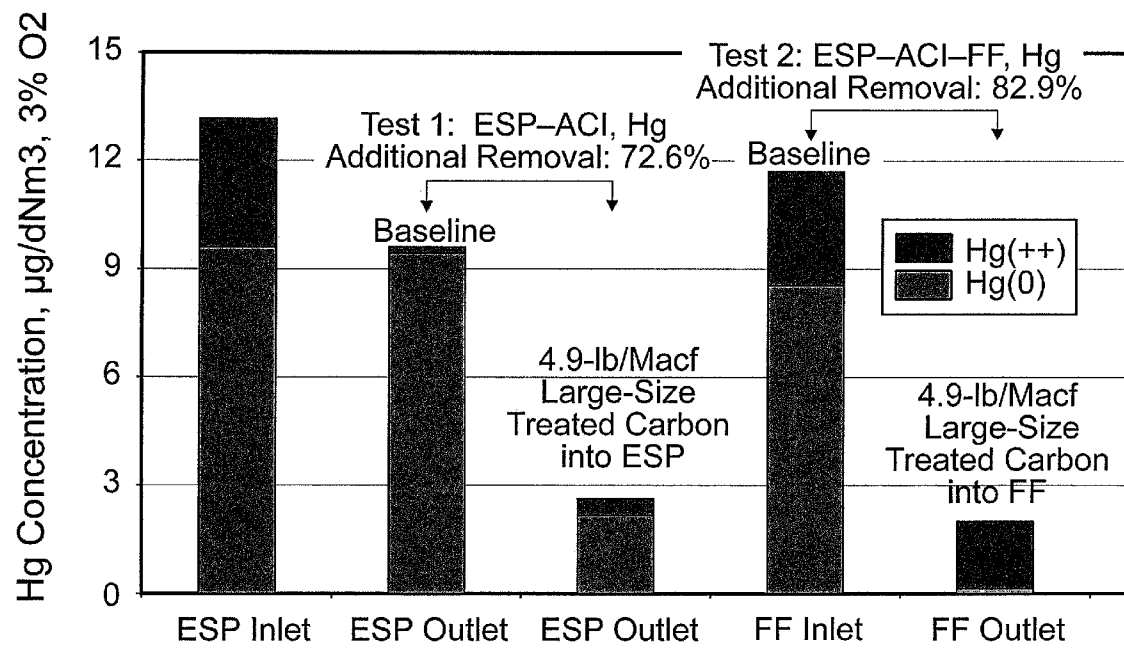


FIG. 6

U.S. Patent

May 1, 2012

Sheet 7 of 10

US 8,168,147 B2

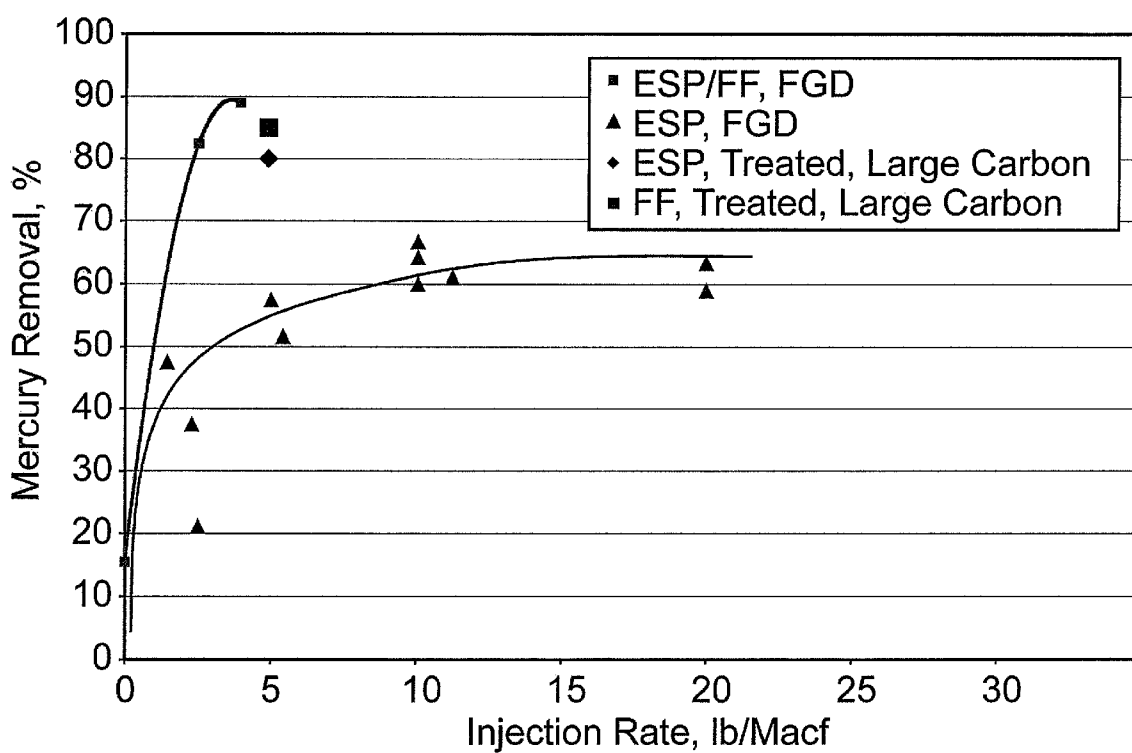


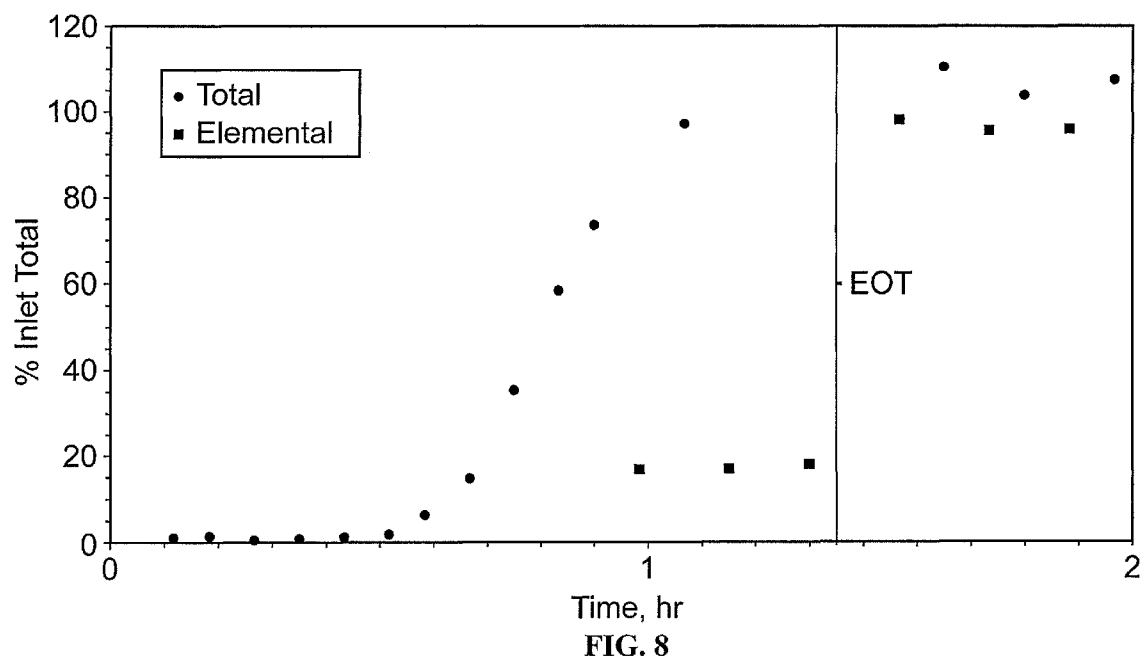
FIG. 7

U.S. Patent

May 1, 2012

Sheet 8 of 10

US 8,168,147 B2

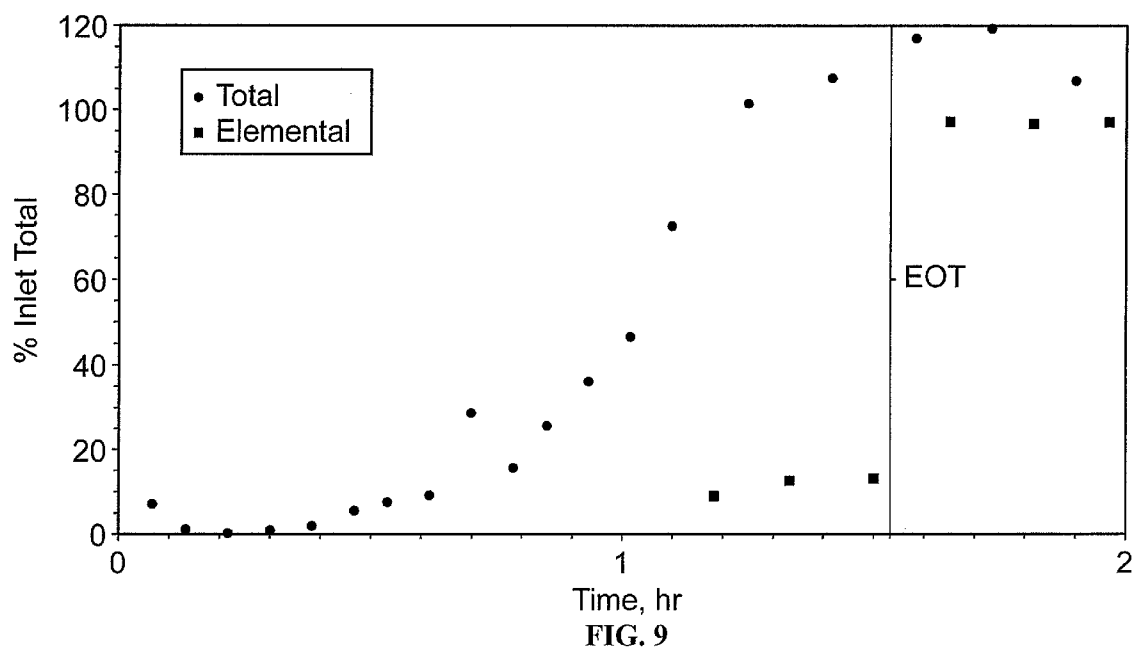


U.S. Patent

May 1, 2012

Sheet 9 of 10

US 8,168,147 B2



U.S. Patent

May 1, 2012

Sheet 10 of 10

US 8,168,147 B2

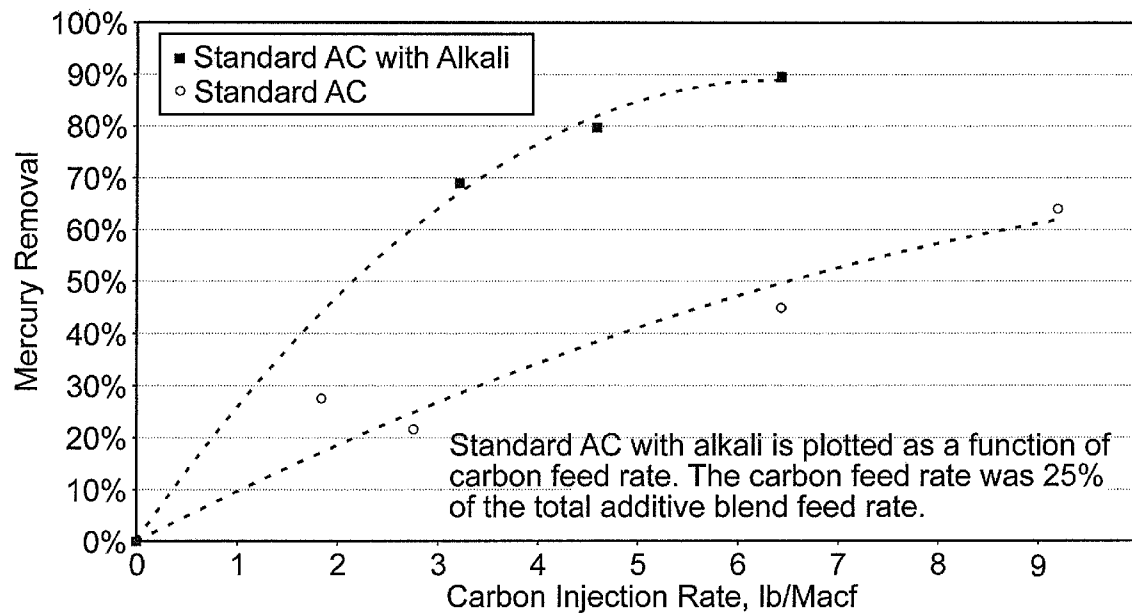


FIG. 10

US 8,168,147 B2

1

**SORBENTS FOR THE OXIDATION AND
REMOVAL OF MERCURY****CROSS-REFERENCE TO RELATED
APPLICATIONS**

This application is a continuation of U.S. patent application Ser. No. 12/201,595 filed on Aug. 29, 2008, which is a division of U.S. patent application Ser. No. 11/209,163, filed on Aug. 22, 2005 (now U.S. Pat. No. 7,435,286), which claims priority to the extent appropriate from provisional application 60/605,640, filed on Aug. 30, 2004. Application Ser. Nos. 12/201,595; 11/209,163; and 60/605,640 are incorporated herein by reference.

**STATEMENT REGARDING FEDERALLY
SPONSORED RESEARCH OR DEVELOPMENT**

This invention was made with United States Government support under Grant Numbers R 827649-01 and CR 830929-01 awarded by the United States Environmental Protection Agency and under Contract Number DE-FC26-98FT40320 awarded by the United States Department of Energy. The United States Government has certain rights in this invention.

BACKGROUND OF THE INVENTION**1. Technical Field of the Invention**

The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

2. Background of the Invention

The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, per day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as off gases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a bag house or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents

2

exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon because the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after extended exposure to the flue gas does the sorbent become effectively seasoned and provide increased reactivity with the mercury in the gas. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY

It is thus an object of the present invention to overcome the deficiencies of the prior art and thereby to provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

A halogen/halide promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new halide-modified carbon form containing a reactive compound produced by the reaction of bromine (or halide or other halogen) with the carbon. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

In some embodiments, a promoted carbon sorbent is provided comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

In an embodiment, a promoted carbon sorbent is provided wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than that of flyash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the base activated carbon may have a mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream

US 8,168,147 B2

3

from which mercury is to be removed. In an embodiment, the base activated carbon may have a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the primary sorbent.

In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base activated carbon. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base activated carbon. In another embodiment, the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

In an embodiment, a method is provided comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream. In a further embodiment, the reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon. In another embodiment the reaction product has an average particle size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment the reaction product has a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment the promoter is in the gas phase when contacting the activated carbon. In another embodiment, the promoter is in an organic solvent when contacting the activated carbon.

In another embodiment, the promoter is selected from the group consisting of Br₂, a Group V bromide, a Group VI bromide, and combinations thereof.

In another embodiment, the method further comprises reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the activated carbon. In another embodiment the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof. In an embodiment, a method is provided for control of mercury in a flue gas

4

with substantially lower sorbent requirements. Through enhanced sorbent reactivity, mercury removal per gram of sorbent is increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas. In embodiments where less than 70 wt-% mercury removal is desired, the required removal may preferably be attained using less than half as much carbon as would be required with standard (non-enhanced) carbon. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent. In another embodiment the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt-% of the promoter content. In another embodiment, the method further comprises adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof.

In an embodiment, the method further comprises co-injecting an optional alkaline material, including without limitation alkaline and alkaline earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent. In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

US 8,168,147 B2

5

In an embodiment, a method for reducing the mercury content of a mercury and ash containing gas stream is provided wherein particulate activated carbon sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the sorbent particles, the sorbent particles are separated from the ash particles on the basis of size, and the sorbent particles are re-injected to the gas stream. In another embodiment, the mercury-containing sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is co-injected into the gas stream. In another embodiment, the sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from fired equipment and gasification systems.

The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

FIG. 1 schematically illustrates methods for preparation of promoted carbon sorbents in accordance with the present invention.

FIG. 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

FIG. 3 schematically illustrates preparation of promoted carbon sorbents and processes for flue gas mercury reduction in flue gases and/or product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon sorbent.

FIG. 4 is a diagram illustrating breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 5 is a diagram illustrating breakthrough curves for non-halogenated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 6 is a bar chart illustrating pilot-scale mercury removal results, including large-size sorbent results.

FIG. 7 is a diagram illustrating the effects of sorbent size and injection rate on mercury removal for ESPs and fabric filters.

FIG. 8 is a diagram illustrating the breakthrough curves for a brominated NORIT Darco FGD sorbent with inert sand.

FIG. 9 is a diagram illustrating the breakthrough curves for brominated NORIT Darco FGD sorbent with a co-injected alkali material.

6

FIG. 10 is a plot of mercury removal vs. carbon injection rate with and without co-injection of alkali material.

DETAILED DESCRIPTION

Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention, and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide promoted carbon sorbents using a bromide (or other halogen/halide) treatment of the carbon, that capture mercury via mercury-sorbent surface reactions, at very short contact times of seconds or less. The sorbent does not require in situ activation (no induction period) in the gas stream to achieve high reactivity, as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants is greatly enhanced and the sorption capacity can be regenerated, the promoted sorbent may be regenerated, recycled and/or reused.

The treated carbons, treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus, it should be understood that the terms combustion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

Referring now to FIG. 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture from flue gas and/or product gas from a gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base activated carbon, and adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, to produce a product promoted carbon sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base activated carbon as shown by block 10, adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product promoted carbon sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A.

US 8,168,147 B2

7

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base activated carbon as illustrated at block 10, and adding a halogen or halide promoter and a secondary component to the activated carbon together, with which they react as illustrated by block 40, producing a product promoted carbon sorbent. As above, in embodiments where vapor additions are made to the activated carbon no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A.

Referring still to FIG. 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a flue gas stream is treated with product promoted carbon sorbent prepared as described above.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product promoted carbon sorbent, or other types as known in the art.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle size greater than fly ash in a flue gas stream to be treated.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle size distribution greater than that of the fly ash or entrained ash in a flue gas stream to be treated, such that the activated carbon and ash can be separated by physical means.

In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the base activated carbon may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2 , respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2 , water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

Referring now to FIG. 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in FIG. 2, hydrogen bromide reacts with the unsaturated structure of the activated carbon. This may be, by way of illustration only, a carbene species on the edge of the graphene sheet structures of the carbon. Molecular bromine or a bromine compound

8

reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury with subsequent capture by the sorbent.

It has now been found that the formation of the new bromide compound with carbon increases their reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus, adding HBr or Br_2 to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Referring now to FIG. 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted carbon sorbents, and flue gas mercury reduction, in accordance with preferred embodiments of the present invention. There is provided base activated carbon reservoir 110, an optional halogen/halide promoter reservoir 120, an optional secondary component reservoir 130, and an optional alkali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the optional alkali component reservoir 180, optional flow control devices 208 and 209 can be used independently, together, or not at all.

Reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Optional alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into contaminated flue gas stream 15. A source of air, nitrogen, or other transport gas(es) may be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such materials, via injection point 119, into flue gas stream 15. Gas sources 170 and 171 may be the same or different, as desired. Alternatively, transport gas(es) may be provided to both transport lines 115 and 118 by gas source 170 (connection from source 170 to line 118 not shown). Although gas sources 170 and 171 are shown in FIG. 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

For clarity, single injection points 116 or 119 are shown in FIG. 3, although one skilled in the art will understand that multiple injection points are within the scope of the present invention. Optical density measuring device (s) 204 is connected to transport line 115 and/or 118 to provide signals representative of the optical density inside transport line 115 and/or 118 as a function of time.

Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 may comprise one or more fabric filters, one or more electrostatic precipitators (hereinafter "ESP"), or other particulate removal devices as are known in the art. It should be further noted that more than one particulate separator 140 may exist, sequentially or in paral-

US 8,168,147 B2

9

lel, and that injection point **116** and **119** may be at a location upstream and/or downstream of **140** when parallel, sequential, or combinations thereof exist. Particulate separator **140** produces at least a predominantly gaseous (“clean”) stream **142**, and a stream **141** comprising separated solid materials. A sorbent/ash separator **150** separates stream **141** into a largely ash stream **152**, and a largely sorbent stream **151**. Stream **151** may then preferably be passed to an optional sorbent regenerator **160**, which yields a regenerated sorbent stream **161** and a waste stream **162**.

An optional Continuous Emission Monitor (hereinafter “CEM”) **205** for mercury is provided in exhaust gas stream **35**, to provide electrical signals representative of the mercury concentration in exhaust stream **35** as a function of time. The optional mercury CEM **205** and flow controllers **201**, **202**, **203**, **208**, and **209** are electrically connected via optional lines **207** (or wirelessly) to an optional digital computer (or controller) **206**, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream **15**.

In operation, promoted carbon sorbent and/or an optional alkali component is injected into contaminated flue gas stream **15**. After contacting the injected material with the contaminated flue gas stream **15**, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, **25**. The injected material is removed from the flue gas **25**, by separator **140**, disposed of or further separated by optional separator **150**, and disposed of or regenerated by an optional regenerator **160**, respectively. The reduced mercury “clean” flue gas stream **142** is then monitored for mercury content by an optional CEM **205**, which provides corresponding signals to an optional computer/controller **206**. Logic and optimization signals from **206** then adjust flow controllers **201**, **202**, **203**, **208**, **209** to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art. Flow controllers **201**, **202**, **203**, **208**, **209** can also be adjusted manually or be some other automated means to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art.

Referring still to FIG. 3, there are illustrated several preferred embodiments for preparation and injection of promoted carbon sorbents and/or alkali components in accordance with the present invention. Stream **111** provides for introduction of base activated carbon from reservoir **110**, as metered by flow controller **201** manually or under the direction of computer **206**. The halogen/halide may be combined and react with the base activated carbon according to any of several provided methods. The halogen/halide may preferably be combined via line **121** directly into transport line **115**, within which it contacts and reacts with the base activated carbon prior to injection point **116**. This option is one form of what is referred to herein as “in-flight” preparation of a promoted carbon sorbent in accordance with the invention. Further, the halogen/halide may be combined via line **121b** with base activated carbon prior to entering transport line **115**. Still further, the halogen/halide may be contacted and react with the base activated carbon by introduction via line **121c** into reservoir **110**. This option is preferably employed when, for example, reservoir **110** comprises an ebulliated or fluidized bed of base activated carbon, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base activated carbon in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in FIG. 3) may

10

then be provided if necessary as mentioned with respect to embodiments discussed with reference to FIG. 1.

Similarly, the optional secondary component may be contacted and react directly in transport line **115** via line **131**, or optionally as described above with respect to the halogen/halide, via lines **131b** and **131c**.

Similarly, the optional alkali component from **180** may either be added in transport line **115** directly, or may be injected separately by transport line **118**, combining downstream in flue gas **15** for synergistic effects with base activated carbon, promoted carbon, or optional secondary components. Being able to vary onsite the amount of the optional alkali component relative to base activated carbon, promoted carbon, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base activated carbon. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br₂, may be passed through an ebulliated or fluidized bed of granular or fibrous activated carbon, with the promoted carbon sorbent so produced removed from the top of the bed via gas entrainment for injection.

In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl₂ and others. In some preferred embodiments, the promoted carbon sorbent may comprise from about 1 to about 30 g halogen/halide per 100 g base activated carbon. In some preferred embodiments, the promoted carbon sorbent may comprise an secondary component in concentration of from about 1 to about 15 wt-% of the concentration of the halogen/halide component.

In still other embodiments, the product promoted carbon sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted carbon sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof.

Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A “halogen” is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB

US 8,168,147 B2

11

(IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F_2 , Cl_2 , Br_2 , and I_2 , the reaction with a hot flue gas components leave little to react with elemental mercury. The atomic elemental halogen form, which includes the fluorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view therefore, a halide-salt-treated activated carbon will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen Promoted Sorbent Characteristics

The sorbent described here has a very high initial reactivity for oxidizing mercury and therefore can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the sorbents produced using the inventive technology. The time interval required for the mercury and the promoted carbon sorbents of the present invention to successfully interact in a flue gas duct, with the subsequent collection of the mercury on the sorbent and ash is very short—less than seconds. Clearly, such collection times require the sorbent to have both high capacity and high reactivity toward mercury. The promoted carbon sorbent can be utilized in a very finely powdered form to minimize mass transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a sorbent containing a halide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for very effective capture of the mercury.

It appears that the inventive sorbents chemically combine molecular bromine, for example, from solution, with activated carbon (edge sites). X-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus, the sorbent produced from halogen and activated carbon does not represent a molecular halogen form, but rather a new chemically modified carbon (or halocarbon) structure. This phenomenon may not occur with the less reactive iodine, where an I_2 molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

12

Optional Second Component

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, typically exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus, the second component is an element with more polarized electrons (4p and 5p).

Optional Alkali Component

It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO_2 , NO_x , HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio onsite in order to overcome and optimize for a given set of site conditions.

The synergy that can be gained when co-injecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e. sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~ an order of magnitude less) than activated carbon, thus more of it can be used still resulting in overall lower costs.

"In-Flight" Sorbent Preparation

Furthermore, we have demonstrated that the halogen promoted carbon sorbent can be readily produced "in-flight". This is accomplished by, for example, contacting the vapors of any combination of halogens and optionally a second component, in-flight, with very fine carbon particles. The particles may be dispersed in a stream of transport air (or other gas), which also conveys the halogen/halide promoted carbon sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

Advantages of on-Site Preparation

In-flight preparation of the halogen/halide promoted carbon sorbent on location produces certain advantages. For example, the treatment system can be combined with the carbon injection system at the end-use site. With this technique, the halogen/halide is introduced to the carbon-air (or other gas) mixture in a transport line (or other part of the sorbent storage and injection system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

US 8,168,147 B2

13

Capital equipment costs at a treatment facility are eliminated.

Costs to operate the treatment facility are eliminated.

There are no costs for transporting carbon and additive to a treatment facility.

The inventive process uses existing hardware and operation procedures.

The inventive technology ensures that the sorbent is always fresh, and thus, more reactive.

No new handling concerns are introduced.

There are no costs for removing carbon from treatment system.

The inventive process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when changing fuels or reducing loads, thus further optimizing the economics.

The inventive technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide promoted carbon sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g. bromine) to the carbon structure.

Sorbent Injection Location

Some of the preferred embodiments contemplate the use of a halogen promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen promoted carbon sorbent comprise a powdered modified activated carbon prepared by adding Br₂ or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjunction with a base activated carbon and/or with the use of a halogen based sorbent and any other combinations of the sorbent technologies provided in this patent. Alternatively, embodiments include methods wherein the sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

Any of the above embodiments of the halogen/halide promoted carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive, conventional methods of adding a reagent (such as peroxide, gold, triiodide, etc.) to a sorbent. The halogen/halide promoted carbon sorbent of the present invention, treated with bromine and/or optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in co-pending, commonly owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal

14

material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

Promoted Carbon Sorbents

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a carbocation that accepts electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine-containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

EXAMPLES

To more clearly illustrate the present invention, several examples are presented below. These examples are intended to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

Example 1

Preparation and Testing of Halogenated Carbon (& Comparative Example) Gas Phase Halogenation

Finely powdered activated carbon (such as NORIT Darco FGD, NORIT Americas, Inc., Marshall, Tex. (USA), although others are suitable, as will be recognized by those skilled in the art), was placed in a rotating plastic barrel with side blades (a 5 ft³ (0.14 m³) cement mixer) fitted with a tight plastic lid to prevent loss of the fine powder during the preparation. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that is warmed to about 40°-50° C. The vapor pressure of the bromine was such that a dark red gas is generated and passed out of the generator. The outlet from the gaseous bromine generator is connected via a ¼ inch (0.64 cm) plastic hose to a stationary metal tube inserted through a flange in the center of the plastic lid and passing into the center of the barrel. The flange is not air tight so that the excess of nitrogen is released after the bromine is transferred to the tumbling carbon. Thus, the bromine gas stream continuously passed into the rotating barrel where it contacted the tumbling carbon. The unit is then operated until the desired amount of bromine has combined with the carbon. Typically, this is 0.4 to 1 kg of bromine to 20 kg of carbon (2-5 wt. %). When the reaction is completed, the carbon is weighed. The treated carbon is odorless and does not cause skin irritation since the bromine has completely reacted with the carbon to produce the brominated carbon.

XPS spectra demonstrate that the brominated carbon contains both covalent carbon-bound (organic) bromide as well as anionic bromide. The product contains the same moisture

US 8,168,147 B2

15

originally present in the activated carbon (5-17 wt %), but does not require further drying for use. The moisture is driven out at higher temperatures ($>150^{\circ}\text{C}$.), and the bromine was not released until very high temperatures

Bench-Scale Testing of Mercury Oxidation and Capture Efficiency

A bench-scale apparatus and procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including bromine-containing activated carbons prepared from a variety of carbons, including commercially available sorbents, aerogel film sorbents, and the original precursor carbons for comparison.

A detailed description of the apparatus and its operation is provided in Dunham, G. E.; Miller, S. J. Chang, R.; Bergman, P. *Environmental Progress* 1998, 17, 203, which is incorporated herein by reference in its entirety. The bench scale mercury sorbent tests in the flue gas compositions were performed with finely (~ 400 mesh) powdered sorbents (37 mg) mixed with 113 mg sand and loaded on a quartz filter (2.5 inch (6.35 cm)). The loaded filter and holder were heated in an oven (125°C .) in the simulated flue gas stream (30 SCFH (standard cubic feet/hr) or 0.79 NCMH (normal cubic meters per hour)) containing the following: O_2 (6%), CO_2 (12%), SO_2 (600 ppm), NO (120 ppm) NO_2 (6 ppm), HCl (1 ppm), Hg^0 (11 $\mu\text{g}/\text{m}^3$), H_2O (15%), and N_2 (balance). Elemental mercury was provided by a standard permeation tube source placed in a double jacketed glass condenser, and heated to the desired temperature. Mercury concentrations in the gas streams were determined with a continuous mercury emission monitor (Sir Galahad mercury CEM mfr. P.S. Analytical Deerfield Beach Fla. USA), and a SnCl_2 cell was used to convert oxidized species to elemental, so that both elemental and oxidized mercury concentration data could be obtained for both the influent and the effluent concentrations from the sorbent bed. Mercury concentrations were calibrated for the flow rates used. Spent sorbents were analyzed for mercury to determine the mass balance.

Referring now to FIG. 4, the effluent mercury concentration data are plotted as a percent of the influent mercury versus time. The resulting curve (breakthrough curve) for the halogenated sorbents typically showed 0%-1% Hg in the effluent (99+% capture) at the beginning, and increasing only after 30-60 minutes (breakthrough point), depending on the sorbent. FIG. 4 illustrates the breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) with synthetic flue gas containing 1 ppm HCl. Total Hg (solid circles) and elemental Hg (solid squares) in the effluent are presented as a percent of the inlet Hg. "EOT" indicates the end of test (the later data points shown are for calibration checks).

FIG. 5 presents the comparative breakthrough curves for the corresponding nonhalogenated sorbents typically initiated at 5%-50% of inlet mercury, depending on the HCl concentration in the synthetic flue gas, thus indicating considerably lower reactivity for oxidation and capture of the mercury for the nonhalogenated sorbents. After breakthrough of either halogenated or nonhalogenated sorbent, most of the mercury in the effluent was oxidized mercury.

Example 2

Gas Phase Halogenation of Fluidized Carbon

A bed of activated carbon supported in a vertical tube by a plug of glass wool was fluidized by a nitrogen stream. The top of the fluidized bed tube was connected to a catching trap for

16

carbon fines that blow out the top of the tube. The bromine gas generator as described in Example 1 was attached to the fluidized carbon bed and the desired amount of gaseous bromine was passed into the bed. The contents of the trap were then mixed with the material in the bed and weighed. The resulting brominated carbon exhibited properties similar to the brominated carbon of Example 1.

Example 3

Liquid Phase (Water) Halogenation

A 5% solution of bromine in water was prepared by carefully adding 50 g of bromine to 1 liter of cold water. One kg of activated carbon was added to the bromine solution in a large metal can. The resulting slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon, as indicated by the disappearance of the red color. The slurry was then filtered using a Buchner funnel under vacuum. The moist carbon that was collected on the filter was dried in an oven at 110°C . for several hours to constant weight. As in Example 1, some moisture remains in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 4

Addition of the Optional Second Halide Component

Brominated carbon was produced by solution phase bromination similar to that described with reference to Example 3. However, before filtration, a solution of hydriodic acid (HI) was added to the slurry in an amount equal to 10% of the bromine amount. The slurry was stirred to complete the reaction and then filtered and dried as described in Example 3.

Example 5

Liquid Phase Phosphohalogenation

A solution of phosphorus tribromide (500 g) in ligroin (10 liters) was stirred in a large metal can and 10 kg of activated carbon was added. The resulting slurry was stirred with a large paddle at ambient temperature to complete the reaction. The slurry was filtered under vacuum on a large Buchner funnel in several batches. The wet filter cake was dried at 110°C . in an oven to constant weight. The dried product was fluffed in the rotating barrel as described in Example 3.

Example 6

Preparation and Sorption on Larger-Particle Carbon

Tests were conducted on a pilot-scale combustor while firing a subbituminous coal, to evaluate mercury control by injecting larger-than-normal sized treated activated carbon. Standard AC sorbents generally are of fine size with a mean particle diameter of less than 20 micrometers, which is also typical of the flyash that is generated from pulverized coal combustion. Consequently, because the sizes of standard AC and flyash are similar, separation of the two is difficult. Injection of larger sized AC is generally not considered because the sorbent effectiveness decreases with size. In a scheme to recycle the injected carbon, the carbon is separated from the flyash. A separation based on size fractionation requires a

US 8,168,147 B2

17

treated larger particle sorbent. To test this concept, a treated larger sized ($>60\text{ }\mu\text{m}$) sorbent was developed, prepared, and tested.

Treatment—Gas Phase Halogenation

Granular activated carbon (Calgon F400) was ground and sieved through conventional mesh screens. The mesh size fraction -170 to $+240$ (corresponding to about 60 to about 88 micrometers) was collected and placed in a rotating vessel as described in Example 1 above. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that was warmed to about 40° – 50° C., and the outlet from this gaseous bromine generator was connected via a $\frac{1}{4}$ inch (6.35 mm) plastic hose to a stationary metal tube inserted through a flange in the center of the lid and passing into the center of the rotating vessel, also as described in Example 1. The unit was operated until the desired amount of bromine had combined with the carbon, in this case 0.05 kg of bromine to 1 kg of carbon (5 wt. %). When the reaction was completed, the carbon was weighed. The treated carbon was odorless as has been described above.

PTC Apparatus

The pilot-scale combustor, known as the “Particulate Test Combustor” (hereinafter “PTC”), is a 550,000-Btu/hr (about 161 kW) pulverized coal (“PC”)-fired unit, designed to generate combustion flue gas properties and fly ash that are representative of those produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle of the PTC fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature. Originally, the PTC used cold-water annular heat exchangers to provide flue gas temperature control to the baghouse (also referred to as a “fabric filter”) or electrostatic precipitator (ESP). However, analysis of ash deposits collected from the heat exchangers indicated that some mercury was collected on the duct walls. To minimize this effect, the heat exchangers were modified to provide for higher duct wall temperatures.

The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device (baghouse, Advanced Hybrid Particle Collector/AHPC™, and/or electrostatic precipitator/ESP) operating data to be monitored continuously and recorded on a data logger.

PTC Procedure

Flue gas samples were taken at combinations of two of the three available system sample points: the furnace exit, the particulate control device inlet, and the particulate control device outlet. After passing through sample conditioners to remove moisture, the flue gas was typically analyzed for O_2 , CO , CO_2 , SO_2 , and NO_x . Each constituent was normally analyzed at both the furnace exit and the outlet of the particulate control device simultaneously, using two analyzers. The concentration values from all of the instruments were recorded continuously. In addition, data were manually recorded at set time intervals. NO_x was determined using a pair of Rosemount Analytical NO_x chemiluminescent analyzers. SO_2 was measured using a pair of Ametek Instruments photometric gas analyzers. The remaining gases were measured by a pair of Rosemount Analytical multi-gas continu-

18

ous emissions monitors. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

The baghouse vessel was a 20 inch (50.8 cm) (ID) chamber that is heat-traced and insulated, with the flue gas introduced near the bottom. The combustor produced about 200 ACFM (actual cubic feet per minute; about 5.7 actual m^3/min) of flue gas at 300° F. (about 150° C.), therefore three 13-ft by 5-inch (3.96 m by 12.7 cm) bags provided an air-to-cloth ratio of 4 ft/min (1.22 m/min). Each bag was cleaned separately in operation with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags were cleaned on a time basis, rather than with the cleaning cycle initiated by pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession on-line.

Tests were also conducted with a single-wire, tubular ESP replacing the fabric filter. The ESP unit was designed to provide a specific collection area of 125 at 300° F. (150° C.). Since the flue gas flow rate for the PTC is 130 SCFM (standard cubic feet per minute; about 3.7 NCMM (normal m^3/min)), the gas velocity through the ESP is 5 ft/min (about 1.52 m/min). The plate spacing for the ESP unit is 11 in (27.9 cm). The ESP was designed to facilitate thorough cleaning between tests so that all tests can begin on the same basis.

PTC Results

Results are illustrated in FIG. 6. As can be observed in FIG. 6, even though the tested sorbent particle size is significantly larger than normal sorbent particles, the treated larger-than-normal sized (that is, >60 micrometers) activated carbon sorbent was quite effective at capturing mercury. Approximately 75% of the mercury was captured when the larger-sized treated AC was injected ahead of the pilot-scale ESP, while approximately 85% of the mercury was captured when injected ahead of the pilot-scale fabric filter (“FF”). Note that in FIG. 6 (and throughout) “Macf” (and “MACF”) indicates million actual cubic feet (1 MACF is about 0.028 million actual cubic meters or “MACM”).

Referring now to FIG. 7, it can be observed that the larger-sized treated AC when injected ahead of the pilot-scale ESP (diamond symbol(s)) performed better than the finer standard AC (triangles) under the same arrangement. In comparison, when injected ahead of the fabric filter (FF), the larger-sized treated AC (square) performed similarly to slightly worse. However, for this application, the larger-sized treated AC can be physically separated from the smaller flyash particles, and the sorbent can then be regenerated, recycled, and reused. This will substantially improve overall utilization and economics. These data thus show that a larger-than-normal sized sorbent can provide effective mercury control and ease flyash and AC separation, thereby also preserving the characteristics of the flyash for sale and beneficial use. Accordingly, because $>60\text{ }\mu\text{m}$ sorbent particles have been successfully demonstrated, superior mercury control can be obtained with $>40\text{ }\mu\text{m}$ particles, which may be preferred in some applications, depending on the sorbent particle/ash separation system used. Note that in FIG. 7 (and throughout) “Macf” (and “MACF”) indicates million actual cubic feet.

Example 7

Liquid Phase (Organic Solvent) Halogenation

A 5% solution of bromine in ligroin was prepared by carefully adding 50 g of bromine to 1 liter of cold ligroin. One kg of activated carbon was added to the bromine solution in a large metal can. The slurry was stirred with a large paddle

US 8,168,147 B2

19

during the addition and for a short time afterwards until all the bromine had reacted with the carbon as indicated by the disappearance of the red color. The slurry was filtered using a Buchner funnel under vacuum. The carbon cake that was collected on the filter was dried in an oven at 110° C. for several hours until it appeared dry and a constant weight was obtained. As in Example 1, some moisture was left in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 8

Promoted Activated Carbon Sorbents

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100° C. in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. The results indicated that adding a second component to the solution improved the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 µg/m³) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM ("continuous emission monitor") (mfr. P S Analytical, Deerfield Beach, Fla., USA). The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer. A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it was treated with 0.1 N HBr, and the powder was collected by centrifugation and drying, revealed that the mercury capture activity increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicated that it not only captured mercury at the same level as before (100% capture) but its capacity was prolonged by several minutes, and thus enhanced. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

Example 9

Fluidized/Ebulliated Bed Preparation

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed or ebulliated bed of the carbon. The amount of bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

20

Example 10

Full-Scale Testing

In this example, a baghouse (fabric filter) or ESP was used to collect particulates in the exhaust of a full-scale commercial pulverized coal-burning facility. A scrubber and sorbent bed were also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In this example, the halogen/halide promoted carbon sorbent was injected into the flue gas after the boiler. In general however, the inventive sorbent can be injected where desired (e.g., before, after, or within the boiler).

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 µg/m³. The ash and injected carbon were collected in the baghouse at 350° F. to 375° F. (about 175-190° C.). Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/MACF ("MACF" and "Macf" represent one million actual cubic feet; 1.0 lb/MACF is about 16 kg/MACM (million actual cubic meters)) resulted in mercury effluent concentrations of 3.8-4.2 µg/m³ (representing 62%-58% removal of the mercury from the gas, respectively), and at 2.0 lb/MACF (about 32 kg/MACM), gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/MACF resulted in 73%-69% removal and at 2.0 lb/MACF gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine promoted carbon sorbent of the present invention.

Example 11A

Addition of Optional Alkaline Component—Bench-Scale

The efficiency of the activated carbons for mercury capture can be improved considerably by employing a basic material co-injected with the activated carbon, in order to capture any oxidized mercury that may be released from the sorbent, or to capture some of the sulfur or selenium oxides in the flue gas that can have a detrimental effect on the sorbent capacity.

Bench-scale testing was conducted by preparing a filter composed of 37 mg of brominated activated carbon mixed with 113 mg of calcium oxide. The test was conducted as described in Example 1 and compared with the same carbon sorbent but with an inert diluent. The breakthrough curve for the mixture of brominated (2%) NORIT Darco FGD sorbent with inert sand is shown in FIG. 8, and the breakthrough curve for the mixture with CaO is shown in FIG. 9. It can be seen that the point of 50% breakthrough improves to 65 minutes with the mixture with CaO from only 48 min with the sand mixture.

Example 11B

Addition of Optional Alkaline Component—Pilot-Scale

Tests were conducted on the pilot-scale PTC combustor described above with reference to Example 6 while firing a Texas lignite to evaluate mercury control by co-injecting a standard activated carbon (also referred to herein as "AC") and an alkali material upstream of a fabric filter. Typical results are illustrated in FIG. 10. As shown in FIG. 10, co-injecting lime with activated carbon vastly improved mercury removal. Mercury removals of approximately 90% were

US 8,168,147 B2

21

achieved with the co-injected sorbents, whereas less than 60% removal was achieved with the use of standard AC alone, even at much higher injection rates. Data from similar tests show that injecting similar quantities of sodium carbonate and AC, and lime and AC, resulted in mercury removals of approximately 80%, and 87%, respectively. These data suggest that other alkali can also be co-injected with AC to improve mercury removal. Other data show that flue gas temperature may impact the effectiveness of the alkali addition. Further test data indicate that flue gas contaminants, flue gas constituents (SO₂, NO_x, HCl, etc.), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This indicates that it may be desirable to be able to adjust and tailor, onsite, the alkali-to-AC ratio in order to optimize removal for a given set of site conditions.

Without wishing to be bound by any particular theory, the synergy observed in the improved performance when co-injecting the two materials can be explained as follows. First, tests indicate that binding sites on AC can be consumed by sulfur species and other contaminants. The alkali material interacts and reacts with these species thus minimizing their consumption of AC mercury binding sites. Second, other work has shown that standard AC will continue to oxidize mercury even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by the particulate control device. Thus, combining alkali with treated and/or non-treated AC synergistically takes advantage of these two mechanisms, resulting in improved mercury capture at reduced costs.

Example 12

Brominated Carbon Sorbent for Gasification Fuel Gas Preparation of 5% Br2W-AC

Using a procedure similar to Example 3, a 2.5 wt/vol % solution of bromine in water was prepared. Granular Calgon F400 was added to the bromine solution to give a 5 wt/wt % brominated carbon product. The bromine solution was stirred with a large paddle during and after the addition until the red color in the water disappeared. The suspension was filtered by vacuum on a large Buchner funnel. The filter cake was dried in air, and then in an oven at 110° C. until a stable weight was obtained. The moisture was reduced to 15%.

Preparation of 5% Br2D-AC

A brominated sorbent was prepared from Br₂ addition in solvent as described in Example 7, except that dichloromethane was used as the solvent instead of ligroin, and granular Calgon F400 was used.

Preparation of 5% PBr3-AC

A phosphohalogenated sorbent was prepared from PBr₃ using the method described in Example 5, except granular Calgon F400 was used.

Testing in Hydrogen Atmosphere—Procedure

To simulate the capture of mercury from a heated fuel gas or syngas from coal gasification, tests were conducted employing a stream comprising 10% vol/vol hydrogen in nitrogen passing through the sorbent at 500 cc/min. The stream contained 26.9 micrograms/m³ of elemental mercury from a commercial mercury permeation source.

In the tests, the sorbent (0.5 g) was placed in a 0.39 inch (1 cm, inside diameter) glass tube fitted with a medium frit sintered glass filter disc to hold the sorbent in the gas stream. The tube containing the sorbent bed was connected to a gas inlet tube for introducing the gas stream containing the mercury vapor and at the outlet to a tube connection to the detec-

22

tor. The detector was a Semtech 2000 continuous mercury emission monitor. The tube was equilibrated in a nitrogen flow (450 cc/min) for 5 minutes at ambient temperature to stabilize the system. The detector showed 0 concentration of mercury in the effluent from the sorbent bed. (The blank run with no sorbent read 26.9 micrograms/m³). The tube was then placed in an oven at the selected temperature for the test (from 250° to 400° C.). Effluent mercury concentration data from the detector were collected until the detector showed a constant reading for 5 minutes. Hydrogen (50 cc/min) was then added to the gas stream and detector readings were taken every 5 min. Tests were conducted at several oven temperatures for various periods of time up to 3 hours, depending on the temperature and sorbent. The elemental mercury concentration data were plotted as a percent of inlet mercury concentration versus time as in Example 1. All the mercury in the effluent was elemental, so a single detector was sufficient, and no SnCl₂ trap was needed to convert to elemental mercury (as in Example 1). The time for 50% breakthrough (time to reach 50% capture) was then determined from the breakthrough curves.

Results

The results are shown in Table 1 (below) for the unbrominated sorbent (Calgon F-400), the brominated sorbents (5% Br2W-AC and 5% BrD-AC), and the phosphobrominated sorbent (5% PBr3-AC). The maximum mercury concentration obtained in the effluent in each run is also reported in Table 1 for the time period indicated in the last column.

Under the reducing hydrogen conditions, the unbrominated sorbent broke through immediately and was exhausted after only 6.5 min. This complete failure occurred because the hydrogen reduces the captured mercury in the unbrominated sorbent at any temperature above 100° C. Both of the brominated sorbents exhibited excellent reactivity and good capacity at all temperatures, up to at least 400° C. The phosphobrominated sorbent exhibited superior reactivity and capacity at all temperatures, up to at least 400° C.

TABLE 1

Times for 50% Breakthrough Maximum Observed Hg Concentrations for Sorbents (10% Hydrogen Streams)				
Sorbent	Temp (° C.)	50% breakthrough (min)	Maximum [Hg] (µg/m ³)	Time (min)
F-400	250	6	20.3	6.5
5% Br2W-AC	250	>150	1.4	150
5% Br2W-AC	300	>180	4.3	180
5% Br2W-AC	350	160	15.1	180
5% Br2W-AC	400	60	13.9	65
5% PBr3-AC	250	>140	0.4	140
5% PBr3-AC	300	>150	0.5	150
5% PBr3-AC	350	>150	1.4	150
5% Br2D-AC	350	>180	2.1	180
5% Br2D-AC	400	>180	10.9	180

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

US 8,168,147 B2

23

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

Although the invention is described herein as a sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

We claim:

1. A method for separating mercury from a mercury containing gas comprising:

(a) promoting at least a portion of a particulate sorbent material comprising activated carbon by chemically reacting the sorbent material with a bromine containing promoter to form a promoted brominated sorbent, wherein the bromine containing promoter is in gaseous form, vapor form, or non-aqueous liquid form, and wherein the activated carbon contains graphene sheets having carbene species edge sites which react with the bromine containing promoter to form a carbocation paired with a bromide anion in the promoted brominated sorbent for oxidation of the mercury;

(b) chemically reacting elemental mercury in the mercury containing gas with the promoted brominated sorbent to form a mercury/sorbent chemical composition; and

(c) separating particulates from the mercury containing gas, the particulates including ash and the mercury/sorbent chemical composition.

2. A method according to claim 1, wherein the bromine containing promoter is in gaseous form.

3. A method according to claim 1, wherein the bromine containing promoter is in an organic solvent.

4. A method according to claim 1, wherein the carbocation paired with a bromide anion chemically react with elemental mercury form the mercury/sorbent composition.

5. A method according to claim 1, wherein at least a portion of the basic binding sites of the activated carbon reacts with oxidized mercury in the mercury containing gas to form another mercury/sorbent chemical composition.

6. A method according to claim 1, wherein the step of separating particulates from the mercury containing gas com-

24

prises separating in a particulate separator comprising one or more electrostatic precipitators.

7. A method according to claim 1, further comprising a step of regenerating a promoted brominated sorbent from the mercury/sorbent chemical composition for reuse.

8. A method according to claim 7, further comprising injecting the regenerated promoted brominated sorbent into a mercury containing gas.

9. A method according to claim 1, further comprising injecting an alkali component into the mercury containing gas for protecting mercury binding sites and capturing oxidized mercury.

10. A method according to claim 9, wherein the alkali component comprises an oxide, hydroxide, carbonate, phosphate of an alkali or alkaline earth element.

11. A method according to claim 1, further comprising adding a second halogen or halide promoter to the promoted halogen containing sorbent.

12. A method according to claim 11, wherein the second halogen or halide promoter comprises HI, HBr, HCl, Group V element with halogen, or Group VI element with halogen.

13. A method according to claim 1, further comprising adding a stabilizing agent to the promoted brominated sorbent.

14. A method according to claim 13, wherein the stabilizing agent comprises at least one of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, or mixtures thereof.

15. A method according to claim 1, wherein the step of promoting at least a portion of the available sorbent material occurs at least partially outside of the mercury containing gas.

16. A method according to claim 1, wherein the promoted brominated sorbent combines with at least 70% of the mercury present in the mercury containing gas.

17. A method according to claim 1, further comprising injecting the particulate sorbent material at a sorbent material injection rate and injecting separately the bromine containing promoter into a gas stream whereby in-flight reaction produces the promoted brominated sorbent, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of the sorbent material.

18. A method according to claim 17, wherein the gas stream is a mercury containing gas.

19. A method according to claim 18, wherein the gas stream is a transport gas.

20. A method according to claim 17, wherein the promoter injection rate and the sorbent injection rate into the gas are determined at least in part on the monitored mercury content of the cleaned gas.

21. A method according to claim 1, wherein the composition of the promoted sorbent is controlled by the mercury content of the cleaned gas stream.

22. A method according to claim 1, wherein the bromine containing promoter comprises at least one of HBr, PBr₃, or Br₂.

23. A method according to claim 1, wherein the bromine containing promoter comprises molecular bromine.

24. A method according to claim 1, wherein the bromine containing promoter comprises a bromine compound.

25. A method according to claim 1, wherein the bromine containing promoter comprises a Group V or Group VI bromide.

* * * * *

EXHIBIT C



US010589225B2

(12) **United States Patent**
Olson et al.

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(45) **Date of Patent:** ***Mar. 17, 2020**

(54) **SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY**

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(58) **Field of Classification Search**

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(57) **ABSTRACT**

A promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new modified carbon form containing reactive forms of halogen and halides. Optional components may be added to increase reactivity and mercury capacity. These may be added directly with the sorbent, or to the flue gas to enhance sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The sorbent can be regenerated and reused. Sorbent treatment and preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

29 Claims, 10 Drawing Sheets

US 10,589,225 B2

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Mar. 17, 2020

Sheet 1 of 10

US 10,589,225 B2

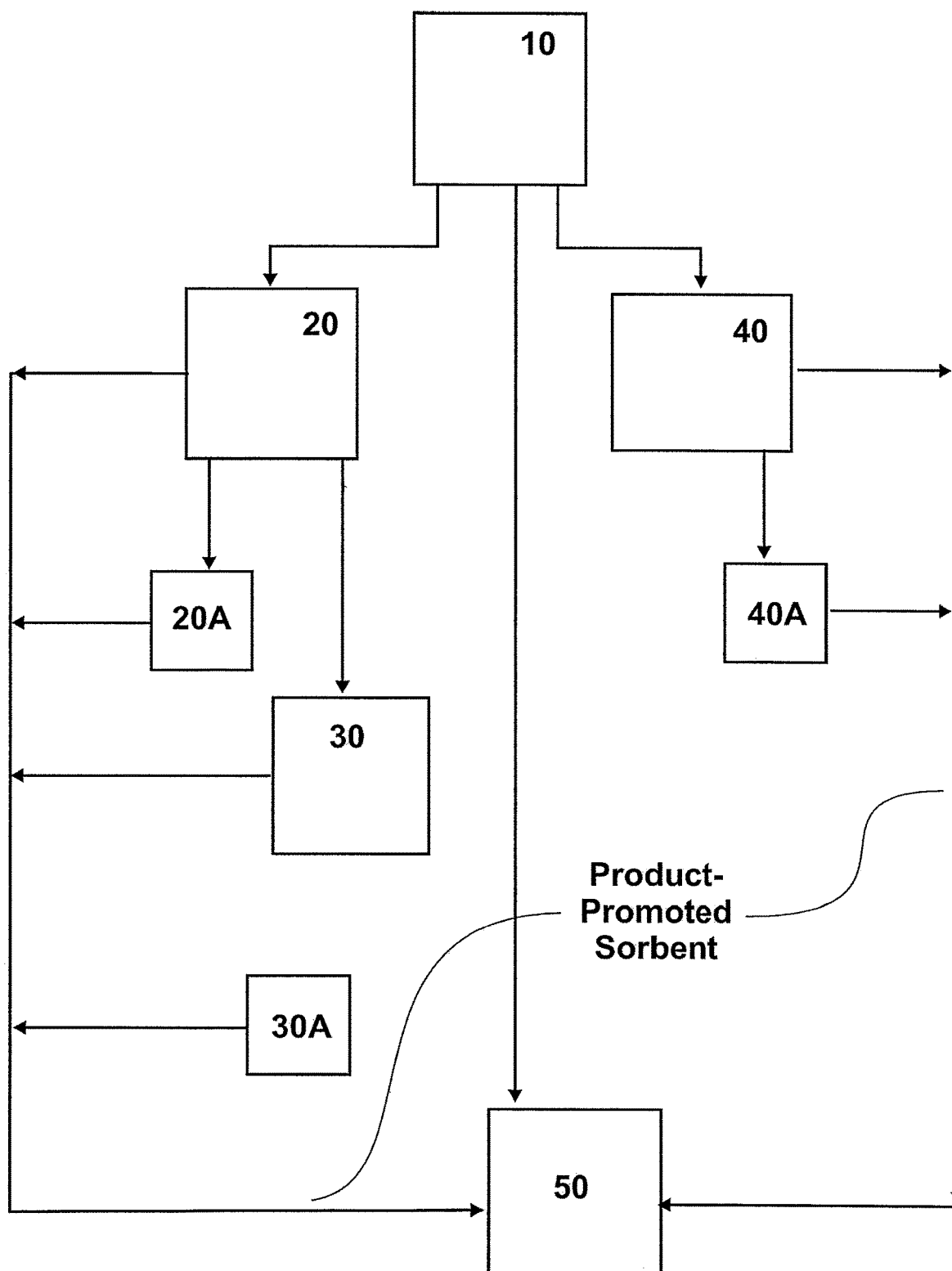


FIG. 1

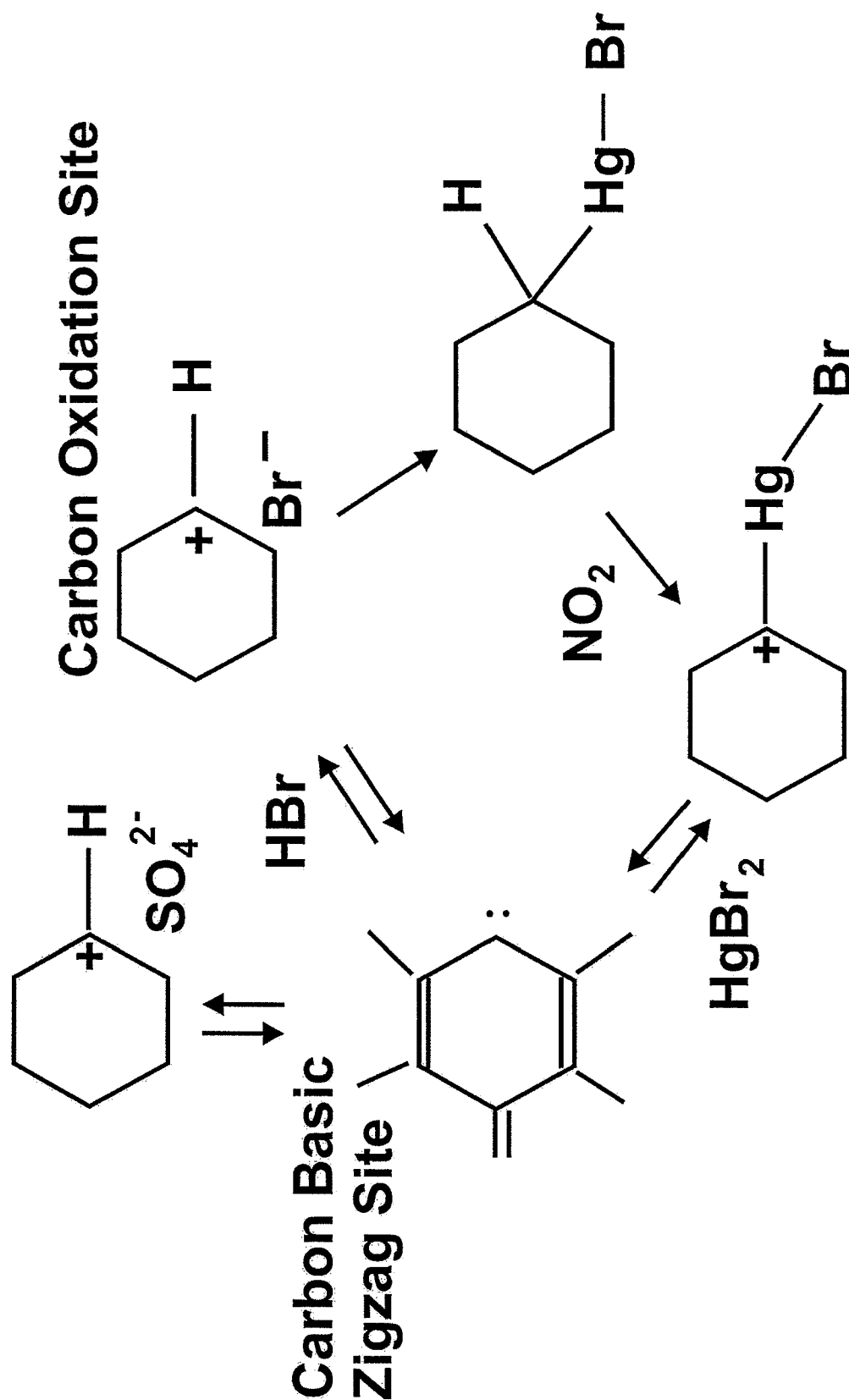


FIG. 2

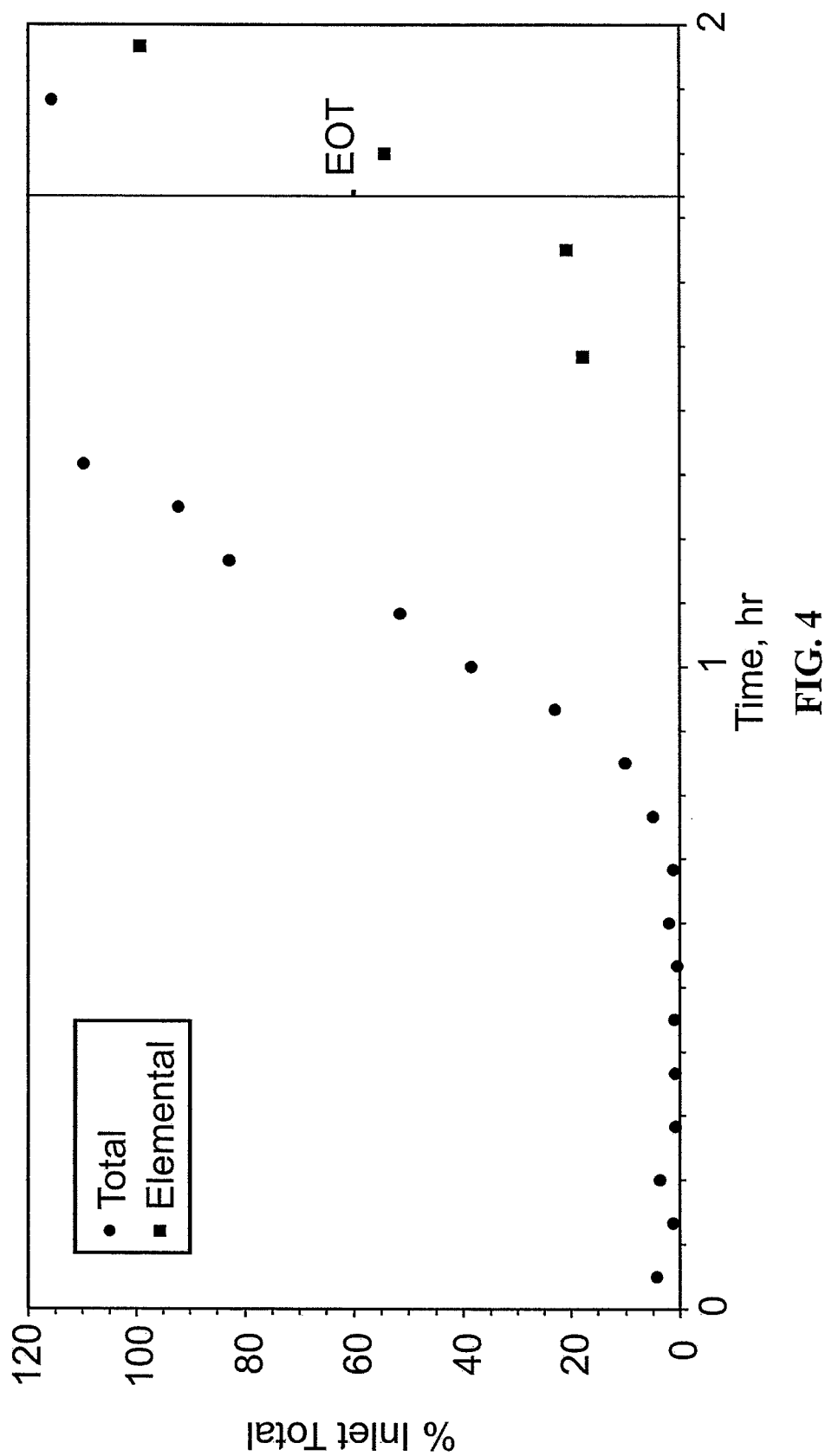


U.S. Patent

Mar. 17, 2020

Sheet 4 of 10

US 10,589,225 B2

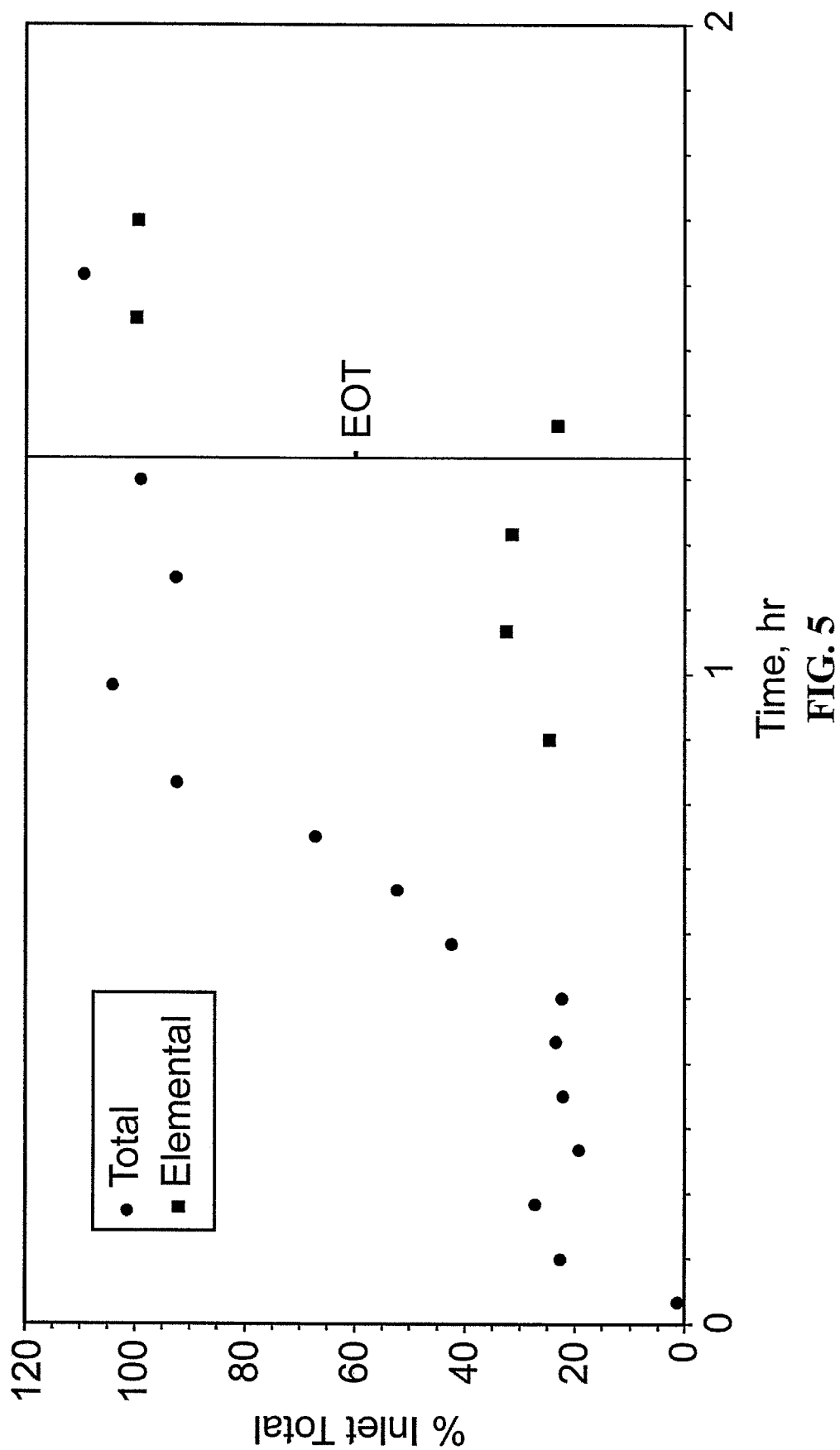


U.S. Patent

Mar. 17, 2020

Sheet 5 of 10

US 10,589,225 B2



U.S. Patent

Mar. 17, 2020

Sheet 6 of 10

US 10,589,225 B2

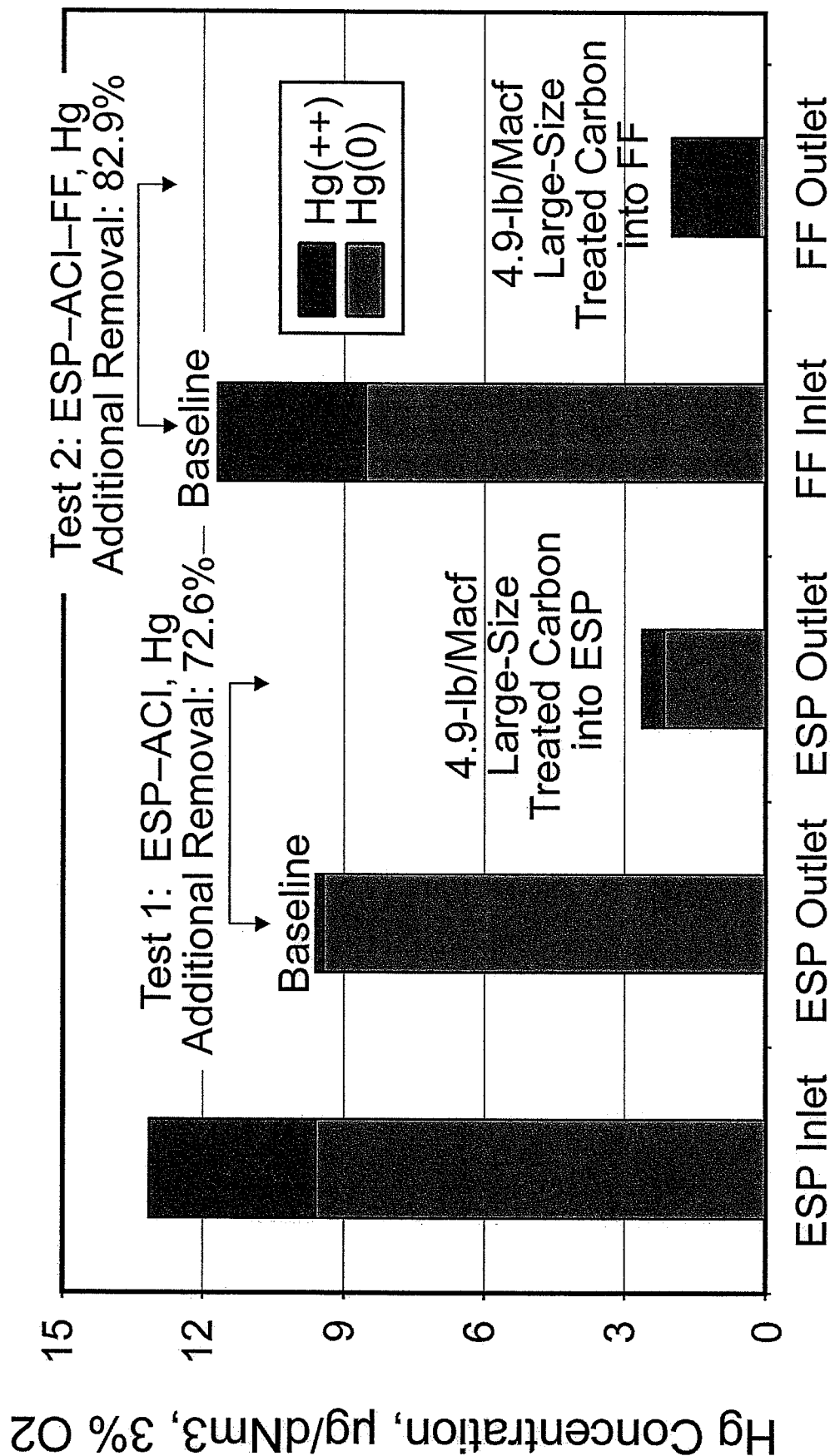


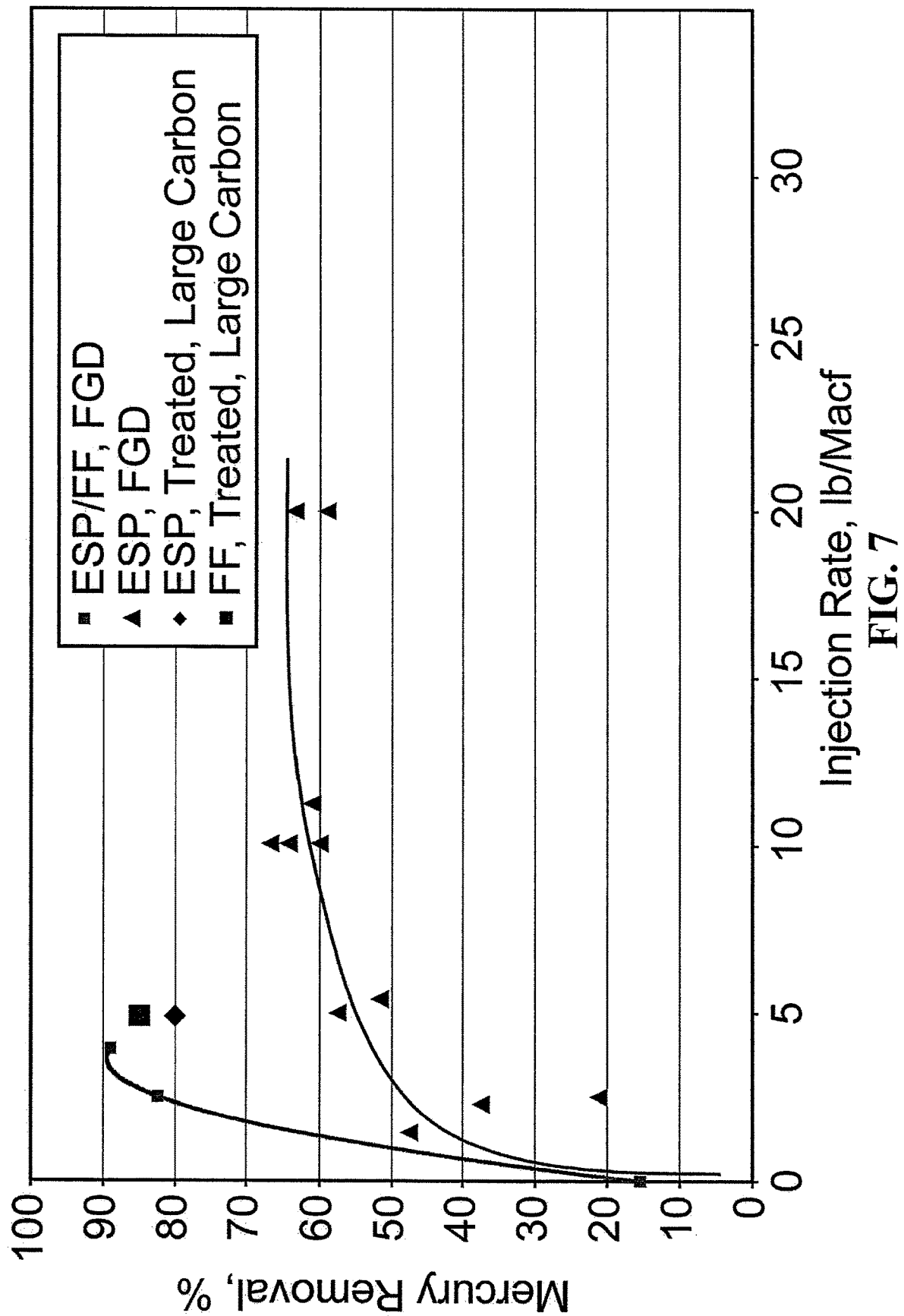
FIG. 6

U.S. Patent

Mar. 17, 2020

Sheet 7 of 10

US 10,589,225 B2

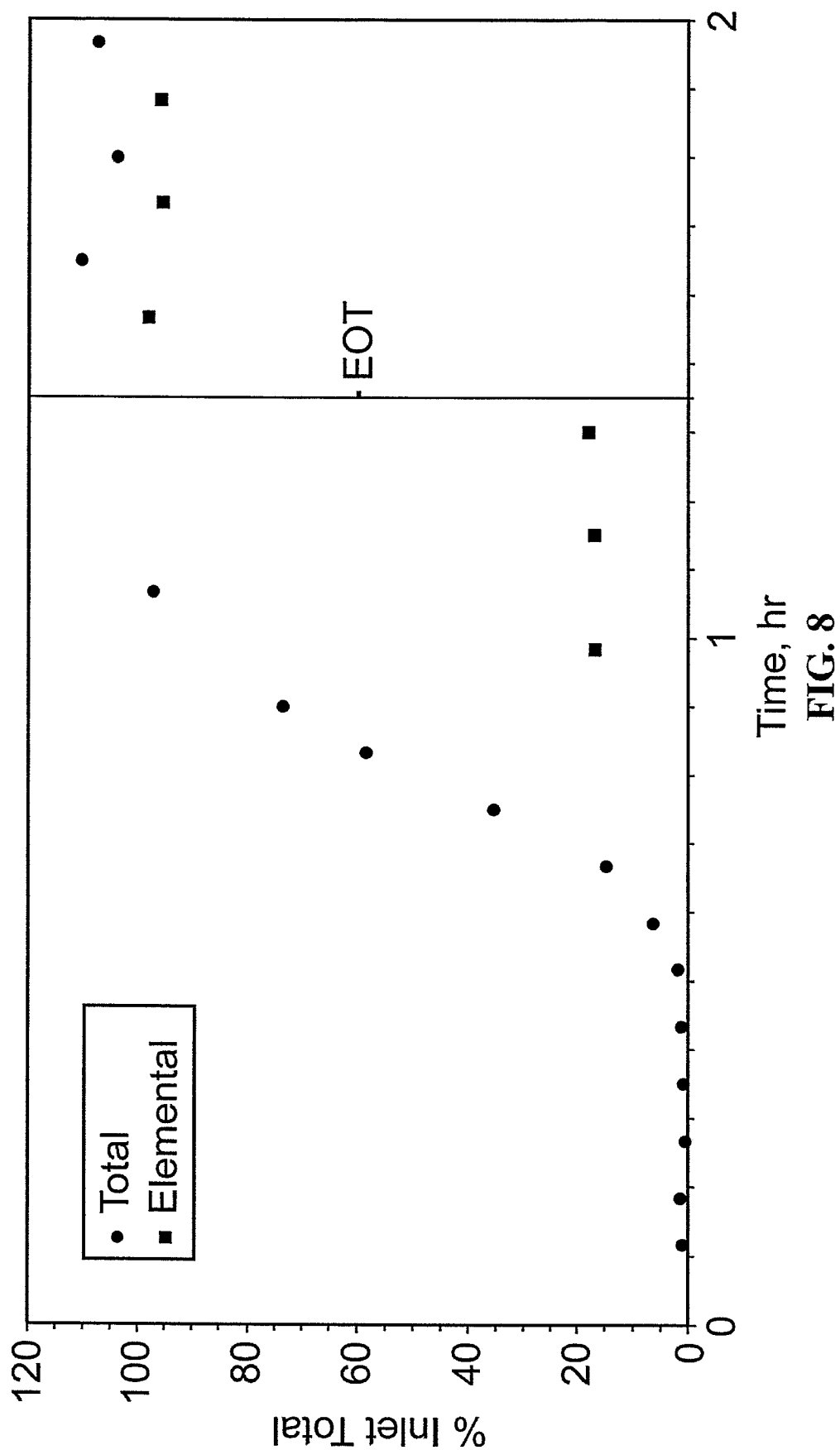


U.S. Patent

Mar. 17, 2020

Sheet 8 of 10

US 10,589,225 B2

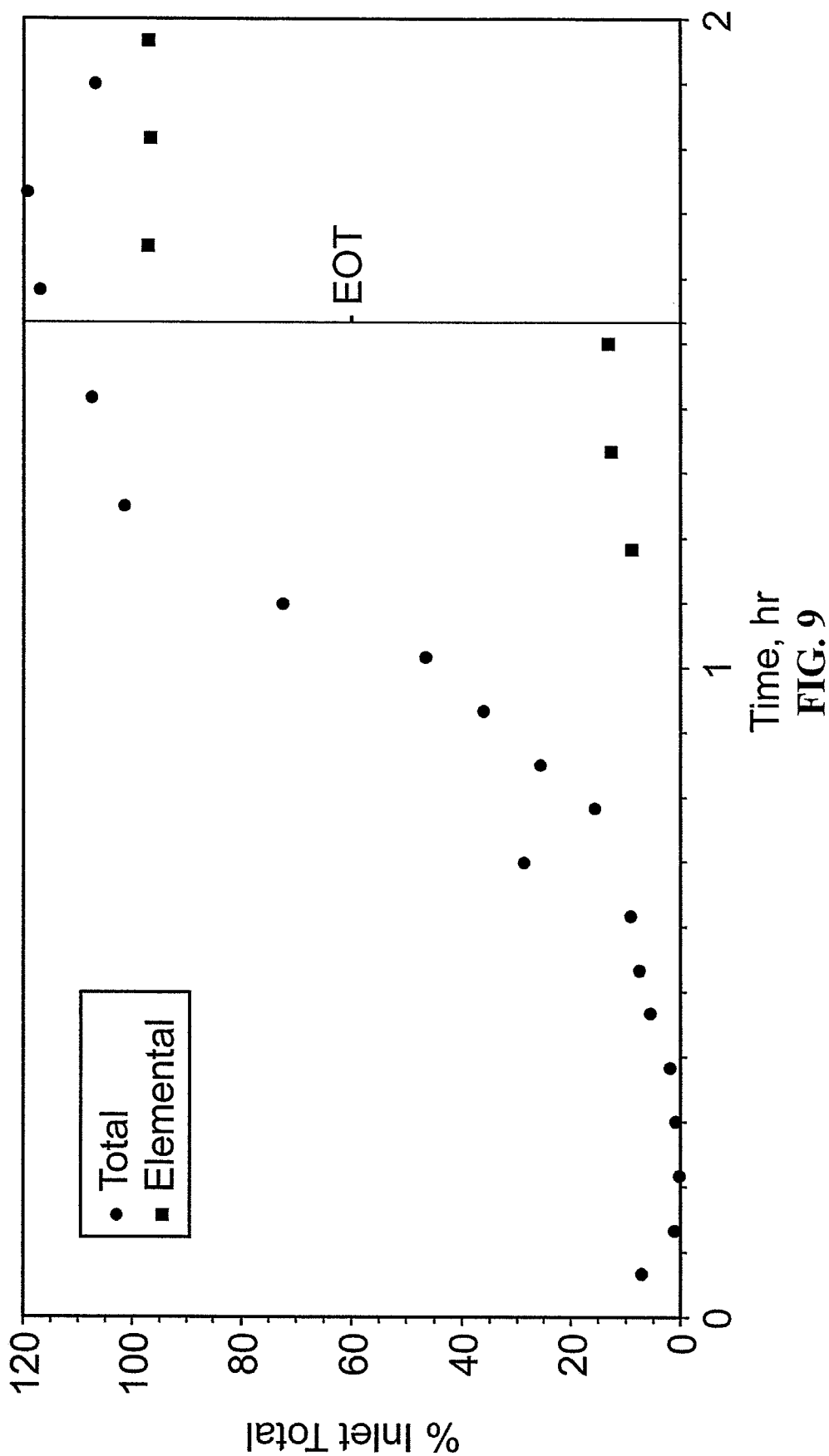


U.S. Patent

Mar. 17, 2020

Sheet 9 of 10

US 10,589,225 B2



U.S. Patent

Mar. 17, 2020

Sheet 10 of 10

US 10,589,225 B2

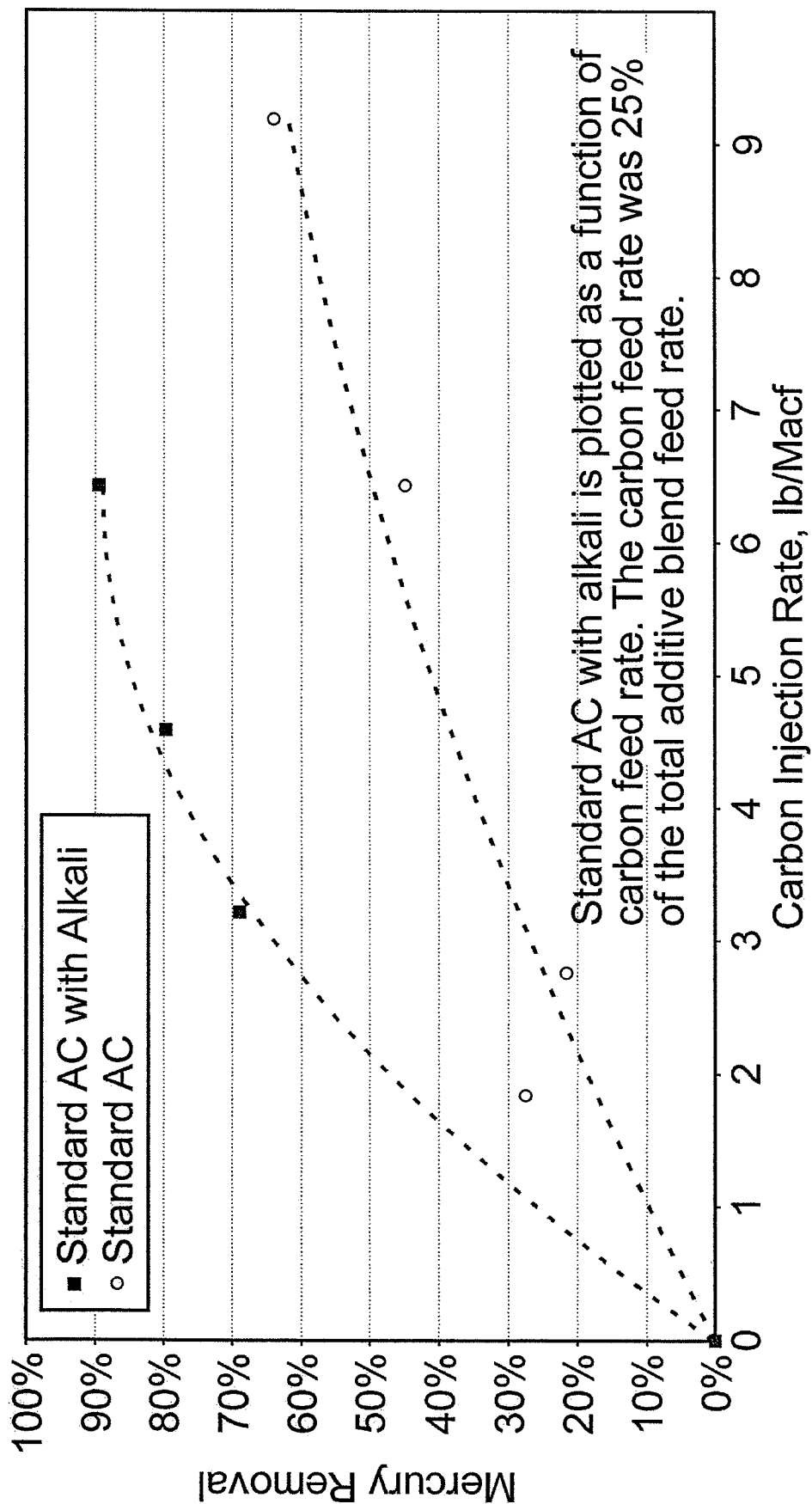


FIG. 10

US 10,589,225 B2

1

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is a divisional of U.S. patent application Ser. No. 11/209,163 filed Aug. 22, 2005, entitled "Sorvents for the Oxidation and Removal of Mercury", which claims the benefit of U.S. Provisional Application Ser. No. 60/605,640, filed Aug. 30, 2004, both applications are hereby incorporated herein by reference in their entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with United States Government support under Grant Numbers R 827649-01 and CR 830929-01 awarded by the United States Environmental Protection Agency and under Contract Number DE-FC26-98FT40320 awarded by the United States Department of Energy. The United States Government has certain rights in this invention.

BACKGROUND OF THE INVENTION**Technical Field of the Invention**

The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

Background of the Invention

The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, per day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as off gases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a bag house or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic silicate and oxide particles are

2

effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon because the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after extended exposure to the flue gas does the sorbent become effectively seasoned and provide increased reactivity with the mercury in the gas. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY

It is thus an object of the present invention to overcome the deficiencies of the prior art and thereby to provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

A halogen/halide promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new halide-modified carbon form containing a reactive compound produced by the reaction of bromine (or halide or other halogen) with the carbon. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

In some embodiments, a promoted carbon sorbent is provided comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

In an embodiment, a promoted carbon sorbent is provided wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than that of flyash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the base activated carbon may have a mass mean particle diameter such that it can be

US 10,589,225 B2

3

substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base activated carbon may have a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the primary sorbent.

In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base activated carbon. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base activated carbon. In another embodiment, the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

In an embodiment, a method is provided comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream. In a further embodiment, the reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon. In another embodiment the reaction product has an average particle size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment the reaction product has a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment the promoter is in the gas phase when contacting the activated carbon. In another embodiment, the promoter is in an organic solvent when contacting the activated carbon.

In another embodiment, the promoter is selected from the group consisting of Br₂, a Group V bromide, a Group VI bromide, and combinations thereof.

In another embodiment, the method further comprises reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the activated carbon. In another embodiment the method further comprises adding a mercury-stabilizing

4

reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof. In an embodiment, a method is provided for control of mercury in a flue gas with substantially lower sorbent requirements.

5 Through enhanced sorbent reactivity, mercury removal per gram of sorbent is increase, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas. In embodiments where less than 70 wt-% mercury removal is desired, the required removal may preferably be attained using less than half as much carbon as would be required with standard (non-enhanced) carbon. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent. In another embodiment the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt-% of the promoter content. In another embodiment, the method further comprises adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof.

In an embodiment, the method further comprises co-injecting an optional alkaline material, including without limitation alkaline and alkaline earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent. In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter

US 10,589,225 B2

5

is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

In an embodiment, a method for reducing the mercury content of a mercury and ash containing gas stream is provided wherein particulate activated carbon sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the sorbent particles, the sorbent particles are separated from the ash particles on the basis of size, and the sorbent particles are re-injected to the gas stream. In another embodiment, the mercury-containing sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is co-injected into the gas stream. In another embodiment, the sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from fired equipment and gasification systems.

The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

FIG. 1 schematically illustrates methods for preparation of promoted carbon sorbents in accordance with the present invention.

FIG. 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

FIG. 3 schematically illustrates preparation of promoted carbon sorbents and processes for flue gas mercury reduction in flue gases and/or product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon sorbent.

FIG. 4 is a diagram illustrating breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 5 is a diagram illustrating breakthrough curves for non-halogenated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 6 is a bar chart illustrating pilot-scale mercury removal results, including large-size sorbent results.

FIG. 7 is a diagram illustrating the effects of sorbent size and injection rate on mercury removal for ESPs and fabric filters.

6

FIG. 8 is a diagram illustrating the breakthrough curves for a brominated NORIT Darco FGD sorbent with inert sand.

FIG. 9 is a diagram illustrating the breakthrough curves for brominated NORIT Darco FGD sorbent with a co-injected alkali material.

FIG. 10 is a plot of mercury removal vs. carbon injection rate with and without co-injection of alkali material.

DETAILED DESCRIPTION

Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention, and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide promoted carbon sorbents using a bromide (or other halogen/halide) treatment of the carbon, that capture mercury via mercury-sorbent surface reactions, at very short contact times of seconds or less. The sorbent does not require in situ activation (no induction period) in the gas stream to achieve high reactivity, as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants is greatly enhanced and the sorption capacity can be regenerated, the promoted sorbent may be regenerated, recycled and/or reused.

The treated carbons, treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus, it should be understood that the terms combustion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

Referring now to FIG. 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture from flue gas and/or product gas form a gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base activated carbon, and adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, to produce a product promoted carbon sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base activated carbon as shown by block 10, adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product promoted carbon

US 10,589,225 B2

7

sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base activated carbon as illustrated at block 10, and adding a halogen or halide promoter and a secondary component to the activated carbon together, with which they react as illustrated by block 40, producing a product promoted carbon sorbent. As above, in embodiments where vapor additions are made to the activated carbon no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A.

Referring still to FIG. 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a flue gas stream is treated with product promoted carbon sorbent prepared as described above.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product promoted carbon sorbent, or other types as known in the art.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle size greater than fly ash in a flue gas stream to be treated.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle size distribution greater than that of the fly ash or entrained ash in a flue gas stream to be treated, such that the activated carbon and ash can be separated by physical means.

In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the base activated carbon may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2 , respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as

8

supercritical CO_2 , water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

Referring now to FIG. 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in FIG. 2, hydrogen bromide reacts with the unsaturated structure of the activated carbon. This may be, by way of illustration only, a carbene species on the edge of the graphene sheet structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury with subsequent capture by the sorbent.

It has now been found that the formation of the new bromide compound with carbon increases their reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer $4p$ orbitals of the ion. Thus, adding HBr or Br_2 to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Referring now to FIG. 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted carbon sorbents, and flue gas mercury reduction, in accordance with preferred embodiments of the present invention. There is provided base activated carbon reservoir 110, an optional halogen/halide promoter reservoir 120, an optional secondary component reservoir 130, and an optional alkali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the optional alkali component reservoir 180, optional flow control devices 208 and 209 can be used independently, together, or not at all.

Reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Optional alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into contaminated flue gas stream 15. A source of air, nitrogen, or other transport gas(es) may be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such materials, via injection point 119, into flue gas stream 15. Gas sources 170 and 171 may be the same or different, as desired. Alternatively, transport gas(es) may be provided to both transport lines 115 and 118 by gas source 170 (connection from source 170 to line 118 not shown). Although gas sources 170 and 171 are shown in FIG. 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

For clarity, single injection points 116 or 119 are shown in FIG. 3, although one skilled in the art will understand that

US 10,589,225 B2

9

multiple injection points are within the scope of the present invention. Optical density measuring device (s) **204** is connected to transport line **115** and/or **118** to provide signals representative of the optical density inside transport line **115** and/or **118** as a function of time.

Downstream from injection point **116** and **119** is provided particulate separator **140**. By way of illustration and not limitation, particulate separator **140** may comprise one or more fabric filters, one or more electrostatic precipitators (hereinafter “ESP”), or other particulate removal devices as are known in the art. It should be further noted that more than one particulate separator **140** may exist, sequentially or in parallel, and that injection point **116** and **119** may be at a location upstream and/or downstream of **140** when parallel, sequential, or combinations thereof exist. Particulate separator **140** produces at least a predominantly gaseous (“clean”) stream **142**, and a stream **141** comprising separated solid materials. A sorbent/ash separator **150** separates stream **141** into a largely ash stream **152**, and a largely sorbent stream **151**. Stream **151** may then preferably be passed to an optional sorbent regenerator **160**, which yields a regenerated sorbent stream **161** and a waste stream **162**.

An optional Continuous Emission Monitor (hereinafter “CEM”) **205** for mercury is provided in exhaust gas stream **35**, to provide electrical signals representative of the mercury concentration in exhaust stream **35** as a function of time. The optional mercury CEM **205** and flow controllers **201**, **202**, **203**, **208**, and **209** are electrically connected via optional lines **207** (or wirelessly) to an optional digital computer (or controller) **206**, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream **15**.

In operation, promoted carbon sorbent and/or an optional alkali component is injected into contaminated flue gas stream **15**. After contacting the injected material with the contaminated flue gas stream **15**, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, **25**. The injected material is removed from the flue gas **25**, by separator **140**, disposed of or further separated by optional separator **150**, and disposed of or regenerated by an optional regenerator **160**, respectively. The reduced mercury “clean” flue gas stream **142** is then monitored for mercury content by an optional CEM **205**, which provides corresponding signals to an optional computer/controller **206**. Logic and optimization signals from **206** then adjust flow controllers **201**, **202**, **203**, **208**, **209** to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art. Flow controllers **201**, **202**, **203**, **208**, **209** can also be adjusted manually or be some other automated means to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art.

Referring still to FIG. 3, there are illustrated several preferred embodiments for preparation and injection of promoted carbon sorbents and/or alkali components in accordance with the present invention. Stream **111** provides for introduction of base activated carbon from reservoir **110**, as metered by flow controller **201** manually or under the direction of computer **206**. The halogen/halide may be combined and react with the base activated carbon according to any of several provided methods. The halogen/halide may preferably be combined via line **121** directly into transport line **115**, within which it contacts and reacts with the base activated carbon prior to injection point **116**. This option is one form of what is referred to herein as “in-flight” prepa-

10

ration of a promoted carbon sorbent in accordance with the invention. Further, the halogen/halide may be combined via line **121b** with base activated carbon prior to entering transport line **115**. Still further, the halogen/halide may be contacted and react with the base activated carbon by introduction via line **121c** into reservoir **110**. This option is preferably employed when, for example, reservoir **110** comprises an ebulliated or fluidized bed of base activated carbon, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base activated carbon in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in FIG. 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to FIG. 1.

Similarly, the optional secondary component may be contacted and react directly in transport line **115** via line **131**, or optionally as described above with respect to the halogen/halide, via lines **131b** and **131c**.

Similarly, the optional alkali component from **180** may either be added in transport line **115** directly, or may be injected separately by transport line **118**, combining downstream in flue gas **15** for synergistic effects with base activated carbon, promoted carbon, or optional secondary components. Being able to vary onsite the amount of the optional alkali component relative to base activated carbon, promoted carbon, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base activated carbon. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br₂, may be passed through an ebulliated or fluidized bed of granular or fibrous activated carbon, with the promoted carbon sorbent so produced removed from the top of the bed via gas entrainment for injection.

In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCI₂ and others. In some preferred embodiments, the promoted carbon sorbent may comprise from about 1 to about 30 g halogen/halide per 100 g base activated carbon. In some preferred embodiments, the promoted carbon sorbent may comprise an secondary component in concentration of from about 1 to about 15 wt-% of the concentration of the halogen/halide component.

In still other embodiments, the product promoted carbon sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted carbon sorbent to produce a bifunctional sorbent. Such stabilizing

US 10,589,225 B2

11

reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof.

Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A “halogen” is defined as a member of the very active elements comprising Group VITA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F₂, Cl₂, Br₂, and I₂, the reaction with a hot flue gas components leave little to react with elemental mercury. The atomic elemental halogen form, which includes the fluorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

The term “halide” as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view therefore, a halide-salt-treated activated carbon will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen Promoted Sorbent Characteristics

The sorbent described here has a very high initial reactivity for oxidizing mercury and therefore can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the sorbents produced using the inventive technology. The time interval required for the mercury and the promoted carbon sorbents of the present invention to successfully interact in a flue gas duct, with the subsequent collection of the mercury on the sorbent and ash is very short—less than seconds. Clearly, such collection times require the sorbent to have both high capacity and high reactivity toward mercury. The promoted carbon sorbent can be utilized in a very finely powdered form to minimize mass transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a sorbent containing a halide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for very effective capture of the mercury.

It appears that the inventive sorbents chemically combine molecular bromine, for example, from solution, with activated carbon (edge sites). X-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus, the sorbent produced from halogen and activated carbon does not represent a molecular halogen form, but rather a new chemically modified carbon (or halocarbon)

12

structure. This phenomenon may not occur with the less reactive iodine, where an I₂ molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, typically exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus, the second component is an element with more polarized electrons (4*p* and 5*p*).

Optional Alkali Component

It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO₂, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio onsite in order to overcome and optimize for a given set of site conditions.

The synergy that can be gained when co-injecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter “AC”) can be consumed by chlorine species, sulfur species (i.e. sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~an order of magnitude less) than activated carbon, thus more of it can be used still resulting in overall lower costs.

“In-Flight” Sorbent Preparation

Furthermore, we have demonstrated that the halogen promoted carbon sorbent can be readily produced “in-flight”. This is accomplished by, for example, contacting the vapors of any combination of halogens and optionally a second component, in-flight, with very fine carbon particles. The particles may be dispersed in a stream of transport air (or other gas), which also conveys the halogen/halide promoted carbon sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be

US 10,589,225 B2

13

removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

Advantages of On-Site Preparation

In-flight preparation of the halogen/halide promoted carbon sorbent on location produces certain advantages. For example, the treatment system can be combined with the carbon injection system at the end-use site. With this technique, the halogen/halide is introduced to the carbon-air (or other gas) mixture in a transport line (or other part of the sorbent storage and injection system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

Capital equipment costs at a treatment facility are eliminated.

Costs to operate the treatment facility are eliminated.

There are no costs for transporting carbon and additive to a treatment facility.

The inventive process uses existing hardware and operation procedures.

The inventive technology ensures that the sorbent is always fresh, and thus, more reactive.

No new handling concerns are introduced.

There are no costs for removing carbon from treatment system.

The inventive process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when changing fuels or reducing loads, thus further optimizing the economics.

The inventive technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide promoted carbon sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g. bromine) to the carbon structure.

Sorbent Injection Location

Some of the preferred embodiments contemplate the use of a halogen promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen promoted carbon sorbent comprise a powdered modified activated carbon prepared by adding Br₂ or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjunction with a base activated carbon and/or with the use of a halogen based sorbent and any other combinations of the sorbent technologies provided in this patent. Alternatively, embodiments include methods wherein the sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

Any of the above embodiments of the halogen/halide promoted carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive, conventional methods of adding a reagent (such as peroxide, gold, triiodide, etc.) to a sorbent. The halogen/halide promoted carbon sorbent of the present invention, treated with bromine and/or optional components, is noncorrosive. Detailed examples of sorbent regeneration

14

techniques are described in co-pending, commonly owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

Promoted Carbon Sorbents

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a carbocation that accepts electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine-containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

EXAMPLES

To more clearly illustrate the present invention, several examples are presented below. These examples are intended to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

Example 1

Preparation and Testing of Halogenated Carbon (& Comparative Example)

Gas Phase Halogenation

Finely powdered activated carbon (such as NORIT Darco FGD, NORIT Americas, Inc., Marshall, Tex. (USA), although others are suitable, as will be recognized by those skilled in the art), was placed in a rotating plastic barrel with side blades (a 5 ft³ (0.14 m³) cement mixer) fitted with a tight plastic lid to prevent loss of the fine powder during the preparation. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that is warmed to about 40°-50° C. The vapor pressure of the bromine was such that a dark red gas is generated and passed out of the generator. The outlet from the gaseous bromine generator is connected via a ¼ inch (0.64 cm) plastic hose to a stationary metal tube

US 10,589,225 B2

15

inserted through a flange in the center of the plastic lid and passing into the center of the barrel. The flange is not air tight so that the excess of nitrogen is released after the bromine is transferred to the tumbling carbon. Thus, the bromine gas stream continuously passed into the rotating barrel where it contacted the tumbling carbon. The unit is then operated until the desired amount of bromine has combined with the carbon. Typically, this is 0.4 to 1 kg of bromine to 20 kg of carbon (2-5 wt. %). When the reaction is completed, the carbon is weighed. The treated carbon is odorless and does not cause skin irritation since the bromine has completely reacted with the carbon to produce the brominated carbon.

XPS spectra demonstrate that the brominated carbon contains both covalent carbon-bound (organic) bromide as well as anionic bromide. The product contains the same moisture originally present in the activated carbon (5-17 wt %), but does not require further drying for use. The moisture is driven out at higher temperatures (>150° C.), and the bromine was not released until very high temperatures.

Bench-Scale Testing of Mercury Oxidation and Capture Efficiency

A bench-scale apparatus and procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including bromine-containing activated carbons prepared from a variety of carbons, including commercially available sorbents, aerogel film sorbents, and the original precursor carbons for comparison.

A detailed description of the apparatus and its operation is provided in Dunham, G. E.; Miller, S. J. Chang, R.; Bergman, P. *Environmental Progress* 1998, 17, 203, which is incorporated herein by reference in its entirety. The bench scale mercury sorbent tests in the flue gas compositions were performed with finely (-400 mesh) powdered sorbents (37 mg) mixed with 113 mg sand and loaded on a quartz filter (2.5 inch (6.35 cm)). The loaded filter and holder were heated in an oven (125° C.) in the simulated flue gas stream (30 SCFH (standard cubic feet/hr) or 0.79 NCMH (normal cubic meters per hour)) containing the following: O₂ (6%), CO₂ (12%), SO₂ (600 ppm), NO (120 ppm) NO₂ (6 ppm), HCl (1 ppm), Hg⁰ (11 µg/m³), H₂O (15%), and N₂ (balance). Elemental mercury was provided by a standard permeation tube source placed in a double jacketed glass condenser, and heated to the desired temperature. Mercury concentrations in the gas streams were determined with a continuous mercury emission monitor (Sir Galahad mercury CEM mfr. P.S. Analytical Deerfield Beach Fla. USA), and a SnCl₂ cell was used to convert oxidized species to elemental, so that both elemental and oxidized mercury concentration data could be obtained for both the influent and the effluent concentrations from the sorbent bed. Mercury concentrations were calibrated for the flow rates used. Spent sorbents were analyzed for mercury to determine the mass balance.

Referring now to FIG. 4, the effluent mercury concentration data are plotted as a percent of the influent mercury versus time. The resulting curve (breakthrough curve) for the halogenated sorbents typically showed 0% -1% Hg in the effluent (99+% capture) at the beginning, and increasing only after 30-60 minutes (breakthrough point), depending on the sorbent. FIG. 4 illustrates the breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) with synthetic flue gas containing 1 ppm HCl. Total Hg (solid circles) and elemental Hg (solid squares) in the effluent are presented as a percent of the inlet Hg. "EOT" indicates the end of test (the later data points shown are for calibration checks).

16

FIG. 5 presents the comparative breakthrough curves for the corresponding nonhalogenated sorbents typically initiated at 5%-50% of inlet mercury, depending on the HCl concentration in the synthetic flue gas, thus indicating considerably lower reactivity for oxidation and capture of the mercury for the nonhalogenated sorbents. After breakthrough of either halogenated or nonhalogenated sorbent, most of the mercury in the effluent was oxidized mercury.

Example 2

Gas Phase Halogenation of Fluidized Carbon

A bed of activated carbon supported in a vertical tube by a plug of glass wool was fluidized by a nitrogen stream. The top of the fluidized bed tube was connected to a catching trap for carbon fines that blow out the top of the tube. The bromine gas generator as described in Example 1 was attached to the fluidized carbon bed and the desired amount of gaseous bromine was passed into the bed. The contents of the trap were then mixed with the material in the bed and weighed. The resulting brominated carbon exhibited properties similar to the brominated carbon of Example 1.

Example 3

Liquid Phase (Water) Halogenation

A 5% solution of bromine in water was prepared by carefully adding 50 g of bromine to 1 liter of cold water. One kg of activated carbon was added to the bromine solution in a large metal can. The resulting slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon, as indicated by the disappearance of the red color. The slurry was then filtered using a Buchner funnel under vacuum. The moist carbon that was collected on the filter was dried in an oven at 110° C. for several hours to constant weight. As in Example 1, some moisture remains in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 4

Addition of the Optional Second Halide Component

Brominated carbon was produced by solution phase bromination similar to that described with reference to Example 3. However, before filtration, a solution of hydriodic acid (HI) was added to the slurry in an amount equal to 10% of the bromine amount. The slurry was stirred to complete the reaction and then filtered and dried as described in Example 3.

Example 5

Liquid Phase Phosphohalogenation

A solution of phosphorus tribromide (500 g) in ligroin (10 liters) was stirred in a large metal can and 10 kg of activated carbon was added. The resulting slurry was stirred with a large paddle at ambient temperature to complete the reaction. The slurry was filtered under vacuum on a large Buchner funnel in several batches. The wet filter cake was

US 10,589,225 B2

17

dried at 110° C. in an oven to constant weight. The dried product was fluffed in the rotating barrel as described in Example 3.

Example 6

Preparation and Sorption on Larger-Particle Carbon

Tests were conducted on a pilot-scale combustor while firing a subbituminous coal, to evaluate mercury control by injecting larger-than-normal sized treated activated carbon. Standard AC sorbents generally are of fine size with a mean particle diameter of less than 20 micrometers, which is also typical of the flyash that is generated from pulverized coal combustion. Consequently, because the sizes of standard AC and flyash are similar, separation of the two is difficult. Injection of larger sized AC is generally not considered because the sorbent effectiveness decreases with size. In a scheme to recycle the injected carbon, the carbon is separated from the flyash. A separation based on size fractionation requires a treated larger particle sorbent. To test this concept, a treated larger sized (>60 µm) sorbent was developed, prepared, and tested.

Treatment—Gas Phase Halogenation

Granular activated carbon (Calgon F400) was ground and sieved through conventional mesh screens. The mesh size fraction -170 to +240 (corresponding to about 60 to about 88 micrometers) was collected and placed in a rotating vessel as described in Example 1 above. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that was warmed to about 40°-50° C., and the outlet from this gaseous bromine generator was connected via a ¼ inch (6.35 mm) plastic hose to a stationary metal tube inserted through a flange in the center of the lid and passing into the center of the rotating vessel, also as described in Example 1. The unit was operated until the desired amount of bromine had combined with the carbon, in this case 0.05 kg of bromine to 1 kg of carbon (5 wt. %). When the reaction was completed, the carbon was weighed. The treated carbon was odorless as has been described above.

PTC Apparatus

The pilot-scale combustor, known as the “Particulate Test Combustor” (hereinafter “PTC”), is a 550,000-Btu/hr (about 161 kW) pulverized coal (“PC”)–fired unit, designed to generate combustion flue gas properties and fly ash that are representative of those produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle of the PTC fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature. Originally, the PTC used cold-water annular heat exchangers to provide flue gas temperature control to the baghouse (also referred to as a “fabric filter”) or electrostatic precipitator (ESP). However, analysis of ash deposits collected from the heat exchangers indicated that some mercury was collected on the duct walls. To minimize this effect, the heat exchangers were modified to provide for higher duct wall temperatures.

18

The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device (baghouse, Advanced Hybrid Particle Collector/AHPC™, and/or electrostatic precipitator/ESP) operating data to be monitored continuously and recorded on a data logger.

PTC Procedure

Flue gas samples were taken at combinations of two of the three available system sample points: the furnace exit, the particulate control device inlet, and the particulate control device outlet. After passing through sample conditioners to remove moisture, the flue gas was typically analyzed for O₂, CO, CO₂, SO₂, and NO_x. Each constituent was normally analyzed at both the furnace exit and the outlet of the particulate control device simultaneously, using two analyzers. The concentration values from all of the instruments were recorded continuously. In addition, data were manually recorded at set time intervals. NO was determined using a pair of Rosemount Analytical NO chemiluminescent analyzers. SO₂ was measured using a pair of Ametek Instruments photometric gas analyzers. The remaining gases were measured by a pair of Rosemount Analytical multi-gas continuous emissions monitors. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

The baghouse vessel was a 20 inch (50.8 cm) (ID) chamber that is heat-traced and insulated, with the flue gas introduced near the bottom. The combustor produced about 200 ACFM (actual cubic feet per minute; about 5.7 actual m³/min) of flue gas at 300° F. (about 150° C.), therefore three 13-ft by 5-inch (3.96 m by 12.7 cm) bags provided an air-to-cloth ratio of 4 ft/min (1.22 m/min). Each bag was cleaned separately in operation with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags were cleaned on a time basis, rather than with the cleaning cycle initiated by pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession on-line.

Tests were also conducted with a single-wire, tubular ESP replacing the fabric filter. The ESP unit was designed to provide a specific collection area of 125 at 300° F. (150° C.). Since the flue gas flow rate for the PTC is 130 SCFM (standard cubic feet per minute; about 3.7 NCMM (normal m³/min)), the gas velocity through the ESP is 5 ft/min (about 1.52 m/min). The plate spacing for the ESP unit is 11 in (27.9 cm). The ESP was designed to facilitate thorough cleaning between tests so that all tests can begin on the same basis.

PTC Results

Results are illustrated in FIG. 6. As can be observed in FIG. 6, even though the tested sorbent particle size is significantly larger than normal sorbent particles, the treated larger-than-normal sized (that is, >60 micrometers) activated carbon sorbent was quite effective at capturing mercury. Approximately 75% of the mercury was captured when the larger-sized treated AC was injected ahead of the pilot-scale ESP, while approximately 85% of the mercury was captured when injected ahead of the pilot-scale fabric filter (“FF”). Note that in FIG. 6 (and throughout) “MacF” (and “MACF”) indicates million actual cubic feet (1 MACF is about 0.028 million actual cubic meters or “MACM”).

Referring now to FIG. 7, it can be observed that the larger-sized treated AC when injected ahead of the pilot-scale ESP (diamond symbol(s)) performed better than the finer standard AC (triangles) under the same arrangement. In comparison, when injected ahead of the fabric filter (FF), the larger-sized treated AC (square) performed similarly to slightly worse. However, for this application, the larger-

US 10,589,225 B2

19

sized treated AC can be physically separated from the smaller flyash particles, and the sorbent can then be regenerated, recycled, and reused. This will substantially improve overall utilization and economics. These data thus show that a larger-than-normal sized sorbent can provide effective mercury control and ease flyash and AC separation, thereby also preserving the characteristics of the flyash for sale and beneficial use. Accordingly, because >60 μm sorbent particles have been successfully demonstrated, superior mercury control can be obtained with >40 μm particles, which may be preferred in some applications, depending on the sorbent particle/ash separation system used. Note that in FIG. 7 (and throughout) “Macf” (and “MACF”) indicates million actual cubic feet.

Example 7

Liquid Phase (Organic Solvent) Halogenation

A 5% solution of bromine in ligroin was prepared by carefully adding 50 g of bromine to 1 liter of cold ligroin. One kg of activated carbon was added to the bromine solution in a large metal can. The slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon as indicated by the disappearance of the red color. The slurry was filtered using a Buchner funnel under vacuum. The carbon cake that was collected on the filter was dried in an oven at 110° C. for several hours until it appeared dry and a constant weight was obtained. As in Example 1, some moisture was left in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 8

Promoted Activated Carbon Sorbents

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100° C. in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. The results indicated that adding a second component to the solution improved the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 $\mu\text{g}/\text{m}^3$) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM (“continuous emission monitor”) (mfr. P S Analytical, Deerfield Beach, Fla., USA). The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer. A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it was treated with 0.1 N HBr, and the powder was collected by centrifugation and drying, revealed that the mercury capture activity increased

20

from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicated that it not only captured mercury at the same level as before (100% capture) but its capacity was prolonged by several minutes, and thus enhanced. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

Example 9

Fluidized/Ebulliated Bed Preparation

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed or ebulliated bed of the carbon. The amount of bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Example 10

Full-Scale Testing

In this example, a baghouse (fabric filter) or ESP was used to collect particulates in the exhaust of a full-scale commercial pulverized coal-burning facility. A scrubber and sorbent bed were also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In this example, the halogen/halide promoted carbon sorbent was injected into the flue gas after the boiler. In general however, the inventive sorbent can be injected where desired (e.g., before, after, or within the boiler).

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 $\mu\text{g}/\text{m}^3$. The ash and injected carbon were collected in the baghouse at 350° F. to 375° F. (about 175-190° C.). Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/MACF (“MACF” and “Macf” represent one million actual cubic feet; 1.0 lb/MACF is about 16 kg/MACM (million actual cubic meters)) resulted in mercury effluent concentrations of 3.8-4.2 $\mu\text{g}/\text{m}^3$ (representing 62%-58% removal of the mercury from the gas, respectively), and at 2.0 lb/MACF (about 32 kg/MACM), gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/MACF resulted in 73%-69% removal and at 2.0 lb/MACF gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine promoted carbon sorbent of the present invention.

Example 11A

Addition of Optional Alkaline Component—Bench-Scale

The efficiency of the activated carbons for mercury capture can be improved considerably by employing a basic material co-injected with the activated carbon, in order to capture any oxidized mercury that may be released from the sorbent, or to capture some of the sulfur or selenium oxides in the flue gas that can have a detrimental effect on the sorbent capacity.

Bench-scale testing was conducted by preparing a filter composed of 37 mg of brominated activated carbon mixed

US 10,589,225 B2

21

with 113 mg of calcium oxide. The test was conducted as described in Example 1 and compared with the same carbon sorbent but with an inert diluent. The breakthrough curve for the mixture of brominated (2%) NORIT Darco FGD sorbent with inert sand is shown in FIG. 8, and the breakthrough curve for the mixture with CaO is shown in FIG. 9. It can be seen that the point of 50% breakthrough improves to 65 minutes with the mixture with CaO from only 48 min with the sand mixture.

Example 11B

Addition of Optional Alkaline
Component—Pilot-Scale

Tests were conducted on the pilot-scale PTC combustor described above with reference to Example 6 while firing a Texas lignite to evaluate mercury control by co-injecting a standard activated carbon (also referred to herein as “AC”) and an alkali material upstream of a fabric filter. Typical results are illustrated in FIG. 10. As shown in FIG. 10, co-injecting lime with activated carbon vastly improved mercury removal. Mercury removals of approximately 90% were achieved with the co-injected sorbents, whereas less than 60% removal was achieved with the use of standard AC alone, even at much higher injection rates. Data from similar tests show that injecting similar quantities of sodium carbonate and AC, and lime and AC, resulted in mercury removals of approximately 80%, and 87%, respectively. These data suggest that other alkali can also be co-injected with AC to improve mercury removal. Other data show that flue gas temperature may impact the effectiveness of the alkali addition. Further test data indicate that flue gas contaminants, flue gas constituents (SO_2 , NO_x , HCl, etc.), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This indicates that it may be desirable to be able to adjust and tailor, onsite, the alkali-to-AC ratio in order to optimize removal for a given set of site conditions.

Without wishing to be bound by any particular theory, the synergy observed in the improved performance when co-injecting the two materials can be explained as follows. First, tests indicate that binding sites on AC can be consumed by sulfur species and other contaminants. The alkali material interacts and reacts with these species thus minimizing their consumption of AC mercury binding sites. Second, other work has shown that standard AC will continue to oxidize mercury even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by the particulate control device. Thus, combining alkali with treated and/or non-treated AC synergistically takes advantage of these two mechanisms, resulting in improved mercury capture at reduced costs.

Example 12

Brominated Carbon Sorbent for Gasification Fuel
Gas

Preparation of 5% Br2W-AC

Using a procedure similar to Example 3, a 2.5 wt/vol % solution of bromine in water was prepared. Granular Calgon F400 was added to the bromine solution to give a 5 wt/wt % brominated carbon product. The bromine solution was stirred with a large paddle during and after the addition until the red color in the water disappeared. The suspension was

22

filtered by vacuum on a large Buchner funnel. The filter cake was dried in air, and then in an oven at 110° C. until a stable weight was obtained. The moisture was reduced to 15%.

Preparation of 5% Br2D-AC

A brominated sorbent was prepared from Br_2 addition in solvent as described in Example 7, except that dichloromethane was used as the solvent instead of ligroin, and granular Calgon F400 was used.

Preparation of 5% PBr3-AC

A phosphohalogenated sorbent was prepared from PBr_3 using the method described in Example 5, except granular Calgon F400 was used.

Testing in Hydrogen Atmosphere—Procedure

To simulate the capture of mercury from a heated fuel gas or syngas from coal gasification, tests were conducted employing a stream comprising 10% vol/vol hydrogen in nitrogen passing through the sorbent at 500 cc/min. The stream contained 26.9 micrograms/ m^3 of elemental mercury from a commercial mercury permeation source.

In the tests, the sorbent (0.5 g) was placed in a 0.39 inch (1 cm, inside diameter) glass tube fitted with a medium frit sintered glass filter disc to hold the sorbent in the gas stream. The tube containing the sorbent bed was connected to a gas inlet tube for introducing the gas stream containing the mercury vapor and at the outlet to a tube connection to the detector. The detector was a Semtech 2000 continuous mercury emission monitor. The tube was equilibrated in a nitrogen flow (450 cc/min) for 5 minutes at ambient temperature to stabilize the system. The detector showed 0 concentration of mercury in the effluent from the sorbent bed. (The blank run with no sorbent read 26.9 micrograms/ m^3). The tube was then placed in an oven at the selected temperature for the test (from 250° to 400° C.). Effluent mercury concentration data from the detector were collected until the detector showed a constant reading for 5 minutes. Hydrogen (50 cc/min) was then added to the gas stream and detector readings were taken every 5 min. Tests were conducted at several oven temperatures for various periods of time up to 3 hours, depending on the temperature and sorbent. The elemental mercury concentration data were plotted as a percent of inlet mercury concentration versus time as in Example 1. All the mercury in the effluent was elemental, so a single detector was sufficient, and no SnCl_2 trap was needed to convert to elemental mercury (as in Example 1). The time for 50% breakthrough (time to reach 50% capture) was then determined from the breakthrough curves.

Results

The results are shown in Table 1 (below) for the unbrominated sorbent (Calgon F-400), the brominated sorbents (5% Br2W-AC and 5% BrD-AC), and the phosphobrominated sorbent (5% PBr3-AC). The maximum mercury concentration obtained in the effluent in each run is also reported in Table 1 for the time period indicated in the last column.

Under the reducing hydrogen conditions, the unbrominated sorbent broke through immediately and was exhausted after only 6.5 min. This complete failure occurred because the hydrogen reduces the captured mercury in the unbrominated sorbent at any temperature above 100° C. Both of the brominated sorbents exhibited excellent reactivity and good capacity at all temperatures, up to at least 400° C. The phosphobrominated sorbent exhibited superior reactivity and capacity at all temperatures, up to at least 400° C.

US 10,589,225 B2

23

TABLE 1

Times for 50% Breakthrough Maximum Observed Hg Concentrations for Sorbents (10% Hydrogen Streams)				
Sorbent	Temp (° C.)	50% breakthrough (min)	Maximum [Hg] (µg/m ³)	Time (min)
F-400	250	6	20.3	6.5
5%Br2W-AC	250	>150	1.4	150
5%Br2W -AC	300	>180	4.3	180
5%Br2W-AC	350	160	15.1	180
5%Br2W-AC	400	60	13.9	65
5%PBr3-AC	250	>140	0.4	140
5%PBr3-AC	300	>150	0.5	150
5%PBr3-AC	350	>150	1.4	150
5%Br2D-AC	350	>180	2.1	180
5%Br2D-AC	400	>180	10.9	180

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

Although the invention is described herein as a sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

We claim:

1. A method for treating a mercury-containing gas, the method comprising:

combusting a mixture comprising coal, pyrolysis char, and an additive comprising HBr, a bromide compound, or a combination thereof, to form the mercury-containing gas; and

24

adding a particulate sorbent material comprising activated carbon into the mercury-containing gas.

2. The method of claim 1, wherein the pyrolysis char is a promoted pyrolysis char.

3. The method of claim 1, wherein the pyrolysis char and the additive are added prior to a combustor that combusts the mixture, within the combustor, or a combination thereof.

4. The method of claim 1, wherein the pyrolysis char and the additive are added within a combustor that combusts the mixture.

5. The method of claim 1, further comprising using a particle separation device to remove mercury from the flue gas and comprising collecting greater than 70 wt % of the mercury in the mercury-containing gas to produce a cleaned gas.

6. The method of claim 5, further comprising: measuring the mercury content of the mercury-containing gas; and

modifying, in response to the measured mercury content: an injection rate of injecting the sorbent into the mercury-containing gas, an amount of the additive in the mixture, or a combination thereof.

7. The method of claim 1, wherein the additive further comprises Br₂.

8. The method of claim 1, wherein the sorbent material is chosen from powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, and combinations thereof.

9. The method of claim 1, further comprising adding an alkaline component to the mercury-containing gas, the alkaline component chosen from alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

10. The method of claim 1, further comprising contacting the sorbent material with a mercury-stabilizing reagent chosen from S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof.

11. The method of claim 1, further comprising contacting the sorbent material with a secondary component chosen from halogens, hydrogen halides, Group V halides, Group VI halides, and combinations thereof.

12. The method of claim 11, wherein the secondary component is chosen from halogens, halide salts, HI, HBr, HCl, and combinations thereof.

13. The method of claim 11, wherein the secondary component is chosen from I₂, HI, and combinations thereof.

14. A method for treating a mercury-containing gas, the method comprising:

combusting coal in a combustor comprising pyrolysis char and an additive comprising HBr, a bromide compound, or a combination thereof, to form the mercury-containing gas; and adding a particulate sorbent material comprising activated carbon into the mercury-containing gas.

15. The method of claim 14, wherein the pyrolysis char is a promoted pyrolysis char.

16. A method for treating a mercury-containing gas, the method comprising:

combusting coal in a combustor and adding within the combustor a pyrolysis char promoted by an additive comprising HBr, a bromide compound, or a combination thereof, to form the mercury-containing gas; and adding a particulate sorbent material comprising activated carbon into the mercury-containing gas.

17. A method for treating a mercury-containing gas, the method comprising:

US 10,589,225 B2

25

combusting a mixture comprising coal, pyrolysis char,
and an additive comprising HBr, a bromide compound,
or a combination thereof, to form the mercury-contain-
ing gas; and

adding a sorbent material comprising activated carbon 5
into the mercury-containing gas.

18. The method of claim 1, further comprising
modifying, in response to a measured mercury content,
an injection rate of injecting the sorbent into the
mercury-containing gas, 10
an amount of the additive in the mixture, or
a combination thereof.

19. The method of claim 1, wherein the coal comprises
added sorbent enhancement additive that comprises the 15
bromide compound.

20. The method of claim 1, wherein the coal is combusted
in a combustion chamber at a coal-combustion facility,
wherein the HBr, bromide compound, or combination
thereof, is added to the coal before the coal enters the
combustion chamber, wherein the addition of the HBr, 20
bromide compound, or combination thereof, to the coal is
performed at the coal-combustion facility.

21. The method of claim 1, wherein the coal is combusted
in a combustion chamber at a coal-combustion facility, 25
wherein the HBr, bromide compound, or combination
thereof, is added to the coal before the coal enters the
combustion chamber, wherein the addition of the HBr,

26

bromide compound, or combination thereof, to the coal is
performed at a site other than the coal-combustion facility.

22. The method of claim 1, wherein the sorbent is
contacted with a halogen or halide promoter prior to the
addition of the sorbent to the mercury-containing gas.

23. The method of claim 1, wherein the sorbent is free of
contact with a halogen or halide promoter prior to the
addition of the sorbent to the mercury-containing gas.

24. The method of claim 6, wherein the measurement of
the mercury content of the mercury-containing gas com-
prises continuous measurement.

25. The method of claim 1, wherein the coal comprises
subbituminous coal.

26. The method of claim 1, wherein the coal comprises
lignite coal.

27. The method of claim 1, wherein the mixture is
combusted in a combustion chamber of a coal-combustion
facility upstream of a scrubber, a particulate control system,
or a combination thereof, wherein the particulate sorbent is
added to the mercury-containing gas before the mercury-
containing gas encounters the scrubber, the particulate con-
trol system, or the combination thereof.

28. The method of claim 26, wherein the particulate
control system comprises an electrostatic precipitator, a
baghouse, a fabric filter, or a combination thereof.

29. The method of claim 19, wherein the combustion
chamber is a coal combustion furnace.

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EXHIBIT D

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(12) **United States Patent**
Olson et al.(10) **Patent No.:** **US 10,596,517 B2**(45) **Date of Patent:** ***Mar. 24, 2020**(54) **SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY**(71) Applicant: **Midwest Energy Emissions Corp.**,
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Lewis Center, OH (US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.This patent is subject to a terminal dis-
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(2013.01); **B01J 20/20** (2013.01); **B01J 20/22**
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None

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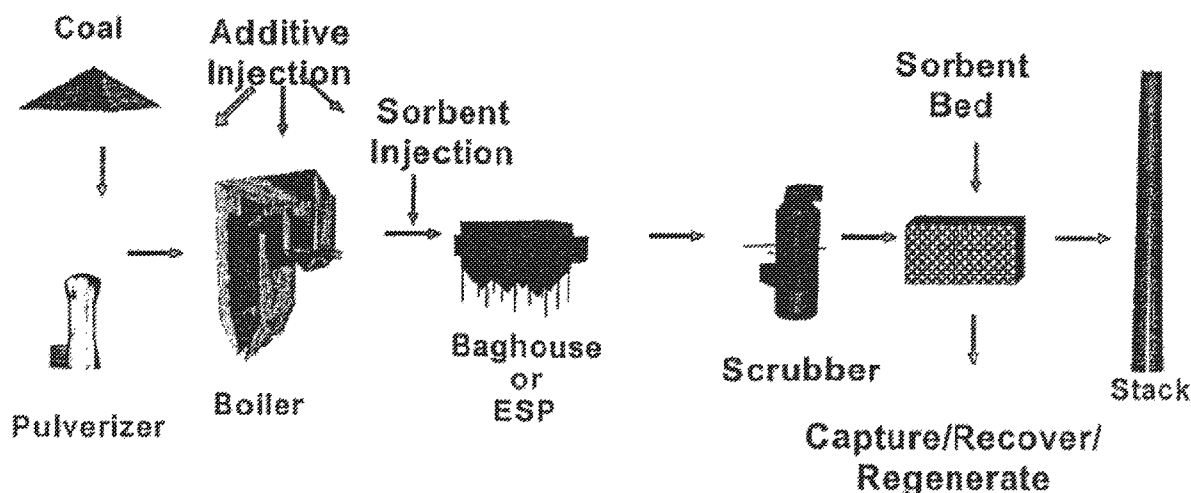
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Primary Examiner — Amber R Orlando(74) *Attorney, Agent, or Firm* — Schwegman Lundberg &
Woessner, P.A.(57) **ABSTRACT**A promoted activated carbon sorbent is described that is
highly effective for the removal of mercury from flue gas
streams. The sorbent comprises a new modified carbon form
containing reactive forms of halogen and halides. Optional
components may be added to increase reactivity and mer-
cury capacity. These may be added directly with the sorbent,
or to the flue gas to enhance sorbent performance and/or
mercury capture. Mercury removal efficiencies obtained
exceed conventional methods. The sorbent can be regener-
ated and reused. Sorbent treatment and preparation methods
are also described. New methods for in-flight preparation,
introduction, and control of the active sorbent into the
mercury contaminated gas stream are described.**30 Claims, 11 Drawing Sheets**

US 10,596,517 B2

Page 2

Related U.S. Application Data

No. 15/951,970, filed on Apr. 12, 2018, which is a continuation of application No. 14/712,558, filed on May 14, 2015, which is a continuation of application No. 14/318,270, filed on Jun. 27, 2014, now Pat. No. 9,757,689, which is a continuation of application No. 13/966,768, filed on Aug. 14, 2013, now Pat. No. 8,821,819, which is a continuation of application No. 13/427,665, filed on Mar. 22, 2012, now Pat. No. 8,512,655, which is a continuation of application No. 12/419,219, filed on Apr. 6, 2009, now Pat. No. 8,168,147, which is a continuation of application No. 12/201,595, filed on Aug. 29, 2008, which is a continuation of application No. 11/209,163, filed on Aug. 22, 2005, now Pat. No. 7,435,286.

(60) Provisional application No. 60/605,640, filed on Aug. 30, 2004.

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Page 7

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US 10,596,517 B2

Page 10

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Mar. 24, 2020

Sheet 1 of 11

US 10,596,517 B2

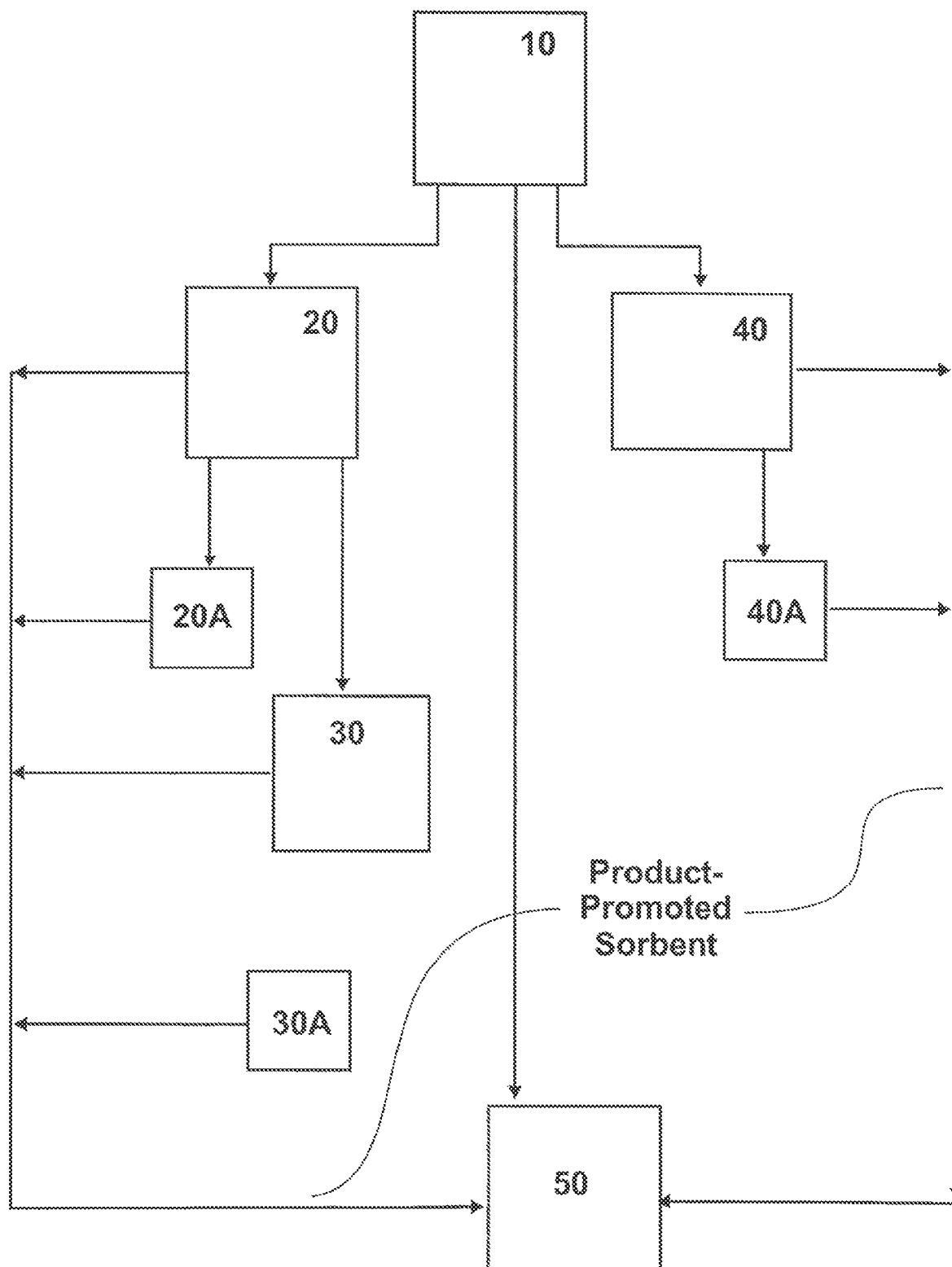


FIG. 1

U.S. Patent

Mar. 24, 2020

Sheet 2 of 11

US 10,596,517 B2

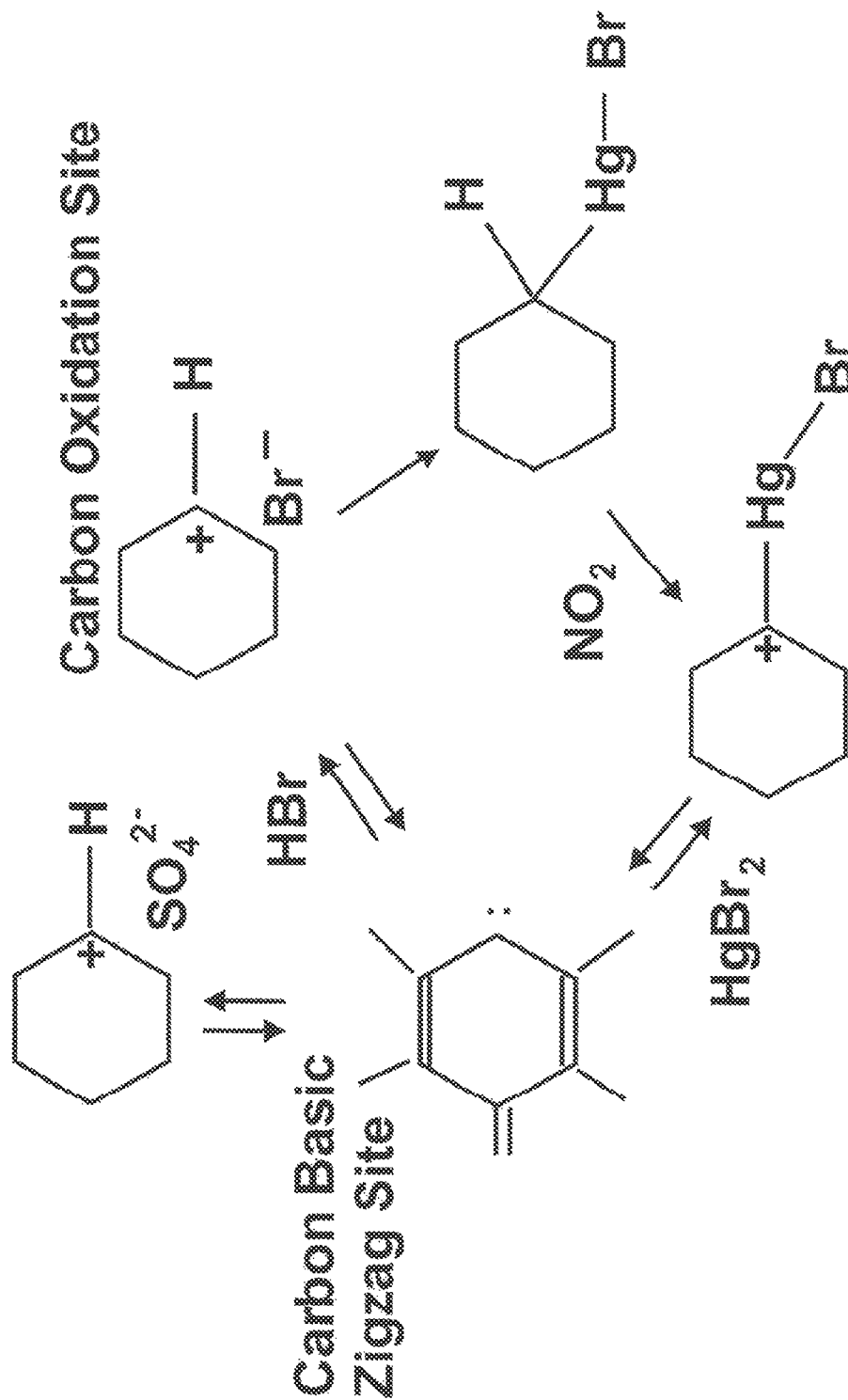


FIG. 2

U.S. Patent

Mar. 24, 2020

Sheet 3 of 11

US 10,596,517 B2

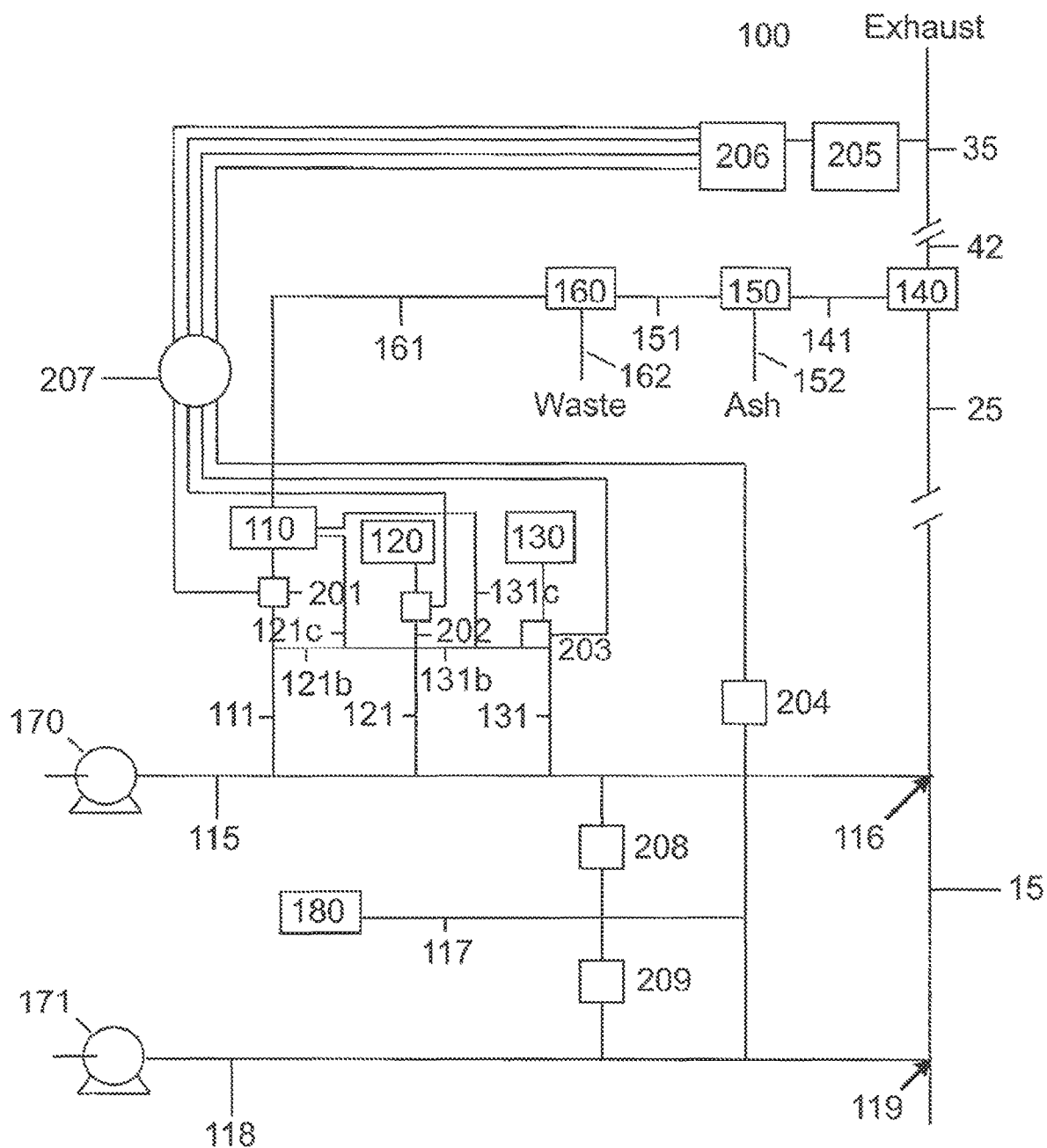


FIG. 3

U.S. Patent

Mar. 24, 2020

Sheet 4 of 11

US 10,596,517 B2

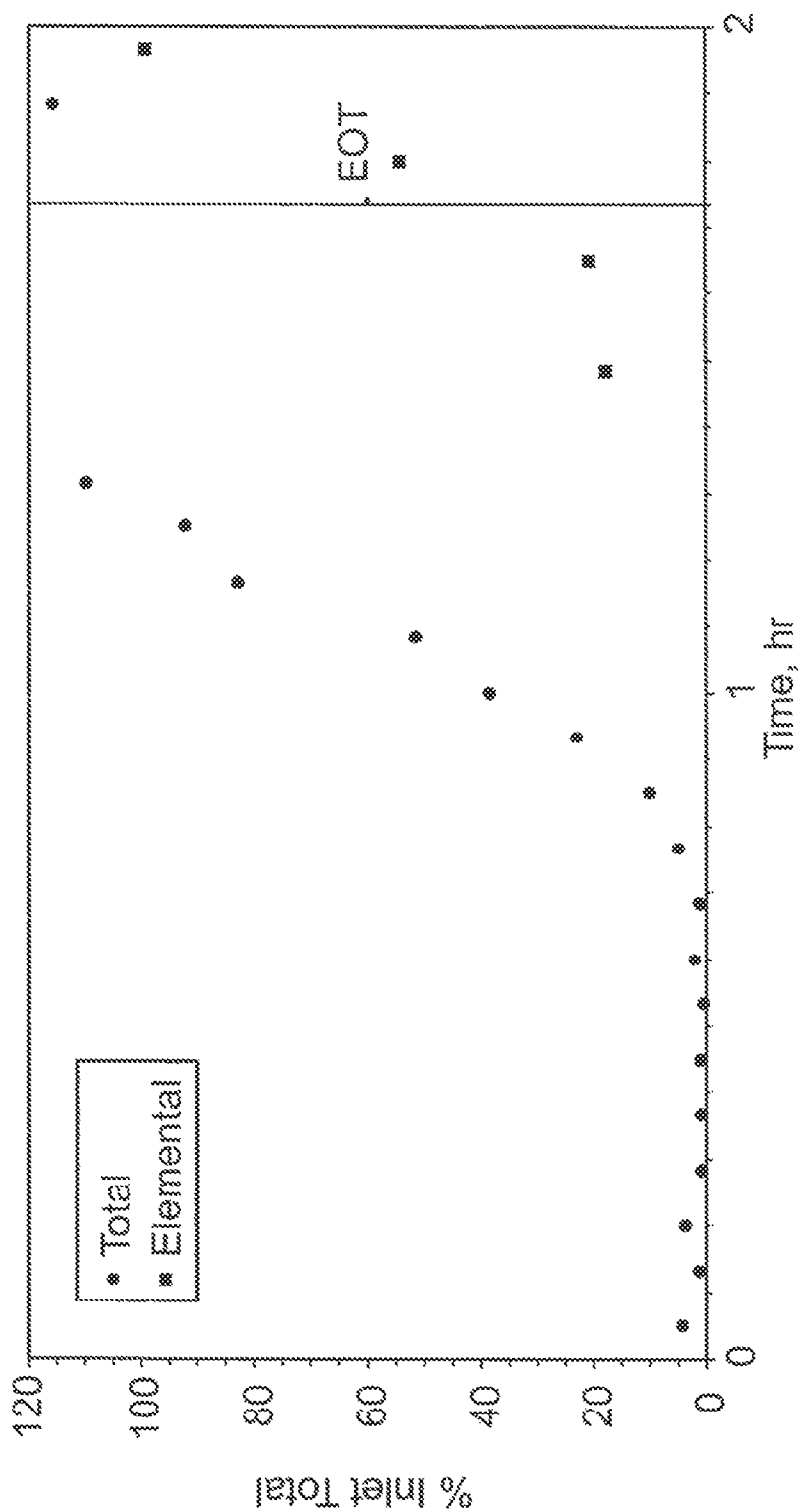


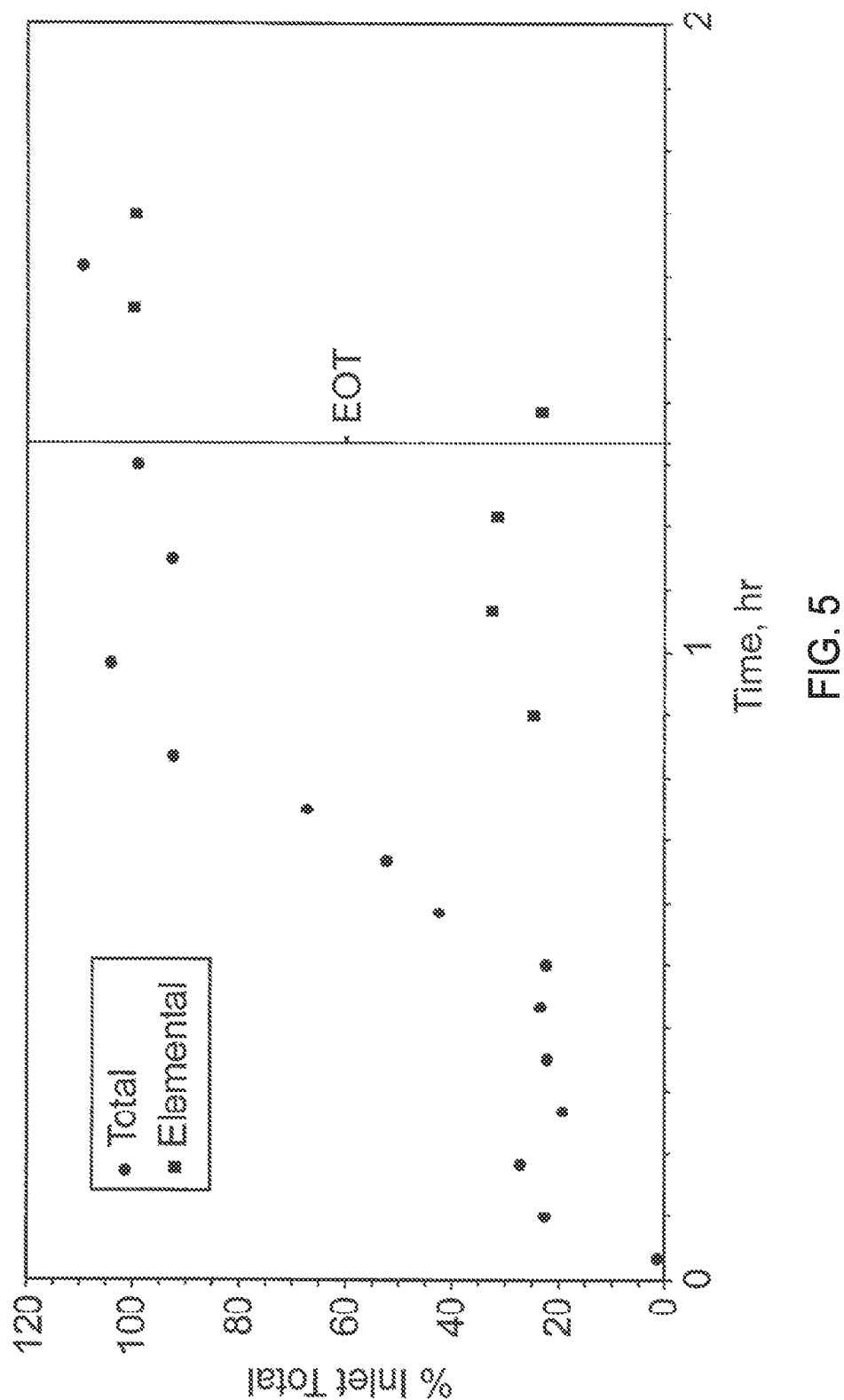
FIG. 4

U.S. Patent

Mar. 24, 2020

Sheet 5 of 11

US 10,596,517 B2



U.S. Patent

Mar. 24, 2020

Sheet 6 of 11

US 10,596,517 B2

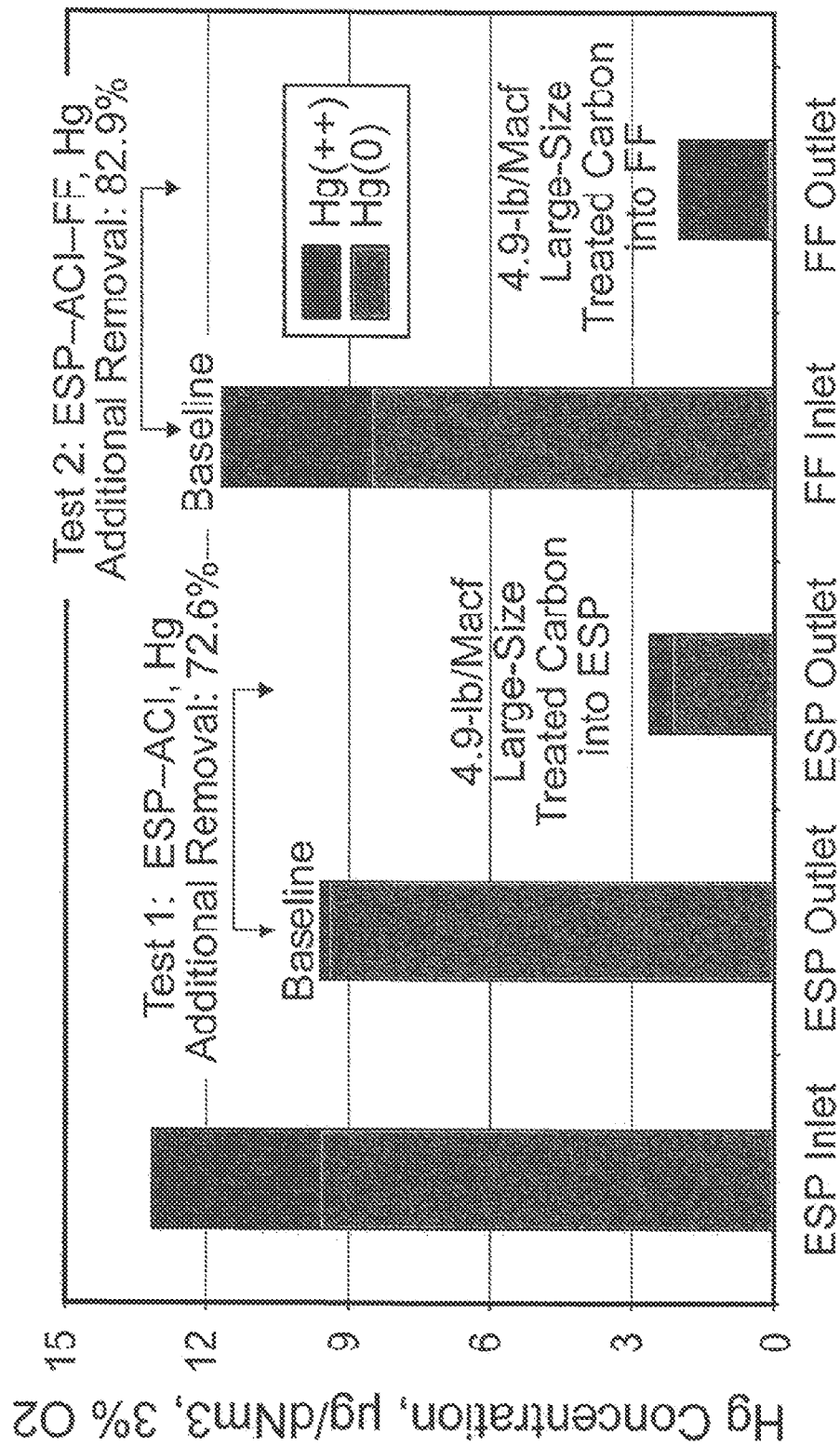


FIG. 6

U.S. Patent

Mar. 24, 2020

Sheet 7 of 11

US 10,596,517 B2

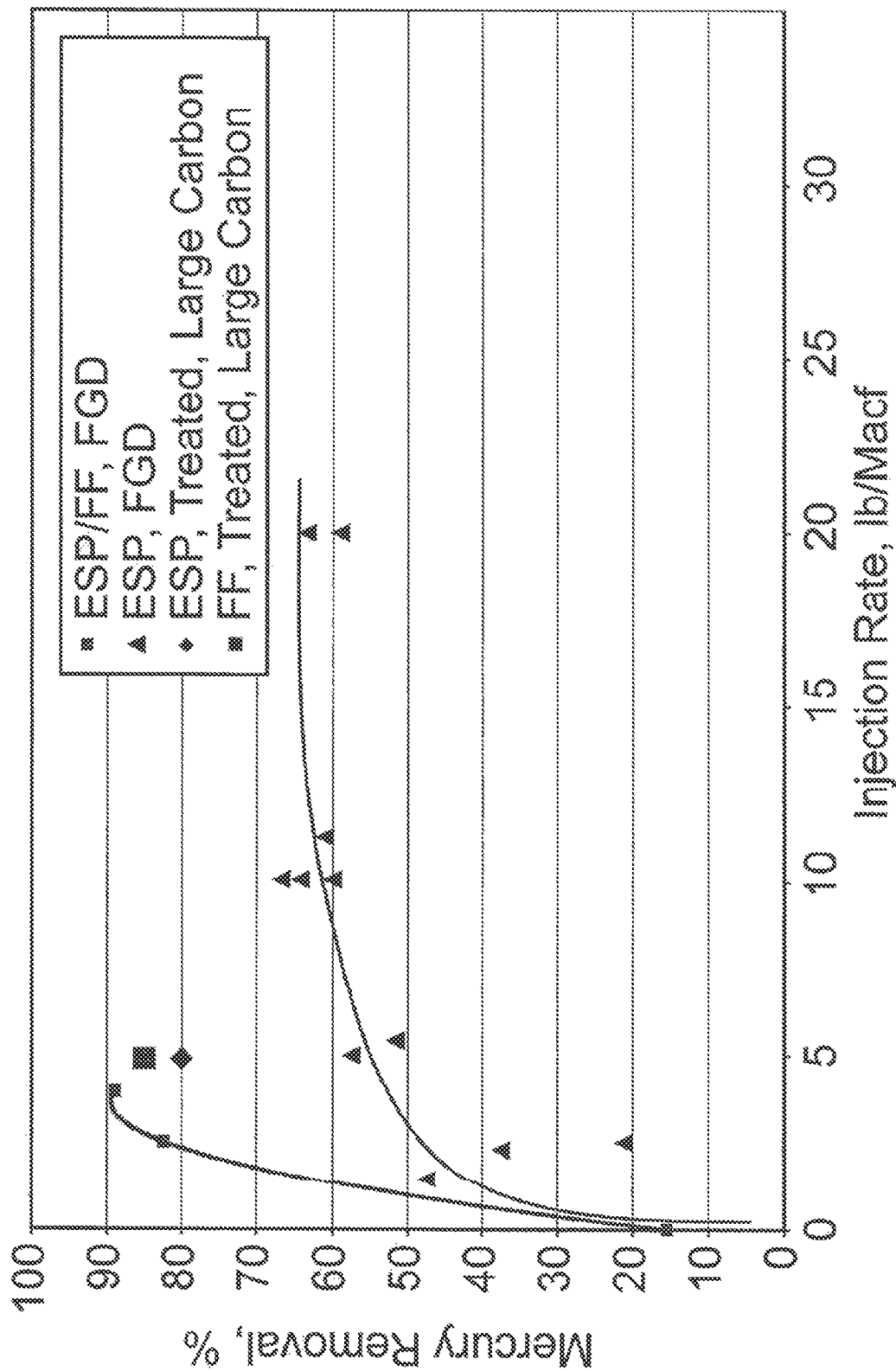


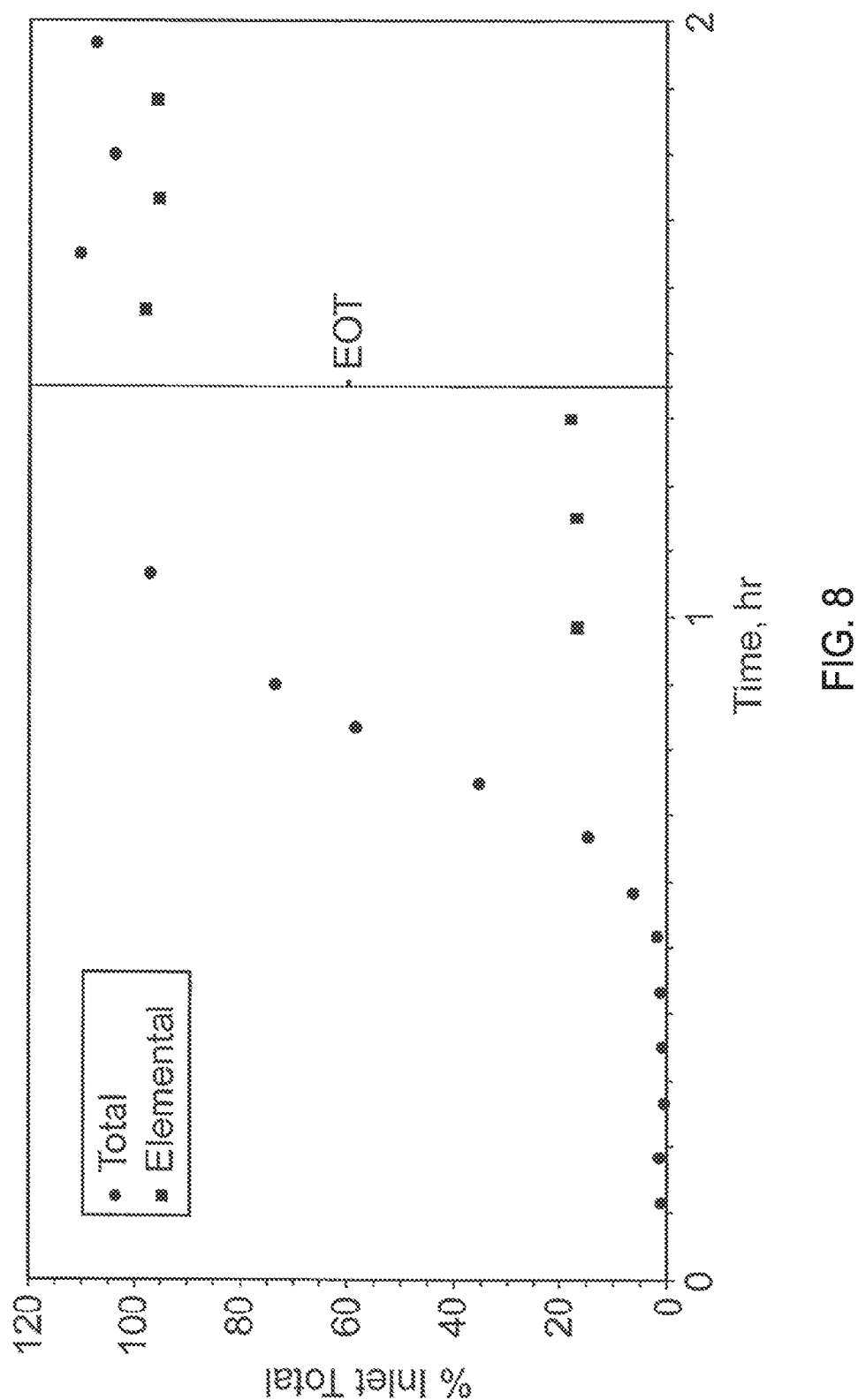
FIG. 7

U.S. Patent

Mar. 24, 2020

Sheet 8 of 11

US 10,596,517 B2



U.S. Patent

Mar. 24, 2020

Sheet 9 of 11

US 10,596,517 B2

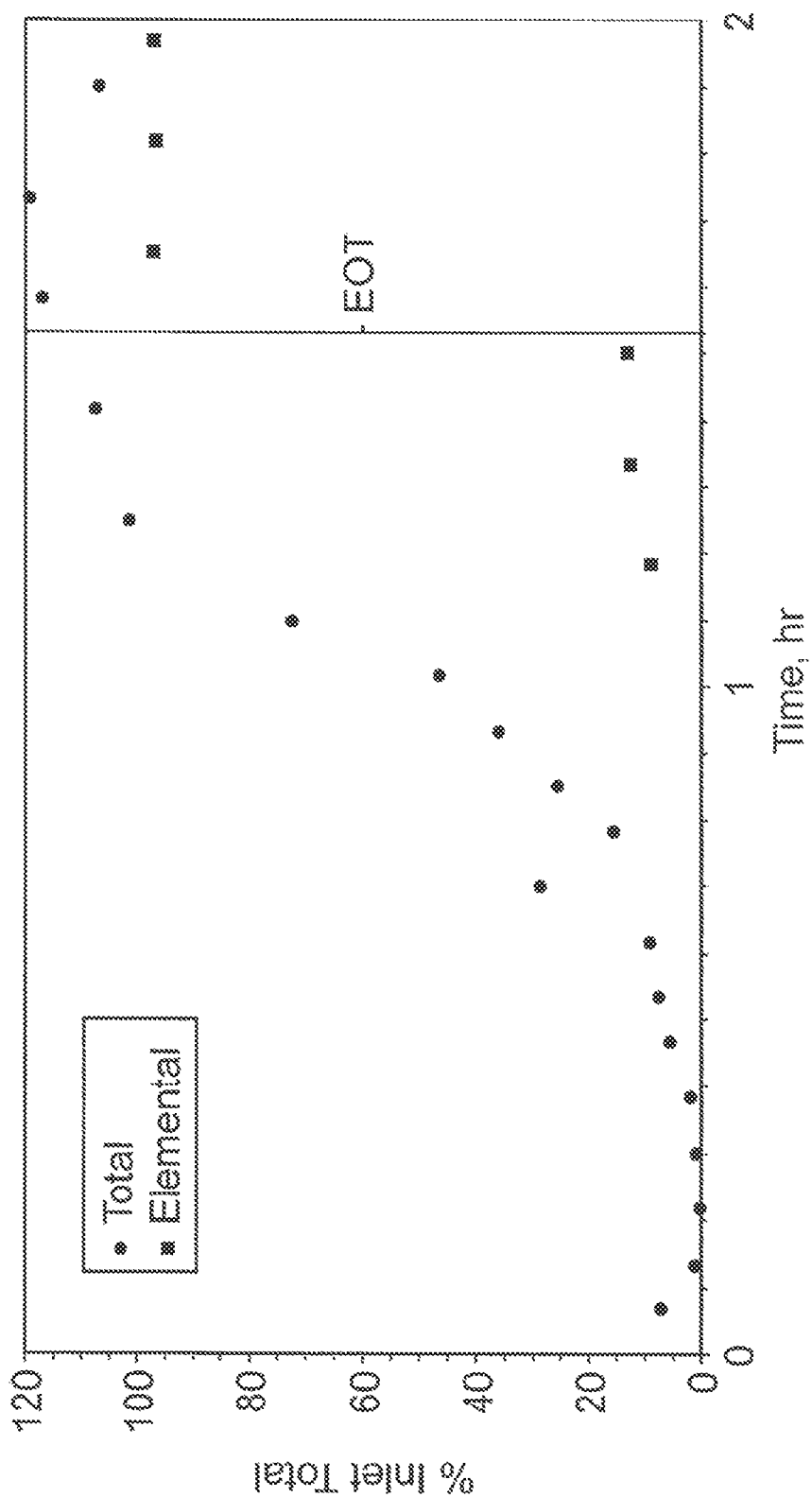


FIG. 9

U.S. Patent

Mar. 24, 2020

Sheet 10 of 11

US 10,596,517 B2

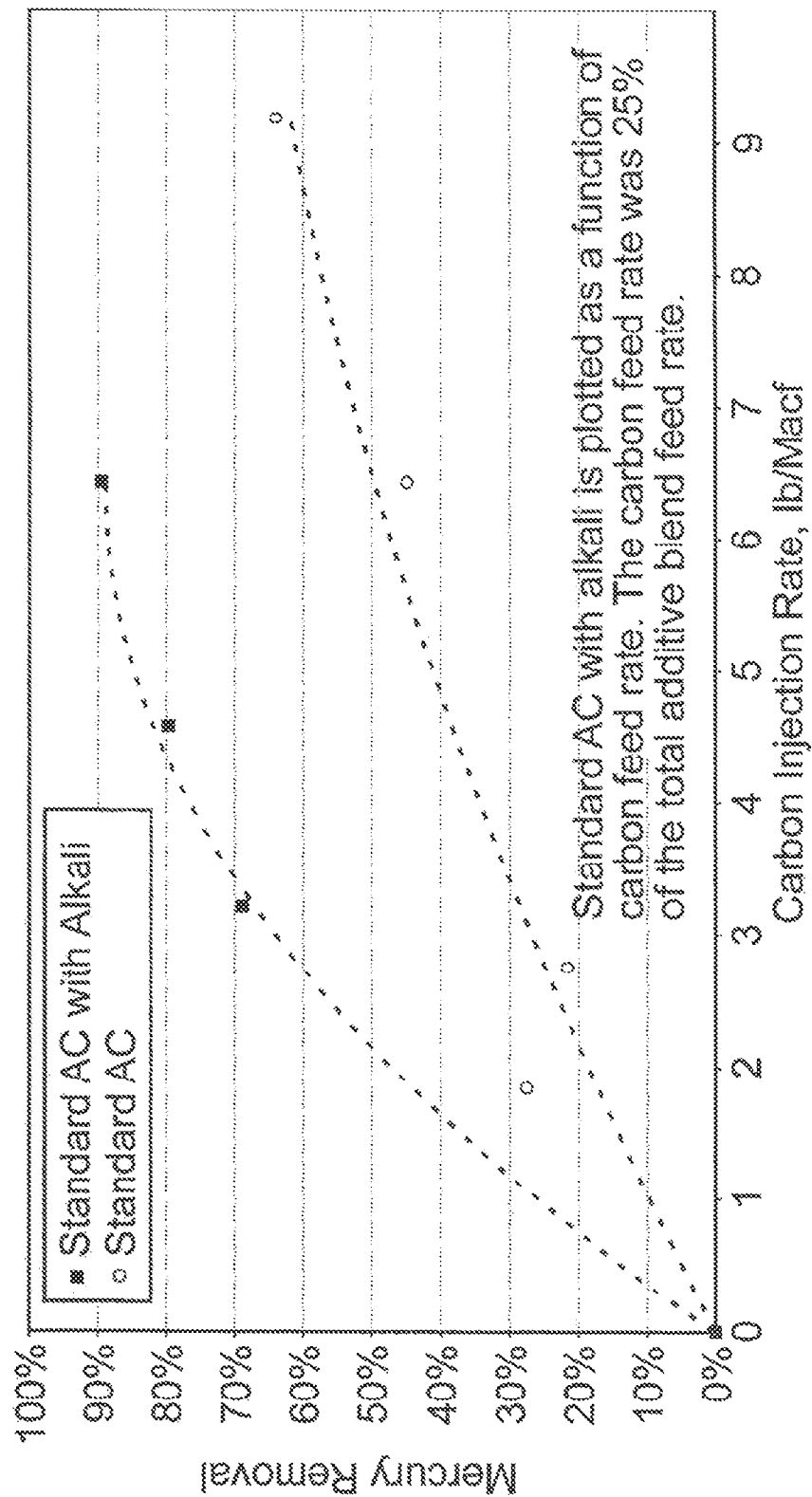


FIG. 10

U.S. Patent

Mar. 24, 2020

Sheet 11 of 11

US 10,596,517 B2

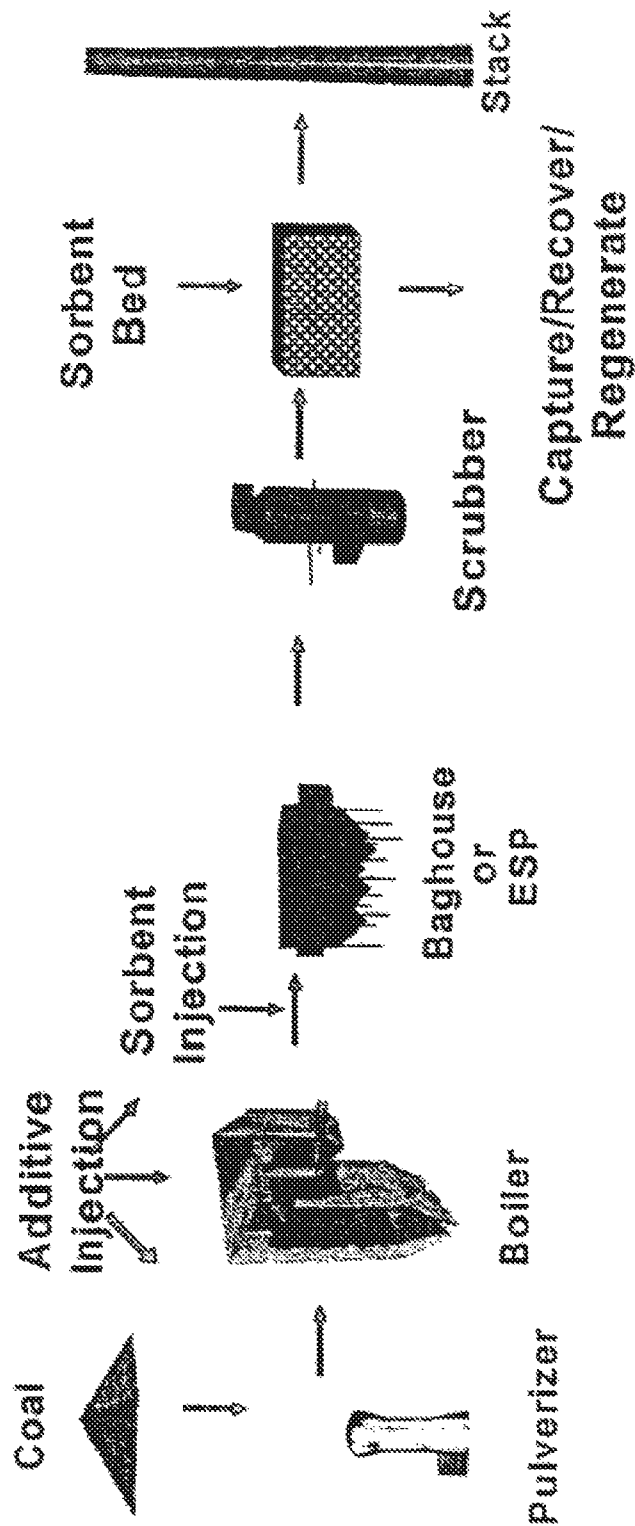


FIG. 11

US 10,596,517 B2

1

**SORBENTS FOR THE OXIDATION AND
REMOVAL OF MERCURY****CROSS-REFERENCE TO RELATED
APPLICATIONS**

This application is a continuation of U.S. patent application Ser. No. 15/974,343, filed May 8, 2018, which is a continuation of U.S. patent application Ser. No. 15/951,970, filed Apr. 12, 2018, which is a continuation of U.S. patent application Ser. No. 14/712,558, filed May 14, 2015, which is a continuation of U.S. patent application Ser. No. 14/318,270, filed Jun. 27, 2014, which is a continuation of U.S. patent application Ser. No. 13/966,768, filed Aug. 14, 2013, issued as U.S. Pat. No. 8,821,819, which is a continuation of U.S. patent application Ser. No. 13/427,665, filed Mar. 22, 2012, issued as U.S. Pat. No. 8,512,655, which is a continuation of U.S. patent application Ser. No. 12/419,219, filed Apr. 6, 2009, issued as U.S. Pat. No. 8,168,147, which is a continuation of U.S. patent application Ser. No. 12/201,595, filed Aug. 29, 2008, which is a division of U.S. patent application Ser. No. 11/209,163, filed Aug. 22, 2005, issued as U.S. Pat. No. 7,435,286, which application claims the benefit under 35 U.S.C. § 119 (e) of U.S. Provisional Patent Application No. 60/605,640 filed Aug. 30, 2004, the disclosure of which is hereby incorporated by reference in its entirety.

**STATEMENT REGARDING FEDERALLY
SPONSORED RESEARCH OR DEVELOPMENT**

This invention was made with United States Government support under Grant Numbers R 827649-01 and CR 830929-01 awarded by the United States Environmental Protection Agency and under Contract Number DE-FC26-98FT40320 awarded by the United States Department of Energy. The United States Government has certain rights in this invention.

BACKGROUND OF THE INVENTION**1. Technical Field of the Invention**

The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

2. Background of the Invention

The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, per day.

2

Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as off gases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a bag house or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon because the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after extended exposure to the flue gas does the sorbent become effectively seasoned and provide increased reactivity with the mercury in the gas. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY OF THE INVENTION

It is thus an object of the present invention to overcome the deficiencies of the prior art and thereby to provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

A halogen/halide promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new halide-modified carbon form containing a reactive compound produced by the reaction of bromine (or halide or other halogen) with the carbon. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

US 10,596,517 B2

3

In some embodiments, a promoted carbon sorbent is provided comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

In an embodiment, a promoted carbon sorbent is provided wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than that of flyash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the base activated carbon may have an mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base activated carbon may have a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the primary sorbent.

In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base activated carbon. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base activated carbon. In another embodiment, the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

In an embodiment, a method is provided comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream. In a further embodiment, the reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon. In another embodiment the reaction product has an average particle size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment the reaction product has a mass mean particle diameter greater than about 40 micrometers.

4

In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment the promoter is in the gas phase when contacting the activated carbon. In another embodiment, the promoter is in an organic solvent when contacting the activated carbon.

In another embodiment, the promoter is selected from the group consisting of Br₂, a Group V bromide, a Group VI bromide, and combinations thereof.

In another embodiment, the method further comprises reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the activated carbon. In another embodiment the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof. In an embodiment, a method is provided for control of mercury in a flue gas with substantially lower sorbent requirements. Through enhanced sorbent reactivity, mercury removal per grain of sorbent is increase, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas. In embodiments where less than 70 wt-% mercury removal is desired, the required removal may preferably be attained using less than half as much carbon as would be required with standard (non-enhanced) carbon. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent. In another embodiment the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt % of the promoter content. In another embodiment, the method further comprises adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof.

US 10,596,517 B2

5

In an embodiment, the method further comprises co-injecting an optional alkaline material, including without limitation alkaline and alkaline earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent. In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

In an embodiment, a method for reducing the mercury content of a mercury and ash containing gas stream is provided wherein particulate activated carbon sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the sorbent particles, the sorbent particles are separated from the ash particles on the basis of size, and the sorbent particles are re-injected to the gas stream. In another embodiment, the mercury-containing sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is co-injected into the gas stream. In another embodiment, the sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from fired equipment and gasification systems.

The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

FIG. 1 schematically illustrates methods for preparation of promoted carbon sorbents in accordance with the present invention.

6

FIG. 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

FIG. 3 schematically illustrates preparation of promoted carbon sorbents and processes for flue gas mercury reduction in flue gases and/or product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon sorbent.

FIG. 4 is a diagram illustrating breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 5 is a diagram illustrating breakthrough curves for non-halogenated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 6 is a bar chart illustrating pilot-scale mercury removal results, including large-size sorbent results.

FIG. 7 is a diagram illustrating the effects of sorbent size and injection rate on mercury removal for ESPs and fabric filters.

FIG. 8 is a diagram illustrating the breakthrough curves for a brominated NORIT Darco FGD sorbent with inert sand.

FIG. 9 is a diagram illustrating the breakthrough curves for brominated NORIT Darco FGD sorbent with a co-injected alkali material.

FIG. 10 is a plot of mercury removal vs. carbon injection rate with and without co-injection of alkali material.

FIG. 11 is a block diagram illustrating the use of the invention in a coal fueled facility.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention, and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide promoted carbon sorbents using a bromide (or other halogen/halide) treatment of the carbon, that capture mercury via mercury-sorbent surface reactions, at very short contact times of seconds or less. The sorbent does not require in situ activation (no induction period) in the gas stream to achieve high reactivity, as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants is greatly enhanced and the sorption capacity can be regenerated, the promoted sorbent may be regenerated, recycled and/or reused.

The treated carbons, treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus, it should be understood that the terms combustion system and flue gas as used throughout

US 10,596,517 B2

7

this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

Referring now to FIG. 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture from flue gas and/or product gas from a gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base activated carbon, and adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, to produce a product promoted carbon sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base activated carbon as shown by block 10, adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product promoted carbon sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base activated carbon as illustrated at block 10, and adding a halogen or halide promoter and a secondary component to the activated carbon together, with which they react as illustrated by block 40, producing a product promoted carbon sorbent. As above, in embodiments where vapor additions are made to the activated carbon no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A.

Referring still to FIG. 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a flue gas stream is treated with product promoted carbon sorbent prepared as described above.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product promoted carbon sorbent, or other types as known in the art.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle size greater than fly ash in a flue gas stream to be treated.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated

8

carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle size distribution greater than that of the fly ash or entrained ash in a flue gas stream to be treated, such that the activated carbon and ash can be separated by physical means.

In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the base activated carbon may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2 , respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2 , water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

Referring now to FIG. 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in FIG. 2, hydrogen bromide reacts with the unsaturated structure of the activated carbon. This may be, by way of illustration only, a carbene species on the edge of the graphene sheet structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury with subsequent capture by the sorbent.

It has now been found that the formation of the new bromide compound with carbon increases their reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus, adding HBr or Br_2 to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Referring now to FIG. 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted carbon sorbents, and flue gas mercury reduction, in accordance with preferred embodiments of the present invention. There is provided base activated carbon reservoir 110, an optional halogen/halide promoter reservoir 120, an optional secondary component reservoir 130, and an optional alkali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the optional alkali component reservoir 180, optional flow control devices 208 and 209 can be used independently, together, or not at all.

US 10,596,517 B2

9

Reservoirs **110**, **120**, **130**, and **180** connect through their respective flow control devices and via associated piping, to transport line **115**. Optional alkali component reservoir **180** may also connect, through respective flow control devices and via associated piping, to transport line **118**. A source of air, nitrogen, or other transport gas(es) is provided by gas source **170** to transport line **115** for the purpose of entraining materials discharged from reservoirs **110**, **120**, **130**, and **180** and injecting such materials, via injection point **116**, into contaminated flue gas stream **15**. A source of air, nitrogen, or other transport gas(es) may be provided by gas source **171** to transport line **118** for the purpose of entraining materials discharged from reservoirs **180** and injecting such materials, via injection point **119**, into flue gas stream **15**. Gas sources **170** and **171** may be the same or different, as desired. Alternatively, transport gas(es) may be provided to both transport lines **115** and **118** by gas source **170** (connection from source **170** to line **118** not shown). Although gas sources **170** and **171** are shown in FIG. 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

For clarity, single injection points **116** or **119** are shown in FIG. 3, although one skilled in the art will understand that multiple injection points are within the scope of the present invention. Optical density measuring device(s) **204** is connected to transport line **115** and/or **118** to provide signals representative of the optical density inside transport line **115** and/or **118** as a function of time.

Downstream from injection point **116** and **119** is provided particulate separator **140**. By way of illustration and not limitation, particulate separator **140** may comprise one or more fabric filters, one or more electrostatic precipitators (hereinafter "ESP"), or other particulate removal devices as are known in the art. It should be further noted that more than one particulate separator **140** may exist, sequentially or in parallel, and that injection point **116** and **119** may be at a location upstream and/or downstream of **140** when parallel, sequential, or combinations thereof exist. Particulate separator **140** produces at least a predominantly gaseous ("clean") stream **142**, and a stream **141** comprising separated solid materials. A sorbent/ash separator **150** separates stream **141** into a largely ash stream **152**, and a largely sorbent stream **151**. Stream **151** may then preferably be passed to an optional sorbent regenerator **160**, which yields a regenerated sorbent stream **161** and a waste stream **162**.

An optional Continuous Emission Monitor (hereinafter "CEM") **205** for mercury is provided in exhaust gas stream **35**, to provide electrical signals representative of the mercury concentration in exhaust stream **35** as a function of time. The optional mercury CEM **205** and flow controllers **201**, **202**, **203**, **208**, and **209** are electrically connected via optional lines **207** (or wirelessly) to an optional digital computer (or controller) **206**, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream **15**.

In operation, promoted carbon sorbent and/or an optional alkali component is injected into contaminated flue gas stream **15**. After contacting the injected material with the contaminated flue gas stream **15**, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, **25**. The injected material is removed from the flue gas **25**, by separator **140**, disposed of or further separated by optional separator **150**, and disposed of or regenerated by an optional regenerator **160**, respectively. The reduced mercury "clean"

10

flue gas stream **142** is then monitored for mercury content by an optional CEM **205**, which provides corresponding signals to an optional computer/controller **206**. Logic and optimization signals from **206** then adjust flow controllers **201**, **202**, **203**, **208**, **209** to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art. Flow controllers **201**, **202**, **203**, **208**, **209** can also be adjusted manually or be some other automated means to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art.

Referring still to FIG. 3, there are illustrated several preferred embodiments for preparation and injection of promoted carbon sorbents and/or alkali components in accordance with the present invention. Stream **111** provides for introduction of base activated carbon from reservoir **110**, as metered by flow controller **201** manually or under the direction of computer **206**. The halogen/halide may be combined and react with the base activated carbon according to any of several provided methods. The halogen/halide may preferably be combined via line **121** directly into transport line **115**, within which it contacts and reacts with the base activated carbon prior to injection point **116**. This option is one form of what is referred to herein as "in-flight" preparation of a promoted carbon sorbent in accordance with the invention. Further, the halogen/halide may be combined via line **121b** with base activated carbon prior to entering transport line **115**. Still further, the halogen/halide may be contacted and react with the base activated carbon by introduction via line **121c** into reservoir **110**. This option is preferably employed when, for example, reservoir **110** comprises an ebullated or fluidized bed of base activated carbon, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base activated carbon in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in FIG. 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to FIG. 1.

Similarly, the optional secondary component may be contacted and react directly in transport line **115** via line **131**, or optionally as described above with respect to the halogen/halide, via lines **131b** and **131c**.

Similarly, the optional alkali component from **180** may either be added in transport line **115** directly, or may be injected separately by transport line **118**, combining downstream in flue gas **15** for synergistic effects with base activated carbon, promoted carbon, or optional secondary components. Being able to vary onsite the amount of the optional alkali component relative to base activated carbon, promoted carbon, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base activated carbon. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br₂, may be passed through an ebullated or fluidized bed of granular or fibrous activated

US 10,596,517 B2

11

carbon, with the promoted carbon sorbent so produced removed from the top of the bed via gas entrainment for injection.

In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl_2 and others. In some preferred embodiments, the promoted carbon sorbent may comprise from about 1 to about 30 g halogen/halide per 100 g base activated carbon. In some preferred embodiments, the promoted carbon sorbent may comprise an secondary component in concentration of from about 1 to about 15 wt-% of the concentration of the halogen/halide component.

In still other embodiments, the product promoted carbon sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted carbon sorbent to produce a bifunctional sorbent. Such stabilizing reagents may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H_2S , SO_2 , H_2Se , SeO_2 , CS_2 , P_2S_5 , and combinations thereof.

Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F_2 , Cl_2 , Br_2 , and I_2 , the reaction with a hot flue gas components leave little to react with elemental mercury. The atomic elemental halogen form, which includes the fluorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view therefore, a halide-salt-treated activated carbon will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen Promoted Sorbent Characteristics

The sorbent described here has a very high initial reactivity for oxidizing mercury and therefore can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the sorbents produced using the inventive technology. The time interval required for the mercury and the promoted carbon sorbents of the present invention to successfully interact in a flue gas duct, with the subsequent collection of the mercury on the sorbent

12

and ash is very short less than seconds. Clearly, such collection times require the sorbent to have both high capacity and high reactivity toward mercury. The promoted carbon sorbent can be utilized in a very finely powdered form to minimize mass transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a sorbent containing a halide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for very effective capture of the mercury.

It appears that the inventive sorbents chemically combine molecular bromine, for example, from solution, with activated carbon (edge sites). X-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus, the sorbent produced from halogen and activated carbon does not represent a molecular halogen form, but rather a new chemically modified carbon (or halocarbon) structure. This phenomenon may not occur with the less reactive iodine, where an I_2 molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, typically exceeding that of both the untreated carbon and the brominated carbon. The second component comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus, the second component is an element with more polarized electrons (4p and 5p).

Optional Alkali Component

It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO_2 , NO_x , HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio onsite in order to overcome and optimize for a given set of site conditions.

The synergy that can be gained when co-injecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e. sul-

US 10,596,517 B2

13

fates), and other flue gas contaminants (arsenates, selenates, etc.). The addition of optional alkali material will interact and react with these species/contaminants thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~an order of magnitude less) than activated carbon, thus more of it can be used still resulting in overall lower costs.

"In-Flight" Sorbent Preparation

Furthermore, we have demonstrated that the halogen promoted carbon sorbent can be readily produced "in-flight". This is accomplished by, for example, contacting the vapors of any combination of halogens and optionally a second component, in-flight, with very fine carbon particles. The particles may be dispersed in a stream of transport air (or other gas), which also conveys the halogen/halide promoted carbon sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

Advantages of On-Site Preparation

In-flight preparation of the halogen/halide promoted carbon sorbent on location produces certain advantages. For example, the treatment system can be combined with the carbon injection system at the end-use site. With this technique, the halogen/halide is introduced to the carbon-air (or other gas) mixture in a transport line (or other part of the sorbent storage and injection system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

- Capital equipment costs at a treatment facility are eliminated.

- Costs to operate the treatment facility are eliminated.

- There are no costs for transporting carbon and additive to a treatment facility.

- The inventive process uses existing hardware and operation procedures.

- The inventive technology ensures that the sorbent is always fresh, and thus, more reactive.

- No new handling concerns are introduced.

- There are no costs for removing carbon from treatment system.

- The inventive process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when changing fuels or reducing loads, thus further optimizing the economics.

- The inventive technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide promoted carbon sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g. bromine) to the carbon structure.

Sorbent Injection Location

Some of the preferred embodiments contemplate the use of a halogen promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash

14

particulates have been removed. Other embodiments of the inventive composition of the halogen promoted carbon sorbent comprise a powdered modified activated carbon prepared by adding Br₂ or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjunction with a base activated carbon and/or with the use of a halogen based sorbent and any other combinations of the sorbent technologies provided in this patent. Alternatively, embodiments include methods wherein the sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

Any of the above embodiments of the halogen/halide promoted carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive, conventional methods of adding a reagent (such as peroxide, gold, triiodide, etc.) to a sorbent. The halogen/halide promoted carbon sorbent of the present invention, treated with bromine and/or optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in co-pending, commonly owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component (s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

Promoted Carbon Sorbents

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a carbocation that accepts electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine-containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

EXAMPLES

To more clearly illustrate the present invention, several examples are presented below. These examples are intended

US 10,596,517 B2

15

to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

Example 1

Preparation and Testing of Halogenated Carbon (& Comparative Example) Gas Phase Halogenation

Finely powdered activated carbon (such as NORIT Darco FGD, NORIT Americas, Inc., Marshall, Tex. (USA), although others are suitable, as will be recognized by those skilled in the art), was placed in a rotating plastic barrel with side blades (a 5 ft³ (0.14 m³) cement mixer) fitted with a tight plastic lid to prevent loss of the fine powder during the preparation. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that is warmed to about 40°-50° C. The vapor pressure of the bromine was such that a dark red gas is generated and passed out of the generator. The outlet from the gaseous bromine generator is connected via a ¼ inch (0.64 cm) plastic hose to a stationary metal tube inserted through a flange in the center of the plastic lid and passing into the center of the barrel. The flange is not air tight so that the excess of nitrogen is released after the bromine is transferred to the tumbling carbon. Thus, the bromine gas stream continuously passed into the rotating barrel where it contacted the tumbling carbon. The unit is then operated until the desired amount of bromine has combined with the carbon. Typically, this is 0.4 to 1 kg of bromine to 20 kg of carbon (2-5 wt. %). When the reaction is completed, the carbon is weighed. The treated carbon is odorless and does not cause skin irritation since the bromine has completely reacted with the carbon to produce the brominated carbon.

XPS spectra demonstrate that the brominated carbon contains both covalent carbon-bound (organic) bromide as well as anionic bromide. The product contains the same moisture originally present in the activated carbon (5-17 wt %), but does not require further drying for use. The moisture is driven out at higher temperatures (>150° C.), and the bromine was not released until very high temperatures

Bench-Scale Testing of Mercury Oxidation and Capture Efficiency

A bench-scale apparatus and procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including bromine-containing activated carbons prepared from a variety of carbons, including commercially available sorbents, aerogel film sorbents, and the original precursor carbons for comparison.

A detailed description of the apparatus and its operation is provided in Dunham, G. E.; Miller, S. J. Chang, R.; Bergman, P. *Environmental Progress* 1998, 17, 203, which is incorporated herein by reference in its entirety. The bench scale mercury sorbent tests in the flue gas compositions were performed with finely (—400 mesh) powdered sorbents (37 mg) mixed with 113 mg sand and loaded on a quartz filter (2.5 inch (6.35 cm)) The loaded filter and holder were heated in an oven (125° C.) in the simulated flue gas stream (30 SCFH (standard cubic feet/hr) or 0.79 NCMH (normal cubic meters per hour)) containing the following: O₂ (6%), CO₂ (12%), SO₂ (600 ppm), NO (120 ppm) NO₂ (6 ppm), HCl (1 ppm), Hg⁰ (11 µg/m³), H₂O (15%), and N₂ (balance). Elemental mercury was provided by a standard permeation tube source placed in a double jacketed glass condenser, and heated to the desired temperature. Mercury concentrations in

16

the gas streams were determined with a continuous mercury emission monitor (Sir Galahad mercury CEM mfr. P.S. Analytical Deerfield Beach Fla. USA), and a SnCl₂ cell was used to convert oxidized species to elemental, so that both elemental and oxidized mercury concentration data could be obtained for both the influent and the effluent concentrations from the sorbent bed. Mercury concentrations were calibrated for the flow rates used. Spent sorbents were analyzed for mercury to determine the mass balance.

Referring now to FIG. 4, the effluent mercury concentration data are plotted as a percent of the influent mercury versus time. The resulting curve (breakthrough curve) for the halogenated sorbents typically showed 0%-1% Hg in the effluent (99+% capture) at the beginning, and increasing only after 30-60 minutes (breakthrough point), depending on the sorbent. FIG. 4 illustrates the breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) with synthetic flue gas containing 1 ppm HCl. Total Hg (solid circles) and elemental Hg (solid squares) in the effluent are presented as a percent of the inlet Hg. "EOT" indicates the end of test (the later data points shown are for calibration checks).

FIG. 5 presents the comparative breakthrough curves for the corresponding nonhalogenated sorbents typically initiated at 5%-50% of inlet mercury, depending on the HCl concentration in the synthetic flue gas, thus indicating considerably lower reactivity for oxidation and capture of the mercury for the nonhalogenated sorbents. After breakthrough of either halogenated or nonhalogenated sorbent, most of the mercury in the effluent was oxidized mercury.

Example 2

Gas Phase Halogenation of Fluidized Carbon

A bed of activated carbon supported in a vertical tube by a plug of glass wool was fluidized by a nitrogen stream. The top of the fluidized bed tube was connected to a catching trap for carbon fines that blow out the top of the tube. The bromine gas generator as described in Example 1 was attached to the fluidized carbon bed and the desired amount of gaseous bromine was passed into the bed. The contents of the trap were then mixed with the material in the bed and weighed. The resulting brominated carbon exhibited properties similar to the brominated carbon of Example 1.

Example 3

Liquid Phase (Water) Halogenation

A 5% solution of bromine in water was prepared by carefully adding 50 g of bromine to 1 liter of cold water One kg of activated carbon was added to the bromine solution in a large metal can. The resulting slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon, as indicated by the disappearance of the red color. The slurry was then filtered using a Buchner funnel under vacuum. The moist carbon that was collected on the filter was dried in an oven at 110° C. for several hours to constant weight. As in Example 1, some moisture remains in the carbon, however.

US 10,596,517 B2

17

The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 4

Addition of the Optional Second Halide Component

Brominated carbon was produced by solution phase bromination similar to that described with reference to Example 3. However, before filtration, a solution of hydriodic acid (HI) was added to the slurry in an amount equal to 10% of the bromine amount. The slurry was stirred to complete the reaction and then filtered and dried as described in Example 3.

Example 5

Liquid Phase Phosphohalogenation

A solution of phosphorus tribromide (500 g) in ligroin (10 liters) was stirred in a large metal can and 10 kg of activated carbon was added. The resulting slurry was stirred with a large paddle at ambient temperature to complete the reaction. The slurry was filtered under vacuum on a large Buchner funnel in several batches. The wet filter cake was dried at 110° C. in an oven to constant weight. The dried product was fluffed in the rotating barrel as described in Example 3.

Example 6

Preparation and Sorption on Larger-Particle Carbon

Tests were conducted on a pilot-scale combustor while firing a subbituminous coal, to evaluate mercury control by injecting larger-than-normal sized treated activated carbon. Standard AC sorbents generally are of fine size with a mean particle diameter of less than 20 micrometers, which is also typical of the flyash that is generated from pulverized coal combustion. Consequently, because the sizes of standard AC and flyash are similar, separation of the two is difficult. Injection of larger sized AC is generally not considered because the sorbent effectiveness decreases with size. In a scheme to recycle the injected carbon, the carbon is separated from the flyash. A separation based on size fractionation requires a treated larger particle sorbent. To test this concept, a treated larger sized (>60 µm) sorbent was developed, prepared, and tested.

Treatment Gas Phase Halogenation

Granular activated carbon (Calgon F400) was ground and sieved through conventional mesh screens. The mesh size fraction -170 to +240 (corresponding to about 60 to about 88 micrometers) was collected and placed in a rotating vessel as described in Example 1 above. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that was warmed to about 40°-50° C., and the outlet from this gaseous bromine generator was connected via a ¼ inch (635 mm) plastic hose to a stationary metal tube inserted through a flange in the center of the lid and passing into the center of the rotating vessel, also as described in Example 1. The unit was operated until the desired amount of bromine had combined with the carbon, in this case 0.05 kg of bromine to 1 kg of carbon (5 wt. %). When the reaction was completed, the carbon was weighed. The treated carbon was odorless as has been described above.

18

PTC Apparatus

The pilot-scale combustor, known as the "Particulate Test Combustor" (hereinafter "PTC"), is a 550,000-Btu/hr (about 161 kW) pulverized coal ("PC")-fired unit, designed to generate combustion flue gas properties and fly ash that are representative of those produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle of the PTC fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature. Originally, the PTC used cold-water annular heat exchangers to provide flue gas temperature control to the baghouse (also referred to as a "fabric filter") or electrostatic precipitator (ESP). However, analysis of ash deposits collected from the heat exchangers indicated that some mercury was collected on the duct walls. To minimize this effect, the heat exchangers were modified to provide for higher duct wall temperatures.

The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device (baghouse, Advanced Hybrid Particle Collector/AHPC™, and/or electrostatic precipitator/ESP) operating data to be monitored continuously and recorded on a data logger.

PTC Procedure

Flue gas samples were taken at combinations of two of the three available system sample points: the furnace exit, the particulate control device inlet, and the particulate control device outlet. After passing through sample conditioners to remove moisture, the flue gas was typically analyzed for O₂, CO, CO₂, SO₂, and NO_x. Each constituent was normally analyzed at both the furnace exit and the outlet of the particulate control device simultaneously, using two analyzers. The concentration values from all of the instruments were recorded continuously. In addition, data were manually recorded at set time intervals. NO_x was determined using a pair of Rosemount Analytical NO_x chemiluminescent analyzers. SO₂ was measured using a pair of Ametek Instruments photometric gas analyzers. The remaining gases were measured by a pair of Rosemount Analytical multi-gas continuous emissions monitors. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

The baghouse vessel was a 20 inch (50.8 cm) (ID) chamber that is heat-traced and insulated, with the flue gas introduced near the bottom. The combustor produced about 200 ACFM (actual cubic feet per minute; about 5.7 actual m³/min) of flue gas at 300° F. (about 150° C.), therefore three 13-ft by 5-inch (3.96 m by 12.7 cm) bags provided an air-to-cloth ratio of 4 ft/min (1.22 m/min). Each bag was cleaned separately in operation with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags were cleaned on a time basis, rather than with the cleaning cycle initiated by pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession on-line.

Tests were also conducted with a single-wire, tubular ESP replacing the fabric filter. The ESP unit was designed to provide a specific collection area of 125 at 300° F. (150° C.). Since the flue gas flow rate for the PTC is 130 SCFM

US 10,596,517 B2

19

(standard cubic feet per minute; about 3.7 NCMM (normal m³/min)), the gas velocity through the ESP is 5 ft/min (about 1.52 m/min). The plate spacing for the ESP unit is it in (27.9 cm). The ESP was designed to facilitate thorough cleaning between tests so that all tests can begin on the same basis.

PTC Results

Results are illustrated in FIG. 6. As can be observed in FIG. 6, even though the tested sorbent particle size is significantly larger than normal sorbent particles, the treated larger-than-normal sized (that is, >60 micrometers) activated carbon sorbent was quite effective at capturing mercury. Approximately 75% of the mercury was captured when the larger-sized treated AC was injected ahead of the pilot-scale ESP, while approximately 85% of the mercury was captured when injected ahead of the pilot-scale fabric filter ("FF"). Note that in FIG. 6 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet (1 MACF is about 0.028 million actual cubic meters or "MACM").

Referring now to FIG. 7, it can be observed that the larger-sized treated AC when injected ahead of the pilot-scale ESP (diamond symbol(s)) performed better than the finer standard AC (triangles) under the same arrangement. In comparison, when injected ahead of the fabric filter (FF), the larger-sized treated AC (square) performed similarly to slightly worse. However, for this application, the larger-sized treated AC can be physically separated from the smaller flyash particles, and the sorbent can then be regenerated, recycled, and reused. This will substantially improve overall utilization and economics. These data thus show that a larger-than-normal sized sorbent can provide effective mercury control and ease flyash and AC separation, thereby also preserving the characteristics of the flyash for sale and beneficial use. Accordingly, because >60 µm sorbent particles have been successfully demonstrated, superior mercury control can be obtained with >40 µm particles, which may be preferred in some applications, depending on the sorbent particle/ash separation system used. Note that in FIG. 7 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet.

Example 7

Liquid Phase (Organic Solvent) Halogenation

A 5% solution of bromine in ligroin was prepared by carefully adding 50 g of bromine to 1 liter of cold ligroin. One kg of activated carbon was added to the bromine solution in a large metal can. The slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon as indicated by the disappearance of the red color. The slurry was filtered using a Buchner funnel under vacuum. The carbon cake that was collected on the filter was dried in an oven at 110° C. for several hours until it appeared dry and a constant weight was obtained. As in Example 1, some moisture was left in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 8

Promoted Activated Carbon Sorbents

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including the bromine-containing activated carbons pre-

20

pared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100° C. in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. The results indicated that adding a second component to the solution improved the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 µg/m³) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM ("continuous emission monitor") (mfr. P S Analytical, Deerfield Beach, Fla., USA). The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer. A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it was treated with 0.1 N HBr, and the powder was collected by centrifugation and drying, revealed that the mercury capture activity increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicated that it not only captured mercury at the same level as before (100% capture) but its capacity was prolonged by several minutes, and thus enhanced. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

Example 9

Fluidized/Ebullated Bed Preparation

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed or ebullated bed of the carbon. The amount of bromine taken up by the carbon ranges one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Example 10

Full-Scale Testing

In this example, a baghouse (fabric filter) or ESP was used to collect particulates in the exhaust of a full-scale commercial pulverized coal-burning facility. A scrubber and sorbent bed were also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In this example, the halogen/halide promoted carbon sorbent was injected into the flue gas after the boiler. In general however, the inventive sorbent can be injected where desired (e.g., before, after, or within the boiler).

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 fg/m³. The ash and injected carbon were collected in the baghouse at 350° F. to 375° F. (about 175-190° C.). Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/MACF ("MACF" and "Macf" represent one million actual cubic

US 10,596,517 B2

21

feet; 1.0 lb/MACF is about 16 kg/MACM (million actual cubic meters)) resulted in mercury effluent concentrations of 3.8-4.2 $\mu\text{g}/\text{m}^3$ (representing 62%-58% removal of the mercury from the gas, respectively), and at 2.0 lb/MACF (about 32 kg/MACM), gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/MACF resulted in 73%-69% removal and at 2.0 lb/MACF gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine promoted carbon sorbent of the present invention.

Example 11A

Addition of Optional Alkaline
Component—Bench-Scale

The efficiency of the activated carbons for mercury capture can be improved considerably by employing a basic material co-injected with the activated carbon, in order to capture any oxidized mercury that may be released from the sorbent, or to capture some of the sulfur or selenium oxides in the flue gas that can have detrimental effect on the sorbent capacity.

Bench-scale testing was conducted by preparing a filter composed of 37 mg of brominated activated carbon mixed with 113 mg of calcium oxide. The test was conducted as described in Example 1 and compared with the same carbon sorbent but with an inert diluent. The breakthrough curve for the mixture of brominated (2%) NORIT Darco FGD sorbent with inert sand is shown in FIG. 8, and the breakthrough curve for the mixture with CaO is shown in FIG. 9. It can be seen that the point of 50% breakthrough improves to 65 minutes with the mixture with CaO from only 48 min with the sand mixture.

Example 11B

Addition of Optional Alkaline
Component—Pilot-Scale

Tests were conducted on the pilot-scale PTC combustor described above with reference to Example 6 while firing a Texas lignite to evaluate mercury control by co-injecting a standard activated carbon (also referred to herein as "AC") and an alkali material upstream of a fabric filter. Typical results are illustrated in FIG. 10. As shown in FIG. 10, co-injecting lime with activated carbon vastly improved mercury removal. Mercury removals of approximately 90% were achieved with the co-injected sorbents, whereas less than 60% removal was achieved with the use of standard AC alone, even at much higher injection rates. Data from similar tests show that injecting similar quantities of sodium carbonate and AC, and lime and AC, resulted in mercury removals of approximately 80%, and 87%, respectively. These data suggest that other alkali can also be co-injected with AC to improve mercury removal. Other data show that flue gas temperature may impact the effectiveness of the alkali addition. Further test data indicate that flue gas contaminants, flue gas constituents (SO_2 , NO_x , HCl, etc.), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This indicates that it may be desirable to be able to adjust and tailor, onsite, the alkali-to-AC ratio in order to optimize removal for a given set of site conditions.

Without wishing to be bound by any particular theory, the synergy observed in the improved performance when co-injecting the two materials can be explained as follows.

22

First, tests indicate that binding sites on AC can be consumed by sulfur species and other contaminants. The alkali material interacts and reacts with these species thus minimizing their consumption of AC mercury binding sites. Second, other work has shown that standard AC will continue to oxidize mercury even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by the particulate control device. Thus, combining alkali with treated and/or non-treated AC synergistically takes advantage of these two mechanisms, resulting in improved mercury capture at reduced costs.

Example 12

Brominated Carbon Sorbent for Gasification Fuel
GasPreparation of 5% Br₂W-AC

Using a procedure similar to Example 3, a 2.5 wt/vol % solution of bromine in water was prepared. Granular Calgon F400 was added to the bromine solution to give a 5 wt/wt % brominated carbon product. The bromine solution was stirred with a large paddle during and after the addition until the red color in the water disappeared. The suspension was filtered by vacuum on a large Buchner funnel. The filter cake was dried in air, and then in an oven at 110° C. until a stable weight was obtained. The moisture was reduced to 15%.

Preparation of 5% Br₂D-AC

A brominated sorbent was prepared from Br₂ addition in solvent as described in Example 7, except that dichloromethane was used as the solvent instead of ligroin, and granular Calgon F400 was used.

Preparation of 5% PBr₃-AC

A phosphohalogenated sorbent was prepared from PBr₃ using the method described in Example 5, except granular Calgon F400 was used.

Testing in Hydrogen Atmosphere—Procedure

To simulate the capture of mercury from a heated fuel gas or syngas from coal gasification, tests were conducted employing a stream comprising 10% vol/vol hydrogen in nitrogen passing through the sorbent at 500 cc/min. The stream contained 26.9 micrograms/ m^3 of elemental mercury from a commercial mercury permeation source.

In the tests, the sorbent (0.5 g) was placed in a 0.39 inch (1 cm, inside diameter) glass tube fitted with a medium fit sintered glass filter disc to hold the sorbent in the gas stream. The tube containing the sorbent bed was connected to a gas inlet tube for introducing the gas stream containing the mercury vapor and at the outlet to a tube connection to the detector. The detector was a Semtech 2000 continuous mercury emission monitor. The tube was equilibrated in a nitrogen flow (450 cc/min) for 5 minutes at ambient temperature to stabilize the system. The detector showed 0 concentration of mercury in the effluent from the sorbent bed. (The blank run with no sorbent read 26.9 micrograms/ m^3). The tube was then placed in an oven at the selected temperature for the test (from 250° to 400° C.). Effluent mercury concentration data from the detector were collected until the detector showed a constant reading for 5 minutes. Hydrogen (50 cc/min) was then added to the gas stream and detector readings were taken every 5 min. Tests were conducted at several oven temperatures for various periods of time up to 3 hours, depending on the temperature and sorbent. The elemental mercury concentration data were plotted as a percent of inlet mercury concentration versus time as in Example 1. All the mercury in the effluent was

US 10,596,517 B2

23

elemental, so a single detector was sufficient, and no SnCl_2 trap was needed to convert to elemental mercury (as in Example 1). The time for 50% breakthrough (time to reach 50% capture) was then determined from the breakthrough curves.

Results

The results are shown in Table 1 (below) for the unbrominated sorbent (Calgon F-400), the brominated sorbents (5% Br2W-AC and 5% BrD-AC), and the phosphobrominated sorbent (5% PBr3-AC). The maximum mercury concentration obtained in the effluent in each run is also reported in Table 1 for the time period indicated in the last column.

Under the reducing hydrogen conditions, the unbrominated sorbent broke through immediately and was exhausted after only 6.5 min. This complete failure occurred because the hydrogen reduces the captured mercury in the unbrominated sorbent at any temperature above 100° C. Both of the brominated sorbents exhibited excellent reactivity and good capacity at all temperatures, up to at least 400° C. The phosphobrominated sorbent exhibited superior reactivity and capacity at all temperatures, up to at least 400° C.

Times for 50% Breakthrough Maximum Observed Hg Concentrations for Sorbents (10% Hydrogen Streams)				
Sorbent	Temp (° C.)	50% breakthrough (min)	Maximum [Hg] ($\mu\text{g}/\text{m}^3$)	Time (min)
F-400	250	6	20.3	6.5
5% Br2W-AC	250	>150	1.4	150
5% Br2W-AC	300	>180	4.3	180
5% Br2W-AC	350	160	15.1	180
5% Br2W-AC	400	60	13.9	65
5% PBr3-AC	250	>140	0.4	140
5% PBr3-AC	300	>150	0.5	150
5% PBr3-AC	350	>150	1.4	150
5% Br2D-AC	350	>180	2.1	180
5% Br2D-AC	400	>180	10.9	180

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. According y, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

24

The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

Although the invention is described herein as a sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

PROVISIONAL APPLICATION

A reactive sorbent material is described for capture of mercury in a vapor stream. The vapor stream includes flue gas from coal combustion or incineration, synthesis gas from gasification, as well as offgases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories. The sorbent is especially suited to, but not limited to, use in low-chlorine flue or exhaust gases where the mercury is mainly elemental. The sorbent comprises a bromide-modified carbon form containing a reactive compound produced by the reaction of bromine with the carbon. Other additional promoting substances can be added in smaller amounts to increase the reactivity with and sorption of elemental mercury. This combination results in a carbon bromide structure in the carbon lattice that can oxidize the mercury to a species that is strongly bonded to the carbon structure and, therefore, easily retained on the sorbent at higher temperatures in the presence of flue gas constituents. In some examples, the sorbent consists of a fine or coarse powdered material for injection into the gas stream or a granular or fibrous material for use in a fixed or moving bed. In some examples, the sorbent does not require in situ activation (an induction period) in a flue gas stream as do conventional activated carbon sorbents. Other additives of base chemistry (Ca, Na, and others) may be added to flue gas as a sorbent mixture, or co-injected to selectively sorb acid gases or other flue gas constituents to keep available reactive sites for mercury oxidation and subsequent capture. The sorbent can be regenerated by washing off contaminating components derived from flue gas that poison the spent sorbent. Novel methods for introduction of the sorbent dispersion into the mercury contaminated gas stream are described.

Following is an outline of examples of the invention. The invention may also take on various other examples or embodiments, as a person skilled in the art would understand.

1. A modified carbon sorbent was prepared by reacting the carbon with molecular bromine by applying a solution of molecular bromine in an organic solvent to the carbon, followed by removal of the modified carbon from the bulk of solvent and further removal of solvent from the pores by drying the carbon in air or nitrogen. The solution may also contain an additional promoting substance in small amounts. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

1A. (Dependent)

Same as 1, carbon is powdered activated carbon.

Carbon is granular activated carbon.

US 10,596,517 B2

25

Carbon is very fine carbon black.

Carbon is very fine carbon fiber.

Carbon is aerogel carbon film.

Carbon is char recovered from pyrolysis process.

Carbon is powdered activated carbon of size distribution 5
larger than fly ash size distribution, so that it can be
physically separated from the ash and regenerated for reuse.

Carbon is regenerated from previous usage cycle and
recycled.

Other desired types of carbon may also be used. 10

1B. (Dependent)

Same as 1, Solvent is chlorinated hydrocarbon such as
dichloromethane.

Same as 1, Solvent is hydrocarbon solvent such as petro-
leum ether or ligroin or pentane or hexane or toluene or 15
benzene.

Same as 1, Solvent is water.

Same as 1, Solvent is carbon disulfide.

Same as 1, Solvent is a waste solvent.

Same as 1, Solvent is an ether. 20

Same as 1, Solvent is recycled from previous batch.

Same as 1, Solvent is supercritical solvent such as CO₂.

Other desired types of Solvents may also be used.

1C. (Dependent)

Same as 1, solution of bromine is applied by stirring the 25
carbon in the bromine solution.

Same as 1, solution of bromine is applied by spraying a
solution of molecular bromine in an organic solvent, fol-
lowed by removal of solvent from the pores by drying the
carbon in air or nitrogen. 30

The bromine may also be applied using other desired
techniques.

1D. (Dependent)

Same as 1, removal of solvent is by filtration, centrifu- 35
gation, settling, and decantation and drying in vacuum, air,
or other gas.

Same as 1, when sprayed or minimal volume, removal of
solvent is by drying in air, vacuum, or other gas.

The solvent may also be removed using other desired
techniques. 40

1E. (Dependent)

Same as 1, additional substance is iodine, at 1%-10% of
the bromine concentration added.

Same as 1, additional substance is hydrohalide (HI, HBr,
HCl), etc., 1%-10% of bromine. 45

Same as 1, additional substance is a compound comprised
of a Group V or VI element or combination of Group V or
VI with Group VII element, such as SCl₂, 1-10 wt % of
bromine.

2. A modified carbon sorbent was prepared by reacting the 50
carbon with molecular bromine by contacting the carbon
with a gas containing molecular bromine. In one example,
the amount of bromine taken up by the carbon ranges
from <1 to about 30 g per 1.00 g of activated carbon,
depending on the proportions used. 55

Contacting is by passing the Br₂ gas through a bed of the
carbon.

Bed is ebullated or fluidized.

Bed is moving bed of granules or fibers.

Contacting is by admitting Br₂ gas to a duct through 60
which the carbon is transported from a reservoir to the flue
gas duct via an air-driven entrainment method, thus promot-
ing the activity of the carbon in-flight.

Same additives as 1E, except these are added in the gas
phase, and added in-flight as in 2 above. 65

3. A modified activated carbon sorbent was prepared by
reacting the carbon with hydrogen bromide (HBr) by

26

stirring the carbon in a solution of HBr in an organic
solvent or in water, followed by removal of the modified
carbon from the bulk of solvent and further removal of
solvent from the pores by drying the carbon in air or
nitrogen. In one example, the amount of bromine taken up
by the carbon ranges from <1 to about 30 g per 100 g of
activated carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon
forms. Same solutions and treatment as 1B, 1C, 1D.

Same additives as 1E, added into the solution phase or
later in the gas phase, and added in-flight as in 2 above.

4. An activated carbon sorbent was prepared by impregnating
hydrogen bromide by passing a gas composition
containing hydrogen bromide diluted with nitrogen or air
through a fluidized bed or ebullated bed of the carbon. In
one example, the amount of bromine taken up by the
carbon ranges from <1 to about 30 g per 100 g of activated
carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon
forms. 20

Contacting options are similar to 2.

5. Sequential treatment of activated carbon with bromine or
HBr, followed by another mercury stabilizing reagent to
generate a highly reactive bifunctional sorbent, the
reagent to include sulfur and selenium species, such as
H₂S, SO₂, H₂Se, Se, SeO₂, CS₂, O₂S₅.

6. Sequential treatment of activated carbon with mercury
stabilizing reagent, followed by bromine or HBr to gen-
erate a highly reactive bifunctional sorbent, the reagent to
include sulfur and selenium species, such as H₂S, SO₂,
H₂Se, Se, SeO₂, CS₂, P₂S₅.

7. Treatment of a carbon with a Group V or VI element
combined with Group VII element, such as PBr₃ or SCl₂.
In one example, the amount of Group V or VI halide is
1-30 wt % of the carbon. The compound is added in vapor
phase or in solution (solvent is hydrocarbon, chlorinated
hydrocarbon, or other solvent as described in 1B, but not
water, since the compound is destroyed in water solution).

8. The process for preparing the bromine-containing acti-
vated carbon sorbent as described in Examples 1-6 and
coupled with the injection of the bromine-containing
fine-particle sorbent into the contaminated gas stream and
subsequent removal of the fine particles of sorbent from
the gas stream in a collection device, such as bag filtration
of electrostatic precipitator (ESP).

9. The process of using additives (1-8) in conjunction with
sorbents to capture acid gases and other flue gas constitu-
ents that block oxidation reactions or consume sorbent
sites that would otherwise capture mercury. The additive
is a compound comprised of Group I or II elements, such
as Ca, Na, and others. These additives of base chemistry
may be added to flue gas as a sorbent mixture or co-
injected to selectively sorb acid gases or other gas con-
stituents that compete for mercury reactive/sorption sites,
thereby improving the effectiveness of activated carbon to
capture mercury. In addition, the base additives can
augment the treated activated carbon by helping to cap-
ture oxidized mercury forms in the flue gas, such as
mercuric chloride, or that are produced on the carbon
sorbent, such as mercuric bromide, but are released to the
gas phase as the sorbent becomes saturated or capacity
limited.

10. The process of preparing a larger-than-normal (>40 μm)
sorbent particle size, promoting with the halogen treat-
ment as described in 1-8, using the treated sorbent for
capture of mercury by injecting in the flue gas, and finally
separating and recovering the sorbent from the ash par-

US 10,596,517 B2

27

ticles. The larger sorbent size thus will allow easy mechanical/physical separation so that sorbent can be regenerated, recycled, and reused, and the ash can be sold as a low-carbon cementitious byproduct for concrete. The separation can be effected by various methods, such as density (gravity), floatation, or sieving methods.

11. The process for preparing the bromine-containing activated carbon sorbent as described in Example 1-10, coupled with the direct injection of the slurry of the prepared fine-particle sorbent in the solvent or aqueous phase, so that the aerosol particles of the slurry achieve a high degree of dispersion in the gas stream and evaporation of the solvent in the hot gas occurs rapidly. The amount of slurry added is flow-controlled, and the concentration of particles in the slurry is monitored by optical density measurements prior to injection. Collection of particles is performed.

12. The process for preparing the bromine-containing activated carbon sorbent, as described in Examples 2 and 4, coupled where the fine-particle dispersion of brominated sorbent in the gas stream at the top of the ebullated bed is led to the flue gas or offgas duct where the said dispersion is contacted with mercury-contaminated flue gas or offgas stream. The amount of aerosol dispersion added is controlled by the gas flow to the ebullated bed, and the concentration of particles in the dispersion can be monitored by optical density measurements prior to injection. Collection of particles is performed by the existing particulate-collection equipment.

13. The process for preparing the bromine-containing activated carbon sorbent bed, coupled with contacting the bed with the mercury-contaminated flue gas or offgas.

14. The process for preparing the bromine-containing activated carbon sorbent, as described in Examples 2 and 4, or untreated activated carbon, coated on a substrate or as activated carbon material. This material is placed in a moving system that geometrically allows for control of rate of exposure, sorption, and exchange of material in a continuous or semicontinuous manner.

15. In the sorbent and mercury removal process outlined in paragraphs above, the bromine reagents promote metal oxidation activity by creating cationic or radical character on the carbon edge structure that attracts mercury atoms and extracts electrons from said mercury atoms, resulting in oxidized mercury, which is more easily captured on a sorbent. A similar mechanism applies to oxidation and capture of reduced arsenic and other pollutant species.

The invention relates to the process for the removal of mercury and other pollutant species from gas streams generated during the burning of fossil fuels, such as in a coal-fired utility or synthesis gas from gasification facilities. This removal process would utilize a sorbent and/or a combination of additives to remove pollutants from the gas stream, which are at the same time interacting with other gas components that result in poisoning or deactivating the sorbent and reducing its capacity or reaction rates with the targeted pollutant species. The present invention provides a cost-effective way to capture the pollutants by utilizing exceptionally active carbon sorbents and promoting mercury sorbent surface reactions, containing a bromide form of the carbon, that capture mercury with high kinetic chemisorption (oxidation) activity, so that capture can occur during contact times of seconds or less. The sorbent does not require in situ activation (induction period) in the gas stream to achieve high activity as do conventional activated carbon

28

sorbents. The reactivity of the sorbent toward the pollutants and the sorption capacity can be regenerated, recycled, and reused.

Burning fossil fuels generates a flue gas that contains mercury (and other trace elements) that was in the coal, plus oxides of sulfur and nitrogen (acid gas emissions) and particulates whose release to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. While control of other elements and/or flue gas pollutants may apply, the discussion provided is focused on mercury. Initially, mercury is released in the elemental form during combustion/gasification, but downstream of the boiler, in the ducts and stack of the combustion system, part of the elemental mercury is oxidized. The amount oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the coal, but a typical concentration of mercury in the stream of combustion gas is about 5 parts per billion (ppb). A pound of mercury or more per day may be emitted in some utilities.

Discussion of Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles (for example, see U.S. Pat. No. 6,214,304), and basic silicate or oxide sorbents (for example, see the Ghorishi reference (Ghorishi, B.; Gullet, B K. Waste Manage Res. 1993, 16, 582) and Lancia references). When particle injection is employed, the mercury chemisorbed to the sorbent particle is removed from the gas stream in a bag house or ESP and collected along with ash particulates (for example, see U.S. Pat. Nos. 4,889,698, 4,956,162, 5,672,323, 5,827,352, 6,027,551, and 5,505,766). The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of approximately 60% was attained with a baghouse to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon, since the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after exposure to the flue gas for about 20 minutes does the seasoned sorbent become effective and provide capture of 60% of the mercury in the gas. Consequently, these sorbents must be used in large amounts (high sorbent-to-mercury ratios) to effectively capture the mercury. These sorbents can be relatively expensive and cannot be easily separated from the ash, regenerated and reused. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash for use in various applications.

Use of Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have not previously been effective. Halogen is defined as a member of the very active elements comprising Group VII-A of the periodic table. In the molecular elemental halogen form, including F₂, Cl₂, Br₂, and I₂, the reaction with elemental mercury is not fast enough to result in the formation of oxidized mercury in a coal combustion flue gas with conventional ash control technology. The atomic elemental halogen form, which includes F atom, Cl atom, Br

US 10,596,517 B2

29

atom, and I atom, is about a million times more reactive to mercury, but the concentrations of these forms are extremely low, and also, therefore, cannot result in oxidation of mercury in a utility flue gas.

A halide is a compound formed from reaction of a halogen with another element or radical. In general, the halide compounds are normally very much less reactive than the molecular halogens, having expended their high chemical potential in forming the low energy halide. The halide is considered a reduced form and cannot therefore oxidize anything by itself. It is for this reason that it is not obvious that a halide-halogen treated activated carbon would be effective at oxidizing elemental mercury and provide effective capture of elemental mercury. In fact, for tests with salts, analytical data show the addition of bromine to an activated carbon or carbon black or soot does form a compound by reacting with the unsaturated groups on the carbon. By applying x-ray photoelectron spectroscopy, it has been determined that bromine or HBr added to carbon black forms chemical compounds within a carbon structure.

A body of theory has been developed from scientific evidence to explain the nature of the promotion effect of the bromine compounds. This principle is illustrated in FIG. 2, which in step 1 shows the reaction of the hydrogen bromide with the unsaturated structure of the activated carbon. This may be a carbene species on the edge of the graphene sheets structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury.

We now teach that the formation of the new bromide compound with carbon increases the reactivity of the carbon forms toward mercury and other pollutants. The resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation results from the promotion effect of the halide exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, which stabilizes the positive charge developing on the mercury and lowers the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus, adding HBr or Br₂ to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

PRIOR ART PUBLICATIONS

The earliest patents that relate to mercury capture on a sorbent are actually not for flue gas mercury control but for capture of mercury from air or other gas mixtures on a carbon or other sorbent. These patents were based on a model that recognized the affinity of halogens for mercury, rather than the formation of a reactive carbon. These patents are discussed below according to the type of halogen used for impregnation.

One patent that teaches a halogen impregnation (Stock, U.S. Pat. No. 1,984,164, issued in 1934) describes the use of activated carbon or other solid impregnated with a halogen for removing Hg from air. The impregnation method is not specified. This seems to be the most general claim with respect to halogen impregnation. All the statements and claims appear to refer to halogen or iodine, but the patent does not appear to address bromides or other halides or bromide compounds or even specifically iodide or an iodine compound. The only example in the description is iodine

30

impregnation. The patent also is restricted to air systems and did not pertain to flue gas systems with reactive acid gases. The description did not assume that the iodine formed a reactive carbon species.

Japanese Patent JP 49-43197 describes the treatment of Hg-contaminated electrolysis cell gas using a metal iodide salt on a support. A similar treatment using a resin impregnated with a metal iodide is described in JP 50-6438. These patents do not appear to represent a carbon bromide compound as specified in this patent application.

Another early patent (Hilgen, U.S. Pat. No. 3,849,267, issued in 1974) describes a method for Hg removal from a gas which claims mixing molecular chlorine (Cl₂) with the gas to be cleaned and passing it through a nonporous sorbent such as glass wool and NaCl (not carbon). This was evidently not an obvious extension of the Stock patent, since a halogen was introduced as part of the gas phase being cleaned.

A later patent (deJong, et al., U.S. Pat. No. 4,196,173, issued in 1980) describes a method for Hg removal in air which claims using a bed of activated carbon impregnated with halogen-only Cl₂ is specified in the other claims and examples, and it is prepared by flowing the Cl₂ stream through a carbon bed.

An improved sorbent for mercury in air was patented by Revoir and Jones (U.S. Pat. No. 3,662,523, issued in 1972), in which ICl and ICl₃ vapors were impregnated into the activated carbon. No explanation of the increased activity was provided. Since these compounds are interhalogen compounds, the patent did not infringe Stock.

U.S. Pat. No. 5,891,324 describes an activated carbon containing an acid (HCl, H₂SO₄, or H₃PO₄) for the removal of mercury contained in a liquid phase, such as would occur in a process steam in the oil industry. In this case, the model presented was that mercury is adsorbed from the liquid into the solid carbon phase at relatively low temperatures.

In U.S. Patent Application 2004/0003716, a method is described for removing mercury from a combustion gas. This method employs an exposure of a finely powdered activated carbon to a molecular bromine gas at an elevated temperature or to HBr to produce a sorbent with good mercury removal ability when injected into the flue gas duct. The model for the efficacy of the Nelson sorbent is not clearly stated, so it can be presumed that the reasoning for using bromine is the simple premise that some bromine form will help capture the mercury, as does iodine and chlorine. The methods for incorporation of the bromine in the Nelson application are not the same as with the present invention, and the Nelson method will not produce the identical carbon bromide species that are obtained in the art described in this application. The Nelson method lacks many of the features described in this application that impart exceptional activity to the sorbent in a convenient way, for example, the addition of smaller amount of a second more powerful promoting agent, the use of facile solvent systems, including aqueous bromine, and the use of in-flight bromine treatment. Additionally, the patent application does not mention regeneration, recycling, or reuse, or the use of moving contactors or larger particle size to facilitate sorbent-ash separation.

EMBODIMENTS OF THE INVENTION

A sorbent that is initially very reactive in oxidizing mercury can be used in very small amounts to achieve high capture efficiencies, thus lowering operation costs and lessening the disposal problem. In addition, further disposal reduction is made possible by recycling and reusing the

US 10,596,517 B2

31

sorbent that is produced using this technology. The time interval for the mercury and sorbent to interact in a flue gas duct and the subsequent collection of the mercury on the sorbent and ash may be very short—only seconds. This requires the sorbent to have high capacity and be very reactive toward mercury. A sorbent can be utilized in a very finely powdered form (e.g., 1-10 μm) to minimize mass transfer limitations. But, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. One feature of this invention is the process to prepare a sorbent containing a bromide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for effective capture of the mercury.

One possible way to do this is to chemically combine molecular bromine from solution with activated carbon (edge sites). X-ray photoelectron spectroscopy established that the addition of bromine formed a chemical compound in the carbon structure. Thus, the sorbent does not represent a molecular bromine halogen form but a new chemically modified carbon structure. This may not occur with the less reactive iodine, where an I_2 -molecular complex can exist on the carbon basal plane. In the bromine case, it is actually the carbon that oxidizes the mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements as described herein. Chlorine treatment resulted in lower-activity carbons because the chloride anion was less effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound from a second halogen, such as HBr . Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus the second component is an element with more polarized electrons (4p and 5p).

Furthermore, we demonstrated that the sorbent can be readily treated with any combination of bromine and the second component in-flight using vapors of these components contacting the very fine carbon particles dispersed in air or other gas stream that conveys the particles to the flue gas duct. There is no particular temperature requirement for this contact. This technology is very simple to implement, so it will result in a great cost savings to the utility using this technology for mercury capture.

A unique, nonobvious technique for preparation of the treated carbon is through combining the treatment system with the carbon injection system at the end-use site. With this technique, the halogen is introduced to the carbon-air mixture in the transport line (or other part of the sorbent storage and injection system). Benefits over current concepts to treat sorbents off-site include the following:

Capital equipment costs at a treatment facility are eliminated.

Costs to operate the treatment facility are eliminated.

There are no costs for transporting carbon and additive to a treatment facility.

32

his process uses existing hardware and operation procedures.

This technology ensures that the sorbent is always fresh, and thus, more reactive.

No new handling concerns are introduced.

There are no costs for removing carbon from treatment system.

This process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as needed when changing fuels or reducing loads, thus further optimizing the economics. This technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the invention, a process for preparing and regenerating carbon sorbents whose activity for mercury capture is promoted by the addition of bromine to the carbon structure.

The invention applies to use of a sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Examples of the composition of the sorbent are a powdered modified activated carbon prepared by adding Br_2 or HBr plus a second optional component. Alternatively, the sorbent is on a moving contactor consisting of particles or fibers containing the compositions listed in the previous sentence. Either type can be regenerated; the poisoning contaminants from the flue gas are removed and an inexpensive promoting agent added to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive art of adding a reagent (such as peroxide, gold, triiodide, etc.) to the sorbent. The activated carbon sorbent treated with bromine and/or the other components is noncorrosive.

Detailed examples of sorbent regeneration techniques are described in co-pending, commonly-owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is incorporated by reference herein.

Although the invention is described herein as a sorbent material, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

The construction and method of operation of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of specific exemplary embodiments.

FIG. 11 is a block diagram illustrating the use of the invention in a coal fueled facility. Of course, the invention can also be used in any other desired type of facility. FIG. 11 shows a boiler for burning pulverized coal. The facility utilizes various devices to clean the exhaust of the boiler. In this example, a baghouse or ESP is used to collect particulates in the exhaust. A scrubber and sorbent bed are also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In the example shown, the sorbent is injected into the flue gas after the boiler. The additive can be injected where desired (e.g., before, after, or within the boiler).

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize the invention. Where possible, the mercury control technology of the present invention will utilize measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent levels in this

US 10,596,517 B2

33

way will ensure mercury removal requirements are met with the minimal sorbent requirements and therefore the associated costs will be minimized. In one example, the emissions are measured at the stack.

Carbon Sorbent

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a carbocation that accept electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine-containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several powdered carbon sorbents, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100° C. in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. Adding a second component to the solution was demonstrated to improve the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 $\mu\text{g}/\text{m}^3$) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM. The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer.

A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it has been treated with 0.1 N HBr, collecting the powder by centrifugation and drying, revealed that the mercury capture activity is increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicates that it not only captures mercury at the same level as before (100% capture) but is enhanced such that its capacity is prolonged by several minutes. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed of ebullated bed of the carbon. The amount of

34

bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 $\mu\text{g}/\text{m}^3$. The ash and injected carbons were collected in the baghouse at 350 E to 375 EF. Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/Macf resulted in mercury effluent concentrations of 3.8-4.2 $\mu\text{g}/\text{m}^3$ (representing 62%-58% removal of the mercury from the gas), and at 2.0 lb/Macf, gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/Macf resulted in 73%-69% removal and at 2.0 lb/Macf gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine-treated carbon.

Addendum: Other References to Hg Sorption Sorbent Beds with Particulate Removal

Carbon beds have also been utilized for mercury capture in flue gas. The German Patent 34 26 059 describes the use of a very thick carbon bed for treatment of flue gases containing polyhalogenated compounds. Although the system employed at Dusseldorf would also have the potential for Hg removal (for example, see the Streng reference), it is not very practical to use such a thick bed. Spent sorbent is burned and not regenerated. The carbons are not pretreated.

The GE-Mitsui-BF system (Tsuji, K.; Shiraishi, I.; Dague, R. F. Proceedings, Sixth International Symposium, Air & Water Management Assoc., New Orleans, La., Mar. 10-12, 1993) employs a recirculating carbon bed, where mercury is removed along with acid gases (as ammonium salts) and the carbon is regenerated at high temperatures where ammonium sulfate is decomposed to SO_2 and N_2 and mercury is converted to the elemental form, which desorbs from the sorbent. Attrition of the sorbent results in a significant sorbent cost. The carbons are not pretreated.

Sorbent Injection After Particulate Removal

A process of injecting manganese oxide sorbent particles is described in U.S. Patent Application 2002/0150516. Regeneration is claimed by removal of spent oxide particles from the reaction zone and rinsing with dilute aqueous acid.

Sorbent Beds After Particulate Removal

Of particular interest in designing a mercury control process is to use the sorbent downstream of a particulate control device so the sorbent is not highly diluted with the ash particles. The sorbent could then be more easily regenerated and recycled. The prior art teaches several examples of this type of configuration and sorbent processing.

U.S. Pat. No. 5,607,496 teaches the oxidation of mercury on a metal oxide sorbent bed and subsequent absorption to sorbent. The sorbent bed follows the particulate-removal equipment and, thus, the gas still contains the SO_x and NO_x , which react with the metal oxide sorbent to form the metal sulfates, which poison the bed. High temperatures are proposed to regenerate the bed. However, Hg is only partially removed from the sorbent at temperatures up to 500° C. The sorbents do not work effectively after regeneration using this technique; the problem may be that manganese sulfate formed during the sorption cycle does not completely decompose back to an active manganese oxide form.

U.S. Pat. No. 6,383,981 describes a fixed MnO_2 or Fe_2O_3 bed for removal of Hg from a hydrocarbon stream. No regeneration method appears to be included.

A recent U.S. Patent application (2001/0003116) describes the regeneration of a plate or honeycomb material composed of transition metal oxides that was used for sorption of mercury in flue gas. The claimed process

US 10,596,517 B2

35

involves heating the sorbent in a reducing gas stream to remove poisons, followed by impregnation with a polyfunctional complex-forming reagent containing the catalyst active component to restore mercury capture capacity. The first of these steps can remove the mercury, but it is unclear whether it actually removes the sulfate poison. The second of these steps is rather expensive, because one is actually reconstituting the reagent on the sorbent

Porous beds containing a mercury oxidizing reagent on a solid support are described in several patents for removal of mercury from gas streams. These include peroxomonosulfate (for example, see U.S. Pat. No. 4,786,483), triiodide or other mixed halogens (for example, see U.S. Pat. Nos. 3,194,629; 3,662,523), or sulfur (for example, see U.S. Pat. Nos. 3,194,629, 4,101,631, 4,708,853, 6,258,334). The reagent material is destroyed either by reaction with the flue gas during sorption or by attempts to regenerate the sorbent; there is no way to regenerate these sorbents, except by reimpregnation of the expensive reagent.

Amalgamating noble metals (gold, silver) on a suitable support can be regenerated by microwave heating (for example, see U.S. Pat. No. 6,136,072), but they are expensive and not especially active for sorption in flue gas.

Hg Sorbents for Air or Natural Gas Treatment

Melkersson (U.S. Pat. No. 3,786,619) described a Hg sorbent comprising SeO_2 or SeS_2 for air treatment. This method did not appear to employ a carbon support or halide.

Yan (U.S. Pat. No. 4,814,152) described a Hg sorbent comprising elemental sulfur and a metal catalyst on a carbon support. This method did not appear to employ a halide.

Attia (U.S. Pat. No. 65,080,281) described a sorbent for mercury and a variety of other contaminants comprising an inorganic aerogel composition. This method did not appear to employ a carbon support or halide.

Following is a List of Various Background References:
Lancia, A.; Musmarra, D.; Pepe, F.; Volpicelli, G. *Combust. Sci. & Technol* 1993, 93, 277.

Streng, S.; Kassebohm, B. *Fuel Proc. Technol.* 1994, 39, 431.

U.S. Pat. No. 6,214,304 Rosenthal

U.S. Pat. No. 4,889,698 Moller

U.S. Pat. No. 4,956,162 Smith

U.S. Pat. No. 5,672,323 Bhat

U.S. Pat. No. 5,827,352 Altman

U.S. Pat. No. 6,027,551 Hwang

U.S. Pat. No. 5,505,766 Chang

U.S. Pat. No. 5,607,496 Brooks

U.S. Pat. No. 6,383,981 Blankenship

U.S. Pat. No. 4,786,483 Audeh

U.S. Pat. No. 3,194,629 Dreibelbis, et al

U.S. Pat. No. 4,101,631 Ambrsini, et al

U.S. Pat. No. 3,662,523 Revoir

U.S. Pat. No. 4,708,853 Matviya

U.S. Pat. No. 6,258,334 Gadkaree

U.S. Pat. No. 6,136,072 Sjoström

U.S. Patent Application 2002/0150516

U.S. Patent Application 2001/0003116 Neufert

The invention claimed is:

1. A method for reducing mercury in a mercury-containing gas, the method comprising:

combusting coal in a combustion chamber, the coal comprising an additive comprising Br_2 , HBr, a bromide compound, or a combination thereof, to form the mercury-containing gas; and

collecting mercury in the mercury-containing gas with a sorbent added to the mercury-containing gas, the sorbent comprising activated carbon.

36

2. The method of claim 1, further comprising injecting an alkaline sorbent into the mercury-containing gas stream.

3. The method of claim 2, wherein the alkaline sorbent is selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

4. The method of claim 1, wherein the activated carbon is chosen from powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, and combinations thereof.

5. The method of claim 1, wherein the sorbent has a composition comprising from about 1 to about 30 grams of the element bromine per 100 grams of activated carbon.

6. The method of claim 1, comprising collecting greater than 70 wt % of the mercury in the mercury-containing gas.

7. The method of claim 1, comprising collecting greater than 70 wt % of the mercury in the mercury-containing gas with the sorbent.

8. The method of claim 1, further comprising: measuring mercury content of the mercury-containing gas; and

modifying, in response to the measured mercury content, an injection rate of injecting the sorbent comprising activated carbon into the mercury-containing gas, an amount of the additive comprising the Br_2 , HBr, bromide compound, or a combination thereof, added to the coal, or a combination thereof.

9. The method of claim 8, wherein the measuring of the mercury content of the mercury-containing gas is performed substantially continuously.

10. The method of claim 1, further comprising: modifying, in response to a measured mercury content, an injection rate of injecting the sorbent comprising activated carbon into the mercury-containing gas, an amount of the Br_2 , HBr, bromide compound, or a combination thereof, added to the coal, or a combination thereof.

11. The method of claim 1, wherein the coal comprises a subbituminous coal.

12. The method of claim 1, wherein the coal comprises a lignite coal.

13. The method of claim 1, wherein the coal comprises the added Br_2 , HBr, the bromide compound, or a combination thereof, added to the coal before the coal enters the combustion chamber.

14. The method of claim 1, wherein the combustion chamber comprises the added Br_2 , HBr, the bromide compound, or a combination thereof.

15. The method of claim 1, wherein the coal is combusted in the combustion chamber at a coal-combustion facility, wherein the Br_2 , HBr, bromide compound, or combination thereof, is added to the coal before the coal enters the combustion chamber, wherein the addition of the Br_2 , HBr, bromide compound, or combination thereof, to the coal is performed at the coal-combustion facility.

16. The method of claim 1, wherein the coal is combusted in the combustion chamber at a coal-combustion facility, wherein the Br_2 , HBr, bromide compound, or combination thereof, is added to the coal before the coal enters the combustion chamber, wherein the addition of the Br_2 , HBr, bromide compound, or combination thereof, to the coal is performed at a site other than the coal-combustion facility.

17. The method of claim 1, wherein the combustion chamber is an electric utility coal combustion chamber.

US 10,596,517 B2

37

18. The method of claim 1, further comprising:
measuring mercury content of the mercury-containing
gas; and
modifying, in response to the measured mercury content,
an injection rate of injecting the sorbent comprising
activated carbon into the mercury-containing gas. 5
19. The method of claim 1, wherein the mercury-contain-
ing gas comprises about 1 g to about 30 g of the element
bromine per 100 g of the sorbent.
20. The method of claim 1, further comprising: 10
measuring mercury content of the mercury-containing
gas; and
modifying, in response to the measured mercury content,
an amount of the additive comprising the Br₂, HBr,
bromide compound, or a combination thereof, added to 15
the coal.
21. The method of claim 1, wherein the sorbent in the
mercury-containing gas comprises about 1 g to about 30 g of
the added Br₂, HBr, the bromide compound, or a combina- 20
tion thereof, per 100 g of the sorbent.
22. The method of claim 1, wherein the Br₂, HBr, or the
bromide compound is contacted with the sorbent in vapor
form, gaseous form, liquid form, or in an organic solvent.
23. The method of claim 1, wherein the sorbent injected 25
into the mercury-containing gas is a sorbent obtained by
contacting a base sorbent with a halogen or halide promoter
prior to injection of the sorbent to the mercury-containing
gas.
24. The method of claim 1, wherein the sorbent injected 30
into the mercury-containing gas is free of contact with a
halogen or halide promoter prior to injection of the sorbent
into the mercury-containing gas.
25. The method of claim 1, wherein the injection of the
sorbent into the mercury-containing gas occurs upstream of 35
a particulate separator or a scrubber.
26. The method of claim 25, wherein the particulate
separator comprises an electrostatic precipitator, a baghouse,
a fabric filter, or a combination thereof.
27. The method of claim 1, wherein the coal comprises 40
added halide sorbent enhancement additive that comprises
the added Br₂, HBr, the bromide compound, or combination
thereof.

38

28. The method of claim 1, wherein the sorbent enhance-
ment additive comprises the bromide compound.
29. A method of separating mercury from a mercury-
containing gas, the method comprising:
combusting coal in a combustion chamber, wherein 5
the coal comprises added Br₂, HBr, bromide com-
pound, or a combination thereof, added to the coal
before the coal enters the combustion chamber, or
the combustion chamber comprises added Br₂, HBr,
bromide compound, or a combination thereof, or 10
a combination thereof; and
collecting mercury in the mercury-containing gas with a
sorbent added to the mercury-containing gas, the sor-
bent comprising activated carbon.
30. A method of separating mercury from a mercury- 15
containing gas, the method comprising:
combusting coal in a combustion chamber, to provide the
mercury-containing gas, wherein the mercury-contain-
ing gas comprises a halogen or halide promoter com-
prising HBr, Br⁻, or a combination thereof, wherein 20
the coal comprises added Br₂, HBr, bromide com-
pound, or a combination thereof, added to the coal
before the coal enters the combustion chamber, or
the combustion chamber comprises added Br₂, HBr,
bromide compound, or a combination thereof, or 25
a combination thereof;
collecting mercury in the mercury-containing gas with a
sorbent added to the mercury-containing gas, the sor-
bent comprising activated carbon;
separating the sorbent contacted with the mercury from 30
the mercury-containing gas;
measuring the mercury content of the mercury-containing
gas; and
modifying, in response to the measured mercury content 35
of the mercury-containing gas,
an injection rate of injecting the sorbent into the
mercury-containing gas,
an amount of the Br₂, HBr, bromide compound, or a
combination thereof, added to the coal or the com- 40
bustion chamber, or
a combination thereof.

* * * * *

EXHIBIT E

US010668430B2

(12) **United States Patent**
Olson et al.(10) **Patent No.:** **US 10,668,430 B2**(45) **Date of Patent:** ***Jun. 2, 2020**(54) **SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY**(71) Applicant: **Midwest Energy Emissions Corp.**,
Corsicana, TX (US)(72) Inventors: **Edwin S. Olson**, Grand Forks, ND
(US); **Michael J. Holmes**, Thompson,
ND (US); **John H. Pavlish**, East Grand
Forks, MN (US)(73) Assignee: **Midwest Energy Emissions Corp.**,
Corsicana, TX (US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.This patent is subject to a terminal dis-
claimer.(21) Appl. No.: **15/974,343**(22) Filed: **May 8, 2018**(65) **Prior Publication Data**

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None

See application file for complete search history.

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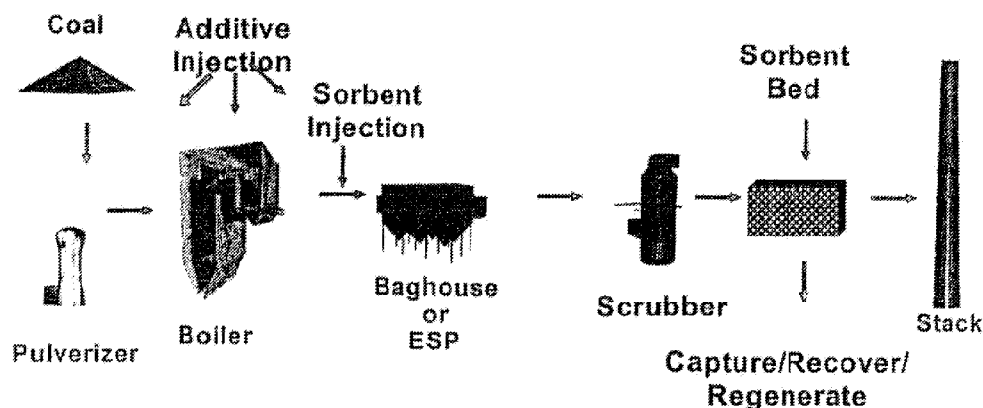
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Primary Examiner — Amber R Orlando(74) *Attorney, Agent, or Firm* — Schwegman Lundberg &
Woessner, P.A.(57) **ABSTRACT**

A promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new modified carbon form containing reactive forms of halogen and halides. Optional components may be added to increase reactivity and mercury capacity. These may be added directly with the sorbent, or to the flue gas to enhance sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The sorbent can be regenerated and reused. Sorbent treatment and preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

29 Claims, 11 Drawing Sheets

US 10,668,430 B2

Page 2

Related U.S. Application Data

No. 14/712,558, filed on May 14, 2015, now Pat. No. 10,589,225, which is a continuation of application No. 14/318,270, filed on Jun. 27, 2014, now Pat. No. 9,757,689, which is a continuation of application No. 13/966,768, filed on Aug. 14, 2013, now Pat. No. 8,821,819, which is a continuation of application No. 13/427,665, filed on Mar. 22, 2012, now Pat. No. 8,512,655, which is a continuation of application No. 12/419,219, filed on Apr. 6, 2009, now Pat. No. 8,168,147, which is a continuation of application No. 12/201,595, filed on Aug. 29, 2008, now abandoned, which is a division of application No. 11/209,163, filed on Aug. 22, 2005, now Pat. No. 7,435,286.		4,956,162 A	9/1990	Smith et al.	
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Page 7

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Jun. 2, 2020

Sheet 1 of 11

US 10,668,430 B2

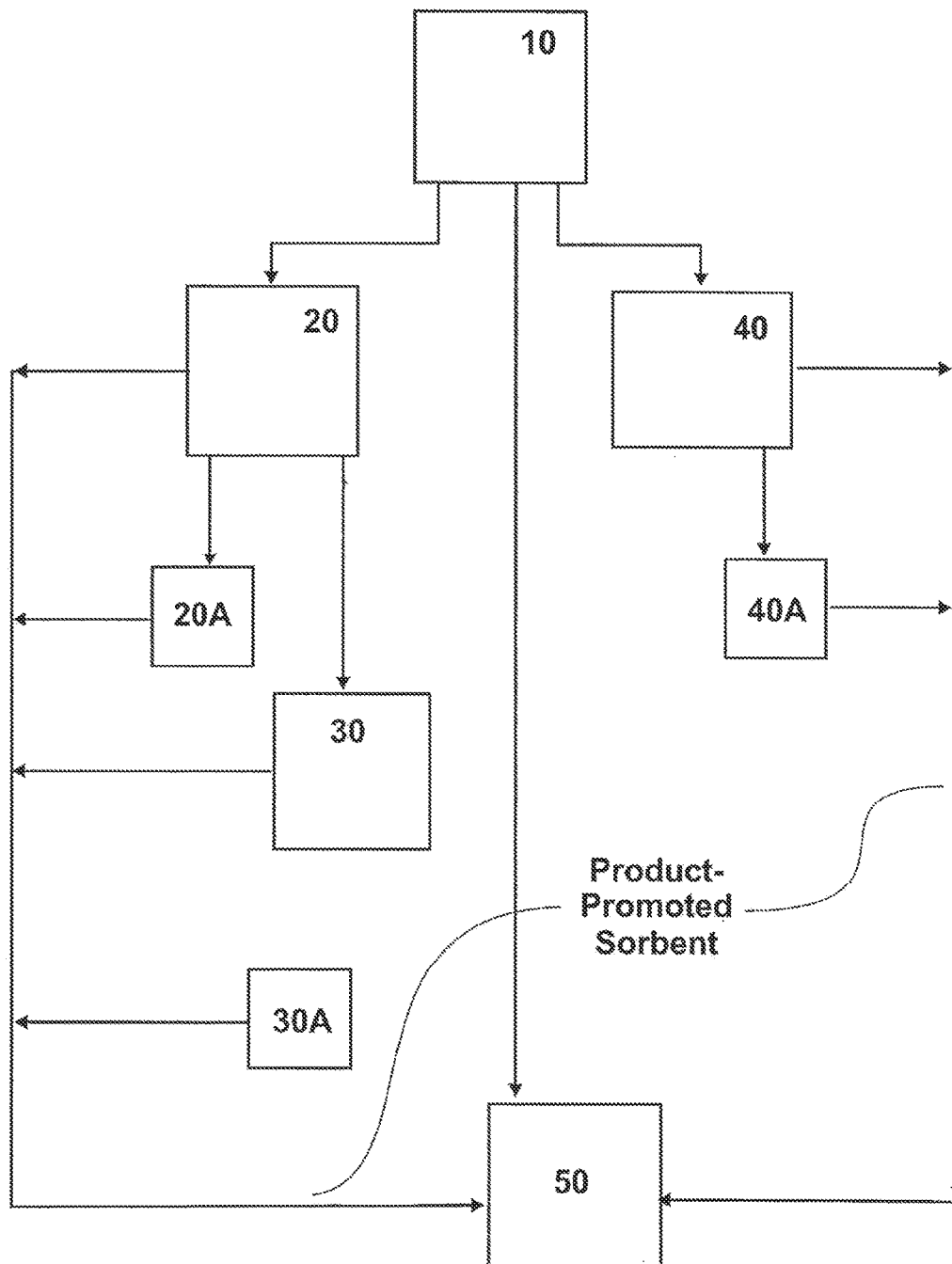


FIG. 1

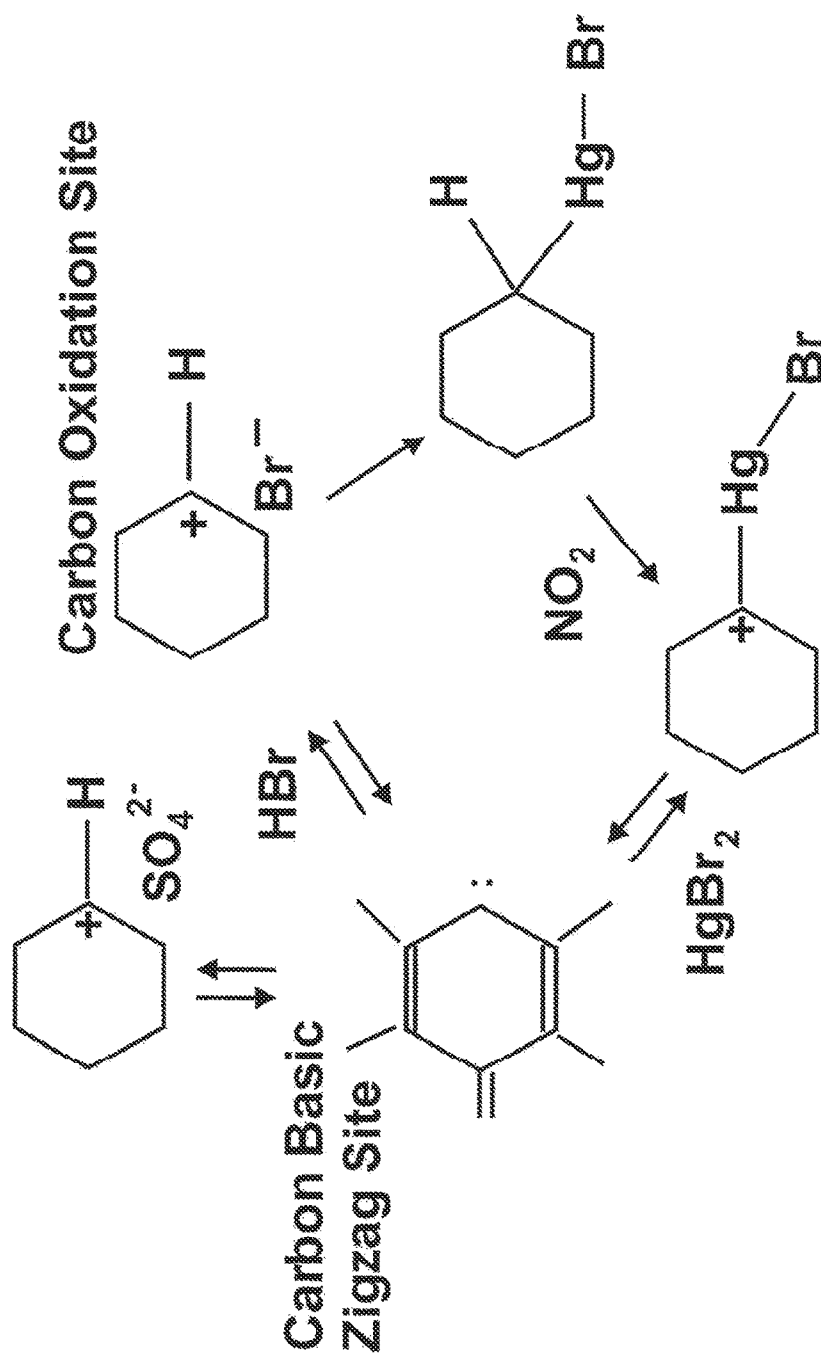


FIG. 2

U.S. Patent

Jun. 2, 2020

Sheet 3 of 11

US 10,668,430 B2

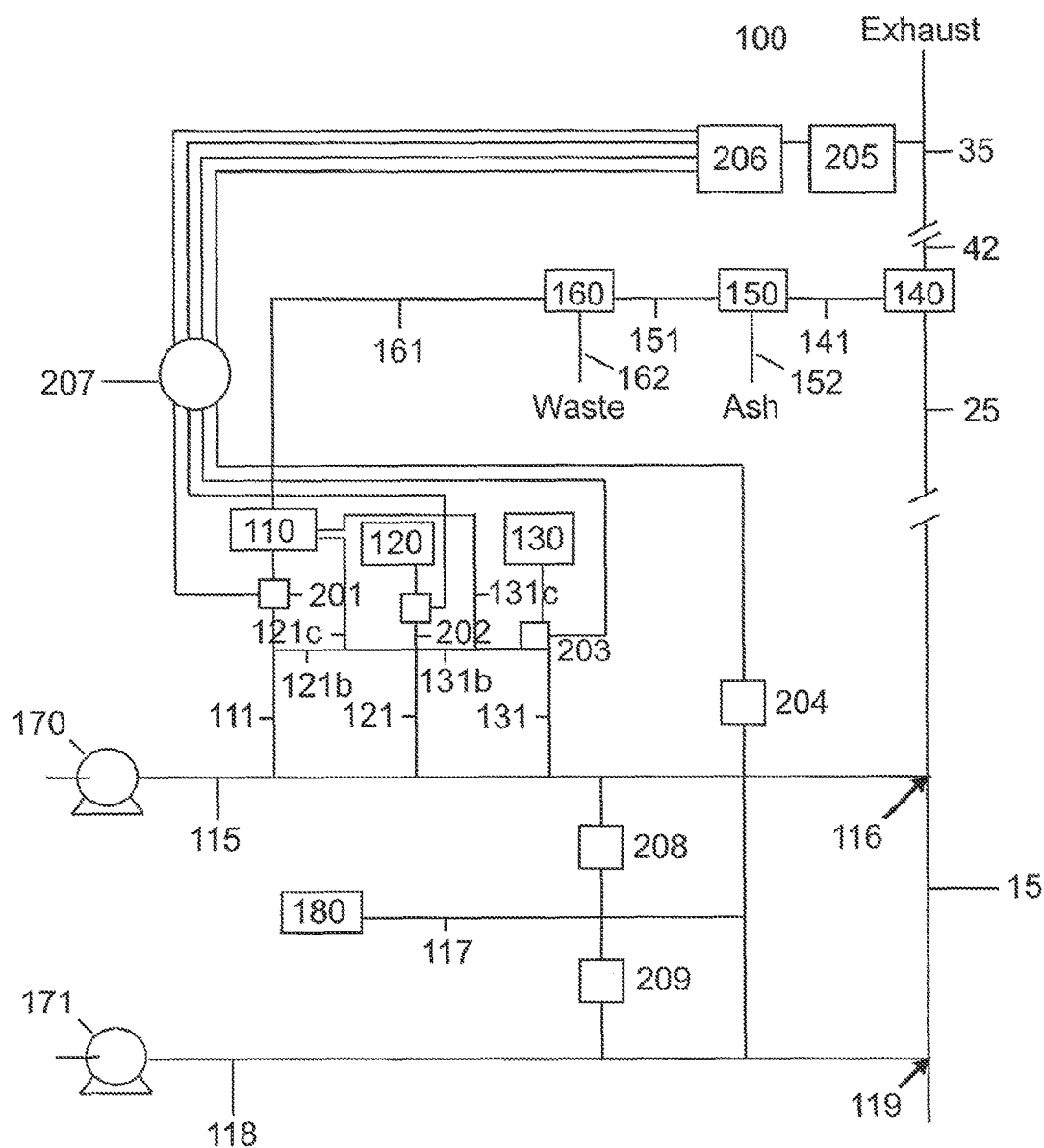


FIG. 3

U.S. Patent

Jun. 2, 2020

Sheet 4 of 11

US 10,668,430 B2

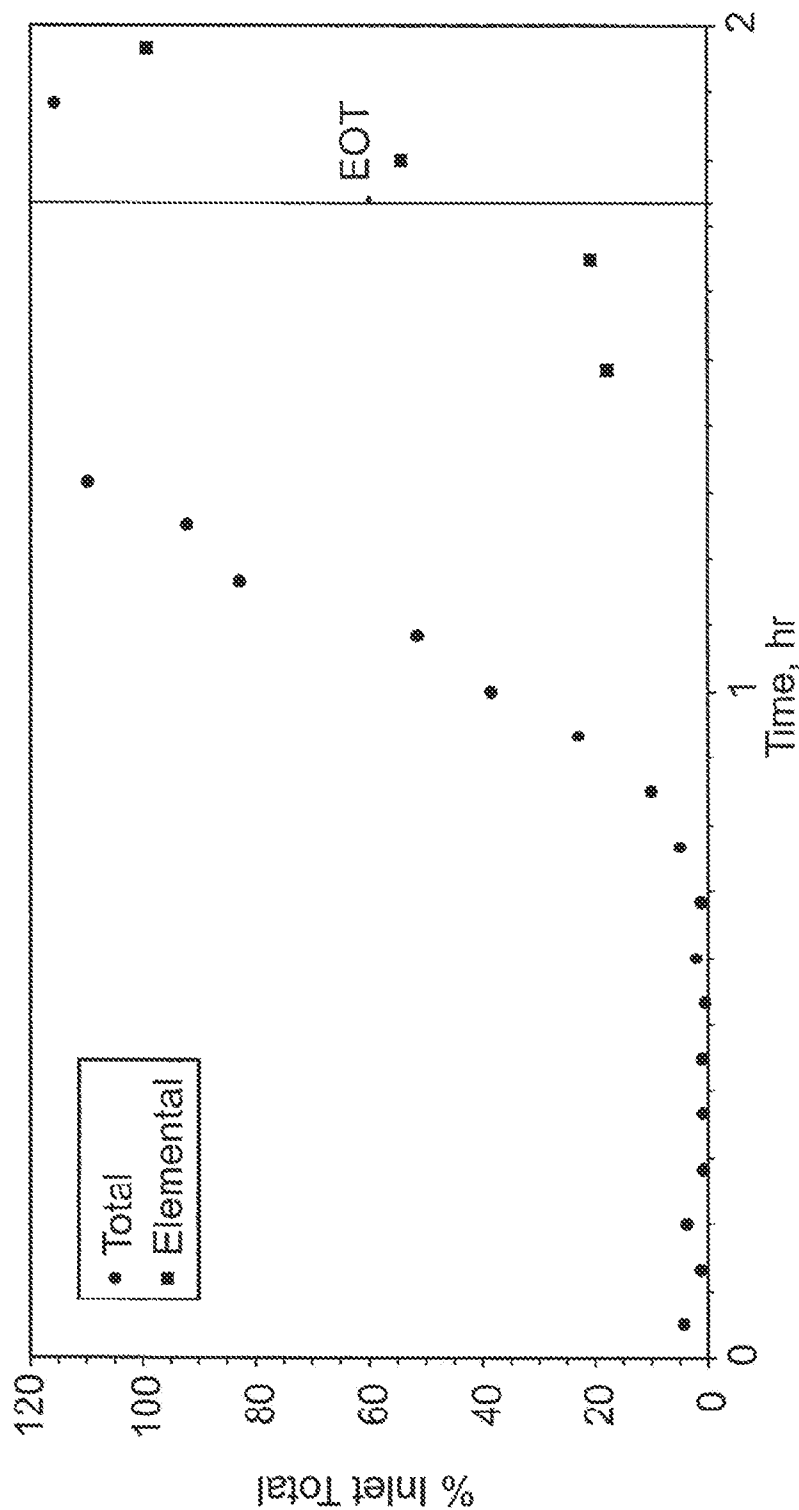


FIG. 4

U.S. Patent

Jun. 2, 2020

Sheet 5 of 11

US 10,668,430 B2

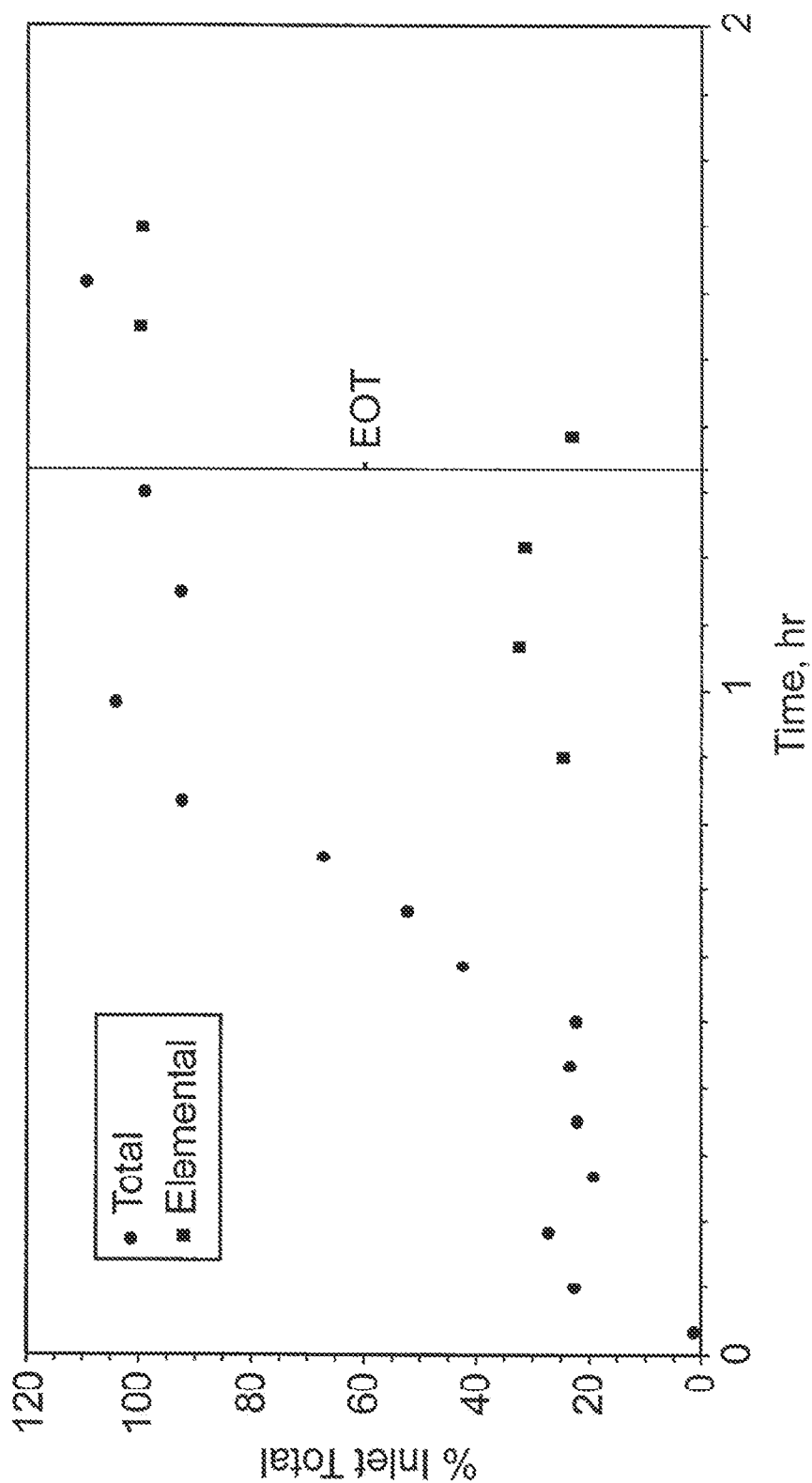


FIG. 5

U.S. Patent

Jun. 2, 2020

Sheet 6 of 11

US 10,668,430 B2

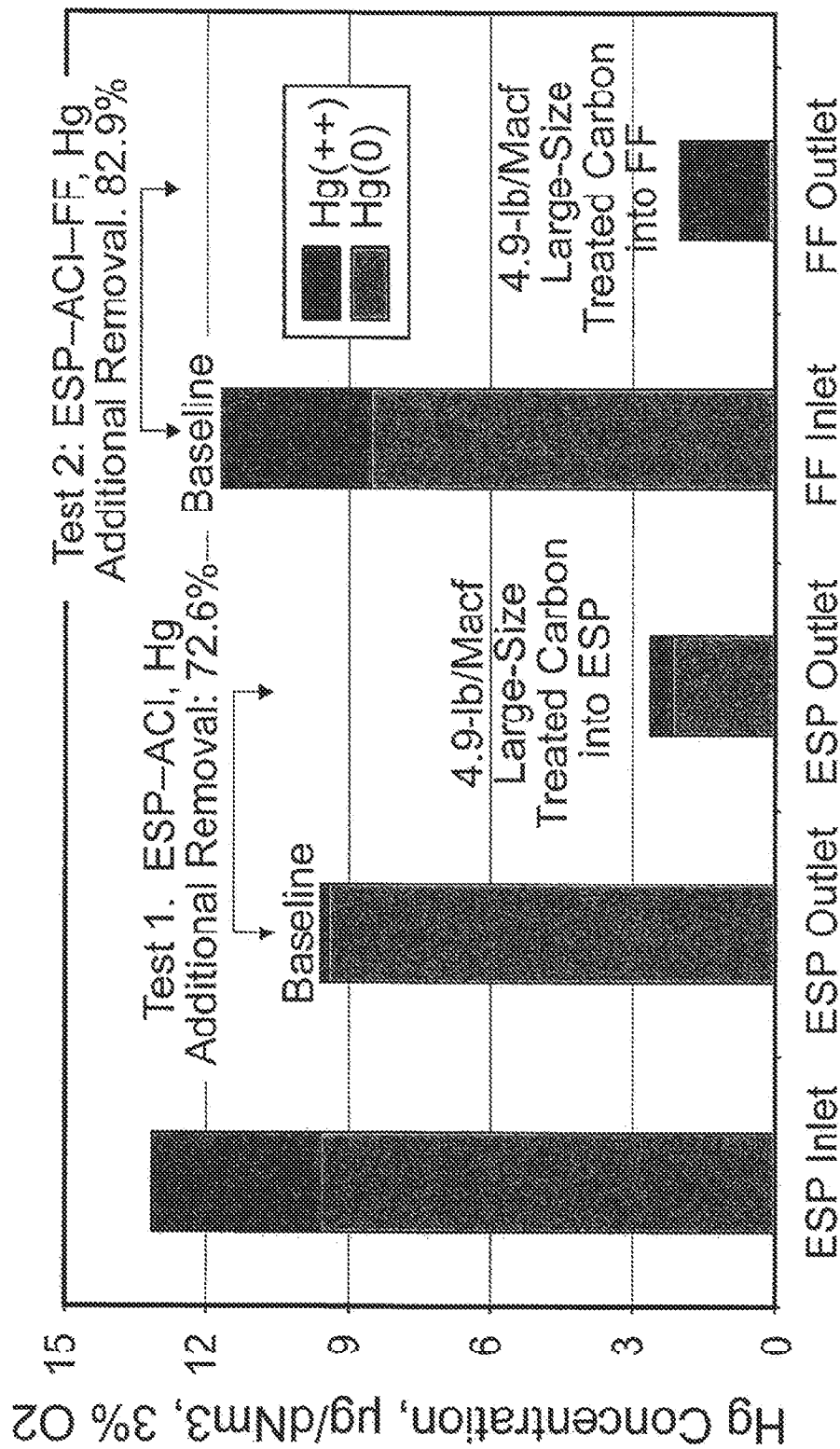


FIG. 6

U.S. Patent

Jun. 2, 2020

Sheet 7 of 11

US 10,668,430 B2

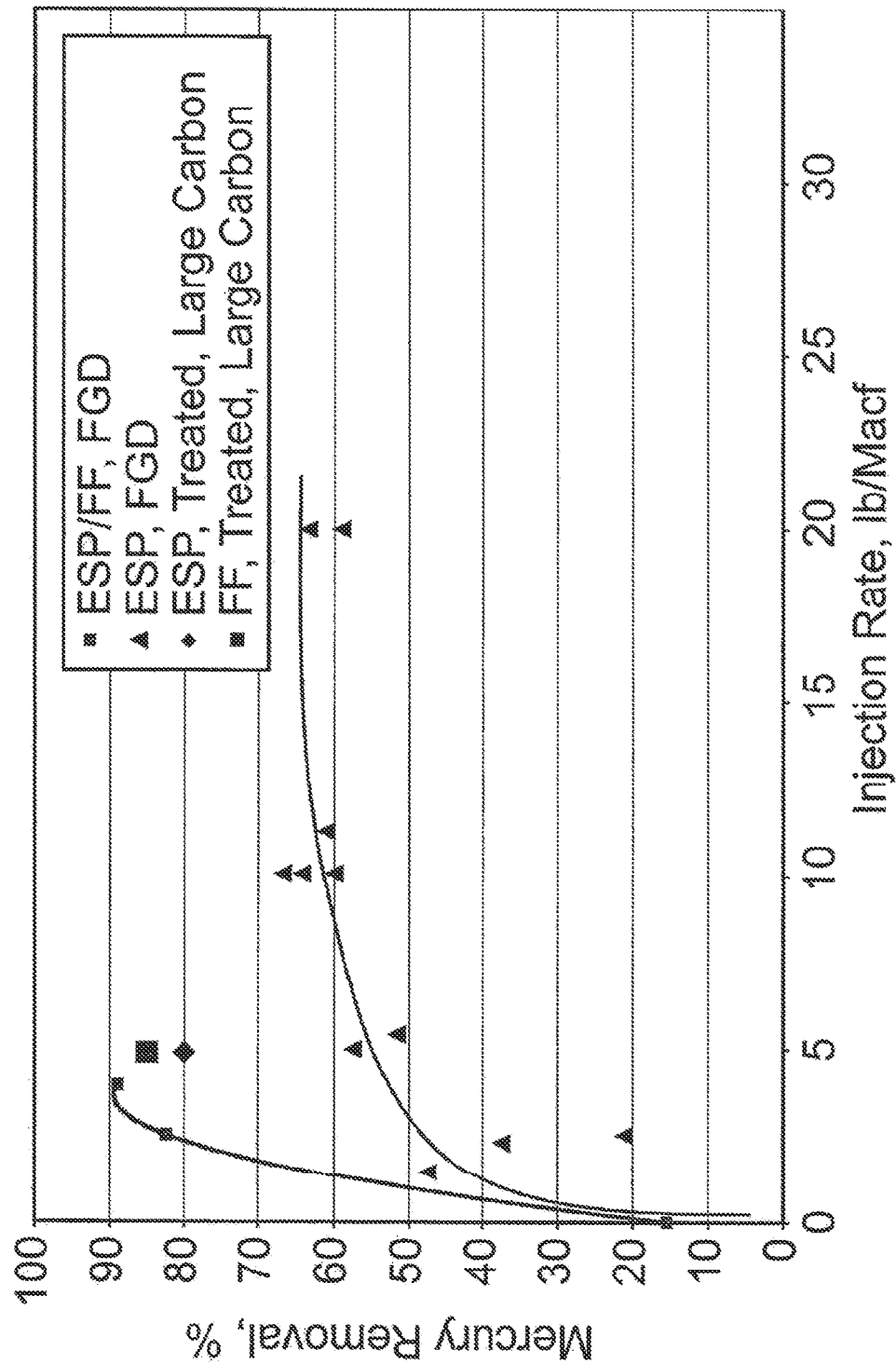


FIG. 7

U.S. Patent

Jun. 2, 2020

Sheet 8 of 11

US 10,668,430 B2

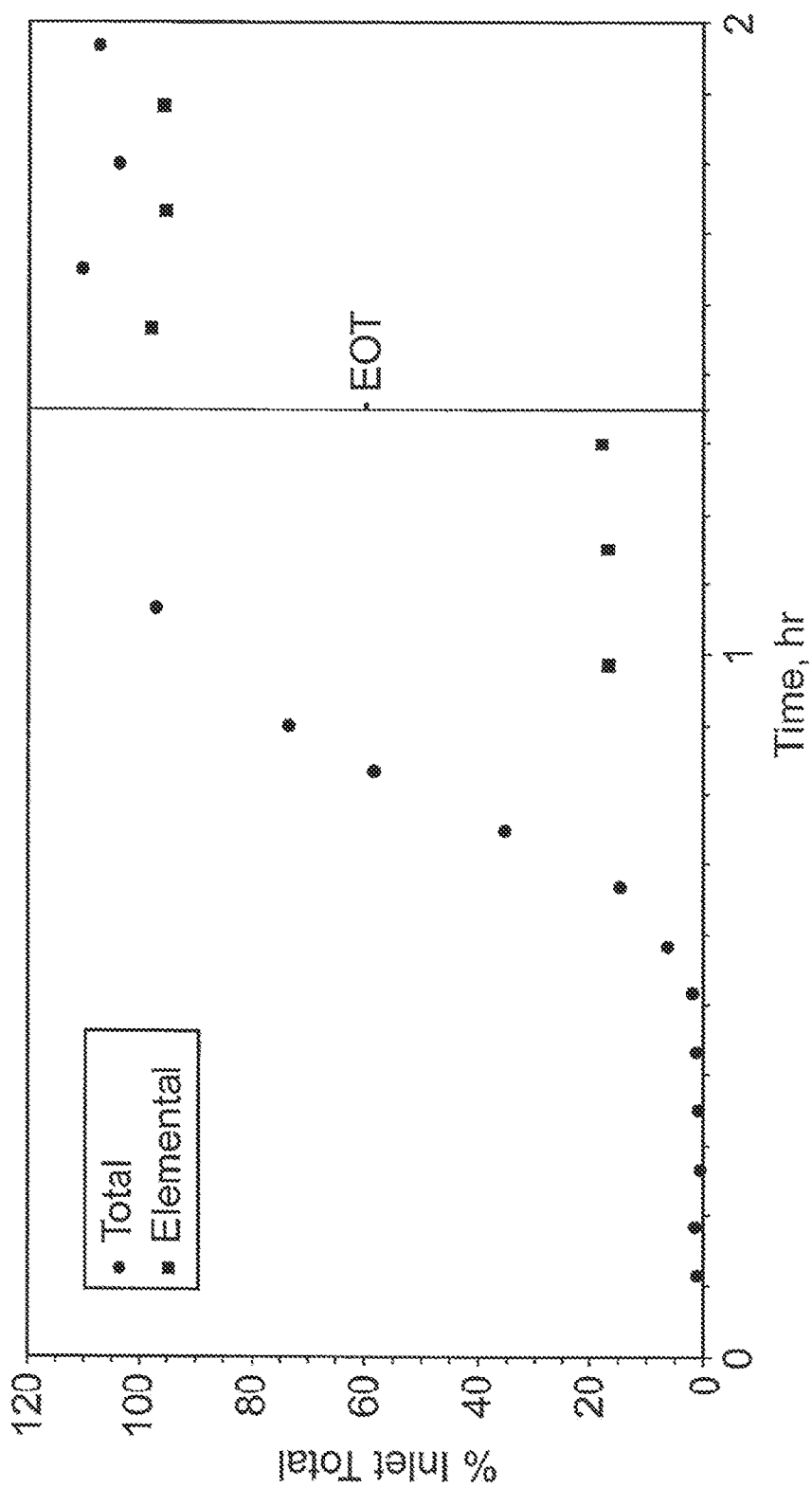


FIG. 8

U.S. Patent

Jun. 2, 2020

Sheet 9 of 11

US 10,668,430 B2

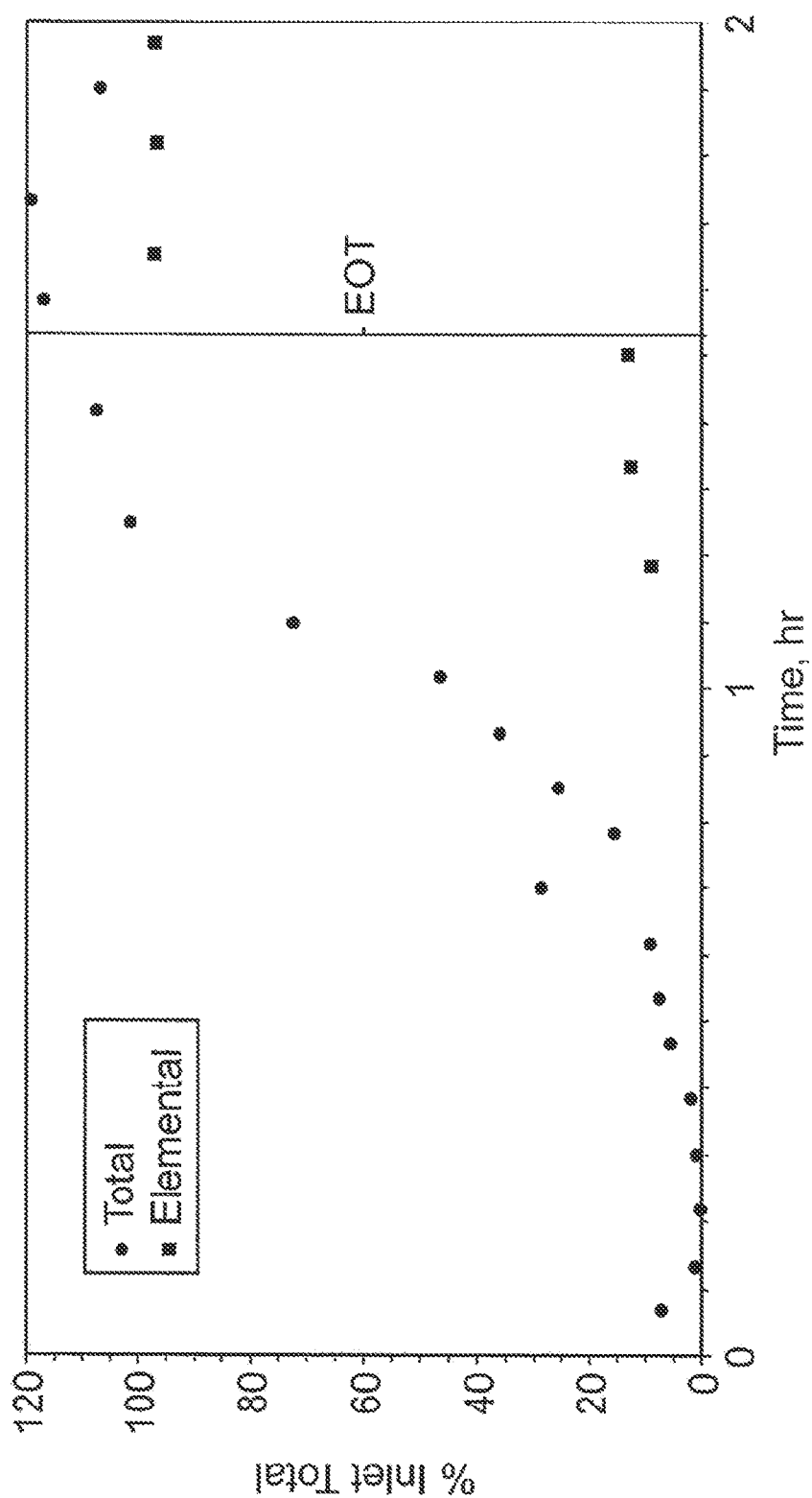


FIG. 9

U.S. Patent

Jun. 2, 2020

Sheet 10 of 11

US 10,668,430 B2

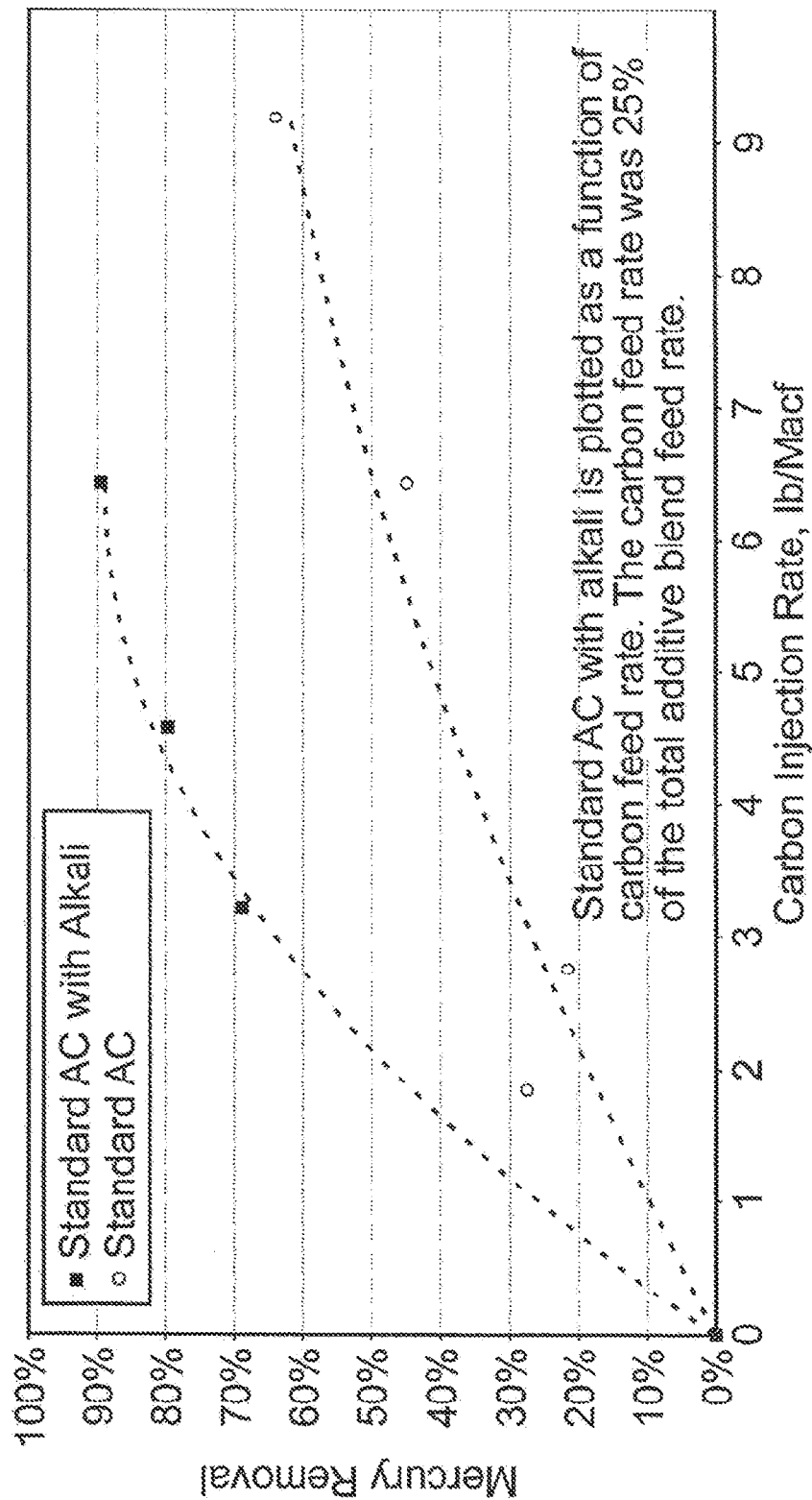


FIG. 10

U.S. Patent

Jun. 2, 2020

Sheet 11 of 11

US 10,668,430 B2

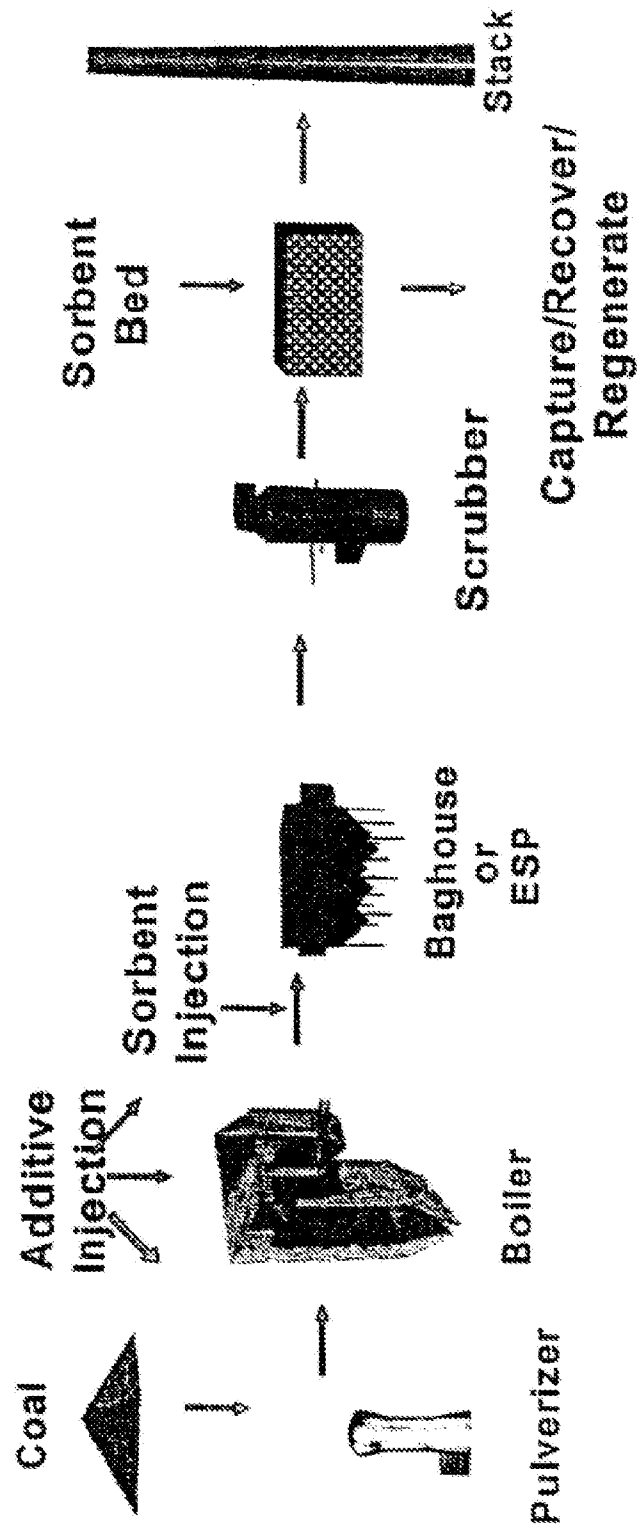


FIG. 11

US 10,668,430 B2

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**SORBENTS FOR THE OXIDATION AND
REMOVAL OF MERCURY****CROSS-REFERENCE TO RELATED
APPLICATIONS**

This application is a continuation of U.S. patent application Ser. No. 15/951,970, filed Apr. 12, 2018, which is a continuation of U.S. patent application Ser. No. 14/318,270, filed Jun. 27, 2014, which is a continuation of U.S. patent application Ser. No. 13/966,768, filed Aug. 14, 2013, issued as U.S. Pat. No. 8,821,819, which is a continuation of U.S. patent application Ser. No. 13/427,665, filed Mar. 22, 2012, issued as U.S. Pat. No. 8,512,655, which is a continuation of U.S. patent application Ser. No. 12/419,219, filed Apr. 6, 2009, issued as U.S. Pat. No. 8,168,147, which is a continuation of U.S. patent application Ser. No. 12/201,595, filed Aug. 29, 2008, which is a division of U.S. patent application Ser. No. 11/209,163, filed Aug. 22, 2005, issued as U.S. Pat. No. 7,435,286, which application claims the benefit under 35 U.S.C. § 119 (e) of U.S. Provisional Patent Application No. 60/605,640 filed Aug. 30, 2004, the disclosure of which is hereby incorporated by reference in its entirety.

**STATEMENT REGARDING FEDERALLY
SPONSORED RESEARCH OR DEVELOPMENT**

This invention was made with United States Government support under Grant Numbers R 827649-01 and CR 830929-01 awarded by the United States Environmental Protection Agency and under Contract Number DE-FC26-98FT40320 awarded by the United States Department of Energy. The United States Government has certain rights in this invention.

BACKGROUND OF THE INVENTION**1. Technical Field of the Invention**

The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

2. Background of the Invention

The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, per day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as off gases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

2

Mercury Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a bag house or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon because the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after extended exposure to the flue gas does the sorbent become effectively seasoned and provide increased reactivity with the mercury in the gas. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY OF THE INVENTION

It is thus an object of the present invention to overcome the deficiencies of the prior art and thereby to provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

A halogen/halide promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new halide-modified carbon form containing a reactive compound produced by the reaction of bromine (or halide or other halogen) with the carbon. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

In some embodiments, a promoted carbon sorbent is provided comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

US 10,668,430 B2

3

In an embodiment, a promoted carbon sorbent is provided wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than that of flyash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the base activated carbon may have a mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base activated carbon may have a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the primary sorbent.

In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base activated carbon. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base activated carbon. In another embodiment, the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

In an embodiment, a method is provided comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream. In a further embodiment, the reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon. In another embodiment the reaction product has an average particle size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment the reaction product has a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment the promoter is in the gas phase when contacting the activated carbon. In another

4

embodiment, the promoter is in an organic solvent when contacting the activated carbon.

In another embodiment, the promoter is selected from the group consisting of Br₂, a Group V bromide, a Group VI bromide, and combinations thereof.

In another embodiment, the method further comprises reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the activated carbon. In another embodiment the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof. In an embodiment, a method is provided for control of mercury in a flue gas with substantially lower sorbent requirements. Through enhanced sorbent reactivity, mercury removal per gram of sorbent is increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas. In embodiments where less than 70 wt-% mercury removal is desired, the required removal may preferably be attained using less than half as much carbon as would be required with standard (non-enhanced) carbon. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent. In another embodiment the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt % of the promoter content. In another embodiment, the method further comprises adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof.

In an embodiment, the method further comprises co-injecting an optional alkaline material, including without limitation alkaline and alkaline earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce sorbent capacity. In another embodi-

US 10,668,430 B2

5

ment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent. In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

In an embodiment, a method for reducing the mercury content of a mercury and ash containing gas stream is provided wherein particulate activated carbon sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the sorbent particles, the sorbent particles are separated from the ash particles on the basis of size, and the sorbent particles are re-injected to the gas stream. In another embodiment, the mercury-containing sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is co-injected into the gas stream. In another embodiment, the sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from fired equipment and gasification systems.

The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

FIG. 1 schematically illustrates methods for preparation of promoted carbon sorbents in accordance with the present invention.

FIG. 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

FIG. 3 schematically illustrates preparation of promoted carbon sorbents and processes for flue gas mercury reduction in flue gases and/or product gases from a gasification

6

system in accordance with the present invention, including in-flight preparation of promoted carbon sorbent.

FIG. 4 is a diagram illustrating breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 5 is a diagram illustrating breakthrough curves for non-halogenated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 6 is a bar chart illustrating pilot-scale mercury removal results, including large-size sorbent results.

FIG. 7 is a diagram illustrating the effects of sorbent size and injection rate on mercury removal for ESPs and fabric filters.

FIG. 8 is a diagram illustrating the breakthrough curves for a brominated NOR IT Darco FGD sorbent with inert sand.

FIG. 9 is a diagram illustrating the breakthrough curves for brominated NORIT Darco FGD sorbent with a co-injected alkali material.

FIG. 10 is a plot of mercury removal vs. carbon injection rate with and without co-injection of alkali material.

FIG. 11 is a block diagram illustrating the use of the invention in a coal fueled facility.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention, and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide promoted carbon sorbents using a bromide (or other halogen/halide) treatment of the carbon, that capture mercury via mercury-sorbent surface reactions, at very short contact times of seconds or less. The sorbent does not require in situ activation (no induction period) in the gas stream to achieve high reactivity, as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants is greatly enhanced and the sorption capacity can be regenerated, the promoted sorbent may be regenerated, recycled and/or reused.

The treated carbons, treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus, it should be understood that the terms combustion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

Referring now to FIG. 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture from flue gas and/or product gas from a gasification system streams. In a pre-

US 10,668,430 B2

7

ferred embodiment illustrated by path 10-20, block 10 illustrates providing a base activated carbon, and adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, to produce a product promoted carbon sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base activated carbon as shown by block 10, adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product promoted carbon sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base activated carbon as illustrated at block 10, and adding a halogen or halide promoter and a secondary component to the activated carbon together, with which they react as illustrated by block 40, producing a product promoted carbon sorbent. As above, in embodiments where vapor additions are made to the activated carbon no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A.

Referring still to FIG. 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a flue gas stream is treated with product promoted carbon sorbent prepared as described above.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product promoted carbon sorbent, or other types as known in the art.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle size greater than fly ash in a flue gas stream to be treated.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle size distribution greater than that of the fly ash

8

or entrained ash in a flue gas stream to be treated, such that the activated carbon and ash can be separated by physical means.

In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the base activated carbon may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SC_2 , respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2 , water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

Referring now to FIG. 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in FIG. 2, hydrogen bromide reacts with the unsaturated structure of the activated carbon. This may be, by way of illustration only, a carbene species on the edge of the graphene sheet structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury with subsequent capture by the sorbent.

It has now been found that the formation of the new bromide compound with carbon increases their reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus, adding HBr or Br_2 to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Referring now to FIG. 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted carbon sorbents, and flue gas mercury reduction, in accordance with preferred embodiments of the present invention. There is provided base activated carbon reservoir 110, an optional halogen/halide promoter reservoir 120, an optional secondary component reservoir 130, and an optional alkali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the optional alkali component reservoir 180, optional flow control devices 208 and 209 can be used independently, together, or not at all.

Reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Optional alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining

US 10,668,430 B2

9

materials discharged from reservoirs **110**, **120**, **130**, and **180** and injecting such materials, via injection point **116**, into contaminated flue gas stream **15**. A source of air, nitrogen, or other transport gas(es) may be provided by gas source **171** to transport line **118** for the purpose of entraining materials discharged from reservoirs **180** and injecting such materials, via injection point **119**, into flue gas stream **15**. Gas sources **170** and **171** may be the same or different, as desired. Alternatively, transport gas(es) may be provided to both transport lines **115** and **118** by gas source **170** (connection from source **170** to line **118** not shown). Although gas sources **170** and **171** are shown in FIG. 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

For clarity, single injection points **116** or **119** are shown in FIG. 3, although one skilled in the art will understand that multiple injection points are within the scope of the present invention. Optical density measuring device(s) **204** is connected to transport line **115** and/or **118** to provide signals representative of the optical density inside transport line **115** and/or **118** as a function of time.

Downstream from injection point **116** and **119** is provided particulate separator **140**. By way of illustration and not limitation, particulate separator **140** may comprise one or more fabric filters, one or more electrostatic precipitators (hereinafter "ESP"), or other particulate removal devices as are known in the art. It should be further noted that more than one particulate separator **140** may exist, sequentially or in parallel, and that injection point **116** and **119** may be at a location upstream and/or downstream of **140** when parallel, sequential, or combinations thereof exist. Particulate separator **140** produces at least a predominantly gaseous ("clean") stream **142**, and a stream **141** comprising separated solid materials. A sorbent/ash separator **150** separates stream **141** into a largely ash stream **152**, and a largely sorbent stream **151**. Stream **151** may then preferably be passed to an optional sorbent regenerator **160**, which yields a regenerated sorbent stream **161** and a waste stream **162**.

An optional Continuous Emission Monitor (hereinafter "CEM") **205** for mercury is provided in exhaust gas stream **35**, to provide electrical signals representative of the mercury concentration in exhaust stream **35** as a function of time. The optional mercury CEM **205** and flow controllers **201**, **202**, **203**, **208**, and **209** are electrically connected via optional lines **207** (or wirelessly) to an optional digital computer (or controller) **206**, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream **15**.

In operation, promoted carbon sorbent and/or an optional alkali component is injected into contaminated flue gas stream **15**. After contacting the injected material with the contaminated flue gas stream **15**, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas. The injected material is removed from the flue gas **25**, by separator **140**, disposed of or further separated by optional separator **150**, and disposed of or regenerated by an optional regenerator **160**, respectively. The reduced mercury "clean" flue gas stream **142** is then monitored for mercury content by an optional CEM **205**, which provides corresponding signals to an optional computer/controller **206**. Logic and optimization signals from **206** then adjust flow controllers **201**, **202**, **203**, **208**, **209** to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art. Flow controllers **201**, **202**,

10

203, **208**, **209** can also be adjusted manually or be some other automated means to maintain the mercury concentration in exhaust stream **35** within desired limits, according to control algorithms well known in the art.

Referring still to FIG. 3, there are illustrated several preferred embodiments for preparation and injection of promoted carbon sorbents and/or alkali components in accordance with the present invention. Stream **111** provides for introduction of base activated carbon from reservoir **110**, as metered by flow controller **201** manually or under the direction of computer **206**. The halogen/halide may be combined and react with the base activated carbon according to any of several provided methods. The halogen/halide may preferably be combined via line **121** directly into transport line **115**, within which it contacts and reacts with the base activated carbon prior to injection point **116**. This option is one form of what is referred to herein as "in-flight" preparation of a promoted carbon sorbent in accordance with the invention. Further, the halogen/halide may be combined via line **121b** with base activated carbon prior to entering transport line **115**. Still further, the halogen/halide may be contacted and react with the base activated carbon by introduction via line **121c** into reservoir **110**. This option is preferably employed when, for example, reservoir **110** comprises an ebullated or fluidized bed of base activated carbon, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base activated carbon in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in FIG. 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to FIG. 1.

Similarly, the optional secondary component may be contacted and react directly in transport line **115** via line **131**, or optionally as described above with respect to the halogen/halide, via lines **131h** and **131c**.

Similarly, the optional alkali component from **180** may either be added in transport line **115** directly, or may be injected separately by transport line **118**, combining downstream in flue gas **15** for synergistic effects with base activated carbon, promoted carbon, or optional secondary components. Being able to vary onsite the amount of the optional alkali component relative to base activated carbon, promoted carbon, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base activated carbon. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br₂, may be passed through an ebullated or fluidized bed of granular or fibrous activated carbon, with the promoted carbon sorbent so produced removed from the top of the bed via gas entrainment for injection.

In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl₂

US 10,668,430 B2

11

and others. In some preferred embodiments, the promoted carbon sorbent may comprise from about 1 to about 30 g halogen/halide per 100 g base activated carbon. In some preferred embodiments, the promoted carbon sorbent may comprise an secondary component in concentration of from about 1 to about 15 wt-% of the concentration of the halogen/halide component.

In still other embodiments, the product promoted carbon sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted carbon sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H₂S, SO₂, H₂Se, SeO₂, CS₂, P₂S₅, and combinations thereof.

Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F₂, Cl₂, Br₂, and I₂, the reaction with a hot flue gas components leave little to react with elemental mercury. The atomic elemental halogen form, which includes the fluorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view therefore, a halide-salt-treated activated carbon will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen Promoted Sorbent Characteristics

The sorbent described here has a very high initial reactivity for oxidizing mercury and therefore can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the sorbents produced using the inventive technology. The time interval required for the mercury and the promoted carbon sorbents of the present invention to successfully interact in a flue gas duct, with the subsequent collection of the mercury on the sorbent and ash is very short—less than seconds. Clearly, such collection times require the sorbent to have both high capacity and high reactivity toward mercury. The promoted carbon sorbent can be utilized in a very finely powdered form to minimize mass transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use

12

of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a sorbent containing a halide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for very effective capture of the mercury.

It appears that the inventive sorbents chemically combine molecular bromine, for example, from solution, with activated carbon (edge sites). X-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus, the sorbent produced from halogen and activated carbon does not represent a molecular halogen form, but rather a new chemically modified carbon (or halocarbon) structure. This phenomenon may not occur with the less reactive iodine, where an I₂ molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed. Optional Second Component

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, typically exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus, the second component is an element with more polarized electrons (4p and 5p).

Optional Alkali Component

It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO₂, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio onsite in order to overcome and optimize for a given set of site conditions.

The synergy that can be gained when co-injecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e. sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and

US 10,668,430 B2

13

subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~an order of magnitude less) than activated carbon, thus more of it can be used still resulting in overall lower costs.

"In-Flight" Sorbent Preparation

Furthermore, we have demonstrated that the halogen promoted carbon sorbent can be readily produced "in-flight". This is accomplished by, for example, contacting the vapors of any combination of halogens and optionally a second component, in-flight, with very fine carbon particles. The particles may be dispersed in a stream of transport air (or other gas), which also conveys the halogen/halide promoted carbon sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

Advantages of On-Site Preparation

In-flight preparation of the halogen/halide promoted carbon sorbent on location produces certain advantages. For example, the treatment system can be combined with the carbon injection system at the end-use site. With this technique, the halogen/halide is introduced to the carbon-air (or other gas) mixture in a transport line (or other part of the sorbent storage and injection system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

- Capital equipment costs at a treatment facility are eliminated.

- Costs to operate the treatment facility are eliminated

- There are no costs for transporting carbon and additive to a treatment facility.

- The inventive process uses existing hardware and operation procedures.

- The inventive technology ensures that the sorbent is always fresh, and thus, more reactive.

- No new handling concerns are introduced.

- There are no costs for removing carbon from treatment system

- The inventive process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when changing fuels or reducing loads, thus further optimizing the economics.

- The inventive technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide promoted carbon sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g. bromine) to the carbon structure.

Sorbent Injection Location

Some of the preferred embodiments contemplate the use of a halogen promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen promoted carbon sorbent comprise a powdered modified activated carbon prepared by adding Br₂ or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjunction with a base activated carbon and/or with the use of a halogen based sorbent

14

and any other combinations of the sorbent technologies provided in this patent. Alternatively, embodiments include methods wherein the sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

Any of the above embodiments of the halogen/halide promoted carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive, conventional methods of adding a reagent (such as peroxide, gold, triiodide, etc.) to a sorbent. The halogen/halide promoted carbon sorbent of the present invention, treated with bromine and/or optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in co-pending, commonly owned PCT patent application No PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

Promoted Carbon Sorbents

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a carbocation that accepts electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine-containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

EXAMPLES

To more clearly illustrate the present invention, several examples are presented below. These examples are intended to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

US 10,668,430 B2

15

Example 1

Preparation and Testing of Halogenated Carbon (& Comparative Example) Gas Phase Halogenation

Finely powdered activated carbon (such as NORIT Darco FGD, NORIT Americas, Inc., Marshall, Tex. (USA), although others are suitable, as will be recognized by those skilled in the art), was placed in a rotating plastic barrel with side blades (a 5 ft³ (0.14 m³) cement mixer) fitted with a tight plastic lid to prevent loss of the fine powder during the preparation. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that is warmed to about 40°-50° C. The vapor pressure of the bromine was such that a dark red gas is generated and passed out of the generator. The outlet from the gaseous bromine generator is connected via a ¼ inch (0.64 cm) plastic hose to a stationary metal tube inserted through a flange in the center of the plastic lid and passing into the center of the barrel. The flange is not air tight so that the excess of nitrogen is released after the bromine is transferred to the tumbling carbon. Thus, the bromine gas stream continuously passed into the rotating barrel where it contacted the tumbling carbon. The unit is then operated until the desired amount of bromine has combined with the carbon. Typically, this is 0.4 to 1 kg of bromine to 20 kg of carbon (2-5 wt %). When the reaction is completed, the carbon is weighed. The treated carbon is odorless and does not cause skin irritation since the bromine has completely reacted with the carbon to produce the brominated carbon.

XPS spectra demonstrate that the brominated carbon contains both covalent carbon-bound (organic) bromide as well as anionic bromide. The product contains the same moisture originally present in the activated carbon (5-17 wt %), but does not require further drying for use. The moisture is driven out at higher temperatures (>150° C.), and the bromine was not released until very high temperatures

Bench-Scale Testing of Mercury Oxidation and Capture Efficiency

A bench-scale apparatus and procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including bromine-containing activated carbons prepared from a variety of carbons, including commercially available sorbents, aerogel film sorbents, and the original precursor carbons for comparison.

A detailed description of the apparatus and its operation is provided in Dunham, G. E.; Miller, S. J. Chang, R.; Bergman, P. *Environmental Progress* 1998, 17, 203, which is incorporated herein by reference in its entirety. The bench scale mercury sorbent tests in the flue gas compositions were performed with finely (-400 mesh) powdered sorbents (37 mg) mixed with 113 mg sand and loaded on a quartz filter (2.5 inch (6.35 cm)). The loaded filter and holder were heated in an oven (125° C.) in the simulated flue gas stream (30 SCFH (standard cubic feet/hr) or 0.79 NCMH (normal cubic meters per hour)) containing the following: O₂ (6%), CO₂ (12%), SO₂ (600 ppm), NO (120 ppm) NO₂ (6 ppm). HCl (1 ppm), Hg⁰ (11 µg/m³), H₂O (15%), and N₂ (balance). Elemental mercury was provided by a standard permeation tube source placed in a double jacketed glass condenser, and heated to the desired temperature. Mercury concentrations in the gas streams were determined with a continuous mercury emission monitor (Sir Galahad mercury CEM mfr. P.S. Analytical Deerfield Beach Fla. USA), and a SnCl₂ cell was used to convert oxidized species to elemental, so that both

16

elemental and oxidized mercury concentration data could be obtained for both the influent and the effluent concentrations from the sorbent bed. Mercury concentrations were calibrated for the flow rates used. Spent sorbents were analyzed for mercury to determine the mass balance.

Referring now to FIG. 4, the effluent mercury concentration data are plotted as a percent of the influent mercury versus time. The resulting curve (breakthrough curve) for the halogenated sorbents typically showed 0%-1% Hg in the effluent (99+% capture) at the beginning, and increasing only after 30-60 minutes (breakthrough point), depending on the sorbent FIG. 4 illustrates the breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) with synthetic flue gas containing 1 ppm HCl. Total Hg (solid circles) and elemental Hg (solid squares) in the effluent are presented as a percent of the inlet Hg "EOT" indicates the end of test (the later data points shown are for calibration checks).

FIG. 5 presents the comparative breakthrough curves for the corresponding nonhalogenated sorbents typically initiated at 5%-50% of inlet mercury, depending on the HCl concentration in the synthetic flue gas, thus indicating considerably lower reactivity for oxidation and capture of the mercury for the nonhalogenated sorbents. After breakthrough of either halogenated or nonhalogenated sorbent, most of the mercury in the effluent was oxidized mercury.

Example 2

Gas Phase Halogenation of Fluidized Carbon

A bed of activated carbon supported in a vertical tube by a plug of glass wool was fluidized by a nitrogen stream. The top of the fluidized bed tube was connected to a catching trap for carbon fines that blow out the top of the tube. The bromine gas generator as described in Example 1 was attached to the fluidized carbon bed and the desired amount of gaseous bromine was passed into the bed. The contents of the trap were then mixed with the material in the bed and weighed. The resulting brominated carbon exhibited properties similar to the brominated carbon of Example 1.

Example 3

Liquid Phase (Water) Halogenation

A 5% solution of bromine in water was prepared by carefully adding 50 g of bromine to 1 liter of cold water. One kg of activated carbon was added to the bromine solution in a large metal can. The resulting slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon, as indicated by the disappearance of the red color. The slurry was then filtered using a Buchner funnel under vacuum. The moist carbon that was collected on the filter was dried in an oven at 110° C. for several hours to constant weight. As in Example 1, some moisture remains in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 4

Addition of the Optional Second Halide Component

Brominated carbon was produced by solution phase bromination similar to that described with reference to Example

US 10,668,430 B2

17

3. However, before filtration, a solution of hydriodic acid (HI) was added to the slurry in an amount equal to 10% of the bromine amount. The slurry was stirred to complete the reaction and then filtered and dried as described in Example 3.

Example 5

Liquid Phase Phosphohalogenation

A solution of phosphorus tribromide (500 g) in ligroin (10 liters) was stirred in a large metal can and 10 kg of activated carbon was added. The resulting slurry was stirred with a large paddle at ambient temperature to complete the reaction. The slurry was filtered under vacuum on a large Buchner funnel in several batches. The wet filter cake was dried at 110° C. in an oven to constant weight. The dried product was fluffed in the rotating barrel as described in Example 3.

Example 6

Preparation and Sorption on Larger-Particle Carbon

Tests were conducted on a pilot-scale combustor while firing a subbituminous coal, to evaluate mercury control by injecting larger-than-normal sized treated activated carbon. Standard AC sorbents generally are of fine size with a mean particle diameter of less than 20 micrometers, which is also typical of the flyash that is generated from pulverized coal combustion. Consequently, because the sizes of standard AC and flyash are similar, separation of the two is difficult. Injection of larger sized AC is generally not considered because the sorbent effectiveness decreases with size. In a scheme to recycle the injected carbon, the carbon is separated from the flyash. A separation based on size fractionation requires a treated larger particle sorbent. To test this concept, a treated larger sized (>60 µm) sorbent was developed, prepared, and tested.

Treatment—Gas Phase Halogenation

Granular activated carbon (Calgon F400) was ground and sieved through conventional mesh screens. The mesh size fraction -170 to +240 (corresponding to about 60 to about 88 micrometers) was collected and placed in a rotating vessel as described in Example 1 above. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that was warmed to about 40°-50° C., and the outlet from this gaseous bromine generator was connected via a ¼ inch (6.35 mm) plastic hose to a stationary metal tube inserted through a flange in the center of the lid and passing into the center of the rotating vessel, also as described in Example 1. The unit was operated until the desired amount of bromine had combined with the carbon, in this case 0.05 kg of bromine to 1 kg of carbon (5 wt %). When the reaction was completed, the carbon was weighed. The treated carbon was odorless as has been described above.

PTC Apparatus

The pilot-scale combustor, known as the “Particulate Test Combustor” (hereinafter “PTC”), is a 550,000-Btu/hr (about 161 kW) pulverized coal (“PC”)-fired unit, designed to generate combustion flue gas properties and fly ash that are representative of those produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Based on

18

the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle of the PTC fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature. Originally, the PTC used cold-water annular heat exchangers to provide flue gas temperature control to the baghouse (also referred to as a “fabric filter”) or electrostatic precipitator (ESP). However, analysis of ash deposits collected from the heat exchangers indicated that some mercury was collected on the duct walls. To minimize this effect, the heat exchangers were modified to provide for higher duct wall temperatures.

The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device (baghouse, Advanced Hybrid Particle Collector/AHPC™, and/or electrostatic precipitator/ESP) operating data to be monitored continuously and recorded on a data logger.

PTC Procedure

Flue gas samples were taken at combinations of two of the three available system sample points: the furnace exit, the particulate control device inlet, and the particulate control device outlet. After passing through sample conditioners to remove moisture, the flue gas was typically analyzed for O₂, CO, CO₂, SO₂, and NO_x. Each constituent was normally analyzed at both the furnace exit and the outlet of the particulate control device simultaneously, using two analyzers. The concentration values from all of the instruments were recorded continuously. In addition, data were manually recorded at set time intervals. NO_x was determined using a pair of Rosemount Analytical NO chemiluminescent analyzers. SO₂ was measured using a pair of Ametek Instruments photometric gas analyzers. The remaining gases were measured by a pair of Rosemount Analytical multi-gas continuous emissions monitors. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

The baghouse vessel was a 20 inch (50.8 cm) (ID) chamber that is heat-traced and insulated, with the flue gas introduced near the bottom. The combustor produced about 200 ACFM (actual cubic feet per minute; about 5.7 actual m³/min) of flue gas at 300° F. (about 150° C.), therefore three 13-ft by 5-inch (3.96 m by 12.7 cm) bags provided an air-to-cloth ratio of 4 ft/min (1.22 m/min). Each bag was cleaned separately in operation with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags were cleaned on a time basis, rather than with the cleaning cycle initiated by pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession on-line.

Tests were also conducted with a single-wire, tubular ESP replacing the fabric filter. The ESP unit was designed to provide a specific collection area of 125 at 300° F. (150° C.). Since the flue gas flow rate for the PTC is 130 SCFM (standard cubic feet per minute; about 3.7 NCM (normal m³/min)), the gas velocity through the ESP is 5 ft/min (about 1.52 m/min). The plate spacing for the ESP unit is 11 in (27.9 cm). The ESP was designed to facilitate thorough cleaning between tests so that all tests can begin on the same basis.

PTC Results

Results are illustrated in FIG. 6. As can be observed in FIG. 6, even though the tested sorbent particle size is significantly larger than normal sorbent particles, the treated larger-than-normal sized (that is, >60 micrometers) acti-

US 10,668,430 B2

19

vated carbon sorbent was quite effective at capturing mercury. Approximately 75% of the mercury was captured when the larger-sized treated AC was injected ahead of the pilot-scale ESP, while approximately 85% of the mercury was captured when injected ahead of the pilot-scale fabric filter ("FF"). Note that in FIG. 6 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet (1 MACF is about 0.028 million actual cubic meters or "MACM").

Referring now to FIG. 7, it can be observed that the larger-sized treated AC when injected ahead of the pilot-scale ESP (diamond symbol(s)) performed better than the finer standard AC (triangles) under the same arrangement. In comparison, when injected ahead of the fabric filter (FF), the larger-sized treated AC (square) performed similarly to slightly worse. However, for this application, the larger-sized treated AC can be physically separated from the smaller flyash particles, and the sorbent can then be regenerated, recycled, and reused. This will substantially improve overall utilization and economics. These data thus show that a larger-than-normal sized sorbent can provide effective mercury control and ease flyash and AC separation, thereby also preserving the characteristics of the flyash for sale and beneficial use. Accordingly, because $>60\ \mu\text{m}$ sorbent particles have been successfully demonstrated, superior mercury control can be obtained with $>40\ \mu\text{m}$ particles, which may be preferred in some applications, depending on the sorbent particle/ash separation system used. Note that in FIG. 7 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet.

Example 7

Liquid Phase (Organic Solvent) Halogenation

A 5% solution of bromine in ligroin was prepared by carefully adding 50 g of bromine to 1 liter of cold ligroin. One kg of activated carbon was added to the bromine solution in a large metal can. The slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon as indicated by the disappearance of the red color. The slurry was filtered using a Buchner funnel under vacuum. The carbon cake that was collected on the filter was dried in an oven at 110°C . for several hours until it appeared dry and a constant weight was obtained. As in Example 1, some moisture was left in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 8

Promoted Activated Carbon Sorbents

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100°C . in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry

20

bed of the activated carbon precursor. The results indicated that adding a second component to the solution improved the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury ($11\ \mu\text{g}/\text{m}^3$) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM ("continuous emission monitor") (mfr. P S Analytical, Deerfield Beach, Fla., USA). The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer. A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it was treated with 0.1 N HBr, and the powder was collected by centrifugation and drying, revealed that the mercury capture activity increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicated that it not only captured mercury at the same level as before (100% capture) but its capacity was prolonged by several minutes, and thus enhanced. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

Example 9

Fluidized/Ebullated Bed Preparation

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed or ebullated bed of the carbon. The amount of bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Example 10

Full-Scale Testing

In this example, a baghouse (fabric filter) or ESP was used to collect particulates in the exhaust of a full-scale commercial pulverized coal-burning facility. A scrubber and sorbent bed were also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In this example, the halogen/halide promoted carbon sorbent was injected into the flue gas after the boiler. In general however, the inventive sorbent can be injected where desired (e.g., before, after, or within the boiler).

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and $11\ \mu\text{g}/\text{m}^3$. The ash and injected carbon were collected in the baghouse at 350°F . to 375°F . (about 175 - 190°C .). Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/MACF ("MACF" and "Macf" represent one million actual cubic feet; 1.0 lb/MACF is about 16 kg/MACM (million actual cubic meters)) resulted in mercury effluent concentrations of 3.8 - $4.2\ \mu\text{g}/\text{m}^3$ (representing 62%-58% removal of the mercury from the gas, respectively), and at 2.0 lb/MACF (about 32 kg/MACM), gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/MACF resulted in 73%-69% removal and at 2.0 lb/MACF gave 86%-84% removal. Thus, a significant increase in the mercury capture was

US 10,668,430 B2

21

exhibited during use of the bromine promoted carbon sorbent of the present invention.

Example 11A

Addition of Optional Alkaline
Component—Bench-Scale

The efficiency of the activated carbons for mercury capture can be improved considerably by employing a basic material co-injected with the activated carbon, in order to capture any oxidized mercury that may be released from the sorbent, or to capture some of the sulfur or selenium oxides in the flue gas that can have a detrimental effect on the sorbent capacity.

Bench-scale testing was conducted by preparing a filter composed of 37 mg of brominated activated carbon mixed with 113 mg of calcium oxide. The test was conducted as described in Example 1 and compared with the same carbon sorbent but with an inert diluent. The breakthrough curve for the mixture of brominated (2%) NORIT Darco FGD sorbent with inert sand is shown in FIG. 8, and the breakthrough curve for the mixture with CaO is shown in FIG. 9. It can be seen that the point of 50% breakthrough improves to 65 minutes with the mixture with CaO from only 48 min with the sand mixture.

Example 11B

Addition of Optional Alkaline
Component—Pilot-Scale

Tests were conducted on the pilot-scale PTC combustor described above with reference to Example 6 while firing a Texas lignite to evaluate mercury control by co-injecting a standard activated carbon (also referred to herein as “AC”) and an alkali material upstream of a fabric filter. Typical results are illustrated in FIG. 10. As shown in FIG. 10, co-injecting lime with activated carbon vastly improved mercury removal. Mercury removals of approximately 90% were achieved with the co-injected sorbents, whereas less than 60% removal was achieved with the use of standard AC alone, even at much higher injection rates. Data from similar tests show that injecting similar quantities of sodium carbonate and AC, and lime and AC, resulted in mercury removals of approximately 80%, and 87%, respectively. These data suggest that other alkali can also be co-injected with AC to improve mercury removal. Other data show that flue gas temperature may impact the effectiveness of the alkali addition. Further test data indicate that flue gas contaminants, flue gas constituents (SO₂, NO_x, HCl, etc.), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This indicates that it may be desirable to be able to adjust and tailor, onsite, the alkali-to-AC ratio in order to optimize removal for a given set of site conditions.

Without wishing to be bound by any particular theory, the synergy observed in the improved performance when co-injecting the two materials can be explained as follows. First, tests indicate that binding sites on AC can be consumed by sulfur species and other contaminants. The alkali material interacts and reacts with these species thus minimizing their consumption of AC mercury binding sites. Second, other work has shown that standard AC will continue to oxidize mercury even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by the particu-

22

late control device. Thus, combining alkali with treated and/or non-treated AC synergistically takes advantage of these two mechanisms, resulting in improved mercury capture at reduced costs.

Example 12

Brominated Carbon Sorbent for Gasification Fuel
Gas

Preparation of 5% Br2W-AC

Using a procedure similar to Example 3, a 2.5 wt/vol % solution of bromine in water was prepared. Granular Calgon F400 was added to the bromine solution to give a 5 wt/wt % brominated carbon product. The bromine solution was stirred with a large paddle during and after the addition until the red color in the water disappeared. The suspension was filtered by vacuum on a large Buchner funnel. The filter cake was dried in air, and then in an oven at 110° C. until a stable weight was obtained. The moisture was reduced to 15%.

Preparation of 50% Br2D-AC

A brominated sorbent was prepared from Br₂ addition in solvent as described in Example 7, except that dichloromethane was used as the solvent instead of ligroin, and granular Calgon F400 was used.

Preparation of 5% PBr3-AC

A phosphohalogenated sorbent was prepared from PBr₃ using the method described in Example 5, except granular Calgon F400 was used.

Testing in Hydrogen Atmosphere—Procedure

To simulate the capture of mercury from a heated fuel gas or syngas from coal gasification, tests were conducted employing a stream comprising 10% vol/vol hydrogen in nitrogen passing through the sorbent at 500 cc/min. The stream contained 26.9 micrograms/m³ of elemental mercury from a commercial mercury permeation source.

In the tests, the sorbent (0.5 g) was placed in a 0.39 inch (1 cm, inside diameter) glass tube fitted with a medium frit sintered glass filter disc to hold the sorbent in the gas stream. The tube containing the sorbent bed was connected to a gas inlet tube for introducing the gas stream containing the mercury vapor and at the outlet to a tube connection to the detector. The detector was a Semtech 2000 continuous mercury emission monitor. The tube was equilibrated in a nitrogen flow (450 cc/min) for 5 minutes at ambient temperature to stabilize the system. The detector showed 0 concentration of mercury in the effluent from the sorbent bed. (The blank run with no sorbent read 26.9 micrograms/m³). The tube was then placed in an oven at the selected temperature for the test (from 250° to 400° C.). Effluent mercury concentration data from the detector were collected until the detector showed a constant reading for 5 minutes. Hydrogen (50 cc/min) was then added to the gas stream and detector readings were taken every 5 min. Tests were conducted at several oven temperatures for various periods of time up to 3 hours, depending on the temperature and sorbent. The elemental mercury concentration data were plotted as a percent of inlet mercury concentration versus time as in Example 1. All the mercury in the effluent was elemental, so a single detector was sufficient, and no SnCl₂ trap was needed to convert to elemental mercury (as in Example 1). The time for 50% breakthrough (time to reach 50% capture) was then determined from the breakthrough curves.

Results

The results are shown in Table 1 (below) for the unbrominated sorbent (Calgon F-400), the brominated sorbents

US 10,668,430 B2

23

(5% Br2W-AC and 5% BrD-AC), and the phosphobrominated sorbent (5% PBr3-AC). The maximum mercury concentration obtained in the effluent in each run is also reported in Table 1 for the time period indicated in the last column.

Under the reducing hydrogen conditions, the unbrominated sorbent broke through immediately and was exhausted after only 6.5 min. This complete failure occurred because the hydrogen reduces the captured mercury in the unbrominated sorbent at any temperature above 100° C. Both of the brominated sorbents exhibited excellent reactivity and good capacity at all temperatures, up to at least 400° C. The phosphobrominated sorbent exhibited superior reactivity and capacity at all temperatures, up to at least 400° C.

Times for 50% Breakthrough Maximum
Observed Hg Concentrations for Sorbents
(10% Hydrogen Streams)

Sorbent	Temp (° C.)	50% breakthrough (min)	Maximum [Hg] (µg/m ³)	Time (min)
F-400	250	6	20.3	6.5
5% Br2W-AC	250	>150	1.4	150
5% Br2W-AC	300	>180	4.3	180
5% Br2W-AC	350	160	15.1	180
5% Br2W-AC	400	60	13.9	65
5% PBr3-AC	250	>140	0.4	140
5% PBr3-AC	300	>150	0.5	150
5% PBr3-AC	350	>150	1.4	150
5% Br2D-AC	350	>180	2.1	180
5% Br2D-AC	400	>180	10.9	180

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term “optionally” with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

24

Although the invention is described herein as a sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

Provisional Application

A reactive sorbent material is described for capture of mercury in a vapor stream. The vapor stream includes flue gas from coal combustion or incineration, synthesis gas from gasification, as well as off gases from mineral processing, metal refining, retorting, cement manufacturing, chlor-alkali plants, dental facilities, and crematories. The sorbent is especially suited to, but not limited to, use in low-chlorine flue or exhaust gases where the mercury is mainly elemental. The sorbent comprises a bromide-modified carbon form containing a reactive compound produced by the reaction of bromine with the carbon. Other additional promoting substances can be added in smaller amounts to increase the reactivity with and sorption of elemental mercury. This combination results in a carbon bromide structure in the carbon lattice that can oxidize the mercury to a species that is strongly bonded to the carbon structure and, therefore, easily retained on the sorbent at higher temperatures in the presence of flue gas constituents. In some examples, the sorbent consists of a fine or coarse powdered material for injection into the gas stream or a granular or fibrous material for use in a fixed or moving bed. In some examples, the sorbent does not require in situ activation (an induction period) in a flue gas stream as do conventional activated carbon sorbents. Other additives of base chemistry (Ca, Na, and others) may be added to flue gas as a sorbent mixture, or co-injected to selectively sorb acid gases or other flue gas constituents to keep available reactive sites for mercury oxidation and subsequent capture. The sorbent can be regenerated by washing off contaminating components derived from flue gas that poison the spent sorbent. Novel methods for introduction of the sorbent dispersion into the mercury contaminated gas stream are described.

Following is an outline of examples of the invention. The invention may also take on various other examples or embodiments, as a person skilled in the art would understand.

1. A modified carbon sorbent was prepared by reacting the carbon with molecular bromine by applying a solution of molecular bromine in an organic solvent to the carbon, followed by removal of the modified carbon from the bulk of solvent and further removal of solvent from the pores by drying the carbon in air or nitrogen. The solution may also contain an additional promoting substance in small amounts. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

1A. (Dependent)

Same as 1, carbon is powdered activated carbon.

Carbon is granular activated carbon.

Carbon is very fine carbon black.

Carbon is very fine carbon fiber.

Carbon is aerogel carbon film.

Carbon is char recovered from pyrolysis process.

Carbon is powdered activated carbon of size distribution larger than fly ash size distribution, so that it can be physically separated from the ash and regenerated for reuse.

Carbon is regenerated from previous usage cycle and recycled.

Other desired types of carbon may also be used.

US 10,668,430 B2

25

1B. (Dependent)

Same as 1, Solvent is chlorinated hydrocarbon such as dichloromethane.

Same as 1, Solvent is hydrocarbon solvent such as petroleum ether or ligroin or pentane or hexane or toluene or benzene.

Same as 1, Solvent is water.

Same as 1, Solvent is carbon disulfide.

Same as 1, Solvent is a waste solvent.

Same as 1, Solvent is an ether.

Same as 1, Solvent is recycled from previous batch.

Same as 1, Solvent is supercritical solvent such as CO₂.

Other desired types of Solvents may also be used.

1C. (Dependent)

Same as 1, solution of bromine is applied by stirring the carbon in the bromine solution.

Same as 1, solution of bromine is applied by spraying a solution of molecular bromine in an organic solvent, followed by removal of solvent from the pores by drying the carbon in air or nitrogen.

The bromine may also be applied using other desired techniques.

1D. (Dependent)

Same as 1, removal of solvent is by filtration, centrifugation, settling, and decantation and drying in vacuum, air, or other gas.

Same as 1, when sprayed or minimal volume, removal of solvent is by drying in air, vacuum, or other gas.

The solvent may also be removed using other desired techniques.

1E. (Dependent)

Same as 1, additional substance is iodine, at 1%-10% of the bromine concentration added.

Same as 1, additional substance is hydrohalide (HI, HBr, HCl), etc, 1%-10% of bromine.

Same as 1, additional substance is a compound comprised of a Group V or VI element or combination of Group V or VI with Group VII element, such as SCl₂, 1-10 wt % of bromine.

2. A modified carbon sorbent was prepared by reacting the carbon with molecular bromine by contacting the carbon with a gas containing molecular bromine. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Contacting is by passing the Br₂ gas through a bed of the carbon.

Bed is ebullated or fluidized.

Bed is moving bed of granules or fibers.

Contacting is by admitting Br₂ gas to a duct through which the carbon is transported from a reservoir to the flue gas duct via an air-driven entrainment method, thus promoting the activity of the carbon in-flight.

Same additives as 1E, except these are added in the gas phase, and added in-flight as in 2 above.

3. A modified activated carbon sorbent was prepared by reacting the carbon with hydrogen bromide (HBr) by stirring the carbon in a solution of HBr in an organic solvent or in water, followed by removal of the modified carbon from the bulk of solvent and further removal of solvent from the pores by drying the carbon in air or nitrogen. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon forms. Same solutions and treatment as 1B, 1C, 1D.

26

Same additives as 1E, added into the solution phase or later in the gas phase, and added in-flight as in 2 above.

4. An activated carbon sorbent was prepared by impregnating hydrogen bromide by passing a gas composition containing hydrogen bromide diluted with nitrogen or air through a fluidized bed or ebullated bed of the carbon. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon forms.

Contacting options are similar to 2.

5. Sequential treatment of activated carbon with bromine or HBr, followed by another mercury stabilizing reagent to generate a highly reactive bifunctional sorbent, the reagent to include sulfur and selenium species, such as H₂S, SO₂, H₂Se, Se, SeO₂, CS₂, P₂S₅.

6. Sequential treatment of activated carbon with mercury stabilizing reagent, followed by bromine or HBr to generate a highly reactive bifunctional sorbent, the reagent to include sulfur and selenium species, such as H₂S, SO₂, H₂Se, Se, SeO₂, CS₂, P₂S₅.

7. Treatment of a carbon with a Group V or VI element combined with Group VII element, such as PBr₃ or SCl₂. In one example, the amount of Group V or VI halide is 1-30 wt % of the carbon. The compound is added in vapor phase or in solution (solvent is hydrocarbon, chlorinated hydrocarbon, or other solvent as described in 1B, but not water, since the compound is destroyed in water solution).

8. The process for preparing the bromine-containing activated carbon sorbent as described in Examples 1-6 and coupled with the injection of the bromine-containing fine-particle sorbent into the contaminated gas stream and subsequent removal of the fine particles of sorbent from the gas stream in a collection device, such as bag filtration of electrostatic precipitator (ESP).

9. The process of using additives (1-8) in conjunction with sorbents to capture acid gases and other flue gas constituents that block oxidation reactions or consume sorbent sites that would otherwise capture mercury. The additive is a compound comprised of Group I or II elements, such as Ca, Na, and others. These additives of base chemistry may be added to flue gas as a sorbent mixture or co-injected to selectively sorb acid gases or other gas constituents that compete for mercury reactive/sorption sites, thereby improving the effectiveness of activated carbon to capture mercury. In addition, the base additives can augment the treated activated carbon by helping to capture oxidized mercury forms in the flue gas, such as mercuric chloride, or that are produced on the carbon sorbent, such as mercuric bromide, but are released to the gas phase as the sorbent becomes saturated or capacity limited.

10. The process of preparing a larger-than-normal (>40 μm) sorbent particle size, promoting with the halogen treatment as described in 1-8, using the treated sorbent for capture of mercury by injecting in the flue gas, and finally separating and recovering the sorbent from the ash particles. The larger sorbent size thus will allow easy mechanical/physical separation so that sorbent can be regenerated, recycled, and reused, and the ash can be sold as a low-carbon cementitious byproduct for concrete. The separation can be effected by various methods, such as density (gravity), floatation, or sieving methods.

11. The process for preparing the bromine-containing activated carbon sorbent as described in Example 1-10, coupled with the direct injection of the slurry of the prepared fine-particle sorbent in the solvent or aqueous phase, so that

US 10,668,430 B2

27

the aerosol particles of the slurry achieve a high degree of dispersion in the gas stream and evaporation of the solvent in the hot gas occurs rapidly. The amount of slurry added is flow-controlled, and the concentration of particles in the slurry is monitored by optical density measurements prior to injection. Collection of particles is performed.

12. The process for preparing the bromine-containing activated carbon sorbent, as described in Examples 2 and 4, coupled where the fine-particle dispersion of brominated sorbent in the gas stream at the top of the ebullated bed is led to the flue gas or offgas duct where the said dispersion is contacted with mercury-contaminated flue gas or offgas stream. The amount of aerosol dispersion added is controlled by the gas flow to the ebullated bed, and the concentration of particles in the dispersion can be monitored by optical density measurements prior to injection. Collection of particles is performed by the existing particulate-collection equipment.

13. The process for preparing the bromine-containing activated carbon sorbent bed, coupled with contacting the bed with the mercury-contaminated flue gas or offgas.

14. The process for preparing the bromine-containing activated carbon sorbent, as described in Examples 2 and 4, or untreated activated carbon, coated on a substrate or as activated carbon material. This material is placed in a moving system that geometrically allows for control of rate of exposure, sorption, and exchange of material in a continuous or semicontinuous manner.

15. In the sorbent and mercury removal process outlined in paragraphs above, the bromine reagents promote metal oxidation activity by creating cationic or radical character on the carbon edge structure that attracts mercury atoms and extracts electrons from said mercury atoms, resulting in oxidized mercury, which is more easily captured on a sorbent. A similar mechanism applies to oxidation and capture of reduced arsenic and other pollutant species.

The invention relates to the process for the removal of mercury and other pollutant species from gas streams generated during the burning of fossil fuels, such as in a coal-fired utility or synthesis gas from gasification facilities. This removal process would utilize a sorbent and/or a combination of additives to remove pollutants from the gas stream, which are at the same time interacting with other gas components that result in poisoning or deactivating the sorbent and reducing its capacity or reaction rates with the targeted pollutant species. The present invention provides a cost-effective way to capture the pollutants by utilizing exceptionally active carbon sorbents and promoting mercury sorbent surface reactions, containing a bromide form of the carbon, that capture mercury with high kinetic chemisorption (oxidation) activity, so that capture can occur during contact times of seconds or less. The sorbent does not require in situ activation (induction period) in the gas stream to achieve high activity as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants and the sorption capacity can be regenerated, recycled, and reused.

Burning fossil fuels generates a flue gas that contains mercury (and other trace elements) that was in the coal, plus oxides of sulfur and nitrogen (acid gas emissions) and particulates whose release to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. While control of other elements and/or flue gas pollutants may apply, the discussion provided is focused on mercury. Initially, mercury is released in the elemental form during combustion/gasification, but downstream of the boiler, in the ducts and stack of

28

the combustion system, part of the elemental mercury is oxidized. The amount oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the coal, but a typical concentration of mercury in the stream of combustion gas is about 5 parts per billion (ppb). A pound of mercury or more per day may be emitted in some utilities.

Discussion of Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles (for example, see U.S. Pat. No. 6,214,304), and basic silicate or oxide sorbents (for example, see the Ghorishi reference (Ghorishi, B.; Gullet, B. K. Waste Manage Res. 1993, 16, 582). and Lancia references). When particle injection is employed, the mercury chemisorbed to the sorbent particle is removed from the gas stream in a bag house or ESP and collected along with ash particulates (for example, see U.S. Pat. Nos. 4,889,698, 4,956,162, 5,672,323, 5,827,352, 6,027,551, and 5,505,766). The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of approximately 60% was attained with a baghouse to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon, since the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after exposure to the flue gas for about 20 minutes does the seasoned sorbent become effective and provide capture of 60% of the mercury in the gas. Consequently, these sorbents must be used in large amounts (high sorbent-to-mercury ratios) to effectively capture the mercury. These sorbents can be relatively expensive and cannot be easily separated from the ash, regenerated and reused. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash for use in various applications.

Use of Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have not previously been effective. Halogen is defined as a member of the very active elements comprising Group VII-A of the periodic table. In the molecular elemental halogen form, including F₂, Cl₂, Br₂, and I₂, the reaction with elemental mercury is not fast enough to result in the formation of oxidized mercury in a coal combustion flue gas with conventional ash control technology. The atomic elemental halogen form, which includes F atom, Cl atom, Br atom, and I atom, is about a million times more reactive to mercury, but the concentrations of these forms are extremely low, and also, therefore, cannot result in oxidation of mercury in a utility flue gas.

A halide is a compound formed from reaction of a halogen with another element or radical. In general, the halide compounds are normally very much less reactive than the molecular halogens, having expended their high chemical potential in forming the low energy halide. The halide is considered a reduced form and cannot therefore oxidize anything by itself. It is for this reason that it is not obvious that a halide-halogen treated activated carbon would be effective at oxidizing elemental mercury and provide effective

US 10,668,430 B2

29

tive capture of elemental mercury. In fact, for tests with salts, analytical data show the addition of bromine to an activated carbon or carbon black or soot does form a compound by reacting with the unsaturated groups on the carbon. By applying x-ray photoelectron spectroscopy, it has been determined that bromine or HBr added to carbon black forms chemical compounds within a carbon structure.

A body of theory has been developed from scientific evidence to explain the nature of the promotion effect of the bromine compounds. This principle is illustrated in FIG. 2, which in step 1 shows the reaction of the hydrogen bromide with the unsaturated structure of the activated carbon. This may be a carbene species on the edge of the graphene sheets structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury.

We now teach that the formation of the new bromide compound with carbon increases the reactivity of the carbon forms toward mercury and other pollutants. The resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation results from the promotion effect of the halide exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, which stabilizes the positive charge developing on the mercury and lowers the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus, adding HBr or Br₂ to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion. Prior Art Publications

The earliest patents that relate to mercury capture on a sorbent are actually not for flue gas mercury control but for capture of mercury from air or other gas mixtures on a carbon or other sorbent. These patents were based on a model that recognized the affinity of halogens for mercury, rather than the formation of a reactive carbon. These patents are discussed below according to the type of halogen used for impregnation.

One patent that teaches a halogen impregnation (Stock, U.S. Pat. No. 1,984,164, issued in 1934) describes the use of activated carbon or other solid impregnated with a halogen for removing Hg from air. The impregnation method is not specified. This seems to be the most general claim with respect to halogen impregnation. All the statements and claims appear to refer to halogen or iodine, but the patent does not appear to address bromides or other halides or bromide compounds or even specifically iodide or an iodine compound. The only example in the description is iodine impregnation. The patent also is restricted to air systems and did not pertain to flue gas systems with reactive acid gases. The description did not assume that the iodine formed a reactive carbon species.

Japanese Patent JP 49-43197 describes the treatment of Hg-contaminated electrolysis cell gas using a metal iodide salt on a support. A similar treatment using a resin impregnated with a metal iodide is described in JP 50-6438. These patents do not appear to represent a carbon bromide compound as specified in this patent application.

Another early patent (Hilgen, U.S. Pat. No. 3,849,267, issued in 1974) describes a method for Hg removal from a gas which claims mixing molecular chlorine (Cl₂) with the gas to be cleaned and passing it through a nonporous sorbent such as glass wool and NaCl (not carbon). This was evi-

30

dently not an obvious extension of the Stock patent, since a halogen was introduced as part of the gas phase being cleaned.

A later patent (deJong, et al., U.S. Pat. No. 4,196,173, issued in 1980) describes a method for Hg removal in air which claims using a bed of activated carbon impregnated with halogen-only Cl₂ is specified in the other claims and examples, and it is prepared by flowing the Cl₂ stream through a carbon bed.

An improved sorbent for mercury in air was patented by Revoir and Jones (U.S. Pat. No. 3,662,523, issued in 1972), in which ICl and ICl₃ vapors were impregnated into the activated carbon. No explanation of the increased activity was provided. Since these compounds are interhalogen compounds, the patent did not infringe Stock.

U.S. Pat. No. 5,891,324 describes an activated carbon containing an acid (HCl, H₂SO₄, or H₃PO₄) for the removal of mercury contained in a liquid phase, such as would occur in a process steam in the oil industry. In this case, the model presented was that mercury is adsorbed from the liquid into the solid carbon phase at relatively low temperatures.

In U.S. Patent Application 2004/0003716, a method is described for removing mercury from a combustion gas. This method employs an exposure of a finely powdered activated carbon to a molecular bromine gas at an elevated temperature or to HBr to produce a sorbent with good mercury removal ability when injected into the flue gas duct. The model for the efficacy of the Nelson sorbent is not clearly stated, so it can be presumed that the reasoning for using bromine is the simple premise that some bromine form will help capture the mercury, as does iodine and chlorine. The methods for incorporation of the bromine in the Nelson application are not the same as with the present invention, and the Nelson method will not produce the identical carbon bromide species that are obtained in the art described in this application. The Nelson method lacks many of the features described in this application that impart exceptional activity to the sorbent in a convenient way, for example, the addition of smaller amount of a second more powerful promoting agent, the use of facile solvent systems, including aqueous bromine, and the use of in-flight bromine treatment. Additionally, the patent application does not mention regeneration, recycling, or reuse, or the use of moving contactors or larger particle size to facilitate sorbent-ash separation.

Embodiments of the Invention

A sorbent that is initially very reactive in oxidizing mercury can be used in very small amounts to achieve high capture efficiencies, thus lowering operation costs and lessening the disposal problem. In addition, further disposal reduction is made possible by recycling and reusing the sorbent that is produced using this technology. The time interval for the mercury and sorbent to interact in a flue gas duct and the subsequent collection of the mercury on the sorbent and ash may be very short—only seconds. This requires the sorbent to have high capacity and be very reactive toward mercury. A sorbent can be utilized in a very finely powdered form (e.g., 1-10 μm) to minimize mass transfer limitations. But, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. One feature of this invention is the process to prepare a sorbent containing a bromide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for effective capture of the mercury.

One possible way to do this is to chemically combine molecular bromine from solution with activated carbon (edge sites). X-ray photoelectron spectroscopy established

US 10,668,430 B2

31

that the addition of bromine formed a chemical compound in the carbon structure. Thus, the sorbent does not represent a molecular bromine halogen form but a new chemically modified carbon structure. This may not occur with the less reactive iodine, where an I₂-molecular complex can exist on the carbon basal plane. In the bromine case, it is actually the carbon that oxidizes the mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements as described herein. Chlorine treatment resulted in lower-activity carbons because the chloride anion was less effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound from a second halogen, such as HBr. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus the second component is an element with more polarized electrons (4p and 5p).

Furthermore, we demonstrated that the sorbent can be readily treated with any combination of bromine and the second component in-flight using vapors of these components contacting the very fine carbon particles dispersed in air or other gas stream that conveys the particles to the flue gas duct. There is no particular temperature requirement for this contact. This technology is very simple to implement, so it will result in a great cost savings to the utility using this technology for mercury capture.

A unique, nonobvious technique for preparation of the treated carbon is through combining the treatment system with the carbon injection system at the end-use site. With this technique, the halogen is introduced to the carbon-air mixture in the transport line (or other part of the sorbent storage and injection system). Benefits over current concepts to treat sorbents off-site include the following:

Capital equipment costs at a treatment facility are eliminated.

Costs to operate the treatment facility are eliminated.

There are no costs for transporting carbon and additive to a treatment facility.

This process uses existing hardware and operation procedures.

This technology ensures that the sorbent is always fresh, and thus, more reactive.

No new handling concerns are introduced.

There are no costs for removing carbon from treatment system.

This process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as needed when changing fuels or reducing loads, thus further optimizing the economics.

This technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the invention, a process for preparing and regenerating carbon sorbents whose activity for mercury capture is promoted by the addition of bromine to the carbon structure.

32

The invention applies to use of a sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Examples of the composition of the sorbent are a powdered modified activated carbon prepared by adding Br₂ or HBr plus a second optional component. Alternatively, the sorbent is on a moving contactor consisting of particles or fibers containing the compositions listed in the previous sentence. Either type can be regenerated; the poisoning contaminants from the flue gas are removed and an inexpensive promoting agent added to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive art of adding a reagent (such as peroxide, gold, triiodide, etc.) to the sorbent. The activated carbon sorbent treated with bromine and/or the other components is noncorrosive.

Detailed examples of sorbent regeneration techniques are described in co-pending, commonly-owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is incorporated by reference herein.

Although the invention is described herein as a sorbent material, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

The construction and method of operation of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of specific exemplary embodiments.

FIG. 11 is a block diagram illustrating the use of the invention in a coal fueled facility. Of course, the invention can also be used in any other desired type of facility. FIG. 11 shows a boiler for burning pulverized coal. The facility utilizes various devices to clean the exhaust of the boiler. In this example, a baghouse or ESP is used to collect particulates in the exhaust. A scrubber and sorbent bed are also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In the example shown, the sorbent is injected into the flue gas after the boiler. The additive can be injected where desired (e.g., before, after, or within the boiler).

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize the invention. Where possible, the mercury control technology of the present invention will utilize measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent levels in this way will ensure mercury removal requirements are met with the minimal sorbent requirements and therefore the associated costs will be minimized. In one example, the emissions are measured at the stack.

Carbon Sorbent

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a carbocation that accept electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active

US 10,668,430 B2

33

sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine-containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several powdered carbon sorbents, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100° C. in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. Adding a second component to the solution was demonstrated to improve the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 µg/m³) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM. The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer.

A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it has been treated with 0.1 N HBr, collecting the powder by centrifugation and drying, revealed that the mercury capture activity is increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicates that it not only captures mercury at the same level as before (100% capture) but is enhanced such that its capacity is prolonged by several minutes. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed of ebullated bed of the carbon. The amount of bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 µg/m³. The ash and injected carbons were collected in the baghouse at 350 E to 375 EF. Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/Macf resulted in mercury effluent concentrations of 3.8-4.2 µg/m³ (representing 62%-58% removal of the mercury from the gas), and at 2.0 lb/Macf, gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/Macf resulted in 73%-69% removal and at 2.0 lb/Macf gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine-treated carbon.

34

Addendum: Other References to Hg Sorption Sorbent Beds with Particulate Removal

Carbon beds have also been utilized for mercury capture in flue gas. The German Patent 34 26 059 describes the use of a very thick carbon bed for treatment of flue gases containing polyhalogenated compounds. Although the system employed at Dusseldorf would also have the potential for Hg removal (for example, see the Streng reference), it is not very practical to use such a thick bed. Spent sorbent is burned and not regenerated. The carbons are not pretreated.

The GE-Mitsui-BF system (Tsuiji, K.; Shiraishi, I.; Dague, R. F. Proceedings, Sixth International Symposium, Air & Water Management Assoc., New Orleans, La., Mar. 10-12, 1993) employs a recirculating carbon bed, where mercury is removed along with acid gases (as ammonium salts) and the carbon is regenerated at high temperatures where ammonium sulfate is decomposed to SO₂ and N₂ and mercury is converted to the elemental form, which desorbs from the sorbent. Attrition of the sorbent results in a significant sorbent cost. The carbons are not pretreated.

Sorbent Injection after Particulate Removal

A process of injecting manganese oxide sorbent particles is described in U.S. Patent Application 2002/0150516. Regeneration is claimed by removal of spent oxide particles from the reaction zone and rinsing with dilute aqueous acid.

Sorbent Beds after Particulate Removal

Of particular interest in designing a mercury control process is to use the sorbent downstream of a particulate control device so the sorbent is not highly diluted with the ash particles. The sorbent could then be more easily regenerated and recycled. The prior art teaches several examples of this type of configuration and sorbent processing.

U.S. Pat. No. 5,607,496 teaches the oxidation of mercury on a metal oxide sorbent bed and subsequent absorption to sorbent. The sorbent bed follows the particulate-removal equipment and, thus, the gas still contains the SO_x and NO_x, which react with the metal oxide sorbent to form the metal sulfates, which poison the bed. High temperatures are proposed to regenerate the bed. However, Hg is only partially removed from the sorbent at temperatures up to 500° C. The sorbents do not work effectively after regeneration using this technique; the problem may be that manganese sulfate formed during the sorption cycle does not completely decompose back to an active manganese oxide form.

U.S. Pat. No. 6,383,981 describes a fixed MnO₂ or Fe₂O₃ bed for removal of Hg from a hydrocarbon stream. No regeneration method appears to be included.

A recent U.S. Patent application (2001/0003116) describes the regeneration of a plate or honeycomb material composed of transition metal oxides that was used for sorption of mercury in flue gas. The claimed process involves heating the sorbent in a reducing gas stream to remove poisons, followed by impregnation with a polyfunctional complex-forming reagent containing the catalyst active component to restore mercury capture capacity. The first of these steps can remove the mercury, but it is unclear whether it actually removes the sulfate poison. The second of these steps is rather expensive, because one is actually reconstituting the reagent on the sorbent.

Porous beds containing a mercury oxidizing reagent on a solid support are described in several patents for removal of mercury from gas streams. These include peroxomonosulfate (for example, see U.S. Pat. No. 4,786,483), triiodide or other mixed halogens (for example, see U.S. Pat. Nos. 3,194,629; 3,662,523), or sulfur (for example, see U.S. Pat. Nos. 3,194,629, 4,101,631, 4,708,853, 6,258,334). The reagent material is destroyed either by reaction with the flue

US 10,668,430 B2

35

gas during sorption or by attempts to regenerate the sorbent; there is no way to regenerate these sorbents, except by reimpregnation of the expensive reagent.

Amalgamating noble metals (gold, silver) on a suitable support can be regenerated by microwave heating (for example, see U.S. Pat. No. 6,136,072), but they are expensive and not especially active for sorption in flue gas.

Hg Sorbents for Air or Natural Gas Treatment

Melkersson (U.S. Pat. No. 3,786,619) described a Hg sorbent comprising SeO_2 or SeS_2 for air treatment. This method did not appear to employ a carbon support or halide.

Yan (U.S. Pat. No. 4,814,152) described a Hg sorbent comprising elemental sulfur and a metal catalyst on a carbon support. This method did not appear to employ a halide.

Atia (U.S. Patent 65/080,281) described a sorbent for mercury and a variety of other contaminants comprising an inorganic aerogel composition. This method did not appear to employ a carbon support or halide.

FOLLOWING IS A LIST OF VARIOUS BACKGROUND REFERENCES

Lancia, A.; Musmarra, D.; Pepe, F.; Volpicelli, G. *Combust. Sci. & Technol.* 1993, 93, 277.

Streng, S.; Kassebohm, B. *Fuel Proc. Technol.* 1994, 39, 431.

U.S. Pat. No. 6,214,304 Rosenthal

U.S. Pat. No. 4,889,698 Moller

U.S. Pat. No. 4,956,162 Smith

U.S. Pat. No. 5,672,323 Bhat.

U.S. Pat. No. 5,827,352 Altman

U.S. Pat. No. 6,027,551 Hwang

U.S. Pat. No. 5,505,766 Chang

U.S. Pat. No. 5,607,496 Brooks

U.S. Pat. No. 6,383,981 Blankenship

U.S. Pat. No. 4,786,483 Audeh

U.S. Pat. No. 3,194,629 Dreibelbis, et al

U.S. Pat. No. 4,101,631 Ambrsini, et al

U.S. Pat. No. 3,662,523 Revoir

U.S. Pat. No. 4,708,853 Matviya

U.S. Pat. No. 6,258,334 Gadkaree

U.S. Pat. No. 6,136,072 Sjostrom

U.S. Patent Application 2002/0150516

U.S. Patent Application 2001/0003116 Neufert

The invention claimed is:

1. A method of separating mercury from a mercury-containing gas, the method comprising:

combusting coal in a combustion chamber, to provide the mercury-containing gas, wherein

the coal comprises an additive comprising Br_2 , HBr, a bromide compound, or a combination thereof, wherein the additive is added to the coal before the coal enters the combustion chamber, or

the combustion chamber comprises an additive comprising Br_2 , HBr, a bromide compound, or a combination thereof or

a combination thereof;

injecting a sorbent comprising activated carbon into the mercury-containing gas downstream of the combustion chamber;

contacting mercury in the mercury-containing gas with the sorbent; and

separating the sorbent contacted with the mercury from the mercury-containing gas.

2. The method of claim 1, wherein the coal comprises the additive comprising the Br_2 , HBr, the bromide compound, or

36

a combination thereof, wherein the additive is added to the coal before the coal enters the combustion chamber.

3. The method of claim 1, wherein the combustion chamber comprises the additive comprising the Br_2 , HBr, the bromide compound, or a combination thereof.

4. The method of claim 1, wherein the coal is combusted in the combustion chamber at a coal-combustion facility, wherein the additive comprising the Br_2 , HBr, bromide compound, or combination thereof, is added to the coal before the coal enters the combustion chamber, wherein the addition of the additive comprising the Br_2 , HBr, bromide compound, or combination thereof, to the coal is performed at the coal-combustion facility.

5. The method of claim 1, wherein the coal is combusted in the combustion chamber at a coal-combustion facility, wherein the additive comprising the Br_2 , HBr, bromide compound, or combination thereof, is added to the coal before the coal enters the combustion chamber, wherein the addition of the additive comprising the Br_2 , HBr, bromide compound, or combination thereof, to the coal is performed at a site other than the coal-combustion facility.

6. The method of claim 1, wherein the combustion chamber is an electric utility coal combustion chamber.

7. The method of claim 1, wherein the combustion chamber is a coal combustion furnace.

8. The method of claim 1, wherein the coal comprises a subbituminous coal.

9. The method of claim 1, wherein the coal comprises a lignite coal.

10. The method of claim 1, further comprising measuring the mercury content of the mercury-containing gas; and

modifying, in response to the measured mercury content of the mercury-containing gas,

an injection rate of injecting the sorbent into the mercury-containing gas,

an amount of the Br_2 , HBr, the bromide compound, or

a combination thereof, added to the coal or the combustion chamber, or

a combination thereof.

11. The method of claim 10, wherein the measuring of the mercury content comprises continuous measurement.

12. The method of claim 1, further comprising:

modifying, in response to a measured mercury content, an injection rate of injecting the sorbent into the mercury-containing gas,

an amount of the Br_2 , HBr, the bromide compound, or

a combination thereof, added to the coal or the combustion chamber, or

a combination thereof.

13. The method of claim 1, wherein the mercury-containing gas comprises about 1 g to about 30 g of the element bromine per 100 g of the sorbent.

14. The method of claim 1, wherein the sorbent contacted with the mercury comprises the element bromine and mercury.

15. The method of claim 1, comprising removing greater than 70 wt % of the mercury in the mercury-containing gas.

16. The method of claim 1, comprising removing greater than 70 wt % of the mercury in the mercury-containing gas with the sorbent.

17. The method of claim 1, wherein the sorbent in the mercury-containing gas comprises about 1 g to about 30 g of the added Br_2 , HBr, the bromide compound, or a combination thereof, per 100 g of the sorbent.

US 10,668,430 B2

37

18. The method of claim 1, wherein the Br₂, HBr, or the bromide compound is contacted with the sorbent in vapor form, gaseous form, liquid form, or in an organic solvent.

19. The method of claim 1, wherein the activated carbon comprises powdered activated carbon, granular activated carbon, or a combination thereof.

20. The method of claim 1, wherein the sorbent injected into the mercury-containing gas is a sorbent obtained by contacting a sorbent with a halogen or halide promoter prior to the injection of the sorbent into the mercury-containing gas.

21. The method of claim 1, wherein the sorbent injected into the mercury-containing gas is free of contact with a halogen or halide promoter prior to injection of the sorbent into the mercury-containing gas.

22. The method of claim 1, wherein the combustion chamber comprises a boiler.

23. The method of claim 1, wherein the mercury-containing gas is a flue gas.

24. The method of claim 1, wherein the injection of the sorbent into the mercury-containing gas occurs upstream of a particulate separator, a scrubber, or a combination thereof.

25. The method of claim 24, wherein the particulate separator comprises a baghouse, an electrostatic precipitator, a fabric filter, or a combination thereof.

26. The method of claim 1, wherein a halide sorbent enhancement additive comprises the added Br₂, HBr, bromide compound, or combination thereof.

27. The method of claim 26, wherein the sorbent enhancement additive comprises the bromide compound.

28. A method of separating mercury from a mercury-containing gas, the method comprising:

combusting coal in a combustion chamber, to provide the mercury-containing gas, wherein the mercury-containing gas comprises a halogen or halide promoter comprising HBr, Br⁻, or a combination thereof, wherein the coal comprises an additive comprising Br₂, HBr, a bromide compound, or a combination thereof, wherein the additive is added to the coal before the coal enters the combustion chamber, or

38

the combustion chamber comprises an additive comprising Br₂, HBr, a bromide compound, or a combination thereof, or a combination thereof,

injecting a sorbent comprising activated carbon into the mercury-containing gas downstream of the combustion chamber;

contacting mercury in the mercury-containing gas with the sorbent; and

separating the sorbent contacted with the mercury from the mercury-containing gas.

29. A method of separating mercury from a mercury-containing gas, the method comprising:

combusting coal in a combustion chamber, to provide the mercury-containing gas, wherein the mercury-containing gas comprises a halogen or halide promoter comprising HBr, Br⁻, or a combination thereof, wherein the coal comprises an additive comprising Br₂, HBr, a bromide compound, or a combination thereof, wherein the additive is added to the coal before the coal enters the combustion chamber, or

the combustion chamber comprises an additive comprising Br₂, HBr, a bromide compound, or a combination thereof, or

a combination thereof;

injecting a sorbent comprising activated carbon into the mercury-containing gas downstream of the combustion chamber such that the activated carbon reacts with the halogen or halide promoter in the mercury-containing gas to form a promoted sorbent;

contacting mercury in the mercury-containing gas with the promoted sorbent;

separating the promoted sorbent contacted with the mercury from the mercury-containing gas;

measuring the mercury content of the mercury-containing gas; and

modifying, in response to the measured mercury content, an injection rate of injecting the sorbent into the mercury-containing gas, an amount of the Br₂, HBr, the bromide compound, or a combination thereof, added to the coal or the combustion chamber, or a combination thereof.

* * * * *

EXHIBIT F

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Laplander
Page: 1 of 806

REFINED COAL SUPPLY AGREEMENT

by and between

BELLE RIVER FUELS COMPANY, LLC

and

THE DETROIT EDISON COMPANY

December 4, 2009

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 2 of 806

TABLE OF CONTENTS

	Page
ARTICLE I DEFINITIONS	1
Section 1.1. Definitions.....	1
Section 1.2. Construction of Certain Terms and Phrases.....	8
ARTICLE II REPRESENTATIONS AND WARRANTIES	9
Section 2.1. Representations and Warranties of Buyer.....	9
Section 2.2. Representations and Warranties of Seller.....	10
ARTICLE III TERM.....	10
Section 3.1. Term.....	10
ARTICLE IV AUTHORIZED REPRESENTATIVES	11
Section 4.1. Authorized Representatives.....	11
ARTICLE V PRODUCTION AND SALE OF REFINED COAL	11
Section 5.1. Production and Sale.....	11
Section 5.2. Sales to Third Parties.....	12
Section 5.3. Annual Forecasts; Adjustments.....	13
Section 5.4. Purchase by Buyer at Termination.....	13
Section 5.5. Consistent Reporting.....	13
ARTICLE VI PURCHASE AND SALES OF SELLER COAL	13
Section 6.1. Coal Purchase Contracts.....	13
Section 6.2. Available Seller Coal.....	14
Section 6.3. Purchase by Buyer at Termination.....	14
ARTICLE VII DELIVERIES; WEIGHTS; TITLE AND RISK OF LOSS	15
Section 7.1. Deliveries.....	15
Section 7.2. Weights.....	15
Section 7.3. Feedstock Inventory Store Reconciliation.....	16
Section 7.4. Measurement Methodology.....	17
Section 7.5. Title and Risk of Loss.....	17
ARTICLE VIII REFINED COAL AND RESOLD COAL SPECIFICATIONS	17
Section 8.1. Coal Specifications.....	17
Section 8.2. Refined Coal Production Specifications and Use.....	18
Section 8.3. Chemical Additives.....	18
Section 8.4. Presumption Regarding Conforming Coal and Refined Coal.....	19
Section 8.5. Warranty Disclaimer.....	19
ARTICLE IX PRICE; BILLING AND PAYMENT	20
Section 9.1. Refined Coal Price.....	20
Section 9.2. Resold Coal Price.....	20
Section 9.3. Coal Consultant Fee Reimbursement.....	20

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 3 of 806

Section 9.4.	O&M and Capital Cost Reimbursement	20
Section 9.5.	Invoicing and Payment.	21
Section 9.6.	Business Days.	23
Section 9.7.	Audit.	23
Section 9.8.	Taxes and Other Liabilities.	23
ARTICLE X	FORCE MAJEURE	23
Section 10.1.	Force Majeure.	23
ARTICLE XI	EARLY TERMINATION	24
Section 11.1.	Early Termination.	24
Section 11.2.	Post-Termination Obligations; Survival.	25
ARTICLE XII	EVENTS OF DEFAULT AND REMEDIES.....	25
Section 12.1.	Event of Default.	25
Section 12.2.	Remedies.	26
Section 12.3.	Limitations of Seller Liability.	27
ARTICLE XIII	DISPUTE RESOLUTION	27
Section 13.1.	Dispute Resolution.	27
ARTICLE XIV	MISCELLANEOUS	28
Section 14.1.	Terms and Conditions of Sale.	28
Section 14.2.	Confidentiality.	28
Section 14.3.	Required Disclosure.	29
Section 14.4.	Compliance with Laws and Governmental Approvals.	29
Section 14.5.	Entire Agreement; Successors and Assigns.	30
Section 14.6.	Notices.	30
Section 14.7.	Assignment.	31
Section 14.8.	Waiver; Invalidity.	31
Section 14.9.	Limitations of Liability and Exclusive Remedies.	31
Section 14.10.	Headings.	32
Section 14.11.	Counterparts.	32
Section 14.12.	Applicable Law.	32
Section 14.13.	Amendment.	32
Section 14.14.	No Third Party Beneficiary.	33

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 4 of 806

EXHIBITS

EXHIBIT A	Belle River Site
EXHIBIT B	Delivery Points
EXHIBIT C	Calculation of Detroit Edison Benefits
EXHIBIT D	Calculation of MPPA Benefits
EXHIBIT E	Operating Protocols

SCHEDULES

SCHEDULE 1.1(a)	Buyer Knowledge
SCHEDULE 1.1(b)	Seller Knowledge
SCHEDULE 2.1	Required Consents and Approvals

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Laplander
Page: 5 of 806

REFINED COAL SUPPLY AGREEMENT

THIS REFINED COAL SUPPLY AGREEMENT (this "Agreement"), is made and entered into as of December 4, 2009, (the "Effective Date"), by and between BELLE RIVER FUELS COMPANY, LLC, a Delaware limited liability company ("Seller"), and THE DETROIT EDISON COMPANY, a Michigan corporation ("Buyer") (Seller and Buyer each a "Party," and collectively, the "Parties").

RECITALS:

WHEREAS, Seller desires to provide refined coal produced at the Facility for use in Buyer's Belle River Power Plant; and

WHEREAS, Buyer desires to purchase all of the feedstock requirements for the Belle River Power Plant in the form of Refined Coal output of the Facility, and otherwise in the form of Resold Coal, as provided herein.

NOW, THEREFORE, in consideration of the mutual covenants, set forth in this Agreement, and for other good and valuable consideration, the receipt and sufficiency of which are hereby acknowledged, the Parties, intending to be legally bound, hereby agree as follows:

ARTICLE I DEFINITIONS

Section 1.1. Definitions.

The following terms, when used in this Agreement, have the following meanings:

"Acceptance Period Coal Inventory Purchase Agreement" means the Acceptance Period Coal Inventory Purchase Agreement, to be entered into on or about the Commercial Operations Date, by and between Detroit Edison and BR Fuels.

"Affiliate" of a specified Person means any Person that directly or indirectly through one or more intermediaries controls, is controlled by, or is under common control with, such specified Person. As used in this definition of Affiliate, the term "control" of a specified Person including, with correlative meanings, the terms, "controlled by" and "under common control with," means (a) the ownership, directly or indirectly, of 50 percent or more of the equity interest in a Person or (b) the power to direct or cause the direction of the management and policies of a Person, whether through ownership of voting securities, by contract or otherwise; provided, however, that notwithstanding the foregoing, for purposes of this Agreement, members of BR Fuels will be deemed to be an Affiliate of Seller, but, in no event will either Party be deemed to be an Affiliate of the other Party.

"Agreement" has the meaning given to such term in the introductory paragraph hereof.

"Authorized Representative" means the individual or individuals designated as such by each Party pursuant to Section 4.1.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 6 of 806

"Available Seller Coal" shall mean an amount of Conforming Coal that is in the Feedstock Inventory Store or in transit (or has been identified for delivery under a Coal Purchase Contract but is not yet in transit), in either case, as to which Seller has determined that is not needed as Feedstock.

"Back-Up Coal Purchase Contract" has the meaning given to such term in Section 6.1(b).

"Belle River Power Plant" means the two fossil fuel-fired steam electric generating units known as Belle River Unit No. 1 and Belle River Unit No. 2, each with a nominal rating of 650 megawatts, together with related facilities, located at the Belle River Site.

"Belle River Site" means that certain property located in St. Clair County, Michigan, on which the Belle River Power Plant is located, more particularly described on Exhibit A.

"BR Fuels" means Belle River Fuels Company, LLC, a Delaware limited liability company.

"Business Day" means any day other than Saturday, Sunday and any day that is a legal holiday or a day on which banking institutions in Michigan are authorized by law or governmental action to close.

"Buyer" has the meaning given such term in the introductory paragraph hereof.

"Buyer Annual Forecast" has the meaning given to such term in Section 5.3.

"Coal Consultant" has the meaning given to such term in the Coal Handling and Consulting Agreement.

"Coal Handling and Consulting Agreement" means the Coal Handling and Consulting Agreement, to be entered into on or about the Commercial Operations Date, by and between Detroit Edison and BR Fuels.

"Coal Consultant Fee" means the Coal Fee and the Coal Consultant Reimbursable Costs as defined in the Coal Handling and Consulting Agreement.

"Coal Inventory Price" means, for any given period, the per Ton amount derived by dividing (i) the sum of (A) the book value of the Seller Coal inventory at the beginning of the period (less the "Inventory Coal Purchase Price," as defined in the MPPA Coal Inventory Purchase Agreement), plus (B) the total quality adjusted cost of all Seller Coal purchased during such period (reflecting all quality and other allowances, adjustments and assessments under the applicable Coal Purchase Contract, all related Third Party Impositions that are imposed on Seller in this Agreement and transportation costs, and all other charges and costs relating to such period and charged to Seller Coal inventory in accordance with Seller's customary inventory accounting procedures consistently applied), by (ii) the sum of (A) the volume in Tons of Seller Coal inventory on hand at the beginning of the period, plus (B) the volume in Tons of Seller Coal inventory purchased during such period.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 7 of 806

"Coal Inventory Purchase Agreement" means the Coal Inventory Purchase Agreement, to be entered into on or about the Commercial Operations Date, by and between Detroit Edison and BR Fuels.

"Coal Purchase Contract" has the meaning given to such term in Section 6.1(a).

"Coal Specifications" means coal type, other specifications and price parameters for the coal that Seller is to use as Feedstock in the production of Refined Coal for sale to Buyer hereunder and that Seller is to sell to Buyer and to other parties to the extent so directed by Buyer as Resold Coal hereunder, as provided in Section 8.1.

"Code" means the Internal Revenue Code of 1986, as amended.

"Collective Coal Inventory Purchase Agreements" means, collectively, the Detroit Edison Coal Inventory Purchase Agreements and the MPPA Coal Inventory Purchase Agreement.

"Commercial Operations Date" has the meaning given to such term in the License Agreement.

"Conforming Coal" means Seller Coal that meets the Coal Specifications in effect at the time that the Coal Purchase Contract relating to such Seller Coal was entered into, and shall include, without limitation, Seller Coal presumed to be Conforming Coal pursuant to Section 8.4 hereof and/or pursuant to the Collective Coal Inventory Purchase Agreements.

"Contract" means any agreement, lease, license, evidence of indebtedness, indenture, or other contract (including any design, construction, equipment or other warranty or guarantee under any of the foregoing).

"Contract Year" means each calendar year during the Term of this Agreement, provided that: (a) the initial Contract Year shall commence on the Commercial Operations Date and shall end on December 31 of that year; and (b) the final Contract Year shall end on the date of termination or expiration of this Agreement and shall commence on the immediately preceding January 1.

"Delivery Point for Feedstock" means the point at transfer gate no. 03zm053 on feed conveyor CV 23 and at transfer gate no. 03zm054 on feed conveyor CV 24, designated as "Delivery Point for Feedstock" on Exhibit B hereto.

"Delivery Point for Resold Coal" means: (a) for Resold Coal that is in transit or that has been identified for delivery under a Coal Purchase Contract but is not yet in transit, the Point of Origin; and (b) for all other Resold Coal, the point at transfer gate no. 03zm053 on feed conveyor CV 23 and at transfer gate no. 03zm054 on feed conveyor CV 24, designated as "Delivery Point for Resold Coal" on Exhibit B hereto.

"Delivery Point for Refined Coal" means the point at which Refined Coal is discharged from the product conveyor extending from the discharge point of the Facility onto product

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Laplander
Page: 8 of 806

conveyors CV 19 and CV 20, designated as "Delivery Point for Refined Coal" on Exhibit B hereto.

"Detroit Edison" means The Detroit Edison Company, a Michigan corporation.

"Detroit Edison Benefits" means the amount equal to the sum of (i) the Detroit Edison FlyAsh Benefit, plus (ii) the Detroit Edison Mercury Benefit, plus (iii) the Detroit Edison SO₂ Benefit.

"Detroit Edison Coal Inventory Purchase Agreements" means (i) the Acceptance Period Coal Inventory Purchase Agreement, and (ii) the Coal Inventory Purchase Agreement.

"Detroit Edison Fly Ash Benefit" means the change in sales revenues and/or disposal expenses for the fly ash produced at the Belle River Power Plant while using Refined Coal as a fuel calculated in accordance with the formulas set forth in Exhibit C.

"Detroit Edison Mercury Benefit" means the benefits achieved as a result of reduced mercury emissions from the Belle River Power Plant while using Refined Coal as a fuel calculated in accordance with the formulas set forth in Exhibit C.

"Detroit Edison PA2 Expense Increase" means the increase in Detroit Edison's cost of purchasing power under PA2 power purchase agreements or any power purchase agreement entered into under the Public Utility Regulatory Policies Act of 1978, if any, that is due to Detroit Edison paying the Detroit Edison Refined Coal Adder calculated in accordance with the formulas set forth in Exhibit C.

"Detroit Edison Refined Coal Adder" means the amount calculated as set forth in Exhibit C.

"Detroit Edison Revenue Requirement" means Detroit Edison's share of BR Fuels' annual revenue requirements calculated in accordance with the formula set forth in Exhibit C.

"Detroit Edison SO₂ Benefit" means the benefits achieved as a result of reduced SO₂ emissions from the Belle River Power Plant while using Refined Coal as a fuel calculated in accordance with the formulas set forth in Exhibit C.

"Effective Date" has the meaning given to such term in the introductory paragraph hereof.

"Environmental Indemnity Agreement" means that certain Environmental Indemnity Agreement, dated as of August 24, 2009, by and between Detroit Edison and BR Fuels.

"Event of Default" has the meaning given to such term in Section 12.1.

"Event of Force Majeure" means any event beyond the reasonable control of the Party affected, including, without limitation, any act of God, strike, work stoppage or other labor disturbance, shortage of supplies, parts, materials, rail cars, barges or other freight transport vehicles customarily used, breakdowns or damage to or destruction of the Facility, the Belle

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Laplander
Page: 9 of 806

River Power Plant, the St. Clair Power Plant or any part thereof or to plants or other facilities (including a forced outage or an extension of a scheduled outage of the Facility, the Belle River Power Plant, the St. Clair Power Plant or such plants, equipment or facilities to make repairs to avoid breakdowns thereof or damage thereto), act of public enemy, act of terrorism, war, blockade, riot, public unrest, lightning, fire, violent storm, flood, frozen river, canal, channel or lake, unforeseeable geological condition, drought, unusually severe weather conditions, explosion, government order or restraint, or other cause or event, whether of a similar or dissimilar nature, which, in the case of any of the foregoing: (a) could not have been reasonably anticipated by the affected Party, and (b) cannot be reasonably avoided or circumvented by the affected Party.

"Excess Amount" has the meaning given to such term in Section 7.3.

"Facility" means the refined coal production facility, comprised of one or more production lines, to be constructed and owned by BR Fuels to be located at the Belle River Site.

"Feedstock" means coal utilized as feedstock by the Facility for the production of Refined Coal.

"Feedstock Inventory Store" means the Seller Coal deposited and present in the areas identified as "Coal Yard" and on all interconnecting conveyors shown in Exhibit B hereto (prior to crossing either the Delivery Point for Resold Coal or the Delivery Point for Feedstock, each as identified on Exhibit B hereto).

"Follow-up Period" means the period commencing at the expiration of the Initial Acceptance Period and ending at the later of (i) the expiration of 60 days or such other period as agreed upon by the Parties, or (ii) such time as the reasonable determination is made by Buyer, after prompt review and analysis of the operating data and information relating to the use of Refined Coal during the Initial Acceptance Period, that use of Refined Coal at the Belle River Power Plant will not likely result in a Reduction Event.

"Governmental Approvals" means any authorization, consent, concession, license, certificate, permit, waiver, privilege or approval from, or filing with, or notice to, any Governmental Body.

"Governmental Body" means the federal government of the United States, any state of the United States or political subdivision thereof, and any entity exercising executive, legislative, judicial, regulatory or administrative functions of or pertaining to government and any other governmental entity, instrumentality, agency, authority or commission.

"Increased Expenses" has the meaning given to such term in Section 9.4.

"Initial Acceptance Period" means the period commencing on the Commercial Operations Date and ending at the later of (i) the expiration of 75 days following the Commercial Operations Date, or (ii) the last of 60 consecutive days during which the Facility is in operation with at least 90 percent availability (or such lesser percentage determined by reducing 90 percent as necessary to reflect any reduction in the production and supply of Refined Coal as directed by

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 10 of 806

Buyer (except by reason of a Reduction Event)), as such availability is measured on a calendar week basis.

“Initial Term” has the meaning given to such term in Section 3.1.

“Knowledge” means, as to Buyer, the actual knowledge, after due inquiry, of those persons identified on Schedule 1.1(a) and, as to Seller, the actual knowledge, after due inquiry, of those persons identified on Schedule 1.1(b).

“Late Payment Rate” means a rate of interest per annum equal to the lesser of: (a) as to each applicable day, the most recent published prime rate, as reported in *The Wall Street Journal* (Eastern Edition) under “Money Rates” or, if such rate does not so appear, in such other nationally recognized publication as Seller may, from time to time, specify to Buyer; or (b) the maximum rate of interest permitted by applicable Law.

“Law” means any law (including common law), statute, act, decree, ordinance, rule, directive (to the extent having the force of law), order, treaty, code or regulation (including any of the foregoing relating to health and safety matters) or any interpretation of any of the foregoing, as enacted, issued or promulgated by any Governmental Body, including all amendments, modifications, extensions, replacements or re-enactments thereof.

“License Agreement” means that certain License and Services Agreement, dated as of August 24, 2009, by and among BR Fuels, Detroit Edison and MPPA.

“Mer-Sorb” is a chemical additive identified in the patents listed in the Amended and Restated License Agreement, dated January 23, 2009, between Chem-Mod LLC and DTE Energy Resources, Inc.

“MPPA” means Michigan Public Power Agency, a public body politic and corporate organized pursuant to Act 448, Public Acts of Michigan 1976.

“MPPA Benefits” means the amount equal to the sum of (i) the MPPA FlyAsh Benefit, plus (ii) the MPPA Mercury Benefit, plus (iii) the MPPA SO₂ Benefit.

“MPPA Coal Inventory Purchase Agreement” means the Coal Inventory Purchase Agreement, to be entered into on or about the Commercial Operations Date, by and between BR Fuels and MPPA.

“MPPA Fly Ash Benefit” means the change in sales revenues and/or disposal expenses for the fly ash produced at the Belle River Power Plant while using Refined Coal as a fuel calculated in accordance with the formulas set forth in Exhibit D.

“MPPA Mercury Benefit” means the benefits achieved as a result of reduced mercury emissions from the Belle River Power Plant while using Refined Coal as a fuel calculated in accordance with the formulas set forth in Exhibit D.

“MPPA Refined Coal Adder” means the lesser of the MPPA Benefits or the MPPA Revenue Requirement.

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Laplander

Page: 11 of 806

"MPPA Revenue Requirement" means MPPA's share of BR Fuels' annual revenue requirements calculated in accordance with the formula set forth in Exhibit D.

"MPPA SO₂ Benefit" means the benefits achieved as a result of reduced SO₂ emissions from the Belle River Power Plant while using Refined Coal as a fuel calculated in accordance with the formulas set forth in Exhibit D.

"NIST" means the National Institute of Standards and Technology.

"Operating Protocols" means those certain operating protocols and procedures set forth as Exhibit E.

"Party" and **"Parties"** have the meanings given to such terms in the introductory paragraph hereof.

"Person" means any corporation, limited liability company, any form of partnership, any joint venture, trust, estate, Governmental Body, or other legal or commercial entity or any natural person.

"Point of Origin" means the location where the Seller Coal is loaded into a railcar (or other form of transport), FOB, for transport to Seller at the Belle River Site or to any other site designated by Buyer.

"Project Documents" means: (a) this Agreement, (b) the Coal Handling and Consulting Agreement, (c) the License Agreement, (d) the Detroit Edison Coal Inventory Purchase Agreements, (e) the MPPA Coal Inventory Purchase Agreement, (f) the Environmental Indemnity Agreement, (g) the Memorandum of Understanding with respect to the Participation Agreement, to be entered into on or about the Commercial Operations Date, by and between MPPA and Detroit Edison, (h) the St. Clair Supply Agreement and (i) the other documents, agreements, certificates and instruments executed or entered into by and between (i) BR Fuels and MPPA and Detroit Edison, (ii) BR Fuels and Detroit Edison, and (iii) BR Fuels and MPPA in connection with the transactions contemplated thereby; provided that, in the case of clause (iii), Detroit Edison has received notice of and approved any such documents, agreements, certificates and instruments, such approval not to be unreasonably withheld.

"Reduction Event" has the meaning given to such term in Section 5.1(b).

"Refined Coal" means the refined coal product produced by Seller for sale to Buyer pursuant to this Agreement.

"Refined Coal Price" means the per Ton amount equal to the sum of (i) the Coal Inventory Price, plus (ii) the Detroit Edison Refined Coal Adder, plus (iii) the MPPA Refined Coal Adder.

"Renewal Term" has the meaning given to such term in Section 3.1.

"Resold Coal" means Available Seller Coal sold hereunder to Buyer or to third parties as directed by Buyer.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 12 of 806

"Resold Coal Price" has the meaning given to such term in Section 9.2.

"S-Sorb III" is a chemical additive identified in the patents listed in the Amended and Restated License Agreement, dated January 23, 2009, between Chem-Mod LLC and DTE Energy Resources, Inc.

"Section 45 Tax Credits" means the credits against federal income tax available under Section 45 of the Code or any successor provision.

"Seller" has the meaning given to such term in the introductory paragraph hereof.

"Seller Coal" means coal purchased by Seller pursuant to a Coal Purchase Contract.

"Shortfall Amount" has the meaning given to such term in Section 7.3.

"St. Clair Fuels" means St. Clair Fuels Company, LLC, a Delaware limited liability company.

"St. Clair Power Plant" means the fossil fuel-fired steam electric generating facility located at the St. Clair Site.

"St. Clair Site" means that certain property located in St. Clair County, Michigan adjacent to the Belle River Site, on which the fossil fuel-fired steam electric generating facility known as the St. Clair Power Plant is owned and operated by Detroit Edison.

"St. Clair Supply Agreement" means the St. Clair Supply Agreement, to be entered into on or about the Commercial Operations Date, by and between St. Clair Fuels and BR Fuels.

"Term" means, collectively, the Initial Term and any Renewal Term.

"Third Party Impositions" has the meaning given to such term in Section 9.7.

"Ton" means two thousand (2,000) pounds avoirdupois weight.

"Unloaded Weight" means the weight of the Seller Coal as documented by the supplier under the applicable Coal Purchase Contract.

Section 1.2. Construction of Certain Terms and Phrases.

Unless the context of this Agreement otherwise requires: (a) words of either gender include the other gender; (b) words using the singular or plural also include the plural or singular, respectively; (c) the terms "hereof," "herein," "hereby," "hereto" and similar words refer to this entire Agreement and not any particular Article, Section, Clause, Exhibit, Appendix or Schedule or any other subdivision of this Agreement; (d) references to "Article," "Section," "Clause," "Exhibit," "Appendix" or "Schedule" are to the Articles, Sections, Clauses, Exhibits, Appendices and Schedules, respectively, of this Agreement; (e) the words "include" or "including" shall be deemed to be followed by "without limitation" or "but not limited to" whether or not they are followed by such phrases or words of like import; and (f) references to

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Laplander
Page: 13 of 806

"this Agreement" or any other agreement or document shall be construed as a reference to such agreement or document, including any Exhibits, Appendices, Attachments and Schedules thereto, as amended, modified or supplemented and in effect from time to time and shall include a reference to any document that amends, modifies or supplements it, or is entered into, made or given pursuant to or in accordance with its terms. Whenever this Agreement refers to a number of days, such number shall refer to calendar days unless Business Days are specified. All accounting terms used herein and not expressly defined herein shall have the meanings given to them under generally accepted accounting principles as promulgated by the Financial Accounting Standards Board and as in effect on the Effective Date.

ARTICLE II REPRESENTATIONS AND WARRANTIES

Section 2.1. Representations and Warranties of Buyer.

Buyer hereby represents and warrants as of the date hereof as follows:

- (a) except as set forth in Schedule 2.1, Buyer's execution and delivery of, and performance under, this Agreement have been duly authorized and do not violate or conflict with any charter, bylaw, Law, Contract, permit or obligation applying to Buyer, the Belle River Power Plant or the Belle River Site, other than such violations or conflicts that would not reasonably be expected to have a material adverse effect on Buyer's ability to perform its obligations under this Agreement;
- (b) except as set forth in Schedule 2.1, this Agreement constitutes a legal, valid and binding contractual obligation of Buyer, enforceable against Buyer in accordance with its terms, except as such enforceability may be limited by applicable bankruptcy, insolvency, reorganization and similar laws affecting the enforcement of creditors' rights generally;
- (c) except as set forth in Schedule 2.1, no permit from, notice to, or consent, approval, authorization or order of any court or other Governmental Body or third party not already given or obtained is required with respect to Buyer in connection with its execution and delivery of, and performance under, this Agreement, including, without limitation, Buyer's purchase, transportation, handling and use of Refined Coal and coal as fuel at the Belle River Power Plant;
- (d) Buyer is validly existing and in good standing under the laws of the State of Michigan and is authorized to do business in each jurisdiction necessary for it to perform its obligations under this Agreement, and Buyer has the right, power and authority, to enter into this Agreement and to perform its obligations hereunder; and
- (e) there is no pending or, to Buyer's Knowledge, threatened action, suit, investigation, arbitration or other proceeding against Buyer that, if adversely determined, would reasonably be expected to have a material adverse effect on the ability of Buyer to perform its obligations under this Agreement.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 14 of 806

Section 2.2. Representations and Warranties of Seller.

Seller hereby represents and warrants as of the date hereof as follows:

- (a) Seller's execution and delivery of, and performance under, this Agreement have been duly authorized and do not violate or conflict with any charter, bylaw, Law, Contract, permit or obligation applying to Seller, other than such violations and conflicts that would not reasonably be expected to have a material adverse effect on Seller's ability to perform its obligations under this Agreement;
- (b) this Agreement constitutes a legal, valid and binding obligation of Seller, enforceable against Seller in accordance with its terms, except as such enforceability may be limited by applicable bankruptcy, insolvency, reorganization and similar laws affecting the enforcement of creditors' rights generally;
- (c) no permit from, notice to, or consent, approval, authorization or order of any court or other Governmental Body or third party not already given or obtained is required with respect to Seller in connection with its execution and delivery of, and performance under, this Agreement, other than any such permit, notice, consent, approval authorization or order required for the construction and operation of the Facility;
- (d) Seller is validly existing and in good standing under the laws of the State of Delaware and is authorized to do business in each jurisdiction necessary for it to perform its obligations under this Agreement, and Seller has the right, power and authority to enter into this Agreement and perform its obligations hereunder; and
- (e) there is no pending or, to Seller's Knowledge, threatened action, suit, investigation, arbitration or other proceeding against Seller, that, if adversely determined, would reasonably be expected to have a material adverse effect on the ability of Seller to perform its obligations under this Agreement.

**ARTICLE III
TERM**

Section 3.1. Term.

Subject to Section 11.1, the term of this Agreement will commence on the Effective Date and will end on the tenth anniversary of the Commercial Operations Date (the "Initial Term"). This Agreement shall automatically renew for one additional five-year period thereafter (the "Renewal Term"), unless one Party provides to the other Party, at least 90 days prior to the expiration of the Initial Term, written notice of its election that this Agreement not be renewed beyond the Initial Term.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 15 of 806

ARTICLE IV AUTHORIZED REPRESENTATIVES

Section 4.1. Authorized Representatives.

The initial Authorized Representative of Seller is Katherine A. Panczak. The initial Authorized Representative of Buyer is Patrick J. Temple. Each Party shall be entitled to rely upon any instructions or information given or provided by the Authorized Representative of the other Party (or any one designated individual if more than one individual is designated as such other Party's Authorized Representative), but no Authorized Representative shall have authority under this Section 4.1 to modify or amend this Agreement. Each Party shall have the right to revoke any appointment of any individual or individuals who had been appointed to act as its Authorized Representative with such revocation being effective upon receipt by the other Party of the notice provided for in the following sentence. Each Party shall give to the other Party written notice of any such revocation of appointment and of the appointment of a new individual or individuals to act as its Authorized Representative.

ARTICLE V PRODUCTION AND SALE OF REFINED COAL

Section 5.1. Production and Sale.

(a) During each Contract Year, in accordance with the terms of, and except as otherwise provided in, this Agreement, (i) Buyer shall procure and purchase from Seller all of its requirements for coal and coal-based fuel at the Belle River Power Plant (other than any coal purchased by Buyer under a Back-Up Coal Purchase Contract in accordance with Section 6.1(c)), and (ii) Seller shall use commercially reasonable efforts, in accordance with the Operating Protocols, to produce and sell to Buyer Refined Coal in amounts necessary to satisfy Buyer's requirements for coal and coal-based fuel at the Belle River Power Plant, and (iii) to the extent that such requirements are not fully satisfied by such Refined Coal as described in clause (ii), including without limitation, during a suspension event under the provisions of Sections 5.1(c), 8.2(c) and 9.4, Seller shall sell to Buyer (and Buyer shall purchase) Available Seller Coal, in amounts necessary to satisfy such requirements, as Resold Coal.

(b) Buyer's purchase of Refined Coal pursuant to this Section 5.1 shall be reduced to the extent necessary (i) to prevent damage (other than normal wear and tear that would be caused by the exclusive use of coal (other than Refined Coal) as fuel at the Belle River Power Plant) to the boilers, pollution control equipment or other operating components that comprise the Belle River Power Plant that would be caused by the use of Refined Coal as a fuel at the Belle River Power Plant, or (ii) to prevent material impairment to or a material adverse effect on the operation and maintenance of the boilers, pollution control equipment or other operating components that comprise the Belle River Power Plant or (iii) to prevent the violation of any permit or Governmental Approval (any of the foregoing circumstances described in clauses (i), (ii) and (iii) being referred to as a "Reduction Event") and, to the extent that Buyer's requirements are not fully satisfied by Refined Coal, Seller shall sell to Buyer (and Buyer shall purchase) Available Seller Coal, in amounts necessary to satisfy such requirements, as Resold Coal. The determination of a Reduction Event shall be made by Buyer in its good faith

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 16 of 806

discretion. Buyer shall notify Seller promptly when Buyer determines that a Reduction Event has occurred. The Reduction Event will terminate when the circumstances bringing rise to the Reduction Event are resolved or mitigated as agreed by Buyer and Seller in accordance with Section 5.1(d). The reduction of Buyer's purchase of Refined Coal due to a Reduction Event shall be of no greater scope and no longer duration than that which is necessary by reason of the Reduction Event.

(c) During the Follow-up Period, unless and until otherwise agreed by the Parties, each Party's obligations under Section 5.1(a) will be suspended to provide the Parties time to review and analyze operating data and other information relating to the use by Buyer of Refined Coal as fuel at the Belle River Power Plant during the Initial Acceptance Period. During the Follow-up Period, Buyer shall have the right, but not the obligation, to purchase Available Seller Coal as Resold Coal from Seller as set forth in Section 5.1(a).

(d) During any Reduction Event, as soon as it is reasonably available, Buyer will provide Seller with all information regarding the cause of the Reduction Event and other operating data and other information relating to the use of Refined Coal, and Buyer and Seller will cooperate, discuss and negotiate in good faith to develop and agree upon any price adjustments or other remedial actions to avoid or limit the circumstances leading to the Reduction Event and otherwise to improve, optimize and maximize the use of Refined Coal as a fuel at the Belle River Power Plant on a going-forward basis. Examples of possible remedial actions include, without limitation, capital improvements to the Facility or the Belle River Power Plant, resetting chemical additive levels as provided in Section 8.3(a), and resetting Buyer's requirements for Refined Coal at a quantity less than 100 percent of its coal-based fuel requirements for the Belle River Power Plant. Notwithstanding the foregoing, neither Party shall be required hereunder to agree to any remedial action that would require it to incur additional costs or expenditures. In addition, Seller need not agree to any remedial action (and may terminate any remedial action agreed to) that Seller believes in its sole discretion, could impair or jeopardize the ability of the Refined Coal to qualify for Section 45 Tax Credits.

(e) At any time that Seller fails to satisfy Buyer's requirements for coal or coal-based fuel at the Belle River Plant as required by Section 5.1(a), and Seller fails to deliver Resold Coal in accordance with Section 5.1(a), then, upon notice by telephone to Seller, Buyer shall have the right to cause transfer gates on the product conveyors extending from the Coal Yard to be switched such that Available Seller Coal bypasses the Facility and is delivered directly to the Delivery Point for Resold Coal for sale to and purchase by Buyer as Resold Coal and to maintain such transfer gate positions until such time as Seller provides to Buyer reasonably adequate assurances of Seller's ability to perform in accordance with Section 5.1(a).

(f) Notwithstanding the foregoing, nothing contained in this Article V will prevent Buyer from discontinuing or reducing operation of one or both of the generating units at the Belle River Power Plant prior to the end of the Term.

Section 5.2. Sales to Third Parties.

Any Refined Coal produced at the Facility and not purchased by Buyer, for any reason, may be sold by Seller to third parties or otherwise disposed of subject to compliance with

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 17 of 806

applicable existing permits, Coal Purchase Contracts and coal transportation agreements. This Section 5.2 is not intended and shall not be construed to limit any remedies available to Seller hereunder or under applicable Law.

Section 5.3. Annual Forecasts; Adjustments.

For each Contract Year during the Term, Buyer shall provide Seller with a good faith projection (the "Buyer Annual Forecast") of the aggregate quantity of Refined Coal and Resold Coal it expects to require during each month of such Contract Year pursuant to the terms of this Agreement. The Buyer Annual Forecast for the initial Contract Year shall be provided no later than the 30th day following the Commercial Operations Date. Each succeeding Buyer Annual Forecast shall be delivered no later than October 1 preceding the start of such Contract Year. Buyer shall update such forecast on a monthly basis to reflect any change in Buyer's projections. Buyer shall provide any such amendment to Seller no less than 15 Business Days before the first Business Day of each such month. The Buyer Annual Forecast is to be used solely for informational purposes.

Section 5.4. Purchase by Buyer at Termination.

On the last day of the Term, to the extent it has not already done so, Buyer shall purchase, and Seller shall sell to Buyer, all Refined Coal on hand.

Section 5.5. Consistent Reporting.

Notwithstanding the means of sourcing fuel for the Belle River Power Plant prior to the Commercial Operations Date, Buyer covenants and agrees that it will not, and it will cause its Affiliates not to, make or give any filing, return, ruling request, representation, allegation, notice or report with or to any Governmental Body or court that contains, or otherwise presents in accounting or financial records, reports or statements, or tax or information returns, characterizations of the transactions (or elements thereof) contemplated by the various Project Documents that are inconsistent with the terms of such Project Documents, such as (by way of example and not limitation) any characterization that Feedstock purchased by Seller under applicable Coal Purchase Contracts was purchased by Buyer or any other Person, or that Refined Coal sold to Buyer hereunder was something other than Refined Coal.

**ARTICLE VI
PURCHASE AND SALES OF SELLER COAL**

Section 6.1. Coal Purchase Contracts.

(a) It is contemplated that Seller, directly or through an Affiliate, will enter into one or more contracts with third-party coal suppliers to purchase coal conforming to the Coal Specifications for use as Feedstock and for sale to Buyer, or others designated by Buyer, as provided herein (each, a "Coal Purchase Contract").

(b) It is further contemplated that included among the Coal Purchase Contracts will be purchase contracts that Buyer has in place with coal suppliers on the

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 18 of 806

Commercial Operations Date and that are to be assigned in whole or in part to Seller pursuant to the Coal Inventory Purchase Agreement.

(c) For each Coal Purchase Contract entered into by Seller, Buyer may, but shall not be obligated to, enter into and maintain a back-up Contract to purchase coal from the same third-party coal supplier on terms substantially similar to the terms contained in the corresponding Coal Purchase Contract, including, without limitation, the quantity of coal to be purchased thereunder, except that Buyer's obligation to purchase a quantity of coal thereunder shall be reduced by the quantity of coal purchased by Seller under the corresponding Coal Purchase Contract (each, a "Back-Up Coal Purchase Contract").

(d) Notwithstanding anything to the contrary herein but subject to the provisions of Sections 5.1(e), 8.2(c) and 9.4, Buyer's sole remedies for Seller's failure to produce and sell Refined Coal hereunder shall be to: (i) purchase Resold Coal pursuant to Section 5.1 and to purchase coal under the Back-Up Coal Purchase Contracts; and (ii) terminate this Agreement in accordance with Section 11.1(f).

Section 6.2. Available Seller Coal.

(a) At any point in time, to the extent that Seller has Available Seller Coal, Buyer may request to purchase, and upon such request Seller will sell to Buyer, or to others to the extent so directed by Buyer, all (or such portion requested by Buyer) of such Available Seller Coal as Resold Coal at the applicable Resold Coal Price and otherwise as provided herein; provided, however, that, as to any Available Seller Coal that is to be sold to others or shipped for use at a location or facility other than the Belle River Power Plant or St. Clair Power Plant, Seller's obligation to sell such Available Seller Coal shall be subject to receiving Buyer's undertaking to replace or cause to be replaced by arranging for one or more Coal Purchase Contracts for Conforming Coal, and providing for delivery in such a manner that Seller's Feedstock requirements for production of Refined Coal, and its Refined Coal production schedule, will not be impaired.

(b) At any point in time, to the extent that Seller has Available Seller Coal, Seller may request that Buyer purchase all or a portion of such Available Seller Coal, and upon such request, Buyer will purchase and Seller will sell to Buyer, or to others to the extent so directed by Buyer, such Available Seller Coal (or the applicable portion thereof) as Resold Coal at the applicable Resold Coal Price and otherwise as provided herein, it being agreed, for the avoidance of doubt, that Seller's exercise of such right shall not cause to arise an obligation by Buyer to replace Conforming Coal under Section 6.2(a).

Section 6.3. Purchase by Buyer at Termination.

At the end of the Term, Buyer shall purchase, and Seller shall sell to Buyer, all Conforming Coal on hand or under contract as Resold Coal. To the extent that there is any Coal Purchase Contract in place at the end of the Term which, by its terms, obligates Seller to purchase Conforming Coal for a period extending beyond the end of the Term, each Party agrees that Seller will assign such Coal Purchase Contract to Buyer and Buyer will assume Seller's rights and obligations thereunder. To the extent any such Coal Purchase Contract is not able to

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 19 of 806

be so assigned, following the end of the Term, Seller shall sell and Buyer shall purchase Conforming Coal as Resold Coal in accordance with the terms and conditions hereof until the applicable Coal Purchase Contract expires or otherwise terminates.

ARTICLE VII DELIVERIES; WEIGHTS; TITLE AND RISK OF LOSS

Section 7.1. Deliveries.

- (a) Refined Coal deliveries will be made at the Delivery Point for Refined Coal based on Buyer's requirements for use of Refined Coal as fuel in the Belle River Power Plant.
- (b) Deliveries of Available Seller Coal will be made at the applicable Delivery Point for Resold Coal as specified herein, and, assuming timely performance by third parties under the Coal Purchase Contracts and by the Coal Consultant under the Coal Handling and Consulting Agreement and except as may be otherwise agreed by the Parties, such deliveries will be made based on Buyer's, or others' to the extent so directed by Buyer, requirements for use of Available Seller Coal as fuel.

Section 7.2. Weights.

- (a) The weight of Refined Coal sold to Buyer hereunder during any applicable period will be established by weights of Feedstock measured by Buyer's belt scales located on product conveyors CV 23 and CV 24, plus an agreed upon allowance for the chemical additive used in the Refined Coal production process.
- (b) The weight of Resold Coal sold to Buyer hereunder during any applicable period will be established by weights of Resold Coal measured by Buyer's belt scales located on product conveyors CV 23 and CV 24.
- (c) Buyer shall maintain and preserve, during the Term and for at least six months after any termination of this Agreement, records of all weights taken under this Section 7.2 and shall maintain the scales as provided below:
 - (i) At least once each calendar year, the accuracy of the scales shall be maintained, tested and, if necessary, adjusted, in accordance with the guidelines outlined by the NIST Handbook #44, or other procedures which shall be mutually acceptable to Seller and Buyer and in accordance with applicable Law. If any such test shows the scales to be in error, Buyer shall cause them to be adjusted to within the tolerance specifications as designated by the scale manufacturer;
 - (ii) Buyer shall give prompt notice by telephone (and confirm such notice in writing or by email or facsimile) to Seller the results of any testing and adjustment of the scales, and otherwise if and when the scales are discovered to be in error beyond the tolerance specifications as designated by the scale manufacturer;

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Laplander

Page: 20 of 806

(iii) Seller shall have the right, but not the duty, to have a representative present at any and all times to observe the determination of weights hereunder. In addition to the testing described in Section 7.2(c)(i), if Seller should at any time question the accuracy of the scales, Seller shall so advise Buyer and confirm the same in writing, and Buyer shall promptly arrange testing of the scales. If such test shows the scales to be in error, Buyer shall cause them to be adjusted to within the tolerance specifications as designated by the scale manufacturer. If such test prompted by Seller pursuant to this Section 7.2(c)(iii) shows the scale to be within the applicable tolerance specifications, then Seller shall pay all costs of such test. Otherwise, Buyer shall pay all costs of maintaining, testing and adjusting the scales hereunder.

(d) During any period when the scales are inoperable, determination of the quantities of Refined Coal and Resold Coal delivered hereunder shall be determined by a procedure to be established at such time by agreement of Seller and Buyer and in accordance with applicable Law.

Section 7.3. Feedstock Inventory Store Reconciliation.

(a) On a quarterly basis, the Coal Consultant shall cause to be performed a physical inventory survey of the Feedstock Inventory Store. Promptly thereafter, a reconciliation of the Feedstock Inventory Store will be made, and the actual weight of Resold Coal sold from the Feedstock Inventory Store, and of Feedstock from the Feedstock Inventory Store used to produce Refined Coal, during such quarter will be determined, based on: (i) the Feedstock Inventory Store as measured on such date; (ii) the Feedstock Inventory Store as measured at the end of the prior quarter; (iii) the record of the Unloaded Weight of Seller Coal unloaded at the Belle River Site during the quarter; (iv) the record of the weight of Resold Coal moved from the Feedstock Inventory Store, as determined pursuant to Section 7.2(b), during the quarter; and (v) the record of the weight of Feedstock used to produce Refined Coal sold to Buyer, as determined pursuant to Section 7.2(a), during the quarter. To the extent that the sum of: (i) the Feedstock Inventory Store as measured at the end of the prior quarter; and (ii) the Unloaded Weight of Seller Coal unloaded at the Belle River Site during the quarter, exceeds the sum of: (x) the Feedstock Inventory Store on the measurement date; (y) the weight of Resold Coal moved from the Feedstock Inventory Store, as determined pursuant to Section 7.2(b), during the quarter; and (z) the weight of Feedstock used to produce Refined Coal sold to Buyer, as determined pursuant to Section 7.2(a), during the quarter, the difference (the "Excess Amount") shall be attributable to Resold Coal sold to Buyer and Feedstock used to produce Refined Coal sold to Buyer, in the same proportions as reflected in clauses (y) and (z) above, and the sum of such Excess Amount and the weights described in clauses (y) and (z) above will constitute the actual weight of Resold Coal sold, and Feedstock used, from the Feedstock Inventory Store during such quarter. Seller will invoice Buyer for such Excess Amount using the Coal Inventory Price and the Resold Coal Price, as applicable, on the date the Excess Amount is recorded by Seller as a reduction of Feedstock Inventory Store, and Buyer will make payment, for such Excess Amount in accordance with Article IX. To the extent that the sum of: (i) the Feedstock Inventory Store as measured at the end of the prior quarter; and (ii) the Unloaded Weight of Seller Coal unloaded at the Belle River Site during the quarter, is less than the sum of: (x) the Feedstock Inventory Store on the measurement date; (y) the weight of Resold Coal moved from the Feedstock Inventory Store, as determined pursuant to Section 7.2(b), during the quarter; and (z) the weight of Feedstock used to produce Refined Coal sold to Buyer, as determined pursuant

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Laplander
Page: 21 of 806

to Section 7.2(a), during the quarter, the deficiency (the "Shortfall Amount") shall be attributable to Resold Coal purchased by Buyer and Feedstock used to produce Refined Coal sold to Buyer, in the same proportions as reflected in clauses (y) and (z) above, and, in such case, Seller will credit Buyer for such Shortfall Amount in accordance with Article IX using the Coal Inventory Price and the Resold Price, as applicable, on the date the Shortfall Amount is recorded by Seller as an increase in Feedstock Inventory Store. For purposes of this Section 7.3, in the case of the first quarter (or partial quarter, as the case may be) following the closing date under the Coal Inventory Purchase Agreement, all references herein to "the Feedstock Inventory Store as measured at the end of the prior quarter" shall mean the aggregate tonnage purchased under the Collective Coal Inventory Purchase Agreements. The costs of taking such physical inventories shall be borne by Buyer.

(b) In addition to the reconciliation of the Feedstock Inventory Store, the Coal Consultant shall cause to be performed a physical survey of Seller's inventory located at the Superior Midwest Energy Terminal annually. The survey shall be performed during either October or November of each Contract Year. Buyer shall provide Seller with the results of the physical survey on or about December 15 of each year during Term. Seller will adjust its inventory using the results of the survey before December 31 of the Contract Year.

Section 7.4. Measurement Methodology.

Notwithstanding Sections 7.2 and 7.3, Buyer shall have the right to increase the frequency of scale testing to a quarterly basis. If Buyer elects to increase scale testing to a quarterly basis, Seller shall direct the Coal Consultant to adjust the frequency of the Feedstock Inventory Store reconciliation to an annual basis.

Section 7.5. Title and Risk of Loss.

(a) Title and risk of loss, damage or destruction with respect to the Refined Coal sold hereunder will pass to Buyer at the Delivery Point for Refined Coal.

(b) Title and risk of loss, damage or destruction with respect to the Resold Coal sold hereunder will pass to Buyer at the applicable Delivery Point for Resold Coal.

ARTICLE VIII REFINED COAL AND RESOLD COAL SPECIFICATIONS

Section 8.1. Coal Specifications.

Buyer will specify to Seller the initial Coal Specifications upon request by Seller, and will subsequently, from time to time during the Term as requested by Seller, confirm the Coal Specifications then in effect. During the Term, Buyer may change the Coal Specifications from time to time. Notification of any such change shall be made in writing to Seller and to the Coal Consultant.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 22 of 806

Section 8.2. Refined Coal Production Specifications and Use.

- (a) Refined Coal produced and sold to Buyer hereunder shall be produced from Feedstock that was purchased pursuant to a Coal Purchase Contract and was Conforming Coal at the time delivered to the Belle River Site.
- (b) Seller hereby covenants and warrants that Refined Coal produced and sold to Buyer hereunder shall be produced in accordance with the Operating Protocols.
- (c) During any time that Seller is delivering Refined Coal without complying with the Operating Protocols:
- (i) Buyer shall have the right to suspend immediately all deliveries of Refined Coal by giving notice of the suspension to Seller. Such suspension shall remain in effect until such time as Seller provides to Buyer reasonably adequate assurances of Seller's ability and intention to comply with the Operating Protocols in accordance with this Section 8.2. After receipt of such notice, Seller shall commence appropriate action and use its best efforts to correct the deficiency; and
- (ii) Buyer shall have the right upon notice by telephone to Seller, to cause transfer gates on the product conveyors extending from the Coal Yard to be switched such that Available Seller Coal bypasses the Facility and is delivered directly to the Delivery Point for Resold Coal for sale to and purchase by Buyer as Resold Coal and to maintain such transfer gate positions until such time as Seller provides to Buyer reasonably adequate assurances of Seller's ability to perform in accordance with the Operating Protocols.
- (d) Buyer hereby covenants that it will use all Refined Coal purchased hereunder solely for use as fuel in the Belle River Power Plant.
- (e) Each Monday, Buyer shall provide to Seller the inputs or estimates of the inputs required for calculating the Detroit Edison Benefits and the MPPA Benefits for the previous week (beginning on the previous Monday and ending on Sunday), as set forth on Exhibit C or Exhibit D.

Section 8.3. Chemical Additives.

- (a) Upon Buyer's request and Seller's approval, Seller will increase the level of chemical additives used in the production of Refined Coal beyond that called for in the Operating Protocols (subject to the physical constraints of the Facility), and, in such event, Buyer shall reimburse Seller for any additional costs and expenses incurred by Seller for and attributable to the use of the additional chemical additive. Notwithstanding the foregoing, if, after such an increase, there occurs a Reduction Event, Seller shall have the right to reduce levels of chemical additives back to levels called for in the Operating Protocols.
- (b) Upon Buyer's request, Seller shall for a period of up to seven days of testing, supply additional Mer-Sorb, at its own expense, and increase the application rate for Mer-Sorb to the level that the Parties mutually agree is likely reduce the mercury emissions from the Belle River Power Plant to the maximum level of mercury emissions reductions that can be

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 23 of 806

reasonably achieved by the application of additional Mer-Sorb to the Conforming Coal (all subject to the physical constraints of the Facility); provided, however, that all costs and expenses (other than the cost of such additional Mer-Sorb) related to such testing shall be borne by Buyer.

(c) During any time during the Term that the Facility is not operating, Buyer shall have the right to purchase from Seller, as Seller's delivered cost, such chemical additives for use at the Belle River Power Plant; provided that Buyer shall be responsible for any capital relating to the handling, storage and use of such chemical additives so purchased, including with limitation, any capital costs associated with or required for Buyer's use of such chemical additives.

Section 8.4. Presumption Regarding Conforming Coal and Refined Coal.

BUYER AGREES THAT ANY RESOLD COAL OR FEEDSTOCK WILL BE CONCLUSIVELY PRESUMED TO HAVE BEEN CONFORMING COAL IF SUCH COAL WAS PURCHASED BY SELLER PURSUANT TO THE COLLECTIVE COAL INVENTORY PURCHASE AGREEMENTS OR: (A) WAS PURCHASED BY SELLER PURSUANT TO A COAL PURCHASE CONTRACT THAT WAS ASSIGNED TO SELLER BY BUYER OR THAT WAS CERTIFIED BY THE COAL CONSULTANT AS PROVIDED IN THE COAL HANDLING AND CONSULTING AGREEMENT, AND (B) WAS NOT RECOMMENDED FOR REJECTION IN ACCORDANCE WITH THE APPLICABLE COAL PURCHASE CONTRACT BY THE COAL CONSULTANT PURSUANT TO THE COAL HANDLING AND CONSULTING AGREEMENT, AND WAS PREPARED, BLENDED AND DELIVERED TO THE APPLICABLE DELIVERY POINT BY THE COAL CONSULTANT PURSUANT TO THE COAL HANDLING AND CONSULTING AGREEMENT. ACCORDINGLY, BUYER WAIVES ANY RIGHT IT MIGHT HAVE TO REJECT OR TO REVOKE ACCEPTANCE OF, OR TO CLAIM DAMAGES OR ANY OTHER RELIEF WITH RESPECT TO ANY SUCH RESOLD COAL OR ANY REFINED COAL PRODUCED FROM SUCH FEEDSTOCK BY REASON THAT SUCH RESOLD COAL OR FEEDSTOCK WAS NOT CONFORMING COAL.

Section 8.5. Warranty Disclaimer.

(a) EXCEPT AS EXPRESSLY PROVIDED IN THIS ARTICLE VIII, ALL RESOLD COAL AND REFINED COAL SOLD PURSUANT TO THIS AGREEMENT IS SOLD "AS IS" AT THE APPLICABLE DELIVERY POINT PROVIDED HEREIN.

(b) EXCEPT AS EXPRESSLY PROVIDED IN THIS ARTICLE VIII, SELLER HEREBY DISCLAIMS ALL WARRANTIES (OTHER THAN THE WARRANTY OF TITLE) WHETHER EXPRESS OR IMPLIED, INCLUDING, WITHOUT LIMITATION, IMPLIED WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE AND ALL WARRANTIES REGARDING THE COMPATIBILITY OF ANY REFINED COAL WITH ANY BUYER EQUIPMENT.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Laplander
Page: 24 of 806

ARTICLE IX PRICE; BILLING AND PAYMENT

Section 9.1. Refined Coal Price.

For each Ton of Refined Coal produced and sold by Seller and purchased by Buyer hereunder during a Contract Year, Buyer shall pay to Seller the Refined Coal Price applicable to such Ton of Refined Coal.

Section 9.2. Resold Coal Price.

Buyer shall pay (or cause to be paid) to Seller for each Ton of Resold Coal purchased and sold hereunder the Resold Coal Price. The "Resold Coal Price" for Resold Coal purchased at a site other than the Belle River Site shall be the same quality adjusted price per Ton incurred or to be incurred directly by Seller under any applicable Coal Purchase Contract, plus any applicable transportation charges or other rail and transloading costs incurred by Seller. The "Resold Coal Price" for Resold Coal sold from the Feedstock Inventory Store shall be the Coal Inventory Price applicable to such Ton of Resold Coal.

Section 9.3. Coal Consultant Fee Reimbursement.

Buyer shall reimburse Seller for the Coal Fee as and when paid under the Coal Handling and Consulting Agreement.

Section 9.4. O&M and Capital Cost Reimbursement.

(a) Seller shall reimburse Buyer for increased operation and maintenance expenses incurred and that Buyer demonstrates are related to Buyer's use of Refined Coal (and not increased levels of chemical additives pursuant to Section 8.3) as a fuel in the Belle River Power Plant that would not have been incurred from use of coal (other than Refined Coal), but only to the extent such costs are not included in the calculation of Detroit Edison Benefits ("Increased Expenses"). Buyer shall give Seller prompt notice upon the occurrence of any Increased Expenses. If the Increased Expense is ongoing, either Party shall have the right to suspend delivery of Refined Coal hereunder unless and until the Parties agree upon a resolution of such Increased Expense; provided, however, that Buyer shall have the right to suspend delivery of Refined Coal hereunder only to the extent that Buyer is not reimbursed for such Increased Expense. If Seller disputes an Increased Expense, Seller shall have the right to withhold reimbursement for such Increased Expense until such dispute has been resolved.

(b) Seller shall reimburse Buyer for any capital investments that Buyer demonstrates are required of Buyer as a result of Buyer's use of Refined Coal (and not increased levels of chemical additives pursuant to Section 8.3) as fuel in the Belle River Power Plant, to the extent agreed to and approved by Seller. Either Party shall have the right to suspend delivery of Refined Coal hereunder unless and until the Parties agree upon such capital investment and reimbursement or upon other resolution of such matter.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 25 of 806

(c) Notwithstanding the foregoing, Seller shall not be required to reimburse Buyer for any costs, expenses or capital investment that Buyer cannot demonstrate are amounts that Buyer would not have incurred but for Buyer's use of Refined Coal.

Section 9.5. Invoicing and Payment.

(a) Buyer shall pay Seller by electronic transfer (recipient's account per Seller's advice) in United States funds for all Refined Coal produced and sold by Seller and purchased by Buyer hereunder. Seller shall submit to Buyer an invoice for the Refined Coal delivered to Buyer hereunder during each week. Such invoice will be submitted within two Business Days after the end of the applicable week and will include the weight of Refined Coal delivered, an estimate of the Refined Coal Price applicable to such Refined Coal, the amount of any applicable true-up adjustment and pertinent wire transfer instructions. Buyer shall make payment within four days after receipt of each Seller invoice. From time to time, Seller, with assistance of the Coal Consultant, shall determine (i) the actual Refined Coal Price, (ii) the actual price of the Detroit Edison Refined Coal Adder, and (iii) the actual price of the MPPA Refined Coal Adder, in each case, applicable to the Refined Coal produced and sold during the most recent period following any prior true-up adjustment and any resulting true-up adjustment will be reflected (as an addition or reduction, as the case may be) on the weekly invoice next submitted by Seller hereunder.

(b) Buyer shall pay Seller by electronic transfer (recipient's account per Seller's advice) in United States funds for all Resold Coal from the Feedstock Inventory Store purchased and sold hereunder. Seller shall submit to Buyer an invoice for the Resold Coal from the Feedstock Inventory Store delivered to Buyer hereunder during each week. Such invoice will be submitted within two Business Days after the end of the applicable week and will include the weight of such Resold Coal delivered, an estimate of the Resold Coal Price applicable to such Resold Coal, the amount of any applicable true-up adjustment and pertinent wire transfer instructions. Buyer shall make payment within four days after receipt of each Seller invoice. From time to time, Seller, with assistance of the Coal Consultant, shall determine the actual Resold Coal Price applicable to the Resold Coal from the Feedstock Inventory Store delivered to Buyer hereunder during the most recent period following any prior true-up adjustment and any resulting true-up adjustment will be reflected (as an addition or reduction, as the case may be) on the weekly invoice next submitted by Seller hereunder. Following each inventory reconciliation (and determination of the actual Unloaded Weight of Resold Coal sold from the Feedstock Inventory Store during such period) as to which it is determined that there is an Excess Amount or a Shortfall Amount as provided in Section 7.3, the amount of such Excess Amount or Shortfall Amount will be reflected (as an addition or reduction, as the case may be) on the weekly invoice next submitted by Seller hereunder.

(c) Buyer shall pay Seller by electronic transfer (recipient's account per Seller's advice) in United States funds for all Resold Coal purchased and sold hereunder other than from the Feedstock Inventory Store. Seller shall submit to Buyer an invoice for the Resold Coal other than from the Feedstock Inventory Store delivered to Buyer hereunder during each week. Such invoice will be submitted within two Business Days after the end of the applicable week and will include the weight of such Resold Coal delivered, the Resold Coal Price

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 26 of 806

applicable to such Resold Coal and pertinent wire transfer instructions. Buyer shall make payment within four days after receipt of each Seller invoice.

(d) Buyer shall pay Seller by electronic transfer (recipient's account per Seller's advice) in United States funds for the reimbursement required under Section 9.3. Seller shall submit to Buyer an invoice for the Coal Fee during each week. Such invoice will be submitted within two Business Days after the end of the applicable week and will include pertinent wire transfer instructions. Buyer shall make payment within four days after receipt of each Seller invoice.

(e) The Parties agree that each Party may, in computing the amount required to be paid by such Party upon termination of this Agreement, reduce the required amount of such payment by offsetting against such amount the aggregate amount due and owing (and not subject to a good faith dispute) to such Party and all Affiliates of such Party by such other Party hereunder and under the other Project Documents.

(f) In case any portion of an invoice submitted pursuant to this Section 9.5 is in bona fide dispute, the undisputed amount shall be payable when due. Any Party disputing any portion of an invoice shall provide the other Party with notice describing the nature of the dispute as soon as reasonably possible.

(g) Invoices shall be mailed, emailed or sent by facsimile to the Persons listed below, or such other Person or address as may be specified by Buyer:

The Detroit Edison Company
One Energy Plaza
634 General Offices
Detroit, Michigan 48226
Attention: John R. Klos
Email: klosj@dteenergy.com

With a copy to:

The Detroit Edison Company
One Energy Plaza
634 General Offices
Detroit, Michigan 48226
Attention: John A. Wagner
Email: wagnerj@dteenergy.com

(h) All amounts owed by a Party to the other Party under this Agreement more than five Business Days beyond the date on which such amount is due and payable shall bear interest at the Late Payment Rate.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 27 of 806

Section 9.6. Business Days.

All payments to be made under this Agreement shall be made on a Business Day. If the day specified for payment is not a Business Day, such payment shall be made on the next succeeding day which is a Business Day.

Section 9.7. Audit.

Notwithstanding the payment of any amount pursuant to this Article IX, each Party shall remain entitled to conduct an audit and review of all costs and expenses subject to reimbursement by such Party hereunder, including, but not limited to, costs incurred and taken into account in the calculation of the Detroit Edison Benefits, together with any supporting documentation, for a period of three years from and after the close of the calendar year in which such costs were incurred, excluding those books and records related to costs based upon the standard allowances and rates. If, pursuant to such audit and review, it is determined that any amount previously paid by such Party did not constitute a due and payable item of costs, such Party may submit a claim to the other Party indicating the amount and reason the cost is believed not to be reimbursable. If the Parties agree on such matter, the Party obligated to pay will remit the amount within 30 calendar days. If there is not agreement on any item of cost, the Parties will then meet and attempt to agree on the disposition of the item of cost. If the Parties are not able to resolve issues raised by such an audit and review, any disputed items will be resolved in accordance with the provisions of Article XIII.

Section 9.8. Taxes and Other Liabilities.

(a) Seller shall be solely responsible for all assessments, fees, costs, expenses and taxes imposed by any Governmental Body or other third parties ("Third Party Impositions") relating to Seller Coal that arise prior to any transfer of title to the Seller Coal hereunder, either as Resold Coal or after its conversion into Refined Coal, as provided herein; provided, however, that such Third Party Impositions shall, for purposes of this Agreement, be included in the definition and calculation of the Coal Inventory Price. Buyer shall be solely responsible for all Third Party Impositions relating to the Resold Coal or Refined Coal imposed at or after the transfer of title to Buyer (other than franchise or income taxes which are related to the sale of the Seller Coal and are the responsibility of Seller), including, but not limited to, sales or use tax if applicable.

(b) Upon Buyer's purchase of Refined Coal from Seller, Buyer shall provide Seller with a sales tax exemption certificate with the "industrial processing" exemption box selected.

**ARTICLE X
FORCE MAJEURE**

Section 10.1. Force Majeure.

(a) Except as otherwise provided in this Section 10.1, a Party shall be excused from performance under this Agreement, and shall not be considered to be in default hereunder for failure to perform obligations under this Agreement, to the extent that such Party is unable to,

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 28 of 806

or otherwise fails to, perform due to an Event of Force Majeure or the failure of the other Party or any of its Affiliates to perform its obligations under any of the Project Documents. No Party shall be relieved of any obligation for the payment of money as a result of an Event of Force Majeure or relieved of any other obligations under this Agreement as a result of an Event of Force Majeure solely because of increased costs or other adverse economic consequences that may result from performance by such Party.

(b) If a Party's ability to perform its obligations under this Agreement is affected by an Event of Force Majeure, such Party shall: (i) promptly notify the other Party in writing of such event and its cause; and (ii) promptly supply such other available information about the Event of Force Majeure and its cause as may be reasonably requested by the other Party.

(c) The suspension of performance by a Party due to an Event of Force Majeure hereunder shall be of no greater scope and no longer duration than that which is necessary by reason of the Event of Force Majeure. The affected Party shall use commercially reasonable efforts to promptly mitigate or remedy its inability to perform. However, no Party shall be required hereunder to accede to the demands of labor or settle any strike or labor dispute. An Event of Force Majeure shall not excuse compliance with any Law or environmental permits unless so provided under the applicable Law or permit.

ARTICLE XI EARLY TERMINATION

Section 11.1. Early Termination.

This Agreement shall terminate on a date prior to the date referred to in Section 3.1 under the following circumstances:

(a) Upon mutual agreement of Buyer and Seller, which termination shall be effective on the date agreed to by Buyer and Seller;

(b) If the Term (as defined in the License Agreement) under the License Agreement expires or is terminated, which termination of this Agreement shall be effective as of the expiration or termination of the Term under the License Agreement;

(c) Upon the date specified in a termination notice sent by a non-breaching Party, so long as such date follows the expiration of any applicable notice and/or cure period, in accordance with Article XII hereof;

(d) Upon the date specified in a notice of termination from Seller to Buyer, so long as such date follows the expiration of 30 days' notice, if a change in Law or circumstances that results in a material increase in costs and expenses or a material reduction in revenue or benefits in respect of Section 45 Tax Credits; provided that to the extent Seller terminates in accordance with this Section 11.1(d), Seller shall not be required to produce and sell Refined Coal pursuant to Section 5.1 from the date of the notice of termination until the effective date of such termination;

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 29 of 806

(e) Upon the date specified in a notice of termination by one Party to the other Party, so long as such date follows the expiration of 30 days' notice, if the other Party's obligation to perform hereunder is excused due to an Event of Force Majeure and, notwithstanding the provisions of Section 10.1, the suspension of such other Party's performance due to the Event of Force Majeure has continued for at least six consecutive months;

(f) Upon the date specified in a notice of termination by Buyer to Seller, so long as such date follows the expiration of 30 days' notice, if after the Follow-up Period, Seller fails to produce Refined Coal for at least three consecutive months and such failure to produce is not attributable in whole or part to Buyer;

(g) Upon the date specified in a notice of termination by one Party to the other Party, so long as such date follows the expiration of 30 days' notice, if after the Follow-up Period, deliveries of Refined Coal are suspended for at least three consecutive months;

(h) Upon the date specified in a notice of termination from Buyer to Seller, so long as such date follows the expiration of 30 days' notice, if an order issued by the Michigan Public Service Commission, or a change in Law, related to Buyer's use of Refined Coal as a fuel in the Belle River Power Plant, this Agreement or any of the transactions contemplated by the Project Documents results in an increase in costs and expenses or a reduction in revenue to Buyer; or

(i) Upon the date specified in a notice of termination from Buyer to Seller, so long as such date follows the expiration of 30 days' notice, if operation of one or both of the generating units at the Belle River Power Plant is discontinued.

Section 11.2. Post-Termination Obligations; Survival.

(a) Any termination of this Agreement, irrespective of the reason therefor, shall not release either Party of any obligations incurred prior to the effective date of such termination nor, subject to Article XII hereof, waive any rights or remedies with respect to a breach of this Agreement giving rise to such termination.

(b) Any termination of this Agreement, irrespective of the reason therefor, shall not release either Party of any applicable rights and obligations pursuant to Section 5.4, Section 5.5, Section 6.3, Section 7.2(b), Section 11.2, Article XII, Article XIII or Article XIV.

ARTICLE XII EVENTS OF DEFAULT AND REMEDIES

Section 12.1. Event of Default.

An "Event of Default" shall mean the occurrence of any one or more of the following events:

(a) A breach by Buyer of its payment obligations under Article IX hereof, which breach is not cured within ten days from the date written notice thereof is given to Buyer by Seller;

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 30 of 806

(b) Any representation or warranty made by either Party in this Agreement shall at any time prove to be false or misleading in any material respect as of the date hereof, unless: (i) the fact, circumstance or condition that is the subject of such representation or warranty is made true within 30 days after such Party becomes aware that it was false or misleading (or within such longer period of time, not to exceed 90 days, as is necessary for such Party with the exercise of diligence to cure such failure, if such failure is susceptible to being made true but cannot be cured with the exercise of diligence within such 30-day period, and if such Party commences within such 30-day period and thereafter diligently and in good faith prosecutes the curing of such failure); and (ii) such cure removes any adverse effect on the other Party of such fact, circumstance or condition being otherwise than as first represented; or unless such fact, circumstance or condition being other than as first represented does not materially adversely affect the other Party, as the case may be;

(c) The failure by Buyer to purchase its requirements for coal, refined coal and coal-based feedstock as required in Section 5.1, which breach is not cured within ten days from the date written notice thereof is given to Buyer by Seller;

(d) A breach of a material provision hereof (other than a breach described in the other subsections of this Section 12.1) by either Party, which breach is not cured within: (i) 60 days from the date written notice thereof is given to the breaching Party by the other Party; or (ii) if such breach cannot reasonably be cured within such 60 days, and the breaching Party has commenced and is diligently pursuing cure, within 90 days of the date written notice is given; or

(e) If either Party shall: (i) become insolvent or generally unable to pay its debts as they become due; (ii) apply for, consent to, or acquiesce in, the appointment of a trustee, receiver, sequestrator or other custodian for it or any of its property, or make a general assignment for the benefit of its creditors; (iii) in the absence of any such application, consent or acquiescence, permit or suffer to exist the appointment of a trustee, receiver, sequestrator or other custodian for it or a substantial portion of its property, and such trustee, receiver, sequestrator or other custodian shall not be discharged within 60 days; (iv) permit or suffer to exist the commencement of any bankruptcy, reorganization, debt arrangement or other case or proceeding under any bankruptcy or insolvency law, or any dissolution, winding up or liquidation proceeding, in respect of it, and, if any such case or proceeding shall be consented to or acquiesced in by it or shall result in the entry of an order for relief or shall remain for 60 days undismissed; or (v) take any formal action authorizing, or in furtherance of, any of the foregoing.

Section 12.2. Remedies.

(a) Upon the occurrence of an Event of Default described in Section 12.1(c), Seller shall have the right, exercisable within 90 days following the occurrence of the Event of Default, by giving written notice to Buyer to such effect, to terminate this Agreement within 30 days after the date of such notice.

(b) Upon the occurrence of the Event of Default described in Section 12.1(a), Section 12.1(b) or Section 12.1(d), the non-breaching Party shall have the right to terminate this Agreement (so long as such Event of Default remains uncured) by giving written notice to the

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 31 of 806

breaching Party to such effect, which notice shall specify a date of termination that is not less than 90 days after written notice of the breach and not more than 120 days after written notice of the breach.

(c) Upon the occurrence of an Event of Default described in Section 12.1(e), the non-breaching Party shall have the right to terminate this Agreement immediately by giving written notice to the breaching Party to such effect.

(d) Notwithstanding any other provision of this Agreement to the contrary, the remedies contained in this Article XII shall not be applicable to any matter governed by the Environmental Law or pertaining to Hazardous Materials, as those terms are defined in the Environmental Indemnity Agreement, and the Parties acknowledge and agree that any indemnification or other remedies as to such environmental matters are governed solely and exclusively by the Environmental Indemnity Agreement.

(e) Except as otherwise provided herein, in addition to the remedies specified in this Article XII, each Party shall have all rights and remedies as are available to it at law or in equity.

Section 12.3. Limitations of Seller Liability.

Notwithstanding anything to the contrary in this Agreement, the total aggregate liability of Seller for the payment of money to Buyer in any Contract Year under this Agreement, including without limitation, Seller's breach or alleged breach of this Agreement but excluding Seller's reimbursement obligations under Section 9.4, shall in no event exceed the aggregate amount paid by Buyer pursuant to Sections 9.1 and 9.2 after deducting the Coal Inventory Price associated therewith and Resold Coal Price for Resold Coal purchased at a site other than the Belle River Site.

ARTICLE XIII DISPUTE RESOLUTION

Section 13.1. Dispute Resolution.

(a) The Parties hereto agree: (i) to attempt to resolve all disputes arising hereunder promptly, equitably and in a good faith manner; and (ii) to provide each other with reasonable access during normal business hours to any and all non-privileged records, information and data pertaining to any such dispute.

(b) Other than a claim for equitable relief, which may be brought directly to any court of competent jurisdiction, any claim or dispute arising out of any of the provisions of this Agreement or the breach thereof which the Parties are unable to resolve pursuant to Section 13.1(a), shall be settled by arbitration to be conducted in Lansing, Michigan in accordance with the American Arbitration Association Commercial Arbitration Rules. The arbitration shall be held before a panel of three arbitrators. Each Party shall appoint an arbitrator within 30 days of the filing of the notice of intent to arbitrate. The arbitrators appointed by the Parties shall attempt to agree on the selection of the third arbitrator who will serve as chairman of the arbitration panel within 30 days from their appointment. If they cannot agree on an arbitrator

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 32 of 806

then either Party may move to have the arbitrator appointed by the American Arbitration Association. Time shall be of the essence in the nomination of the arbitrators. If a Party fails to appoint an arbitrator within such 30 day period, that Party shall waive its right to appoint an arbitrator and the arbitration shall proceed with the appointed arbitrator. The arbitration award by the arbitrator shall be final and binding and, unless the arbitrator expressly determines them to be appropriate, shall not include costs or attorney's fees. A judgment to enforce the arbitration award may be entered in any court of appropriate jurisdiction. Each Party shall bear the cost of its appointed arbitrator and the Parties shall share equally the cost of the third arbitrator and the American Arbitration Association. Upon the date of an arbitration award, if it is determined that an amount is due from one Party to the other, then such amount will be paid to the Party to whom it is due within 15 days from the final settlement, or written determination of the arbitrator, as the case may be.

(c) During resolution of any dispute under this Article XIII, the Parties shall continue to perform all of their respective obligations under this Agreement without interruption or slow down, except to the extent a Party is prevented from performing due to the nature of the dispute, until such dispute is resolved.

(d) The Parties agree that they may be joined as an additional party to an arbitration involving BR Fuels, MPPA or Detroit Edison under any of the other Project Documents; provided, that the Party joined as an additional party to the arbitration is a proper respondent in the arbitration. If more than one arbitration is begun under the Agreement or the Project Documents and any Person contends that two or more arbitrations involve substantially the same issues and should be heard in one proceeding, then the arbitration(s) that have been commenced shall be dismissed and a new arbitration proceeding involving all of the parties shall be commenced and a new arbitration panel shall be selected.

ARTICLE XIV MISCELLANEOUS

Section 14.1. Terms and Conditions of Sale.

The terms and conditions of sale applicable to each sale of Refined Coal under this Agreement will be those stated in this Agreement, unless the Parties otherwise agree in writing. The terms and conditions of sale applicable to each sale of Resold Coal under this Agreement will be those stated in this Agreement, unless the Parties otherwise agree in writing; provided that any inconsistencies between the terms and conditions of this Agreement and any purchase order shall be resolved in favor of the terms and conditions set forth in this Agreement.

Section 14.2. Confidentiality.

Each Party shall hold, and shall use its best efforts to cause its Affiliates, agents, advisors (including counsel and consultants), any lender, potential lender, investor or potential investor to hold, in strict confidence from any other Person (other than any such Affiliate, agent or advisor or any lender, potential lender, investor or potential investor as permitted hereby) all documents and information concerning the other Party or any of its Affiliates furnished to it, or its Affiliates,

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 33 of 806

agents or advisors (including counsel and consultants) which are marked confidential or can reasonably be interpreted to contain confidential information, whether before or after the Effective Date, by or on behalf of the other Party in connection with this Agreement or the transactions contemplated hereby, and neither Party nor their Affiliates or any agent, advisor, lender, potential lender, investor or potential investor shall disclose any such information unless, subject to Section 14.3, required to disclose any such information by judicial or administrative process (including in connection with obtaining from Governmental Bodies the necessary approvals of this Agreement and the transactions contemplated hereby) or by other requirements of Law. Each Party may disclose such documents or information to its agents and advisors and any lender or potential lender or any investor or potential investor, provided that prior to receipt of any such information any such agent, advisor, lender, potential lenders, investor or potential investor shall have executed a confidentiality agreement with such Party that incorporates the restrictions and exceptions set forth in this Section 14.2, and may disclose such documents or information in an action or proceeding brought by either Party in pursuit of its rights or in the exercise of its remedies hereunder. Notwithstanding the foregoing, this Section 14.2 shall not apply to such documents or information that were (i) previously known by the Party receiving such documents or information without breach of any confidentiality requirement or obligation, (ii) in the public domain (either prior to or after the furnishing of such documents or information hereunder) through operation of Law, or by no fault of such receiving Party, or (iii) later acquired by such receiving Party from another source if such receiving Party is not aware that such source is under an obligation to the other Party to keep such documents and information confidential.

Section 14.3. Required Disclosure.

Any Party reasonably determining in good faith that it is required by Law or in the course of tax audits or administrative or judicial proceedings to disclose information that is otherwise required to be maintained in confidence pursuant to Section 14.2 may make disclosure notwithstanding the provisions of Section 14.2; provided, however, that the Party making the disclosure shall, to the extent possible, give prior notice to the other Party of the requirement and the terms thereof and shall cooperate to the maximum extent practicable to minimize the disclosure of the information to allow such Party at its cost and expense to obtain proprietary or confidential treatment of such information by the third party to whom the information is disclosed and, to the extent such remedies are available, to seek protective orders limiting the dissemination and use of the information. This Agreement does not alter the rights of either Party to object to the Law or proceedings requiring the disclosure.

Section 14.4. Compliance with Laws and Governmental Approvals.

In connection with the performance of this Agreement, each Party agrees to comply in all material respects with all Laws, and each Party hereto agrees that it or its agent will use commercially reasonable efforts to acquire and maintain, in a timely manner, all Governmental Approvals required by Law or Governmental Bodies to perform its obligations under this Agreement.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Laplander
Page: 34 of 806

Section 14.5. Entire Agreement; Successors and Assigns.

This Agreement, together with the other Project Documents, constitutes the entire agreement and understanding between the Parties with respect to the subject matter herein and therein and the transactions contemplated hereby and thereby, and any and all previous understandings, proposals, negotiations, agreements, commitments and representations, whether oral or written, are merged herein and are superseded hereby. This Agreement shall be binding upon and inure to the benefit of the Parties and their respective successors and permitted assigns.

Section 14.6. Notices.

Except as otherwise set forth in this Agreement, all notices, requests and other communications hereunder must be in writing and shall be delivered personally (by hand delivery or by overnight courier) or by facsimile transmission (with receipt of transmission confirmation) or mailed (certified mail postage prepaid, return receipt requested) to the Parties at the following addresses or facsimile numbers and shall be effective upon receipt (when sent by personal delivery or certified mail) and upon receipt of transmission confirmation (when sent by facsimile):

If to Buyer, to: The Detroit Edison Company
One Energy Plaza
634 General Offices
Detroit, Michigan 48226
Attention: Manager, Business Development and
Administration - Fuel Supply
Facsimile: (313) 235-6992

With a copy to: The Detroit Edison Company
One Energy Plaza
641 General Offices
Detroit, Michigan 48226
Attention: Director - Fuel Supply
Facsimile: (313) 235-6992

If to Seller, to: Belle River Fuels Company, LLC
414 South Main Street
Suite 600
Ann Arbor, MI 48104
Attention: General Counsel
Facsimile: (734) 302-8245

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 35 of 806

With a copy to:

Belle River Fuels Company, LLC
414 South Main Street
Suite 600
Ann Arbor, MI 48104
Attention: Katherine A. Panczak
Facsimile: (734) 302-5335

provided, however, that either Party from time to time may change its address, facsimile number or other information for the purposes of notices to such Party by giving notice specifying such change to the other Party.

Section 14.7. Assignment.

Neither this Agreement, nor any of the rights and obligations hereunder, may be assigned, transferred or delegated by either Party without the express prior written consent of the other Party, which consent shall not be unreasonably withheld or delayed, except that either Party may assign this Agreement to an Affiliate thereof without the prior written consent of the other Party; provided that any assignment to an Affiliate shall not release the assignor from any obligations under this Agreement unless otherwise expressly consented to by the other Party. For purposes of this Section 14.7, any change in control or majority ownership of Seller which causes Seller no longer to be an Affiliate of DTE Energy Company (determined without regard to the proviso in the definition of "Affiliate" contained herein) shall be deemed an assignment.

Section 14.8. Waiver; Invalidity.

Any term or condition of this Agreement may be waived at any time by the Party that is entitled to the benefit thereof, but no such waiver shall be effective unless set forth in a written instrument duly executed by such waiving Party. The failure or delay of either Party to require performance by the other Party of any provision of this Agreement shall not affect its right to require performance of such provision unless and until such performance has been waived by such Party in writing in accordance with the terms hereof. No waiver by either Party of any term or condition of this Agreement, in any one or more instances, shall be deemed to be or construed as a waiver of the same or any other term or condition of this Agreement on any future occasion. All remedies, either under this Agreement or by Law or otherwise afforded, shall be cumulative and not alternative. The invalidity or unenforceability of any provision of this Agreement shall be determined only by a court of competent jurisdiction. The Parties hereby agree to use good faith efforts to negotiate an equitable adjustment to any provisions of this Agreement determined to be invalid or unenforceable with a view toward effecting the purposes of this Agreement, and the validity or enforceability of the remaining provisions of this Agreement shall not be affected thereby.

Section 14.9. Limitations of Liability and Exclusive Remedies.

(a) **NEITHER PARTY NOR ITS AFFILIATES SHALL BE LIABLE UNDER THIS AGREEMENT TO THE OTHER PARTY OR ITS AFFILIATES FOR CONSEQUENTIAL OR INDIRECT LOSS OR DAMAGE, INCLUDING, WITHOUT**

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 36 of 806

LIMITATION, LOSS OF PROFIT, LOSS OF TAX BENEFIT OR CREDITS, LOSS OF GOODWILL OR ANY OTHER SPECIAL, PUNITIVE OR INCIDENTAL DAMAGES RESULTING FROM ANY VIOLATION OF OR DEFAULT UNDER THIS AGREEMENT.

(b) **THE PROVISIONS OF THIS SECTION 14.9 SHALL APPLY TO ALL CLAIMS BASED ON OR ARISING UNDER THIS AGREEMENT, WHETHER IN CONTRACT, EQUITY, TORT OR OTHERWISE, REGARDLESS OF FAULT, GROSS OR OTHER NEGLIGENCE (IN WHOLE OR IN PART), STRICT LIABILITY, BREACH OF CONTRACT OR BREACH OF WARRANTY AND SHALL EXTEND TO THE MEMBERS, MANAGERS, TRUSTEES, DIRECTORS, OFFICERS AND EMPLOYEES, AGENTS AND RELATED PERSONS OR AFFILIATES OF EACH PARTY, AND THEIR RESPECTIVE MEMBERS, MANAGERS, DIRECTORS, TRUSTEES, OFFICERS, EMPLOYEES AND AGENTS.**

Section 14.10. Headings.

The headings contained in this Agreement are solely for the convenience of the Parties and shall not be used or relied upon in any manner in the construction or interpretation of this Agreement.

Section 14.11. Counterparts.

The Parties may execute this Agreement in counterparts, which shall, in the aggregate, when signed by both Parties constitute one and the same instrument, and, thereafter, each counterpart shall be deemed an original instrument as against any Party who has signed it.

Section 14.12. Applicable Law.

This Agreement, including the interpretation, construction, validity and enforceability hereof, and the transactions contemplated herein, and all disputes between the Parties under or related to this Agreement or the facts and circumstances leading to its execution or performance, whether in contract, tort or otherwise will be governed by the laws of the State of Michigan without regard to the conflict of laws rules thereof. IN ADDITION, EACH PARTY, KNOWINGLY AND INTENTIONALLY, IRREVOCABLY AND UNCONDITIONALLY, WAIVES TRIAL BY JURY IN AND AS TO ANY LEGAL ACTION OR PROCEEDING RELATING TO THIS AGREEMENT AND FOR ANY CLAIM, COUNTERCLAIM, CROSS CLAIM OR THIRD PARTY CLAIM THEREIN.

Section 14.13. Amendment.

No modification or amendment of any provisions of this Agreement shall be valid unless it is in writing and signed by both Parties.

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Laplander

Page: 37 of 806

Section 14.14. No Third Party Beneficiary.

The terms and provisions of this Agreement are intended solely for the benefit of each Party and their respective successors or permitted assigns, and it is not the intention of the Parties to confer third-party beneficiary rights upon any other Person.

[Remainder of page intentionally left blank]

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 38 of 806

IN WITNESS WHEREOF, the Parties have executed this Refined Coal Supply Agreement by their authorized representatives as of the date first above written.

BELLE RIVER FUELS COMPANY, LLC

By: *David R. Ryan*
Name: DAVID RYAN
Title: PRESIDENT

REVIEWED BY:
SSC
LEGAL

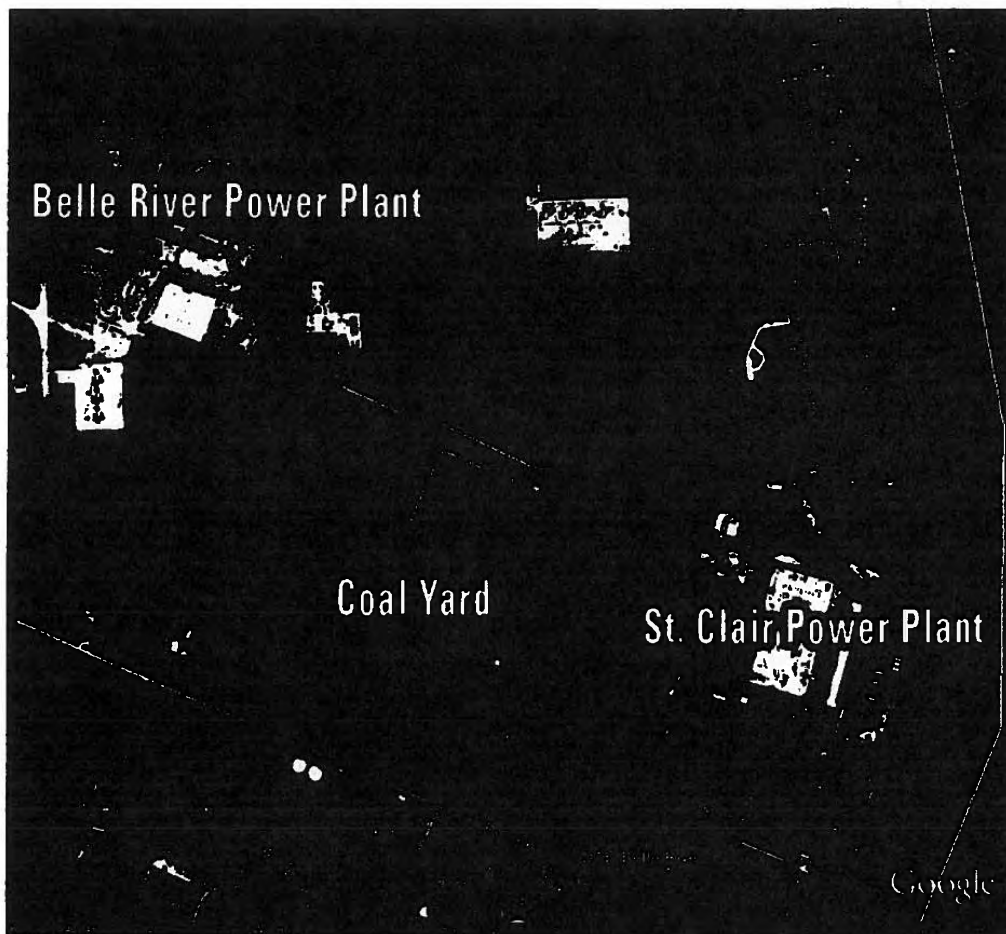
THE DETROIT EDISON COMPANY

By: *Anthony F. Earley, Jr.*
Name: ANTHONY F. EARLEY, JR.
Title: CHAIRMAN

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 39 of 806

EXHIBIT A

BELLE RIVER SITE



A-1

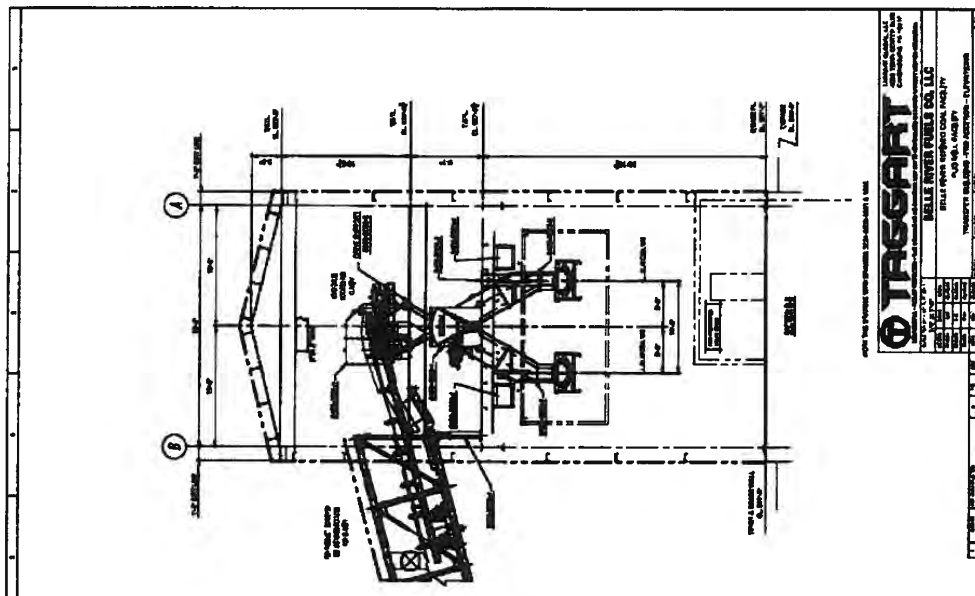
Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 40 of 806

EXHIBIT B

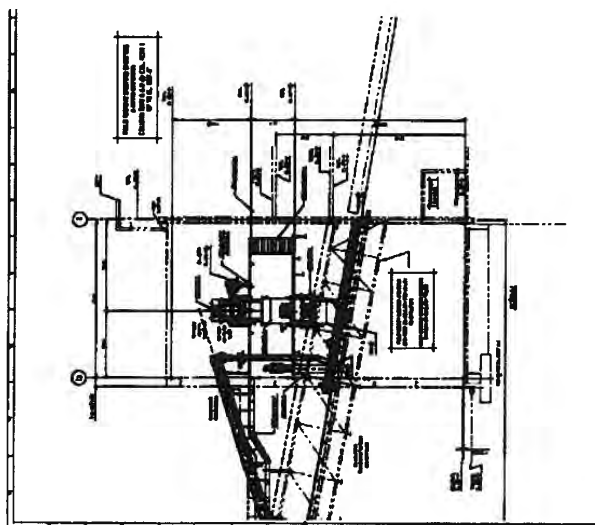
DELIVERY POINTS

See attached on the next page.

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 41 of 806



B-2



Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 42 of 806

EXHIBIT C

CALCULATION OF DETROIT EDISON BENEFITS

See attached.

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 43 of 806

Calculation of Detroit Edison Benefits

DECo Refined Coal Adder Calculation:

DECo Refined Coal Adder = Minimum(DECo Environmental Benefit, DECo's
Share of BRFC's Revenue Requirement) – PA2 Expense Increase + DECO
Avoided Hg Capital Amortization

DECo Environmental Benefit = DECo SO2 Benefit + DECo Mercury Benefit
+ DECo Fly Ash Benefit

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 44 of 806

Environmental Benefit Calculation SO₂ Benefit

DECo SO₂ Benefit

$$\text{DECo SO}_2 \text{ Benefit}_{\text{year}} = \sum_{\text{Jan}}^{\text{Dec}} \text{DECo SO}_2 \text{ Benefit}_{\text{month}}$$

Monthly SO₂ Benefit Calculation:

$$\text{If Actual SO}_2 \text{ Emissions}_{\text{month}} \geq \text{Status Quo SO}_2 \text{ Emissions}_{\text{month}}, \text{ then DECo SO}_2 \text{ Benefit}_{\text{month}} = 0$$

$$\text{If Actual SO}_2 \text{ Emissions}_{\text{month}} < \text{Status Quo SO}_2 \text{ Emissions}_{\text{month}}, \text{ then DECo SO}_2 \text{ Benefit}_{\text{month}} = 0.8139 \times \text{Transacted SO}_2 \text{ Allowance Benefit}_{\text{month}}$$

Status Quo Calculation:

$$\text{Status Quo SO}_2 \text{ Emissions}_{\text{month}} (\text{tons SO}_2) = \text{Emission Factor}_{\text{unit}} \times \% \text{ Sulfur in Coal}_{\text{monthly avg}} \times \text{Actual Tons Coal Combusted}_{\text{month}} \times 0.0005$$

Table defining terms on next page

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 45 of 806

Environmental Benefit Calculation SO₂ Benefit Continued

Defined Terms	Unit	Data Source
Actual SO ₂ Emissions _{Month}	(tons SO ₂)	= Tons of SO ₂ emissions for the calendar month, as reported by the SO ₂ Continuous Emissions Monitors installed at Belle River Unit 1 and 2 stack(s). Data shall be provided by Buyer to Seller by the 5 th day of the month for the prior month's emissions.
Emission Factor Unit 1	$\frac{\text{lbs SO}_2}{\text{tons coal}}$	= 33.0 Fixed number, developed by adjusting AP-42 Emission Factor of 35 to better correlate with annual SO ₂ emissions reported for Belle River Unit 1 to the United States Environmental Protection Agency (USEPA) from 1998 through 2007. If Buyer installs additional control technology on the unit to comply with future environmental regulations, the Emission Factor shall be adjusted to account for changes in Belle River Unit 1 emissions due to the installation of the control technology.
Emission Factor Unit 2	$\frac{\text{lbs SO}_2}{\text{tons coal}}$	= 33.4 Fixed number, developed by adjusting AP-42 Emission Factor of 35 to better correlate with annual SO ₂ emissions reported for Belle River Unit 2 to the USEPA from 1998 through 2007. If Buyer is installing additional control technology on the unit to comply with future environmental regulations, the Emission Factor shall be adjusted to account for changes in Belle River Unit 2 emissions due to the installation of the control technology.
% Sulfur In Coal _{Monthly Avg.}	$\frac{\text{lbs S}}{\text{lbs coal}}$ (tons)	= Average percent sulfur content of coal for month as determined by averaging, for the calendar month, the daily sample percent sulfur content (% Sulfur) results reported by the Buyer's Central Fuel Lab. The Buyer shall provide daily coal samples for Belle River Unit 1 and Unit 2 to the Buyer's Central Fuel Lab, which shall each be analyzed for % Sulfur in accordance with ASTM standards and reported to Seller within 5 calendar days.
Allowances Not Consumed		= The number of SO ₂ allowances that would have been surrendered to the USEPA if the difference between Status Quo SO ₂ Emissions and Actual SO ₂ Emissions were emitted by the Belle River Power Plant. For example, in 2010 under the current Clean Air Interstate Rule (CAIR), two SO ₂ allowances are required to be surrendered for every one ton of SO ₂ emitted; therefore Allowances Not Consumed = (Status Quo SO ₂ Emissions _{Month} - Actual SO ₂ Emissions _{Month}) x 2.
Actual Tons Coal Combusted _{Month}	(tons coal)	= Actual tonnage of coal consumed for the calendar month as reported in P3M as COAL_CONS
Transacted SO ₂ Allowance Benefit _{Month}	(\$)	= The actual sale price realized by Buyer for the sale of monthly Allowances Not Consumed. Buyer shall use commercially reasonable efforts to sell the number of Allowances Not Consumed during a calendar month by the 12 th day of the following month. In the event Buyer does not sell the Allowances Not Consumed, the Argus Air Daily monthly index price (ADI) for one SO ₂ allowance, as published by Argus Air daily on the last business day of the month, shall be multiplied by the number of Allowances Not Consumed during that same calendar month to estimate the monthly Transacted SO ₂ Allowance Benefit. The estimated Transacted SO ₂ Allowance Benefit will be reconciled within 30 days to reflect actual sales price if Buyer makes a transaction for Allowances Not Consumed within 3 months after the estimated value was used. It is the Parties' intent that the SO ₂ price index used for purposes of the calculations specified above are representative of the current SO ₂ market price. In the event that the ADI becomes unavailable, or if the Parties agree that the above-specified does not accurately represent the current SO ₂ market price, the Parties shall mutually agree to an alternative or replacement SO ₂ price index for the calculations.

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 46 of 806

Environmental Benefit Calculations Mercury Benefit

Mercury Benefit Calculation:

⊗ DECo Mercury Benefit_{Year} = 0.8139 X Avoided Mercury Compliance Cost_{Year}

Avoided Mercury Compliance Cost Calculations:

⊗ If Actual Mercury Compliance Cost_{Year} ≥ Status Quo Mercury Compliance Cost_{Year}, then Avoided Mercury Compliance Cost_{Year} = 0

⊗ If Actual Mercury Compliance Cost_{Year} < Status Quo Mercury Compliance Cost_{Year}, then Avoided Mercury Compliance Cost_{Year} = (Status Quo Mercury Compliance Cost_{Year} - Actual Mercury Compliance Cost_{Year})

Status Quo Calculations:

⊗ Status Quo Mercury Compliance Cost_{Year} = SQ Sorbent Cost_{Year} + SQ Fixed O&M_{Year}

⊗ If Year = Hg Compliance Date - 1, SQ Capital Cost_{Year} = DECo Hg Capital Cost_{Year}

⊗ If Year ≠ Hg Compliance Date - 1, SQ Capital Cost_{Year} = \$0

Status Quo Sorbent Cost Calculations:

⊗ If Year < Hg Compliance Date, SQ Sorbent Cost Calculations_{Year} = 0

⊗ If Year ≥ Hg Compliance Date, SQ Sorbent Cost Calculations_{Year} = Sorbent Usage Rate ($\frac{\text{lb}}{\text{mmacf}}$) X Flue Gas Flow Rate ($\frac{\text{mmacf}}{\text{min}}$) X 525,600 ($\frac{\text{min}}{\text{year}}$) X Plant Capacity Factor_{Year} X Delivered Sorbent Unit Price ($\frac{\$}{\text{lb}}$)

Status Quo Fixed O&M Calculations:

⊗ If Year < Hg Compliance Date, SQ Fixed O&M_{Year} = 0

⊗ If Year ≥ Hg Compliance Date, SQ Fixed O&M_{Year} = DECo Hg O&M_{Year}

Avoided Capital Effect Calculations:

⊗ If Year < Hg Compliance Date, Avoided Capital Effect_{Year} = 0

⊗ If Year = Hg Compliance Date, Avoided Capital Effect_{Year} = (SQ Capital Cost_{Year} - 1) - Actual Capital Cost_{Year} * DECo Capital Fixed Charge Rate

⊗ If Year > Hg Compliance Date, Avoided Capital Effect_{Year} = Avoided Capital Effect_{Year-1} - (Actual Capital Cost_{Year-1} * DECo Capital Fixed Charge Rate)

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 47 of 806

Environmental Benefit Costs Mercury Benefit

Defined Terms	Unit	Data Source
Actual Mercury Compliance Cost _{Year}	(\$)	= Actual Belle River Mercury Compliance Cost as determined from discrete accounts dedicated to Belle River mercury control equipment, which will be the sum of all mercury control related expenditures, excluding capital
Actual Capital Cost _{Year}	(\$)	= Actual annual capital cost for mercury control equipment for Belle River Power Plant as determined from discrete accounts dedicated to Belle River mercury control equipment
Hg Compliance Date	(year)	= First year Hg emissions are required to be removed from Belle River stack emissions due to State and/or Federal requirements
DECo Hg O&M _{Year}	(\$)	= Actual O&M expenses incurred for mercury control at Detroit Edison plants not consuming Refined Coal, adjusted for Belle River Power Plant requirements without Refined Coal consumption. If actual Detroit Edison cost data is unavailable, EPRI O&M ₂₀₀₆ will be used.
EPRI O&M ₂₀₀₆	(\$)	= 1,000,000 x Inflation Adjustment Factor. 1,000,000 is a fixed value, determined using the EPRI-based Hg Cost Table that was developed using the September 2006 EPRI Mercury Control Technology Selection Guide
Sorbent Usage Rate	$\frac{\text{lb}}{\text{mmacf}}$	= Determined from EPRI-based Sorbent Injection Rate Table, based on Hg Removal % and Coal Type; such table to be updated as more current or relevant data is published by EPRI. In the event Detroit Edison conducts appropriate activated carbon injection testing at Belle River or another plant suitable to simulate Belle River conditions, the Sorbent Usage Rate value determined from that testing will be used.
Inflation Adjustment Factor _{Year}	-	= Gross Domestic Product Implicit Price Deflator (GDPIDP) _{Year} is annually computed and published by US Department of Commerce
Flue Gas Flow Rate	$\frac{\text{mmacf}}{\text{min}}$	= 2.75. Fixed value, based on design data assuming full load operation
Plant Capacity Factor _{Year}	-	= Annual Capacity Factor for Belle River for specified year, as determined from P3M OUTPUT_FAC
Delivered Sorbent Unit Price	$\frac{\$}{\text{lb}}$	= Unit cost for the purchase of treated activated carbon, as determined using average annual prices paid by Detroit Edison for treated activated carbon plus cost for delivery to Belle River
DECo Hg Capital Cost _{Year}	(\$)	= Actual capital costs incurred for mercury control at Detroit Edison plants, adjusted for Belle River Power Plant conditions and installation year. If actual Detroit Edison cost data is unavailable, EPRI Capital Cost _{Year} will be used and installation year.
EPRI Capital Cost ₂₀₀₆	(\$)	= 5,000,000 x Inflation Adjustment Factor. 5,000,000 is a fixed value, determined using the EPRI-based Hg Cost Table that was developed using the September 2006 EPRI Mercury Control Technology Selection Guide
DECo Capital Fixed Charge Rate	-	= .15

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 48 of 806

Environmental Benefit Calculation Fly Ash Benefit

Fly Ash Benefit Calculation:

$$\text{DECo Fly Ash Benefit}_{\text{year}} = 0.8139 \times (\text{Fly Ash Revenue Benefit}_{\text{year}} + \text{Fly Ash Disposal Expense Benefit}_{\text{year}})$$

Fly Ash Revenue Benefit Calculation:

$$\text{Fly Ash Revenue Benefit}_{\text{year}} = \text{Actual Fly Ash Revenue}_{\text{year}} - \text{Status Quo Fly Ash Revenue}_{\text{year}}$$

$$\text{If Year} < \text{Hg Compliance Date, Status Quo Fly Ash Revenue}_{\text{year}} = \text{Total Guaranteed Payment}_{\text{year}}$$

$$\text{If Year} \geq \text{Hg Compliance Date, Status Quo Fly Ash Revenue}_{\text{year}} = 0$$

$$\text{Actual Fly Ash Revenue}_{\text{year}} = \text{Project Contracted Fly Ash Volume}_{\text{year}} \times \text{Project Contracted Fly Ash Unit Price}_{\text{year}}$$

Fly Ash Disposal Expense Benefit Calculation:

$$\text{Fly Ash Disposal Expense Benefit}_{\text{year}} = (\text{Project Contracted Fly Ash Volume}_{\text{year}} - \text{Status Quo Contracted Fly Ash Volume}_{\text{year}} - \text{Incremental Fly Ash Increase}_{\text{year}}) \times \text{Variable Unit Disposal Cost}$$

$$\text{If Year} < \text{Hg Compliance Date, Status Quo Contracted Fly Ash Volume}_{\text{year}} = \text{Total Guaranteed Volume}_{\text{year}}$$

$$\text{If Year} \geq \text{Hg Compliance Date, Status Quo Contracted Fly Ash Volume}_{\text{year}} = 0$$

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 49 of 806

Environmental Benefit Contract Fly Ash Benefit Continued

Defined Terms	Unit	Data Source
Project Contracted Fly Ash Volume _{Year}	(tons)	= Volume of Fly Ash committed for sale under contracts in place when Refined Coal is used as fuel at Belle River Power Plant
Project Contracted Fly Ash Unit Price _{Year}	(\$/ton)	= Unit price committed to be paid to Detroit Edison under fly ash contracts in place when Refined Coal is used as fuel at Belle River Power Plant
Variable Unit Disposal Cost _{Year}	(\$/ton)	= $\frac{\text{Actual Annual Variable Disposal Cost}_{\text{Year}}}{\text{Actual Annual Fly Ash Tons Landfilled}_{\text{Year}}}$
Actual Annual Variable Disposal Cost _{Year}	(\$)	= Cost for landfilling fly ash produced at Belle River for specified year, as reported in [Plant Maximo Account]. This cost excludes fixed costs associated with landfill.
Actual Annual Fly Ash Tons Landfilled _{Year}	(tons)	= Actual annual tons of fly ash produced at Belle River for specified year that were disposed by landfilling, as reported in [Plant Maximo Account]
Hg Compliance Date	(year)	= First year that Hg emissions are required to be removed from Belle River stack emissions due to State and/or Federal requirements
Incremental Fly Ash Increase _{Year}	(tons)	= Annual volume of additives mixed with coal by BRFC to produce Refined Coal, as determined from BRFC data acquisition system
Total Guaranteed Volume _{Year}	(tons)	= Value determined from Belle River Fly Ash Contracts Table for specified year. Table will be amended to incorporate future contract adjustments not attributed to the use of Refined Coal.
Total Guaranteed Payment _{Year}	(\$)	= Value determined from Belle River Fly Ash Contracts Table for specified year. Table will be amended to incorporate future contract adjustments not attributed to the use of Refined Coal.

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 50 of 806

DECo's Share of BRFC Revenue

DECo's Share of BRFC's Revenue Requirement:

- DECo's Share of BRFC's Revenue Requirement_{Year} =

$$81.39\% \times (\text{Expenses}_{\text{Year}} + \text{DECo Allowed Return} \times (1/(1 - \text{Tax Rate})) \times (\text{Net Plant}_{\text{Year}} + \text{Non Coal Working Capital}_{\text{Year}})) \\ + \text{DECo Allowed Return} \times (1/(1 - \text{Tax Rate})) \times \text{DECo Coal Inventory}_{\text{Year}}$$

Defined Terms	Unit	Data Source
Expenses _{Year}	(\$)	Total BRFC reasonable and prudent expenses incurred for the year less all coal and coal handling expenses for which BRFC is reimbursed by either Edison or MPPA - See Note 1.
DECo Allowed Return	%	= 7.16%.
Tax Rate	(\$)	= Federal Statutory Tax Rate + ((1 - Federal Statutory Tax Rate) X (State Income Tax Rate including Surcharges) e.g. for 2009: 35% + ((1 - 35%) X (4.95% + 0.8%))) = 38.74%
Net Plant _{Year}	(\$)	= BRFC's Net Book Value of Capital Assets at December 31 st of the applicable year Note: If the number of facilities exceeds the appropriate number of facilities, Net Plant _{Year} will be reduced by the net book value of excess facilities.
Non Coal Working Capital _{Year}	(\$)	= BRFC's Working Capital at December 31 st of the applicable year Less Coal Inventory (Coal Intransit + Coal Yard) at the Same Date (i.e. Current Assets - Current Liabilities - Coal Inventory)
DECo Coal Inventory _{Year}	(\$)	= BRFC's Coal Inventory stored in Coal Intransit and Coal Yard (excluding the MPPA's portion of BRFC's inventory) at Year End.

Note: When it is anticipated that DECo's Share of BRFC's Revenue Requirement will be less than the DECo Environmental Benefit, monthly invoices will be estimated using prior year Expenses, prior year Tax Rate, prior year Net Plant, prior year Non Coal Working Capital and prior year DECo Coal Inventory.

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Laplander

Page: 51 of 806

Avoided Hg Capital Amortization

DECo Avoided Hg Capital Amortization Calculations:

$$\text{DECo Avoided Hg Capital Amortization}_{\text{year}} = \text{Minimum}(\text{Avoided Hg Capital Balance}_{\text{year-1}}, \text{Maximum}(\text{DECo Environmental Benefit} - \text{DECo's Share of BRFC's Revenue Requirement}, 0), \text{DECo Avoided Capital Amortization Cap}_{\text{year}})$$

$$\text{If Year} = 2009, \text{Avoided Hg Capital Balance}_{\text{year}} = 0$$

$$\text{If Year} > 2009, \text{Avoided Hg Capital Balance}_{\text{year}} = \text{Avoided Hg Capital Balance}_{\text{year-1}} + 8139 * (\text{SQ Capital Cost}_{\text{year-1}} - \text{Actual Capital Cost}_{\text{year}}) - \text{DECo Avoided Hg Capital Amortization}_{\text{year}}$$

DECo Avoided Capital Amortization Cap Calculations:

$$\text{If Year} < \text{Hg Compliance Date}, \text{DECo Avoided Capital Amortization Cap} = 0$$

$$\text{If Year} = \text{Hg Compliance Date}, \text{DECo Avoided Capital Amortization Cap} = 0.8139 * ((\text{SQ Capital Cost}_{\text{year-1}} - \text{Actual Capital Cost}_{\text{year-1}}) / (\text{2020 - Hg Compliance Date}))$$

$$\text{If Year} > \text{Hg Compliance Date}, \text{DECo Avoided Capital Amortization Cap} = \text{DECo Avoided Capital Amortization Cap}_{\text{year-1}} + (\text{DECo Avoided Capital Amortization Cap}_{\text{year-1}} - \text{DECo Avoided Hg Capital Amortization}_{\text{year-1}})$$

Status Quo Calculations:

$$\text{If Year} = \text{Hg Compliance Date} - 1, \text{SQ Capital Cost}_{\text{year}} = \text{DECo Hg Capital Cost}_{\text{year}}$$

$$\text{If Year} \neq \text{Hg Compliance Date} - 1, \text{SQ Capital Cost}_{\text{year}} = \$0$$

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 52 of 806

Avoided Hg Capital Amount Continued

Defined Terms	Unit	Data Source
Hg Compliance Date	(year)	= First year Hg emissions are required to be removed from Belle River stack emissions due to State and/or Federal requirements
Actual Capital Cost _{Year}	(\$)	= Actual annual capital cost for mercury control equipment for Belle River Power Plant as determined from discrete accounts dedicated to Belle River mercury control equipment
DECo Hg Capital Cost _{Year}	(\$)	= Actual capital costs incurred for mercury control at Detroit Edison plants, adjusted for Belle River Power Plant conditions and installation year. If actual Detroit Edison cost data is unavailable, EPRI Capital Cost ₂₀₀₆ will be used and installation year.
EPRI Capital Cost ₂₀₀₆	(\$)	= 5,000,000 x Inflation Adjustment Factor. 5,000,000 is a fixed value, determined using the EPRI-based Hg Cost Table that was developed using the September 2006 EPRI Mercury Control Technology Selection Guide
DECo Capital Fixed Charge Rate	-	= .15

Case No.: U-16434-R
 Exhibit: A-30
 Witness: G. E. Laplander
 Page: 53 of 806

Expense Increase Calculation

PA2 Expense Increase Calculation:

$$\text{PA2 Expense Increase}_{\text{Year}} = \frac{\text{PA2 MWH}_{\text{Year}}}{\text{BR MWH}_{\text{Year}}} * (\text{DECo SO2 Benefit}_{\text{Year}} + \text{DECo Avoided Hg Capital Amortization}_{\text{Year}}) / (1 + \text{PA2 MWH/BR MWH}_{\text{Year}})$$

Defined Terms	Unit	Data Source
PA2 MWH _{Year}	MWH	= The quantity of electricity purchased by Detroit Edison through contracts where the price paid by Detroit Edison is a function of Belle River Power Plant fuel expense.
DECo SO2 Benefit _{Year}	(\$)	= As defined earlier in this Exhibit
DECo SQ Hg Capital Amortization _{Year}	(\$)	= As defined earlier in this Exhibit
BR MWH _{Year}	MWH	= The quantity of electricity produced at Belle River Power Plant by Detroit as used in calculating the price Detroit Edison pays is a function of Belle River Power Plant fuel expense.

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 54 of 806

Acronym/Symbol Definitions

Acronym/Symbol	Definition
\$	U.S. Dollar
lb	pound
mmacf	million actual cubic feet
min	minute
SQ	Status Quo
O&M	Operations & Maintenance
MWH	Mega Watt Hour
USEPA	United States Environmental Protection Agency
BACT	Best Available Control Technology

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 55 of 806

EPRI-based Sorbent Injection Rate Table

Sorbent	Hg Removal (%)	Sorbent Usage (lb/MMacf) by Coal Type ⁽¹⁾	
		Powder River Basin	Low Sulfur Eastern Blend
Untreated Activated Carbon	50	2.6	3.3
	60	9.4	5.7
	70	16.2	9.0
	75	NA	10.8
	80	NA	13.6
	85	NA	16.4
Treated Activated Carbon	90	NA	19.2
	50	0.7	2.9
	60	1.3	4.4
	70	1.9	5.8
	75	2.7	7.2
	80	3.6	8.6
	85	4.4	9.9
	90	6.2	11.3

⁽¹⁾ Data pulled from EPRI Report, "Mercury Control Technology Selection Guide (Technical Report 1012672) September 2006, Table 3-3

NA = Limited or no data available, not appropriate option, or not achievable or not consistently achievable based on available test data

Bold numbers were provided in EPRI Report referenced in footnote (1)
Italicized numbers were not provided in EPRI report but developed through linear interpolation using closest EPRI-provided usage rates for Hg Removal % greater and lower than italicized value.

EPRI-based Hg Cost Table

Hg Reduction	Belle River	
	EPRI Capital Cost (\$)	EPRI Fixed O&M (\$)
50	5,000,000	1,000,000
60	5,000,000	1,000,000
70	5,000,000	1,000,000
75	5,000,000	1,000,000
80	5,000,000	1,000,000
85	5,000,000	1,000,000
90	5,000,000	1,000,000

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Laplander

Page: 56 of 806

Calculation of MPPA Benefits

MPPA Refined Coal Adder Calculation:

**MPPA Refined Coal Adder = Minimum(MPPA Environmental Benefit, MPPA's
Share of BRFC's Revenue Requirement) + MPPA Avoided Hg Capital
Amortization**

**MPPA Environmental Benefit = MPPA SO₂ Benefit + MPPA Mercury Benefit
+ MPPA Fly Ash Benefit**

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 57 of 806

Environmental Benefit Calculation SO₂ Benefit

MPPA SO₂ Benefit

$$\text{MPPA SO}_2 \text{ Benefit}_{\text{Year}} = \sum_{\text{Jan}}^{\text{Dec}} \text{MPPA SO}_2 \text{ Benefit}_{\text{Month}}$$

Monthly SO₂ Benefit Calculation:

If Actual SO₂ Emissions_{Month} ≥ Status Quo SO₂ Emissions_{Month}, then MPPA SO₂ Benefit_{Month} = 0

If Actual SO₂ Emissions_{Month} < Status Quo SO₂ Emissions_{Month}, then MPPA SO₂ Benefit_{Month} = 0.1861 X Transacted SO₂ Allowance Benefit_{Month}

Status Quo Calculation:

$$\text{Status Quo SO}_2 \text{ Emissions}_{\text{Month}} (\text{tons SO}_2) = \text{Emission Factor}_{\text{Unit}} \times \% \text{ Sulfur in Coal}_{\text{Monthly Avg}} \times \text{Actual Tons Coal Combusted}_{\text{Month}} \times 0.0005$$

Table defining terms on next page

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 58 of 806

Environmental Benefit Calculation SO₂ Benefit Continued

Defined Terms	Unit	Data Source
Actual SO ₂ Emissions _{Month}	(tons SO ₂)	Tons of SO ₂ emissions for the calendar month, as reported by the SO ₂ Continuous Emissions Monitors installed at Belle River Unit 1 and 2 stack(s). Data shall be provided by Detroit Edison to BRFC by the 5 th day of the month for the prior month's emissions.
Emission Factor _{Unit 1}	$\frac{\text{lbs SO}_2}{\text{tons coal}}$	33.0 Fixed number, developed by adjusting AP-42 Emission Factor of 35 to better correlate with annual SO ₂ emissions reported for Belle River Unit 1 to the United States Environmental Protection Agency (USEPA) from 1998 through 2007. If additional control technology is installed on the unit to comply with future environmental regulations, the Emission Factor shall be adjusted to account for changes in Belle River Unit 1 emissions due to the installation of the control technology.
Emission Factor _{Unit 2}	$\frac{\text{lbs SO}_2}{\text{tons coal}}$	33.4 Fixed number, developed by adjusting AP-42 Emission Factor of 35 to better correlate with annual SO ₂ emissions reported for Belle River Unit 2 to the USEPA from 1998 through 2007. If additional control technology is installed on the unit to comply with future environmental regulations, the Emission Factor shall be adjusted to account for changes in Belle River Unit 2 emissions due to the installation of the control technology.
% Sulfur In Coal _{Monthly Avg.}	$\frac{\text{lbs SO}_2}{\text{tons coal}}$	Average percent sulfur content of coal for month as determined by averaging, for the calendar month, the daily sample percent sulfur content (% Sulfur) results reported by the Detroit Edison's Central Fuel Lab. Detroit Edison shall provide daily coal samples for Belle River Unit 1 and Unit 2 to their Central Fuel Lab, which shall each be analyzed for % Sulfur in accordance with ASTM standards and reported to BRFC within 5 calendar days.
Allowances Not Consumed	$\frac{\text{lbs S}}{\text{lbs coal (tons)}}$	The number of SO ₂ allowances that would have been surrendered to the USEPA if the difference between Status Quo SO ₂ Emissions and Actual SO ₂ Emissions were emitted by the Belle River Power Plant. For example, in 2010 under the current Clean Air Interstate Rule (CAIR), two SO ₂ allowances are required to be surrendered for every one ton of SO ₂ emitted; therefore Allowances Not Consumed = (Status Quo SO ₂ Emissions _{Month} - Actual SO ₂ Emissions _{Month}) x 2.
Actual Tons Coal Combusted _{Month}	(tons coal)	Actual tonnage of coal consumed for the calendar month as reported in P3M as COAL_CONS
Transacted SO ₂ Allowance Benefit _{Month}	(\$)	The actual sale price realized by Detroit Edison for the sale of monthly Allowances Not Consumed. Detroit Edison shall use commercially reasonable efforts to sell the number of Allowances Not Consumed during a calendar month by the 12 th day of the following month. In the event Detroit Edison does not sell the Allowances Not Consumed, the Argus Air Daily monthly index price (ADI) for one SO ₂ allowance, as published by Argus Air daily on the last business day of the month, shall be multiplied by the number of Allowances Not Consumed during that same calendar month to estimate the monthly Transacted SO ₂ Allowance Benefit. The estimated Transacted SO ₂ Allowance Benefit will be reconciled within 30 days to reflect actual sales price if Detroit Edison makes a transaction for Allowances Not Consumed within 3 months after the estimated value was used. It is the Parties' intent that the SO ₂ price index used for purposes of the calculations specified above are representative of the current SO ₂ market price. In the event that the ADI becomes unavailable, or if the Parties agree that the above-specified does not accurately represent the current SO ₂ market price, the Parties shall mutually agree to an alternative or replacement SO ₂ price index for the calculations.

Case No.: U-16434-R
 Exhibit: A-30
 Witness: G. E. Lapplander
 Page: 59 of 806

Environmental Benefit Calculations Mercury Benefit

Mercury Benefit Calculation:

$$\text{MPPA Mercury Benefit}_{\text{year}} = 0.1861 \times \text{Avoided Mercury Compliance Cost}_{\text{year}}$$

Avoided Mercury Compliance Cost Calculations:

$$\text{If Actual Mercury Compliance Cost}_{\text{year}} \geq \text{Status Quo Mercury Compliance Cost}_{\text{year}}, \text{ then Avoided Mercury Compliance Cost}_{\text{year}} = 0$$

$$\text{If Actual Mercury Compliance Cost}_{\text{year}} < \text{Status Quo Mercury Compliance Cost}_{\text{year}}, \text{ then Avoided Mercury Compliance Cost}_{\text{year}} = (\text{Status Quo Mercury Compliance Cost}_{\text{year}} - \text{Actual Mercury Compliance Cost}_{\text{year}})$$

Status Quo Mercury Compliance Cost Calculations:

$$\text{Status Quo Mercury Compliance Cost}_{\text{year}} = \text{SQ Sorbent Cost}_{\text{year}} + \text{SQ Fixed O\&M}_{\text{year}}$$

SQ Sorbent Cost Calculations:

$$\text{If Year} < \text{Hg Compliance Date}, \text{ SQ Sorbent Cost Calculations}_{\text{year}} = 0$$

$$\text{If Year} \geq \text{Hg Compliance Date}, \text{ SQ Sorbent Cost Calculations}_{\text{year}} = \text{Sorbent Usage Rate} \left(\frac{\text{lb}}{\text{mmcd}} \right) \times \text{Flue Gas Flow Rate} \left(\frac{\text{mmcd}}{\text{min}} \right) \times 525,600 \left(\frac{\text{min}}{\text{year}} \right) \times \text{Plant Capacity Factor}_{\text{year}} \times \text{Delivered Sorbent Unit Price} \left(\frac{\$}{\text{lb}} \right)$$

SQ Fixed O&M Calculations:

$$\text{If Year} < \text{Hg Compliance Date}, \text{ SQ Fixed O\&M}_{\text{year}} = 0$$

$$\text{If Year} \geq \text{Hg Compliance Date}, \text{ SQ Fixed O\&M}_{\text{year}} = \text{DECo Hg O\&M}_{\text{Fixed}}$$

SQ Capital Cost Calculations:

$$\text{If Year} = \text{Hg Compliance Date} - 1, \text{ SQ Capital Cost}_{\text{Hg}}(\text{year}) = \text{DECo Hg Capital Cost}_{\text{year}}$$

$$\text{If Year} \neq \text{Hg Compliance Date} - 1, \text{ SQ Capital Cost}_{\text{Hg}}(\text{year}) = \$0$$

Avoided Capital Effect Calculations:

$$\text{If Year} < \text{Hg Compliance Date}, \text{ Avoided Capital Effect}_{\text{year}} = 0$$

$$\text{If Year} = \text{Hg Compliance Date}, \text{ Avoided Capital Effect}_{\text{year}} = (\text{SQ Capital Cost}_{\text{Hg}}(\text{year} - 1) - \text{Actual Capital Cost}_{\text{Hg}}(\text{year} - 1)) \times \text{DECo Capital Fixed Charge Rate}$$

$$\text{If Year} > \text{Hg Compliance Date}, \text{ Avoided Capital Effect}_{\text{year}} = \text{Avoided Capital Effect}_{\text{year-1}} - (\text{Actual Capital Cost}_{\text{Hg}}(\text{year-1}) \times \text{DECo Capital Fixed Charge Rate})$$

Case No.: U-16434-R
Exhibit: A-30
Witness: G. E. Lapplander
Page: 60 of 806

Environmental Benefit Calculation Mercury Benefit

Defined Terms	Unit	Data Source
Actual Mercury Compliance Cost _{Year}	(\$)	= Actual Belle River Mercury Compliance Cost as determined from discrete accounts dedicated to Belle River mercury control equipment, which will be the sum of all mercury control related expenditures, excluding capital
Actual Capital Cost _{Year}	(\$)	= Actual annual capital cost for mercury control equipment for Belle River Power Plant as determined from discrete accounts dedicated to Belle River mercury control equipment
Hg Compliance Date	(year)	= First year Hg emissions are required to be removed from Belle River stack emissions due to State and/or Federal requirements
DECo Hg O&M _{Year}	(\$)	= Actual O&M expenses incurred for mercury control at Detroit Edison plants not consuming Refined Coal, adjusted for Belle River Power Plant requirements without Refined Coal consumption. If actual Detroit Edison cost data is unavailable, EPRI O&M ₂₀₀₈ will be used.
EPRI O&M ₂₀₀₈	(\$)	= 1,000,000 x Inflation Adjustment Factor. 1,000,000 is a fixed value, determined using the EPRI-based Hg Cost Table that was developed using the September 2006 EPRI Mercury Control Technology Selection Guide
Sorbent Usage Rate		= Determined from EPRI-based Sorbent Injection Rate Table, based on Hg Removal % and Coal Type; such table to be updated as more current or relevant data is published by EPRI. In the event Detroit Edison conducts appropriate activated carbon injection testing at Belle River or another plant suitable to simulate Belle River conditions, the Sorbent Usage Rate value determined from that testing will be used.
Inflation Adjustment Factor _{Year}	-	= GDPIDP _{Year} is annually computed and published by US Department of Commerce
Flue Gas Flow Rate		= 2.75. Fixed value, based on design data assuming full load operation
Plant Capacity Factor _{Year}	-	= Annual Capacity Factor for Belle River for specified year, as determined from PJM OUTPUT_FAC
Delivered Sorbent Unit Price		= Unit cost for the purchase of treated activated carbon, as determined using average annual prices paid by Detroit Edison for treated activated carbon plus cost for delivery to Belle River
DECo Hg Capital Cost _{Year}	(\$)	= Actual capital costs incurred for mercury control at Detroit Edison plants, adjusted for Belle River Power Plant conditions and installation year. If actual Detroit Edison cost data is unavailable, EPRI Capital Cost ₂₀₀₈ will be used and installation year.
EPRI Capital Cost ₂₀₀₈	(\$)	= 5,000,000 x Inflation Adjustment Factor. 5,000,000 is a fixed value, determined using the EPRI-based Hg Cost Table that was developed using the September 2006 EPRI Mercury Control Technology Selection Guide
DECo Capital Fixed Charge Rate	-	= .15

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Laplander

Page: 61 of 806

Environmental Benefit Calculation Fly Ash Benefit

Fly Ash Benefit Calculation:

$$\text{MPPA Fly Ash Benefit}_{\text{Year}} = 0.1861 \times (\text{Fly Ash Revenue Benefit}_{\text{Year}} + \text{Fly Ash Disposal Expense Benefit}_{\text{Year}})$$

Fly Ash Revenue Benefit Calculation:

$$\begin{aligned} \text{Fly Ash Revenue Benefit}_{\text{Year}} &= \text{Actual Fly Ash Revenue}_{\text{Year}} - \text{Status Quo Fly Ash Revenue}_{\text{Year}} \\ \text{If Year} < \text{Hg Compliance Date, Status Quo Fly Ash Revenue}_{\text{Year}} &= \text{Total Guaranteed Payment}_{\text{Year}} \\ \text{If Year} \geq \text{Hg Compliance Date, Status Quo Fly Ash Revenue}_{\text{Year}} &= 0 \\ \text{Actual Fly Ash Revenue}_{\text{Year}} &= \text{Project Contracted Fly Ash Volume}_{\text{Year}} \times \text{Project Contracted Fly Ash Unit Price}_{\text{Year}} \end{aligned}$$

Fly Ash Disposal Expense Benefit Calculation:

$$\begin{aligned} \text{Fly Ash Disposal Expense Benefit}_{\text{Year}} &= (\text{Project Contracted Fly Ash Volume}_{\text{Year}} - \text{Status Quo Contracted Fly Ash Volume}_{\text{Year}} - \text{Incremental Fly Ash Increase}_{\text{Year}}) \times \text{Variable Unit Disposal Cost} \\ \text{If Year} < \text{Hg Compliance Date, Status Quo Contracted Fly Ash Volume}_{\text{Year}} &= \text{Total Guaranteed Volume}_{\text{Year}} \\ \text{If Year} \geq \text{Hg Compliance Date, Status Quo Contracted Fly Ash Volume}_{\text{Year}} &= 0 \end{aligned}$$

Case No.: U-16434-R

Exhibit: A-30

Witness: G. E. Lapplander

Page: 62 of 806

Environmental Benefit Calculation Fly Ash Benefit Continued

Defined Terms	Unit	Data Source
Project Contracted Fly Ash Volume _{year}	(tons)	= Volume of Fly Ash committed for sale under contracts in place when Refined Coal is used as fuel at Belle River Power Plant
Project Contracted Fly Ash Unit Price _{year}	(\$/ton)	= Unit price committed to be paid to Belle River under fly ash contracts in place when Refined Coal is used as fuel at Belle River Power Plant
Variable Unit Disposal Cost _{year}	(\$/ton)	= $\frac{\text{Actual Annual Variable Disposal Cost}_{\text{year}}}{\text{Actual Annual Fly Ash Tons Landfilled}_{\text{year}}}$
Actual Annual Variable Disposal Cost _{year}	(\$)	= MPPA cost for landfilling fly ash produced at Belle River for specified year, as reported in [Plant Maximo Account]. This cost excludes fixed costs associated with landfill.
Actual Annual Fly Ash Tons Landfilled _{year}	(tons)	= Actual annual tons of fly ash produced at Belle River for specified year that were disposed by landfilling, as reported in [Plant Maximo Account]
Hg Compliance Date	(year)	= First year that Hg emissions are required to be removed from Belle River stack emissions due to State and/or Federal requirements
Incremental Fly Ash Increase _{year}	(tons)	= Annual volume of additives mixed with coal by BRFC to produce Refined Coal, as determined from BRFC data acquisition system
Total Guaranteed Volume _{year}	(tons)	= Value determined from Belle River Fly Ash Contracts Table for specified year. Table will be amended to incorporate future contract adjustments not attributed to the use of Refined Coal.
Total Guaranteed Payment _{year}	(\$)	= Value determined from Belle River Fly Ash Contracts Table for specified year. Table will be amended to incorporate future contract adjustments not attributed to the use of Refined Coal.