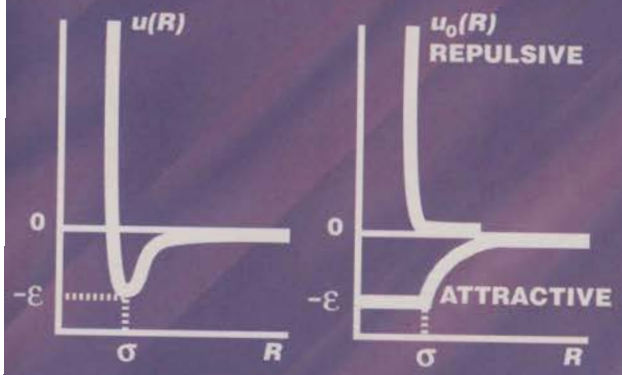
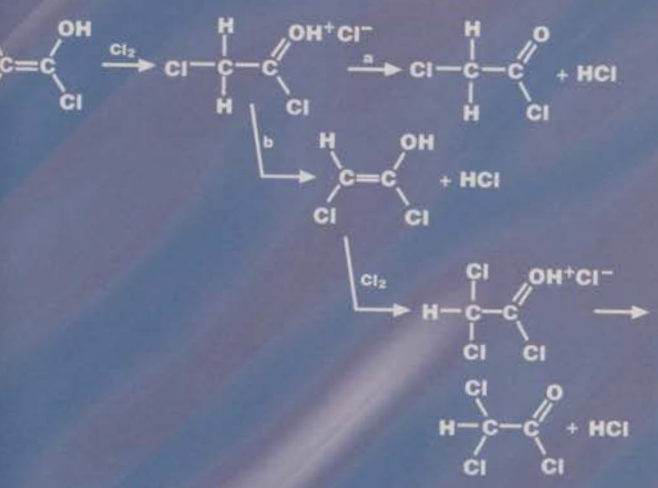
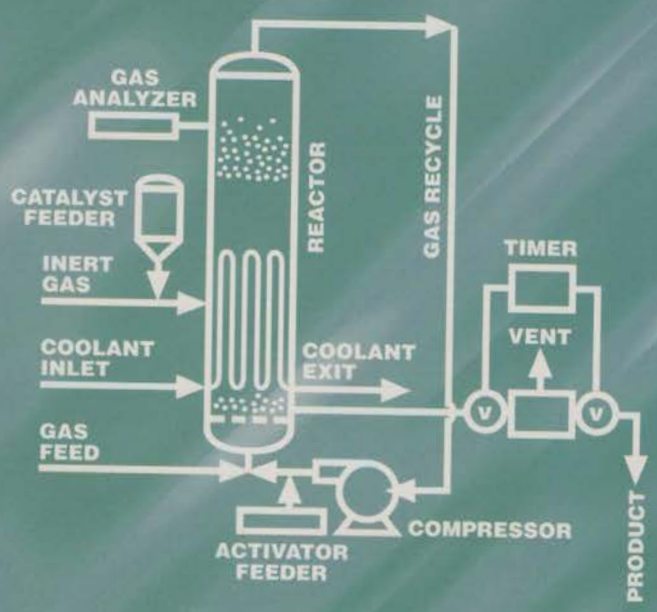
Volume 39, Number 4
http://pubs.acs.org/IECR
April 2000

INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH

A PUBLICATION OF THE AMERICAN CHEMICAL SOCIETY
FOR APPLIED CHEMISTRY & CHEMICAL ENGINEERING







AMEREN UE EXHIBIT 1078
Page 1

INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH

UNIVERSITY OF PITTSBURGH
APR 1 1 2000
COMPUTER SCIENCE LIBRARY

EDITOR

DONALD R. PAUL
Department of Chemical Engineering, University of Texas at Austin
Austin, Texas 78712-1062
(512) 471-5392; Fax (512) 471-0542
E-mail iecr@che.utexas.edu

ASSOCIATE EDITORS

Spiro D. Alexandratos
University of Tennessee

David T. Allen
University of Texas at Austin

John L. Anderson
Carnegie-Mellon University

Lorenz T. Biegler
Carnegie-Mellon University

Milorad P. Dudukovic
Washington University

Babatunde A. Ogunnaike
DuPont Central Research & Development

UNIVERSITY OF PITTSBURGH
APR 1 3 2000
BEVIER ENGINEERING LIBRARY

ADVISORY BOARD

Joan F. Brennecke
University of Notre Dame

Joseph M. DeSimone
University of North Carolina—Chapel Hill

Christodoulos A. Floudas
Princeton University

David S. Hacker
Highland Park, Illinois

Bal K. Kaul
ExxonMobil Research & Engineering Company

M. J. Lockett
Praxair, Inc.

William L. Luyben
Lehigh University

Paul Mathias
Aspen Technology, Inc.

Patrick L. Mills
DuPont Company

Massimo Morbidelli
ETH Zürich

K. J. L. Paciorek
Corona Del Mar, California

Richard J. Quann
Mobil Technology Company

G. V. Reklaitis
Purdue University

Steven F. Rice
Sandia National Laboratories

Dominique Richon
Ecole des Mines de Paris, France

Robin D. Rogers
The University of Alabama

Shivaji Sircar
Air Products

P. R. Westmoreland
University of Massachusetts

AMERICAN CHEMICAL SOCIETY
Science That Matters.

Quick...what alerts you to ACS Web Edition Articles ASAP*?

[ASAP Alerts]

It's Free!

Sign up today—it's FREE!

1. Go to http://pubs.acs.org
2. Click on the ASAP Alerts icon.
3. Complete the registration form.

***Articles ASAP**™ (**As Soon As Publishable**) delivers fully accepted articles within 48 hours of final author approval—in both HTML and PDF full-text formats—weeks before appearing in print—only from ACS.

ACS WEB EDITIONS
Know it Now!
http://pubs.acs.org

SEPARATIONS

Novel Sorbents for Mercury Removal from Flue Gas

Evan J. Granite,* Henry W. Pennline, and Richard A. Hargis

National Energy Technology Laboratory, United States Department of Energy, P.O. Box 10940, Pittsburgh, Pennsylvania 15236-0940

A laboratory-scale packed-bed reactor system is used to screen sorbents for their capability to remove elemental mercury from various carrier gases. When the carrier gas is argon, an on-line atomic fluorescence spectrophotometer (AFS), used in a continuous mode, monitors the elemental mercury concentration in the inlet and outlet streams of the packed-bed reactor. The mercury concentration in the reactor inlet gas and the reactor temperature are held constant during a test. For more complex carrier gases, the capacity is determined off-line by analyzing the spent sorbent with either a cold vapor atomic absorption spectrophotometer (CVAAS) or an inductively coupled argon plasma atomic emission spectrophotometer (ICP-AES). The capacities and breakthrough times of several commercially available activated carbons as well as novel sorbents were determined as a function of various parameters. The mechanisms of mercury removal by the sorbents are suggested by combining the results of the packed-bed testing with various analytical results.

Introduction

Over 32% of anthropogenic mercury emissions in the United States are from coal-burning utilities. This percentage will increase over the next few years because of the mandated control of mercury emissions from municipal solid waste and medical waste incinerators. A low concentration of mercury, on the order of 1 ppbv, exists in flue gas when coal is burned. The primary forms in the flue gas are elemental mercury and mercuric chloride.[1]

Control technologies for removing mercury from flue gas include scrubbing solutions and activated carbon sorbents. Mercuric chloride is soluble in water; elemental mercury is not. Dry sorbents have the potential to remove both elemental and oxidized forms of mercury. Activated carbons have been successfully applied for the control of mercury emissions from incinerators.[1,2]

Several sorbents, such as activated carbons, can remove mercury from flue gas produced by the combustion of coal. However, there are problems associated with the use of activated carbons for mercury removal from flue gas. Activated carbons are general adsorbents; most of the components of flue gas will adsorb on carbon, with some in competition with mercury. Carbon sorbents operate effectively over a limited temperature range, typically working best at temperatures well below 300 °F. The projected annual costs for an activated carbon cleanup process are high, not only because of the high cost of the sorbent but also because of its poor utilization/selectivity for mercury. Carbon-to-mercury weight ratios of 3000:1 to 100 000:1 have been projected.[1,3−5] In addition, activated carbons can only be regenerated a few times before they exhibit unacceptably low activity for mercury removal. Therefore, the development of improved activated carbons as well as novel sorbents merits further research.

A sorbent can capture mercury via amalgamation, physical adsorption, chemical adsorption, and/or chemical reaction. The noble metal sorbents[6−14] can capture mercury via amalgamation. Unpromoted activated carbons and aluminosilicates[15] physisorb elemental mercury. Both amalgamation and physisorption are low-temperature processes, typically occurring below 300 °F. Chemically promoted (with sulfur, iodine, or chlorine) activated carbons,[16−21] selenium,[22,23] and manganese dioxide or hopcalite[24,25] are examples of sorbents which chemisorb or chemically react with mercury. Chemisorption and chemical reaction can occur over a wider range of temperatures than physical adsorption and amalgamation. The enthalpy and activation energies of chemisorption/chemical reaction are typically larger than those for physical adsorption.

In this work, which is sponsored by the Advanced Research and Environmental Technology Power Subprogram of the U.S. Department of Energy's Fossil Energy Program, various sorbents were examined for the removal of elemental mercury from argon. It was realized that elemental mercury in flue gas would be more difficult to remove than oxidized mercury, and thus the thrust was to initially identify sorbents that could remove the less reactive elemental mercury. Very few techniques can be used to make an on-line and continuous determination of elemental mercury down to ppb levels, and the exact mechanism by which most sorbents remove mercury is unresolved. The atomic fluorescence spectrophotometer can be used to measure the concentration of elemental mercury in argon on a continuous basis[26] and was used in determining the breakthrough curves of sorbents in a packed bed. When more complex carrier gases were used, the capacity was

* To whom correspondence should be addressed. Tel.: (412) 386-4607. Fax: (412) 386-6004. E-mail: evan.granite@netl.doe.gov.

10.1021/ie990758v CCC: $19.00 © 2000 American Chemical Society
Published on Web 03/10/2000

AMEREN UE EXHIBIT 1078
Page 3

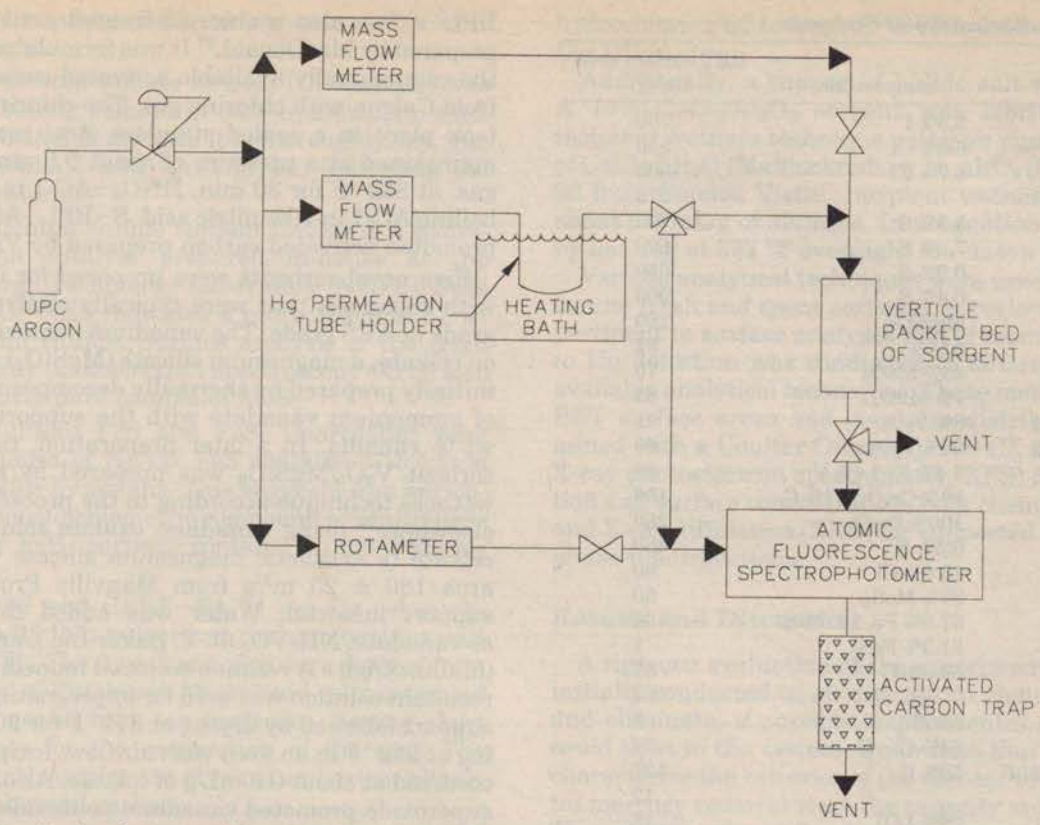


Figure 1. Schematic of sorbent screening unit.

determined off-line via ICP-AES or CVAAS. The capacities of several commercially available activated carbons, metal oxides, a halide salt, metal sulfides, silicates, chlorinated sorbents, a noble metal, and fly ashes were determined.

Experimental Procedures

The assembly used for measuring sorbent capacities consists of an elemental mercury permeation tube, a packed-bed reactor, an on-line atomic fluorescence spectrophotometer, and a data acquisition system. The reactor scheme is shown in Figure 1. A certified Dynacal permeation tube from VICI Metronics is used as the source of elemental mercury. The permeation tube has been certified by the manufacturer to release 144 ng of Hg/min at 212 °F. The permeation tube is located at the bottom of a Dynacal glass U-tube, which is maintained at 212 ± 1.6 °F at all times by immersing it in a Hacke L oil bath. A flow (30 mL/min) of ultra-high-purity carrier-grade (99.999%) argon gas passes over the permeation tube and is maintained at all times with a thermal conductivity mass flow controller. The output of the permeation tube and the flow rate of argon yields a calculated concentration of mercury in argon of 585 ppb. The mercury output of the tube has been verified on a monthly basis via weight loss measurement and has been found to be consistent (155 ng of Hg/min) with the certified release. After a year in service, the output of the permeation tube dropped to 139 ng of Hg/min and was replaced with a second certified tube rated for 119 ng of Hg/min. The output of this tube has also been verified by weight loss measurement and has been found to be consistent (107 ng/min) with the certified release. Sorbent capacities have all been normalized to reflect the output of the original permeation tube.

The reactor (adsorber) is a quartz tube (20 in. in length with an outer diameter of $^1/_4$ in. and inner diameter of $^1/_6$ in.) held in a vertical position. All of the plumbing and valves which come into contact with mercury are constructed from either stainless steel or Teflon. These materials have been demonstrated to have good chemical resistance and inertness toward mercury. The packed bed of sorbent is surrounded by a large clam-shell furnace. A Self-tune Plus 300 PID controller is used to maintain the bed at the desired temperature. The temperature at the top of the bed has been determined to be within 1.8 °F of the temperature at the bottom of the bed.

The detector for elemental mercury is a Brooks Rand CVAFS-2 cold vapor atomic fluorescence spectrophotometer (AFS). When used as a continuous on-line monitor for elemental mercury in argon, the detection limit is below 0.1 ppb. The AFS is an ultraviolet (UV) detector for elemental mercury; mercury atoms absorb 253.7-nm light and re-emit (fluoresce) this wavelength. A mercury bulb serves as the UV source, and a photomultiplier tube serves as the UV fluorescence detector. Any gas can be used as a carrier, although sensitivity varies dramatically with inertness, because of quenching of the excited Hg atoms by collisions with polyatomic species. Maximum sensitivity (ppt) is achieved with high-purity argon or helium carrier gases. When the AFS was used as an on-line detector for elemental mercury, argon was used as the carrier gas. For the more complex carrier gases, the sorbent capacity was determined off-line by analyzing the spent sorbent with ICP-AES or CVAAS. The ICP-AES is a Perkin-Elmer Optima 3000 radial view spectrometer. The CVAAS is a Cetac M-6000A unit dedicated for the analysis of elemental mercury.

Key process parameters were recorded with a data acquisition system. This on-line data acquisition system was used to take and store the various voltage signals

AMEREN UE EXHIBIT 1078
Page 4

Table 1. Characterization of Sorbents

sorbent	composition	BET surface area (m^2/g)
I−AC	3.5% I	750
Cl−AC-1	6.0% Cl	550
Cl−BPL-AC	6.7% Cl	1000
HNO_3−AC-1		575
S−BPL-AC	5.9% S	790
S−AC	7.6% S	690
AC-1	0.9% S	650
AC-2	0.4% S	900
celkate	$MgSiO_3$	160
alumina	Al_2O_3	82
$MoO_3/MgSiO_3$	46% MoO_3	70
MnO_2/Al_2O_3	7% MnO_2	65
V_2O_5−$MgSiO_3$-1	8% V_2O_5	91
V_2O_5−$MgSiO_3$-2	50% V_2O_5	60
KO_2−V_2O_5	3.4% K, 1.4% V	85
Cr_2O_3/Al_2O_3	13% Cr_2O_3, 11% C	156
Fe_2O_3	100% Fe_2O_3	250
TS-7	3.5% S	450
Cl−celkate	15.0% Cl	80
MoS_2	87% MoS_2	50
FeS	57.8% Fe, 22.6% S	32
FeS_2	81.3% FeS_2	1
CERF−FA-#2	59.3% C	37
CERF−FA-#4	37% C	24
FA-1	5% C	5
WCFA-1	64% C	32
WCFA-1−air-750F	50% C	127
Cl−WCFA-1		12
DCFA-1	29% LOI	16
DCFA-2	52% LOI	25
DCFA-3	82% LOI	34
$CaCl_2/Al_2O_3$	10% $CaCl_2$	41
Pt/wool	40% Pt	20

from the thermocouples, flowmeters, and the atomic fluorescence spectrophotometer. Data logging occurred every 15 s.

Typically, 10 milligram (mg) of 200/325-mesh (45−75-μm) sorbent is placed in the center of the tube and is supported by about 50 mg of quartz wool. The quartz wool and reactor tube have been demonstrated to be inert toward elemental mercury. Separate argon gas streams flow through the bed and through the permeation tube holder. The latter flow is sent to the AFS to determine a baseline for the mercury concentration. Once thermal stability is reached in the reactor, the mercury/argon mixture is diverted to flow through the reactor. Breakthrough curves were generated by plotting the atomic fluorescence spectrophotometer voltage signal at the reactor exit versus time. Sorbent capacities were determined by integration under the breakthrough curve.

Sorbent Preparation

The sorbents examined in this study and their characterization are listed in Table 1. The sorbents I−AC, S−AC, AC-1, and AC-2 are commercially available activated carbons. I−AC is an iodine-promoted activated carbon, containing both elemental iodine and potassium iodide. S−AC is a sulfur-promoted activated carbon. AC-1 and AC-2 are unpromoted carbons from Calgon and CarboChem, respectively. Some typical mercury control applications for AC-1 include municipal waste combustors, hazardous waste combustors, and hospital waste incinerators.[2] AC-2 is a food-grade activated carbon used commercially for decolorizing corn syrup.

Cl−AC-1 is a chlorine-promoted activated carbon, prepared by boiling AC-1 in 37% hydrochloric acid. Cl−BPL−AC is also a chlorine-treated activated carbon prepared by MacDonald.[27] It was formulated by treating the commercially available activated carbon BPL−AC from Calgon with chlorine gas. The chlorine treatment took place in a sealed stainless steel reaction vessel maintained at a pressure of about 0.5 atm of chlorine gas, at 330 °F for 30 min. HNO_3−AC-1 is prepared by boiling AC-1 in 70% nitric acid. S−BPL−AC is a sulfur-promoted activated carbon prepared by Vidic.[17]

Five novel sorbents were prepared for investigation with chemicals that were typically analytical reagent grade or ACS grade. The vanadium pentoxide dispersed on celkate, a magnesium silicate ($MgSiO_3$) support, was initially prepared by thermally decomposing a mixture of ammonium vanadate with the support to obtain 8 wt % vanadia. In a later preparation, the supported sorbent $V_2O_5/MgSiO_3$ was prepared by the incipient wetness technique according to the procedure outlined elsewhere[28] using vanadium oxalate solution and the celkate (a synthetic magnesium silicate with surface area 180 ± 25 m^2/g from Manville Products Corp.) support material. Water was added to ammonium *m*-vanadate, NH_4VO_3 (J. T. Baker Inc.), and oxalic acid (Mallinckrodt). A reaction occurred immediately and the resultant solution was used for impregnating the celkate support followed by drying at 572 °F for 2 h and calcining at 932 °F in an oven with air flow. Incipient wetness occurred at about 0.9 mL/g of celkate. Also, a potassium superoxide-promoted vanadium pentoxide (KO_2−V_2O_5) celkate-supported sorbent, whose preparation was similar to the preceding sorbent, was fabricated as well.

The supported sorbent $MoO_3/MgSiO_3$ was prepared by the incipient wetness technique by dissolution of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Fisher Scientific Co.), with ammonium hydroxide in distilled water, and then contact with the celkate. The solution pH was 8. Impregnation was followed by drying at 248 °F for 24 h and then calcination at 932 °F for 6 h.[29]

The alumina-supported MnO_2 sorbent was prepared by the incipient wetness technique using an aqueous solution of manganese nitrate, $Mn(NO_3)_2\cdot 4H_2O$ (Sigma Chemical Corp.), with alumina, Al_2O_3 (Catalox SCFA 90 with surface area 82 ± 25 m^2/g from Condea Vista). Incipient wetness occurred at about 0.6 mL/g of alumina. Impregnation was followed by the thermal decomposition of manganese nitrate in air at 261 °F as outlined elsewhere.[30] Preliminary X-ray diffraction data did not show a MnO_2 diffraction pattern, indicating that the MnO_2 phase was well-dispersed over the alumina and that the crystallite size was below 5 nm.

The chromium oxide sorbent Cr_2O_3/Al_2O_3 that was obtained from Cadus was prepared by impregnation of alumina by chromic acid at room temperature for 30 min.[31] Immediately after impregnation, the sorbent was dried overnight to 122 °F in a vacuum oven and then calcined at 1202 °F in air for 7 h.

MACH I Inc. supplied the ferric oxide sorbent Fe_2O_3. It was the Nanocat superfine iron oxide, which is a dark brown amorphous powder. The particle size is 3 nm.

The platinum sorbent Pt/wool was prepared by deposition of Engelhard metallo organic platinum ink upon quartz wool. The ink was fired in air at red heat to form a platinum film.

Pacific Northwest National Laboratory provided a novel self-assembled monolayer thiol-promoted aluminosilicate sorbent (TS-7). [illegible] applied to purify mercury-contaminated water [illegible]s.

AMEREN UE EXHIBIT 1078
Page 5

This sorbent has a high BET surface area and is 3.5% sulfur by weight.

A chlorine-treated celkate sorbent (Cl−celkate) was prepared by boiling celkate in 37% hydrochloric acid. The slurry is boiled in air until it is thoroughly dry. The boiling hydrochloric acid turns green, indicating the evolution of chlorine.

The molybdenum sulfide sorbent (MoS_2) is a hydrodesulfurization catalyst prepared in-house at the National Energy Technology Laboratory (NETL). Bulk analysis by ICP-AES indicates a composition of 87 wt % molybdenum sulfide. Surface analysis of the fresh sorbent by X-ray photoelectron spectroscopy (XPS) also indicates a fairly pure sample of MoS_2.

The iron sulfides FeS and FeS_2 (marcasite) were prepared in-house at NETL. FeS contains 57.8% iron and 22.6% sulfur by weight. This suggests iron enrichment as in a nonstoichiometric compound or multiphase mixture. The FeS_2 sorbent contains 81.3% FeS_2 by weight.

CERF−FA-#2 and CERF−FA-#4 are fly ashes obtained from a 35 lb/h pulverized coal combustion unit located at NETL. The fly ash samples were derived from the combustion of Pittsburgh #8 coal and were extracted from the furnace at high temperatures, having short residence times for the combustion of the coal. The resulting fly ash samples are atypical and extraordinarily high in unburned carbon.

Sorbents were prepared from fly ash in an effort to utilize unburned carbon from the fly ash. The starting material, FA-1, is fly ash obtained from the combustion of Blacksville coal in the 500 lb/h pilot-scale coal combustion unit located at NETL. FA-1 contains 5% carbon and has a BET surface area of 5 m^2/g. WCFA-1 is a unburned carbon separated from fly ash obtained from the 500 lb/hr combustion unit. The carbon is concentrated from the fly ash through a wet separation technique. WCFA-1 contains 64% carbon and has a BET surface area of 32 m^2/g.

Cl−WCFA-1 is a chlorine-treated carbon derived from fly ash. It is prepared by soaking WCFA-1 in aqua regia for 24 h and drying in air. Also, WCFA-1−air-750F is prepared by heating the carbon WCFA-1 in air at 750°F for 2 h. This is done to increase the BET surface area of the carbon.[32] Thermal oxidation in air increases the microporosity of carbon resulting from the chemical reaction. WCFA-1 has a BET surface area of 32 m^2/g, whereas WCFA-1−air-750F has a higher surface area of 127 m^2/g. The oxidation in air decreases the carbon content from the original 64% down to 50%.

DCFA-1 is a fly ash that is high in carbon content because of poor combustion at a commercial utility; DCFA-2 and DCFA-3 are unburned carbon fractions separated from the DCFA-1 fly ash. The two carbon samples are obtained from the fly ash by a dry separation method (triboelectrostatic) where the first sample is a one-pass separation and the second is a two-pass separation. The elements present in these sorbents were determined via ICP-AES and are silicon, aluminum, iron, titanium, potassium, calcium, magnesium, phosphorus, and sodium. Sulfur, chlorine, and several other elements were not determined by ICP-AES, suggesting that the mass balances obtained (near 90%) are reasonable. Silicon and aluminum accounted for 70−80 wt % of these sorbents (excluding the carbon). These carbons were subsequently treated with chlorine by soaking in hydrochloric acid to form Cl−DCFA-1, Cl−DCFA-2, and Cl−DCFA-3.

Additionally, a supported halide salt was prepared. A 10% $CaCl_2/Al_2O_3$ sorbent was fabricated by the incipient wetness technique using an aqueous solution of $CaCl_2 \cdot 2H_2O$ (Mallinckrodt) with Al_2O_3 (Catalox SCFA 90 from Condea Vista). Incipient wetness occurred at about 0.6 mL/g of alumina. Impregnation was followed by heating at 392 °F overnight to remove the moisture.

Various analytical techniques were used to characterize the fresh and spent sorbents. A review of literature pertinent to surface analyses and of reports pertaining to Hg detection was conducted to determine the best available analytical techniques. These methods included BET surface areas and pore size distributions determined with a Coulter Omnisorp 100 CX apparatus, an X-ray photoelectron spectrometer (XPS) for Hg speciation and surface concentration, bulk chemical analyses, and X-ray diffraction (XRD) for supported oxide sorbent phase identifications.

Results and Discussion

A rigorous evaluation of the experimental setup was initially conducted in an attempt to identify, quantify, and eliminate, if possible, experimental artifacts that could exist in the system. Quantities that were used to characterize the behavior of the sorbent toward elemental mercury removal were the capacity and breakpoint. The capacity was defined as the amount of elemental mercury removed by the sorbent after 350 min on stream. When the continuous on-line AFS monitor for elemental mercury was used, the breakpoint was defined as the time when the outlet concentration of mercury emerging from the reactor bed equaled 10% of the inlet mercury concentration.

The reproducibility of the experimentally determined 350-min capacity and the 10% breakpoint were determined for the baseline sorbent, iodine-promoted activated carbon. Ten milligrams of 200/325-mesh iodine-promoted activated carbon was exposed to 585 ppb of elemental mercury in a 30 cm^3/min flow of argon at 350 °F in order to generate the breakthrough curves. This sorbent was used in this exercise because it represented the most reactive sorbent to date. The experiment was replicated with good results. The capacity determined via the on-line AFS in argon was reproducible to within ±0.2 mg/g and the breakpoint time to within ±25%.

The capacity determined with the on-line AFS was compared with the results obtained from analyzing the spent sample with cold vapor atomic absorption spectrophotometry (CVAAS) and the inductively coupled argon plasma atomic emission spectrophotometer (ICP-AES). The on-line AFS is the most reliable technique for determining sorbent capacity. Unfortunately, this technique is primarily limited to argon (or other noble gas) or nitrogen carrier gas streams.[33] The AFS also has a detection limit for mercury which is an order of magnitude less than the detection limit for the atomic absorption spectrophotometer (AAS).

CVAAS is the next most reliable method for capacity determination and is the preferred analytical technique for the quantitative determination of trace levels of mercury in solids because of the elimination of the background matrix. Great care is taken to transfer the mercury into a noble carrier gas, providing good reproducibility. In CVAAS, the sorbent is dissolved into solution. Mercury is reduced from solution with tin chloride,

AMEREN UE EXHIBIT 1078
Page 6

Table 2. Sorbent Experimental Results: Argon Carrier Gas

sorbent	capacity (mg/g)[a]	breakpoint (min)	temperature (°F)
I−AC	3.1		350
I−AC	4.8	330	350
S−AC	0.4	4	350
S−AC	3.5	7	280
S−BPL−AC	1.9		280
Cl−AC-1	4.0	70	280
Cl−BPL−AC	2.6		280
HNO_3−AC-1	1.2	3	280
AC-1	0.37		280
AC-2	0.4	4	280
celkate	0.5	2.5	350
alumina	0.6	2.5	140
MnO_2/Al_2O_3	2.2	3	350
MnO_2/Al_2O_3	2.4	11	280
MnO_2/Al_2O_3	2.4	40	140
V_2O_5−$MgSiO_3$-1	0.4	3	350
V_2O_5−$MgSiO_3$-2	0.1	2	350
$MoO_3/MgSiO_3$	0.2	3	350
Cr_2O_3/Al_2O_3	1.2	2	140
Cr_2O_3/Al_2O_3	3.1		280
Cr_2O_3/Al_2O_3	3.3	9	350
Fe_2O_3	0.1		280
TS-7	0.01 (ICP-AES)		150
Cl−celkate	0.8	0.5	280
MoS_2	8.8 (ICP-AES)		280
MoS_2	3.9		280
MoS_2	3.6	17	280
MoS_2	4.5	194	140
FeS	cap < 0.01		280
FeS_2	0.2		280
CERF−FA-#2	1.7	4	280
CERF−FA-#2	1.4		280
CERF−FA-#4	2.2	20	280
CERF−FA-#4	1.7		280
FA-1	0.02		280
WCFA-1	0.1		280
WCFA-1	0.04		350
Cl−WCFA-1	2.5		280
Cl−WCFA-1	0.64		350
DCFA-1	0.03		280
DCFA-2	0.12		280
DCFA-3	0.15		280
Cl−DCFA-1	0.24		280
Cl−DCFA-2	0.30		280
Cl−DCFA-3	0.41		280
Pt/wool	5.0		280
$CaCl_2/Al_2O_3$	0.6	2	140

[a] Capacity determined via on-line AFS when a breakpoint time is given; otherwise, the capacity was determined by CVAAS, except as noted.

aerated onto a gold trap, thermally desorbed from the gold trap, and swept into an argon stream to an ultraviolet (AAS) detector. Chemical (tin chloride reduction) and physical (amalgamation) steps are taken to separate the mercury. The detection limit of CVAAS is 10 ng/g.[34] The typical precision for measurement of mercury concentrations in solids is 5−10% relative standard deviation.[34] A comparison of capacity determinations via the on-line AFS and CVAAS shown in Tables 2 and 3 for I−AC in argon at 350 °F, MoS_2 in argon at 280 °F, CERF−FA #2 in argon at 280 °F, and CERF−FA #4 in argon at 280 °F shows a fair agreement.

The ICP-AES is the least reliable of the three techniques for trace-level mercury determinations. It can be seen from Table 2 that the ICP-AES yields capacities which are high by a factor of 2. The ICP-AES is the most versatile tool for multielement analysis, but it is not the preferred method for trace-level mercury measurements in solids. No steps are taken to separate the mercury from the other elements present in the solid sample.

Table 3. Sorbent Experimental Results: Air Carrier Gas

sorbent	capacity (mg/g)	analysis method	temperature (°F)
KO_2−V_2O_5	0.02	CVAAS	280
KO_2−V_2O_5	0.04	CVAAS	350
MnO_2/Al_2O_3	3.50	CVAAS	280
TS-7	0.00	ICP-AES	140
S−BPL−AC	0.53	ICP-AES	280
S−BPL−AC	0.28	ICP-AES	350
MoS_2	5.6	ICP-AES	140
MoS_2	5.2	ICP-AES	280
MoS_2	1.1	ICP-AES	350
AC-1[a]	0.04	CVAAS	280
AC-1[a]	0.19	AFS	280

[a] 4% O_2 in N_2 carrier gas.

Other elements could interfere in the detection of mercury. For example, the cobalt emission line at 253.649 nm could interfere in the determination of mercury by the 253.652-nm emission line.[35] The concentration of the interfering element (in this case cobalt), monochromator slit width, and relative intensity of the shared emission line are factors in determining the extent of spectral interference. Experiments with the Perkin-Elmer Optima 3000 radial view ICP-AES confirmed that cobalt will interfere in the trace-level determination of mercury in solids. Additionally, because of their emission lines close to 253.7 nm, iron and manganese[36] will also interfere in the determination of mercury by ICP-AES.

The effect of intraparticle mass-transfer resistance due to the diffusion of mercury within the pores was determined by carrying out the same experiment but with various size fractions of the baseline iodine-promoted activated carbon. For a sub-400-mesh size fraction of the same carbon, the 350-min capacity was 4.9 mg of Hg/g and the breakpoint was 405 min. This is in good agreement with the data for the larger size fraction (see I−AC in Table 2), suggesting that mass-transfer resistance due to the diffusion of mercury into the sorbent at the sizes used in the testing is negligible. Calculations further indicated that bulk mass-transfer effects, heat-transfer effects, channeling, and pressure drop would not be significant in the experimentation.

Most of the experiments used a gas feed of 585 ppb elemental mercury in argon. This is dramatically different than the composition of a typical flue gas from a coal-fired utility. Most of the components in a typical flue gas (e.g., acid gases, etc.) can adsorb on an activated carbon and could possibly hinder or help the adsorption of mercury on carbon. As pointed out above, the ultra-high-purity argon carrier gas was selected to maximize the sensitivity of the AFS for elemental mercury. However, the capacity of the sorbents in argon can be quite different from the capacity in flue gas. Also, the temperatures at which sorbent capacities were typically determined are 140, 280, and 350 °F. These temperatures were chosen because of their potential relevance to coal-fired utilities. If a sorbent were contacted with the flue gas by injection into the duct work of a coal-fired utility after the air preheater but before the particulate collection device, it would experience temperatures in the range of 350−280 °F. If a sorbent was placed downstream of a wet scrubber, it would encounter a temperature near 140 °F.

The 350 min capacities and the 10% breakpoint times for the sorbents are listed in Table 2. The baseline sorbent—the iodine-promoted activated carbon—exhibited

AMEREN UE EXHIBIT 1078
Page 7

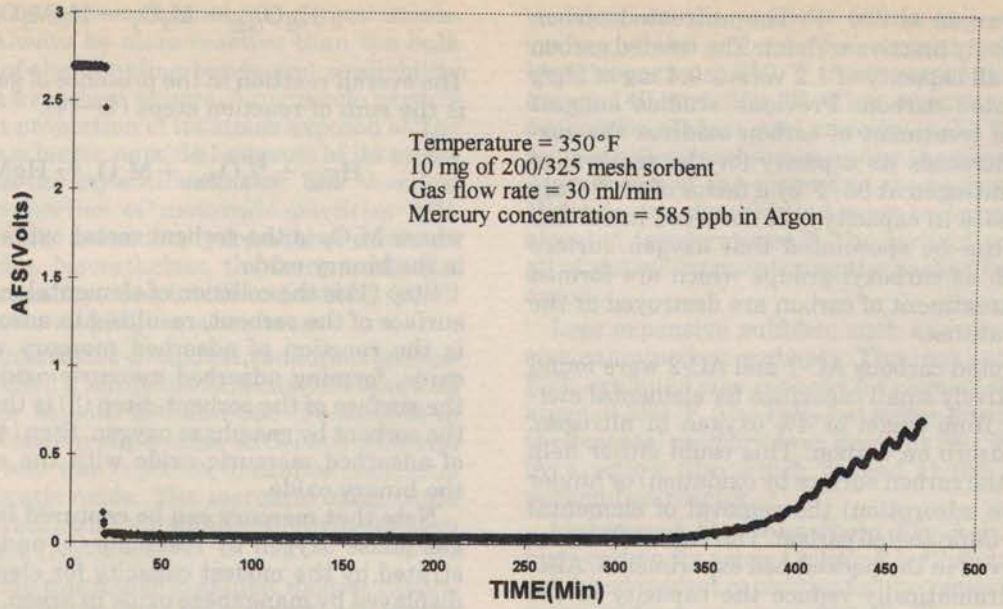


Figure 2. Breakthrough curve for I-AC using the AFS for mercury detection.

both the largest, most reliably determined (on-line AFS) capacity and longest breakpoint time. A typical breakthrough curve for the iodine-promoted activated carbon is shown in Figure 2.

Activated Carbons. With the activated carbons, the effect of the chemical promoter on the capacity for elemental mercury was determined by comparing the capacities of the commercially available unpromoted carbon with the capacities of the sulfur, iodine, chlorine, and nitric acid-treated carbons at the same temperature. The sulfur- and iodine-promoted carbons are available commercially. The carbons, when chemically promoted, exhibited a far greater capacity for elemental mercury. An unpromoted carbon primarily captures elemental mercury via physical adsorption. Chemically promoted carbons capture elemental mercury by both physical adsorption and chemisorption/chemical reaction, where mercuric sulfide, mercuric iodide, and so forth formation enables the promoted carbons to remove more elemental mercury.

Various analyses were performed on the spent baseline iodated carbon sorbent to elucidate the role of the promoter. A 3-day run in the packed bed was performed on 35 mg of iodated activated carbon so that gross differences, if any, between the fresh sorbent and spent sorbent could be differentiated by the BET surface analysis. Results indicate a reduction in surface area from 780 to 300 m^2/g. Additionally, after it was determined that the vacuum treatment would not impact the mercury concentration, XPS studies with the spent iodated activated carbon showed that the Hg species on the surface was oxidized and in the form of HgI_2; no elemental Hg was detected. Potassium iodide was also detected. The total iodide concentration was 0.4% atomic and the Hg surface concentration was 0.13% atomic. Also, the capacity of the spent iodine-promoted carbon was confirmed by atomic absorption analysis. The used sorbent was digested in acid, and the concentration of mercury in the solution was measured by an atomic absorption spectrophotometer. The capacity (gaseous determination) of the iodine-promoted carbon found by integration under the breakthrough curve (4.8 mg/g) was in reasonably good agreement with the capacity (solid determination) established by atomic absorption (3.1 mg/g).

The effect of flue gas temperature was studied by examining the breakthrough curves for the sulfur-promoted carbon S−AC at 280 and 350 °F. The capacity of this carbon at 280 °F was 3.5 versus 0.4 mg of Hg/g at 350 °F. As many studies have demonstrated, activated carbons perform much better at lower temperatures. The temperatures at which activated carbons have been reported to possess good capacities for mercury range from 70 to 500 °F.[1−6,13,16−19,23,37−46] This suggests that physical adsorption may be the first step in the removal of mercury for both unpromoted and promoted carbons. Physical adsorption, analogous to condensation, is a low-temperature process. For a chemically promoted carbon, such as sulfur-impregnated carbon, chemisorption/reaction between the physically adsorbed mercury and sulfur promoter to form mercuric sulfide could be the second step in the mechanism of mercury removal.

The hydrochloric acid-treated activated carbon Cl−AC-1 exhibited a large capacity of 4.0 mg of Hg/g when tested in argon at 280 °F, making it one of the most active sorbents studied to date. Additionally, the chlorine gas-treated activated carbon, Cl−BPL−AC, exhibited a modest capacity for elemental mercury removal. One previous study suggests that hydrochloric acid treatment yields activated carbons which have chemisorbed chlorine.[47] Quimby demonstrated that HCl-treated activated carbon will adsorb mercuric chloride from air at 300 °F.[21] Mercury is known to primarily form the tetrachloromercury complex $HgCl_4^{2-}$ on the surface of activated carbons used for the removal of mercuric chloride from wastewater; little mercuric chloride was found on the surface of these carbons.[48] Other prior studies have shown that HCl treatment of silica increases its capacity for mercury. It can be speculated that elemental mercury reacts with chemisorbed chlorine to form the tetrachloromercury complex on the surface of the carbon.

A nitric acid-treated activated carbon, HNO_3−AC-1, was examined as a sorbent for the removal of elemental

AMEREN UE EXHIBIT 1078
Page 8

mercury from argon at 280 °F. The untreated carbon AC-1 is a relatively inactive sorbent. The treated carbon exhibited a small capacity of 1.2 versus 0.4 mg of Hg/g for the untreated carbon. Previous studies suggest that nitric acid treatment of carbon oxidizes the surface[20,47] and increases its capacity for the removal of mercury from nitrogen at 86 °F by a factor of 20.[20] Only a modest increase in capacity was observed in our lab at 280 °F. It can be speculated that oxygen surface complexes such as carboxyl groups which are formed by nitric acid treatment of carbon are destroyed at the higher temperatures.

The unpromoted carbons AC-1 and AC-2 were found to possess relatively small capacities for elemental mercury, whether from argon or 4% oxygen in nitrogen. Oxygen will adsorb on carbon. This could either help (by promoting the carbon surface by oxidation) or hinder (by competitive adsorption) the removal of elemental mercury by an unpromoted carbon. The latter effect was probably observed in the packed-bed experiments. Also, oxygen may dramatically reduce the capacity of the sulfur-promoted carbon as the capacity dropped from 3.5 mg/g in argon for S−AC to 0.5 mg/g in air at 280 °F for S−BPL−AC. S−AC and S−BPL−AC both exhibit high capacities for elemental mercury from inert carrier gases.[17] This suggests that oxygen competitively adsorbs on sulfur, reducing the capacity.

The results obtained from the packed-bed unit require judicious interpretation when attempting to extrapolate their relevance to activated carbon sorbent duct injection as a mercury control technique for industrial size combustors. AC-1 was also studied in the NETL 500 lb of coal/h pilot-scale combustor unit for the removal of mercury from the flue gas.[49] When introduced at a large sorbent-to-mercury ratio of around 5000:1, AC-1 used in the 500 lb/h unit achieved a high level of mercury removal. However, the used AC-1 recovered from the baghouse had mercury levels of less than 300 ppm (0.3 mg of Hg/g), but a high level of mercury removal is achieved. Unpromoted activated carbons sequester elemental mercury via physical adsorption and therefore exhibit small capacities. Duct injection at large sorbent-to-mercury ratios from 5000:1 to 100 000:1 allows them to, nevertheless, achieve high levels of removal of mercury from flue gas.

Metal Oxides. Metal oxides are proposed as novel alternatives to activated carbon sorbents. It is noted that there are many binary oxides of mercury, such as mercury vanadates, mercury molybdates, and mercury manganates.[50−52] Vanadium pentoxide, molybdenum trioxide, and manganese dioxide are all partial oxidation oxide catalysts for the oxidation of various hydrocarbons.[26,53] In the oxidation of various hydrocarbons, lattice oxygen serves as the oxidant in a Mars-Maessen mechanism. This suggests that lattice oxygen of partial oxidation oxides could also serve as the oxidant of mercury. The reaction mechanism for the capture of mercury by oxide catalysts can be written as

$$Hg_{(g)} + \text{surface} \rightarrow Hg_{(ad)} \quad (1)$$

$$Hg_{(ad)} + M_xO_y \rightarrow HgO_{(ad)} + M_xO_{y-1} \quad (2)$$

$$HgO_{(ad)} + M_xO_{y-1} + {}^1/_2O_{2(g)} \rightarrow HgO_{(ad)} + M_xO_y \quad (3)$$

$$HgO_{(ad)} + M_xO_y \rightarrow HgM_xO_{y+1} \quad (4)$$

The overall reaction in the presence of gas-phase oxygen is the sum of reaction steps (1)−(4):

$$Hg_{(g)} + {}^1/_2O_{2(g)} + M_xO_y \rightarrow HgM_xO_{y+1} \quad (5)$$

where M_xO_y is the sorbent metal oxide and HgM_xO_{y+1} is the binary oxide.

Step (1) is the collision of elemental mercury with the surface of the sorbent, resulting in adsorption. Step (2) is the reaction of adsorbed mercury with the metal oxide, forming adsorbed mercuric oxide and reducing the surface of the sorbent. Step (3) is the reoxidation of the sorbent by gas-phase oxygen. Step (4) is the reaction of adsorbed mercuric oxide with the sorbent to form the binary oxide.

Note that mercury can be captured in the absence of gas-phase oxygen by reactions (1) and (2), as demonstrated by the modest capacity for elemental mercury displayed by manganese oxide in argon, shown in Table 2. There are many potential rate-limiting factors which can impact oxide capacity for mercury, including surface area, activity of the sorbent as an oxidation catalyst, stability of lower oxides, oxygen partial pressure, and tendency to form the binary oxide. Mercury is a semi-noble metal with a standard reduction potential similar to palladium's. Mercury may not be easily oxidized by the metal oxide sorbent. An oxide's tendency to form sulfates is a critical factor for sorbent performance in flue gas because sulfur dioxide is present at concentrations orders of magnitude greater than mercury's.

Alumina (Al_2O_3) or celkate ($MgSiO_3$), which were used as supports for some of the novel sorbents, were examined as sorbents for the removal of elemental mercury from argon. Both exhibit small capacities, demonstrating their inertness toward elemental mercury. The role of the alumina or celkate support is to provide a high surface area substrate for maximizing the number of collisions between mercury and the sorbent.

Supported vanadium pentoxide and supported molybdenum trioxide exhibited low capacities for the removal of elemental mercury from argon at 350 °F. Preparation of the V_2O_5-supported sorbent either via the thermal decomposition of ammonium vanadate or via incipient wetness did not impact the sorbent capacity. Manganese dioxide supported on alumina was examined as a sorbent for the removal of elemental mercury from argon at 350, 280, and 140 °F. Manganese dioxide has been reported to remove elemental mercury from both air and argon at room temperature.[24,25] MnO_2 exhibited modest 350-min capacities of 2.2 mg of Hg/g at the higher temperature and 2.4 mg of Hg/g, at both 140 and 280 °F.

In the Mars-Maessen mechanism, gas-phase oxygen can serve to reoxidize the reduced oxide. Oxygen was absent from the gas phase in these experiments. Manganese dioxide is the most powerful oxidation catalyst[53] of the oxide oxidation catalysts examined and exhibited the largest capacity for mercury. A Mars-Maessen redox mechanism for the removal of mercury has been proposed above for partial oxidation oxide sorbents. The capacity of the manganese dioxide sorbent was observed to be larger in air than in argon at 280 °F (see Table 3).

Nanoscale iron oxide was examined as a sorbent for mercury removal from argon at 280 °F. Each particle

AMEREN UE EXHIBIT 1078
Page 9

contains about 600 iron atoms and 900 oxygen atoms. A surface will always be more reactive than the bulk lattice because of the dangling bonds and availability for collision with a reactant species. A nanoscale particle has a significant proportion of its atoms exposed on the surface whereas a larger particle has most of its atoms contained within the crystalline lattice. The chemical and physical properties of nanoscale particles will, therefore, often differ dramatically from those exhibited by larger particles. Nevertheless, the ferric oxide displayed a poor capacity, despite the unusually small (3-nm) particle size and high surface area.

A potassium superoxide-promoted vanadium pentoxide sorbent exhibited a miniscule capacity for elemental mercury from air at both 280 and 350 °F, as seen in Table 3. The potassium superoxide (KO_2) is a powerful oxidizing agent and was expected to oxidize elemental mercury to mercuric oxide. The mercuric oxide could then chemisorb/react with vanadium pentoxide to form mercury vanadate (HgV_2O_6).

Chromium oxide was found to exhibit modest capacities for elemental mercury. Cr_2O_3 is a fairly strong oxidation catalyst, with a catalytic activity for the deep oxidation of methane comparable to manganese dioxide.[53] A crude correlation was found between the catalytic activity for deep oxidation exhibited by the oxide and the sorbent capacity for elemental mercury removal. Sorbents that are active catalysts for the deep oxidation of methane Cr_2O_3/Al_2O_3 and MnO_2/Al_2O_3 exhibit large capacities, whereas the inactive oxide catalysts Fe_2O_3, MoO_3/Al_2O_3, and $V_2O_5-MgSiO_3$-1 show small capacities.

Promotion of metal oxide supports was also investigated. The chlorine-promoted magnesium silicate Cl–celkate exhibited a small capacity for the removal of elemental mercury from argon at 280 °F. Braman demonstrated that HCl-treated Chromosorb-W, a diatomite chromatographic packing, will adsorb mercuric chloride vapors at 70 °F.[7] Additionally, the novel thiol-promoted aluminosilicate sorbent (TS-7) exhibited very small capacities for elemental mercury both in argon and in air. Thiols are the sulfur analogues of alcohols. Thiols are also called mercaptans, from the Latin, *mercurium captans*, meaning "capturing mercury".[54] Mercaptans react with mercuric ions and the ions of other heavy metals to form precipitates. The sorbent was developed for the removal of oxidized mercury from contaminated water. Elemental mercury is insoluble in water. Oxidized forms of mercury are known to react efficiently with thiols. The low decomposition temperatures of thiols as well as the lack of reactivity with elemental mercury suggest that thiols are not practical promoters for the removal of elemental mercury from flue gas.

Metal Sulfides. Molybdenum sulfide (MoS_2) displayed a large capacity for the removal of elemental mercury from argon and air. This sorbent was originally developed as a hydrodesulfurization catalyst for the conversion of thiopene and mercaptans to hydrogen sulfide and alkanes. A possible mechanism of mercury capture is chemisorption/chemical reaction to form mercuric sulfide. XPS analysis of the used sorbent run in argon at 280 °F confirms the presence of mercury on the surface. Elemental mercury was not detected on the surface of the used MoS_2 sorbent. This rules out physical adsorption of elemental mercury as the primary means of sequestration. The X-ray excited photoelectron spectra suggests the presence of mercuric sulfide on the surface of the sorbent. The sorbent exhibits a much lower capacity at 350 °F in air versus the capacities in air at 140 and 280 °F. This suggests that physical adsorption of elemental mercury is the first step in the sequestration mechanism and/or the physical–chemical degradation of the sorbent at the higher temperature. Molybdenum disulfide is known to decompose in air at elevated temperatures.[36] The sorbent removed nearly all of the mercury entering the packed bed at 140 °F in argon.

Less expensive sulfides, such as iron sulfides, were also examined as sorbents. The iron sulfides FeS and FeS_2 exhibited poor capacity for elemental mercury from argon at 280 °F. The FeS_2 lost sulfur during the sorption of elemental mercury from argon at 280 °F, as evidenced by a yellow film which formed at the bottom of the packed-bed reactor.

Unburned Carbons from Fly Ash. The atypical high-carbon fly ashes CERF–FA-#2 and CERF–FA-#4 exhibited modest capacities for the removal of elemental mercury from argon at 280 °F. These capacities are, however, significantly higher than those exhibited by the unpromoted carbon and the alumina and celkate supports. Further characterization of these fly ash sorbents is needed to determine the mechanism of mercury capture. These carbons were extracted from the combustor at high temperatures of around 2300 °F. It is speculated that novel forms of carbon present in these samples could positively impact capacity.

The fly ash obtained from the combustion of Blacksville coal, FA-1, exhibited a miniscule capacity for elemental mercury at 280 °F. The carbon separated from this fly ash, WCFA-1, exhibited a small capacity for the removal of elemental mercury from argon at 280 °F. Nevertheless, WCFA-1 does exhibit a larger capacity than the parent fly ash, FA-1. The capacity of WCFA-1 was smaller at 350 °F, as expected. The unpromoted activated carbons show similarly low capacities. The chlorine-promoted carbon extracted from fly ash, Cl–CFA-1, exhibited a much larger capacity for elemental mercury, much like the chlorine-promoted activated carbons. The capacity was lower at the higher temperature, as expected.

DCFA-2 and DCFA-3 are carbons separated from the parent fly ash, DCFA-1, by a dry separation method and exhibit small capacities for elemental mercury. The capacity increases with increasing carbon content. The chlorine-treated materials Cl–DCFA-1, Cl–DCFA-2, and Cl–DCFA-3 showed significantly larger, but still small, capacities. The capacity again increases with increasing carbon content.

Halide salts are also proposed as an alternative to carbon sorbents. There are many binary halides of mercury such as calcium chloromercurate and potassium iodomercurate.[50] These are double salts of calcium chloride and mercuric chloride and potassium iodide and mercuric iodide, respectively. Potassium iodide is used as a chemical promoter in some of the commercially available activated carbons,[18,19] such as the baseline sorbent in this study. However, the thermal stability of the binary halides of mercury is poor, as evidenced by their low decomposition temperatures.[50] Mercuric chloride was absent from the gas phase in these experiments. The absence of mercuric chloride could explain the small capacity exhibited by the calcium chloride sorbent. Mercuric chloride can be present in the flue gas

AMEREN UE EXHIBIT 1078
Page 10

obtained from the combustion of coal, municipal waste, and medical waste.[1]

Noble Metals. The platinum sorbent Pt/wool exhibited a large capacity for elemental mercury from argon at 280 °F. Breakthrough was not observed. After the absorption experiment, the used Pt/wool sorbent was slowly heated in argon to 770 °F over a 70-min period, with the effluent sent directly to the AFS. Over 99.4% of the mercury remained sequestered on the platinum. A minor desorption spike of mercury was observed at 320 °F, likely due to unburned carbon from the organometallic platinum paint precursor. The noble metals are often used for small-scale sampling of gases for mercury, i.e., mercury is often collected on gold, thermally desorbed, and sent to a UV detector for its analytical determination. Thermal desorption of the mercury is accomplished by heating the noble metal to 1470 °F,[13] greater than the 770 °F maximum temperature in the desorption experiment.

Conclusions

A packed-bed reactor system was used to screen sorbents for the removal of elemental mercury from a carrier gas. An on-line atomic fluorescence spectrophotometer was used to measure elemental mercury in argon on a continuous basis. For more complex carrier gases, sorbent capacities were determined off-line via CVAAS or ICP-AES. Chemically promoted activated carbons exhibit a far greater capacity for mercury than unpromoted carbons. The activated carbons possess higher capacities at lower temperatures. Chlorine could be a cost-effective chemical promoter for carbon sorbents for the removal of mercury.

Metal oxides and sulfides are proposed as a possible alternative to activated carbon sorbents, with MnO_2, Cr_2O_3, and MoS_2 exhibiting moderate capacities for mercury removal among the candidates investigated. Unburned carbon sorbents from fly ash typically showed poor performance toward mercury removal, although promotion of these increases the activity for elemental mercury removal. Future work will concentrate on testing inexpensive chlorine-promoted carbons as well as metal oxides and sulfides in a simulated flue gas matrix which includes acid gases, oxygen, water, and mercuric chloride. Promising sorbent candidates will be further evaluated on a pilot-scale system.[49,55]

Acknowledgment

Evan Granite acknowledges the support of a postdoctoral fellowship at the U.S. Department of Energy administered by Oak Ridge Institute For Science and Education (ORISE). George Haddad, also through the ORISE program, provided project support. Michael Hilterman, Edward Zagorski, Dennis Stanko, Sheila Hedges, John Baltrus, Mac Gray, Yee Soong, Rod Diehl, Murphy Keller, Mark Freeman, Anthony Cugini, James Hoffman, Karl Schroeder of the Department of Energy, Robert Thompson and Joseph Niedzwicki of Parsons Infrastructure, Donald Floyd of EG&G Technical Services, and Mark Wesolowski of SSI Services, Inc. provided outstanding technical assistance. Several individuals and organizations provided sorbent samples for examination by the DOE. Professor Radisav Vidic of The University of Pittsburgh supplied a sulfur-promoted carbon sorbent. Professor Jayne MacDonald of the Royal Military College of Canada provided a chlorinated carbon sample. CarboChem Inc. donated an unpromoted activated carbon sorbent. Dr. Shas Mattigod of Pacific Northwest National Laboratory provided the thiol-promoted aluminosilicate. Professor Luis Cadus of INTEQUI Instituto de Investigaciones en Tecnologia Quimica, San Luis, Argentina supplied the chromium oxide sorbent. Dr. John Stencel of the Kentucky Center For Applied Energy Research provided carbons derived from fly ash. MACH I Inc. of King of Prussia Pennsylvania contributed the iron oxide sample.

Disclaimer

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement by the U.S. Department of Energy.

Literature Cited

(1) *Mercury Study Report to Congress*; EPA 452/R-97-003; U. S. Environmental Protection Agency, Office of Air Quality Planning and Standards: Washington, DC, Dec 1997.

(2) *Flue Gas Treatment Reference Bulletin*; Calgon Carbon Corporation: Pittsburgh, PA, Nov 1994.

(3) Ghorishi, B.; Jozewicz, W.; Gullet, B. K.; Sedman, C. B. Mercury Control: Overview of Bench-Scale Research at EPA/APPCD. Presented at the First Joint Power & Fuel Systems Contractors Conference, Pittsburgh, PA, July 1996.

(4) Waugh, E. G.; Jensen, B. K.; Lapatnick, L. N.; Gibbons, F. X.; Haythornthwate, S.; Sjostrom, S.; Ruhl, J.; Slye, R.; Chang, R. Mercury Control on Coal-Fired Flue Gas Using Dry Carbon-Based Sorbent Injection: Pilot-Scale Demonstration. Presented at the Fourth International Conference on Managing Hazardous Air Pollutants, Washington, DC, Nov 1997.

(5) Brown, T. D.; Smith, D. N.; Hargis, R. A.; O'Dowd, W. J. Mercury Measurement and Its Control: What We Know, Have Learned, and Need to Further Investigate. *J. Air Waste Manage. Assoc.* **1999**, *6*, 1.

(6) Attari, A.; Chao, S. Trace Constituents in Natural Gas; Sampling and Analysis. *Oper. Sect. Proc. Am. Gas Assoc.* **1994**, 28−32.

(7) Braman, R. S.; Johnson, D. L. Selective Absorption Tubes and Emission Technique for Determination of Ambient Forms of Mercury in Air. *Environ. Sci. Technol.* **1974**, *8* (12), 996.

(8) Williston, S. H. Mercury in the Atmosphere. *J. Geophys. Res.* **1968**, *73* (22), 7051.

(9) Henriques, A.; Isberg, J.; Kjellgren, D. Collection and Separation of Metallic Mercury and Organo-mercury Compounds in Air. *Chem. Scr.* **1973**, *4* (3), 139.

(10) Henriques, A.; Isberg, J. A New Method for Collection and Separation of Metallic Mercury and Organomercury Compounds in Air. *Chem. Scr.* **1975**, *8* (4), 173.

(11) Roberts, D. L.; Stewart, R. M. Novel Process for Removal and Recovery of Vapor Phase Mercury. Presented at the First Joint Power & Fuel Systems Contractors Conference, Pittsburgh, PA, July 1996.

(12) Yan, T. Y. A Novel Process for Hg Removal from Gases. *Ind. Eng. Chem. Res.* **1994**, *33*, 3010.

(13) Dumarey, R.; Dams, R.; Hoste, J. Comparison of the Collection and Desorption Efficiency of Activated Charcoal, Silver, and Gold for the Determination of Vapor-Phase Atmospheric Mercury. *Anal. Chem.* **1985**, *57*, 2638.

(14) Roberts, D. Novel Process for Removal and Recovery of Vapor-Phase Mercury. Presented at the Advanced Coal-Based Power and Environmental Systems '97 Conference, Pittsburgh, PA, July 1997.

(15) Livengood, C. D.; Huang, H. S.; Mendelsohn, M. H.; Wu, J. M. Enhancement of Mercury Control in Flue Gas Cleanup Systems. Presented at the First Joint Power & Fuel Systems Contractors Conference, Pittsburgh, PA, July 1996.

(16) Walker, P. L.; Sinha, R. K. Removal of Mercury by Sulfurized Carbons. *Carbon* **1972**, *10*, 754.

(17) Korpiel, J.; Vidic, R. Effect of Sulfur Impregnation Method on Activated Carbon Uptake of Gas-Phase Mercury. *Environ. Sci. Technol.* **1997**, *31* (8), 2319.

(18) *Material Safety Data Sheet for Activated Carbon 117*; Barnebey & Sutcliffe: Columbus, OH, Sept 1996.

AMEREN UE EXHIBIT 1078
Page 11

(19) *Carbon Product Bulletin HGR-LH*; Calgon Carbon Corp.: Pittsburgh, PA, Feb 1994.

(20) Matsumura, Y. Adsorption of Mercury Vapor on the Surface of Activated Carbons Modified by Oxidation or Iodization. *Atmos. Environ.* **1974**, *8*, 1321.

(21) Quimby, J. M. Mercury Emissions Control From Combustion Systems. Proceedings of Annual Meeting, Air Waste Management Association: Pittsburgh, PA, 1993.

(22) Hogland, W. K. H. Usefulness of Selenium for the Reduction of Mercury Emissions From Crematoria. *J. Environ. Qual.* **1994**, *23*, 1364.

(23) Tsuji, K.; Shiraishi, I.; Olson, D. G. *EPRI Report no. TR-105258*; EPRI: Palo Alto, CA, 1995; conf-950332, Vol. 3, pp 66.1–66.15.

(24) Janssen, J.; Van Den Enk, J.; De Groot, D. Determination of Total Mercury in Air by Atomic Absorption Spectrometry After Collection on Manganese Dioxide. *Anal. Chim. Acta* **1977**, *92*, 71.

(25) Rathje, A.; Marcero, D.; Dattilo, D. Personal Monitoring Technique for Mercury Vapor in Air and Determination by Flameless Atomic Absorption. *J. Am. Ind. Hyg. Assoc.* **1974**, *35*, 571.

(26) Granite, E. J.; Pennline, H. W.; Hargis, R. A. Sorbents For Mercury Removal From Flue Gas. *Topical Report DOE/FETC/TR-98-01*; National Energy Technology Laboratory: Pittsburgh, PA, Jan 1998.

(27) MacDonald, J.; Evans, M.; Halliop, E.; Liang, S. The Effect of Chlorination On Surface Properties Of Activated Carbon. *Carbon* **1998**, *36*, *6* (11), 1677.

(28) Oyama, S. T.; Went, G. T.; Lewis, K. B.; Bell, A. T.; Somarjai, G. A. *J. Phys. Chem.* **1989**, *93*, 6786.

(29) Mahipal Reddy, B.; Padmanabha Reddy, E.; Srinivas, S.T. *J. Catal.* **1992**, *136*, 50.

(30) Maltha, A.; Favre, T. L. F.; Kist, H. F.; Zuur, A. P.; Ponec, V. *J. Catal.* **1994**, *149*, 364.

(31) Mentasty, L.; Gorriz, O.; Cadus, L. Chromium Oxide Supported on Different Al_2O_3 Supports. *Ind. Eng. Chem. Res.* **1999**, *38*, 396.

(32) MacDonald, J. A. F.; Halliop, E.; Evans, M. J. B. The Production of Chemically-Activated Carbons. *Carbon* **1999**, *37*, 269.

(33) Granite, E. J.; Pennline, H. W.; Hoffman, J. S. Effects of Photochemical Formation of Mercuric Oxide. *Ind. Eng. Chem. Res.* **1999**, *38*, 5034.

(34) Golightly, D. W., Simon, F. O., Eds. Methods For Sampling and Inorganic Analysis of Coal. *U.S. Geological Survey Bulletin 1823*; USGS: Reston, VA, 1995.

(35) Reeves, R. D.; Brooks, R. R. *Trace Element Analysis of Geological Materials*; John Wiley: New York, 1978.

(36) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 63rd ed.; CRC Press: Boca Raton, FL, 1982.

(37) *Brochure on Sorbalit*; Dravo Corp.: Pittsburgh, PA, June 1994.

(38) Teller, A. J.; Hsieh, J. Y. Control of Hospital Incineration Emissions-Case Study. Presented at the 84th Annual Meeting of Air & Waste Management Association, Vancouver, Canada, 1991.

(39) Hsieh, J. Y.; Confuorto, N. Operation of a Medical Waste Incinerator and the Emission Control System. *Proc. SPIE-Int. Soc. Opt. Eng.* **1993**, *1717* (Industrial, Municipal, and Medical Waste Incineration Diagnostics and Control), 46.

(40) Tsuji, K.; Shiraishi, I. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1996**, *41* (1), 404.

(41) Tsuji, K.; Shiraishi, I. *EPRI Report no. TR-101054*; EPRI: Palo Alto, CA, 1992; conf-911226, Vol.3, p 8A.1.

(42) Dunham, G. E.; Miller, S. J. Evaluation of Activated Carbon For Control of Mercury From Coal-Fired Boilers. Presented at the First Joint Power & Fuel Systems Contractors Conference, Pittsburgh, PA, July 1996.

(43) Livengood, C.D.; Huang, H. S.; Wu, J. M. Experimental Evaluation of Sorbents for the Capture of Mercury in Flue Gases. Presented at the 87th Annual Meeting Air & Waste Management Association, Cincinnati, Ohio, June 1994.

(44) McNamara, J. D.; Wagner, N. J. *Gas Sep. Purif.* **1996**, *10* (2), 137.

(45) Roberts, D. L.; Stewart, R. M. Characterization of Sorbents for Removal of Vapor Phase Mercury. Presented at the EPRI Mercury Sorbent Workshop, Grand Forks, ND, July 1996.

(46) Van Wormer, M. Control of Mercury Emissions From Combustion Applications. Presented at the 1992 AIChE National Meeting, Aug 1992.

(47) Castilla, C. M.; Marin, F. C.; Hodar, F. J. M.; Utrilla, J. R. Effects Of Non-Oxidant And Oxidant Acid Treatments On The Surface Properties Of An Activated Carbon With Very Low Ash Content. *Carbon* **1998**, *36* (1–2), 145.

(48) Carrott, P. J. M.; Carrott, M. M. L. R.; Nabais, J. M. V. Influence of Surface Ionization On The Adsorption Of Aqueous Mercury Chlorocomplexes By Activated Carbons. *Carbon* **1998**, *36* (1–2), 11.

(49) Hargis, R. A.; O'Dowd, W. J.; Pennline, H. W. Mercury Investigations in a Pilot-Scale Unit. Presented at the AIChE National Meeting, Houston, TX, March 1999.

(50) Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Longmans Green and Co.: New York, 1952.

(51) Angenault, J. *Rev. Chim. Miner.* **1970**, *7*, 651.

(52) Wessels, A. L.; Jeitschko, W. The Mercury Vanadates with the Empirical Formulas $HgVO_3$ and Hg_2VO_4. *J. Solid State Chem.* **1996**, *125* (2), 140.

(53) Golodets, G. I. *Heterogeneous Catalytic Reactions Involving Molecular Oxygen*; Elsevier: New York, 1983.

(54) Solomons, T. W. G. *Organic Chemistry*; John Wiley: New York, 1980.

(55) Hargis, R. A.; Pennline, H. W. Trace Element Distribution and Mercury Speciation in A Pilot-Scale Combustor Burning Blacksville Coal. Presented at the 90th AWMA Annual Meeting, Toronto, Canada, June 1997; paper no. 97-WP72B.04.

Received for review October 18, 1999
Revised manuscript received February 5, 2000
Accepted February 7, 2000

IE990758V