

Effect of Calcium in Field-Spent GACs on Pore Development During Regeneration

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Thermal regenerations were conducted on a granular activated carbon (GAC) that had become exhausted (spent) in a water treatment plant where it had been in service nearly four years. This GAC contained 2 percent calcium. With this field-loaded calcium intact, proper regeneration restored the spent GAC to the same pore structure and surface area that was exhibited by several virgin GACs. When calcium appeared inside the spent GAC, it always caused micropores to be converted to small mesopores during thermal oxidation. In contrast, if the calcium was leached out of the spent GAC with acid, thermal oxidation increased only the micropore volume. Several regeneration variables were tested, including pyrolysis temperature (650–950°C), oxidation temperature (650–950°C), oxidant gas (steam and CO₂), oxidant flow rate, and oxidant extent. All regenerated products of the spent GAC that had been taken to the same targeted apparent density displayed the same surface area and pore structure except those regenerated at low temperatures (650–750°C) with both steam and CO₂ together: these produced carbons with lower volumes of small pores and lower surface areas.

The primary role of granular activated carbon (GAC) in water treatment is to adsorb organic compounds that could potentially harm humans or impart tastes and odors. While the GAC is in service, however, it can also accumulate metals. When the GAC's capacity to adsorb organic compounds becomes exhausted (spent), the GAC can be thermally regenerated for reuse.

This metals accumulation could be high when the GAC serves as a filter adsorber, i.e., when GAC replaces anthracite coal or sand in a conventional filter bed. In such cases the GAC is downstream of iron, aluminum, or lime coagulation process, or a softening process,

and it could become heavily laden with these metals.

The goal of this research was to explore how these accumulated metals affected thermal regeneration and to determine whether thermal regeneration could restore the spent GAC's virgin adsorption capacity despite the metals.

When a GAC becomes spent, water utility managers face a major decision. Should the spent GAC be disposed of in a landfill or incinerated and replaced with virgin GAC, or should the GAC be regenerated so it can be reused? If utility managers select the landfill option, they waste a renewable resource and contribute to a national waste disposal dilemma.

Moreover, they may be asked some day to prove that the adsorbed organic compounds have not subsequently desorbed from the GAC in the landfill and contaminated the groundwater.

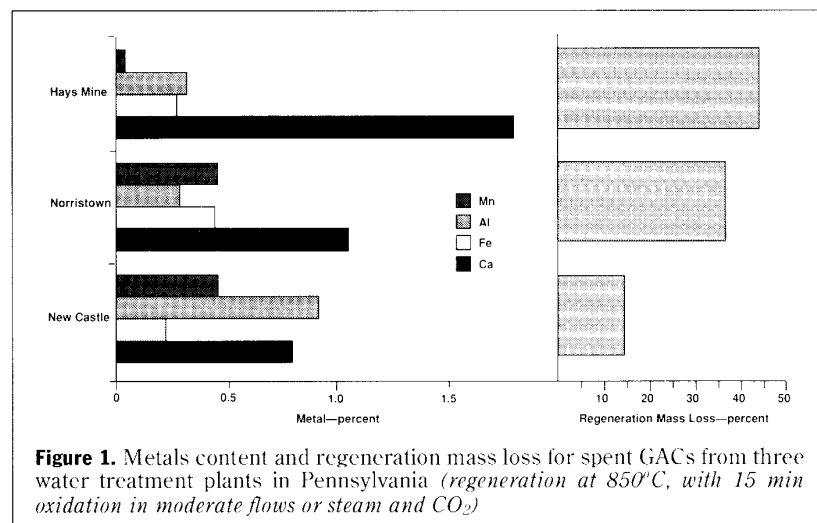
On the other hand, if they select regeneration, they can reuse the GAC rather than discard it. The regeneration process employs the same methods as those used to manufacture virgin GAC or incinerate spent GAC.

Regeneration potentially offers the most economical, energy-efficient, and environmentally sound option. However, any cost or energy analysis would be very sensitive to the adsorption capacity of regenerated carbon relative to virgin carbon. GAC bed volume losses would also weigh heavily, because any lost GAC volume would have to be made up with equal volumes of virgin carbon.

One practical research goal, then, has been to create a thermally regenerated GAC product that manifested the same adsorption properties as its virgin counterpart. As an alternative to monitoring adsorption capacities for the myriad organic compounds present in water, the authors substituted nitrogen pore volumes and surface areas. It was inferred that these parameters were somewhat usefully correlated to adsorption capacities for organic compounds.

Regeneration method and strategies

Thermal regeneration includes both a pyrolysis step and an oxidation step. During pyrolysis, the spent GAC is exposed to an inert gas environment at 650–850°C. This step vaporizes the GAC's water, volatilizes volatile organic compounds, and converts nonvolatile organic compounds to char. Volatilization vacates pores, and charring creates very narrow fissures between aromatic units that had previously been associated with one another. Char is an amorphous carbon pyrolysis product generally devoid of oxygen and hydrogen. A larger percentage of the mass of aromatic and unsaturated aliphatic compounds is usually



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converted to char than that of saturated aliphatics.^{1,2}

During oxidation, the second step of regeneration, the pyrolyzed GAC is exposed to an environment of steam or CO₂ or both at 700–900°C. These gases partly gasify the solid GAC internal surface and slightly widen the pyrolyzation fissures. One could say that optimum oxidation would widen these fissures sufficiently to accommodate organic carbon adsorption but not so excessively that the solid layer between one fissure and another would be destroyed. If excessive, one wide pore with two adsorption surfaces would be created where two narrower pores with four adsorption surfaces had previously existed.

Metals accumulation and catalysis

Metals analyses of spent GACs^{3–5} from American Water Works Service Company (AWWSC) and Compagnie Générale des Eaux (CGE) water treatment plants showed significant metal buildup during use (see representative data in Figure 1; not all data shown herein). In spent GACs, calcium contents were the highest (0.4–7 percent), followed by aluminum (0.3–3.7 percent), iron (nonpyritic—0.1–0.5 percent), manganese (0.02–0.6 percent), and magnesium (0.06–0.3 percent). Calcium, iron, manganese, and magnesium are not known to be harmful to human health.

These metals appear naturally in raw waters. Calcium, iron, and aluminum may be added during chemical treatment. The metals can become loaded onto GAC via chemical precipitation, chelation with natural organic matter, or ion exchange onto the GAC surface. Buildup could be particularly significant when GAC replaces anthracite filtration in a GAC filter-adsorber.⁶

Of these metals, calcium is the most catalytic^{3,4,7,8} (Figure 1). Moreover, iron catalyzes gasification dramatically when sulfur is absent, but it has only a marginal effect when sulfur is present.^{3,4,9} Sulfur always appears in GAC, either from the pyrite that commonly occurs in coal or from organically bound sulfur. Coal-based GACs contain 0.5–0.8 percent sulfur. Screening experiments also showed that aluminum, manganese, and magnesium are not catalytic.^{3,4} Other metals exhibit low concentrations (<0.03 percent), most notably potassium, sodium, nickel, strontium, and barium. At higher concentrations, these five metals measurably catalyze carbon gasification.¹⁰

Literature review

The following review surveys how uncatalyzed and catalyzed oxidation have influenced pore development and adsorption behavior. It also addresses how pore structure potentially influences adsorption behavior by comparing pore sizes with molecular dimensions.

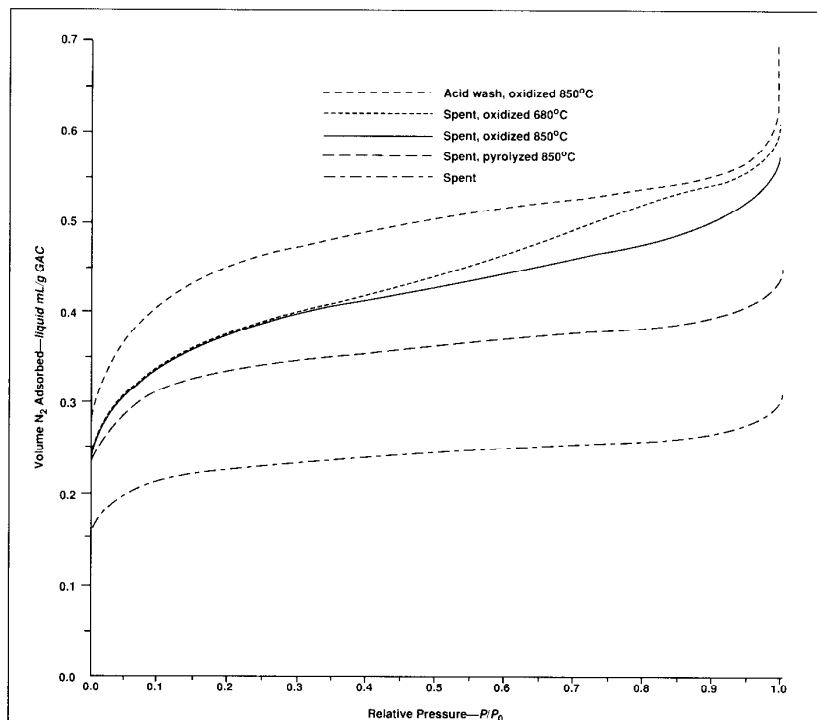


Figure 2. Nitrogen adsorption isotherms for spent Hays Mine GAC treated as shown (oxidation in moderate flows of steam and CO₂ to an apparent density of 0.43 g/mL)

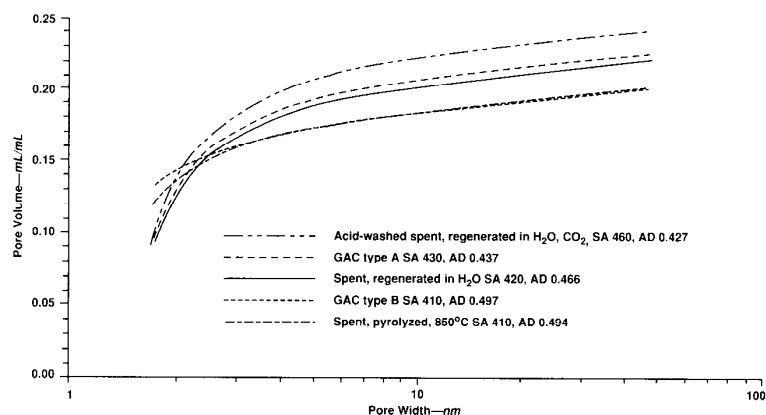


Figure 3. Cumulative pore volume distribution and surface area (m²/mL) for spent Hays Mine GAC pyrolyzed and regenerated at 850°C to the apparent density shown (compared with virgin GAC types A and B)

Size comparisons of GAC pores versus organic compounds. Pore sizes have been categorized into three ranges:¹¹ micropores that are less than 2 nm in width, mesopores that are 2–50 nm in width, and macropores that are larger than 50 nm in width. In comparison, dissolved organic molecules that predominate in natural freshwaters are mostly within the 0.5–5-nm-diameter range. Single-ring aromatic compounds have dimensions in the range of 0.5–0.6 nm,¹² and 1,000-Dalton organic molecules span 1.3 nm (Table 1).

Several researchers have proposed correlations between adsorbate molecular size and adsorbent pore size, including Kasaoka et al.,¹⁹ who observed that adsorption dramatically increased when the carbon's mean pore size exceeded the molecule's second widest dimension by 1.5–2 times. To test this, adsorption was monitored onto an array of carbons that had progressively wider pore sizes. The pores were widened by subjecting a microporous parent carbon to progressively greater oxidation. Methylene blue's adsorption capacity, for example,

TABLE 1
Molecular and pore size comparisons

Size—nm	Parameter	Reference
0.13–0.15	Bond length between carbon atoms	13
0.2	Calcium ionic diameter*	13
0.4 × 0.4	Surface area for condensed N ₂	14
0.3–0.4	Carbon graphitic interlayer spacing	15,16
0.5–0.6	<i>p</i> -nitrophenol width	17
0.5	I ₂ diameter	13
0.6	Diameter of 100-Dalton molecule	12
1–2	Estimated diameter, aquatic fulvic and humic compounds, MW of 800–30,000 Daltons	12,18
1.3	Diameter of 1,000-Dalton molecule	12
1.5–1.9	Estimated critical pore diameter for methylene blue adsorption	17,19
<2	Micropore width	19
2.9	Diameter of 10,000-Dalton molecule	12
6.2	Diameter of 100,000-Dalton molecule	12
2–50	Mesopore width	11
>50	Macropore width	11
450	Blue light wavelength	—

*Hydrated calcium is several times wider.

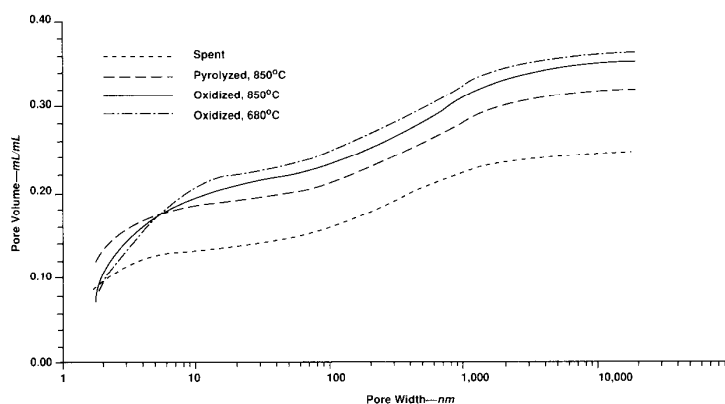


Figure 4. Cumulative pore volume distribution for spent Hays Mine GAC that was pyrolyzed and oxidized in steam and CO₂ to an apparent density of 0.43 g/mL

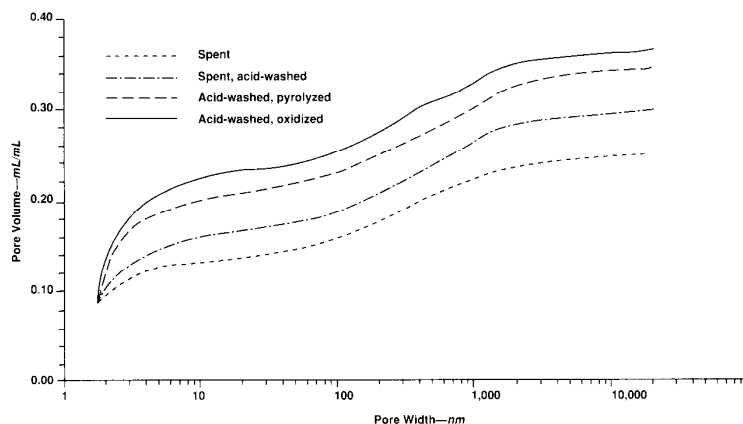


Figure 5. Cumulative pore volume distribution for acid-washed spent Hays Mine GAC that was pyrolyzed and oxidized at 850°C in steam and CO₂ to an apparent density of 0.43 g/mL

increased abruptly when the carbon's mean pore size surpassed 1.5 nm.

Although further research regarding size correlations is warranted, the literature suggests that the low-molecular-weight organic compounds that appear in water supplies would be small enough to

fit into medium-sized GAC micropores but not into the narrowest micropores. Low-molecular-weight compounds might include small carboxylic acids, phenols, amino acids, small hydrocarbons, and a number of the regulated synthetic and halogenated organic compounds. In-

deed, Hölzel and Sontheimer²⁰ and Sontheimer et al²¹ propose that a large number of small organic compounds adsorb into pores smaller than 2 nm in width. In comparison, moderate-sized waterborne compounds such as cellulose and carbohydrates have dimensions that would allow them to fit only into the larger micropores or mesopores.

While evaluating several raw water samples from Southern California, Amy et al²² observed the following apparent molecular sizes for dissolved organic carbon (DOC) composition: 5–30 percent of the DOC was contained among >30,000-Dalton molecules, 10–30 percent was among 10,000- to 30,000-Dalton molecules, 20–35 percent was among 1,000- to 10,000-Dalton molecules, and 20–65 percent was among <1,000-Dalton molecules. According to Perry and Chilton,¹² these would have corresponding diameter ranges of >4.5 nm, 2.9–4.5 nm, 1.3–2.9 nm, and <1.3 nm, respectively. McCarthy and Suffet¹⁸ and Thurman²³ have also characterized the typical molecular weights of river water DOC.

If these organic compounds could only adsorb into pores that were 1.5–2 times greater than their molecular dimension, then only the 20–65 percent of the organic carbon that occurred within <1,000-Dalton molecules could potentially fit within micropores. The remainder would potentially fit into nothing smaller than mesopores. Most of the specific synthetic organic compounds targeted for removal are smaller than 1,000 Daltons.

Pore structure and adsorptive capacity following uncatalyzed oxidation. With catalysts absent, the pore structure and adsorptive capacity of spent GAC have been adequately restored by thermal regeneration, as reported by several researchers. Waer et al²⁴ and Waer²⁵ tested GACs that were regenerated without catalysts being present and found the GACs could be restored to their virgin surface area, micropore volume, iodine capacity, *p*-nitrophenol capacity, and methylene blue capacity. Best adsorptive properties and pore structure occurred when apparent density (AD) of the regenerated GAC was equal to or slightly lower than that of the virgin GAC.

Jüntgen²⁶ regained virgin phenol capacity in repetitive (uncatalyzed) regenerations of GAC. Chihara et al²⁷ restored sucrose adsorption capacity after one (uncatalyzed) regeneration, but capacity deteriorated in subsequent regenerations.

Uncatalyzed oxidation has also effectively developed superior activated carbons from lignocellulosic chars without destroying the carbon micropores. This was found in experiments by Cannon and Roberts²⁸ and Cannon²⁹ that employed a prune-pit char. They attained the highest pore volumes and adsorption capacities when the char was oxidized the longest

in CO₂. As oxidation mass loss increased from 37 to 67 percent, the micropore volume increased from 0.27 to 0.47 mL/g, the mesopore volume increased from 0.14 to 0.35 mL/g, the N₂-BET surface area increased from 930 to 1,700 m²/g, and the adsorption capacity for filtered wastewater secondary effluent DOC increased from 13 to 63 mg DOC/g powdered activated carbon. Although no metals analysis was conducted on this char, fruit pits are generally known to contain very little ash.³⁰ When comparing these prune-pit carbons to GAC type A,* it was observed that DOC adsorption capacity correlated better to the lower range of mesopore volume than to micropore volume. Other parameters may have also influenced adsorption capacity.

Calcium effect on micropore structure and adsorptive properties. Calcium accelerates the gasification rate and thus allows a desired mass loss to be achieved in less time or at lower temperature than when calcium is not present. But uncontrolled calcium catalysis can adversely affect pore structure and surface area.

Sebastiani³¹ regenerated spent GAC from a GAC contactor that served the Upper Occoquan Sewage Authority in Virginia. This contactor followed activated sludge treatment and multimedia filtration. The coal-based spent GAC contained 0.85 percent calcium, compared with 0.2 percent in the corresponding virgin GAC, and had an AD of 0.51 g/mL. This compared with an AD of 0.43 for a virgin GAC type A (12 × 16-mesh fraction, 1.7 mm × 1.18 mm). Sebastiani compared the regeneration products of spent GAC with acid-washed spent GAC and found that when both had been regenerated to an AD of 0.43, they exhibited identical DOC isotherms for wastewater secondary effluent, although their pore

size distributions were presumably different. Moreover, the DOC isotherms for these two GACs were statistically undistinguishable from isotherms that employed virgin GAC or ones that employed spent GAC that had been regenerated to ADs of 0.47 or 0.41. These all had different pore size distributions.

Juhola³² measured the adsorption properties of regenerated spent GAC from an advanced wastewater treatment plant. The spent GAC had accumulated roughly 1.5–2.5 percent ash above virgin levels. Regenerations to virgin AD at 930°C resulted in 10–15 percent lower iodine adsorption numbers than in virgin GAC type A and 0–20 percent higher molasses numbers. Regenerations with steam alone generally caused higher iodine numbers than with CO₂ alone. In comparison, the regeneration product of acid-washed GAC exhibited iodine adsorption capacity 4–10 percent lower than virgin GAC and molasses numbers 0–13 percent lower. Iodine has been perceived to adsorb primarily in large micropores and molasses in small mesopores.

In Juhola's experiments, micropore volume appeared to be restored to virgin values for a spent GAC that was regenerated at 930°C in steam alone or for an acid-washed GAC regenerated in steam and CO₂. However, micropore volume was not restored for a spent GAC that was regenerated in CO₂ alone.³² None of these three regeneration conditions restored the 2–5-nm pores or surface area to virgin values. These pore structure analyses were conducted using water adsorption isotherms (the modeling method was not reported). It is not known how these would compare with nitrogen adsorption isotherms. As the spent GAC experienced three field-loadings and regeneration cycles, iodine capacity de-

creased (0–10 percent each cycle), ash content increased (1 percent each cycle), and molasses numbers increased (0–20 percent each cycle).

Van Vliet and Venter³³ were able to restore only 70 percent of virgin micropore volume (on a unit bed volume basis) after a fourth regeneration cycle. The spent GAC came from a wastewater secondary effluent GAC contactor, and steam oxidation was applied in an infrared furnace. Optimum regeneration conditions were 8 min oxidation at 800°C. Data were not available on the pore size distribution following the third regeneration, just prior to the fourth loading and regeneration cycle. Although ash analyses were not provided, the pore structure behavior suggested catalytic influence.

Linares-Solano et al³⁴ found that uncatalyzed CO₂ gasification caused an increase in micropores but no increase in mesopores, whereas calcium-catalyzed CO₂ gasification caused a dramatic increase in mesopores and a slight decrease in micropores. These GAC samples were loaded with calcium acetate and then were oxidized in a thermogravimetric analyzer (TGA) at 900°C. Catalyzed oxidation also caused a considerable increase in "supermicropore" volumes, defined as the difference between the N₂ and CO₂ micropore volumes. Linares-Solano et al did not assign a pore size to these. In comparison, calcium-catalyzed steam oxidation (at 0.02-MPa pressure) created a pore distribution that was similar to uncatalyzed steam oxidation and exhibited a reactivity that equaled uncatalyzed reactivity. Linares-Solano et al attributed this unusually low catalytic activity to the low partial pressure of steam.

*Filtrisorb 400, Calgon Carbon Corp., Pittsburgh, Pa.

TABLE 2
Comparison of regeneration products for Hays Mine GAC

Parameter	Spent, Hays Mine	Spent, Pyrolyzed	Spent, Pyrolyzed, Mildly Oxidized	Acid- Washed, Pyrolyzed, Oxidized	Type A	Type B*
Regeneration conditions						
Temperature—°C		850	850	850		
Oxidation time—min	0	0	3	35		
Mass loss—percent	0	13.7	18.6	24.5		
Volume loss—percent	0	3.8	3.4	6.8		
Oxidant employed— g H ₂ O/g GAC	0	0	0.4	4.7†		
Product characterization						
Apparent density—g/mL	0.548	0.494	0.466	0.428	0.437	0.497
Ash-free apparent density—g-C/mL	0.492	0.440	0.414	0.406	0.410	0.473
Micropore volume—mL/mL	0.100	0.134	0.124	0.134	0.130	0.142
Mesopore volume—mL/mL	0.049	0.065	0.097	0.107	0.094	0.057
(Volumetric) surface area—m ² /mL	300	410	420	460	430	410
(Gravimetric) surface area—m ² /g-GAC	540	820	900	1,080	990	820
Ash content—percent	9.9	10.8	11.1	5.1	6.22	4.92

*This virgin GAC type B sample was not from the same batch that became spent at Hays Mine, Pa.

†Plus 6.5 g CO₂/g GAC

Full-scale and pilot-scale regenerations at the Cincinnati Water Works have been reported by Miller and Hartman³⁵ and by De Marco et al.³⁶ These data indicated that after virgin GACs had become spent at this water treatment plant and then regenerated through one cycle, the regenerated product GACs exhibited 7–14 percent lower iodine numbers and BET surface areas than their virgin predecessors (on a volumetric basis of comparison). Following the second, third,

and fourth regeneration cycles, there was no further decline in iodine numbers. Although calcium content was not specifically monitored during these tests, the data depicted considerable ash buildup.

Pore blockage by calcium and other inorganic metals has not been noticeable within activated carbons and chars. Linares-Solano et al.³⁷ and Hippo and Walker³⁸ saw no change in pore structure and a slight increase in N₂-BET surface

area when 12 percent calcium and an array of other metals were loaded by chelation or ion exchange into porous chars.

In summary, calcium-catalyzed oxidation has generally been found to slightly deteriorate GAC micropores, surface areas, and iodine adsorption capacity. This deterioration has been the least when the spent GACs were regenerated to their virgin AD. If the spent GACs were acid-washed before regeneration, they exhibited less micropore deterioration and in some cases gained micropore volume.

Recognizing this research, the authors have sought the most favorable conditions for regenerating a spent GAC that contained high levels of calcium and therefore have subjected a spent GAC that contained calcium to a wide array of oxidant gases, oxidant flow rates, oxidation temperatures, pyrolysis temperatures, and extents of oxidation.

Materials and methods

Spent and acid-washed GACs were regenerated in a fluidized-bed furnace, and the regenerated products were compared with virgin GACs by employing nitrogen adsorption isotherms and mercury porosimetry. Spent adsorptive capacity was monitored for select samples by measuring iodine, *p*-nitrophenol, and methylene blue adsorption.

Spent and virgin GACs. Experiments were conducted with a spent GAC from the Hays Mine, Pa., water treatment plant (subsequently called “spent GAC”) and with virgin GAC types B and A.* Both are bituminous-based carbons, and both GAC type A and type B are commonly used in water and wastewater treatment applications.

The Hays Mine plant serves Pittsburgh, Pa., and treats Monongahela River water. At this plant, GAC type B had been used in a filter adsorber for three years and eight months prior to sampling. The spent GAC contained 1.8 percent calcium and 9.9 percent ash and had an AD of 0.55 g/mL.

Acid-washing. Acid-washing was accomplished by passing 10 or more bed volumes of 1 M HCl up through a GAC filter bed followed by 10 or more bed volumes of deionized distilled water. The HCl washing extracted 98 percent of the GAC’s calcium; 90 percent of its available aluminum, manganese, and magnesium; and 50 percent of its iron. The HCl did not appear to extract pyritic iron, sulfur, or aluminosilicates.³⁹

Fluidized-bed regenerations. The fluidized-bed regeneration furnace was as described by Waer et al.²⁴ Standard (“moderate”) steam-CO₂ fluidized-bed regenerations included 10 min of pyrolysis in nitrogen followed by oxidation in 8

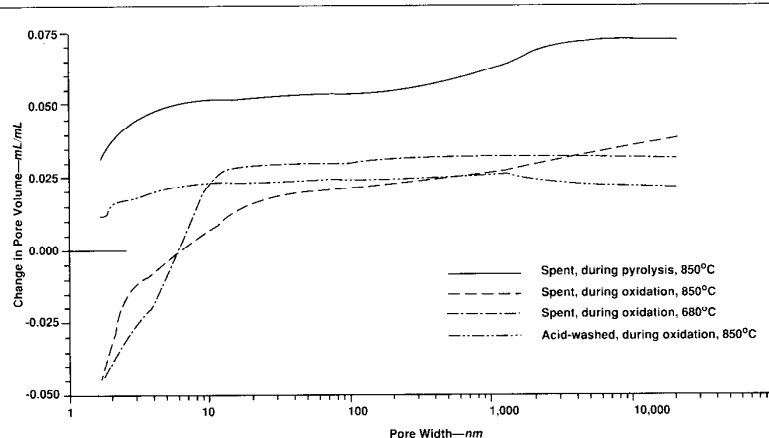


Figure 6. Change in cumulative pore volume distribution for spent Hays Mine GAC during pyrolysis and for pyrolyzed GACs during oxidation in steam and CO₂ to an apparent density of 0.43 g/mL.

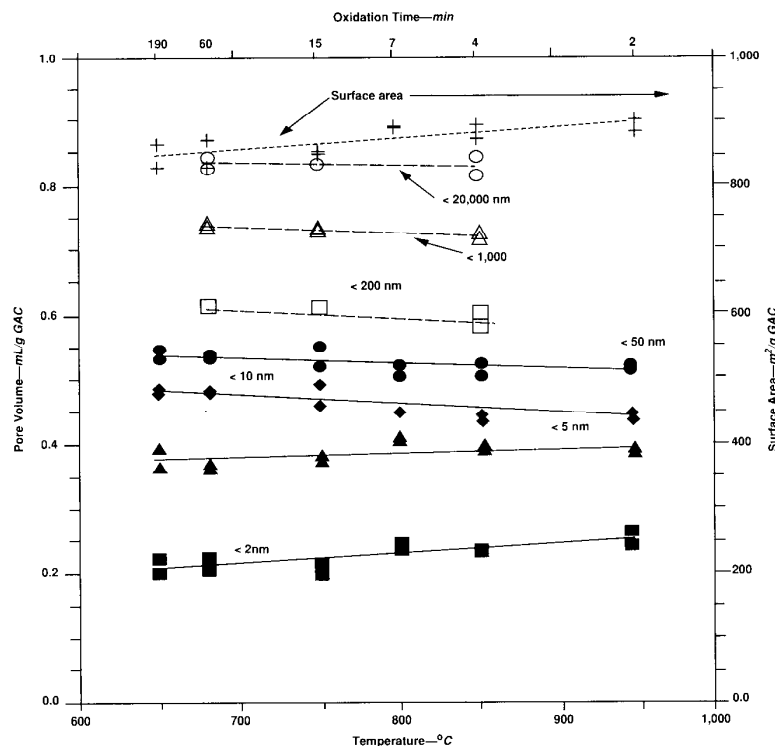


Figure 7. Pore volume distribution and surface area for spent Hays Mine GAC regenerated in steam and CO₂ at various temperatures to an apparent density of 0.43 g/mL.

*Type B—Filtrisorb 200 and type A—Filtrisorb 400, Calgon Carbon Corp., Pittsburgh, Pa.

g H₂O/g GAC-h, 11 g CO₂/g GAC-h, and 30 g N₂/g GAC-h. In these regenerations, 10 g of 16- × 20-mesh (1.18- × 0.85-mm mesh) GAC was used, and the changes in mass, unstratified bed volume, and AD were monitored per ASTM D 2854-83.⁴⁰ This narrow mesh range was employed to minimize variations in oxidation rate that could have resulted from variations in grain size.

Thermogravimetric analysis. Thermogravimetric analyses were conducted with a unit* that continuously monitored mass loss of 10–20-mg GAC samples while they were being pyrolyzed in nitrogen or oxidized in 20 mL/min CO₂ plus N₂ at preprogrammed temperatures. Steam was not used because TGAs are limited to very low water flow rates.³⁴ Moreover, volume losses and changes in AD could not be monitored during TGA experiments.

Metals analysis. Metals analysis was conducted by ashing GAC in a 600°C muffle furnace for 12–16 h, dissolving the ash in 25 mL concentrated HCl for 4–8 h, filtering the solution through 0.45-μm filter paper, and then diluting it to 100 mL with deionized distilled water. This solution was analyzed for metals by employing an inductively coupled plasma (ICP) unit† in the University of Illinois Chemistry Department. Hydrochloric acid is expected to dissolve all pertinent metals except for aluminosilicates, pyrites (FeS₂), and some claybound iron.^{39,40} All ashings and metals analyses were duplicated, and values from duplicate ashings agreed within ±10 percent.

Sulfur was analyzed using an automated total sulfur analyzer‡ at the University of Illinois Forestry Department⁴¹ or at the Illinois State Geological Survey. Samples were duplicated, and values agreed within ±10 percent.

Apparent density, mass loss, and volume loss. The AD of GAC was obtained by dividing the mass of a GAC sample by the volume that the sample occupies when randomly stratified. For this research project, AD measurements were performed according to ASTM procedure D 2854-83⁴⁰ with the modification that 5- to 10-g samples were vibrated into a 25-mL graduated cylinder.

The mass loss resulting from the thermal regeneration process was determined for a batch-type process by weighing the carbon on an analytical balance before and after the regeneration. Mass loss has been expressed as a percentage of unregenerated GAC mass. For samples regenerated in duplicate, the average difference in mass loss between two samples was 0.8 percent (for example, replicate regenerations could have exhibited 25.0 and 25.8 percent mass loss).

The volume of a randomly stratified GAC sample was measured by vibrating a GAC sample into a graduated cylinder as described in the AD procedure. By

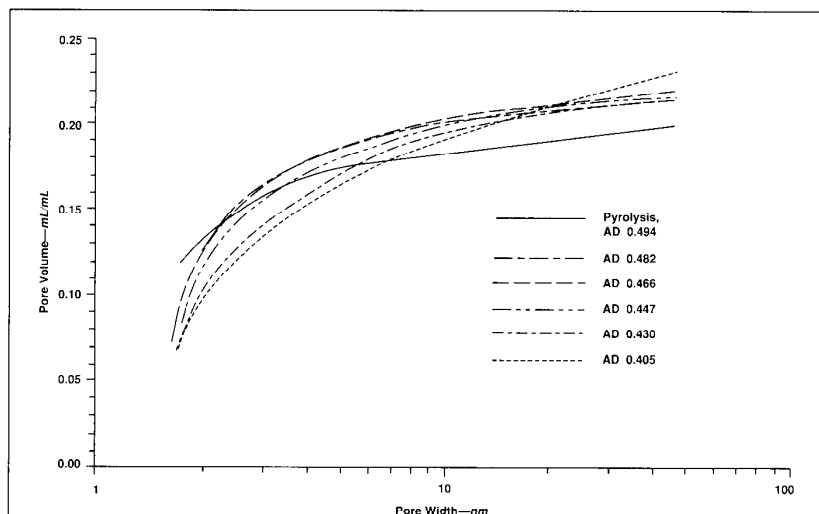


Figure 8. Pore volume distribution for spent Hays Mine GAC regenerated at 850°C to various apparent densities in steam

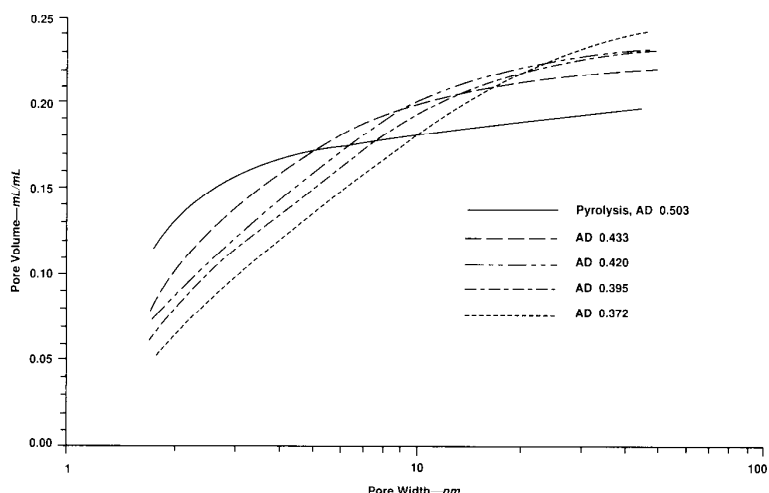


Figure 9. Pore volume distribution for spent Hays Mine GAC regenerated at 750°C to various apparent densities in steam and CO₂

measuring the volume that GAC samples were occupying before and after thermal regeneration, the percentage of volume loss could be calculated and expressed as a percentage of the spent GAC volume.

For samples regenerated in duplicate, the average difference in volume loss between two samples was 0.7 percent (for example, average replicate regenerations could have exhibited 4.0 and 4.7 percent volume loss).

The volume loss occurring during regeneration is an important parameter because it determines the amount of virgin GAC that needs to be purchased to refill the GAC bed to its design volume.

Iodine number, p-nitrophenol, and methylene blue capacity. The iodine number has been defined as the mass of iodine (in milligrams) adsorbed by 1 g of carbon when the residual iodine concentration is

0.02 N. At the University of Illinois, the authors followed ASTM method D4607-86⁴⁰ for measuring the iodine number. However, both the initial concentration of the iodine solution and the amount of carbon were reduced by half to conserve carbon needed for subsequent analyses. p-nitrophenol and methylene blue adsorption capacities were determined from isothermal measurements.²⁵

Nitrogen adsorption at 77 K. Nitrogen adsorption isotherms were obtained at 77.15 K, the boiling point of liquid N₂ at 1 atm (0.1 MPa) of pressure. These isotherms provided the information required to calculate the BET surface area as well as the micropore and mesopore volume of GAC samples. N₂ adsorption

*PC Series TGA7, Perkin-Elmer, Norwalk, Conn.

†Plasma P 2000, Perkin-Elmer, Norwalk, Conn.

‡SC-132, LECO, St. Joseph, Mich.

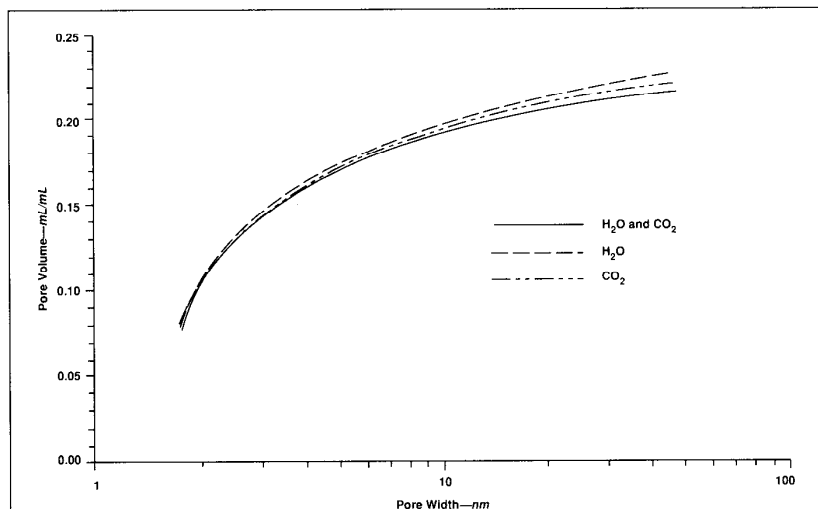


Figure 10. Pore volume distribution for spent Hays Mine GAC regenerated to an apparent density of 0.43 at 850°C in steam, CO₂, and steam plus CO₂

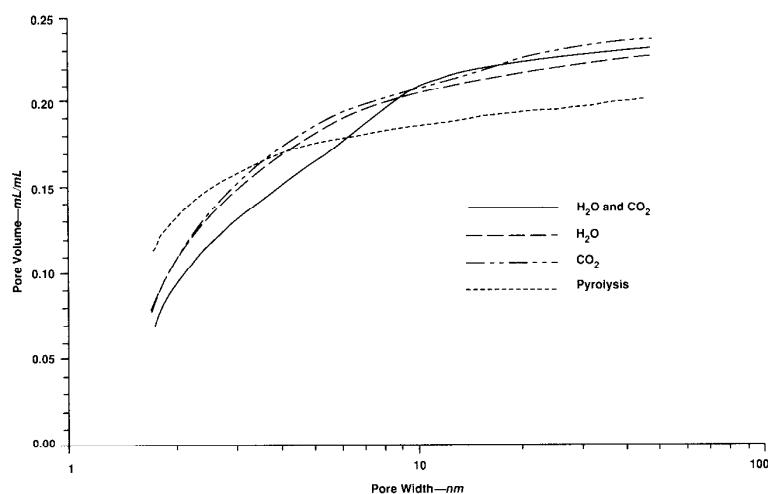


Figure 11. Pore volume distribution for spent Hays Mine GAC regenerated to an apparent density of 0.43 g/mL at 680°C in steam, CO₂, and steam plus CO₂

experiments were conducted on a nitrogen surface analyzer* at the Center for Cement Composite Materials at the University of Illinois. This instrument measured the nitrogen volumes adsorbed versus relative pressures, in which relative pressure was the equilibrium pressure (P) divided by the saturation pressure of N₂ (P_0) at 77 K.

For each GAC sample, the nitrogen surface analyzer automatically monitored roughly 45 adsorption equilibrium points, which spanned relative pressures from 0.005 to 1.00. For each of these data points, a known volume of gaseous nitrogen was pulsed into a glass bulb that contained 0.13–0.17 g of sample. This glass bulb was immersed in liquid nitrogen. As the gaseous nitrogen within the bulb condensed and adsorbed into the GAC sample (at a density approximately equal to that of

liquid nitrogen), the pressure within the bulb dropped to an equilibrium value. This pressure was automatically recorded, and then another pulse of gaseous nitrogen was introduced to repeat the adsorption cycle.

The authors have included representative isotherm examples in Figure 2, which represents experiments that are considered further in the "Results and discussion" section. Several researchers^{14,24,25,42,43} have proposed models that interpret these isotherms to derive the GAC surface area and micropore and mesopore volumes. In most cases, N₂ isotherms were obtained for duplicate regenerations. Typical differences in pore volumes and surface areas were within 5 percent for duplicate regenerations.

Surface area. Total surface area was computed using the model of Brunauer et al.,¹⁴ by employing the portion of the

nitrogen data that spanned relative pressures from 0.005 to 0.124. The Barrett et al model (BJH model)⁴² provided mesopore surface areas, and mercury porosimetry provided macropore surface areas.[†]

Mesopore volume. The mesopore volume range contains pores with diameters spanning from 2 to 50 nm as defined by the International Union of Pure and Applied Chemistry (IUPAC).¹¹ The total mesopore volume and the mesopore volume distribution were calculated from the data of the adsorption leg of the N₂ isotherm via the BJH model.⁴²

Barrett et al⁴² presumed that nitrogen adsorbed by two simplified mechanisms: (1) capillary condensation within small pores and (2) layered physical adsorption onto larger pore walls. Relative pressure dictated the pore size where condensation and layered adsorption occurred, and trigonometric functions distinguished between them. Barrett et al⁴² built their model on the Kelvin equation, which identified the relative pressure that caused nitrogen condensation within the "inner capillary volume" of a pore. The "inner capillary volume" was defined as the vacant volume that was not occupied by either carbon or layered nitrogen at the preceding relative pressure. Thus, the inner capillary width equaled the pore width minus twice the layered nitrogen thickness.

Barrett et al championed their model for situations in which pores were "cylindrical, or more precisely, when the pore volume and the capillary volume were related to each other as the square of some adequate measure of their cross sections."⁴² In this article the authors propose that the wedge-shaped pores found in GAC conform to this criterion. The cross-section dimensions computed by this method may not, however, represent true pore widths, and they therefore offer relative rather than quantitative comparisons. Thus, throughout this article, the term "2-nm pores" refers to pores having a computed cross-section dimension of 2 nm.

The equation used for determining nitrogen layer thickness, t_N , in the BJH model was provided by Waer:²⁵

$$t_N = 24.6164 / (0.034 - \log [P/P_0])^{0.429} \quad (1)$$

For duplicate analyses of duplicated regenerations, the difference in mesopore volumes was usually found to be within 5 percent.

Micropore volume. The recovery of GAC micropore volume within a regenerated product is especially important for restoring the adsorption capacity of low-molecular-weight organic compounds.

*2400 ASAP, Micromeritics, Norcross, Ga.

†Autopore II Mercury Porosimeter, Micromeritics, Norcross, Ga.

Micropores are defined by IUPAC as pores having diameters <2 nm.¹¹ To determine micropore volume, a procedure was developed that expanded the scope of the BJH model.⁴² As developed during the research, the authors propose that at a relative pressure of 0.12, all pores smaller than 2 nm are filled with nitrogen by capillary condensation,^{44,45} and all surfaces in pores larger than 2 nm have adsorbed a 0.4-nm-thick layer of nitrogen.^{24,25} The micropore volume could then be computed by the procedure:

1. Convert gaseous volume of N₂ adsorbed to equivalent liquid N₂ volume (V_{total}) at a relative pressure of 0.12 (cm³ at STP/g GAC). The density of liquid N₂ at 77.15 K is 0.808 g/cm³.¹³

2. Derive the adsorbed layer volume (V_{layer}) in pores larger than 2 nm at a relative pressure of 0.12 by multiplying the mesopore plus macropore surface area by the thickness of the adsorbed liquid N₂ layer (0.4 nm). The mesopore surface area was determined from the nitrogen isotherm data by use of the BJH model; the macropore surface area was determined by mercury porosimetry.

3. Compute the micropore volume (V_{micro}) by taking the difference between the total and layered volumes (Eq 2):

$$V_{\text{micro}} = V_{\text{total}} - V_{\text{layer}} \quad (2)$$

For the coal-based virgin and regenerated GACs, V_{micro} generally amounted to two thirds of V_{total} , and V_{layer} amounted to roughly one third of V_{total} . For analyses of duplicated regenerations, the difference in micropore volumes was usually within 5 percent.

Total pore volume under 50 nm. Similarly, a relative pressure of 0.96 filled all pores smaller than 50 nm per the Kelvin equation⁴³ and blanketed macropore surfaces with a 1.4-nm-thick adsorption layer per Waer et al²⁴ and Waer.²⁵ Thus their difference equaled the <50-nm volume. These computations were cross-checked by comparing micropore volumes (at $P/P_0 = 0.12$), mesopore volumes (by the BJH model), and volume below 50 nm (at $P/P_0 = 0.96$). The last value consistently exceeded the sum of the first two values by only 0–7 percent. This good agreement implied model accuracy or consistently compensating inaccuracies. One cannot independently distinguish between these possibilities. Nonetheless, this modified BJH model has been considered useful when making comparisons among GAC samples.

Several researchers^{7,24,25,43} have employed the thickness-volume (t - V) method when computing micropore volumes. The t - V method has relied on the same assumptions that have been used in this research. However, after several trials, the authors abandoned the t - V method because (1) the authors could not interpret all data with it and (2) it

apparently overestimated micropore volumes. When t - V micropore volumes that were computed from data were added to corresponding BJH mesopore volumes, they exceeded the under-50-nm volume by 10 to 25 percent.

An example of one of the curves that could not be interpreted by the t - V method is labeled in Figure 2 as the "Spent, oxidized 680°C" curve. No single micropore volume could be computed for this because it was described by two t - V slopes between relative pressures of 0.2 and 0.93.

Representative nitrogen adsorption isotherms. Several representative nitrogen isotherms have been shown on a unit mass basis in Figure 2 as they appeared before they were mathematically manipulated. The BJH model results (see subsequent discussion) depicted the same trends as these isotherms, as expected.

Mercury porosimetry. IUPAC defines macropores as pores with diameters >50 nm.¹¹ Pore volume distributions in the macropore range up to pore diameters of 20 μ m (20,000 nm) were obtained using mercury intrusion porosimetry (MIP)* at the Center for Cement Composite Materials at the University of Illinois. In MIP, mercury is forced into GAC pores at pressures up to 60,000 psi. Increasing pressures correspond to decreasing pore diameters so that a pore volume distribution is obtained. The cumulative intrusion volume was plotted against the corresponding pore diameters.

For duplicated regenerations, mercury porosimetry agreement was within ± 6 percent.

Comparisons per unit bed volume. Throughout this article, the authors have reported GAC data per unit of unstratified bed volume. The volume is that occupied by the GAC including the volume of voids between grains (ASTM D2584-83).⁴⁰ When values were measured on a mass basis, they were converted to a unit bed volume basis by multiplying the values by their corresponding ADs.

The unit bed volume basis was preferred over the unit mass basis for two reasons: (1) the capacity per unit volume is more directly related to the capacity of a fixed-bed adsorber and (2) comparisons based on a unit bed volume more accurately depict how pore development progresses. This latter reason was true for three reasons. First, the volume of GAC grains changed very little during regeneration, whereas a considerable fraction of the solid mass was volatilized or gasified. For example, when coal-based regenerated samples experienced 25–29 percent mass loss, they correspondingly lost only 3–9 percent of their volume. Second, most of the mass loss was internal, and third, some of the bed volume loss appeared to be caused by abrasion, which probably did not change pore size distribution per unit volume.

Results and discussion

Objectives. Specific objectives of the experiments described were to (1) restore a field-spent GAC to virgin pore structure and adsorptive properties while the calcium remained within the GAC, (2) understand how calcium in a field-spent GAC affected pore development during regeneration, (3) determine whether pretreatment with acid substantially improved the regeneration product, and (4) determine how an array of different regeneration conditions affected field-spent GAC pore structure.

Regeneration to restore virgin properties. *Spent GAC.* Virgin pore structure could be virtually restored by appropriate thermal regeneration of the spent Hays Mine GAC while its 1.8 percent calcium remained intact. When the spent GAC was merely pyrolyzed at 850°C, its pore structure became nearly identical to that of virgin GAC type B, with 13 percent more mesopores, 6 percent fewer micropores, and the same surface area (Figure 3 and Table 2). Pyrolysis caused 14–16 percent

*Autopore II Mercury Porosimeter, Micromeritics, Norcross, Ga.

TABLE 3
Adsorption capacity* of spent Hays Mine GAC regenerated at various temperatures to an apparent density of 0.43–0.44

Regeneration Temperature °C	Iodine Number mg I ₂ /g C	Methylene Blue Capacity† mg MB/g C	p-Nitrophenol Capacity‡ mg PNP/g C	Ash Content percent
650	980	198	140	11.5
680	940	201	160	11.5
750	960	207	160	11.5
850	1,010	214	165	11.5
910	930	201	160	11.5
Pyrolyzed, 900°C§	960	200	175	10.8
Acid-washed, oxidized, 850°C	1,060	218	160	4.4
Virgin type A			195**	6.2

*Adsorption data listed on the unit basis of ash-free carbon mass

†For initial concentrations of 1.2 g/L methylene blue and 4.0 g/L GAC, 30-min adsorption

‡For equilibrium PNP concentration of 3 mg/L

§Apparent density following pyrolysis was 0.48 g/mL

**Data provided by C. Feizoulou, University of Illinois

mass loss and 3–4 percent bed volume loss. This same trend in pore structure was also observed at other pyrolysis temperatures, as discussed later in this article. The authors did not test whether these pore structures could be sustained through several regeneration cycles. (The virgin GAC type B tested in the laboratory was from a different batch than the GAC type B used at Hays Mine.) The curves shown in Figure 3 and in all subsequent figures represent cumulative pore volume distributions.

In comparison, the regenerated GAC exhibited a pore structure most like GAC type A when it had received 10 min of pyrolysis at 850°C and 2–3 min of oxidation with moderate steam flows at 850°C. These products had surface areas, micropore volumes, and mesopore volumes that were within 2–5 percent of values for GAC type A (Figure 3 and Table 2). Mild oxidation to an AD of 0.466–0.484 g/mL achieved these results and employed 0.27–0.40 g H₂O/g GAC. Corresponding mass loss was 14.5–18.5 percent, and volume loss was 3–4 percent. At 0.466, the AD of this regenerated GAC was 7 percent higher than GAC type A's AD, but the ash-free apparent densities were the same at 0.41 g ash-free carbon/mL. Although GAC type A is not the same GAC as was used initially, it has been considered a high-grade, popular GAC among water utilities.

Thus, within the range of statistical significance, the pore structures of two popular virgin GACs could be attained by employing controlled regeneration of a spent GAC, even though 1.8 percent calcium remained within this spent GAC.

Comparison with acid-washed GAC. Spent GAC was washed in 10 bed volumes of 1 M HCl (subsequently called "acid-washed GAC") and then pyrolyzed and oxidized in moderate flows of steam and CO₂ at 850°C for 35 min. This GAC product had 7–9 percent higher surface area, micropore volume, and mesopore volume than the regenerated product (with AD 0.47) that had not been acid-washed (Figure 3 and Table 2). The AD of the acid-washed product, at 0.43 g GAC/mL, was lower than the 0.47 AD for the mildly oxidized spent product previously discussed. But on an ash-free basis, the two products had the same AD of 0.41 g ash-free carbon/mL.

Attaining this level of oxidation with acid-washed GAC required 4.7 g H₂O/g GAC, 6.5 g CO₂/g GAC, and 35 min of oxidation time. These values were an order of magnitude greater than those necessary when the spent GAC was loaded with calcium. This difference highlighted how calcium dramatically improved oxidation efficiency, a factor that could offer advantages during full-scale, carefully controlled regenerations.

When all issues are weighed for the spent Hays Mine GAC, the slight im-

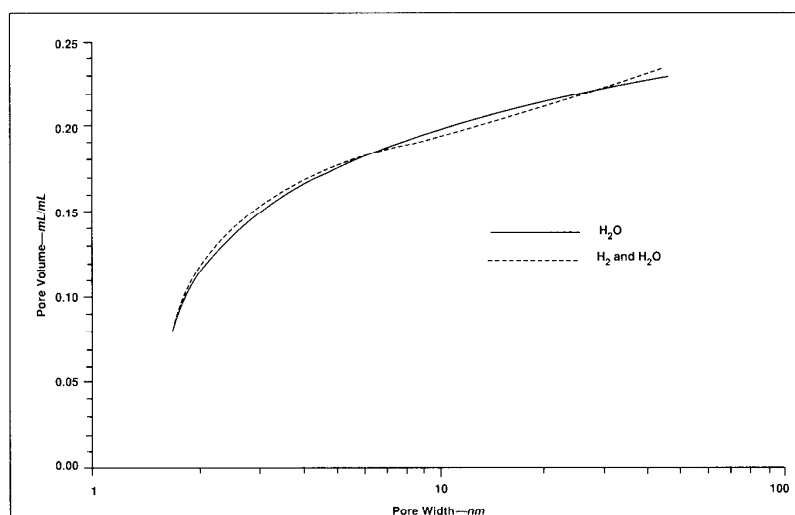


Figure 12. Pore volume distribution for spent Hays Mine GAC regenerated to an apparent density of 0.43 at 850°C in steam and H₂ plus H₂O

provements in pore structure gained by acid-washing would not justify the disadvantages incurred by using acid. Disadvantages include longer regeneration times, higher steam or CO₂ consumption, higher capital expense, stricter safety precautions, and acid waste streams that must be disposed of. Indeed, the calcium catalyst would allow a higher GAC throughput through a regeneration furnace, which probably would offset the potential need for more frequent regeneration cycles. This overall recommendation regarding acid-washing would also apply to another coal-based GAC with 0.9 percent calcium that has been studied at the University of Illinois,³¹ but it might not apply to several wood-based GACs that contained 6 percent and 3 percent calcium studied at the University of Illinois.^{3,4,8}

Pore development progression. Spent GAC and acid-washed GAC had similar pore size distributions following pyrolysis, but the pore size distributions differed dramatically following oxidation. For both GACs, pyrolysis increased the micropores, small mesopores, and 600–2,000-nm macropore volumes. During oxidation, calcium-loaded spent GAC always lost some micropore volume, whereas acid-washed GAC always gained micropores. These trends are observed in Figures 4–6, which show BJH nitrogen adsorption data for pores <50 nm and mercury porosimetry data for pores >50 nm. Figure 6 shows the change in cumulative pore volume that occurred during a single regeneration step. For example, the curve appearing in Figure 6 labeled "Spent, during oxidation, 850°C" represents the difference between the curves labeled "Oxidized, 850°C" and "Pyrolyzed, 850°C" in Figure 4.

An AD of 0.43 was targeted in these (and other subsequently discussed) experiments. This AD was intentionally slightly low so trends could be exaggerated and accurately quantified. This AD was achieved following 25–29 percent regeneration mass loss and 4–9 percent bed volume loss.

Pyrolysis. During pyrolysis, most porosity developed in pores <10 nm wide (Figures 4–6). This presumably represented the volatilization of organic matter from within the small pores and the release of oxygen functional groups from the carbon surface. Pores also developed in the range 600–2,000 nm. The 600–2,000-nm pore development had consistent magnitude whether spent GAC was pyrolyzed at 850°C or 680°C or whether acid-washed GAC was pyrolyzed at 850°C. (The latter two cases are not shown.) Development of pores in this range could have biological significance, because the narrow dimension of bacteria can be as small as 1,000–2,000 nm (1–2 μm).

Spent GAC oxidation. Oxidation always caused spent GAC to lose micropore volume and gain mesopore volume, but the temperature and oxidant dictated where mesopores developed. When CO₂ and steam were combined, 850°C oxidation caused pore widening throughout all pore ranges from 2 to 20,000 nm, but 680°C oxidation with both gases caused pore volume to increase solely between 6 and 10 nm. This implied that steam and CO₂ together attacked different carbon sites at low temperatures than they did at high temperatures.

At both temperatures, volumes declined in pores <5 nm, but the decline was greater at the lower temperature. The <5-nm pore size range is believed to be

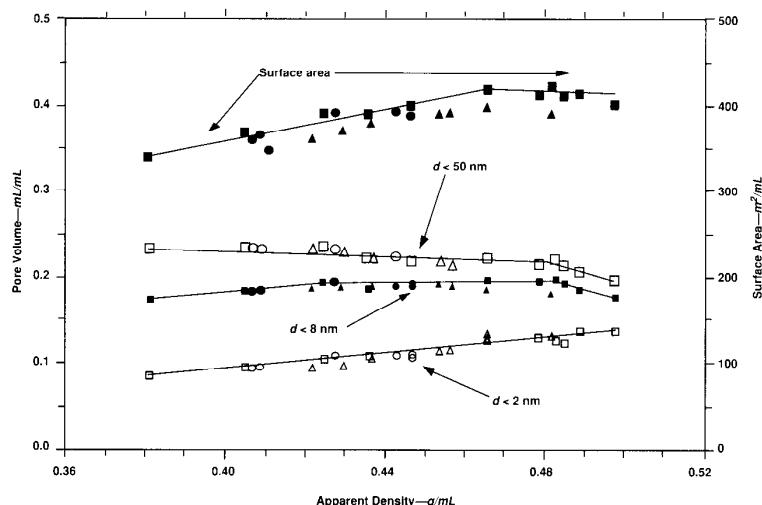


Figure 13. Pore volume distribution and surface area for spent Hays Mine GAC regenerated in steam at 850°C to various apparent densities (triangles—low flow, prepyrolyzed at 950°C, squares—moderate flow, circles—high flow)

important, and for most water treatment applications the pore volume distribution at 680°C would probably be inferior.

The effect of widening micropores implied that calcium catalyst either appeared in the micropores or facilitated oxidant transfer into the micropores along the carbon surface. If dissolved calcium had been conveyed into the GAC in association with a small anion during water treatment service, the calcium presumably would have fit into micropores, even in hydrated form (Table 1).

Acid-washed GAC oxidation. Oxidation of acid-washed GAC increased its micropore volumes but did not affect its mesopores or macropores (Figures 5 and 6). Only the pyrolysis step developed 2–10-nm mesopores for this acid-washed GAC. After the GAC was acid-washed and pyrolyzed, it took 35 min of oxidation to attain a 0.43 AD, compared with 4 min if it was not acid-washed, when both oxidations employed moderate steam and CO₂ flows. The ninefold rate increase implies that when the catalyst was present, it induced nearly all the oxidation that occurred. Thus, the spent GAC pore size that was widened probably correlated to the pore size that hosted the calcium. The larger micropore volume for acid-washed GAC suggested that steam and CO₂ could penetrate micropores more deeply than calcium could.

Potential blockage of pores by metals. The metals present in ash itself did not significantly impair pore structure by themselves. To test this, several spent Hays Mine GACs were acid-washed after they had been regenerated. The GACs' surface areas, micropore volumes, and mesopore volumes remained unchanged by the acid-washing when compared on an ash-free mass basis.

However, the metals that accumulate within GAC during water treatment service could potentially block pores by other possible association mechanisms. When humic compounds and metals become chelated to one another, they can form flocs⁴⁶ that would be large enough to mask the GAC's macropores. If this phenomenon occurred, it might prevent smaller organic compounds from subsequently penetrating through this mask into the GAC's smaller internal pores. Similarly, the hydrated water molecules associated with metals might span wide enough dimensions to clog small pores.

Because the nitrogen adsorption preparatory procedure includes a dehydration step, this method would not detect such hydrated water pore constriction. Perhaps subsequent research will provide perspective on these possibilities.

Volume and mass balance. Volume and mass balances were conducted for the oxidations shown in Figure 6 by using the equation

$$\Delta U_{OX} = \Delta PV_{OX} \times SD_N + \Delta BV_{OX} \times AD_{ur} \quad (3)$$

in which ΔU_{OX} —mass loss during oxidation per unit volume (g/mL unregenerated GAC), ΔPV_{OX} —change in internal pore volume during oxidation (mL/mL), SD_N —nitrogen skeletal density (g/mL), ΔBV_{OX} —bed volume loss during oxidation (mL/mL unregenerated GAC), and AD_{ur} —AD of unregenerated GAC (g/mL).

Balancing units were grams GAC lost/millilitres unregenerated bed volume. The nitrogen skeletal density was the mass of GAC/volume of carbon solid plus voids that nitrogen could not enter. This was calculated as 2.0 g/mL and was derived from nitrogen adsorption and

mercury porosimetry experiments. Eq 3 balanced within 6–10 percent for all three of these oxidations. This was believed to be good, considering the experimental errors inherent for each parameter in this equation.

It was determined that 70–85 percent of the mass loss occurred internally and 15–30 percent occurred externally (i.e., outside 20,000-nm-diameter pores). The spent GAC that was oxidized at 850°C lost the least mass externally, and the acid-washed GAC lost the most externally. When regeneration was prolonged, a higher portion of the external mass loss could be attributed to the agitation-induced attrition of micron-sized aggregates, and a lower proportion could be attributed to burnout by the oxidizing gases. For the acid-washed GAC, nearly all of the external losses appeared to be caused by attrition and none by oxidizing gases.

Temperature effect on combined steam and CO₂ oxidation. Effect on pore volumes.

When steam and CO₂ were combined, pore development during oxidation to a uniform 0.43 AD varied with temperature. With decreasing temperature from 944°C to 650°C, micropore volume decreased, 2–10-nm pore volume increased, and 10–1,000-nm pore volume decreased (Figure 7). The total pore volume (<20,000 nm) remained constant at all temperatures, as would be expected when regenerating to the same AD. Oxidation times required to achieve this AD ranged from 2 min at 944°C to 190 min at 650°C. The Figure 7 data are presented on a unit mass basis, because all these GACs were regenerated to the same AD, the same trends would have been observed on a unit bed volume basis.

Effect on surface area. Decreasing temperature correlated to decreasing total N₂-BET surface area: from 890 m²/g GAC at 944°C to 850 m²/g GAC at 650°C (Figure 7). However, the BJH mesopore surface area increased with declining temperature from 250 m²/g GAC at 944°C to 310 m²/g GAC at 650°C. Macropore surface areas generally ranged between 3 to 5 m²/g GAC as determined by mercury porosimetry.

From these and similar analyses, it is discerned that roughly one third of the total surface area in these coal-based regenerated and virgin GACs appeared within the mesopore range, roughly two thirds was in the micropore range, and less than 1 percent was in the macropore range.

Mesopore surface area might relate to adsorption performance when adsorbing large fulvic or humic acids or other high-molecular-weight compounds that would be too large to penetrate micropores; whereas total surface area may correlate to adsorption performance for the organic compounds that would be small enough to fit within micropores (see pre-

vious discussion). Many of the regulated synthetic organic compounds have low molecular weights.

Adsorption capacity for I_2 , PNP, and methylene blue. Adsorption capacities for iodine, *p*-nitrophenol, and methylene blue were compared for (1) spent GAC that had been oxidized to an AD of 0.43–0.44 over the 650–910°C temperature range; (2) spent GAC that had been pyrolyzed at 900°C (AD 0.48); and (3) acid-washed GAC that had been regenerated at 850°C to AD 0.435. Capacities were reported on an ash-free mass basis of comparison. Within the accuracy of measurement, the adsorption capacities were roughly equal for all these GACs and exhibited no consistent temperature-related trend (Table 3). This suggested that the range of these pore size distributions was not wide enough to detect significant differences among adsorption capacities.

Temperature effect with decreasing apparent density. Nitrogen pore volume distribution was monitored as AD declined with progressively increasing oxidation of the spent GAC. When oxidation occurred at 850°C with moderate steam flows, the pore distribution progressed as shown in Figure 8. When oxidation occurred at 750°C with moderate flows of both steam and CO_2 , the pore distribution progressed as shown in Figure 9. At 750°C, pores widened solely within the <15-nm range, where the distributions were linear and parallel.

At 850°C, in contrast, the pore development occurred throughout the 2–50-nm region (which could be monitored by nitrogen adsorption) and resulted in curvilinear pore distributions. Initial steam oxidations to an AD of 0.482–0.466 widened some micropores to the 2–5-nm size and markedly increased the total pore volume <5 nm. Continued oxidation appeared to widen these pores to progressively larger sizes. Perhaps much of the easily oxidized char was gasified during the first few minutes, and extended oxidation attacked primarily the GAC skeletal structure.

Effect of oxidant gas. Steam, CO_2 , or steam plus CO_2 . No pore structure differences appeared whether steam, CO_2 , or steam plus CO_2 was employed at 850°C (Figure 10). Moreover, 680°C oxidations caused this same pore distribution when steam alone or CO_2 alone was employed (Figure 11). However, when steam and CO_2 were used together at 680°C, a different distribution resulted, which was linear between 2 and 10 nm (Figure 11). These distinctions were manifested as a trend throughout the 650–950°C range when steam and CO_2 were used together: as temperature decreased, the destruction of small pores became more pronounced (Figure 7).

In light of these pore distributions, coupled with experimental findings per-

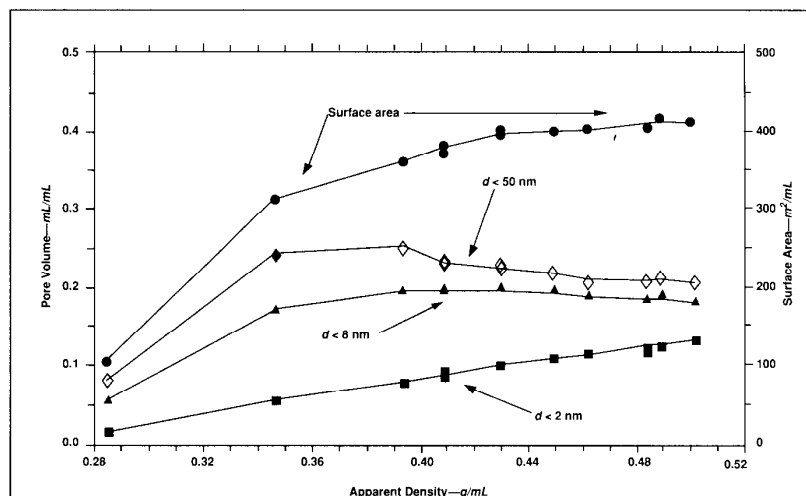


Figure 14. Pore volume distribution and surface area for spent Hays Mine GAC regenerated in moderate flow of steam at 680°C to various apparent densities

taining to the catalyzed reaction kinetics,^{3,4,5} the authors have proposed that the manner of pore development was influenced by which reaction step was rate limiting. At higher temperatures (>800°C), the water–gas shift reaction has been proposed to limit overall rate, and pore development was characterized by nonfocused gasification that was dispersed throughout all pore size ranges.

In contrast, when lower temperatures (<750°C) were employed, the gasification of solid $-C(O)$ to gaseous CO has been proposed to limit overall rate, and pore development was characterized by a focused attack on the pores <5 nm, which caused more pore development in the 5–10-nm range.^{3–5}

Reduced gas environment: steam plus H_2 . Gasification was also tested with a hydrogen–steam mixture. These experiments were motivated by the findings of Matsumoto and Walker,⁴⁷ which showed that hydrogen inhibited calcium catalysis. In tests, 5 g H_2 /g GAC/h plus 5 g H_2O /g GAC/h was applied to spent GAC for 160 min at 850°C before it reached the targeted AD of 0.43. This required more than an order of magnitude longer time than had been necessary to achieve this AD when the H_2 was excluded and steam was used alone. Nonetheless, the pore distribution following this gasification was nearly identical to that following steam alone (Figure 12). The surface area, at 390 m^2/mL , was also about the same as that following steam oxidation. Thus, H_2 dramatically inhibited calcium catalysis and the rate of carbon gasification, but this inhibition did not influence the product pore structure.

Effect of steam flow rate. Steam flow rate made no difference to pore development when oxidations were carried to

any given AD (Figures 13, 14, and 15). Three flows were tested: a moderate rate of 8 g H_2O /g GAC/h, a high rate of 50 g H_2O /g GAC/h, and a low rate of 0.4 g H_2O /g GAC/h. The moderate flow rate was within the range commonly employed at full-scale regeneration facilities; the high rate was an order of magnitude greater; and the low rate was an order of magnitude lower. The low flow reaction rate was slowed even further by prepyrolyzing these GAC samples at 950°C. High-temperature prepyrolysis sintered the calcium and decreased its surface area of reaction.^{7,8,48,49}

The oxidation rates varied considerably. For example, achieving an AD of 0.43 required 2 min at the highest flow, 9 min at the moderate flow, and 45 min at the lowest flow. Despite this, all flow rates created nearly identical pore volume distributions and surface areas when compared at the same ADs (Figures 13 and 15). As an exception, the GAC prepyrolyzed at 950°C exhibited 10 percent lower surface areas than the others. This probably reflected more on the high-temperature sintering effects than on the low-flow oxidation effects. Because pore size distribution was the same at a given AD over this wide range of flow rates, it could be reasoned that pore diffusion limitations were not manifested. This reasoning was confirmed by diffusion computations.^{3,4}

During steam oxidation, temperature also did not affect the pore size distribution. Whether 680 or 850°C was used, the same pore distributions and surface areas resulted at a given AD (compare Figures 13 and 14). The 680°C oxidation to AD 0.43 took 100 min. Thus, steam alone apparently attacked the same carbon sites at 680°C as it did at 850°C.

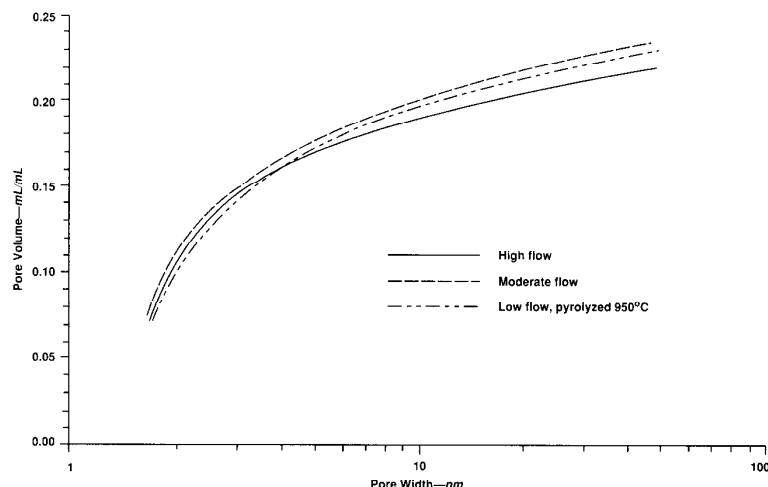


Figure 15. Effect of steam flowrate on pore volume distribution of spent Hays Mine GAC regenerated to an apparent density of 0.43 g/mL (pyrolysis at 850°C, except as indicated)

As AD decreased, the pore structure progressed through stages that were common for all three flow rates and both temperatures. Progressing from an initial 0.49 AD (for pyrolyzed GAC) down to the range of 0.44–0.47, the 2–8-nm pore volume increased slightly while the <2-nm pore volume decreased slightly and surface area remained fairly constant. This corresponded to 14–18 percent mass loss. With further oxidation to AD 0.40–0.42 and 26–28 percent mass loss, micropore volumes continued to decline, 2–8-nm pore volumes remained unchanged, 8–50-nm pore volumes increased, and surface area declined. This represented the widening of micropores to progressively larger mesopores.

Finally, below ADs in the range of 0.38–0.40 (corresponding to 28–35 percent mass loss), micropores and surface areas had deteriorated dramatically (with losses of 20–40 percent), indicating that the GAC was severely overregenerated. Severe overregeneration took only 13 min of moderate steam oxidation at 850°C or 1.7 g H₂O/g GAC, which was within the range of common oxidation conditions employed at full-scale regeneration facilities. This highlights how important it is to tailor regeneration conditions to the GAC's calcium content. A regeneration strategy that works well for a low-calcium GAC may seriously deteriorate a catalyst-laden GAC.

Effect of pyrolysis. Pyrolysis alone. Pyrolysis alone, without oxidation, most effectively restored micropores. If the spent pyrolyzed GAC was also oxidized, it always lost a fraction of its micropores. Moreover, pyrolyzed spent GAC possessed high adsorption capacity for iodine, PNP, and methylene blue (Table 3). It would be useful to determine whether

this quality could still be restored after several adsorption and pyrolysis cycles.

Mere pyrolysis at any temperature between 650 and 950°C created products that were nearly identical to one another and were also similar to virgin GAC type B. Pore structure similarities can be seen by comparing the representative curves for pyrolysis at 850, 750, and 680°C in Figures 8, 9, and 11 and by comparing the product of 850°C pyrolysis with GAC type B in Figure 3. Surface areas throughout the 650–950°C pyrolysis temperature span were also consistently the same, ranging between 390 and 410 m²/mL (790–840 m²/g GAC).

Pyrolysis temperature did affect GAC mass loss and volume loss, however. With an increase from 650 to 950°C, bed volume loss in 10 min increased from 2 percent to 5 percent, mass loss increased from 10 percent to 16 percent, and AD decreased from 0.50 to 0.48.

There was no attempt to optimize pyrolysis times in these experiments, because the rate of pyrolytic mass loss appeared unrelated to the calcium content. Ten minutes was used merely because it allowed ample time to stabilize temperature, complete volatilization, and facilitate quantitative comparisons during oxidation. However, shorter pyrolysis times would suffice for full-scale regenerations. When spent GAC was pyrolyzed in the TGA, volatilization appeared complete within 1–3 min following 5 min of temperature rampup time.

Similarly, when spent GAC was pyrolyzed at 900°C in a fluidized bed for 3, 10, and 30 min, mass losses were 14.2, 14.7, and 16.9 percent, respectively; volume losses were 3.5, 3.5, and 4.0 percent; and final ADs were 0.49, 0.48, and 0.47 g/mL. This compared with a spent-GAC AD of

0.55. This implied that the volatilization was virtually complete within 3 min. The temperature rampup procedure added another 2–5 min of pyrolysis time to those values listed previously.

Effect of pyrolysis temperature on subsequent oxidation. High-temperature pyrolysis influenced subsequent oxidation behavior by dramatically slowing the oxidation rate and slightly affecting the resulting pore distribution. When spent GAC was pyrolyzed at 900°C before being oxidized at 750°C, its oxidation rate was half as fast as when it was pyrolyzed at 750°C before being oxidized at 750°C. Moreover, when pyrolyzed at 900°C and oxidized at 750°C to AD 0.42, it exhibited a curvilinear pore volume distribution in the small-mesopore range and linear distribution in the large-mesopore range (Figure 16). This small-mesopore distribution imitated that of spent GAC that had been pyrolyzed at 920°C and oxidized at 910°C rather than one that had been both pyrolyzed and oxidized at 750°C.

Radovic et al.⁴⁸ suggested that high-temperature pyrolysis caused calcium oxide crystallites to sinter and congregate into larger pores and become less reactive catalysts. The experiments described in this article confirmed the lower reactivities but were not designed to identify where the calcium congregated. All three of these regenerations achieved the same surface area of 360–380 m²/mL (850–890 m²/g GAC). Thus, high-temperature presintering influenced the subsequent oxidation rate, but not in a manner that substantially improved the regenerated GAC quality.

Summary and conclusions

Metals accumulation in spent GAC. In summary, spent GACs from water treatment plants were found to contain high concentrations of calcium (0.4–7 percent) and moderate concentrations of iron (nonpyritic: 0.1–0.5 percent), aluminum (0.3–3.7 percent), manganese (0.02–0.6 percent), and magnesium (0.06–0.3 percent). Calcium, iron, manganese, and magnesium are not known to be harmful to human health. Other metals appeared in low concentrations (<0.03 percent). The GAC with the highest calcium loadings often came from water treatment plants in which lime treatment preceded the GAC filter adsorbers. However, lime treatment did not cause calcium to accumulate at all the plants where it was employed.

Acid-washing in 1 M HCl extracted most of these metals, and acid-washed spent GAC exhibited far lower oxidation reaction rates than spent GAC that had not been acid-washed. Of these metals extracted by acid, calcium was isolated as the one that catalyzed oxidation the most vigorously during thermal regenerations.

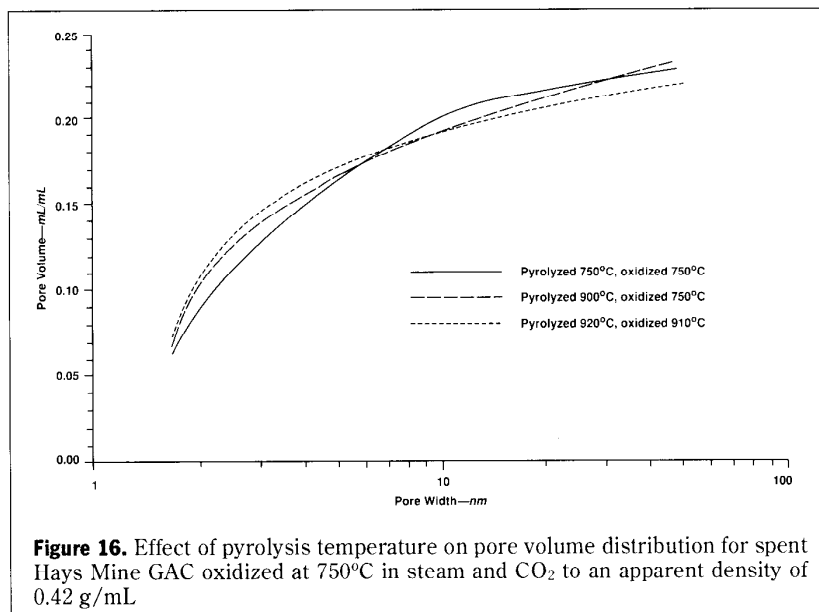


Figure 16. Effect of pyrolysis temperature on pore volume distribution for spent Hays Mine GAC oxidized at 750°C in steam and CO₂ to an apparent density of 0.42 g/mL

Restoration of pore structure in calcium's presence. The authors therefore evaluated how field-loaded calcium affected pore structure following an array of regeneration conditions. It was determined that when a spent GAC type B was thermally regenerated under the proper conditions, its virgin pore characteristics could be restored despite the presence of 1.8 percent calcium. This implied that the regeneration option for this calcium-loaded GAC provided potential as a viable alternative to discarding or incinerating spent GAC and replacing it with virgin GAC.

Pyrolysis of this spent GAC at 850°C created a product that had 6 percent fewer micropores, 13 percent more mesopores, and the same surface area as a virgin GAC type B. Comparisons have been made on a unit volume basis. Mere pyrolysis caused 14–16 percent mass loss and 3–4 percent bed volume loss.

If this pyrolyzed spent GAC also received 2–3 min of steam oxidation at 850°C, the product's characteristics became nearly identical to virgin GAC type A, with virtually the same micropore volume, surface area, and mesopore volume. This regeneration corresponded to 14–19 percent mass loss and 3–4 percent volume loss and resulted in an AD of 0.46–0.48 g/mL. The authors believe this regeneration strategy was not the only one that could have produced these pore characteristics for this spent GAC. The same pore structure would be expected when regenerations achieved this same AD with just steam or just CO₂ at any temperature or with both steam and CO₂ at temperatures above 800°C.

Influence of temperature on pore structure. The spent GAC was regenerated to a uniform AD of 0.43 g/mL under a range of regeneration conditions. All condi-

tions caused decreased micropore volumes, decreased surface areas, and increased mesopore volumes compared with their pyrolyzed counterparts. Moreover, all but one condition caused pores to widen throughout the mesopore range. The exception occurred when both steam and CO₂ were used at temperatures below 750°C. These oxidations caused lower total surface areas, higher mesopore surface area, lower micropore volumes, higher 2–10-nm pore volumes, and a linear pore size distribution between 2 and 10 nm. These low-temperature oxidations primarily widened pores of the <5-nm range, forming pores in the 5–10-nm range. They caused negligible increase in pores >10 nm. The <5-nm pores are probably the most important for many water treatment applications. Therefore, the author recommends that field regeneration strategies avoid low temperatures (<800°C) when both steam and CO₂ are employed together and the spent GAC is loaded with calcium.

Acid-washing. By treating the spent GAC with 1 M HCl, the authors could produce a slightly superior regeneration product. The authors recommend that the slight improvement would not justify the added nuisance and expense incurred by employing an acid-washing step before regenerating coal-based GACs that contain <2 percent calcium.

Influence of rate-limiting step on pore development. When both steam and CO₂ were combined, the manner of pore development was proposed to be influenced by which reaction step was rate-limiting.^{3–5} At higher temperatures (>800°C), the water–gas shift reaction appeared to limit overall rate, which caused non-focused gasification that was dispersed throughout all pore size ranges.

In contrast, when lower temperatures (<750°C) were employed, the gasification of solid -C(O) to gaseous CO appeared to limit overall rate, which resulted in a focused attack on the pores <5 nm and caused more pore development in the 5–10-nm range.

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