

# Effect of Calcium on Thermal Regeneration of GAC

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Calcium commonly accumulates on granular activated carbon (GAC), and when it is chelated by natural organic matter (NOM), it is drawn into the pores of the GAC. Internally loaded calcium greatly catalyzes regeneration reactions, leading to accelerated internal mass loss. Optimal conditions for the regeneration of a GAC not loaded with calcium lead to severe overregeneration if applied to a calcium-loaded GAC. The pore structure and capacity of the GAC are adversely affected by this overregeneration. The authors of this article found that calcium-loaded GACs could be regenerated to yield a GAC with the properties of the virgin GAC by reducing the regeneration time or temperature.

Interest in thermal regeneration of granular activated carbon (GAC) has been growing as the disposal of spent GAC is becoming more costly and difficult. Use of GAC in drinking water treatment is expected to expand because of the required and desired control of synthetic organic compounds, including pesticides, volatile organic chemicals, and disinfection by-products. GAC is also effective in controlling tastes and odors and in producing a biologically stable water after ozonation. Disposal of spent GAC in landfills is a problem because of potential leaching of adsorbed compounds into nearby groundwater. Consequently, the reuse of spent GAC that has been thermally regenerated on-site or by a regional facility should become an attractive alternative.

A thorough understanding of the factors influencing the thermal regeneration of GAC from treatment plants and the quality of the regenerated product is needed. Of special importance are the metals that accumulate on GAC during water treatment because some metals catalyze the reactions that are taking

place during thermal regeneration. It is necessary to determine how regeneration conditions should be modified as a function of metal concentration and speciation in the water.

The objective of this research was to determine the effect of calcium (Ca) on the thermal regeneration of GAC. The accumulation of Ca on GAC during water treatment is common because Ca is ubiquitous in natural waters, it readily forms complexes with natural organic matter (NOM), and it is often added in the form of lime during water treatment. Calcium is expected to adsorb inside GAC pores, especially when chelated by organic anions, such as humates, or to precipitate as calcium carbonate ( $\text{CaCO}_3$ ) on the GAC surface as a result of supersaturation. Both loading mechanisms were addressed in this research project, but the major focus was on internally loaded Ca, which is discussed in this article.

## Background

**Thermal regeneration of GAC.** The process of thermal regeneration has been divided into four steps:

- drying of the GAC at temperatures less than about 200°C,
- vaporization of volatile adsorbates and decomposition of unstable adsorbates to form volatile fragments at temperatures between 200 and 500°C,
- pyrolysis of nonvolatile adsorbates and adsorbate fragments to form a char on the activated carbon surface at temperatures of about 500 to 700°C, and
- oxidation of the pyrolyzed residue with steam and carbon dioxide ( $\text{CO}_2$ ) as the oxidizing agents at temperatures above about 700°C.<sup>1</sup>

Past research has shown that the quality of the regenerated product is mainly influenced by the parameters affecting the oxidation step, whereas the manner in which the drying and pyrolysis steps are carried out does not have any significant effect on the final product.<sup>2</sup> One important factor affecting the oxidation step is the presence of metals that can catalyze the oxidation reactions. In particular, Ca has been observed to catalyze the reactions of steam and  $\text{CO}_2$  with carbon.

## Accumulation of inorganic compounds.

The evidence for accumulation of metals on GAC in water treatment plants is clear when the data presented in Table 1 are compared with the metal concentrations of virgin GACs (Table 2). Metals such as calcium, iron, aluminum, and manganese were found to accumulate on GAC as a result of their ubiquity in natural waters or their presence in chemicals used in water treatment. Mechanisms for the buildup of inorganics on GAC include

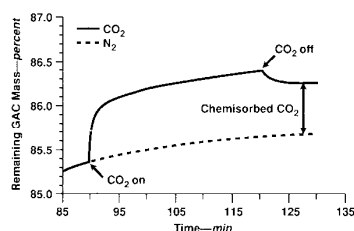


Figure 1. Carbon dioxide adsorption experiment for the determination of calcium oxide surface area

TABLE 1  
Concentrations of metals on GAC used in drinking water treatment

| Location                           | Type of Virgin Carbon | Ca mg/kg | Fe mg/kg | Al mg/kg | Mn mg/kg |
|------------------------------------|-----------------------|----------|----------|----------|----------|
| Norristown, Pa. <sup>3</sup>       | C*                    | 10,593   | 3,490    | 1,923    | 3,228    |
| New Castle, Pa. <sup>3</sup>       | A†                    | 13,159   | 1,181    | 7,633    | 5,201    |
| Hopewell, Va. <sup>3</sup>         | B‡                    | 35,861   | 85       | 35,908   | 5,522    |
| Hays Mine, Pa. <sup>3</sup>        | B‡                    | 22,186   | 1,796    | 4,047    | 809      |
| Choisy-le-Roi, France <sup>4</sup> | D§ (wood base)        | 33,500   | 620      | 7,640    | 670      |
| Méry-sur-Oise, France <sup>4</sup> | D§ (coconut base)     | 49,700   | 4,350    | 13,400   | 220      |
| Louveciennes, France <sup>4</sup>  | D§ (wood base)        | 67,600   | 1,700    |          | 2,600    |
| Rouen, France <sup>4</sup>         | D§ (coconut base)     | 29,900   | 560      | 800      | 380      |

\*F400, Calgon Corp., Pittsburgh, Pa.

†CECARBON GAC40, Atochem Ceca Div., Pryor, Okla.

‡F200, Calgon Corp., Pittsburgh, Pa.

§PICA, Levallois, France

**TABLE 2**  
*Concentrations of metals on virgin GACs\**

| GAC Type           | Ca<br>mg/kg  | Fe<br>mg/kg | Al<br>mg/kg | Mn<br>mg/kg |
|--------------------|--------------|-------------|-------------|-------------|
| C†,‡               | 743          | 355         | 665         | 2           |
| A†,§               | 8,610        | 1,600       | 8,280       | 50          |
| D** (wood base)    | 5,000–10,000 | 100–200     | 25–70       | 25–70       |
| D** (coconut base) | 300–1,500    | 100–400     | 50–300      | 10–50       |

\*F400 and F200 (carbons C and B, respectively) have essentially similar inorganic compositions.<sup>5</sup>

†University of Illinois analyses

‡F400, Calgon Corp., Pittsburgh, Pa.

§CECARBON GAC40, Atochem Ceca Div., Pryor, Okla.

\*\*PICA, Levallois, France; analyses conducted there

**TABLE 3**  
*Characteristics of virgin GACs\**

| Carbon Type | US Standard<br>(Particle Size—mm) | Apparent Density<br>g/cm <sup>3</sup> | Iodine Number<br>mg/g |
|-------------|-----------------------------------|---------------------------------------|-----------------------|
| A†          | 12 × 40 (1.68 × 0.42)             | 0.487                                 | 1,043                 |
| B†          | 12 × 40 (1.68 × 0.42)             | 0.46                                  | >850                  |
| C§          | 12 × 40 (1.68 × 0.42)             | 0.43                                  | >1,000                |

\*Data provided by respective manufacturers

†CECARBON GAC 40, Atochem Ceca Div., Pryor, Okla.

‡F200, Calgon Corp., Pittsburgh, Pa.

§F400, Calgon Corp., Pittsburgh, Pa.

**TABLE 4**  
*Effect of acid-washing on ash and metal content of virgin GAC\**

| Parameter   | Virgin GAC | Acid-Washed Virgin GAC |
|-------------|------------|------------------------|
| Ash—percent | 13.8       | 7.6                    |
| Ca—mg/kg    | 8,610      | 300                    |
| Al—mg/kg    | 8,280      | 890                    |
| Fe—mg/kg    | 1,600      | 550                    |
| Mg—mg/kg    | 3,060      | 110                    |
| Mn—mg/kg    | 50         | 2                      |

\*CECARBON 40, Atochem Ceca Div., Pryor, Okla.

**TABLE 5**  
*Total loading, ash content, and calcium content for GAC internally loaded with calcium*

| Sample                | Total Loading<br>percent by weight | Ash<br>percent | Calcium<br>mg/kg |
|-----------------------|------------------------------------|----------------|------------------|
| Ca-EDTA 1             | 6.9                                | 10.1           | 15,380           |
| Ca-EDTA 2             | 21.1                               | 13.2           | 40,710           |
| Ca-EDTA + MB 1        | 20.5                               | 11.4           | 17,610           |
| Ca-EDTA + MB 2        | 24.0                               | 13.0           | 22,800           |
| Acid-washed Ca-EDTA 2 | 5.3*                               | 7.2            | 490              |

\*Loading estimated by AD after acid-washing

**TABLE 6**  
*Ash and metal contents for Norristown and Hays Mine GACs*

| Parameters  | Norristown | Hays Mine |
|-------------|------------|-----------|
| Ash—percent | 9.2        | 8.9       |
| Ca—mg/kg    | 10,480     | 13,760    |
| Al—mg/kg    | 2,710      | 3,270     |
| Fe—mg/kg    | 4,370      | 2,680     |
| Mg—mg/kg    | 700        | 740       |
| Mn—mg/kg    | 4,440      | 210       |

precipitation on the surface of GAC, adsorption of metallo-organic complexes in the presence of NOM, particle deposition, and ion exchange. Precipitation of Ca can be expected when a supersaturated water is applied to a GAC adsorber. The GAC particles serve as nuclei for the precipitation process, and the resulting

precipitate coats the activated carbon granules. Adsorption via complex formation with anionic organics, such as humates, can be envisioned for all metals; this mechanism will draw metal ions inside the GAC pores. Particle deposition is expected mainly when ferric or aluminum precipitates from the coagulation

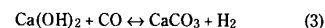
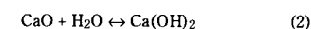
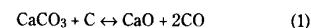
process enter the GAC filter and are deposited on the exterior surface of the GAC. Finally, ion exchange is expected to occur only to a limited extent because of the low ion exchange capacity of GAC.<sup>6</sup>

Juhola<sup>7</sup> was the first to find evidence that the accumulation of inorganics on GAC used in tertiary wastewater treatment caused increased mass losses during regeneration under constant oxidizing conditions. An analysis of the ash showed that the GAC had accumulated calcium, magnesium, potassium, sodium, iron, and chromium during the loading process. In the presence of loaded inorganics, pore enlargement resulted in a decreased capacity for small molecules, such as iodine, whereas the capacity for large molecules, such as molasses, was increased. Juhola<sup>7</sup> showed that the removal of inorganics by acid-washing with hydrochloric acid (HCl) alleviated these problems and concluded that an increase in ash content resulted in a catalytic effect.

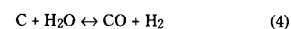
**Calcium as a catalyst.** Although the effect of Ca on the thermal regeneration of activated carbon has not been studied thus far, the catalytic characteristics of Ca salts on the gasification of carbonaceous materials such as coal char or graphite have been documented in the literature. Although a catalyst in the traditional sense reduces the activation energy of a reaction, Ca catalyzes the gasification reactions of carbon with steam and CO<sub>2</sub> merely by increasing the number of active sites, not by reducing the activation energy.<sup>8–10</sup>

The most widely accepted catalytic reaction mechanism that describes the interaction between calcium, carbon, and the oxidizing gases (steam and CO<sub>2</sub>) is the oxygen-transfer mechanism in which CaCO<sub>3</sub> plays the role of the catalyst. The oxygen-transfer mechanism involves a carbonate-oxide cycle, during which oxygen is extracted from the oxidizing gases by the catalyst and supplied to the carbon in an active form.<sup>11</sup> McKee<sup>12</sup> studied the catalytic gasification of graphite with alkaline earth salts and described the process by the following reactions:

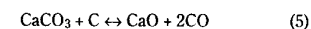
with steam as oxidant:



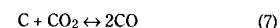
which results in the overall reaction



with CO<sub>2</sub> as oxidant:



which results in the overall reaction



The overall reactions are typical of the noncatalytic gasification of carbonaceous materials with steam or CO<sub>2</sub>. The presence of either calcium oxide (CaO) or CaCO<sub>3</sub> is required to initiate the oxygen transfer mechanism. Also, the catalytic activity of Ca should be greatest at temperatures at which the cyclic conversion between the carbonate and oxide forms is most favorable. Studies by Ohtsuka and Tomita,<sup>13</sup> as well as McKee,<sup>14,15</sup> showed that Ca was catalytic between temperatures of 600 and 1,000°C, a range that includes typical regeneration temperatures.

Linares-Solano et al<sup>16</sup> showed that the reactivity of carbonaceous materials was linearly related to the CaO surface area present after pyrolysis. Furthermore, they found that CaO surface areas started to level off with increasing Ca content; CaO surface areas were essentially constant for carbons with Ca concentrations in the range of 6.0–9.4 percent, and the resulting reactivities of the chars were uniform. Salinas-Martínez de Lecea et al<sup>19</sup> suggested that the plateau value for CaO area relates to the saturation of carbon-carboxyl groups with Ca.

#### Effects of externally loaded calcium.

When Ca was loaded in the form of a CaCO<sub>3</sub> precipitate on the exterior surface of methylene-blue-loaded GAC (up to 1.8 percent Ca by weight), the regenerated GAC samples had characteristics that were very similar to those of a control GAC that was loaded with methylene blue only. A more detailed presentation of the data for the external loading of Ca on GAC is available elsewhere.<sup>17</sup>

#### Materials and methods

**GAC.** The GAC\* used in the laboratory studies was a subbituminous-based carbon (carbon A). In addition, GAC samples from the American Water Works Service Company plants at Hays Mine, (carbon B)† Pittsburgh, Pa., and Norristown, (carbon C)‡ Pa., were examined. Both employ bituminous-based carbons. Table 3 shows the characteristics of the virgin GACs used in this project.

In Norristown, GAC is utilized in a filter-adsorber. Ferric iron is used as a coagulant, and the pH of the water is adjusted with lime just prior to GAC treatment. The filter-adsorber was put into service in June 1988, and the sample for this project was taken in November 1989.

Hays Mine also employs GAC in a filter-adsorber; here, potassium permanganate, lime, and cationic polymer are added during the treatment process. The sample used in this research was taken from filter 30 in October 1989, just prior to regeneration. At the time of sampling, the GAC had been in place for two and one-half years.

**Acid-washing of GAC.** Acid-washing of GAC was performed by applying 10 bed volumes of 1 N HCl to a GAC column in

| Sample                 | Mass Loss<br>(Pyrolysis +<br>Oxidation)<br>percent | Volume<br>Loss<br>percent | AD <sub>reg.</sub><br>g/cm <sup>3</sup> | AD <sub>reg.</sub><br>g/cm <sup>3</sup> |
|------------------------|----------------------------------------------------|---------------------------|-----------------------------------------|-----------------------------------------|
| Acid-washed virgin GAC | 10.3                                               | 2.5                       | 0.438                                   | 0.404                                   |
| Ca-EDTA 1              | 33.0                                               | 3.0                       | 0.466                                   | 0.322                                   |
| Ca-EDTA 2              | 41.2                                               | 3.0                       | 0.527                                   | 0.320                                   |
| Ca-EDTA + MB 1         | 39.4                                               | 2.7                       | 0.525                                   | 0.327                                   |
| Ca-EDTA + MB 2         | 35.2                                               | 2.8                       | 0.541                                   | 0.361                                   |
| Acid-washed Ca-EDTA 2  | 12.7                                               | 1.9                       | 0.461                                   | 0.411                                   |

\*Temperature of regeneration—850°C; time—15 min

| Sample                                                                       | Micropore<br>Volume<br>cm <sup>3</sup> /cm <sup>3</sup><br>GAC | Mesopore<br>Volume<br>cm <sup>3</sup> /cm <sup>3</sup><br>GAC | BET Surface<br>Area<br>m <sup>2</sup> /cm <sup>3</sup><br>GAC | Iodine<br>Number<br>mg/cm <sup>3</sup><br>GAC |
|------------------------------------------------------------------------------|----------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------|
| Acid-washed virgin GAC<br>(AD—0.438 g/cm <sup>3</sup> )                      | 0.190                                                          | 0.229                                                         | 510                                                           |                                               |
| Acid-washed virgin GAC regenerated at 850°C<br>(AD—0.404 g/cm <sup>3</sup> ) | 0.196                                                          | 0.206                                                         | 510                                                           | 370                                           |
| Ca-EDTA 1 regenerated at 850°C<br>(AD—0.322 g/cm <sup>3</sup> )              | 0.140                                                          | 0.203                                                         | 380                                                           | 310                                           |
| Ca-EDTA 2 regenerated at 850°C<br>(AD—0.320 g/cm <sup>3</sup> )              | 0.124                                                          | 0.222                                                         | 360                                                           | 280                                           |
| Ca-EDTA + MB 1 regenerated at 850°C<br>(AD—0.327 g/cm <sup>3</sup> )         | 0.120                                                          | 0.234                                                         | 370                                                           | 310                                           |
| Acid-washed Ca-EDTA 2 regenerated at 850°C<br>(AD—0.411 g/cm <sup>3</sup> )  | 0.199                                                          | 0.201                                                         | 510                                                           |                                               |

upflow mode. Following the acid, 10 bed volumes of deionized, distilled water were pumped up through the GAC column to raise the pH back to between 4 and 5. The GAC was then removed from the column and dried.

**Adsorbates.** Methylene blue (MB), a surrogate for NOM,<sup>18</sup> was loaded onto the 16 × 20-mesh (1.19 × 0.84-mm) fraction of the virgin GAC in batch experiments. A known mass of dried carbon was placed in an acid bottle, and a mass of MB equal to 1.5 times the final loaded mass of MB desired was added along with 2 L of deionized, distilled water. The sealed mixture was then placed on a shaker for seven days. After the loading, the supernatant was filtered through a 0.45-μm-pore-size membrane filter to catch the fines, and the MB-loaded GAC was placed on a 20.3-cm-diameter sieve (<74 μm) and dried.

To achieve an internal Ca loading, Ca chelated by ethylene diamine tetraacetic acid (EDTA) was loaded onto GAC in the same fashion as MB. In place of MB, known amounts of EDTA in the acid form and Ca hydroxide were added to 2 L deionized, distilled water. Two 16 × 20-mesh (1.19 × 0.84-mm) portions each of acid-washed virgin GAC and acid-washed MB-loaded GAC were contacted with Ca-EDTA solutions of different concentrations to yield the following samples: Ca-EDTA 1, Ca-EDTA 2, Ca-EDTA + MB 1, and Ca-EDTA + MB 2.

**Regeneration of GAC.** GAC samples were regenerated in a batch-type fluid-

ized-bed furnace that has been described in detail by Waer et al.<sup>18</sup> Unless otherwise noted, all GAC samples were dried and then subjected to a 10-min pyrolysis step in an inert nitrogen (N<sub>2</sub>) atmosphere, immediately followed by a 15-min reactivation step in an oxidative environment. The pyrolysis and reactivation temperatures were always the same for an individual regeneration; typically the temperature was 850°C. For all regenerations, dried GAC samples ranging in volume from 18 to 20 mL were introduced into the reaction chamber. The oxidative environment was created by adding steam, CO<sub>2</sub>, or, most commonly, a mixture of the two gases into the reaction chamber. Throughout this research, the oxidant flow rates were 1.75 L/min steam and 0.55 L/min CO<sub>2</sub>, each at standard temperature and pressure (STP: 0°C, 101 kPa). For a 15-min regeneration, the oxidant flow rates were equivalent to adding 2.0–2.5 g steam/g GAC and 1.6–2.0 g CO<sub>2</sub>/g GAC, conditions similar to those used by Waer et al.<sup>18</sup> to recover the characteristics of virgin GAC for GAC samples loaded with MB or NOM. To facilitate direct comparison between samples, only the representative 16 × 20-mesh fraction (1.01-mm mean diameter) of the GAC samples was regenerated, which eliminated any variability attributable to the effects of particle size. When the sam-

\*Carbon A—CECARBON GAC40, Atochem Ceca Div., Pryor, Okla.

†Carbon B—F200, Calgon Corp., Pittsburgh, Pa.

‡Carbon C—F400, Calgon Corp., Pittsburgh, Pa.

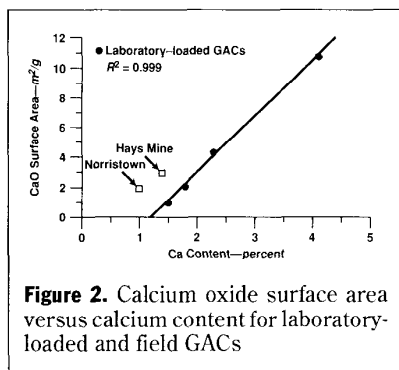


Figure 2. Calcium oxide surface area versus calcium content for laboratory-loaded and field GACs

ple size was sufficient, all regenerations were performed in duplicate.

**Thermogravimetric analyses (TGA).** During TGA,\* high-purity N<sub>2</sub> (99.99 percent) was used to create an inert atmosphere in the balance and sample compartments. Nitrogen flow rates were 30 mL/min for the balance purge line and 20 mL/min for the sample purge line. The sample purge line was switched to CO<sub>2</sub> (20 mL/min) when desired.

After zeroing the electrobalance, a small amount of GAC (about 15 mg) was placed on the pan of the electrobalance and heated to 100°C in the N<sub>2</sub> atmosphere. After approximately 5 min, the sample was weighed, and the temperature program was started. Two sets of experiments were performed by TGA: (1) CO<sub>2</sub> kinetic studies for the determination of the rate of mass loss in the presence of CO<sub>2</sub> alone and (2) CO<sub>2</sub> adsorption experiments for the determination of CaO surface area.

For CO<sub>2</sub> kinetic studies, the temperature program was

(1) ramp in N<sub>2</sub> environment to 850°C at a rate of 150°C/min,

(2) soak in N<sub>2</sub> environment at 850°C for 10 min,

(3) soak in CO<sub>2</sub> environment at 850°C for 30 min, and

(4) ramp in N<sub>2</sub> environment to 100°C at a rate of 50°C/min.

The CO<sub>2</sub> kinetic studies were performed in duplicate.

For isothermal CO<sub>2</sub> adsorption studies, the multiramp program described by Linares-Solano et al<sup>16</sup> was used:

(1) ramp in N<sub>2</sub> environment to 900°C at a rate of 20°C/min,

(2) soak in N<sub>2</sub> environment at 900°C for 10 min,

(3) ramp in N<sub>2</sub> environment to 300°C at a rate of 20°C/min,

(4) soak in N<sub>2</sub> environment at 300°C for 10 min,

(5) soak in CO<sub>2</sub> environment at 300°C for 30 min, and

(6) soak in N<sub>2</sub> environment at 300°C for 10 min.

For blank runs, the CO<sub>2</sub> in step 5 was replaced by N<sub>2</sub>.

Figure 1 illustrates the phenomenon of CO<sub>2</sub> adsorption. The CaO surface area

was computed from the amount of CO<sub>2</sub> that chemisorbed isothermally at 300°C by assuming that one molecule of CO<sub>2</sub> chemisorbed per exposed CaO molecule and that one CaO molecule occupied an area of  $1.15 \times 10^{-19} \text{ m}^2$ .<sup>16,19</sup> Thus, the CaO surface area could be calculated, according to Eq 8, in units of m<sup>2</sup> CaO/g pyrolyzed GAC:

$$\begin{aligned} \text{CaO area (m}^2\text{/g)} = & \frac{\text{mass of CO}_2 \text{ adsorbed (g)}}{\text{mass of GAC remaining after pyrolysis (g)}} \quad (8) \\ & \times \frac{1.574 \text{ m}^2 \text{ CaO}}{1 \text{ g CO}_2} \end{aligned}$$

in which the conversion factor includes the molecular weight of CO<sub>2</sub> (44 g) and Avogadro's number ( $6.02 \times 10^{23}$  molecules/mole) as well as the area of a CaO molecule.

**Analysis of GAC.** GAC samples were analyzed for mass loss, volume loss, apparent density (AD), iodine number, macropore volume (pores with diameters >50 nm), mesopore volume (pores with diameters between 2 and 50 nm), micropore volume (pores with diameters <2 nm), and BET surface area. The procedures for these analyses have been presented in detail by Knappe<sup>17</sup> and by Waer et al.<sup>18</sup> In addition, the GAC ash content was determined, and metal analyses were performed.

**Ash content.** Samples were ashed by placing a known mass of dried GAC into a crucible, which was introduced into a muffle furnace at 600°C for 24 h. After the ashed sample was cooled in a desiccator, it was weighed on an analytical balance. The ash content, expressed in percent of spent GAC, was calculated by Eq 9:

$$\begin{aligned} \text{ash content (percent of spent GAC)} = & \frac{\text{mass of ash (g)}}{\text{mass of spent GAC (g)}} \times 100 \text{ percent} \quad (9) \end{aligned}$$

**Metal analysis.** To obtain a solution that could be analyzed for metals, ashed GAC samples were dissolved in 25 mL of concentrated HCl. After a minimum contact time of 24 h, the solution was filtered through an acid-resistant, ash-free cellulose acetate membrane (0.45-μm pore size) to retain the insoluble portion of the ash. The filtrate was then diluted to 250 mL, and a portion was transferred to a 40-mL, nitric acid (HNO<sub>3</sub>)-washed polyethylene bottle. Solutions were analyzed for metals by the inductively coupled plasma (ICP) method† in the microanalysis laboratory of the Chemistry Department at the University of Illinois, Urbana. The microanalyst performed two or three replications of each sample; if the coefficient of variation was less than 2 percent, the analysis was accepted. Metal contents were expressed in milligrams of metal per kilograms of spent dry GAC or as percentage by weight (with respect to

spent GAC), in which 1 percent by weight corresponds to 10,000 mg/kg.

## Experimental results

### Total loading, ash, and calcium content.

Table 4 illustrates the effect acid-washing had on virgin GAC with regard to ash and metal content. Acid-washing reduced the ash content by 45 percent and the concentrations of the metals of interest in this study by approximately one order of magnitude. Apart from Ca, metal concentrations stayed at this low level throughout the internal loading experiment. Table 5 summarizes the total loading (percent by weight) of the adsorbed compounds, ash content, and Ca content for internally loaded samples. The Ca content varied from 0.03 percent for the acid-washed virgin GAC to 4.1 percent for sample Ca-EDTA 2. A portion of sample Ca-EDTA 2 was also acid-washed, which effectively removed the loaded Ca. Table 6 shows the ash and metal contents for the Norristown and Hays Mine GAC samples. The Ca content was 1.0 percent for Norristown GAC and 1.4 percent for Hays Mine GAC.

**CO<sub>2</sub> adsorption as a measure of CaO surface area.** Because Linares-Solano et al<sup>16</sup> showed that the increase in reactivity of a char resulting from the presence of Ca correlated best with the CaO surface area after pyrolysis, the GAC samples used in this experiment were also analyzed for CaO surface area. Finding a sizable CaO area after pyrolysis was especially significant for the field carbons because it was an indication of internal Ca loading. Figure 2 shows that a linear relationship existed between CaO surface area and Ca content for the laboratory-loaded carbons; however, the data for the Norristown and Hays Mine GACs show that the direct relationship between CaO surface area and Ca content cannot be generalized. It is surprising that Ca dispersion, i.e., the percentage of the total CaO exposed, was higher for the field GACs than for the laboratory-loaded carbons. The presence of other alkaline earth and alkali metal oxides could have contributed to an increase in CO<sub>2</sub> adsorption, but because the combined concentration of magnesium, sodium, and potassium was an order of magnitude lower than the Ca concentration in the ash of Norristown and Hays Mine GACs, the contribution to CO<sub>2</sub> adsorption from those metals was assumed to be minor. Salinas-Martínez de Lecea et al<sup>9</sup> found that a greater degree of Ca dispersion was related to a larger concentration of carboxyl groups on the carbon surface. Thus, it is possible that the abundance of carboxyl functional groups found in humic substances could have contributed to higher CaO surface areas in the field carbons.

\*PC Series TGA7, Perkin-Elmer, Norwalk, Conn., interfaced with an IBM PS/2 Model 50 PC

†Plasma 2 ICP unit, Perkin-Elmer, Norwalk, Conn.

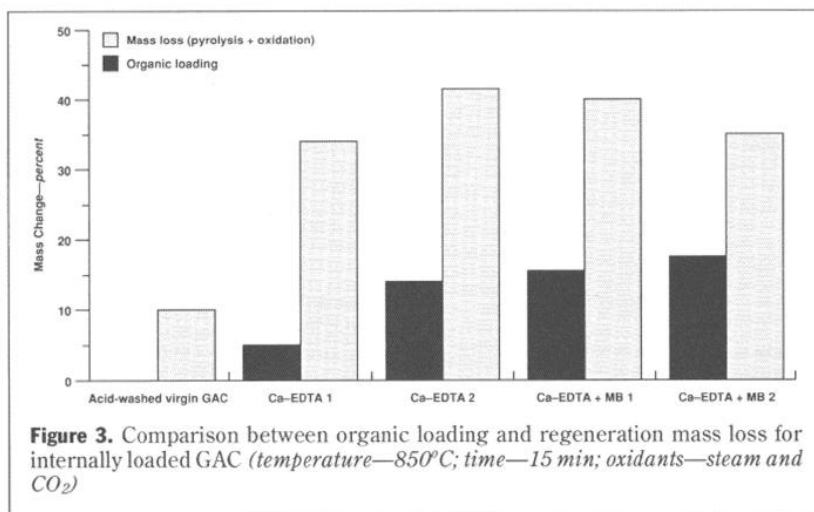


**Figure 3.** Comparison between organic loading and regeneration mass loss for internally loaded GAC (temperature—850°C; time—15 min; oxidants—steam and CO<sub>2</sub>)

**Effect of calcium on regeneration behavior.** To determine the effect of internally loaded Ca on the regeneration behavior of GAC, all laboratory-loaded samples were regenerated at 850°C for 15 min. During the reactivation step, steam and CO<sub>2</sub> flows were such that the quantity of steam applied was equivalent to 2.2–2.5 g H<sub>2</sub>O/g GAC, and the quantity of CO<sub>2</sub> applied was equivalent to 1.7–2.0 g CO<sub>2</sub>/g GAC. Although the mass of oxidant applied per unit mass of GAC varied, the mass of oxidant was constant per unit volume of GAC. A normalization on a unit volume basis was deemed more important because the same volume of GAC differed in mass depending on the degree of internal loading. Thus, oxidant flows translated into 1.2 g H<sub>2</sub>O/cm<sup>3</sup> GAC and 0.9 g CO<sub>2</sub>/cm<sup>3</sup> GAC. A nitrogen flow rate of 2 L N<sub>2</sub>/min at STP was required for fluidization throughout each regeneration. Used by Waer et al.,<sup>18</sup> these regeneration conditions were considered optimal for regenerating the GAC that was loaded with MB only.

Table 7 summarizes mass and volume losses as well as spent and regenerated ADs. When the mass losses for the two acid-washed GACs are compared with those for the Ca-loaded samples, it becomes apparent that the presence of internally loaded Ca greatly increases regeneration mass loss. Also, the observed mass losses for the Ca-loaded GACs greatly exceeded the degree of total loading, which is an indication of large base-carbon losses. The severity of base-carbon loss is further illustrated in Figure 3, which compares the total mass loss with the amount of loaded organic adsorbate.

Even though mass losses increased greatly, increases in volume loss were small, showing that the excessive mass loss occurred inside the GAC pores, where the Ca was present. As a consequence, the regenerated ADs for the Ca-loaded samples decreased to levels well below the AD of the acid-washed virgin

GAC, another indication of extensive internal mass loss and overregeneration.

**Pore structure and capacity.** Pore structure and capacity are also important parameters for the evaluation of regenerated GAC. Table 8 summarizes micropore and mesopore volumes, BET surface areas, and iodine numbers for acid-washed virgin GAC as well as for GAC samples regenerated with steam and CO<sub>2</sub> at 850°C for 15 min. For comparative purposes, all values were normalized on a unit bed volume (nonstratified) basis to better relate the data to full-scale adsorbers that have a fixed volume. Micropore volumes varied between 0.19 and 0.20 cm<sup>3</sup>/cm<sup>3</sup> GAC for acid-washed virgin and acid-washed regenerated GACs; however, the presence of internally loaded Ca caused micropore volumes to decrease to values between 0.12 and 0.14 cm<sup>3</sup>/cm<sup>3</sup> GAC in the regenerated products. A decrease in micropore volume could be expected for the Ca-loaded samples because the increased internal mass losses observed during regeneration should have caused pore enlargement, which would have led to a decrease in micropore volume and an increase in mesopore volume. However, mesopore volume analysis did not produce a clear trend; in general, mesopore volumes varied between 0.20 and 0.23 cm<sup>3</sup>/cm<sup>3</sup> GAC. No definite increase in mesopore volume was observed to explain a concurrent loss in micropore volume. Thus, it was hoped that the answer could be obtained from the macropore volume analysis.

Figure 4 shows the cumulative macropore volume distribution for acid-washed virgin GAC and for the regenerated Ca-EDTA + MB 1 sample. The graph clearly shows that the presence of Ca leads to an increase in macropore volume. For the regenerated Ca-EDTA + MB 1 sample, the macropore volume increased by 0.022 cm<sup>3</sup>/cm<sup>3</sup> GAC (or 20 percent) over the macropore volume of acid-washed

virgin GAC. The enlargement in macropore volume was not expected, particularly because Waer et al.<sup>18</sup> found that macropore volume was very constant for a variety of regeneration conditions. However, the increase in macropore volume explained why the mesopore volume change was not directly related to the loss in micropore volume. It was concluded that in addition to the conversion of micropores to mesopores, mesopores were converted to macropores as a result of the presence of Ca in the mesopores. Thus, the gains and losses in mesopore volume roughly canceled each other out.

In addition to pore volume, BET surface areas were analyzed. Table 8 shows that the BET surface area for acid-washed virgin GAC and acid-washed regenerated samples was 510 m<sup>2</sup>/cm<sup>3</sup> GAC, whereas Ca-loaded samples had surface areas of only 360–380 m<sup>2</sup>/cm<sup>3</sup> GAC after regeneration. The loss in BET surface area for the Ca-loaded samples is consistent with the loss in the volume of micropores where the largest portion of the BET surface area is found. On average, BET surface areas for the Ca-loaded regenerated samples were 27 percent less than for the acid-washed samples.

Finally, iodine numbers served as a measure of capacity for regenerated products. As can be seen in Table 8, the iodine number for an acid-washed virgin sample was 370 mg I<sub>2</sub>/cm<sup>3</sup> GAC after regeneration, whereas the capacities for the Ca-loaded regenerated samples varied between 280 and 310 mg I<sub>2</sub>/cm<sup>3</sup> GAC, approximately 20 percent lower.

**Ash and calcium content after regeneration.** Table 9 shows the ash and Ca contents for laboratory-loaded GAC samples regenerated with steam and CO<sub>2</sub> at 850°C for 15 min. When the values for ash and Ca contents after regeneration are compared with the values prior to regeneration, it can be determined that the values prior to regeneration are lower by approximately the percentage of mass lost for each sample during regeneration. Therefore, essentially all of the loaded Ca stayed on the regenerated product. The implications of this finding deserve attention and future research. First, the accumulated ash might have an adverse effect on the capacity of the regenerated product, thus shortening the GAC bed life. Second, whether the buildup of inorganics proceeds while the regenerated product is in place and what effect this continued accumulation has on subsequent regenerations should be studied.

**Effect of CO<sub>2</sub> on regeneration.** To investigate the effect of CO<sub>2</sub> on the regeneration of Ca-containing GACs, samples Ca-EDTA 1, Ca-EDTA + MB 1, and Norristown GAC were regenerated under two conditions: (1) steam as the only oxidant (2 g H<sub>2</sub>O/g GAC) and (2) both steam and CO<sub>2</sub> as oxidants (2 g H<sub>2</sub>O/g GAC, 1.6 g CO<sub>2</sub>/g GAC).

All samples were regenerated at 850°C for 15 min; in addition, Norristown GAC was regenerated at 750°C for 15 min. Table 10 summarizes the observed mass and volume losses as well as spent and regenerated ADs. At 850°C, the addition of CO<sub>2</sub> increased mass losses by 7.1 percent for sample Ca-EDTA 1, by 8.3 percent for Norristown GAC, and by 12.0 percent for sample Ca-EDTA + MB 2. At 750°C, however, CO<sub>2</sub> caused only a 1.8 percent increase in mass loss for the Norristown GAC. Volume loss was also higher upon addition of CO<sub>2</sub>, but the increase was less dramatic. Thus, ADs were much lower when CO<sub>2</sub> was added during the reactivation step at 850°C.

Also, the products regenerated at 850°C with steam alone had larger micropore volumes, BET surface areas, and iodine numbers because the milder regeneration condition without CO<sub>2</sub> was less destructive to the GAC structure. At a regeneration temperature of 750°C, however, CO<sub>2</sub> addition resulted in trivial reductions of micropore volume, BET surface area, and iodine number.

It was also of interest to correlate mass loss with CaO surface area for the regenerations that used steam as the only oxidant and compare the behavior with that of the regenerations in which both steam and CO<sub>2</sub> were employed (see Figure 5). The graph shows that regenerations with steam alone behaved similarly to regenerations with steam and CO<sub>2</sub> with respect to CaO surface area; mass losses increased significantly in the presence of Ca, but a plateau was reached at CaO surface areas >1 m<sup>2</sup>/g. Figure 5 also illustrates that CO<sub>2</sub> was an important oxidant at 850°C when Ca was present and that mass losses were much higher as a consequence. In future work, it would be interesting to show whether the addition of an equivalent amount of steam would have led to the same increase in mass loss or whether the steam reaction was already zero order and proceeded at its maximum rate. The correlation between mass loss and Ca content, the main reason being the use of Norristown GAC whose CaO surface area correlated differently with Ca content than the CaO areas of the laboratory-loaded GACs, as shown in Figure 2.

**Steam kinetics.** The kinetics of the steam reaction at 850°C were studied extensively for the GAC sample Ca-EDTA + MB 2 by regenerating it for different amounts of time in the fluidized-bed furnace. The steam application was equivalent to 2.1 g H<sub>2</sub>O/g GAC for a 15-min regeneration. Mass loss increased linearly over the 30-min regeneration range ( $R^2 = 0.994$ ), and the rate of mass loss was 1.22 percent/min. The direct proportionality between mass loss and time is consistent with the findings of Waer et al.,<sup>18</sup>

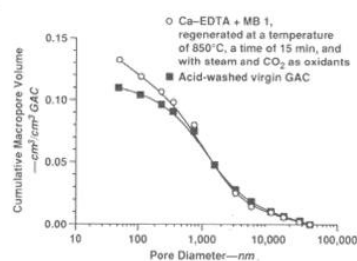


Figure 4. Macropore volume distributions for acid-washed virgin GAC

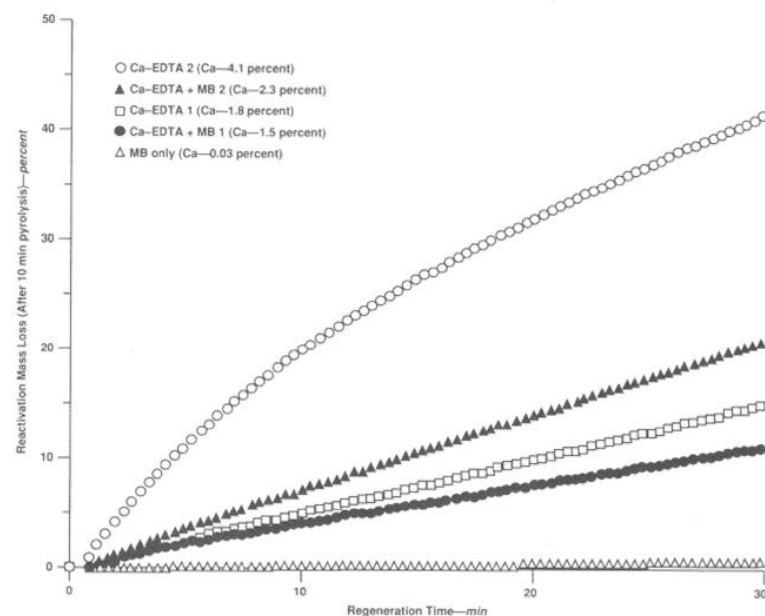


Figure 6. Effect of calcium concentration on CO<sub>2</sub> regenerations at 850°C

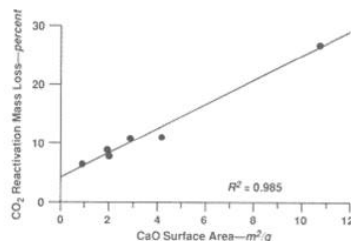


Figure 7. Carbon dioxide reactivation mass loss after 15 min versus calcium oxide surface area

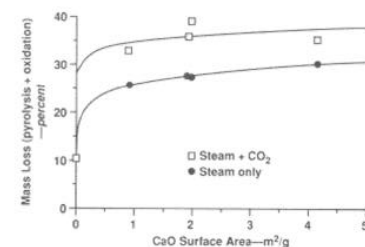


Figure 5. Effect of CO<sub>2</sub> on mass loss as a function of calcium oxide surface area (temperature—850°C; time—15 min)

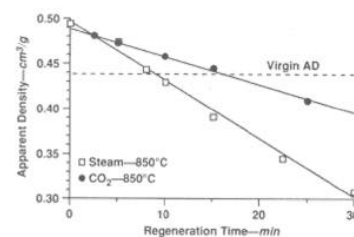


Figure 8. Apparent density versus regeneration time

who observed the same relationship for a variety of temperatures and GACs. But they observed mass loss rates on the order of 0.24 percent/min when MB-loaded virgin GAC was being regenerated with steam and CO<sub>2</sub> at 850°C. Thus, the rate of mass loss for the steam regeneration was five times higher in the presence of 2.3 percent Ca (4.2 m<sup>2</sup> CaO/g GAC) than the rate of mass loss for a

regeneration with steam and CO<sub>2</sub> in the absence of loaded Ca.

**CO<sub>2</sub> kinetics.** The kinetics of the CO<sub>2</sub> reaction were studied in the absence of steam as a function of Ca by TGA. Figure 6 shows that CO<sub>2</sub> regeneration mass losses at 850°C increased with increasing Ca loading. For a Ca content up to 2.3 percent, the rate of mass loss was essentially constant with time, whereas the re-

activity of the GAC with a 4.1 percent Ca content decreased over the 30-min regeneration period. The higher initial rate for the GAC with 4.1 percent Ca might indicate that the reactivity of EDTA char is greater than that of GAC (a pure compound analysis of EDTA showed that 16 percent char remained at 850°C), but, on the other hand, the high initial rate is also consistent with the findings of Linares-Solano et al.,<sup>16</sup> who observed a significant decrease in reactivity for a carbon sample with a 3.2 percent Ca loading that was gasified at 800°C in a CO<sub>2</sub> atmosphere. They attributed the decrease in reactivity to the sintering (crystallite growth) of CaCO<sub>3</sub>, which resulted in a lesser degree of Ca dispersion. This phenomenon was much less pronounced for the samples with lower Ca loadings, which raises the question of whether the severity of sintering is a function of Ca loading. Salinas-Martínez de Lecea et al.<sup>9</sup> found that CaO crystallite sizes started to increase once the loading saturation level (LSL) was reached; they related the LSL to the abundance of carbon carboxyl groups.

The reactivity of the Ca-loaded carbons was much greater than the reactivity of an acid-washed carbon loaded with MB. For the latter carbon, the CO<sub>2</sub> reaction rate was essentially negligible at 0.027 percent/min.

In addition, Ca-EDTA + MB 2 samples were also regenerated with CO<sub>2</sub> in the fluidized-bed furnace at 850°C. The CO<sub>2</sub> flow rate was equivalent to 1.6 g CO<sub>2</sub>/g GAC at 15 min. A mass loss rate of 0.64 percent/min was obtained, which was in excellent agreement with the average TGA rate of 0.69 percent/min. Because the mass flow rate of CO<sub>2</sub> per unit mass GAC was >30 times greater in the TGA than in the furnace, the similarity of the rates implied that the reaction was proceeding at its maximum rate and was zero order with respect to CO<sub>2</sub>.

The maximum rate of mass loss for the CO<sub>2</sub> regeneration was about one half of the value obtained for the steam regeneration presented earlier; however, it was not known whether the steam reaction proceeded at the maximum rate. Also, the rate of mass loss for the CO<sub>2</sub> regeneration was 2.7 times greater than the rate of mass loss found by Waer et al.<sup>18</sup> for an MB-loaded GAC regenerated with steam and CO<sub>2</sub> at 850°C.

Furthermore, the reactivities of Norristown and Hays Mine GACs were measured in a CO<sub>2</sub> environment at 850°C by TGA. The average rate of mass loss over 30 min was 0.50 percent/min for Norristown GAC and 0.62 percent/min for Hays Mine GAC. Again, the rate of mass loss was greater for the GAC with the higher Ca content.

Once CO<sub>2</sub> reactivity data were obtained for a variety of GACs with different Ca loadings, it was desired to establish a relationship between GAC reactivity and

| <b>TABLE 9</b><br><i>Ash and calcium contents for internally loaded GAC before and after regeneration *</i> |             |       |          |        |
|-------------------------------------------------------------------------------------------------------------|-------------|-------|----------|--------|
| Sample                                                                                                      | Ash—percent |       | Ca—mg/kg |        |
|                                                                                                             | Before      | After | Before   | After  |
| Ca-EDTA 1<br>(mass loss—33.7 percent)                                                                       | 10.1        | 14.5  | 15,380   | 22,520 |
| Ca-EDTA 2<br>(mass loss—41.2 percent)                                                                       | 13.2        | 21.0  | 40,710   | 66,860 |
| Ca-EDTA + MB 1<br>(mass loss—39.4 percent)                                                                  | 11.4        | 17.8  | 17,610   | 26,840 |
| Acid-washed Ca-EDTA 2<br>(mass loss—12.7 percent)                                                           | 7.2         | 8.1   | 490      | 530    |

\*Temperature of regeneration—850°C; time—15 min

| <b>TABLE 10</b><br><i>Effect of CO<sub>2</sub> addition on mass and volume losses as well as apparent densities</i> |                                                    |                           |                                         |                                         |
|---------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|---------------------------|-----------------------------------------|-----------------------------------------|
| Sample                                                                                                              | Mass Loss<br>(Pyrolysis +<br>Oxidation)<br>percent | Volume<br>Loss<br>percent | AD <sub>appt</sub><br>g/cm <sup>3</sup> | AD <sub>reg.</sub><br>g/cm <sup>3</sup> |
| Ca-EDTA 1, 850°C                                                                                                    |                                                    |                           |                                         |                                         |
| Steam only                                                                                                          | 25.9                                               | 2.2                       | 0.470                                   | 0.356                                   |
| Steam + CO <sub>2</sub>                                                                                             | 33.0                                               | 3.0                       | 0.466                                   | 0.322                                   |
| Ca-EDTA + MB 1, 850°C                                                                                               |                                                    |                           |                                         |                                         |
| Steam only                                                                                                          | 27.4                                               | 2.2                       | 0.516                                   | 0.383                                   |
| Steam + CO <sub>2</sub>                                                                                             | 39.4                                               | 2.7                       | 0.525                                   | 0.327                                   |
| Norristown, 850°C                                                                                                   |                                                    |                           |                                         |                                         |
| Steam only                                                                                                          | 27.6                                               | 5.4                       | 0.575                                   | 0.440                                   |
| Steam + CO <sub>2</sub>                                                                                             | 35.9                                               | 8.1                       | 0.580                                   | 0.405                                   |
| Norristown, 750°C                                                                                                   |                                                    |                           |                                         |                                         |
| Steam only                                                                                                          | 16.9                                               | 3.2                       | 0.580                                   | 0.498                                   |
| Steam + CO <sub>2</sub>                                                                                             | 18.7                                               | 3.7                       | 0.581                                   | 0.490                                   |

| <b>TABLE 11</b><br><i>Micropore and mesopore volumes for regenerated GAC samples when virgin AD was used as a regeneration control parameter</i> |                         |                                                         |                                                        |
|--------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------|---------------------------------------------------------|--------------------------------------------------------|
| Sample                                                                                                                                           | AD<br>g/cm <sup>3</sup> | Micropore<br>Volume<br>cm <sup>3</sup> /cm <sup>3</sup> | Mesopore<br>Volume<br>cm <sup>3</sup> /cm <sup>3</sup> |
| Acid-washed virgin GAC                                                                                                                           | 0.438                   | 0.190                                                   | 0.229                                                  |
| Ca-EDTA + MB 2 regenerated at 850°C<br>1.2 g steam/g GAC                                                                                         | 0.443                   | 0.187                                                   | 0.202                                                  |
| Ca-EDTA + MB 2 regenerated at 850°C<br>1.6 g CO <sub>2</sub> /g GAC                                                                              | 0.445                   | 0.182                                                   | 0.155                                                  |
| Ca-EDTA + MB 2 regenerated at 750°C<br>1.9 g steam/g GAC + 1.5 g CO <sub>2</sub> /g GAC                                                          | 0.442                   | 0.180                                                   | 0.210                                                  |
| Ca-EDTA + MB 2 regenerated at 850°C<br>2.2 g steam/g GAC + 1.7 g CO <sub>2</sub> /g GAC                                                          | 0.327                   | 0.120                                                   | 0.234                                                  |

CaO surface area. Figure 7 shows a linear dependence of the reactivation mass loss after 15 min on the CaO surface area. The linear relationship between the reactivity of the different GACs and their respective Ca contents (percent by weight) was not as clear. Therefore, the CaO area after pyrolysis was a better parameter for judging the reactivity of a carbon; this is in complete agreement with the findings of Linares-Solano et al.<sup>16</sup>

Finally, the reactivity of a Ca-EDTA + MB 2 sample was also measured in a CO<sub>2</sub> environment at 750°C by TGA. The average rate of mass loss over the 30-min regeneration period was only 0.066 percent/min, an essentially negligible rate that was 10 times lower than the rate observed at 850°C.

The CO<sub>2</sub> rate study showed that CO<sub>2</sub> plays an important role as an oxidant at a

regeneration temperature of 850°C in the presence of Ca but not in its absence. At 750°C, however, Ca did not noticeably catalyze the CO<sub>2</sub> reaction. In addition, reactivity increased linearly with increasing CaO surface area.

**Apparent density.** In large-scale operations, regeneration is often monitored by measuring the AD of the regenerated product. If the regenerated AD is close to the AD of the virgin GAC, a regeneration is judged successful. In the absence of inorganics, Waer et al.<sup>18</sup> showed that the AD of the virgin GAC is a valid goal for the regeneration of spent GAC. To further examine the validity of the virgin AD as a measure of a successful regeneration, portions of sample Ca-EDTA + MB 2 were regenerated to virgin AD under three different conditions:

- 850°C with CO<sub>2</sub> only (1.6 g/g GAC),
- 850°C with steam only (1.2 g/g GAC), and
- 750°C with steam (1.9 g/g GAC) and CO<sub>2</sub> (1.5 g/g GAC).

During the steam and CO<sub>2</sub> kinetic studies, the change in AD over time was also monitored, as shown in Figure 8. Thus, the time required to reach the virgin AD could easily be predicted for the first two conditions.

Table 11 shows the ADs of the regenerated products and compares the obtained micropore and mesopore volumes with the values for acid-washed virgin GAC, which was the starting material for sample Ca-EDTA + MB 2. In addition, an overregenerated Ca-EDTA + MB 1 sample was included for comparative purposes. Regeneration to virgin AD produced micropore volumes that were very close to the value of 0.19 cm<sup>3</sup>/cm<sup>3</sup> GAC, whereas overregeneration resulted in a loss of micropore volume. The mesopore volume analysis produced one unexpected result. With a value of 0.16 cm<sup>3</sup>/cm<sup>3</sup> GAC, the CO<sub>2</sub> regeneration at 850°C resulted in a mesopore volume that was lower than the mesopore volumes for the other samples that varied between 0.20 and 0.23 cm<sup>3</sup>/cm<sup>3</sup> GAC. The reasons for this reduction in mesopore volume are unknown, and more work needs to be done to further investigate this phenomenon.

The third regeneration condition (steam and CO<sub>2</sub> at 750°C) provided an interesting side result; for sample Ca-EDTA + MB 2, 1.9 g steam/g GAC and 1.5 g CO<sub>2</sub>/g GAC were required at 750°C to recover virgin AD, whereas Waer et al.<sup>18</sup> required 2.25 g steam/g GAC and 1.5 g CO<sub>2</sub>/g GAC at 850°C to recover virgin AD for GAC that had approximately the same MB loading as sample Ca-EDTA + MB 2. Combined with the knowledge that the CO<sub>2</sub> rate at 750°C was negligible for Ca-loaded GACs and that it was also negligible at 850°C in the absence of Ca, this experiment showed that the steam reaction at 750°C proceeded slightly faster in the presence of Ca than at 850°C in its absence. This finding suggests that a regeneration furnace could be operated at a 100°C lower temperature and achieve the same results, which would translate into significant energy savings. However, several questions need to be answered before regeneration to virgin AD in the presence of inorganics can be recommended. Most important, the effect of ash accumulation on GAC capacity needs to be investigated.

### Discussion and conclusions

The presence of internally loaded Ca greatly affected the regeneration behavior of GAC. Calcium acted as a catalyst by increasing the number of reactive sites, and its presence resulted in excessive mass losses compared with non-Ca-

loaded GACs when samples were regenerated under the same conditions. These increased mass losses resulted in a reduction of micropore volume, BET surface area, and iodine number as well as in an increase of macropore volume. There was evidence that the presence of Ca in the micropores caused a conversion of micropores to mesopores and that the presence of Ca in the mesopores caused a conversion of mesopores to macropores when samples were overregenerated.

In addition, kinetic studies at 850°C showed that the presence of 2.3 percent Ca (4.2 m<sup>2</sup> CaO/g GAC) increased the rate of mass loss for steam by a factor of five and for CO<sub>2</sub> by a factor of 25 over the respective rates observed in the absence of Ca. Nonetheless, the catalyzed steam reaction proceeded at nearly twice the rate of the catalyzed CO<sub>2</sub> reaction at 850°C. At 750°C, the CO<sub>2</sub> reaction rate became negligible in the presence of Ca, but the steam reaction proceeded at a rate that still exceeded the reaction rate of a non-Ca-loaded GAC at 850°C. Therefore, regeneration of GAC can be performed at a lower temperature in the presence of Ca if the accumulation of ash in the regenerated product does not affect capacity.

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