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REACTION MECHANISM OF CALCIUM-CATALYZED THERMAL REGENERATION OF SPENT GRANULAR ACTIVATED CARBON

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Abstract—Thermal regenerations were conducted on a spent granular activated carbon (GAC) that had served in a water treatment plant for about four years, and contained 1.8% calcium. Oxidation was conducted in steam, CO₂, or steam plus CO₂, at 650–950°C. As described earlier, when steam and CO₂ were employed together, the regenerated product's pore structure maintained greater micropore volume at high temperatures (>800°C) than at low temperatures (<750°C). The work herein has linked this distinction to differences in reaction rate limitations: at high temperatures, with both oxidants employed together, the water-gas shift reaction ($\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2$) limited overall rate, whereas at low temperatures, the C(O) gasification step limited overall rate. The CO₂ created via the water gas shift reaction served as the primary oxidant. Although steam served only as a secondary oxidant, its presence also facilitated more extensive oxidant transfer to the carbon surface.

Key Words—Activated carbon, calcium catalysis, carbon gasification, diffusion, water-gas shift.

1. INTRODUCTION

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[3,4]. While the GAC is in service, however, it can also accumulate metals, particularly calcium. When the GAC's capacity to adsorb organic compounds becomes exhausted (spent), water utility managers face a major decision. Should the spent GAC be landfilled and replaced with virgin GAC, or should the GAC be regenerated[5] 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. Regeneration, alternatively, may offer the most economical, energy-efficient, and environmentally sound option. However, any cost or energy analysis would be very sensitive to the extent that the adsorption capacity of regenerated carbon is renewed, as compared to that of virgin carbon.

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°C to 850°C. This step vaporizes the water associated with the GAC, volatilizes volatile organic compounds, and converts nonvolatile organic compounds to char. During oxidation, the second step of regeneration, the py-

rolyzed GAC is exposed to an environment of steam or CO₂ or both at 650–950°C. These gases partly gasify the char and solid GAC internal surface. This process slightly widens the GAC pores.

While the GAC is in water treatment service, it accumulates calcium to levels of 0.4 to 7% within spent GACs[1,6,7]. During regeneration, this calcium catalytically accelerates the oxidation rate, and tends to widen the smallest pores (micropores)[1,6,8]. In contrast, with calcium excluded, oxidation increases microporosity and small mesoporosity[8,9,10,11].

In this paper, the authors propose a mechanism to describe calcium catalysis behavior when spent GAC experiences oxidation by steam, CO₂, or steam plus CO₂. This mechanism offers fundamental explanation for the differences in pore development that have been presented earlier[1,6,8] when steam plus CO₂ serve as oxidants at low temperatures, as compared to high temperatures.

In earlier work, Cannon *et al.*[1,6] and Cannon[8] employed nitrogen adsorption isotherms to characterize GAC pore structure changes during regeneration. These authors found that under favorable conditions, thermal regeneration could restore virgin pore structure despite the presence of calcium and other metals. Experiments also explored how pores developed when regenerations altered the apparent density (AD) of

spent GAC from an initial 0.54 g/mL to a final 0.43 g/mL under an array of oxidation conditions. When the GAC was regenerated to a given apparent density under various conditions, the total amount of added pore space was likewise consistent for all oxidation conditions, although its location could vary. Thus, true distinctions could be discerned as to where this pore development was occurring within the GAC.

It was observed that when steam plus CO₂ served as oxidants of calcium-loaded GAC, lower oxidation temperatures (650–750°C) caused greater destruction of micropores than did higher temperatures (850–950°C). Also, if steam alone or CO₂ alone were employed as the oxidant at any temperature, the same pore development resulted as occurred using steam and CO₂ at high temperatures. Micropore preservation has been deemed important for adsorbing small organic compounds[3], and thus, the low-temperature regenerations that employed both oxidants were thought to produce an inferior GAC for water treatment applications in which small organic compounds are targeted.

The purpose of this paper is to explore the fundamental reasons why these differences in pore development occurred by characterizing the mechanistic behavior of calcium catalysis in thermal regeneration.

Many authors have observed significant catalysis displayed by calcium when carbonaceous materials have been gasified in steam or CO₂[7,12–52]. However, only a few of these have specifically addressed the regeneration of spent GACs in calcium's presence [7,46,47,51,52].

The work herein has built upon the research of Knappe *et al.*[7], who determined that calcium caused a five- to twenty-five-fold increase in the rate of regeneration of coal-based GAC when steam and/or carbon dioxide were employed. Reaction rates were determined at 850°C for acid-washed virgin GAC loaded with methylene blue, 2.3% calcium, and EDTA. Knappe[22] also studied the regeneration behavior of a highly calcium-loaded, wood-based GAC, and surmised that the oxidant attacked the outer surface of the wood-based GAC grains in the presence of calcium, whereas oxidation occurred inside the GAC pores after the calcium had been extracted with acid. This shrinking core-like behavior was not observed for coal-based GACs.

2. UNIFIED CATALYSIS MECHANISM

The authors propose that the following unifying mechanism describes the calcium-catalyzed oxidation of GAC in a steam and/or CO₂ environment. This mechanism integrates the fundamentals from several disciplines into one unified whole. This has been derived from literature review[20,53–60], from basic thermodynamic data[35,36,37,57,58,59], and from the authors' interpretation of the results reported herein and in related research[1,2,6,8].

2.1 Diffusion and oxidation steps of catalysis mechanism

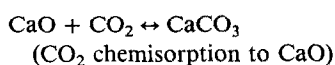
The proposed mechanism includes diffusion, chemisorption, catalysis, surface-phase oxidation reactions, and gas phase reactions. It proceeds as follows:

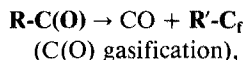
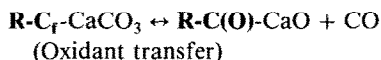
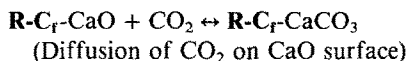
1. CO₂ is generated from steam and CO via the gas phase water-gas shift reaction ($\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2$). CO₂ acts as the primary (predominant) oxidant of the carbon surface. Steam acts as a secondary (subordinate) oxidant.
2. Oxidant gas diffuses via bulk and film (molecular) diffusion to the external surface of the GAC grain[55].
3. Oxidant gas diffuses via molecular diffusion through the large macropores. This is governed by collisions between one gas molecule and another[55].
4. Oxidant gas diffuses via Knudsen diffusion through the smaller macropores, mesopores, and large micropores. This is governed by collisions between gas molecules and pore walls[55]. By convention, micropores have widths smaller than 2 nm, mesopores have widths between 2 and 50 nm, and macropores have widths greater than 50 nm[57].
5. Oxidant gas diffuses via restricted diffusion through the smaller micropores (this step is usually precluded). This is governed by activated interactions between gas molecules and the pore wall[53,54,55,60].
6. The oxidant becomes chemisorbed to CaO crystallites[30].
7. Oxidant diffuses via surface diffusion along the CaO crystallite surface to the CaO-C interface[30].
8. The oxidant chemically transforms and transfers to the carbon surface.
9. Oxidant diffuses via surface diffusion to a free active carbon site.
10. Solid carbon-oxygen functional groups are gasified to form CO.
11. Gasification products diffuse out of the GAC grain via restricted, Knudsen, molecular, and film diffusion[55,57].

In order to evaluate this mechanism experimentally and discern rate limiting steps, the authors have evaluated reaction kinetics and effective activation energies for catalyzed gasification.

2.2 CO₂ oxidation mechanism

The authors concur that when CO₂ serves as the sole oxidant, the calcium-catalyzed chemical reaction mechanism apparently proceeds as described by McKee[35,36,37], Cazorla-Amoros *et al.*[14], and Linares-Solano *et al.*[30]:





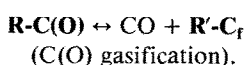
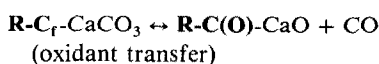
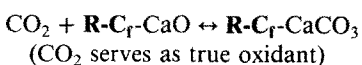
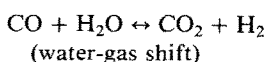
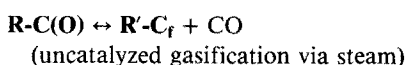
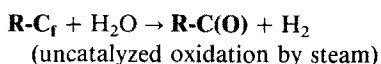
where all solid-phase carbon groups are shown in bold. **R-C_f** represents a solid carbon active site that is free of oxygen, and **R-C(O)** represents a solid carbon-oxygen functional group. The **R-C_f-Ca(O)** represents a solid carbon-calcium oxide interface, and the **R'-C_f** represents an active site that becomes exposed following the gasification of the C(O) group that previously covered it.

2.3 Roles of steam in calcium catalyzed oxidation

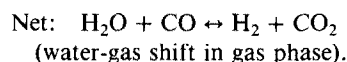
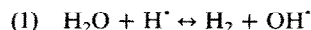
The authors propose that steam plays four roles in calcium catalyzed oxidation of activated carbon:

1. Steam provides a source of CO₂ via the water-gas shift reaction that occurs in the gas phase. The CO₂ created by this reaction serves as the primary oxidant via the CaO-CaCO₃ cycle described above.
2. Steam allows more extensive oxidant transfer across CaO to the carbon surface.
3. Steam serves as a secondary oxidant at lower oxidation temperatures, via a CaO-Ca(OH)₂ cycle.
4. The water-gas shift reaction could also be catalyzed at the CaO surface (although this only occurs to a thermodynamically limited extent at regeneration temperatures). This reaction could provide an additional source of CO₂.

2.3.1 Role 1: Steam as source of CO₂. Steam and CO provide a source of CO₂ via the water-gas shift reaction. This process is initiated via uncatalyzed carbon gasification by steam: The CO produced by this C(O) gasification in turn fuels the water-gas shift reaction, as described by the following mechanism:

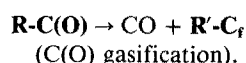
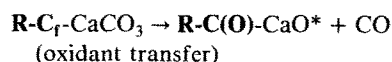
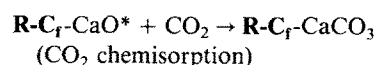
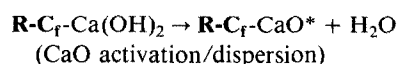
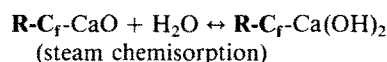


In the gas phase, with oxygen excluded, the water-gas shift reaction proceeds via two steps, per Card[57]:



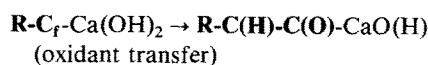
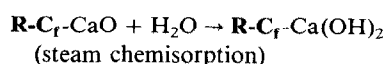
Over the 650°C to 950°C temperature range, the first step is rate limiting and relatively slow; it has an effective activation energy of 90 kJ/mole[57]. If oxygen were present, this mechanism would be limited by other steps and would be far more rapid. But oxygen is specifically excluded from regeneration environments.

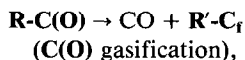
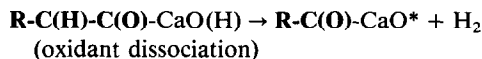
2.3.2 Role 2: Steam causes more extensive oxidant transfer. Steam also transiently interacts directly with the CaO surface to cause more extensive oxidant transfer across the CaO to the carbon surface. This mechanism proceeds as follows:



The CaO* that has been activated by H₂O can more extensively transfer CO₂ oxidant across its surface to the carbon interface than can CaO that has not been influenced by H₂O. This is either because the steam physically disperses the CaO or because it causes structural or chemical alterations to the CaO. This phenomenon effectively increases the number of active carbon sites that interface with the CaO* surface. The authors herein observed considerable evidence that steam caused more extensive CO₂ transfer even at temperatures as high as 850°C (see discussion below).

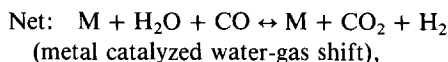
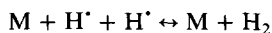
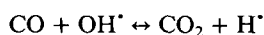
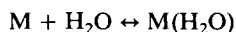
2.3.3 Role 3: Steam as secondary oxidant. Steam could perhaps also serve as a secondary oxidant, particularly at the lowest regeneration temperatures, by means of the following mechanisms (compare to [35,37]):





where **R-C(H)-C(O)-CaO(H)** represents the carbon-calcium interface as H_2O is dissociating to create oxygen plus two Hs. The dissociated Hs would quickly recombine to form an H_2 molecule.

2.3.4 Role 4: Steam as source of CO_2 via metals catalysis. Conceptually, metal oxide surfaces such as CaO could catalyze the water-gas shift reaction. However, for CaO, this would only occur at lower temperatures than were employed in the regeneration conditions. Metal oxide surface catalysis, if occurring, would proceed via the following mechanism[57,58]:



where M represents a metal or metal oxide such as CaO. All the steps in this metal-catalyzed reaction mechanism are very rapid, and would exceed the rate of C(O) gasification if the hydrated metal were thermodynamically predominant, as has been reported for potassium catalysis by Meijer *et al.* [61], Meijer[62], and Mims and Pabst[63]. However, when calcium serves as the catalyst at regeneration temperatures, it will not participate significantly in the metal-catalyzed water-gas shift reaction because the intermediate species Ca(OH)_2 is scarce for thermodynamic reasons that are discussed below.

3. LITERATURE BASIS FOR PROPOSED MECHANISM

The above proposed mechanism builds upon the fundamentals developed in the literature regarding CaO thermodynamics, activation energies, lime manufacturing, water-gas shift reaction thermodynamics, CaO catalysis mechanism, and diffusion theory. In citing this literature, the authors have intended to integrate concepts from several diverse disciplines into one unified model.

3.1 Thermodynamics of calcium oxide

The predominant calcium species is dictated by both the temperature and by the steam or CO_2 partial pressures it experiences, as shown in the phase predominance diagram in Fig. 1. As indicated by this figure, for example, if calcium oxide is placed in a gaseous environment containing 0.2 atm steam (log 0.2 =

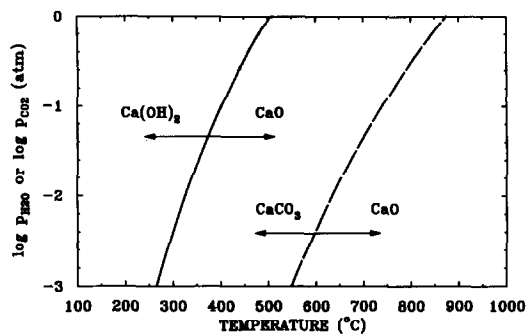
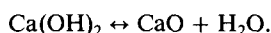
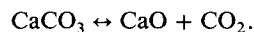


Fig. 1. Phase predominance diagram for the reactions $\text{Ca(OH)}_2 = \text{CaO} + \text{H}_2\text{O}$ and $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$ [35,56].

−0.7), which is within a typical range for regenerations), the species Ca(OH)_2 will predominate below 430°C, and CaO will predominate above 430°C[35,36, 37,56]. This predominance is governed by the reaction:



Similarly, in 0.2 atm CO_2 at equilibrium, the species CaCO_3 will predominate below 775°C, and CaO will predominate above 775°C, as governed by the expression:



Above these phase boundaries, only CaO would exist at equilibrium, in accordance with the Gibb's phase rule. However, the non-predominant species could also be present in a transitory manner above this boundary due to kinetic and sintering limitations, and internal pressure constraints. This was recognized by Joly *et al.* [21], who observed that CO_2 was released from CaCO_3 over a band of temperatures spanning roughly 700 to 900°C. In contrast, however, most water vapor (but not all of it) was released from Ca(OH)_2 at temperatures below 600°C.

For the Ca(OH)_2 -CaO system, the regeneration temperatures of 650°C to 950°C exceed the Ca(OH)_2 -CaO predominance boundary by 200°C to 500°C. At the lower end of this temperature range, perhaps there would be some Ca(OH)_2 available to interact in reactions; but at the upper end of this range, Ca(OH)_2 would be very scarce (but perhaps not non-existent). Thus, on a thermodynamic and kinetic basis, H_2O would be far less prominently involved in oxidant transfer than would CO_2 at thermal regeneration temperatures.

3.2 Activation energy as indicator of the rate limiting step for calcium catalyzed oxidation

The oxidized gasification rate increases with increasing temperature in accordance with the Arrhenius expression[64],

$$\text{rate} = Ae^{-E_a/RT},$$

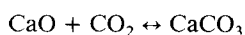
where E_a is the activation energy, A is the pre-exponential factor, R is the ideal gas constant, T is temperature, °K, and e is the natural base. Several researchers have observed the same activation energy for calcium catalyzed gasification in CO_2 as for uncatalyzed gasification, while also noting that the Arrhenius pre-exponential factor A was higher for catalyzed than for uncatalyzed gasification. Typical activation energy values have been in the range of 150 to 250 KJ/mole[28,29,36,45], and rate limitation has been attributed to the C(O) gasification step. Other alkaline earth metals have also manifested similar activation energies[36]. Several authors have cited this similarity in activation energy as evidence that calcium and other alkaline earth metals do not alter the rate limiting step in carbon gasification. Rather, they increase the extent of oxygen transfer to the carbon surface by increasing the number of effectively active sites on the carbon surface. Thus, calcium distinguishes itself from traditional catalysts, which reduce overall activation energy by bypassing high energy barriers.

3.3 Lime calcination and sintering

The relative importance of CO_2 and steam interaction with CaO is illuminated by reviewing the thermal behavior of limestone, since the calcium in GAC has a chemical composition similar to limestone. The limestone calcination process at 800–1000°C expels CO_2 from limestone (CaCO_3) and forms lime (CaO), also known as quicklime. Water hydrates quicklime vigorously and exothermically at room temperature, and disintegrates the CaO structure[65]. Perhaps this CaO disintegration could also occur at regeneration temperatures (see below).

In contrast, CaCO_3 tends to sinter the CaO surface, making it less reactive for oxidation[12,28,65,66, 67]. Linares-Solano *et al.* [28] proposed that in a hot CO_2 environment, calcium species transformed from the (presumably) active CaO to the less active CaCO_3 . Those authors cited a declining gasification rate of char in CO_2 as confirmation of such a transformation. In a steam environment, however, they did not see a declining gasification rate. In steam, they reasoned, less CaCO_3 could form, so there was not the same tendency toward sintering as in a CO_2 environment.

3.3.1 Catalytic effect of steam on calcination or recarbonation. There is some evidence in the limestone calcining literature that steam catalyzes both the calcination of CaCO_3 and the recarbonation of CaO. Thus, the reaction



could proceed more effectively either to the right or to the left when water vapor is present. At room temperatures, it is commonly acknowledged that dry CO_2 gas will not react with CaO, whereas wet CO_2 gas will react with CaO quite readily[65]. Moreover, there has been some evidence that even at elevated temperatures, a trace of steam will enhance either the calcination or recarbonation reaction[68,69,70].

MacIntire and Stansel[70] observed complete conversion of CaCO_3 to $\text{CaO} + \text{CO}_2$ when they subjected small calcite limestone grains to flowing steam at 700°C for 3 hours. In contrast, without steam, the conversion was far slower. Mitchell[68] monitored CO_2 partial pressure when CaCO_3 samples were calcined at elevated temperatures and then cooled and recarbonated at lower temperatures. He noted that the CO_2 would not recombine with the lime so as to revert the CO_2 partial pressure to its equilibrium level unless Ca(OH)_2 was also added.

The findings of Beruto *et al.* [71] may shed light on this behavior: they showed that when Ca(OH)_2 was dissociated to CaO, the product CaO had higher surface area and greater X-ray diffraction peak widths than did the CaO that resulted from CaCO_3 dissociation.

In summary, there appears to be a common (but non-universal) notion among lime manufacturers that water vapor may enhance both the calcination and recarbonation reactions[65]. This principal is reflected in the second proposed role of steam as an enhancer of more extensive oxidant transfer (see discussion above).

3.3.2 Thermodynamics and kinetics of water-gas shift reaction. The water-gas shift reaction ($\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2$) is governed by an equilibrium K of 0.88 at 850°C, 1.25 at 750°C, and 1.9 at 650°C[72]. During calcium catalyzed gasification, the CO released by C(O) oxidation will react with steam to form more CO_2 . This encourages the calcium catalyzed gasification reaction to progress yet further in the forward direction. Since the equilibrium K values are moderately high, much CO_2 could be created by this reaction. However, CO oxidation proceeds relatively slowly[62,63,64,72,73]. Therefore, one cannot assume that the water-gas shift reaction always reaches equilibrium within the fluidized bed environment. Recognition of these facts has prompted the authors to consider the water-gas shift reaction as a rate limiting step under some circumstances.

3.4 Effects of catalyst surface area and dispersion on reaction rate

The surface area and dispersion of calcium have been identified as the proper methods of characterizing the reactivity of a calcium loaded char, rather than mere calcium weight percentage. Dispersion has been defined by Radovic *et al.* [41] as the percentage of CaO that is exposed, relative to the total CaO loading. Cazorla-Amoros *et al.* [13] further suggested that only the calcium at the calcium-carbon interface is catalytically active; the rest of the CaO surface serves merely as an avenue for CO_2 transfer to this interface. This concept is important when considering the significance of CO_2 sintering vs steam dispersion of CaO particles.

3.5 Reaction vs diffusion limitations

In principle, either the rate of oxidation or the rate of diffusion could limit the overall gasification rate, and careful analysis is required to determine which mechanism is most likely to be limiting. Several modes

of diffusion occur within an activated carbon grain, including (a) bulk and film diffusion of oxidant gas to the external surface of the GAC grain; (b) molecular diffusion of oxidant gas through the GAC's larger macropores; (c) Knudsen diffusion of oxidant gas through the GAC's smaller macropores, mesopores, and large micropores; and (d) restricted diffusion of oxidant gas through the small GAC micropores (when applicable)[53,54,55,60].

3.5.1 Test for diffusion limitations. A test for diffusion limitation during reactions within porous materials can be conducted by using the Thiele modulus, which compares the reaction rate to the diffusion rate. The Thiele modulus for a spherical pellet, as adapted from Smith[55] and Hurt *et al.* [53] is given by:

$$\phi = \left(\frac{1}{3}\right)(r^2 k_v / D_e \theta)^{1/2},$$

where r is the characteristic radius, D_e is the effective diffusivity, r^2/D_e is the characteristic time, k_v is the intrinsic rate constant, and θ is the porosity. The intrinsic rate constant is given by:

$$1/k_v = [C_r MW_c / n \rho_p] \Gamma,$$

where C_r is the concentration of the reaction gas, MW_c is the molecular weight of carbon, n is the number of moles of reacting gas consumed per mole of carbon gasified, ρ_p is the particle density, and Γ is the reciprocal of the intrinsic reaction rate with units of g/(sec g). When ϕ is less than 0.33, the intrinsic reaction rate can be approximated by the observed reaction rate, as determined from regeneration experiments. When ϕ is greater than 0.33, iteration is necessary to determine the intrinsic reaction rate.

From the Thiele modulus, the effectiveness factor, η , can be calculated as [55]:

$$\eta = \left((1/\tanh 3\phi) - \left(\frac{1}{3\phi} \right) \right) / \phi.$$

This factor represents the ratio of:

$$\eta = \frac{\text{actual rate for the whole GAC grain}}{\text{rate evaluated at outer surface conditions}}.$$

A ratio of $\eta = 1.0$ would indicate that there is no diffusion limitation and that the reaction would proceed uniformly throughout the aggregate. A ratio approaching zero would indicate severe diffusion limitation, resulting in reaction on the exterior of the aggregate only. A ratio in the 0.4 to 0.7 range would indicate some diffusion limitations, manifest by a measurable decline in the apparent activation energy, as compared to that which would be observed without diffusion limitations[53,55].

3.5.2 Possible effect of diffusion limitations on apparent activation energy. Van Heek and Muhlen[74] observed a shift in activation energy from the range of 200 to 250 kJ/mol, down to the range of

90 to 110 kJ/mol as temperatures increased above 780°C to 920°C for H₂O gasification of an anthracite and metallurgical coke. They attributed this change to a transition into the diffusion limiting zone.

However, Ergun and Mentser[73] suggested that any such change in activation energy would be caused by changes occurring among the rates of competitive chemical reactions, or changes in the structure of the solid. Moreover, Ergun[75] calculated diffusion rates to be two or three orders of magnitude higher than (uncatalyzed) gasification rates of coke by steam at 1200°C. We agree that based on fundamental principles, this change in slope would not likely be related to diffusion limitations, and propose another explanation, in the Results section below.

Pore diffusion limitations have been inferred by Walker *et al.* [76] as a cause for variations in a char's surface area development, although the findings of Rodriguez-Reinoso[44] would appear to contradict this diffusion-limitation premise.

As shown by this discussion, there appears to be no simple consensus in the literature on whether pore diffusion is limiting during typical regeneration conditions. A practical concern herein has been that if pore diffusion were to limit the overall rate, most gasification would likely occur in the outer pores of the spent GAC, causing a nonuniformly regenerated and inferior product. This issue is discussed further in the Results section below.

4. MATERIALS AND METHODS

Materials and Methods were as described previously[1,6,7,8,77]. In overview, an extensive study was performed with a field-spent GAC from the American Water Works Service Company plant at Hays Mine (Pittsburgh, PA)[78,79]. This activated carbon, subsequently identified as "spent GAC," contained 1.8% calcium and 9.9% ash. Hays Mine employed Filtrasorb 200 GAC, a bituminous-based GAC manufactured by Calgon Carbon Corporation (Pittsburgh, PA). At Hays Mine, GAC is used in filter adsorbers, which follow a treatment train that uses potassium permanganate, ferric chloride, lime, and cationic polymer.

Several experiments were also conducted with a Filtrasorb 400 spent GAC from Norristown, PA, which has been described previously[1,6,8]. For the experiments described herein, this spent GAC was washed in 1 M HCl to remove most of its available metals[6], and then loaded in water with varying amounts of calcium plus ethylene diamine tetraacetic acid (EDTA).

4.1 Fluidized bed furnace

Thermal regenerations were performed in a bench-scale, batch-type fluidized bed furnace, as described by Waer *et al.* [78] and Cannon *et al.* [6]. Unless otherwise noted, 10-gram GAC samples were subjected to a 10-minute pyrolysis step in an inert N₂ atmosphere. This was followed by oxidation in steam,

CO₂, or steam plus CO₂. "Moderate" flowrates included 8 g H₂O/g GAC-hr (1.74 L/min steam at STP), 11 g CO₂/g GAC-hr (0.8 L/min CO₂ at STP), and 30 g N₂/g GAC-hr. "High" flowrates were comprised of 50 g H₂O/g GAC-hr, 40 g CO₂/g GAC-hr, and 15 to 30 g N₂/g GAC-hr. Most regenerations were performed in duplicate, and some were performed in triplicate.

4.2 Thermogravimetric analyses

Thermogravimetric analyses were performed on a Perkin-Elmer PC Series TGA7 (Norwalk, CT) interfaced to an IBM PS/2 Model 50 PC[6,7].

4.3 Reactivity

The observed reaction rate during oxidation, also defined as the reactivity, has been defined as:

$$r = \frac{ML_r - ML_p}{100 - \left(\frac{ML_r - ML_p}{2} \right) - ML_p} \times \frac{1}{1 - A} \times \frac{60}{t},$$

where

ML_r = % mass loss during regeneration (pyrolysis plus oxidation);

ML_p = % mass loss during pyrolysis at same temperature;

A = ash fraction within GAC sample;

t = time, minutes; and

r = reactivity (average), g gasified/g solid C-hr.

The experimental error inherent in reactivity measurements was compounded by the repetitive experimental errors inherent in each mass loss measurement, plus the true differences between one GAC sample and the next. Reactivities for duplicate regenerations were generally within 20 to 30% of each other. Under some oxidation conditions, average reactivity declined as gasification progressed (see discussion below).

5. RESULTS AND DISCUSSION

Calcium catalyzed gasification rate was monitored for an array of oxidants (CO₂, steam, or steam plus CO₂), oxidation temperatures (650–950°C), oxidant flow rate, and oxidation times. The results have then been interpreted in accordance with the numerous steps that proceed in the catalyst mechanism, described above. Specifically, these studies revealed what circumstances resulted in limitations by:

- the C(O) gasification rate: $R-C(O) \leftrightarrow CO_{(g)} + R-C_f$,
- the gas-phase water-gas shift reaction: $H_2O + CO \leftrightarrow H_2 + CO_2$, and
- diffusion into the GAC grains.

These experiments also revealed what conditions caused an increased number of active carbon sites that

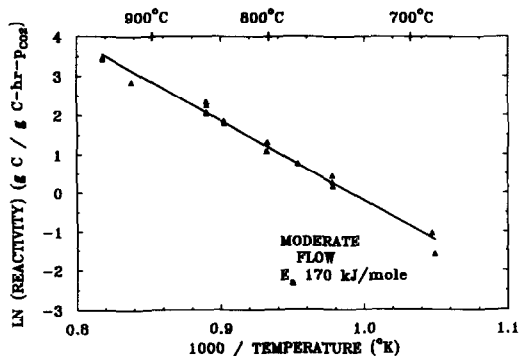


Fig. 2. Arrhenius plot for spent Hays Mine GAC in moderate flows of carbon dioxide; fluidized bed.

effectively participated in transferring oxidant. The nature of these limitations and conditions influenced the GAC pore structure that resulted from regeneration.

5.1 Effect of temperature on reactivity

5.1.1 Influence of oxidant gas. The effect of temperature on reactivity was compared when steam, CO₂, or steam plus CO₂ were used as the oxidants in the fluidized bed furnace (Figs. 2 through 7). Both moderate and high oxidant flow rates were employed. Arrhenius plots of these data suggested that a different mechanism limited overall reaction rate when CO₂ was employed alone than when steam or steam plus CO₂ were employed.

When CO₂ served as the sole oxidant, the C(O) gasification step appeared to limit the overall rate. The slope of these Arrhenius plots depicted activation energies of 170 and 200 kJ/mole (Figs. 2 and 3). These are within the range of activation energies that have been observed by Radovic *et al.* [43], McKee [36], and Lizzio *et al.* [31] for the reaction rate limitation by C(O) gasification.

However, when steam plus CO₂ were combined as oxidants, the Arrhenius plots exhibited two slopes, with the steeper slope occurring in the lower temperature ranges, corresponding to 200 to 220 kJ/mole; and a more gradual slope occurring in the upper tem-

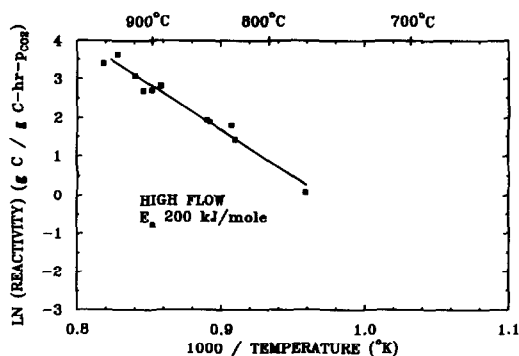


Fig. 3. Arrhenius plot for spent Hays Mine GAC in high flows of carbon dioxide; fluidized bed.

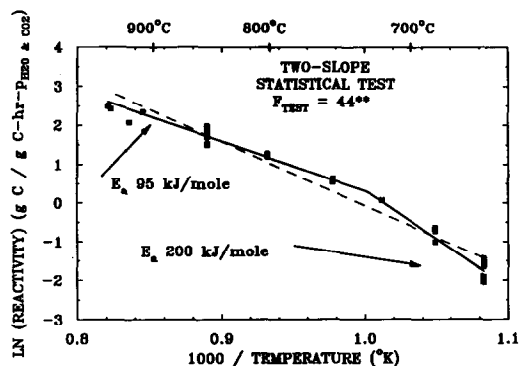


Fig. 4. Arrhenius plot for spent Hays Mine GAC in moderate flows of steam and carbon dioxide; fluidized bed.

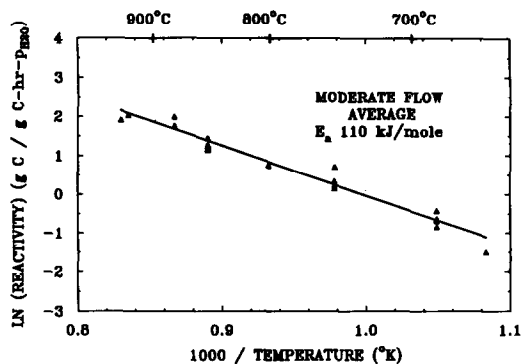


Fig. 6. Arrhenius plot for spent Hays Mine GAC in moderate flows of steam; fluidized bed.

perature ranges, corresponding to 95 to 110 kJ/mole. The higher slopes conformed to activation energies for C(O) gasification limitation, whereas the lower slopes approximated the activation energy for the gas-phase water-gas shift reaction of 90 kJ/mole[57].

The distinction between these two discrete slopes was statistically significant, both at moderate and high oxidant flow rates. This was determined by employing a statistical *F*-test method[80] for discerning whether the data could best be characterized by two slopes rather than one. Since the experimental *F*-test values of 44 and 130 were greater than the tabulated *F*-critical value of 14, the two-slope hypothesis was accepted. Statistically, the probability of being incorrect in accepting the two-slope hypothesis was less than 0.1%[81]. This level of statistical significance is denoted conventionally with a double asterisk, as in Figs. 4 and 5. This analysis implicated the C(O) gasification step as rate limiting in the lower temperature range, and the gas-phase water-gas shift reaction as rate limiting in the upper temperature range.

Likewise, when steam was used alone, the Arrhenius plot reflected a lower average activation energy of 110 kJ/mole for the moderate flow, and an average of 140 kJ/mole for the high flow (Figs. 6 and 7). The former approximated the activation energy of 90

kJ/mole for the gas-phase water-gas shift reaction. Moreover, the plot for high steam flow appeared to qualitatively exhibit some curvature, with slopes closer to 110 kJ/mole depicting the upper temperature range, and slopes closer to 170 kJ/mole depicting the lower temperature range. These slopes, if truly representative, could correspond to limitations by the water-gas shift and C(O) gasification reactions, respectively.

Diffusion limitations were ruled out as an explanation for these changes in slope, as discussed below. Moreover, chemisorption limitations could not have explained these effects in the steam or steam plus CO₂ experiments because this two-slope phenomenon did not appear when CO₂ alone was employed (Fig. 2). Any such potential chemisorption limitations would have had to be manifest under all three oxidation conditions if chemisorption had indeed limited overall rate.

5.1.2 Influence of calcium catalyst. The influence of calcium on activation energy was isolated by measuring CO₂ Arrhenius plots for (a) spent Hays Mine GAC that was pyrolyzed at the same temperature as it was oxidized, and (b) acid-washed spent Hays Mine GAC that was pyrolyzed at the same temperature as it was oxidized (Fig. 8). These measurements employed a thermogravimetric analyzer (TGA). The acid washing removed most of the calcium from

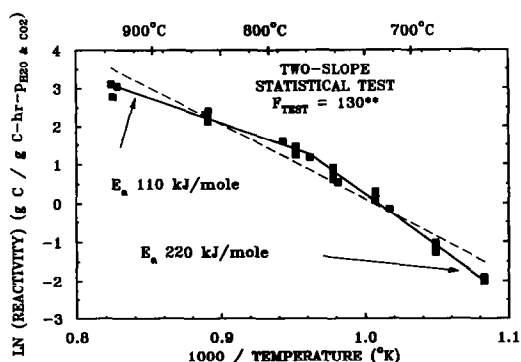


Fig. 5. Arrhenius plot for spent Hays Mine GAC in high flows of steam and carbon dioxide; fluidized bed.

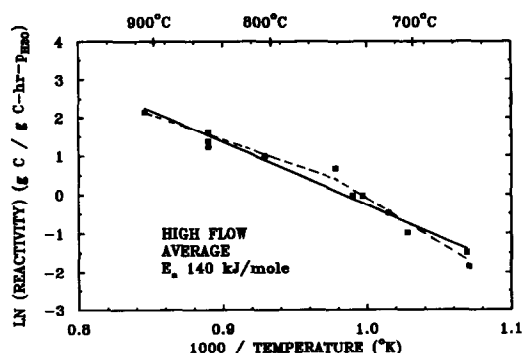


Fig. 7. Arrhenius plot for spent Hays Mine GAC in high flows of steam; fluidized bed.

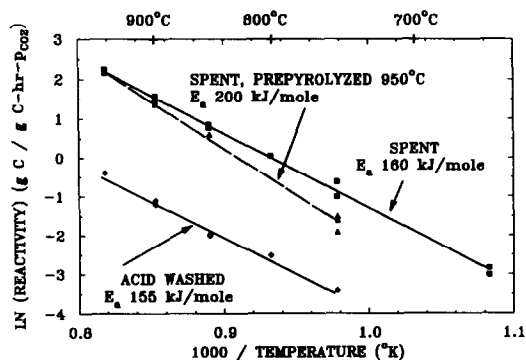


Fig. 8. Arrhenius plots for Hays Mine GAC oxidized with CO_2 in TGA.

the GAC. Although the spent GAC, which contained 1.8% calcium, was 15 times more reactive than the acid-washed GAC, they both exhibited a similar activation energy of 155 to 160 kJ/mole. This indicated that the same reaction step limited the uncatalyzed reaction as limited the catalyzed reaction. The reaction step common to both these mechanisms is the $\text{C}(\text{O})$ gasification step, and thus, this step is the most probable rate limiting step when CO_2 is used as the oxidant[36].

The catalytic role of calcium was to broaden the extent of oxidant transfer to the carbon surface (i.e., to increase the number of effectively active sites on the carbon surface). However, calcium did not change the activation energy of the rate limiting $\text{C}(\text{O})$ gasification step. This interpretation has previously been proposed by several other researchers (see discussion above), and is consistent with the results herein for CO_2 as the oxidant.

5.1.3 Influence of high-temperature pre-pyrolysis. TGA experiments also compared the above oxidation rates to those of a spent GAC that had been pre-pyrolyzed at 950°C before it was oxidized with CO_2 at various temperatures. The 950°C pre-pyrolyzed samples exhibited an activation energy of 200 kJ/mole (Fig. 8). Moreover, at a 750°C oxidation temperature, the GAC that had been pre-pyrolyzed at 950°C displayed half as rapid a reactivity as its counterpart that was pre-pyrolyzed at 750°C. The decreased reactivity caused by 950°C pretreatment can be attributed either to CaO sintering, carbon graphitization, or both.

5.2 Effect of flow rate on reactivity

The influence of flow rate on reactivity was monitored during 850°C oxidations of spent Hays Mine GAC. These experiments employed CO_2 , steam, and steam plus CO_2 in the fluidized bed regeneration furnace (Figs. 9 and 10). Oxidant efficiency was also computed from these data, as shown in Figs. 11, 12, and 13.

5.2.1 Influence of CO_2 flowrate. Over the lower range of CO_2 flow rates (Fig. 10), reactivity increased linearly with increasing CO_2 flow, in a manner characteristic of first-order reaction kinetics.

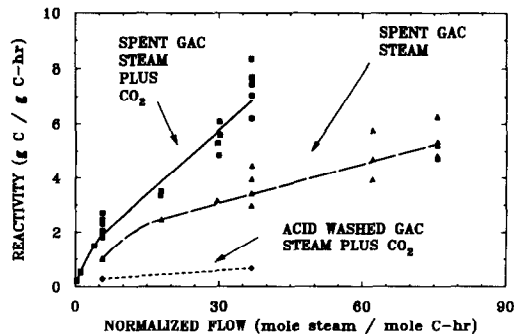


Fig. 9. Reaction rate vs inlet gas flow rate for spent and acid washed Hays Mine GAC, oxidized at 850°C in steam alone, and steam plus CO_2 combined.

However, when flow rates exceeded 11 to 15 moles CO_2 /mole C-hr, reactivity plateaued at 4 gC/g C-hr and manifested zero order reaction kinetics above that flow rate. This behavior appeared to conform to the Langmuir-Hinshelwood model[73,82,83], which is abbreviated as:

$$r = \frac{k_1 C_t P_{\text{CO}_2}}{1 + \frac{k_2}{k_3} P_{\text{CO}} + \frac{k_1}{k_3} P_{\text{CO}_2}}$$

where C_t is the total number of active carbon sites, including both sites that are free (unoccupied) and sites that are occupied by oxygen. The constant k_3 is the rate constant for the $\text{C}(\text{O})$ gasification step. The rate constants k_1 and k_2 characterize the rates of surface oxide formation from CO_2 and the reverse reaction, respectively.

The Langmuir-Hinshelwood model predicts that within the low range of CO_2 partial pressures, an increase in CO_2 partial pressure will cause increasing reactivity that conforms to a simplified first order expression:

$$r = k' C_t P_{\text{CO}_2},$$

where k' is a compilation of rate constants.

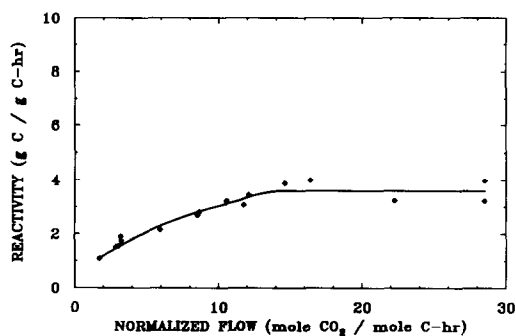


Fig. 10. Reaction rate vs inlet flow rate for spent Hays Mine GAC at 850°C in CO_2 .

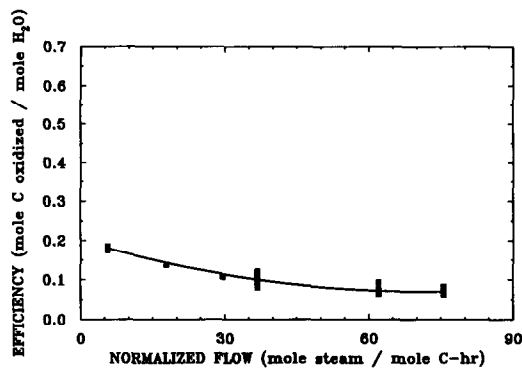


Fig. 11. Efficiency of oxidation with steam for spent Hays Mine GAC at 850°C.

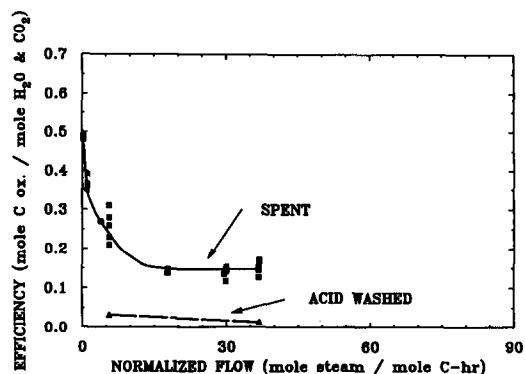


Fig. 13. Efficiency of oxidation with steam plus CO₂ for spent and acid washed Hays Mine GAC at 850°C.

As the flow rate of CO₂ increases beyond this low range, the CO₂ partial pressure will eventually greatly exceed that of product CO, and the reaction rate will reach a plateau and exhibit a zero order reaction rate with respect to CO₂. At this point, the Langmuir-Hinshelwood expression is simplified as:

$$r = k_3 C_t.$$

Mathematically speaking, the reaction rate could be increased further only by increasing the number of active carbon sites (C_t), or by increasing the gasification rate constant k_3 . However, k_3 is a function solely of temperature for a given carbon type and catalyst loading, and is unaltered by oxidant type or oxidant flow rate. Therefore, k_3 could not increase at constant temperature. Thus, according to the Langmuir-Hinshelwood model, the only way that the 850°C reaction rate could have exceeded 4 g C/g C-hr would be if the number of active carbon sites (C_t) increased.

5.2.2 Influence of steam. Reactivities did indeed exceed 4 g C/g C-hr when steam alone or when steam plus CO₂ served as the oxidants (Fig. 9). When steam alone was employed, reactivity reached 5.5 g C/g C-hr. Moreover, steam-induced reactivity never plateaued, even at 70 moles H₂O/mole C-hr. (There are eight data points at this highest steam flow.) This

was the maximum flow rate achievable for this fluidized bed equipment.

Similarly, when steam and CO₂ were combined, reactivity reached 7 to 8 g C/g C-hr at the flow limitations of the regeneration furnace, corresponding to 33 moles steam/mole C-hr plus 33 moles CO₂/mole C-hr (Fig. 9). This far exceeded the 4 gC/gC-hr reactivity achievable when only CO₂ was employed (Fig. 10), and could best be attributed to only one phenomenon: Steam must have increased the number of effectively active carbon sites (C_t) available for gasification, causing increased extent of oxidant transfer to the carbon surface.

This could have occurred either because (a) the steam caused the CaO to disperse and exhibit greater calcium oxide-carbon interface, or (b) because the steam facilitated more extensive surface diffusion of dissociated oxidant to sites that were more remote from the CaO, or (c) because the steam decreased the stability of the carbon matrix and made more sites susceptible to attack by oxidant. The first of these is the most likely mechanism, and would be consistent with the findings of Beruto *et al.* [71].

5.2.3 Oxidation efficiency. With CO₂ alone, oxidation efficiency was greatest at low flow rates, and dropped dramatically at progressively higher flow rates (Fig. 12). In contrast, when steam was employed either by itself or with CO₂, oxidation efficiency remained fairly constant above a threshold level (Figs. 11 and 13). This implied that when steam was employed, reactivity above this threshold was limited by steam flowrate (i.e., the water-gas shift reaction), and was not limited by the number of active carbon sites available. This in turn suggested that the water-gas shift reaction was limiting the production of CO₂ as the primary oxidant, and it was also limiting overall reaction rate.

The rate expression for the forward water-gas shift reaction would take the form:

$$r = k P_{H_2O} P_{CO}.$$

Increasing P_{H_2O} should be directly proportional to increasing water gas-shift reaction rate when P_{CO} re-

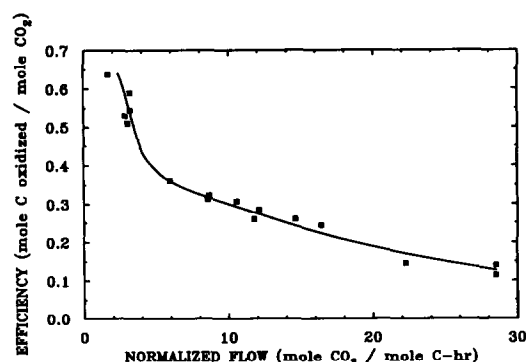


Fig. 12. Efficiency of oxidation with CO₂ for spent Hays Mine GAC at 850°C.

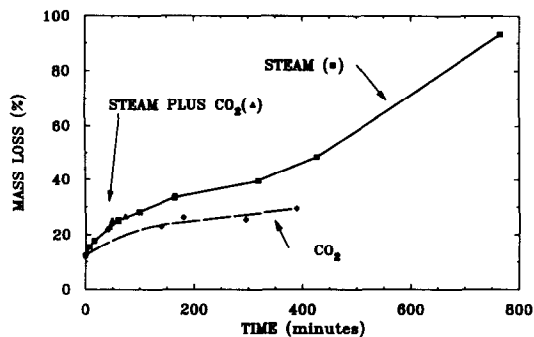


Fig. 14. Regeneration mass loss vs oxidation time for spent Hays Mine GAC at 680°C in moderate flows of oxidants shown.

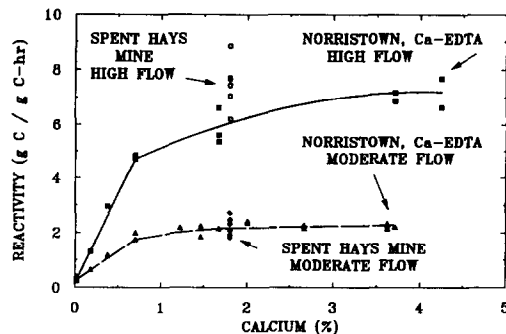


Fig. 16. Reactivity vs calcium content for acid-washed spent Norristown GAC loaded with calcium-EDTA; fluidized bed at 850°C, in steam and CO₂.

mains relatively constant. This would also be directly proportional to overall carbon gasification rate. Such a pattern matches the observed behavior in Figs. 9, 11, and 13.

It is noteworthy that at the lowest flow rates of CO₂ alone, or of steam and CO₂ combined, efficiency equalled 0.5 to 0.6 moles C gasified/mole of oxidant (Figs. 12 and 13). This meant that roughly half of all the steam and CO₂ that passed through the furnace became engaged in gasifying the solid carbon at the lowest flows. Such high efficiency would be favorable for full-scale regenerations.

5.3 Effect of oxidation extent on reactivity

Reactivity declined dramatically with extended oxidation time at 680°C (Fig. 14), whereas it declined only slightly at 850°C (Fig. 15). This behavior was observed for fluidized bed regenerations in steam, CO₂, and steam plus CO₂. Furthermore, reactivity became almost completely retarded with CO₂ alone at 680°C. The authors interpret these data to imply that at the higher temperatures, there were more surface carbon sites with which the CO₂ or steam could react. Also, at the lower temperature, CaCO₃ was a thermodynamically stable species[21] that was presumably not the catalytically active species[28]. Its bulk formation

with time probably exhausted the catalytically active CaO.

When steam was employed at 680°C, reactivity did not become completely retarded with prolonged oxidation. This distinction probably occurred because steam altered the surface of the CaO in a manner that maintained its ability to transfer oxidant. Perhaps steam somewhat thwarted the buildup of a CaCO₃ layer that would become impenetrable to oxidant transfer[21,28,71].

5.4 Effect of calcium content on reactivity

Calcium content strongly influenced the reaction rate, as shown in Figs. 16, 17, and 18. The experiments represented in these figures were conducted with a spent GAC from the Norristown, PA, water treatment plant. After this spent GAC had been washed in 1 M HCl, it was loaded with various amounts of calcium and EDTA. Corresponding data for the spent Hays Mine GAC have also been plotted on this graph.

5.4.1 High-temperature behavior, steam, and CO₂. When steam and CO₂ were employed at 850°C, plots of reactivity vs calcium content revealed two distinct regions of curvature (Fig. 16). Below 0.7% calcium, reaction rate increased linearly with increasing calcium content, in conformance to behav-

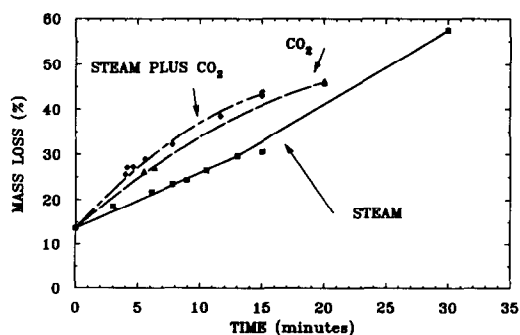


Fig. 15. Regeneration mass loss vs oxidation time for spent Hays Mine GAC at 850°C in moderate flows of oxidants shown.

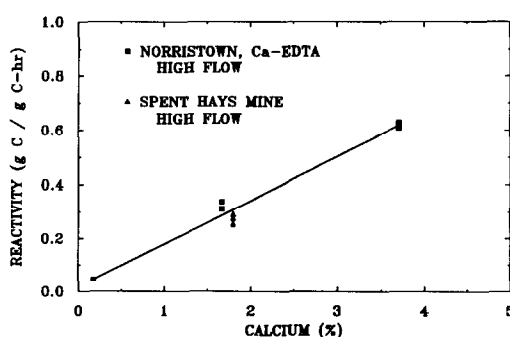


Fig. 17. Reactivity vs calcium content for acid-washed spent Norristown GAC loaded with calcium-EDTA; fluidized bed at 680°C, in steam and CO₂.

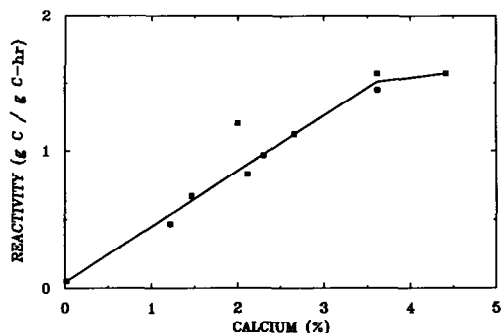


Fig. 18. Reactivity vs calcium content for acid-washed spent Norristown GAC loaded with calcium-EDTA; TGA at 850°C, in CO₂.

ior expected when C(O) gasification limited overall rate, and a higher calcium content resulted in a higher C_i value. Above 0.7 to 2% calcium, a plateau rate was reached, and further increases in calcium loading caused no further increase in oxidation rate. This behavior suggested that above the plateau, the gas-phase water-gas shift reaction limited overall rate, since such a reaction would be unaffected by calcium content.

This concept is pertinent to full-scale regeneration design; if several similar grade carbons with varying calcium content (above this plateau level) are pooled (combined) together, they could all be expected to manifest the same reactivity, so long as regeneration is operated in the water-gas shift limiting zone.

5.4.2 Absence of metal catalyzed water gas-shift. One of the potential roles of calcium identified above in the mechanism section was to catalyze the water-gas shift reaction. However, the flatness of the plateau above 0.7 to 2% calcium in Fig. 16 offered evidence that the metal-catalyzed water-gas shift reaction played a negligible role, compared to its gas-phase counterpart.

5.4.3 Low-temperature behavior, steam, and CO₂. The calcium-loaded Norristown GAC was also regenerated at 680°C in high flows of steam and CO₂ together (Fig. 17). Based on the Arrhenius plots in Figs. 4 and 5, one would have predicted that the C(O) gasification rate would have governed overall rate at this low temperature. Indeed, the linearly increasing rate with increasing calcium content (and consequent increase in both C_i and C(O) gasification rate) matched this expectation.

5.4.4 High-temperature behavior, CO₂. Reactivity in CO₂ alone at 850°C was monitored in TGA experiments, as shown in Fig. 18 (similar results were observed by Knappe *et al.* [7]). The C(O) gasification reaction limited the overall rate, as manifested by the increasing reactivity with increasing calcium content. Above 3.6% calcium, the curve appeared to reach a plateau level, suggesting that further CaO loading did not cause further increase in CaO surface area. Linares-Solano *et al.* [30] observed this same plateau at 3.5 to 4% calcium in TGA experiments, and

attributed it to a maximum achievable value for the CaO surface area.

5.5 Influence of oxidation mechanism on pore distributions

The above-described oxidation mechanisms shed light on the pore size distributions observed under various oxidation conditions by Cannon *et al.* [1]. These distributions revealed that at low temperature, steam plus CO₂ oxidation was active within pores smaller than 5 nm, and created more pores between 5 and 10 nm. In contrast, at high temperatures, steam plus CO₂ uniformly widened all pore sizes in the micropore and mesopore range. Similarly, when steam or CO₂ was used individually at any temperature, the pore development was the same as for steam and CO₂ at high temperatures.

These results could be explained by the above proposed mechanism as follows:

1. When steam plus CO₂ was used in 650°C to 750°C, the steam activated or dispersed the CaO* surface and catalyzed its ability to transfer CO₂ to the carbon surface. When there was ample CO₂ available, all C-CaO interfaces were involved in oxidant transfer, but the C-CaO interface activated by H₂O would have transferred oxidant most rapidly. The result was a focused attack at the C-CaO interface that had been influenced by H₂O, resulting in focused conversion of pores <5 nm into pores between 5 and 10 nm.

2. At high temperatures (>800°C), the primary oxidant was the CO₂. Whether steam, CO₂, or steam plus CO₂ was introduced, the pore development resulted from catalyzed CaO-CO₂ interactions, and was characterized by unfocused pore widening throughout the micropore and mesopore range. The influence of steam in catalytically focusing attack became less pronounced as temperature increased and Ca(OH)₂ became more scarce because of its conversion to CaO.

3. When steam alone was introduced at 650 to 750°C, a synergistic interaction at the CaO surface would not have been specifically focused within the <5 nm pore range for two reasons: (a) It took longer to oxidize CO than it did to transfer CO₂ across CaO to the carbon surface [14,72,73]. (b) CaCO₃ was a stable species at these temperatures. This implied that the entire CaO surface would have been "starved" for CO₂, and therefore, the whole CaO surface would readily adsorb CO₂. As soon as CO₂ was formed from H₂O and CO, the CO₂ would have immediately adsorbed to the closest CaO surface. Proximity would have prevailed over efficiency of transfer under these conditions that employed steam alone.

5.6 Test for diffusion limitations

Before one can isolate which chemical reaction steps are rate limiting, one must consider whether mere diffusion causes any limitations. Several types of diffusion occur within a GAC particle during thermal regeneration, as repeated from above:

1. bulk and film diffusion to the external surface of the GAC grain,
2. molecular diffusion through the GAC grain's larger macropores,
3. Knudsen diffusion through the GAC grain's smaller macropores, mesopores, and large micropores,
4. restricted diffusion through carbon's smaller micropores (this step is sometimes precluded), and
5. restricted or solid phase diffusion through the CaO lattice.

Bulk and film diffusion limitations would not be observed for steam and CO₂ oxidation unless the reaction temperatures were far greater than those employed herein[60,73]. Furthermore, the analysis herein of the Thiele modulus (ϕ) and effectiveness factor (η) revealed that Knudsen diffusion never limited the reaction rate, and molecular diffusion only slightly limited overall rate at the highest temperatures. Restricted diffusion limitations, at the other extreme, were so severely limiting that oxidant did not penetrate into the smallest micropores.

The Thiele modulus (ϕ), as discussed above, compares the reaction rate to the diffusion rate. The effectiveness factor (η) represents the ratio of the actual rate for the whole GAC grain, as compared to the rate evaluated at outer surface conditions.

The most critical step in calculating the Thiele modulus and effectiveness factor is to properly characterize the appropriate radius (r), effective diffusivity (D_e), and characteristic time (r^2/D_e). These values differ for each type of diffusion (Table 1), and have been evaluated as follows (see sample calculations by Cannon[8]).

5.6.1 Types of diffusion. Diffusion theory indicates that at atmospheric pressure, molecular diffusion predominates in pores greater than 500 nm width, and Knudsen diffusion predominates in pores between 1 $\pm$ and 500 nm[55]. Moreover, restricted (or activated) diffusion predominates in pores smaller than 0.5 to 1 nm in width[53,60]. Molecular diffusion is relatively fast, Knudsen diffusion is slightly slower, and restricted diffusion is very slow.

5.6.2 Characteristic aggregate radius. The appropriate characteristic radius varies for each type of diffusion. This is recognized when one conceptually views the GAC grain as comprised of thousands of primary aggregates. Each of these primary aggregates is in turn comprised of thousands of amorphous graphitic crystallites (secondary aggregates). Diffusion within a GAC grain occurs in three steps. First, molecular diffusion transfers oxidant through the GAC grain to the periphery of the primary aggregates. Next, Knudsen diffusion transfers oxidant through the primary aggregates to the periphery of the graphitic crystallites. Finally, activated, or restricted diffusion (when involved) transfers oxidant through the graphitic crystallites to the site of the oxidation reaction. In cases where restricted diffusion is much slower than reactivity, the oxidant would not penetrate the graphitic crystallites, and most oxidation would occur outside of the graphitic crystallites.

For molecular diffusion through large pores, the appropriate radius to be used in the Thiele modulus calculations is that of the GAC grain itself. The average GAC grain radius in the present study was 500 microns.

For Knudsen diffusion into primary aggregates, the authors used a characteristic aggregate radius of 5 to 10 microns. This characteristic radius was determined by measuring the surface area exposed to pores with widths greater than 500 nm and comparing them to the corresponding GAC volume that these large pores surrounded. The volume equalled that of solid carbon plus voids smaller than 500 nm in width. This surface area and volume were determined from mercury porosimetry, and confirmed qualitatively by electron micrographs.

For restricted diffusion, a characteristic radius could not be independently discerned. Rather, a characteristic time was measured, from which an approximate characteristic radius could be inferred.

5.6.3 Effective diffusivity. The molecular and Knudsen diffusion coefficients were determined from the standard constants and formulas described in Smith[55]. A tortuosity factor of 2 was used for molecular diffusion[10], and a tortuosity factor of 10 was

Table 1. Characterization of diffusion in spent Hays Mine GAC

Predominate diffusion type	Molecular (within pores)	Knudsen	Restricted (activated)
Pore width (nm)	$w > 500$	$1 \pm < w < 500$	$w < 0.5$ to 1.0
Diffusion coefficient at 700°C to 850°C (cm ² /sec)	1 to 2	2×10^{-3} to 4×10^{-3}	10^{-10} to 10^{-14}
Characteristic aggregate radius (microns)	500	5 to 10	0.02 to 0.2
Characteristic time (r^2/D_e) (seconds)	70×10^{-4}	2×10^{-4}	30 to 50 ^b
ϕ Thiele modulus ^a	0.35	0.01	40
η Effectiveness factor ^a	0.94	1.0	nil

^aThiele modulus and effectiveness factor calculated for moderate flow conditions of steam plus CO₂ at 850°C, or for high flow conditions at 750°C.

^bSome authors would interpret these characteristic times as reflecting chemisorption behavior (see discussion in text).

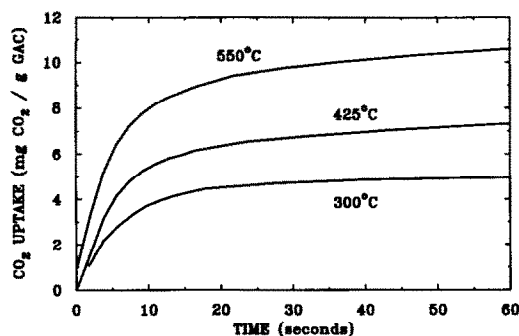


Fig. 19. Rate of CO_2 uptake onto spent Hays Mine GAC, pre-pyrolyzed at 830°C , then exposed to CO_2 at temperature shown.

used for Knudsen diffusion. For restricted diffusion, diffusivity could not be directly measured; rather, the characteristic time (r^2/D_e) was measured, and an approximate diffusion rate was inferred from this.

5.6.4 Characteristic time. Characteristic times (r^2/D_e) for molecular and Knudsen diffusion were computed by employing the independently determined aggregate radii and effective diffusion coefficients described above.

For restricted diffusion, in contrast, characteristic time (r^2/D_e) was determined from CO_2 adsorption data (Figs. 19 and 20), using plots of $dM/dt^{1/2}$ vs $t^{1/2}$, in accordance with the method of Walker[60] and Hurt[53]. In these plots, M was the mass, t was the time, and d was the derivative. Characteristic times ranged from 30 to 50 seconds. In this part of the experiment, spent Hays Mine GAC samples were pre-pyrolyzed in the TGA in 830°C . Then CO_2 uptake kinetics were monitored gravimetrically during exposure of the GAC to 300 mL/minute CO_2 at temperatures ranging from 200°C to 650°C (see representative data in Fig. 19). The first 10 to 20 seconds of uptake data were used to measure characteristic time.

CO_2 uptake data and characteristic times were monitored at 200°C to 650°C , because at these low temperatures, the GAC gasification rate was very slow, and did not confound the interpretation of the

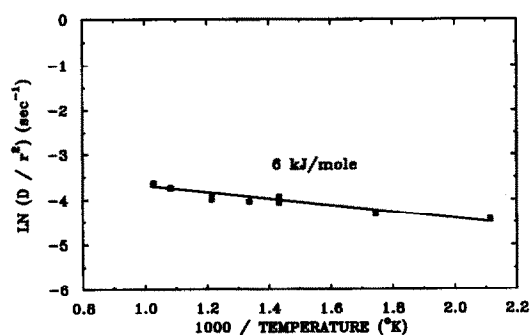


Fig. 20. Arrhenius plot of characteristic time (D/r^2) for CO_2 uptake into spent Hays Mine GAC pre-pyrolyzed at 830°C .

results. Characteristic times were then extrapolated to the 750°C to 850°C range via an Arrhenius plot (Fig. 20). The activation energy for restricted diffusion was found to be 6 kJ/mole, a value consistent with the 8 kJ/mole found by Walker *et al.*[60].

CO_2 uptake data similar to that shown in Figs. 19 and 20 has been interpreted by Walker *et al.*[60] and Hurt *et al.*[53] to depict restricted diffusion, but they have been interpreted by Mickelson and Rostam-Abadi[84], Cazorla-Amoros *et al.*[16], and Floess *et al.*[85] to depict the rate of chemisorption. Moreover, Hayward and Trapnell[86] have invoked both models, citing a temperature dependence for determining which governs.

To shed light on this, the GAC samples were pre-ashed, in several experiments. This effectively gasified all of the carbon that the CO_2 could have otherwise diffused through. Even in these cases, the authors found CO_2 uptake rates similar to those shown in Fig. 19. But this did not distinguish whether restricted diffusion into the ash or chemisorption onto the ash was limiting. Chemisorption activation energies are often considerably larger than 6 kJ/mole[87].

Regardless of whether restricted diffusion or chemisorption was reflected by these measurements, the experiments manifested an effective activation energy of 6 kJ/mole. This value was far below the 95 to 200 kJ/mole measured for the rate-limiting step in GAC oxidation (Figs. 2–8). Thus, neither restricted diffusion nor chemisorption characterized the rate-limiting step in GAC oxidation.

5.6.5 Computed effectiveness factors. On the basis of the above measurements of radius and effective diffusivity, the Thiele modulus and effectiveness factors were computed for molecular, Knudsen, and restricted diffusion, as listed in Table 1. As can be seen, Knudsen diffusion would never have limited gasification rate, since the effectiveness factors closely approached 1.0 (see discussion above). Likewise, molecular diffusion would not have measurably limited the overall rate at moderate oxidant flow rates. Even at the highest reactivities of 17 g C/g C-hr at the highest temperatures and oxidant flow rates (Fig. 5), the effectiveness factor was conservatively estimated to be 0.7, and the molecular diffusion could have limited overall rate by only about 20%[8].

Any such minor limitations would not have noticeably influenced the Arrhenius plots in Figs. 2 through 8. Specifically, this slight limitation could not account for the decline in steam plus CO_2 reactivity at high temperatures, relative to CO_2 reactivity at the same high temperatures (Figs. 2 through 8) because (a) the five-fold declines were of greater magnitude than the 30% reduction that could be attributed to diffusion, and (b) if diffusion limitations had occurred, they would have been equally manifest for all oxidant conditions, whereas changes in slope did not appear for the CO_2 Arrhenius plots.

At the other extreme, the effectiveness factors computed for restricted diffusion approached zero (if truly a manifestation of restricted diffusion). These values

suggested that the reaction rate was so much faster than the restricted diffusion rate that almost no gasification would have occurred within amorphous graphitic crystallites (secondary aggregates) during gasification (i.e., within pores smaller than 0.5 to 1.0 nm width). This was perhaps with the exception of the very lowest temperatures and reactivities.

6. SUMMARY AND CONCLUSIONS

6.1 Influence of temperature on pore structure

In summary, a spent GAC from the Hays Mine water treatment plant of Pittsburgh, PA, was regenerated to a consistent apparent density of 0.43 g/mL under a range of regeneration conditions[1]. By regenerating to a consistent AD, the relative regions within the pore structure that were most gasified by various oxidation conditions could be quantitatively compared. For all conditions, GACs that contained calcium showed decreased micropore volumes, decreased surface areas, and increased mesopore volumes, as compared to their pyrolyzed counterparts.

Moreover, all but one gasification condition resulted in the same pore development behavior, which was characterized by pores widened throughout the micropore and mesopore range. The exception occurred when both steam and CO₂ were used at temperatures below 750°C. These oxidations caused even lower total surface areas, higher mesopore surface area, lower micropore volumes, higher 2 to 10 nm pore volumes. They also resulted in 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 to 10 nm range. They caused a negligible increase in pores greater than 10 nm. The <5 nm pores are probably the most important for most water treatment applications. Therefore, the authors recommended 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.

6.2 Calcium catalysis mechanism

In order to provide a fundamental basis for these pore structure observations, the authors have proposed a calcium-catalyzed oxidation mechanism that involves diffusion, chemisorption, oxidant transformation, and C(O) gasification. Of these steps, the C(O) gasification step generally limited overall rate. However, at high temperatures when steam alone or steam plus CO₂ were employed, the water-gas shift reaction limited overall rate. The authors observed no evidence of significant diffusion or chemisorption rate limitations under any regeneration conditions.

The authors propose that steam played four roles:

1. It combined with product CO to form CO₂ via the water-gas shift reaction. This CO₂ in turn acted as the primary oxidant via a CaO-CaCO₃ cycle.

2. Steam acted as a secondary oxidant with Ca(OH)₂ as an intermediary species. This occurred more at low temperatures than at high temperatures.
3. Steam allowed more extensive CO₂ transfer across the CaO to the carbon surface. That is, steam dramatically increased the quantity of active carbon sites available to the CaO interface.
4. The water-gas shift reaction could also have been catalyzed at the surface of the CaO; however, for thermodynamic reasons, this was not extensive.

6.3 Influence of rate limiting step on pore development

When both steam and CO₂ were combined, the manner of pore development was influenced by which reaction step was rate limiting. At higher temperatures (>800°C±), the water-gas shift reaction limited overall rate, and pore development was characterized by nonfocused gasification dispersed throughout all pore size ranges.

In contrast, when lower temperatures (<700°C to 750°C) were employed with both steam and CO₂, the C(O) gasification step limited overall rate, and pore development was characterized by a focused attack on the pores smaller than 5 nm, which created more pore development in the 5 to 10 nm range. With both oxidants combined at low temperatures, a synergistic behavior apparently developed between the steam, CO₂, CaO, and carbon, which caused most efficient development of active carbon sites within the pores smaller than 5 nm.

6.4 Overview

In overview, a calcium-loaded, coal-based GAC requires a different and more controlled regeneration strategy than does a GAC that contains little calcium. However, with proper precautions, the presence of calcium need not be adverse. Indeed, the calcium can be employed advantageously. The calcium will cause the oxidation step to proceed an order of magnitude more rapidly than for uncatalyzed oxidation, and it will allow a target apparent density to be achieved with far less time, steam, and energy. However, this calcium also widens pores, and in overall balance, spent GACs with low calcium and ash buildup are favored over spent GACs with high calcium buildup. In-plant lime treatment modifications may help control calcium buildup. However, the authors do not recommend that regenerators expend the effort to wash their spent GACs in acid before regenerating them.

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