

THE ROLE OF CALCIUM IN AND METHODOLOGIES FOR OVERCOMING pH
EXCURSIONS FOR REACTIVATED GRANULAR ACTIVATED CARBON

By

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This document is dedicated to my mother and sister

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THE ROLE OF CALCIUM IN AND METHODOLOGIES FOR OVERCOMING pH
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Water contact pH experiments employing several reactivated granular activated carbons (GAC) showed that reactivated carbons exhibit pH excursions (i.e., pH > 8.5) when wetted. Moreover, when the water contact pH was predicted based on the log of the quantity of calcium that leached out of the GAC during the pH experiments, good agreement was obtained with the measured water contact pH of reactivated GACs that contained a range of calcium content, typically 0 to 1% wt. Ca. Treatments employing air exposure at 400°C for 1 hour and carbon dioxide exposure at ambient temperature for 20 minutes were found to create pH stable carbons (i.e., water contact pH < 8.5). An evaluation of total surface acidity suggested that the pH excursion was balanced by the acidic oxygen-containing functional groups created on the surface of the air treated reactivated GAC. Physisorption of carbon dioxide and subsequent desorption forming

carbonic acid upon water immersion was proposed as the means behind balancing pH excursions with the carbon dioxide treated reactivated GAC.

In a comparison of adsorption performance with 2-methylisoborneol (MIB), a taste and odor causing compound often found in surface water, in deionized water the untreated reactivated GAC removed more MIB than the air treated reactivated GAC. It is proposed that the increase in surface acidity with the air treated reactivated GAC created preferential adsorption of water onto the GAC surface over MIB adsorption. In adsorption experiments with MIB in water containing natural organic matter (NOM), a ubiquitous surface water component shown to compete with MIB for adsorption sites, the air treated reactivated GAC removed more MIB than did an untreated reactivated GAC. The proposed explanation for this is that the negatively charged NOM is attracted to the positively charged surface of the untreated carbon via electrostatic forces, thus out-competing MIB for adsorption sites. In both deionized water and water containing NOM, the carbon dioxide treated reactivated GAC removed the most MIB, though the mechanism behind this is unclear and warrants further research. Regardless of the mechanism, the results show that treatments to create pH stable carbons will change the carbon's adsorption capabilities and, thus, use of these treatments should be based on more than their ability to create pH stable carbons.

CHAPTER 1 INTRODUCTION/LITERATURE REVIEW

1.1 Activated Carbon

Activated carbon is created when a carbonaceous precursor, generally wood, peat, lignite-coal, bituminous-coal, or other material possessing relatively high carbon content, undergoes a thermal process involving pyrolysis and oxidation to increase the surface area and develop a range of pore sizes within the precursor. Pyrolysis is carried out in an inert environment, or oxygen starved, to ensure that the raw material does not gasify but rather is transformed into char. The oxidation process, or simply activation, is performed in the presence of an oxidizing gas, such as air, steam, carbon dioxide (CO₂), or a combination of these, at temperatures between 800-900°C in order to oxidize the surface of the carbon pores and further develop the internal pore structure. In physical activation, the pyrolysis and oxidation steps are separate, while in chemical activation the two processes are combined (Snoeyink and Summers 1999). Powdered activated carbon (PAC) is activated carbon ground in various types of mills so that 65-90% passes through a number 325 mesh (45µm) sieve. Granular activated carbon (GAC) consists of any larger activated carbon particles and is the portion of activated carbon used in the packed bed contact basins of water treatment plants.

1.2 Adsorption

Adsorption of a substance onto activated carbon in water occurs when the substance is concentrated more on the surface of the activated carbon than it is in the bulk

solution. The substance that accumulates is called the adsorbate and the activated carbon is termed the adsorbent. Physisorption, or physical adsorption, occurs when the accumulation results from dispersion forces while chemisorption, or chemical adsorption, results from an exchange or sharing of electrons between the adsorbate and the surface of the activated carbon. The properties of activated carbon that make it ideal as an adsorbent are a significant surface area to which the adsorbate may accumulate and an extensive internal pore structure in which the adsorbate may become trapped, thus encouraging its accumulation.

The relative hydrophobicity of the adsorbate is a driving force for its accumulation on the adsorbent. Thus, the adsorption of a substance generally decreases with increased contaminant solubility in water (Snoeyink and Summers 1999). The pore size of the activated carbon also plays a major role in adsorption as, for example, a large fulvic acid molecule will be unable to fit into small pores, or micropores, which have diameters less than 2 nm. An activated carbon with a large volume of mesopores, with diameters between 2 and 50 nm, and macropores, with diameters greater than 50 nm, would be better suited for fulvic acid removal. Conversely, a larger microporous volume is preferred when the target compound is a small molecule. The surface chemistry of the activated carbon also affects adsorption, particularly the presence of surface oxygen functional groups as will be discussed extensively in Section 4.1.2.

The rate of removal, or adsorption kinetics, is governed by the rates of the four steps composing physical adsorption. The first step, bulk transport, where the adsorbate moves from the bulk solution to the boundary layer of the adsorbate, is encouraged by the turbulent flow created in a packed bed of GAC. Film resistance to transport follows bulk

transport and involves the transport of the adsorbate through the stationary layer of water surrounding the adsorbent. Film resistance may also be minimized by increased flow rate past the adsorbent. The third step is internal pore transfer where the adsorbate travels through the adsorbent's pores via surface or pore diffusion to existing adsorption sites. The third step is often the rate-limiting step as the final step, physical adsorption, occurs almost instantaneously, so it has little effect on the rate of the overall reaction (Snoeyink and Summers 1999). The rate of adsorption, therefore, is influenced by the same variables affecting diffusion rate, including the concentration gradient and the temperature of the system (Bansal et al. 1988).

1.3 Current Uses of Activated Carbon

GAC can be used as a substitute for typical granular filter media, in that it removes suspended matter, though, through adsorption, GAC is also capable of removing organic compounds such as synthetic organic chemicals, natural organic matter, and taste and odor causing compounds. Synthetic organic chemicals (SOCs), such as most pesticides, may be contaminants in both ground and surface water. SOCs at chronic exposure levels may cause neurological and kidney effects and, for some pesticides, cancer (Hammer and Hammer 2001). Natural organic matter (NOM), a mixture of fulvic and humic acids, as well as hydrophilic acids, and carbohydrates, can impart color to water and may also react with chlorine, added for disinfection purposes, to create disinfection by-products (DBPs). DBPs, such as chloroform, a trihalomethane, are considered carcinogenic (Hammer and Hammer 2001). It is, therefore, important to reduce the NOM concentration in the water before disinfection with chlorine occurs. The adsorption of NOM onto GAC is enhanced if calcium complexes with the NOM prior to

adsorption by activated carbon (Frederick et al. 2001a). The effects of this enhanced adsorption relationship will be discussed throughout this paper. Taste and odor causing compounds, considered the primary reason water treatment utilities use activated carbon, may be consequences of biological growth or industrial activities. An example of a taste and odor causing compound resulting from biological growth is 2-methylisoborneol (MIB), which can be produced by cyano-bacteria, or blue-green algae. MIB, described as having an earthy-musty odor, enters a water treatment plant when the source water is surface water experiencing a bloom in the growth of the MIB producing organism.

1.4 Reactivation of Activated Carbon

During normal use, activated carbon will eventually become saturated with adsorbates so that the treated water exceeds the desired level of adsorbate removal, or reaches breakthrough. At this point, the spent activated carbon can be reactivated to restore the adsorption capacity of the GAC so that it can be reused rather than simply disposed of and replaced with virgin GAC. The time to reactivate a GAC bed can range from 6 months to 5 years, depending on the type of adsorbate, the influent concentration, and the desired treatment level.

Steam or chemical regeneration may be employed, though thermal reactivation is the most commonly employed activation scheme. Thermal reactivation consists of four steps: drying, desorption, pyrolysis, and gasification. The drying process removes water and some highly volatile adsorbates. At higher temperatures, thermal desorption occurs with vaporization of volatile adsorbates and decomposition of unstable adsorbates to more volatile components. A pyrolytic process follows using high temperatures, between 650-850°C, in an inert environment that converts heavy or non-volatile adsorbates to

char. The final step, gasification at temperatures above 700°C in steam, CO₂, or a combination of both, involves desorption of the vapors and gaseous products of char and their exit from the pores of the reactivated carbon (Clark and Lykins 1989, Cannon et al. 1993, Snoeyink and Summers 1999).

Reactivation has several effects on the activated carbon, aside from the intended effect of, ideally, restored adsorption capacity. Mass loss during the activation process may range from 10-15% of the original GAC and is the result of loss through the transfer of GAC from the treatment site to the regeneration site and/or burning of the GAC during reactivation (Clark and Lykins 1989). The loss is compensated for by the addition of virgin GAC before the reactivated GAC is returned to service. The surface chemistry of the activated carbon is also affected by reactivation as most oxygen-containing functional groups are stripped during reactivation at temperatures greater than 700°C and in an inert environment (Menendez et al. 1996, Pereira et al. 2003).

Inorganic molecules, such as calcium, may be adsorbed during normal operation of a GAC filter and are not removed during the activation or reactivation processes. The inorganic molecules remaining on the surface of the reactivated carbon prevent these adsorption sites from being freed for further adsorption and thus compromise the ability of the reactivation process to restore the adsorption capacity of the carbon (Clark and Lykins 1989). One well-documented effect of calcium presence in the reactivation process is calcium catalysis (Knappe et al. 1992, Cannon et al. 1993, Mazyck and Cannon 2000, Mazyck and Cannon 2002). Calcium catalysis increases the number of active sites on the surface of the carbon rather than, in the traditional sense of a catalyst, reducing the activation energy. Calcium catalyzes the gasification step of reactivation and is

characterized by increased mass losses during the reaction process and pore enlargement (Knappe et al. 1992). As discussed in Section 1.2, the pore size of the activated carbon can affect its ability to adsorb certain compounds, and an increase in pore size may make it unsuitable for certain applications. There is also cost associated with the addition of virgin GAC to replace the increased mass lost during the reactivation process.

Another result of reactivation is the incidence of pH excursions, an increase in the pH of treated water when reactivated carbon is returned to service (Farmer et al. 1996, Farmer et al. 1998). The duration and extent of the pH excursion will determine its impact on the system. Water with high pH levels is unfit for distribution to customers and also exceeds national pollution discharge elimination system (NPDES) discharge limits due to environmental impact concerns. An anion-exchange mechanism has been proposed for pH excursions with virgin activated carbons, in which anions present in the water displace hydroxyl (OH⁻) ions from the GAC surface (See Section 3.1.3) (Dussert et al. 1995). Methods to reduce the pH of the treated water on-site can be both time-consuming and expensive. Oxidation of the reactivated carbon using air has been proposed for the creation of a pH stable carbon as well as treatment with carbon dioxide (CO₂) (Dussert et al. 1995, Farmer et al. 1996, Farmer et al. 1998). Methods to overcome pH excursions will be discussed in-depth in Section 4.1.1.

CHAPTER 2 HYPOTHESIS AND OBJECTIVES

2.1 Hypothesis

- Calcium chemistry ($\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$), rather than the chemistry of other inorganic constituents of carbon or carbon basicity, dominates in pH excursions;
- Air treatments
 - The addition of carboxylic acid groups to the carbon surface via air treatment between 350°C and 450°C will balance the basicity effect created by calcium chemistry;
 - Air treatments add acidic oxygen-containing functional groups to the carbon surface via chemisorption of oxygen;
 - Air treatments decrease adsorption capacity for MIB due to the preference of the acidic oxygen-containing functional groups for water adsorption;
- CO₂ treatments
 - The physisorption of CO₂ to activated carbon will combat pH excursions because the CO₂ will desorb from the carbon upon wetting, forming carbonic acid (H₂CO₃);
 - CO₂ treatments do not add oxygen-containing functional groups to the carbon surface, but rather the CO₂ is physisorbed to the carbon;

2.2 Objectives

- Determine whether calcium within reactivated GAC contributes to pH excursions, due to the transformation of calcium oxide to calcium hydroxide, which can further dissociate to calcium ions and hydroxides;
- Determine if an anion exchange phenomenon that is associated with the carbon surface (versus with calcium) contributes to pH excursions via

anion adsorption and subsequent release of hydroxide ions for reactivated carbons;

- Create pH stable carbons using air treatments and CO₂ treatments;
- Determine the total acidity ($\mu\text{eq/g}$) of the air and CO₂ treated carbons and evaluate the effect of total acidity on the carbon's adsorption of MIB

CHAPTER 3

THE ROLE OF CALCIUM IN PH EXCURSIONS FOR REACTIVATED GAC

Water and wastewater utilities thermally reactivate their spent granular activated carbon (GAC) because thermal reactivation offers an economical approach for reusing the exhausted material. These utilities save money by reactivating the spent GAC versus wasting it and replacing it with virgin GAC. For example, together, American Carbon Services (a subsidiary of the American Water Works Company), the Cincinnati Water Works, and NORIT Americas reactivate more than 25 million pounds of spent GAC per year. Because thermal reactivation is more economical than virgin carbon replacement, and because it has been shown that reactivated carbon performs as well as or better than virgin carbon (Goins 2000), thermal reactivation is an increasingly attractive industrial operation.

Over the years, research has been carried out on two recurring issues that pertain to thermal reactivation. The first is related to calcium catalysis (Knappe 1992, Cannon et al. 1993, Cannon et al. 1994) and has been addressed through the development of a new thermal reactivation protocol that overcomes the deleterious effects of calcium catalysis (Mazyck and Cannon 2000, Mazyck and Cannon 2002). This new protocol not only reduced the mass, volume, and micropore loss compared to conventional reactivation, but also has been shown to increase GAC performance for removing the common odorant MIB compared to conventionally reactivated and virgin GAC (Goins 2000).

The second issue is pH excursion: when reactivated carbon is returned to service, several water and wastewater utilities have found that the pH of the subsequently treated water is excessively high. Indeed, some water utilities have reported pH excursions greater than pH 11 that have lasted for several weeks. Furthermore, many carbonaceous precursors such as bituminous and sub-bituminous coals, wood, coconut, peat, and acid-washed carbons have been found to produce pH excursions (Dussert et al. 1995). If left unmitigated, this deviation in pH could cause some water utilities that discharge backwash water to rivers to operate out of compliance, and risk being fined because their NPDES permits often require that water pH be maintained between 6 and 9. Therefore, some utilities request that their reactivated GAC maintain a stable pH of 6.5 to 8.5 when it is placed back in service (i.e., with a certain “safety buffer”). Currently, to overcome pH excursions, water utilities often either a) backwash their GAC until the pH is less than 8.5–9, b) add acid, or c) recirculate their water until the pH excursion is abated. All of these solutions are time-consuming and expensive.

The objective of this study was to elucidate the role that calcium plays in pH excursions. Several other pH excursion mechanisms have also been proposed in the literature (see Section 3.1). The intent of this paper has not been to disprove any of these other mechanisms. It is deemed plausible that calcium could cause pH excursions, thus, the role of calcium on pH excursions was the primary focus of this study.

3.1 Literature Review

3.1.1 pH Excursions in Water Treatment

During potable water treatment, water-soluble calcium can adsorb onto GAC as a complex with natural organic matter (NOM) (Nowak and Cannon 1997, Nowak and

Cannon 1999, Frederick and Cannon 2001, Frederick et al. 2001a, Frederick et al. 2001b). Moreover, calcium is abundant in many coal-based carbons. Thermal reactivation of spent GAC at temperatures above 850°C decomposes the oxygenated functionality of the NOM that complexes with Ca. This process results in the formation of CaO, which is thermodynamically the most stable species at these high temperatures (Mazyck and Cannon 2000). When the reactivated carbon is returned to service, the calcined CaO can react with water to form Ca(OH)₂ (equation 1). Furthermore, Ca(OH)₂ can dissolve and subsequently dissociate as Ca²⁺ and 2OH⁻ (equation 2). The release of OH⁻ would elevate the pH of the subsequently treated water.



Calcium chemistry and thermodynamics as related to GAC and thermal reactivation have been previously discussed at length (Cannon et al. 1994, Mazyck and Cannon 2000, Mazyck and Cannon 2002).

A water utility in the Virginia-American Water Company, under the umbrella of the American Water Works Company, measured increases in both pH and Ca²⁺ concentration in their backwash water when a reactivated GAC was placed back in service (Figure 1). These data are representative of a full-scale GAC filter bed adsorber. As shown, the reactivated GAC posed an adverse effect on water quality in that it elevated the filter bed adsorber's effluent pH to greater than 11. Even after 6 days, the pH was still above 8.5. In addition to the pH, the utility also measured the concentration of calcium in the effluent for two days. As shown in Figure 1, as the calcium concentration decreased, the water contact pH likewise decreased. The influent calcium

concentration in their backwash water was relatively constant over the two days. No other operational changes could have contributed to the higher Ca^{2+} and OH^- levels; and these results are fairly typical, as reported by American Water Works Company personnel. These results led to the hypothesis that the manner by which the reactivated GAC was contributing both calcium and hydroxyl to the water was via the mechanisms described in equations 1 and 2 above. Furthermore, it was rationalized that the deviation from a $[\text{OH}^-]$ (molar concentration of hydroxyl ions) to $[\text{Ca}^{2+}]$ (molar concentration of calcium ions) ratio of 2, in that the released OH^- that originated from $\text{Ca}(\text{OH})_2$ would have also been consumed to some extent by the natural buffering capacity of the water. Thus, the data from the Virginia-American Water Company could be taken as a semi-quantitative example of the mechanisms described in equations 1 and 2.

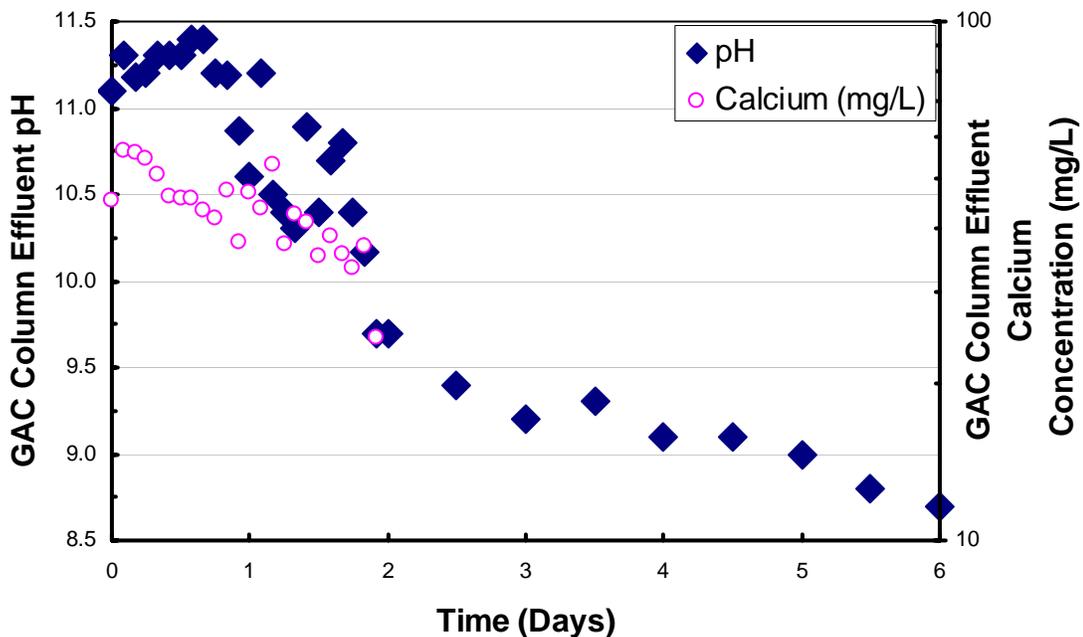
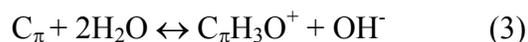


Figure 1. Full-scale water treatment plant effluent pH and calcium concentration data after reactivated GAC was returned to service

3.1.2 Carbon Basic Properties

Leon y Leon et al. (1992) investigated the basic (alkaline) nature of carbons and proposed a mechanism that involved electron donor/acceptor and pyrone-type interactions. They showed that the oxygen content of the carbon dictated the importance of either interaction, and that these basic sites were created as a result of high temperature (> 700°C) heat treatments. Indeed, Papirer et al. (1991) have also shown that the number of basic sites can be maximized by heat treatment between 750°C and 850°C. Temperatures higher than 700°C are commonly employed when manufacturing and reactivating GAC.

Leon y Leon et al. (1992) used highly pure (i.e., inorganic-free) carbons, which were chemically or thermally treated, in order to determine the surface basicity. Through HCl adsorption, stepped temperature-programmed desorption, electrophoresis and mass titration, they argued in favor of the following mechanism:



where C_{π} is a graphene layer in which the itinerant π electrons may become partially localized as a result of H_3O^{+} addition. Leon y Leon et al. (1992) showed that these oxygen-free C_{π} sites can adsorb protons from solution, and thus render the surface positively charged. Therefore, this electron donor/acceptor interaction was proposed to be responsible for the basicity of the carbon surface. In addition to this mechanism, they could not discount that pyrone-type surface groups were also responsible for carbon basicity. The electron donor/acceptor mechanism is predominant in carbons with low oxygen concentrations, while interactions with pyrone groups could predominate in carbons with high oxygen content. Barton et al. (1997) also investigated acidic and basic

sites on carbon and confirmed that acid functionalities are associated with chemisorbed oxygen, whereas basic sites are concentrated at delocalized electrons (C_{π}) in the basal plane. However, they have not supported the notion that pyrones can contribute to carbon basicity. Darmstadt and Christian's (2003) findings support those of Barton et al. (1997) in that no significant correlation between oxygen groups and basic equivalents on the surface of carbon blacks was found and that the dominant portions of the basic sites present on the carbon blacks are associated with the basal planes of the graphine layer. Menendez et al. (1999) did show, however, that complex (tricyclic) pyrones, which are located at the edges of graphene layers, could have a pK_a around 12.7 and that they can contribute significantly to carbon basicity. It is evident that there is no general consensus as to the dominant contributor to carbon basicity or to the basic strength of the contributor. Montes-Moran et al. (2004) provide a summary of the virtues and drawbacks of the two proposed contributors to carbon basicity discussed herein, basic-oxygen-containing groups and delocalized π -electrons of the basal planes.

3.1.3 pH Excursion Mechanism for Virgin Carbons

A mechanism involving anion exchange with hydroxide ions following carbon protonation has been proposed by Farmer and coworkers to explain pH excursions (Carr and Farmer 1995, Dussert et al. 1995, Farmer et al 1996). These authors suggested that pH excursions are a function of the carbon surface that is altered during high temperature activation or reactivation. Activated carbons exposed to high temperatures in a reducing atmosphere during manufacturing and reactivation tended to adsorb strong acids in water. Garten and Weiss (1957) classified these as H-type carbons. In contrast, L-type carbons are those produced by surface oxidation; and these are known to adsorb strong bases in

water (Garten and Weiss 1957). Farmer et al. (1996) argued that this acid adsorption during water treatment might involve the protonation of pyrone-type surface groups or other similar functionalities on the carbon surface, in agreement with Leon y Leon et al. (1992). In addition, they suggested that loading the carbon with sulfate, chloride, or other anions that are present in water could neutralize the positive charge on the carbon surface. Furthermore, they proposed that this charge neutralization could also occur through an anion exchange process involving sulfates and hydroxides on the carbon surface. In other words, they surmised that the carbon could adsorb sulfates or other anions from water while releasing hydroxyls, and that this ion exchange process could cause the pH to rise. Farmer et al. (1996) did acknowledge that this anion exchange mechanism requires additional testing and confirmation. To date, however, there has been no further evaluation presented in the literature that would either prove or disprove their hypothesis.

Dussert et al. (1995) supported this anion exchange mechanism because they found no significant pH excursion when virgin GAC was immersed in Milli-Q (anion-free) water, and they concurred that anions were required to trigger a pH effect. In contrast, as discussed below, the results show that pH excursions occur even in Milli-Q water when using reactivated carbons. Dussert et al. (1995) came to their conclusions after studying virgin GACs that removed 2 to 9 mg of sulfate/g GAC. In Milli-Q water spiked with 80 mg sulfate/L, they measured the water contact pH and sulfate capacity for several virgin carbons. Not only did they find that pH excursions only occurred when anions such as sulfate were present, but they also reported that, as the sulfate capacity increased, pH also increased. In their study, the carbons that did not exhibit pH

excursions also did not significantly remove sulfate ions from solution (< 0.7 mg/g). They also found that sulfate (SO_4^{2-}) removal was greater than nitrate (NO_3^-) or chloride (Cl^-) removal. They did not measure calcium concentrations for their carbons; however, they did find that the ash content of the carbon could not be correlated with pH excursions.

3.2 Experimental

3.2.1 Activated Carbon Samples

Several coal-based reactivated GAC samples were received from the NORIT Americas, Inc. plant in Pryor, OK. These carbons had served in potable water treatment, had become spent, and had been subsequently reactivated in Pryor, OK. The calcium content of these carbons, or the GAC calcium concentration, was determined by ashing the GAC, dissolving the ash in acid, then analyzing for calcium via inductively coupled plasma (ICP) emission spectroscopy (Leeman Labs PS3000UV, Framingham, MA) following the procedure described by Nowack and Cannon (1997), except that emission spectroscopy was used instead of absorption spectroscopy. (Analyses were conducted at the Materials Characterization Laboratory, PSU.) The reproducibility of the results was within $\pm 5\%$.

3.2.2 Water Contact pH

The water contact pH for these carbons was determined by mixing approximately 2 grams of as-received GAC with 80 mL of Milli-Q water for 30 minutes, then measuring the pH. This ratio of GAC to solution was the same used by Dussert et al. (1995) and Farmer et al. (1996). In initial exploratory experiments, pH measurements (Standard Methods for the Examination of Water and Wastewater procedure 4500-H⁺) were taken

every five minutes, and it was observed that after 20 or 30 minutes the pH reached a pseudo-equilibrium level (less than 0.1 change in pH over 5 minutes). Dussert et al. (1995) used a similar technique and concluded that this protocol provides a good prediction of the pH that would be measured during water treatment service. For the experiments described herein, each reactivated carbon was sampled twice and the pH for these two samples was within ± 0.4 pH units. (Six of the seven samples varied by less than ± 0.1 pH units.)

3.2.3 Calcium Solution Concentration

After the water contact pH experiment was completed, the GAC was separated from the solution by utilizing a vacuum filtration apparatus (0.45 μm Whatman filter paper), and the 80 mL of Milli-Q water was analyzed for calcium by inductively coupled plasma (ICP) emission spectroscopy, as above. Calcium levels leached out of the GAC during the 30-minute water contact pH experiment were determined. The measured concentrations of the replicas were within $\pm 3.5\%$ of one another. Aluminum, iron, and magnesium concentrations leached from the samples were also measured.

3.2.4 GAC Sulfate Capacity

In selected experiments, the water contact pH was measured in Milli-Q water that contained 80 mg $\text{SO}_4^{2-}/\text{L}$. The sulfate concentration of this solution was verified using a HACH DR/2000 spectrophotometer (Loveland, CO) by utilizing their sulfate method 680 (SulfaVer 4). After each experiment, the carbon was separated from the solution using vacuum filtration with a 0.45 μm Whatman filter paper. The filtrate was then analyzed for sulfate concentration as described above. The difference in sulfate concentration

between the stock solution and the filtrate represented the sulfate adsorbed on the activated carbon. The reproducibility of sulfate concentrations was within $\pm 5\%$.

3.3 Results and Discussion

3.3.1 Calcium Content Versus Water Contact pH

Water contact pH experiments were conducted for seven reactivated carbons. The duplicated results are summarized in Figure 2. As shown, all the pH values were above 8.5 and none of the carbons exhibited pH greater than 11.0. It is anticipated from empirical experience that most activated carbons that had become loaded with calcium-NOM complexes will exhibit pH excursions with pH values greater than 8.5. These data confirmed the pH excursions that water utilities face when they use reactivated carbons.

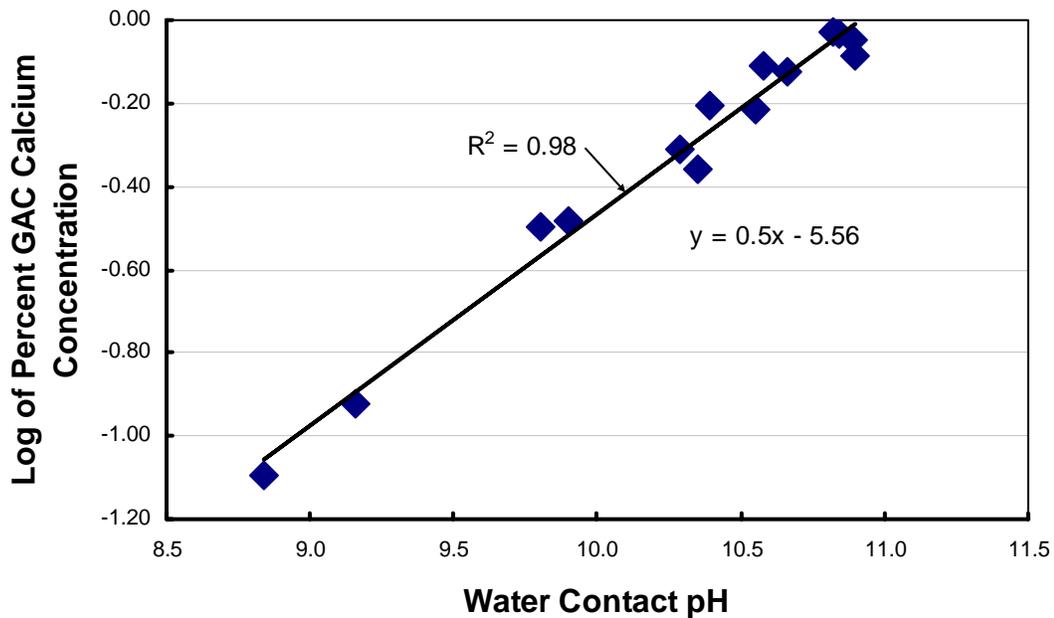


Figure 2. Correlation between log GAC calcium content and water contact pH exhibited by reactivated carbon

Calcium chemistry is obviously important for pH excursions, since the water contact pH increased linearly ($R^2 = 0.98$) with the log of the calcium content of the GAC.

Also, the slope of the line, 0.5, is reminiscent of equation 2, which designates a 1:2 ratio of moles of calcium to moles of hydroxyl ion. The slope, therefore, supports the relationship between calcium and pH excursions.

It should be noted that not all of the GAC calcium content would be accessible to water. The portion that would be fully accessible is that which resulted from complexation with NOM and subsequent adsorption onto the GAC surface where it would be expected to undergo the reactions shown in equations 1 and 2. In contrast, the calcium that was a component of the original activated carbon may or may not have been accessible to the water, since it could have been imbedded within the graphene layers of the carbon. For the reactivated GACs of somewhat consistent parent source that were evaluated herein, the inaccessible carbon posed a fairly uniform background calcium level.

Figure 2 showed that the contact pH increased as calcium accumulated during normal operation in a water treatment plant. Despite the interesting correlation between calcium content of the GAC and water contact pH, only calcium leached from the GAC, as discussed in Section 3.3.2, should be used to predict pH excursions. Whether there exists a cause-and-effect relationship in the correlation of the calcium content of the GAC to the water contact pH is the focus of the ensuing discussion. Each one of these reactivated carbons exhibited a pH excursion in Milli-Q water; and this contrasted with the behavior of virgin GACs that were studied by Dussert et al. (1995). Those authors did not measure a significant pH excursion for virgin carbons in Milli-Q water. This discrepancy highlights the distinction between the accessible calcium that originates from

adsorbed calcium-NOM, versus the partially accessible calcium that occurs in virgin activated carbons.

3.3.2 Predicted pH Based on Calcium Leached from GAC

After each water contact pH experiment, the concentration of calcium that leached out of the GAC and into solution was measured. This amount of calcium was used to predict the pH of the water based on equations 1 and 2: for every mole of Ca^{2+} released from dissociated $\text{Ca}(\text{OH})_2$, two OH^- moles would be released. This relation is shown in Equation 4.

$$2[\text{Ca}^{2+}] = [\text{OH}^-] \quad (4)$$

To calculate the water contact pH in an open system, with contributions to acidity from dissolved CO_2 , and the resulting formation of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions, a charge balance was used to relate the molar concentrations of the pertinent ions according to

$$[\text{H}^+] + 2[\text{Ca}^{2+}] = [\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] \quad (5)$$

The equation was then solved for the concentration of H^+ , and the resulting water contact pH, through trial and error for each sample and its related concentration of calcium in solution.

The results are presented in Figure 3. Duplicate analyses are plotted; and a good linear relationship is evident. The dotted line in Figure 3 corresponds to a perfect match where the predicted water contact pH (excluding reactions with carbonate acidity) is exactly equal to the measured water contact pH. The predicted water contact pH in an isolated system is seen to be always higher than the measured value by about 0.3 ± 0.1 pH units. The discrepancy reflects a uniform amount of bicarbonate anion and H^+ that

was generated by the side reaction $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+$. This reaction occurred in the mixing beaker that was open to the atmosphere. An additional experiment was performed on the sample with the highest GAC calcium content to test this explanation. The sample was split to perform water contact pH experiments in open air and an analogous experiment in a nitrogen filled glove box. The open-air experiment yielded a water contact pH of 10.8 and the glove box experiment yielded a water contact pH of 11.3. The water contact pH predicted by equations 1 and 2, based on leached calcium for this sample, was found to be 11.3. This experiment demonstrates the role of ambient CO_2 in altering the measured pH values compared to the predicted values. As the slope of 1.0 in Figure 3 suggests, if the acidic effects of CO_2 were removed, the line would be expected to lie on the perfect match line represented by the dotted line in Figure 3.

It should be noted that the predicted water contact pH based on an open atmosphere is far below the water contact pH measured in the open atmosphere, with an approximate 2.7 unit decrease in pH compared to the predicted water contact pH in an isolated system. It is possible that the system is not at equilibrium when the water contact pH is measured, and therefore not enough time has passed for the water contact pH to decrease to the level predicted. It would therefore be expected that if the water contact pH experiments were carried out for longer than 30 minutes, that the water contact pH would decrease and eventually reach the theoretical water contact pH as predicted by Equation 4. Contributions to basicity via EDA or pyrone-type groups on the surface of the carbon may also affect the pH. The carbon's contribution to basicity is not included in the theoretical calculations of an open atmosphere water contact pH, and

therefore this theoretical calculation would be expected to under predict the final water contact pH.

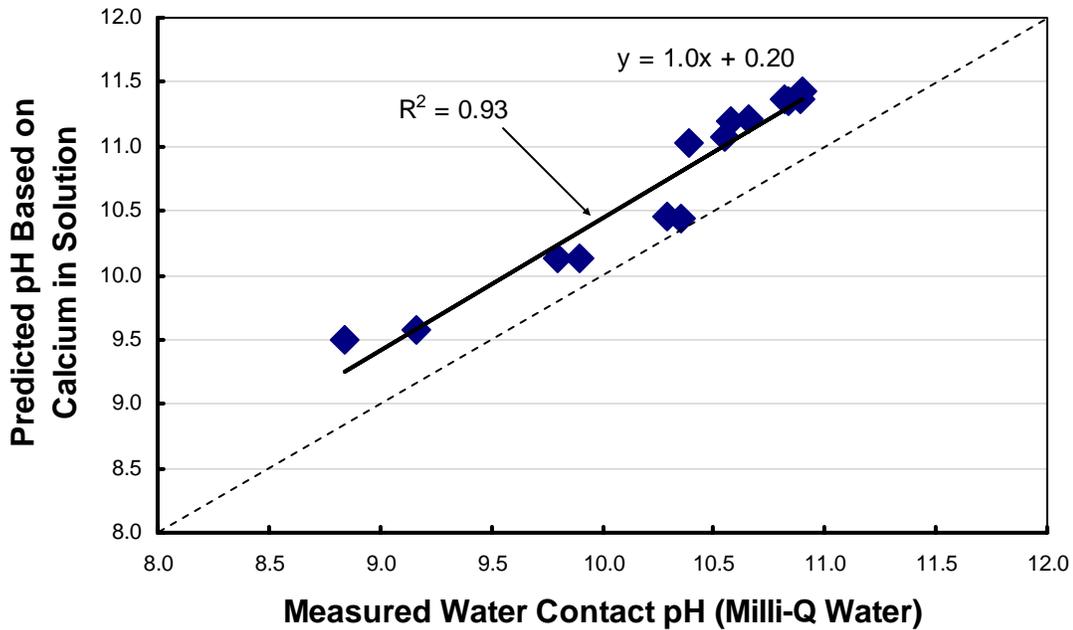


Figure 3. Predicted pH based on the calcium that leached out of the reactivated carbon in an isolated and an open system versus the water contact pH measured in Milli-Q water

To verify that calcium is primarily responsible for the pH excursions, rather than other inorganics, the leaching of other inorganics was also measured namely aluminum, iron, and magnesium (Table 1). Aluminum, iron, and magnesium appear ubiquitously in raw water and they may be added during chemical treatment in the water treatment plant (Knappe et al. 1992, Cannon et al. 1993). The minimum detection limit (MDL) for iron on the ICP is 0.02 ppm and for aluminum the MDL is 0.03 ppm. As was proposed, it is evident that calcium accumulates onto the GAC samples, and therefore leaches, to a greater extent than aluminum, magnesium, or iron. In fact, calcium concentrations are at least ten times higher than the concentrations of other metals leached from the samples, signifying that the chemistry of calcium indeed dominates the pH excursion effects.

Table 1: Metal concentrations leached from the activated carbon samples

Water Contact pH	Aluminum (ppm)	Iron (ppm)	Magnesium (ppm)	Calcium (ppm)
8.9	Below MDL	Below MDL	0.03	0.88
9.6	0.11	Below MDL	0.17	4.85
10.1	0.80	Below MDL	0.20	7.00
10.6	1.17	Below MDL	1.01	16.8
10.6	1.82	Below MDL	1.38	29.0
10.7	3.80	Below MDL	1.37	34.2
10.9	3.46	Below MDL	0.76	38.5

3.3.3 pH of Steam-Cured Plus Ramped-Temperature Reactivated Carbons

A spent bituminous coal-based carbon that contained 2.4 wt. % calcium was thermally reactivated by means of the steam-curing plus ramped-temperature protocol that was previously developed to overcome calcium catalysis (Mazyck and Cannon 2000, Mazyck and Cannon 2002). Briefly, this protocol entailed steam-curing at 375°C for 1 h followed by ramping in N₂ to either 650°C, 750°C, or 850°C. The carbon was not held at these high temperatures for any extended time, and reactivation was terminated as soon as the final temperature was reached. Immediately after reactivation, the water contact pH was measured in each case and the results are shown in Figure 4. It is well known from the literature that as the final ramped-temperature increases above the calcining temperature of 800°C-850°C; CaCO₃ would have increasingly decomposed to CaO (Boynton 1980, Babushkin et al. 1985, Cannon et al. 1994, Mazyck and Cannon 2000). Because of this calcining effect, the spent GAC exposed to 850°C had the highest pH. The significance of the highest temperature is that CaO is formed and is available to react via equations 1 and 2. Other calcium species (e.g., CaCO₃ or CaSO₄) are less likely to participate in these reactions because they tend to dissolve less readily in water that has a neutral or basic pH. Samples exposed to 650°C or 750°C had lower pH values because

neither was heated enough to promote complete CaO formation, as this calcining reaction is diffusion limited (Boynton 1980).

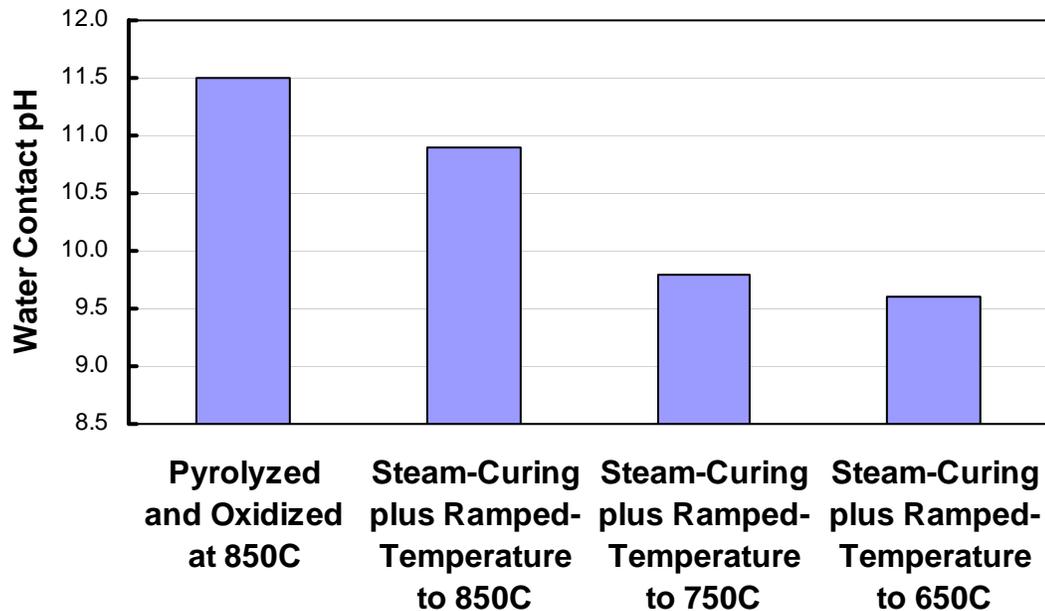


Figure 4. Comparison of water contact pH for conventionally reactivated and steam-cured reactivated carbons to 3 different temperatures

The same spent carbon (from above) that was steam-cured was also reactivated conventionally using pyrolysis and steam-activation at 850°C. Its water contact pH was 11.5 (see Figure 4); this significantly higher pH occurred because this GAC had been exposed to steam at 850°C for 15 minutes. At temperatures above ca. 527°C for any partial pressure of steam, $\text{Ca}(\text{OH})_2$ decomposes to CaO (Mazyck and Cannon 2000).

Total calcium concentration provided a stronger correlation with pH than did CaO surface area (data not shown). This is because CaO surface area measurements reflect only the external fraction of the total CaO available for reaction with water.

3.3.4 Influence of Acid and Base Washing on Water Contact pH

It is noted that high-temperature pyrolysis or steam exposure could also gasify oxygen-containing functionality on the carbon surface, and this could also elevate the pH.

Thus, to further distinguish the role of calcium from the role of diminished surface acidity, a non-oxidizing acid was employed to remove the calcium from the GAC to isolate the surface acidity effect. Specifically, a spent carbon was treated with ten bed volumes of 1 M HCl. This treatment reportedly removes essentially all of the metals, including calcium, from the GAC (Knappe et al. 1992, Cannon et al. 1993). After acid washing, this sample was washed with ten bed volumes of 15.8 M NaOH to remove any residual H^+ , then rinsed with 30 bed volumes of deionized distilled water to neutralize the pH and desorb any previously sorbed H^+ or OH^- . Then, the carbon was reactivated. The pH of this conventionally reactivated carbon, that had been acid-base treated, was considerably lower (8.5) than the pH of the conventionally reactivated Ca-containing carbon (11.5) as shown in Figure 4. These results are as would be expected by the mechanism of equations 1 and 2.

3.3.5 Comparisons of pH in Milli-Q and Sulfate-Containing Water

Dussert et al (1995) hypothesized that an ion exchange mechanism was responsible for pH excursions on virgin GAC. To discern if this mechanism was also valid in describing pH excursions on reactivated GAC, this protocol was tested on the reactivated carbons herein. The concentration of sulfate was measured and plotted versus the water contact pH as measured in water that contained 80 mg sulfate/L (Figure 5). Sulfate uptake was very low for the reactivated GACs; and in some cases it was negative, indicating that the reactivated GAC itself contributed sulfate to the solution. In light of these results, it was concluded that the uptake of sulfate and the subsequent release of hydroxyl ions were not responsible for the observed pH excursions on the reactivated GACs. Commercial GAC contains a considerable level of sulfur in its pyrite content

(Boynton 1980, Cannon et al. 1997). It is proposed that during thermal reactivation, sulfur dioxide formed from the inorganic pyrite impurities in GAC, and then the residual SO_2 (i.e., that which remained present as the reactivated GAC cooled) adsorbed onto CaO to form CaSO_3 or CaSO_4 (Munoz-Guillena 1994), and these subsequently leached out of the GAC and dissolved in the effluent water. Also, this sulfate could have adsorbed, to a limited extent, out of the municipal water source. Then, at the high water contact pH that was incurred by the $\text{Ca}(\text{OH})_2$ mechanism, the base ion-exchanged with the adsorbed sulfate.

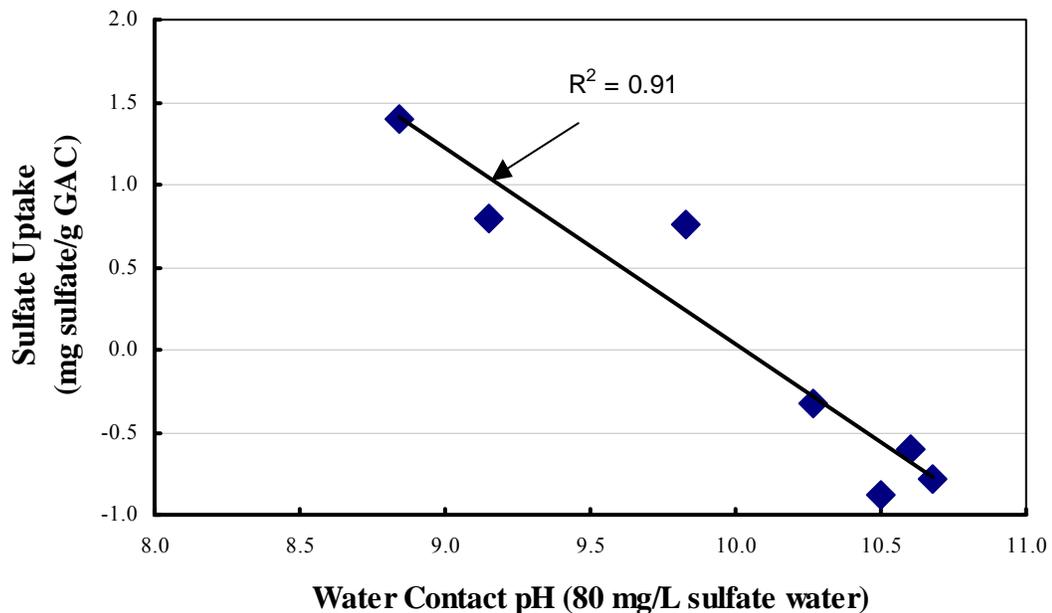


Figure 5. Sulfate uptake for several reactivated carbons versus their water contact pH as measured in 80 mg/L sulfate water

3.4 Conclusions

The data shown here support the contention that calcium chemistry (i.e., equations 1 and 2) is a plausible mechanism to account for pH excursions of reactivated carbons because as the calcium concentration increased, the water contact pH also increased.

Indeed, the correlation coefficient (R^2) between the log of the calcium content and water contact pH exceeded 0.9.

When calcium is removed from reactivated carbons, the magnitude of the pH excursion is drastically decreased. The acid (HCl) and base (NaOH) washing procedures removed the calcium, but did not significantly influence the carbon's functional groups that existed prior to this treatment, since the HCl and NaOH were neither oxidizing nor reducing agents. Typically, organic free water has a pH of 5-6. When the acid and base washed reactivated carbon, assumed to be free of accumulated calcium, was tested, it altered the pH to 8.5. In contrast, when calcium was present on the reactivated carbon, the pH rose to 11.5. Therefore, one could conclude that for these reactivated carbons, calcium exerted the greater influence in causing high pH excursions.

Sulfate uptake and hence an anion exchange mechanism did not provide an explanation for pH excursions for reactivated carbons because as the sulfate uptake increased, the water contact pH decreased.

CHAPTER 4 CREATING A pH STABLE CARBON

Previous experiments have shown that calcium chemistry is a plausible mechanism behind the pH excursions experienced in water treatment when reactivated GAC is returned to service. In addition, the anion exchange mechanism proposed by other researchers as the mechanism behind pH excursion in virgin GAC was not found to explain the pH excursions experienced with reactivated GAC. An understanding of the mechanisms behind pH excursions with reactivated GAC will aid in the formulation of a method to overcome these pH excursions.

The option of not reactivating the GAC, thus avoiding the reaction process and the resulting pH excursions, is not a cost-saving solution, as reactivation of GAC is a more economical approach than simply replacing the spent GAC with virgin GAC. Furthermore, as demonstrated by Farmer et al. (1996), virgin carbons can cause pH excursion as well. Currently, water treatment plants treat the pH excursions as they occur, including adjustment of the pH of the treated water and backwashing the GAC until the GAC no longer creates a pH excursion. Altering the reactivation process to avoid the creation of calcium species that will participate in the proposed calcium chemistry reactions, using a reactivation scheme proposed by Mazyck and Cannon (2000 and 2002) has been investigated in this paper as a successful means of avoiding pH excursions experienced with reactivated GAC. Patents are held on methods to overcome

pH excursions that propose treatments of reactivated GAC with either air or carbon dioxide will create pH stable carbons that will not create pH excursions when the reactivated GAC is returned to service (Dussert et al. 1995, Farmer et al. 1998)

The objective of this study was to investigate the effects of air and carbon dioxide treatments on the water contact pH of a reactivated GAC. The mechanism responsible for the creation of a pH stable carbon via these treatments was also investigated, with a focus on the effect of the treatments on the surface chemistry of the reactivated GAC. Finally, the performance of the treated GAC was investigated through equilibrium batch studies using MIB as the adsorbate.

4.1 Literature Review

4.1.1 Methods to Overcome pH Excursions

The three broad categories of methods to overcome pH excursions are on-site treatments, tailoring of the reactivation process, and post-reactivation treatments performed before the reactivated GAC is returned to service.

One on-site method that would occur prior to reactivation is the reduction of the calcium adsorbed onto the activated carbon during water treatment. To achieve this, either the NOM complexes with a stronger cation, thus out-competing calcium, or the calcium-NOM complex is removed before it comes into contact with the GAC. The use of an iron coagulant would be ideal as it could facilitate both of the above goals. Iron (Fe^{3+}) is a stronger cation than calcium and would displace the calcium from the NOM though competition with NOM by hydroxyl species may hinder the process near a neutral pH. Nowack et al. (1999) proposed that, at near neutral pH, soluble iron hydroxide would precipitate depleting the amount of iron available for further reactions with NOM.

At adequate pH levels, the iron would also coagulate the calcium-NOM complexes already formed and this floc would be allowed to settle out before reaching the GAC. Nowack et al. (1999) and Frederick et al. (2001) have shown that the addition of iron coagulant to a system containing both calcium and NOM yielded a decrease in the amount of calcium-NOM complexes adsorbed to the carbon as well as a relatively level iron loading onto the GAC. These results indicate that, not only is iron addition successful in decreasing calcium loading, but that the primary mechanism responsible for this is coagulation of the iron-NOM and/or calcium-NOM complexes. The accumulation of iron is not detrimental to the reactivation process as iron catalysis is suppressed by the presence of sulfur, which is ubiquitous in coal-based carbons (Nowack et al. 1999). A near neutral pH was indeed found to hinder iron-NOM formation as the hydroxide species out-competed the NOM for complexation with the iron ions. Therefore, Nowack et al. (1999) and Frederick et al. (2001) concluded that a combination of pH adjustment to approximately 6.0 pH and iron addition, on the order of 5 mg/L, are the most effective in reducing calcium loading. Water treatment facilities that operate above this range of pH are expected to accumulate higher levels of calcium onto their GAC.

Other on-site treatments to overcome pH excursions after the reactivated carbon is returned to service include backwashing, recycling of the high pH water, and pH adjustments before the treated water is discharged. Both backwashing and recycling involve running water through the GAC until the pH reaches acceptable levels, which reduces the yield of treated water through the system (Farmer et al. 1998). In addition, backwashing may require a holding tank, as the high pH water cannot be discharged, which will restrict the allowable backwashing time (Carr and Farmer 1995). Acid

treatment of the high pH water prior to discharge to stabilize the pH can be time-consuming and expensive, due to additional monitoring equipment

Acid-washing a traditionally reactivated carbon prior to use, aside from being time-consuming and expensive, may not even produce a pH stable carbon (Dussert et al. 1995). In addition, oxygen surface complexes are introduced to the surface of the carbon if an oxidizing acid is used and this can impact the adsorption capabilities of the reactivated carbon, to be discussed further in Section 4.1.2. Depending on the acid, the micropore volume may also decrease as a result of treatment.

Section 3.3.3 described a reactivation protocol that can overcome calcium catalysis and the resulting pH excursions by reactivating the carbons at temperatures below that at which CaO is formed, 850°C. The CaO form participates in the calcium chemistry mechanism discussed in Section 3. A decrease in the amount of CaO available to participate in the calcium chemistry reactions will result in a decreased pH excursion.

Oxidizing the reactivated carbon, outlined in a patent by Dussert et al. (1995), or treating the reactivated carbon with carbon dioxide, outlined in a patent by Farmer et al. (1998), have been offered as means to create a pH stable carbon. Both patents propose that oxidation or CO₂ treatment, depending on the patent, neutralizes the surface of the reactivated carbon, thus inhibiting any anion-exchange during water treatment. As the focus of Section 3 was the role of calcium in pH excursions and the result was that the anion-exchange mechanism does not fully explain the excursions found in reactivated carbons, there must be an additional explanation for why these treatments are able to create pH stable carbons.

The optimum temperature for chemisorption of oxygen, using air as the oxidizing agent, occurs around 400°C (Wiegand 1937, Puri 1970). The maximum capacity for a carbon to adsorb bases, or its acidic nature, has also been shown to lie close to 400°C (Puri 1970). The fact that the maximum chemisorption of oxygen and the maximum capacity to adsorb bases occur at the same temperature has led many researchers to the conclusion that the acidic nature of carbon is closely related to its oxygen content. Subsequent research has supported this conclusion (Puri 1970, Otake and Jenkins 1993, Barton 1997, Ania et al. 2004). The carboxyl group (COOH) has been suggested as the oxygen-containing functional group responsible for the acidic nature of carbon by several researchers (Krut and de Kadt 1931, Puri 1970). The temperature at which these carboxyl groups were developed was 400°C in either oxygen or air. More recently, Otake and Jenkins (1993) researched air treated carbons and found a positive linear relationship between the chemisorbed oxygen concentration desorbed as a CO₂ complex and total acidity of the carbon. Otake and Jenkins (1993) proposed that the oxygen functional groups existing on the air-oxidized char were carboxyl groups and were formed following the mechanism of Figure 6.

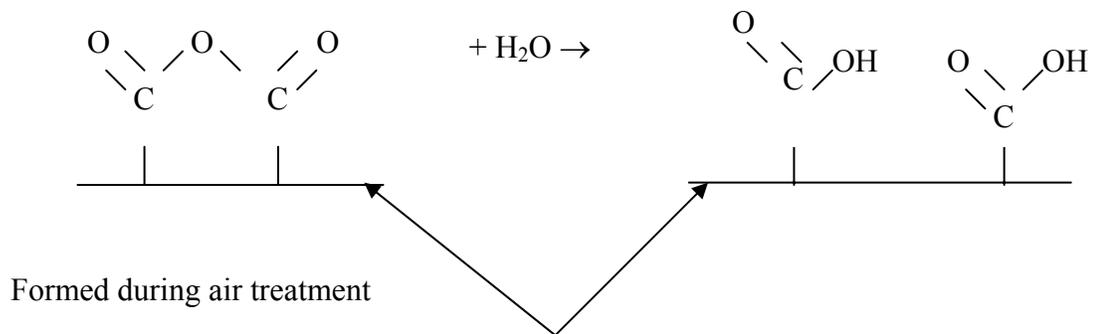


Figure 6. Proposed mechanism for the formation of COOH (Otake and Jenkins, 1993)

Given this information, it can be proposed that air treatment of reactivated carbons adds acidic oxygen-containing functional groups, in the form of carboxyl groups, which upon addition to water form carboxylic acid. Thus, air treatment balances the increased pH caused by either the anion-exchange or the calcium chemistry mechanism rather than inhibiting these mechanisms.

Treatment with CO_2 is advantageous in that it takes place at ambient temperatures, thereby avoiding problems with elevated temperature oxidation, while avoiding the lengthy treatment times and high gas volumes required for air oxidation at ambient temperatures (Farmer et al. 1998). Here, the mechanism that creates a pH stable carbon is believed to be physisorption of CO_2 to the carbon surface. Upon immersion into water, the CO_2 desorbs and reacts with water to form carbonic acid (H_2CO_3). As with air treatment, it is proposed that the CO_2 treatment balances out the basic effects of the anion-exchange or calcium chemistry mechanisms.

4.1.2 Effect of Oxidation on Activated Carbon

The addition of oxygen to the surface of an activated carbon has been shown to alter its wettability, catalytic and electronic properties, as well its adsorption capabilities (Puri 1970, Bansal et al. 2002, Szymański 2002). Acidic oxygen-containing functional groups are mainly present on the outer surface or edge of the basal plane due to limited diffusion into the micropores (Puri 1970, Menendez et al. 1996, Ania et al. 2004). As these outer sites constitute the majority of the adsorption surface, the concentration of oxygen on the surface has a great impact on the adsorption capabilities of the carbon (Puri 1970).

The presence of oxygen imparts a polar nature to the activated carbon, which results in a preference for removal of the more polar component of a solution, e.g., H₂O (Kipling and Gasser 1960). El-Sayed et al. (2003) found that the adsorption of valeric acid onto activated carbon decreased as the density of acid groups on the surface increased. El-Sayed et al. (2003) suggested that the polar nature of the activated carbon surface, associated with its high surface oxygen group content, resulted in the preferential adsorption of water molecules. In addition, the presence of carboxylic groups acted as physical obstacles to the interaction of the valeric acid and the activated carbon surface. Bansal et al. (2002) also attributed the decrease in phenol adsorption with increased oxidation of activated carbon to the increasing hydrophilic character of the oxidized carbons. Ania et al. (2004) found a decrease in the adsorption of salicylic acid as the oxygen-containing functional groups increased at low adsorbate concentrations. At high levels of salicylic acid, however, Ania et al. (2004) found that the adsorption capacity of the carbon was similar to an activated carbon that had not been oxidized and proposed that the higher concentration of valeric acid allowed the water molecules adsorbed onto the hydrophilic carbon sites to be displaced.

Pendleton et al. (1997) researched the effects of surface chemistry on the adsorption of MIB and linked decreased adsorption with an increase in the hydrophilic nature of the oxidized carbon. They also found a strong correlation ($R^2=0.99$) between oxygen content and the number of hydrophilic sites. A subsequent study by the same research team (Considine et al. 2001) further supported the link between oxygen content and decreased adsorption of MIB. In this study, the adsorption of MIB in a dichloromethane solvent, a non-polar solvent, was investigated as well, as opposed to

previous experiments in water. The results showed that adsorption of MIB was independent of oxygen content in this solvent; further supporting the contention that adsorption of water as a result of oxidation impedes MIB adsorption.

Karanfil and Kitis (1999) found that surface oxidation, and the resulting density of strong acid functionalities, also decreased the adsorption of dissolved organic matter (DOC) (the dissolved portion of NOM). Water clusters forming around the polar (hydrophilic) functional groups on the surface reduced the ability of the DOC to reach the smaller pore sizes needed for its adsorption.

The chemisorption of oxygen and the resulting functional groups have been found to destroy π -electrons due to electron localization (Leon y Leon et al. 1992, Ania et al. 2004). The adsorption of phenol has been attributed to the electron-donor acceptor complexes formed between the basal planes on the surface of the carbon and the aromatic ring of the phenol (Bansal et al. 2002, Ania et al. 2004). A decrease in phenol adsorption on oxidized samples has been shown by a number of researchers (Bansal et al. 2002, Ania et al. 2004). As the bonding sites are destroyed through chemisorption of oxygen, the adsorption of phenol decreases (Ania et al. 2004). Pereira et al. (2003) performed a study on anionic dye (acidic), where the presumed adsorption mechanism involved the delocalized π -electrons of the carbon surface and the free electrons of the dye molecule, and found that the adsorption of the anionic dye was hindered by the presence of acidic oxygen-containing functional groups on the surface of the activated carbon. It should be noted that, in addition to both the increased hydrophilicity and the destruction of π -bonds, the chemisorption of oxygen may lead to the formation of acidic-oxygen containing

functional groups creating a weakening in the donor-acceptor (acid/base) adsorption mechanism (Ania et al. 2004).

4.2 Experimental

4.2.1 Air Treatments and CO₂ Treatments

Air treatments were conducted in ambient air using a muffle furnace; a front-loading box-type oven used for high temperature applications up to 1200°C. A composite of the three reactivated NORIT samples containing the highest calcium content was created and three grams of this composite were placed in crucibles for 15, 30, and 60-minute increments at the desired temperature inside the muffle furnace. The air treatment temperatures used were 350°C, 400°C, and 450°C. These temperatures were chosen based on research showing that the maximum chemisorption of oxygen and maximum capacity to adsorb bases occurs around 400°C (Puri 1970). After treatment, the samples were allowed to cool in a desiccator before water contact pH and Boehm titration experiments were performed.

A clamshell furnace similar to that used by Mazyck and Cannon (2000 and 2002) held a quartz-fluidized bed wherein CO₂ treatments were carried out at ambient temperatures. A porous plate near the center of the quartz-fluidized bed allowed a flow of 0.5 L/min of CO₂ to contact three grams of sample for 20 minutes for an exposure of 0.15 mole CO₂/g composite.

4.2.2 Boehm Titration

The concentrations of acidic oxygen complexes created on the surface of the reactivated composite samples were determined according to the Boehm titration method (Boehm 1966). An allotment of 0.5 g of composite and 25 mL of 0.1 N NaOH were

shaken in sealed vials for three days. The suspensions were then filtered using a 0.45 μm filter and 20 mL of the filtrate was titrated with 0.1 N H_2SO_4 . The amount of base (NaOH) consumed by each sample was determined by comparing each titration to that of a blank. Any base consumed by the sample is expected to result from the neutralization of carboxylic, lactonic, and phenolic groups, thereby quantifying the surface acidity of the composite samples.

4.2.3 Equilibrium Isotherms

Equilibrium isotherms were used to compare the adsorption capabilities of the composite samples. The target compound was MIB as the removal of this substance represents the primary use of GAC; removal of taste and odor causing compounds. First, a 0.5 L stock solution of 153 ng radiolabeled MIB/L was created by blending 95.7 μL of an 800,000 ng MIB/L-methanol stock solution with 500 mL of either deionized water or raw water influent to the Manatee County Water Treatment Plant. From the 153 ng radiolabeled MIB/L solution, 4-50 mL allotments were added to separate gas tight syringes followed by addition of enough of a powdered composite sample to create 5, 10, 20, or 40 ppm powdered reactivated carbon solutions. Grinding the treated composites in a crucible and sieving the resulting particles through a 325 mesh (45 μm) sieve created the powdered composites. The syringe was then sealed, permitting for a small amount of headspace and allowed to mix on a rotisserie style mixer. After 24 hours, a 0.45 μm luer-lock nylon filter, attached to the syringe, separated the powdered composite from 3 mL of the solution which was then tested according to previous studies using radiolabeled MIB (Gillogly et al. 1998, Tennant and Mazyck 2003, Nowack et al. 2004). Each sample was measured twice for MIB and the mean of these two runs was used for the final value.

The measurements of the replicates were within $\pm 2\%$ of one another. The entire process, starting with 4-50 mL samples of either deionized or raw water influent to the Manatee County Water Treatment Plant were repeated for each composite for which an equilibrium isotherm was desired.

Adsorption is usually modeled by isotherms, which relate the relative concentrations of solute adsorbed to the solid to the concentration in solution. The adsorption isotherm is defined as the constant temperature relationship between the quantities of adsorbate that is adsorbed per unit of adsorbent combined with the equilibrium concentration of adsorbate in solution.

When a mass of adsorbent and a waste stream are in contact for a sufficiently long time, equilibrium between the amount of pollutant adsorbed and the amount remaining in solution will develop. For any system under equilibrium conditions, the amount of material adsorbed onto the media can be calculated using the mass balance of

$$q_e = (C_{in} - C_e) \frac{V}{M} \quad (6)$$

where q_e is the mass of pollutant per mass of media [expressed as mg target contaminant /g powdered composite], C_{in} is the initial target contaminant concentration in solution, C_e is the concentration of the target contaminant in solution after equilibrium has been reached, V is the volume of the solution to which the powdered composite mass is exposed, and M is the mass of the powdered composite.

The most commonly used isotherm to model the adsorption of contaminants onto activated carbon is the Freundlich isotherm (Snoeyink and Summers 1999). The general form of the Freundlich model is

$$q_e = K_F C_e^{1/n} \quad (7)$$

where K_F and n are calculated from graphing the linear form of the equation shown below.

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln C_e \quad (8)$$

4.3 Results and Discussion

4.3.1 Air and CO₂ Treatments Versus Water Contact pH

A composite of the three reactivated GACs with the highest calcium content was subjected to several treatments with either air or carbon dioxide in an attempt to create a pH stable carbon, i.e., a composite with a water contact pH less than 8.5 pH units, as this pH falls between the NPDES permitted discharge pH of 6 to 9 while still allowing for a small safety factor. The resulting water contact pH of the treated composites are shown in Figure 7. A dashed line at a water contact pH of 8.5 highlights those treatments that created a pH stable carbon, those beneath this dashed line. The first bar shows the water contact pH of the untreated composite. A treatment time of 15 minutes in the presence of air did not create a pH stable carbon regardless of the temperature used, though these water contact pHs are less than the untreated composite. Treatment times of both 30 and 60-minutes in the presence of air are shown to create pH stable carbons regardless of the treatment temperature. It is expected that the longer treatment times would yield a decreased water contact pH compared to the 15-minute treatment time, as more oxygen would be chemisorbed to the surface to create more of the acidic oxygen-containing functional groups that will overcome the addition of hydroxyl ions due to the proposed calcium chemistry mechanism. The carbon dioxide treatment scenario, carried out at ambient temperature with a carbon dioxide flow of 0.5L/min for 20 minutes also created

a pH stable carbon. The results of these treatments support the patents that claim to overcome pH excursions via air treatments (Dussert et al. 1997) and carbon dioxide treatments (Farmer et al. 1998).

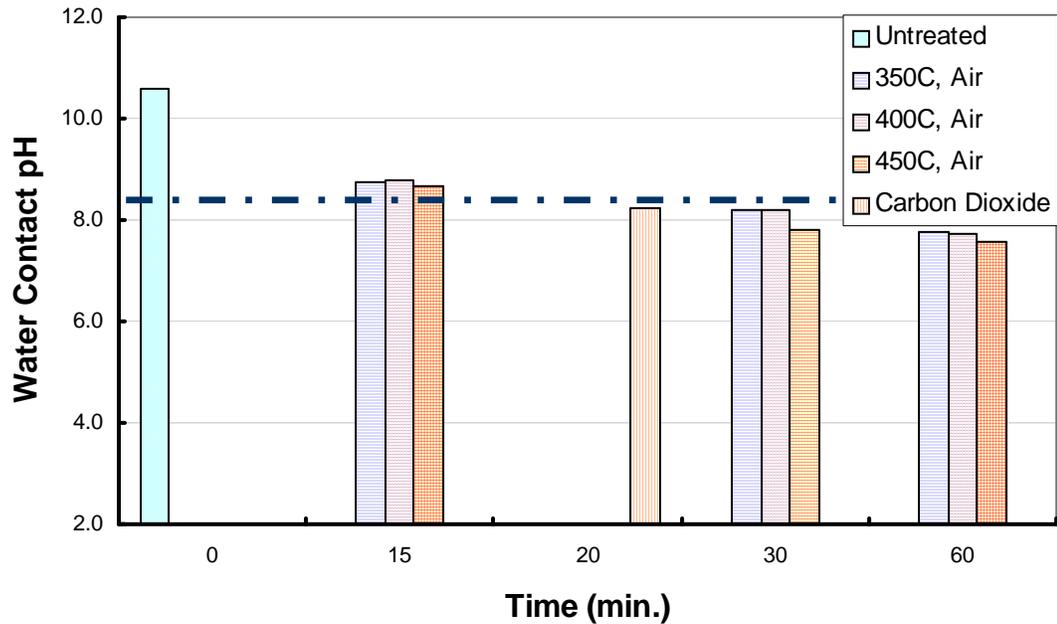


Figure 7. Effect of air and CO₂ treatments on water contact pH. Dashed line represents a pH of 8.5.

4.3.2 Total Surface Acidity of Treated Carbons

The proposed mechanism behind air treatments yielding a pH stable carbon is that oxygen chemisorbs to the surface of the GAC creating acidic oxygen-containing functional groups. The total acidity of the treated composites is shown in Figure 8. As expected, the air treated composites show an increase in total acidity compared to the untreated composite. Air treatment of increased duration yields an increasing total acidity, reflecting the finding that increased duration of air treatments yields pH stable carbons. The highest total acidity for each time-increment is at an air treatment temperature of 400°C. This result is expected from Puri's (1970) finding that the

maximum chemisorption of oxygen and creation of acidic carboxylic groups on the surface of the GAC occur around 400°C.

The carbon dioxide treatment yielded a total acidity close to the total acidity of the untreated composite. The result supports the hypothesis that a pH stable carbon is created with carbon dioxide treatment as a result of physisorbed carbon dioxide which dissolves upon contact with water, rather than by the addition of acidity, as is the case with air treatments.

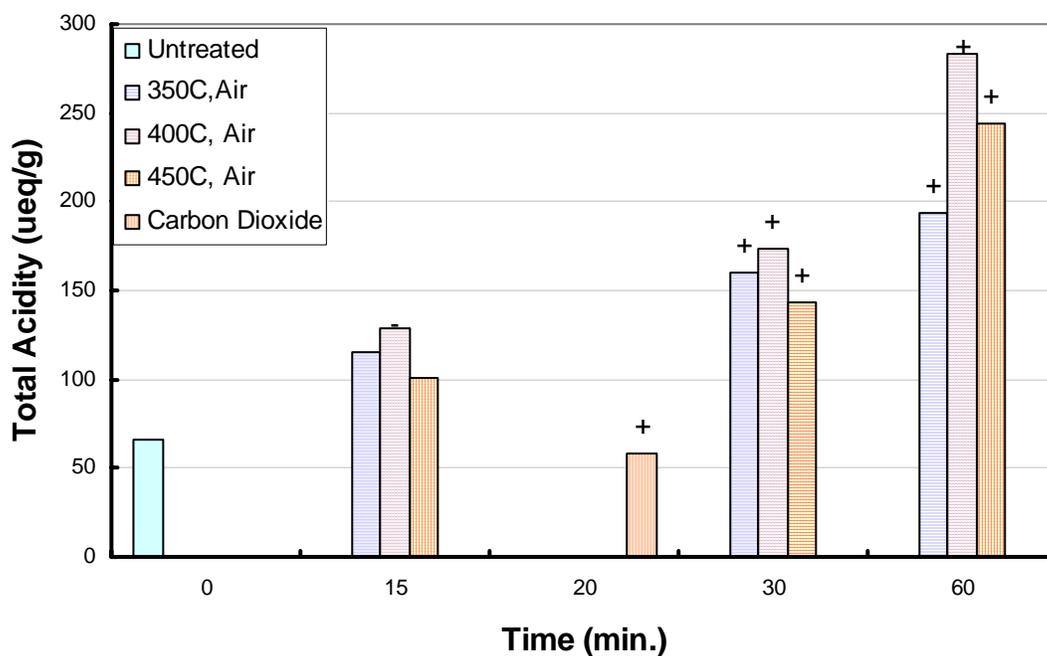


Figure 8. Effect of air and CO₂ treatments on total surface acidity. A pH stable carbon is indicated by a (+).

4.3.3 Comparison of MIB Adsorption Capability

To determine the effect that the treatments designed to create pH stable carbons have on adsorption, the air treated composite that yielded the highest total acidity, the carbon dioxide treated composite, and an untreated composite were evaluated for their removal of MIB in both deionized water and natural water (containing NOM). The

percent removal of MIB in deionized water versus the dose of composite is shown in Figure 9.

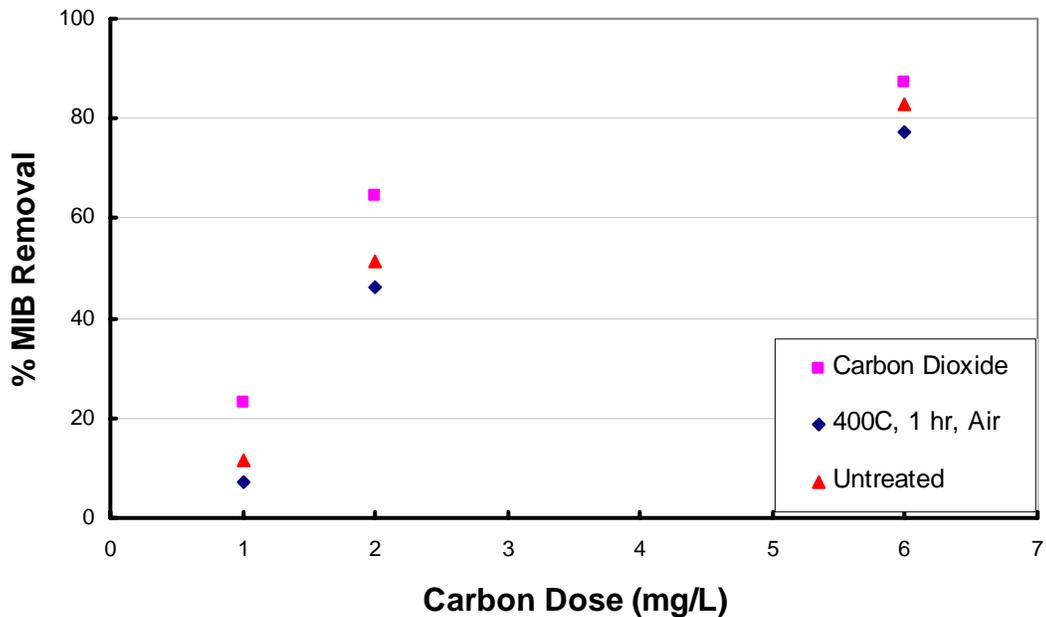


Figure 9. Equilibrium adsorption of MIB in deionized water versus the dose of the composite.

The air treated composite does not remove as much MIB as the untreated composite because the air treated composite has a higher total surface acidity. An increase in total surface acidity has been shown to have a negative effect on the adsorption of MIB due to the preference of the created acidic functional groups for water adsorption, as opposed to the adsorption of MIB (Pendleton et al. 1997, Considine et al. 2001). Given this explanation, one would expect that the carbon dioxide treated composite and the untreated composite would have comparable MIB removal, as their total surface acidity is similar (Figure 8). The results of Figure 9, however, show that the carbon dioxide treated composite removes significantly more MIB than the untreated composite.

A preliminary explanation for this occurrence was that some of the carbon dioxide to which the activated carbon was exposed chemisorbed to the active sites on the carbon surface, rendering them inactive. Active carbon sites would form acidic functional groups upon water contact and, as has been discussed, the resulting sites will prefer adsorption of water to MIB adsorption. By inactivating these sites, the carbon dioxide treated composite would have less water adsorption than an untreated sample. To determine if this proposed mechanism is plausible, approximately 0.14 g of sample were suspended in an enclosed bottle containing 150 mL of deionized water. After 36 hrs, the sample was weighed and the percent of water vapor adsorbed was determined. The carbon dioxide treated composite was found to adsorb 6% less water vapor than the untreated composite. However, the 6% difference in water vapor adsorption may not adequately explain the approximate 15% difference in MIB removal between the carbon dioxide treated composite and the untreated composite. Also, Figure 8 shows comparable surface acidity between the carbon dioxide treated and untreated composite and the carbon dioxide treated composite should have a lower surface acidity than an untreated composite if the inactivity theory is correct and such is not the case. Though, it may be that the type of acidic functional group is important, rather than the total acidity. The mechanism behind the increase in adsorption of MIB with a carbon dioxide treated composite remains unclear and warrants further research.

In typical water treatment, other constituents in the influent water may compete with MIB for adsorption onto the carbon surface. NOM is ubiquitous in surface waters and the concentration of NOM can be 100,000 times that of the trace contaminant MIB. The presence of NOM has been shown to decrease the removal of MIB via competitive

adsorption (Newcombe et al. 2002, Tennant 2004). To determine how the composites perform in natural water, i.e., that containing NOM, a solution was made with influent water from the Manatee County Water Treatment Plant and subsequently dosed with enough MIB to make 153 ng/L MIB. As with the deionized water experiments, four separate doses of the composites were added to the Manatee solution and allowed to mix for 24 hrs. The MIB removal results in Manatee water are found in Figure 10.

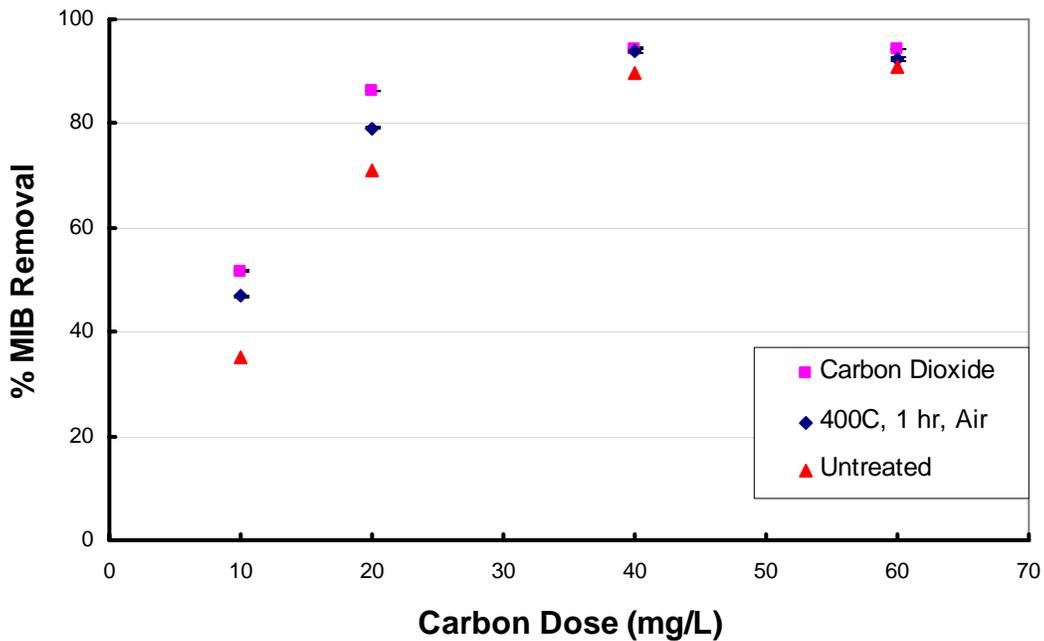


Figure 10. Equilibrium adsorption of MIB in Manatee water versus the dose of the composite.

Unlike the deionized water scenario, the air treated composite removed more MIB in natural water than did the untreated composite. NOM can adsorb through electrostatic forces, wherein the negative charge of the NOM is attracted to a positive charge on the carbon surface (Newcombe et al. 1999). Tennant (2004) has shown that an increase in adsorption of NOM onto carbon is linked to a decrease in the adsorption of MIB. The point of zero charge (PZC) is the pH at which the carbon surface is neutral. Any water

pH below the PZC will produce a positively charged surface and a water pH above the PZC will create a negatively charged surface. An acidic PZC is often indicative of a wealth of surface acidic groups, while a basic PZC has a low number of surface functional groups. The PZC can be related to the water contact pH in that both experiments employ conditions where carbon dominates the system, 10% by weight for the PZC measurements and 2.5% by weight for the water contact pH experiment. A water pH below the water contact pH will create a positively charged surface that will attract the negatively charged NOM. The untreated composite, with a water contact pH of 10.6, in contact with a Manatee water pH of approximately 7, will have a significant positive surface charge. The untreated composite will therefore adsorb more NOM and, as there are fewer adsorption sites available after NOM adsorption, less MIB adsorption would occur. The air treated composite, with a water contact pH of 7.75, in contact with a Manatee solution pH of approximately 7, will have less of a positive surface charge and will therefore not attract as much NOM, leaving more adsorption sites available for MIB.

As in deionized water, the carbon dioxide treated composite removes more MIB than both the air treated composite and the untreated composite in the natural water system. The mechanism may or may not be the same mechanism that causes carbon dioxide treated composites to remove more MIB than other composites in deionized water. Again, the mechanism behind increased adsorption of MIB with a carbon dioxide treated composite is unclear and warrants further research.

The conversion of the removal data into a Freundlich isotherm supports the finding that carbon dioxide treatment creates a carbon better suited for the removal of MIB compared to air treated composites and untreated composites. A linear trendline

was added to each of the composite data points in order to determine the Freundlich values. The equations of the linear trendlines, as well as the R^2 values for the trendlines and the calculated K_F and $1/n$ values, Equation 8, for each of the composites are shown in Table 3.

Table 2: Freundlich values for MIB removal in Manatee water

Composite	Linear Equation	R^2	K_F	$1/n$
Carbon Dioxide Treated	$y = 0.47x + 0.14$	0.78	1.56	0.47
Air Treated	$y = 0.45x + 0.07$	0.77	1.08	0.45
Untreated	$y = 0.64x - 0.69$	0.95	0.93	0.64

The trend in K_F follows the removal trend shown in Figure 10, in that the carbon dioxide treated composite has a higher adsorption capacity for MIB than either the air treated or untreated composite and the air treated composite has slightly less of an adsorption capacity for MIB compared to carbon dioxide treated composites. While the untreated composite shows a much higher $1/n$ value than either the air or carbon dioxide treated, which is expected, the difference in the $1/n$ value for air and carbon dioxide treated is small. The similar $1/n$ values with air and carbon dioxide treated composites suggest a common adsorption mechanism that yields similar strengths of adsorption.

4.4 Conclusions

The results of this research support the patents of Dussert et al. (1995) and Farmer et al. (1998), which state that air treatments and carbon dioxide treatments can create pH stable carbons. A comparison of the total surface acidity of the treated carbon showed that air treatments have a higher surface acidity than both carbon dioxide treated and untreated carbons. These findings suggest that air treatments add acidic oxygen-

containing functional groups, which balances the basic solution pH resulting from the calcium chemistry mechanism. Carbon dioxide treatments, on the other hand, were not found to yield an increase in total surface acidity. Carbon dioxide is thought to physisorb to the carbon surface and upon immersion in water it desorbs forming carbonic acid in solution that balances the basic solution pH produced by the calcium chemistry mechanism.

The performance of the treated composites was evaluated via removal of MIB. The air treated carbon removed the least amount of MIB in deionized water as the acidic oxygen-containing functional groups on the surface of the carbon create a preferential adsorption of water over MIB. MIB in deionized water was adsorbed more by carbon dioxide treated carbons than either the untreated or air treated carbons. The mechanism behind the increase in MIB adsorption with carbon dioxide is not clear but it was not found to result from a decrease in the number of active sites, as this would be linked with a decrease in total surface acidity for the carbon dioxide treated carbon compared to the untreated carbon, which was not supported by the data.

Evaluation of MIB removal in a natural water containing NOM, found that, unlike MIB removal in deionized water, the air treated composite removed more MIB than the untreated composite. The difference here is that NOM out-competes MIB for adsorption sites. The surface of the untreated composite has a positive charge that attracts the negatively charged NOM, thus leaving fewer sites for MIB adsorption. Air treatment creates a more acidic surface, where the positive charge of the surface is not as strong, thus not as much NOM is attracted to the surface, so that MIB may adsorb with minimal competition from NOM. In both deionized water and natural water containing NOM,

carbon dioxide treatment performed better in removal of MIB than the untreated carbon or the air treated carbon. The reason behind this is unclear and warrants further research. The results do indicate, however, that treatments to create pH stable carbon affect the adsorption capacity of the carbon and, as such, a treatment to create pH stable carbons should be evaluated for its affect on adsorption capabilities before being used to create pH stable carbons for use in a water treatment plant.

CHAPTER 5 CONTRIBUTIONS TO SCIENCE

- Calcium chemistry ($\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$; $\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$) is a plausible mechanism behind pH excursion when reactivated carbon is returned to service. Also, the concentration of other metals in the reactivated carbon, such as aluminum, iron, and magnesium, were minimal compared to the concentration of calcium in solution, thus highlighting the role of calcium chemistry in pH excursion over the chemistry of other metals;
- The anion exchange mechanism was not found to explain pH excursions with reactivated carbon as pH excursions occurred even when nanopure water was used in the experiments. Nanopure water is not expected to contain the anions required to participate in the anion exchange mechanism;
- Air and carbon dioxide treatments created pH stable carbons. Air treatments at 350-450°C for 0.5-1 hr balanced pH excursions through the creation of acidic oxygen-containing functional groups on the carbon surface. Carbon dioxide treatment at ambient temperatures for 20 min. were proposed to allow carbon dioxide to physisorb to the carbon surface and then desorb upon contact with water, resulting in the creation of carbonic acid, which balances the pH excursions;
- Carbon dioxide treated GACs removed more MIB, a trace contaminant, than either air treated or an untreated composite. The relative removal of MIB for air treated and untreated composites likely depended on the preference of the carbon for water adsorption and also surface charge, which will have an effect on the electrostatic attraction of the carbon for NOM, which competes with MIB for adsorption onto the carbon surface. The mechanism behind the increased removal of MIB with carbon dioxide treated composites is unclear and warrants further research.

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BIOGRAPHICAL SKETCH

I was born on July 25, 1980, in St. Petersburg, Florida, where my mother, Teresa Bach, also raised me. I graduated from Gibbs High School in June 1998. From there, I traveled to Gainesville, Florida, to attend the University of Florida where I received my Bachelor of Science degree in Environmental Engineering Sciences with highest honors.

I stayed on at the University of Florida to work on my Master of Engineering degree with Dr. David W. Mazyck in the field of environmental engineering sciences. Subsequent to the completion of my master's work, I will endeavor to attain a Doctor of Philosophy degree in environmental engineering sciences, also under the guidance of Dr. David W. Mazyck.