

pH EXCURSIONS IN WATER TREATMENT FOLLOWING INSTALLATION OF REACTIVATED GAC: CAUSATION AND CONTROL

David W. Mazyck,¹ Fred S. Cannon,² and Ljubisa R. Radovic³

¹Department of Environmental Engineering Sciences,

306 AP Black Hall, PO Box 116450, University of Florida, Gainesville, FL 32611

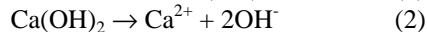
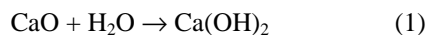
²Department of Civil and Environmental Engineering, 212 Sackett Building,

³Department of Energy and Geo-Environmental Engineering, 205 Hosler Building,
The Pennsylvania State University, University Park, PA 16802

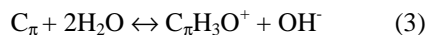
Introduction

Water utilities reactivate their spent granular activated carbon (GAC) to return this exhausted material close to its virgin capacity because reactivation is less expensive than purchasing virgin carbon. Thermal reactivation has its advantages, but the solution to two potential problems can help improve its effectiveness. The first is to avoid the deleterious effects of calcium catalysis; it is addressed by developing a new thermal reactivation protocol (steam-curing) [1-3]. The second is to avoid pH excursions [4]: some utilities have reported that the water pH becomes as high as 11 over a period of several weeks, and they now require that their reactivated GAC maintain a stable pH (6.5-8.5) when it is placed back in service.

The objective of this study was to scrutinize the possible mechanisms for these pH excursions and to tailor the carbon so that, when returned to service, water pH is not affected. One explanation for these pH excursions is calcium chemistry. During potable water treatment, calcium can adsorb onto GAC as a complex with natural organic matter (NOM) [5]; Ca is also native in many coal-based carbons. During thermal reactivation, the adsorbed Ca converts to CaO upon decomposition of NOM [1]. When the reactivated carbon is returned to service, CaO is converted to Ca(OH)₂ (equation 1). Furthermore, Ca(OH)₂ can dissolve and subsequently dissociate to Ca²⁺ and 2 OH⁻ (equation 2). The release of OH⁻ would elevate the pH of the subsequently treated water.



Mechanisms based on carbon basicity are also plausible. Leon y Leon et al. [6] support a mechanism involving electron donor/acceptors (EDA) (equation 3) and pyrone-type sites.



The basic C_π sites could adsorb protons from solution with enough strength to render the surface positively charged. The basicity of pyrone-type sites is another possibility. Menendez et al. [7] supported their importance and argued

that complex (tricyclic) pyrones, which are located at the edges of graphene layers, can have a pK_a ca. 12.7.

A mechanism involving anion exchange with hydroxide ions following carbon protonation has also been proposed. Because of exposure to high temperatures in a reducing atmosphere during manufacturing and reactivating, Farmer and coworkers [4,8] suggested that the H-type activated carbons preferentially adsorb strong acids [6]. After such protonation, the carbon surface will charge-neutralize with sulfate, chloride, or other anions present in water. If these anions are absent, the neutralization of the carbon surface would occur with the hydroxide ions formed upon hydrolysis of water that provided the protons. Furthermore, these authors proposed that charge neutralization occurs on the carbon surface by exchange between sulfate and hydroxide anions.

In none of these studies [4,6,8] was the concentration of Ca monitored, so Ca chemistry was the focus of our investigation.

Experimental Section

Several coal-based reactivated GAC samples were received from NORIT Americas, Inc. from their Pryor, OK plant. These carbons had been used for potable water treatment, became spent, and were subsequently reactivated. Their Ca contents were measured by emission spectroscopy; the reproducibility of these determinations was within ± 0.2%.

The water contact pH for the carbons was determined by dispersing ca. 2 g GAC in 80 mL of Milli-Q (organic free) water for 30 min [4,8]. In initial exploratory experiments, pH measurements (following standard procedure 4500-H⁺) were taken every 5 min; after 20-30 min a pseudo-equilibrium level was reached (< 0.1 pH units change over 5 min). This batch test [4] predicted quite well the pH of water that passed through a full-scale GAC adsorber. The reproducibility was good also: the pH of six out of seven samples varied less than ± 0.2 units.

Results and Discussion

Figure 1 illustrates typical pH excursion and Ca concentration changes immediately following the installation of reactivated carbon. It is seen that, as the pH excursion diminished, the calcium concentration in the effluent decreased; this result supports the hypothesis that calcium hydroxide leached out of the GAC and dissociated to form Ca^{2+} and OH^- .

When the reactivated carbons were received, their water contact pH and Ca content were determined immediately. Figure 2 also suggests a very strong correlation between the two variables.

Based on equation 2, if Ca concentration in solution is measured after the pH excursion, it can be used to predict the water pH based on simple stoichiometry. Figure 3 shows the result: the relationship is very linear and the predicted pH was always over-predicted by the same amount (ca. 0.4 pH units).

To isolate further the importance of Ca chemistry, a spent carbon was first washed with HCl, then freed from any residual H^+ by rinsing with deionized distilled water, and then reactivated. Its pH was compared to that of the conventionally reactivated carbon, which contained Ca, and found to be considerably lower (8.5 vs. 11.5). Interestingly, this is still greater than the pH of water (i.e., 6-7), suggesting that the other pH excursion mechanisms (e.g., those due to carbon basicity) may also be important.

Conclusions

The controlled laboratory tests presented here demonstrate that calcium chemistry plays a key role in pH excursions which are of so much concern to the water utilities. While this study does suggest ways to eliminate some of the deleterious side-effects of thermal reactivation, additional work will focus on further quantifying the relative contributions of the various mechanisms responsible for the pH excursions.

References

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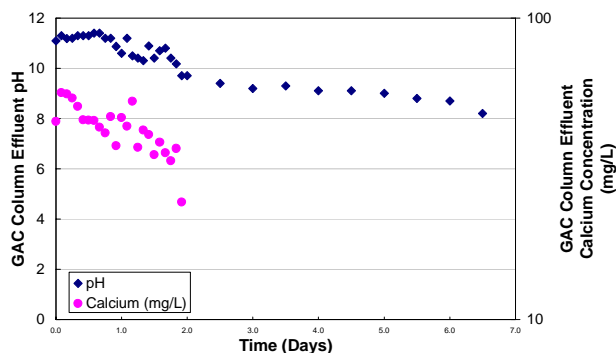


Figure 1. Effluent pH and calcium concentration immediately following installation of reactivated GAC.

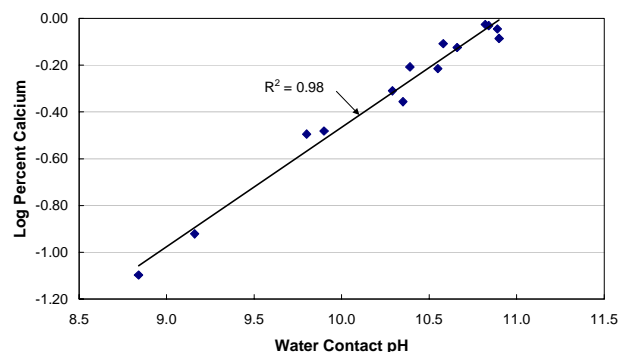


Figure 2. Log of GAC percent calcium versus the water contact pH exhibited by each carbon sample.

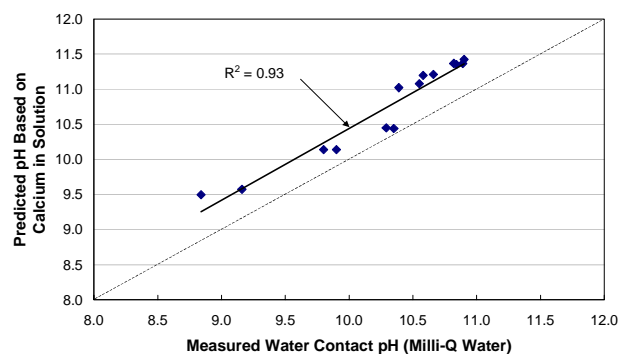


Figure 3. Predicted pH based on calcium that leached out of the GAC during the water contact pH experiment versus the actual measured water contact pH.