

CALCIUM ACCUMULATION BY GAC IN THE PRESENCE OF NOM

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Introduction

Calcium is abundant in raw waters and can impact several facets of water treatment. Calcium can complex with natural organic matter (NOM). In water service operation, calcium can load onto GAC in amounts reaching 1% of the GAC mass.¹ Upon return of regenerated carbons to water service operation, the pH of the treated water becomes elevated possibly resulting from $\text{Ca}(\text{OH})_2$ release from the regenerated GAC. Calcium can catalyze the gasification of carbon when thermally regenerating water treatment GACs.¹ This catalysis results in a wider pore structure and a loss of micropores, thus preventing the restoration of the virgin pore structure and reducing efficiencies for removing small organic compounds. Thus by reducing calcium buildup in GAC, a utility can improve GAC reactivation. In order to understand and control the impacts of calcium, the fundamental question of how calcium loads onto GAC must be addressed. The objective of the research presented here was to determine the effects of NOM and time on calcium accumulation by GAC.

Experimental

Batch tests were conducted. Four liters of a raw water from New Castle, PA were reacted with 0.6 g acid washed Filtrasorb 400. This raw water contained 4.5 to 5.5 mg/L TOC, 25 to 35 mg/L Ca, and 0.1 to 1.0 mg/L Fe. The pH and iron dose were varied. The reactors were incubated for 1 to 5 weeks. The contents of the reactors were separated after this incubation period. GAC was removed using a 100 mesh sieve, dried to a constant weight at 105°C, ashed in a 550°C furnace and treated with nitric acid to extract the metals. Iron and calcium concentrations in the resulting solution were measured and used to determine the iron and calcium loading by the GAC. The reactor solution was filtered through a 0.7 micron Whatman glass fiber filter. The filtrate was analyzed for total organic carbon (TOC) using a Dohrmann Carbon Analyzer. Calcium and iron measurements in the filtrate and ash extract were made using a Perkin Elmer 3030b Atomic Adsorption Spectrophotometer.

Results and Discussion

Initially, several batch reactors were incubated for a 1 week pseudo-equilibrium period. Below a pH of 5.5 the calcium accumulation was generally consistent with the background levels (135 ± 27 mg/kg Ca). Above a pH of 5.5, calcium accumulation increased. When ferric chloride was added to the reactors, this increase was not as significant as without the iron.^{2,3}

Several tests were performed to assess the impact of NOM on calcium accumulation. When NOM was present (Figure 1 [■]), calcium accumulation was significantly greater than when deionized (DI) water was used and NOM was absent (Figure 1 [*]). Experimentally, calcium accumulation has been shown to be strongly dependent upon TOC. For a 1 week incubation time at a constant pH with no added iron but variable GAC doses, the calcium accumulation has a strong linear correlation with the TOC adsorbed (Figure 2).

Several reactors were incubated with New Castle raw water for two weeks (Figure 1 [▲]). This source water is designated as source B and was sampled at a different time than previously (source A). The calcium accumulation was much greater in the GAC incubated for 2 weeks with source B than in the GAC incubated for 1 week with source A (Figure 1 [■]), although additional TOC removal during week 2 was minimal and initial TOC levels in the two batches of source water was comparable.

Intriguingly, the difference in calcium accumulation between these two conditions was not observed when ferric chloride was added to the reactors.² When 5 mg/L iron was added, calcium accumulation by GAC was approximately the same for the two conditions. As determined previously,³ the addition of iron interferes with the mechanism of calcium accumulation by GAC, thereby reducing the overall calcium accumulation. This reduced accumulation may be a result of the ability of metals to coagulate the NOM and alter its characteristics.⁴

The next set of experiments tested if the increased calcium loading was a result of the increased

incubation time or the effect of source water variations. A common source water from New Castle, PA (source C) was incubated for 1, 2, and 5 weeks at various pH values from 5 to 7.5. Calcium accumulation for these time intervals was the same regardless of incubation time as shown in Figure 3. This result demonstrates that calcium accumulation by GAC has reached equilibrium in a 1 week incubation period. The variability in calcium accumulation that was observed in previous experiments was most likely a result of the variations in the source water. Although these two waters had comparable TOC levels, the character of the water was apparently different and it caused the changes in the calcium loading.

Conclusions

The following conclusions were developed based on this research:

- 1) Calcium loading by GAC can be correlated to NOM loading onto GAC.
- 2) Iron coagulants interfere with calcium loading onto GAC.
- 3) Longer incubation time does not result in increased calcium loading by GAC in batch reactors.
- 4) Variability in the chemistry of the source water apparently causes variations in calcium loading in the presence of NOM.

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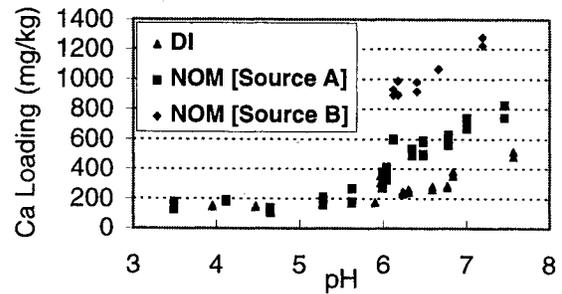


Figure 1. Calcium loading by GAC in the presence and absence (DI) of NOM.

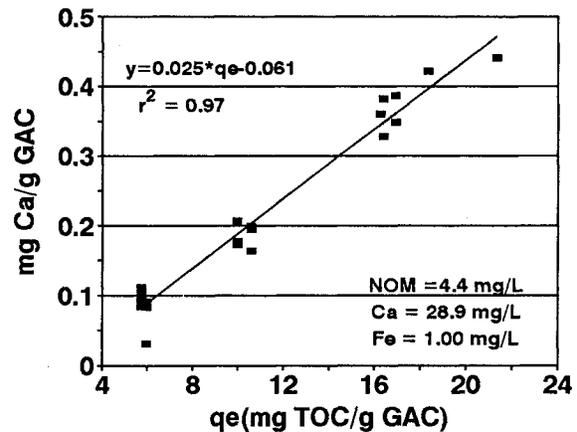


Figure 2. Calcium loading by GAC versus TOC adsorbed at pH 7.3.

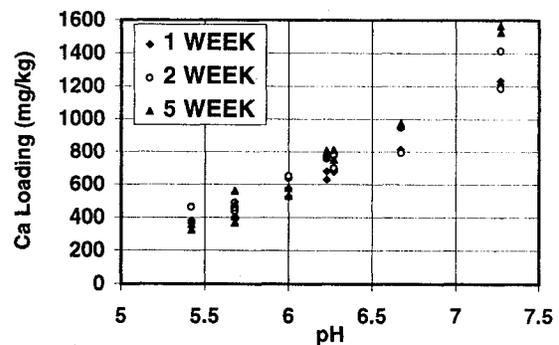


Figure 3. Calcium loading by GAC at various incubation times with identical source water (source C).