The Role of Aluminum within MnO$_x$(s)-Coated Filtration Media in Drinking Water Treatment

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ABSTRACT

The Mn oxide (MnO$_x$(s)) surfaces of water treatment filtration media are known to aid in the capture of dissolved Mn species, but the discovery of significant deposits of Al within these coatings raised several questions about the MnO$_x$(s) surface. A series of experiments and analyses were performed to examine the presence of Al within MnO$_x$(s) coatings formed on water treatment filtration media. It was hypothesized that the presence of Al within the MnO$_x$(s) coatings might have an impact on the capture of Mn by the MnO$_x$(s) surface. A 2008 study of oxide coated filtration media found that Mn and Al are present in nearly equimolar quantities within the oxide coatings. This led to questions of how and why the Al became incorporated into the surface. This phenomenon was analyzed by conducting a series of bench-scale column studies, treatment plant data collection, and analysis of the MnO$_x$(s) surface utilizing an electron microscope. The results confirm that Al deposits onto the MnO$_x$(s) media surface by two separate mechanisms; adsorption of dissolved Al species and the deposition of colloidal and particulate Al(OH)$_3$(s) precipitate species onto the surface. Analysis of the MnO$_x$(s) coating by electron microscopy shows a heterogeneous surface composed of a mix of crystalline Mn oxides existing alongside amorphous Al(OH)$_3$(s) species. The deposition of Al onto the media surface does not have any significant effect on the removal of soluble Mn, but the potential impact that Al might have on the capture of other dissolved species should be explored further.
Dedicated to my father, who inspired me to become an engineer
ACKNOWLEDGMENTS

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INTRODUCTION

The use of Aluminum (Al)-based coagulants has been standard practice in municipal drinking water treatment processes for decades. Al serves as a highly effective coagulant aiding in the capture of solids through sedimentation and filtration processes (Amirtharajah, 1990).

The addition of Al in water treatment has several intended and well-studied effects on the final water quality of the treated effluent, but one unexpected outcome of Al addition has not been previously studied in detail and is the subject of this research study. A 2008 study on drinking water Manganese (Mn) control suggested the potential for a previously unrecognized chemical relationship between Mn and Al (Tobiason et al., 2008). The questions raised by this study provided the impetus for this new research study, which sought to more closely examine how the Mn and Al might interact in a water treatment setting and what effect Al might have on the capture of soluble Mn by Mn oxide coated filtration media.

It is not uncommon for water treatment plants to apply a dosage of free chlorine (HOCl) across their filters in order to achieve a high degree of Mn removal in drinking water. This practice allows for the capture of soluble Mn by adsorption and then subsequent oxidation on the surface of the filtration media. Oxidation by the free chlorine converts the adsorbed soluble Mn (Mn^{2+}) to an insoluble Mn oxide (MnO_{x(s)}) which is then incorporated into the oxide coating. The formation of an oxide coating has been observed on several different types of media, including anthracite coal and sand filtration media (Knocke et al., 1988, Coffey et al., 1993, Islam et al., 2010).

The 2008 AWWARF report on drinking water Mn control gathered filtration media from several Mid-Atlantic region surface water treatment facilities. Several of the facilities that participated in the study applied free chlorine across their filters in order to achieve Mn control. During the study, samples were collected and the accumulated MnO_{x(s)} coatings of the filtration media were extracted in order to quantitatively measure the metal composition of the coatings. The extraction analysis of the MnO_{x(s)} coatings yielded an unexpectedly high Al content. Even more surprising was the relatively consistent molar ratio of Al to Mn found in the coatings. A similar molar ratio between the two metals was observed even when comparing media from different depths in a particular filter, media from different treatment plants, and/or media exposed to differing Mn loadings. The reported molar ratios of Al and Mn in media coatings analyzed in the study generally ranged from 1.0 to 2.0 (moles Al/mole Mn) (Tobiason et al., 2008).

The fact that the two elements existed in nearly equal molar quantities was perplexing; in plants that utilize Al based coagulants the concentration of Al generally exceeds the concentration of Mn by orders of magnitude in the water in direct contact with the filter media. This led to
speculation that there might be a relationship between the mechanism that drives the deposition of Mn and the mechanism that drives the deposition of Al onto the coatings.

The reason for the presence of Al within the MnO$_x$(s) surface has not been identified to date. Knowledge of how and why the Al becomes integrated into the surface could have practical implications regarding both soluble Mn removal and finished water Al levels. The specific objectives of this study are as follows:

1. To determine whether Al impacts the uptake of soluble Mn onto MnO$_x$(s)-coated filtration media by comparing uptake in the presence and absence of Al;
2. To determine the physical or chemical mechanism that leads to the integration of Al within the MnO$_x$(s) surface; and,
3. To analyze an MnO$_x$(s) surface and to observe the state of Al and Mn solids present within the surface.

These objectives were achieved by analyzing data produced by conducting numerous controlled bench scale filtration column studies, analyzing measurements taken at a local water treatment facility, and by conducting an analysis of MnO$_x$(s)-coated media using electron microscopy.
LITERATURE REVIEW

This literature review will focus principally on issues and studies related to the chemistry of Al and Mn. Though this research study was focused primarily on Al, the initial motivation for this work was to determine what effect the presence of Al in MnO$_x$ coated filtration media might have on the removal of soluble Mn. Therefore, an understanding of the motivations for Mn treatment and the mechanisms of Mn oxidation in a water treatment setting are important to include in a discussion of the chemical relationship between Al and Mn.

Mn as an Aesthetic Concern

Many different metals, chemical compounds and biological organisms are monitored in public drinking water in order to protect the health of public water consumers. Chronic exposure to even low levels of some contaminants can result in serious adverse health effects. For these types of contaminants the EPA has outlined enforceable Maximum Contaminant Levels (MCLs) in order to reduce the public's exposure. There is currently no MCL for Mn. Instead, a non-enforceable Secondary Maximum Contaminant Level (SMCL) of 0.05 mg/L has been defined for Mn. This guideline is meant to define a suggested maximum concentration for Mn in order to avoid potential aesthetic effects that can result from high levels of Mn (EPA, 1979).

In a public drinking water distribution system, Mn can build up on the inner diameters of pipe walls and can contribute to the formation of metal oxide scales. In extreme cases these scales can contribute to a reduction in the pipeline cross section and result in significant head losses (Kothari, 1988, Peng et al., 2010). Excessive build-up of Mn within pipeline distribution systems can lead to a phenomenon known as black water. Black water can occur when reduced Mn adsorbs to the inner walls of the distribution pipe and accumulates over time. There are documented cases in which a sudden increase in water demand coupled with the accumulation of Mn in pipe scales led to a blackwater event (Roscoe, 2002). A change in the flow or water quality conditions can cause the accumulated Mn to slough off of the pipe walls and arrive at the water user's tap as a black precipitate. The result is the staining of fixtures and laundry. The sudden deterioration of water quality results in a spike of consumer complaints and an erosion of consumer confidence in the safety of the drinking water (Sly et al., 1990).

Some research suggests that in order to avoid aesthetic issues such as black water, finished water Mn concentrations should not exceed 0.02 mg/L (Casale et al., 2002). Other researchers believe that Mn concentrations should be maintained below 0.01 mg/L in order to avoid aesthetic issues (Sly et al., 1990).
Health Effects of Mn

Several factors determine whether or not a particular compound is harmful to human health. In the case of Mn exposure in humans, research has demonstrated that an individual's age, the route of exposure, and diet are all important in determining how the compound will be absorbed by the body (Lönnertal et al., 1987). In humans, the intake of Mn in very low levels is necessary for enzymatic processes in the body. However, because Mn is found naturally in such a wide variety of foods, the incidence of health complications resulting from a lack of Mn is believed to be rare (W.H.O., 2011). A condition known as manganism, with symptoms similar to Parkinson's disease, occurs in individuals that are exposed to high levels of Mn dioxide via inhalation (Cook et al., 1974). Historically, Mn exposure via oral ingestion in drinking water has been regarded as benign (Bull and Craun, 1977, Wong, 1984), but emerging research is challenging this idea.

A number of studies released in the last decade are changing how Mn exposure in drinking water is viewed, most notably in the potential impact on children. A 2005 study demonstrated a statistical correlation between high levels of drinking water Mn and decreased cognitive abilities in children (Liu, 2005). A 2011 study also identified a decrease in the cognitive ability of both mothers and children related to elevated drinking water Mn exposure from the use of a well water source (Menezes-Filho et al., 2011). One group of researchers calls into question the basis upon which World Health Organization (WHO) Mn drinking water health standards were established and calls for a reevaluation of the standards in light of the apparent exposure risk to vulnerable populations such as children (Ljung and Vahter, 2007). These studies illustrate that Mn exposure through drinking water deserves more scrutiny as a public health concern than has been previously acknowledged.

Traditional Methods of Mn Treatment

Mn commonly occurs in natural waters, especially in groundwater. A recent report by the USGS surveyed groundwater sources from all over the United States and found that 31% the raw groundwaters sampled for the study exceeded the SMCL for Mn (Ayotte et al., 2011). Mn issues are certainly not exclusive to groundwater sources, but the concentrations of Mn in groundwater can potentially exceed those of a typical surface water source by orders of magnitude (Von Gunten et al., 1991). Issues of elevated Mn concentrations in surface waters tend to be more seasonally based, especially in lakes and reservoirs that are subject to thermal stratification. In these situations removal of Mn is often required for only part of the year (typically summer and/or fall months). Oxidation of Mn from a soluble to an insoluble form is one of the most commonly applied strategies for removal in drinking water treatment (Knocke et al., 2010). However, the large number of possible oxidation states of Mn can make removal challenging. Table 1 shows the various oxidation states of Mn that have been found to occur in nature (Tobiason et al., 2008).
When discussing the treatment of drinking water contaminants, iron (Fe) and Mn are often paired together. The pairing is due to their numerous similarities; both are metal contaminants that have the potential to cause aesthetic issues, both are abundant, and both can be removed by oxidation processes. Fe and Mn enter the treatment process in either reduced or oxidized form. Since both Fe and Mn are insoluble in their oxidized forms, an oxidant dosage is determined in order to oxidize all of the Fe and Mn in solution. Once all of the Fe and Mn oxidized a coagulant is applied in order to capture the oxidized metal particles and allow the particles to aggregate. The aggregated particles then either settle out or go on to be captured by filtration processes (Singer and Reckhow, 1999).

Fe can be readily oxidized in the bulk solution, even by relatively weak oxidants such as oxygen. However, Mn often requires much stronger oxidants such as ozone or permanganate (MnO₄⁻) to be effectively oxidized in the bulk solution under typical surface water pH conditions. Chlorine can be used to oxidize Mn in the bulk solution, but only under alkaline pH conditions or in conjunction with a dosage of permanganate. The fact that Al-based coagulation processes are best conducted at somewhat acidic pH conditions renders Mn removal by chlorine in the bulk solution incompatible with coagulation processes (Knocke et al., 1987, Knocke et al., 1988). Chlorine dioxide (ClO₂) is a stronger oxidant than chlorine and is extremely effective at oxidizing Mn under a variety of pH conditions (Knocke et al., 1991b). However, the necessity for onsite generation and the added risks of generating regulated compounds such as chlorate and chlorite make it at least somewhat undesirable for some applications (Haas, 1999). The equations in Table 2 characterize the theoretical stoichiometry necessary to achieve oxidation of Mn by permanganate, ozone, and chlorine dioxide. Once the Mn is oxidized to an insoluble for such as Mn dioxide (MnO₂(s)), it can then be removed by subsequent solids separation processes.
Table 2 - Stoichiometric Oxidation of Mn by Various Oxidants -
Adapted from (Philip C. Singer, 2011)

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Chemical Oxidation Equation</th>
<th>Eqn. #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanganate</td>
<td>$3Mn^{+2} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2(s) + 4H^+$</td>
<td>1</td>
</tr>
<tr>
<td>Ozone</td>
<td>$Mn^{+2} + O_3 + H_2O \rightarrow O_2 + MnO_2(s) + 2H^+$</td>
<td>2</td>
</tr>
<tr>
<td>Chlorine Dioxide</td>
<td>$Mn^{+2} + 2ClO_2 + 2H_2O \rightarrow MnO_2(s) + 2ClO_2^- + 4H^+$</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Theoretical Oxidant Demand (mg Oxidant / mg Mn$^{+2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanganate</td>
<td>1.45</td>
</tr>
<tr>
<td>Ozone</td>
<td>0.87</td>
</tr>
<tr>
<td>Chlorine Dioxide</td>
<td>2.45</td>
</tr>
</tbody>
</table>

There are obvious drawbacks associated with the cost of using chemicals such as permanganate to control Mn or the cost of generating ozone onsite. In either case, the reliability of these approaches is subject to the accuracy of the operator’s estimation of the oxidant demand. The applied dosage of either permanganate or ozone has to be carefully chosen and must be constantly varied to accommodate changes in the raw water (Singer and Reckhow, 1999). Several factors influence the effectiveness of the oxidant: the concentration of Fe and Mn in the raw water, the amount of organics present, the raw water pH, and the raw water temperature (Wilczak et al., 1993).

If the oxidant dosage is too low reduced Mn will remain soluble, pass through the filters and will exit the plant. If the oxidant dosage is too high, Mn in solution could be oxidized too much and will pass through the filters as soluble permanganate. The permanganate gives the water a characteristic pink color (Wilczak et al., 1993). Faced with uncertain oxidant dosages, some treatment plants have opted for a completely different approach to the problem.

**Removal of Soluble Mn by MnO$_x$(s)-Coated Filtration Media**

Some water treatment facility operators have opted to both reduce their chemical costs and to achieve nearly 100% removal of soluble Mn across their conventional filters by applying a chlorine residual across their filtration media (Wong, 1984, Knocke et al., 1987, Knocke et al., 1988). The effect, over time, is the generation of a MnO$_x$(s) layer on the media surface. The number of oxygen atoms associated with each atom of oxidized Mn is represented as an ‘x’ because several different forms of oxidized Mn can form on the oxide surface. The number of associated oxygen atoms for each atom of oxidized Mn can vary between 1.3 and 1.9 (Stumm and Morgan, 1996).
As was mentioned previously, this oxide layer is composed primarily of Mn and has the potential to adsorb multivalent metal cations onto its surface. In the case of Mn, the adsorbed cation is then oxidized by free chlorine in the water flowing through the filter. The adsorbed, reduced Mn becomes oxidized and becomes part of the MnO$_x$(s) surface. The recently oxidized Mn in then available as a sorption site for Mn$^{+2}$ and the process repeats itself (Knocke, 1991).

The nature of the MnO$_x$(s) surface is complex; also, the high surface area provides numerous sites for Mn adsorption (Merkle, 1996). Previous laboratory studies have demonstrated that a greater level of MnO$_x$(s) coating has a greater absorptive capacity for Mn (Knocke et al., 1991a, Tobiason et al., 2008). It is important to understand how the high surface area of the MnO$_x$(s) plays a role in this process. A higher surface area allows for much more adsorption and thus more potential reaction sites for free chlorine to come into contact with the adsorbed reduced species of Mn. Data presented in Figure 1 demonstrate the correlation between the extractable Mn content of the MnO$_x$(s) surface and the measured surface area of the media per gram of dry media. In effect, the surface catalyzes the oxidation reaction between absorbed Mn$^{+2}$ and free chlorine (Morgan and Stumm, 1964). In general, free chlorine does not react very quickly with dissolved Mn in the bulk solution where nucleation sites are scarce. The two will interact and reduced Mn will oxidize given enough time, but the kinetics are so slow that it is generally regarded as impractical as a means of Mn removal in a water treatment setting (Knocke et al., 1987). However, if a media with a high surface area is available to catalyze the reaction, it greatly increases the number of nucleation sites and thus increases the potential for interactions between the reduced Mn and the chlorine.

A group of researchers sought to analyze the role that the high surface area of MnO$_x$(s) coated media plays in Mn oxidation. MnO$_x$(s)-coated media was allowed to adsorb reduced Mn species in the absence of a strong oxidant. A subsequent analysis of the oxidation state of Mn species within that MnO$_x$(s) surface was conducted using a technique called X-ray Photoelectron Spectroscopy (XPS). The authors found that while the predominant oxidation states of the surface Mn were Mn(II) and Mn(IV), the detected presence of Mn(III) on the surface suggested that the surface itself had catalyzed the oxidation of reduced Mn species (Cerrato et al., 2011).

Previous studies on MnO$_x$(s)-coated filtration media have clearly demonstrated that the ability of metal cations like reduced Mn to adsorb to the surface is highly dependent on pH (Morgan and Stumm, 1964). The MnO$_x$(s) surface bears a slight negative charge which helps to account for the surface’s affinity for multivalent cations (Morgan and Stumm, 1964). The ability of the MnO$_x$(s) surface to adsorb metal cations is pH dependent because the metal cations in solution compete with the hydronium ion (H$_3$O$^+$) for sorption sites. As the pH of the water decreases, the concentration of hydronium increases. The high surface area of the MnO$_x$(s)-coated media provides a large number of sorption sites that are rapidly saturated by the sorption of H$_3$O$^+$. Reduced Mn$^{+2}$ that adsorbs to the MnO$_x$(s) surface will have to compete with H$_3$O$^+$ for adsorption sites. When the pH is low, the concentration of H$_3$O$^+$ is high and the adsorption of Mn is less favorable. When the pH is high, the adsorption of Mn$^{+2}$ is much more favorable because there is
Figure 1 - Extractable Mn and Measured Surface Area for MnO$_{x(s)}$-Coated Media Samples (Tobiason et al., 2008)
much less competition for adsorptive sites. The competition with $H_3O^+$ has been demonstrated by previous researchers who observed a decrease in pH that corresponded with decreased $Mn^{2+}$ sorption (Morgan and Stumm, 1964, Knocke et al., 1991a).

**Al Incorporation into $MnO_{x(s)}$-Coated Media**

A review of water research publications was conducted in an effort to seek out any previously performed study related to the presence of Al in $MnO_{x(s)}$-coated water treatment filtration media. Despite the lengthy search, no such study was found. The only publication that made any mention of the presence of Al within $MnO_{x(s)}$-coated media was the recent AWWARF study (Tobiason et al., 2008) on $MnO_{x(s)}$-coated filtration media which was the inspiration for this study.

One study related to the treatment of coal mine drainage (CMD) did confirm that Al deposited along with Mn during the treatment of the CMD (Tan et al., 2010). The authors of this study conducted an analysis of $MnO_{x(s)}$ formed during the treatment of CMD. The authors used electron microscopy and other techniques that confirmed the presence of Al in the environmental deposits of oxidized Mn.

Another study examined naturally deposited $MnO_{x(s)}$ coatings on pebbles in a riverbed. The coatings were likely the result of Mn oxidizing bacteria. That study did note that small amounts Al were found in the coatings, but the researchers felt that Al was bound up in silicate minerals and found that Fe and silicon were much more abundant than Al in the $MnO_{x(s)}$ coating (Seyama et al., 2008).

Several published papers have focused on the potential for $MnO_{x(s)}$ to adsorb and sequester heavy metals onto the $MnO_{x(s)}$ surface (Gray, 1981, Bajpai, 1999, Lisha et al., 2010, Tan et al., 2010). One study examined the adsorptive capacity of various Mn oxides for lead. The authors found that the adsorptive capacity varied significantly between the different types of natural and synthetically prepared $MnO_{x(s)}$ samples examined in the study (O'Reilly and Hochella, 2003). This has obvious potential implications for industrial waste streams or contaminated waters, but surprisingly even in municipal drinking water treatment $MnO_{x(s)}$-coated filter media appears to have some capacity to remove heavy metals from solution in the presence of a chlorine residual. The researchers involved with the 2008 AWWARF report found, through chemical extraction and microprobe analysis of the coatings, that the coatings were composed not just of Mn, but a variety of different heavy metals. Significant amounts of heavy metals such as copper, lead, and chromium were found in the coatings (Tobiason et al., 2008).

The specific origins of the heavy metals are not always clear, but it is reasonable to assume that one source of these heavy metals is the raw water influent in which they are present in very low concentrations. For instance, drinking water facilities represented in the 2008 AWWARF study
that utilized a reservoir for their raw water source showed significantly higher concentrations of copper in their MnO$_x$(s)-coated filtration media. This is almost certainly due to the fact that copper sulfate was used as an algaeicide in the raw water reservoir (Tobiason et al., 2008). Another group of researchers showed that the presence of heavy metals in water treatment is often a consequence of utilizing contaminated water treatment chemicals (Eyring et al., 2002). In any case, it is clear that a wide range of dissolved metal cations have an affinity for the Mn oxide surface; they adsorb, oxidize and are then sequestered within the surface by the continued precipitation of Mn oxides. For MnO$_x$(s) coatings generated in water treatment facilities the majority of the coating is composed of Mn and Al, while heavier metals have always been shown to compose only a small portion of the total metals present in the coating.

Redox active metals such as Fe and Mn are thought to adsorb to the surface in a reduced state and then utilize the surface as a means to react with chlorine and oxidize to a more insoluble form. This cannot be the case for Al since the element is rarely if ever found outside of its trivalent (+3) redox state in nature. Al is only redox active under much more extreme environmental conditions (Srinivasan et al., 1999), conditions that would not be present in a water treatment setting. This seems to indicate that the mechanism of Al incorporation into the MnO$_x$(s) surface must be different from that of Fe or Mn.

Data collected by the authors of the 2008 AWWARF study seem to confirm that the MnO$_x$(s) surface has a strong affinity for Al species even when Al is not added to the treatment process. A significant quantity of Al was found to be present in the MnO$_x$(s)-coated media in each of the facilities surveyed that applied free chlorine across their filtration media. Interestingly, significant concentrations of Al occurred not only in the MnO$_x$(s) coatings of one treatment plant that utilized Al-based coagulants but also in a facility that applied an Fe-based coagulant (Tobiason et al., 2008).

If any determination is to be made about how Al becomes incorporated within the MnO$_x$(s) surface, an understanding of the solution chemistry of Al is necessary. Al chemistry is highly complex. While it is generally not redox active in nature, the various hydrolysis products formed are highly dependent on solution pH. The pH of the solution has a large role in determining whether the Al hydroxide species present in solution is cationic, anionic, or neutral in charge. Additionally, at elevated concentrations of Al, there is a high potential to form polymeric, colloidal, and particulate species (Smith, 1996).

**Aesthetic and Health Effects of Al**

The fact that Al does appear to integrate into the MnO$_x$(s) coatings of water treatment filtration media seems to suggest a potential for the coatings to impact finished water Al levels. The motivation for a reduction in finished water Al levels is driven by both aesthetic and health concerns that result from the accumulation of Al in a drinking water distribution system (Costello, 1984).
The concerns over Al in drinking water can be at least partially attributed to potential health effects; or at least addressing public perceptions about health concerns. Al has been demonstrated to be a neurotoxicant in laboratory animals that were exposed to high dosages. In past decades, it had been speculated by some that there was a link between the ingestion of Al and Alzheimer’s disease (Ganrot, 1986, Srinivasan et al., 1999).

Today, research seems to be somewhat divided on whether or not the link between Al exposure and Alzheimer’s disease has any validity. Many researchers feel that the link between Al exposure in drinking water and Alzheimer’s is unfounded (Reiber and Kukull, 1996). One group of researchers hypothesized that exposure to Al through the use of consumer products might be correlated to Alzheimer’s disease. However, the data were ultimately inconclusive and did not show a definitive connection (Graves et al., 1990).

Regardless of whether or not there is a link between the two, the perceptions and fears of the public may be a greater driver to reduce finished water Al levels than any potential health effects. The EPA regulates Al under its list of secondary drinking water regulations. In the interest of preventing water discoloration the suggested maximum effluent concentration is listed as high as 0.2 mg/L.

**Previous Electron Microscopy Analysis of the MnO₅(s) Surface**

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) analysis of the MnO₅(s) surface are important components of this research. Along with laboratory experiments, an analysis of the surface itself on a nano scale is necessary in order to show the type of Al present in the surface. If the chemistry and structure of the Al on the surface can be accurately characterized then it becomes possible to make intelligent conjectures about the possible mechanism(s) by which the Al integrates into the surface. Images of the MnO₅(s) surface generated by previous researchers investigating the NGE led to speculation that an analysis of the surface might assist in determining this mechanism. Figure 2 shows an SEM image of an MnO₅(s)-coated anthracite coal media grain from a treatment plant filter (Tobiason et al., 2008).

Visual inspection of Figure 2 indicates that the surface is not entirely homogeneous. The cross section cut actually resembles the rings of a tree. The ring pattern of deposition onto the surface is most likely indicative of changes in water chemistry over time. Because many surface water treatment plants experience seasonal variations in Mn loadings, it stands to reason that the deposition behavior onto the surface also varies by season and produces this ring pattern when the coating is viewed in cross section.

MnO₅(s) coatings have been shown to occur in nature even in the absence of a strong oxidant. A 2008 study of Mn oxide coatings on pebbles within riverbed sediments was conducted in order to
Figure 2 - SEM Image of an Anthracite Coal Particle from a Water Treatment Plant in Newport News, VA
(© 1996-2012 Water Research Foundation.)
characterize the surface. The researchers employed methods very similar to those utilized in this research study including mapping of the oxide surface using SEM (Seyama et al., 2008).

**Energy Dispersive Spectroscopy (EDS)**

By utilizing an Environmental Scanning Electron Microscope (ESEM) to perform a scan of the MnO\(_x\)(s) surface it is possible to quantify the elemental composition of the surface at several points along the MnO\(_x\)(s) surface. This is accomplished by measuring the response of a high energy (5 - 20kV) electron beam when it comes into contact with a specific point on the surface. When an electron beam makes contact with the surface several interactions take place. The path that each individual electron takes is complex, but the resulting X-rays produced can indicate the elemental composition of the sample. The energetic electrons in the beam serve to excite other electrons in the atoms of the sample from their ground state to a higher energy state. For an atom that comes into contact with an electron from the beam the result is the ejection of the ground state electron from the sample along with a characteristic X-ray. These ejected X-rays travel in all directions, but a select few are cast back up at the EDS detector. The unique characteristics of each X-ray can be detected and matched to a specific element. In this way, the backscatter detector on the SEM allows for an elemental characterization of a sample. If this analysis is repeated thousands of times over the surface of a sample, the result is a map of the sample showing the elemental composition. If the analysis is conducted at several points in a straight line, the result is a plot showing the number of times the presence of a specific type of element was detected (Goldstein et al., 1981).

**Transmission Electron Microscope (TEM) Analysis**

Alternatively, by performing an analysis in a TEM it is possible to identify not only the elemental composition of a sample, but the specific crystal structure of the compound present at one point within the sample. This is possible though electron diffraction, which has been an important aspect of TEM ever since it was first developed in 1939 (Goldstein et al., 1981). More specific information on the methods utilized for the electron diffraction analysis can be found in the methods chapter. The resolution of the microscope is a function of several contributing factors: the wavelength of the incident electron (which is in turn a function of the energy of the electron beam), the quality of the electron lenses, and the properties of the analyzed sample itself (thickness, morphology etc.) (Williams and Carter, 2009).

In the case of this current laboratory study, a determination about whether Al within the oxide coating is crystalline, amorphous, or bound up in conjunction with Mn in a mineral form provides important clues about how the Al arrived on the MnO\(_x\)(s) surface in the first place. Whether the Al becomes integrated into the surface by adhering to the surface in its solid phase
or if dissolved Al interacts with the surface and adheres in conjunction was unclear prior to TEM analysis.

Though previous researchers did generate SEM images of the MnO$_x$ surface, the mineral state of the Al on the surface was never analyzed using TEM. Researchers working in the fields of materials science and chemical engineering have utilized various electron microscopy techniques to examine Mn oxides from both natural and laboratory environments (Hochella et al., Junta and Hochella, 1994, O'Reilly and Hochella, 2003). Analysis of Mn oxides from water treatment facilities was conducted by the authors of the 2008 AWWARF study who utilized X-ray diffraction on select samples of coated media. The resulting output was compared to published data in order to determine to attempt to identify a mineral phase containing both Al and Mn, but no such phase could be definitively identified within the MnO$_x$ surface (Tobiason et al., 2008).
EXPERIMENTAL DESIGN AND METHODS

The following section details the methods used to quantify the interactions of Mn and Al with the MnO\textsubscript{x(s)} surface during the research study. The bench-scale experiments conducted can be broken down into several categories: soluble Al studies, particulate Al(OH)\textsubscript{3(s)} studies, and batch studies. This section also describes the analytical methods and sample preparation techniques that were used to examine the chemical composition of the MnO\textsubscript{x(s)} surface through the use of electron microscopy.

Bench-Scale Column Experiments

It was important to simulate conditions present in a treatment facility on a smaller scale in the laboratory so that the process could be monitored with some analytical precision. This precision was necessary in order to effectively characterize the behavior of the MnO\textsubscript{x(s)}-coated filtration media. The analysis was carried out by pumping prepared feed water through short beds of filtration media (3.5” or 6”) enclosed in small diameter glass columns (7/16” ID). The metals content of the influent and effluent of each column was carefully monitored throughout all of the experimental trials.

All of the column studies utilized similar materials and equipment in the construction of each experimental apparatus. Peristaltic pumps (Cole-Parmer Masterflex) were used to convey carefully prepared feed water from bulk storage vessels (five gallon HDPE buckets), through the column media until the water was discharged to the sink. Short lengths of polyethylene tubing (1/4” ID / 3/8” OD) were used to transport the feed water through the experimental setup. The short beds of media were enclosed within small glass tubes (7/16” ID). Glass was chosen over plastic for ease of cleaning between experiments. PVC connectors were used to connect pieces of polyethylene tubing to the peristaltic pump tubing, to connect any feed lines that were needed, and to connect to the column containing the short media bed. A small (1/2”) plug of glass wool was placed at the bottom of the column media in order to act as a support bed for the column media. Glass wool was chosen as a support media because it was thought to be inert and would therefore not interfere with the effluent metal concentrations. The specific setup of each experimental configuration is described where appropriate, but the materials described above were common to each experiment.
Experiments Applying ‘Soluble’ Al Species

Defining ‘Soluble’

It is worth clarifying certain aspects of the nomenclature that will be used throughout this thesis to describe the experiments conducted for this research study. Specifically, it is important to clearly define what is meant when a chemical species is designated as ‘soluble’. Essentially, there is a discrepancy between what could be termed as an ‘operational’ definition of soluble and the ‘academic’ definition of the term. The operational definition is primarily the consequence of a desire to quantitatively describe a water sample when faced with limited analytical techniques, while the academic definition has much more to do with the physical/chemical behavior of a substance in solution. The two definitions can potentially be at odds with one another.

A worker at a water treatment facility might apply an ‘operational’ definition of solubility by filtering a sample of water through a 0.45 µm glass fiber filter in order to comply with existing water treatment monitoring regulations. From the worker’s perspective, anything passing through the filter could be reported as ‘soluble’ material. However, this definition of soluble would tend to over-estimate the amount of soluble material present in an ‘academic’ sense of the word.

From an academic standpoint, the definition of soluble has to do with the behavior of a particular chemical species in solution. Reported values for solubility are the subject of disagreement among academics, but it is clear that questions of whether or not a substance is truly soluble in an academic sense go beyond a simple discussion of particle size (Dyer et al., 1998). In the case of supersaturated solutions of Al, colloidal particles of Al(OH)$_3$(s) exist in solution which are smaller than 0.45 µm. These materials would pass through a 0.45 µm filter, but would not be truly soluble (Lai et al., 2007).

The purpose of this discussion is simply to address the fact that at least two different interpretations of the word ‘soluble’ are used frequently in discussions of water treatment. For the purposes of the Al column experiments applying soluble Al, a dosage was chosen in order to satisfy both definitions of the term. The dosage chosen was lower than academically reported solubility limits of Al in solution. A brief bench-scale study of Al was also performed in order to consider the equilibrium that exists between the amorphous Al(OH)$_3$(s) solid phase that is characteristically formed in water treatment coagulation processes and soluble Al species. The published values for Al solubility as well as the bench-scale study results were considered when the Al dosage was chosen. In experiments that applied soluble dosages of Al, the dosage chosen was less than both values (published values were determined to be ~27 ppb as Al at pH 6.3 and ~85 ppb as Al at pH 7.2) (Vanbenschoten and Edzwald, 1990).
**Bench-Scale Study of Al Solubility**

A brief study was conducted in order to experimentally verify the solubility of Al hydroxides under varying pH conditions. Five 250 mL flasks were filled with 200 mL of Blacksburg tap water. Each container was then dosed with a small volume of a concentrated stock solution of Al sulfate in order to produce solutions that each contained roughly 500 ppb of Al. Finally, using a 1M stock solution of NaOH, each flask was pH adjusted to a different pH value (pH 5.5 - pH 8.0). Stoppers were then inserted into the flasks in order to prevent interactions with the atmosphere and any resulting changes in pH. The samples were placed on a shake table and gently shaken for 4 hours. Finally, a 10 mL sample was taken from each flask and filtered through a 0.2 µm glass fiber filter. The resulting filtrate was analyzed using ICP-MS and the concentration of filtered Al was reported for a range of pH values. The resulting experimentally determined values of Al solubility were comparable to published values reported in the literature.

**Experimental Setup – Soluble Al Experiments**

Several columns were operated in parallel during each of the experimental trials in which soluble Al was applied to MnO$_x$(s)-coated filtration media. Several important experimental parameters are summarized in Table 3. The flow of feed water to each column was driven by a single pump head on a peristaltic pump. Materials described previously were used to construct the experimental apparatus shown in the schematic in Figure 3.

The media used in each of the experimental trials was ‘regenerated’ prior to being loaded into the glass column. It was important to ensure that the MnO$_x$(s) surface was free of absorbed Mn species. This was achieved by placing the media into an Erlenmeyer flask and contacting it for at least 12 hours with a solution composed of deionized water and sodium hypochlorite (NaOCl) which yielded a free chlorine concentration of 100 mg/L. After the media was rinsed with DI water it was ready to be placed into the column.

In selected experimental trials a free chlorine residual was applied to the column media. NaOCl was dosed from a feed stock solution and was introduced just upstream of the glass column shown in Figure 3 using a PVC tee connection. This minimized the oxidation of Mn in the bulk solution by minimizing the contact time with free chlorine in the bulk solution.

The use of peristaltic pumps ensured that the columns received a consistent flow of water. In each of the experimental trials the hydraulic loading rate was set at 3.8 – 4.0 gpm/ft$^2$ to approximate the loading rate present in a conventional treatment plant filter. In each experimental trial the flow rate was measured a minimum of three times and averaged to attain a single value for the flow rate. The column effluent was discharged into a nearby sink. The outlet into the sink was placed above the level of the column media bed in an effort to prevent any potential suction that might have resulted from a significant head differential between the
Table 3 - Summary Table of Parameters in Employed in Soluble Al Experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Numerical Value</th>
<th>Notes / Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic Loading Rate</td>
<td>3.8 – 4.0 gpm/ft²</td>
<td>Loading rate was selected to simulate that of a conventional filtration plant</td>
</tr>
<tr>
<td>Media Bed Depth</td>
<td>3.5”</td>
<td>Short bed of media</td>
</tr>
<tr>
<td>pH</td>
<td>6.3</td>
<td>Low pH condition</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>High pH condition</td>
</tr>
<tr>
<td>Mn Concentration</td>
<td>0 – 0.3 mg/L</td>
<td>Concentrations were selected to model seasonal Mn loadings in treatment plants</td>
</tr>
<tr>
<td>Al Concentration</td>
<td>0.0 mg/L</td>
<td>Adsorption of Mn in the absence of Al</td>
</tr>
<tr>
<td></td>
<td>‘Saturated’</td>
<td>Soluble Al dosage was adjusted for pH conditions (pH 6.3, 12 to 16 ppb; pH 7.2, 35 to 43 ppb)</td>
</tr>
<tr>
<td>Free Chlorine</td>
<td>0.0 mg/L</td>
<td>Free chlorine was absent during soluble Al and Mn adsorption experiments.</td>
</tr>
<tr>
<td></td>
<td>1.0 mg/L</td>
<td>Effluent free chlorine was maintained for non-adsorption experiments.</td>
</tr>
</tbody>
</table>
Figure 3 - Schematic Showing Laboratory Setup for Experiments Applying Soluble Species of Al to MnO$_{x(s)}$-Coated Media
media bed and the outlet. During the course of the experiment samples were collected by collecting the drips of the column effluent in capped 16 mL polystyrene ICP sample tubes.

The time at which these samples were collected was recorded in order to quantify the volume of water that had passed through the column by that time. That is, the product of the flow rate and the time of operation yielded the volume of feed water passed through the column. Analysis of the concentration of metals in both the feed water and the effluent for each column was calculated several times during the column operation. The amount of each metal taken up by the column media was calculated using the following equation.

$$\left( [Mn]_{\text{Influent}} - [Mn]_{\text{Effluent}} \right) \times (\text{Flow}) \times (\text{Time}) = \text{Mass of Mn} \quad \text{Equation 4}$$

This allowed for a calculation of the mass of each metal taken up by the column media under varying experimental conditions. A similar approach was used in order to quantify the uptake of Al onto the column media. These results could then be graphed and analyzed in order to compare the uptake of Mn and Al under a variety of experimental conditions.

**Stock Solutions**

Stock solutions of both Mn and Al were utilized during all of the column trials. During all of the experimental trials, the Mn stock was prepared using a hydrated powder of Mn(II) chloride (MnCl$_2$$\cdot$4H$_2$O). The dry powder was placed on a weigh boat and then added to a volume of nanopure water that had been measured in a volumetric flask. This mixture was then placed in a labelled polypropylene Nalgene bottle. After vigorously shaking the solution of Mn, the concentration of the stock solution was verified on the AA instrument. As discussed previously, the kinetics of Mn oxidation by oxygen are extremely unfavorable, especially in acidic environments. Though the pH of the un-buffered stock solution was generally less than 5, the Mn stock solution was changed bi-weekly in order to minimize experimental errors that would have resulted from partial oxidation of the Mn in the stock.

The Al stock was prepared in a similar manner. Al sulfate octadecahydrate hydrate (Al$_2$(SO$_4$)$_3$$\cdot$18H$_2$O) was weighed and added to a precisely measured volume of nanopure water. The need to periodically replace the Al stock solution was motivated by concern over the continued solubility of the Al in solution rather than redox concerns. The pH of the stock solution was maintained below 3 in order to prevent the formation of insoluble Al species such as Al(OH)$_3$(s). The Al stock solution’s interaction with the atmosphere over time may have affected the solubility of the Al in solution and thus it was important to change the solution periodically. Al is not redox active under typical environmental conditions, but the Al stock
solution was changed with the same frequency as the Mn stock in order to ensure consistency. Each time a stock solution was prepared, the concentration of Al present in the solution was verified using the ICP-MS.

**Feed Water Preparation**

Water for the columns was prepared in order to observe the uptake of soluble Mn and Al onto the surface. The pH of the water, the alkalinity, and specific metals available to the columns were carefully controlled. The feed was prepared by adding alkalinity and hardness to the water at levels considered typical of a Mid-Atlantic surface water source. Sodium bicarbonate (NaHCO₃) was added in order to apply 1.0 meq/L of alkalinity to the water. Calcium chloride (CaCl₂) was added to achieve a total hardness of 0.5 meq/L. After alkalinity and hardness were added to the water, the pH of the water was adjusted. This was achieved by the careful addition of a 1M stock solution of nitric acid (HNO₃) or a 1M stock solution of sodium hydroxide (NaOH) as was needed. After pH adjustment the appropriate doses of Mn and Al were applied to the water. Because the added amounts of Al and Mn were so small, stock solutions of alum and Mn were prepared in order to more accurately dose the chemicals rather than adding hydrated salts of the metals directly to the water. The Mn stock was prepared using a hydrated powder of Mn(II) chloride (MnCl₂•4H₂O). The Al stock solution was prepared using Al sulfate octadecahydrate hydrate (Al₂(SO₄)₃•(18H₂O)).

During pH adjustment the use of strong acids and bases has the tendency to create temporary areas of extremely high or extremely low pH. It was important to adjust the pH of the solution prior to the addition of Mn because of the tendency of reduced Mn (Mn²⁺) to oxidize to Mn dioxide (MnO₂(s)) under highly alkaline (>9) pH conditions. Thus, if certain areas of the solution saw momentary pH conditions that were highly basic, reduced Mn might have oxidized in the bulk solution by even trace levels of dissolved oxygen present. Oxidized Mn present in the feed water would not have been able to adsorb to the oxide surface of the media in the same way as reduced Mn and would have introduced an error into the analysis.

**Varying Media Source**

In order to observe differences in the adsorptive behavior of the columns, several different media types were used. The media used in the experiments were selected for their variable amount of MnOₓ(s) coating present in each of the media samples. Based on the work of previous researchers, it was thought that a media with a greater amount of MnOₓ(s) coating would possess a greater adsorptive capacity for soluble Mn (Knocke et al., 1991a, Tobiason et al., 2008).
Table 4 shows the various media sources utilized during the column experiments and the different levels of oxide coating present on each. The method for determining the amount of coating present on each media is described later in this chapter.

Table 4 - Varying Level of MnO$_{x(s)}$ in Coated Media Utilized In Column Experiments

<table>
<thead>
<tr>
<th>Media Type</th>
<th>Approximate MnO$_{x(s)}$ Coating (mg Mn/dry gram media)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin Anthracite Coal</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Blacksburg, Christiansburg, VPI Water Authority</td>
<td>5</td>
</tr>
<tr>
<td>Harwood’s Mill WTP (Newport News, VA)</td>
<td>37</td>
</tr>
<tr>
<td>Synthetically Coated Anthracite Coal</td>
<td>0.2</td>
</tr>
<tr>
<td>Lee Hall WTP (Newport News, VA)</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Pure Pyrolusite</td>
<td>100% MnO$_2$(s)</td>
</tr>
</tbody>
</table>

The Blacksburg, Christiansburg, VPI Water Treatment Facility (BCVPIWTF) provided both MnO$_{x(s)}$-coated anthracite coal media from their filters as well as anthracite coal not yet used in the filter. Media from the Harwood’s Mill (Newport News, VA) treatment facility arrived with a significant coating on the surface of the anthracite coal. This was due to the fact that the media had been exposed to free chlorine and significant concentrations of raw water Mn over the course of years. Another media sample from the Lee Hall (Newport News, VA) treatment facility was also obtained for the column studies. The Lee Hall anthracite had not been exposed to free chlorine and had not developed any significant MnO$_{x(s)}$ coating.

Two types of media, commercially produced pyrolusite and synthetically coated anthracite coal, were also gathered for use in the column studies. Pyrolusite was analyzed for chemical composition by chemical extraction and was found to be almost entirely composed of Mn oxides with minimal impurities. The synthetically coated anthracite coal was prepared utilizing a coating method developed by Merkle et al. (1997). Following this method of coating, 500 grams of uncoated anthracite was first rinsed with tap water. This washed anthracite was then placed in a continuously mixed 10 liter glass carboy containing 9.0 liters of water. To this mixture was added 13.25 g MnCl$_2$•4H$_2$O and 36 mg SnCl$_2$•2H$_2$O. Two stock solutions were also prepared; an oxidant solution comprised of a dilute (0.11%) solution of sodium hypochlorite (NaOCl) and a 6200 mg/L sodium bicarbonate (NaHCO$_3$) solution. The two solutions were added to the stirred mixture of media according to a dosing schedule outline in the procedure. The result was a media with a light MnO$_{x(s)}$ coating (~ 0.2mg/g).
Varying Mn Concentrations

The influent concentrations of Mn were varied between column experiments in order to observe differences in the adsorptive behavior of soluble Al species as a function of the concentration of Mn present in solution. Prior to conducting the experimental trials it was hypothesized that Al and Mn might compete for adsorptive sites on the MnO_{x(s)} surface. Previous work on the subject has confirmed that Mn adsorption is impacted by the adsorption of H_3O^+ and this is why the adsorptive behavior of Mn varies with the solution pH (Morgan and Stumm, 1964, Tobaison et al., 2008). It was thought that cationic Al species in solution could potentially compete in a similar fashion.

Varying the influent dose of Mn allowed for the adsorptive uptake of Al under differing feed water conditions to be compared in order to confirm or reject the hypothesis that soluble Al species compete for adsorption sites with reduced Mn.

Varying Al Concentrations

The concentration of Al that each column was exposed to did vary between each of the different experimental trials. Some trials were conducted in the presence of soluble Al while others were conducted in the absence of Al. It is important to note that the solubility of Al is highly dependent on the pH. Two different concentrations of feed water Al were chosen based on published data (Vanbenschoten and Edzwald, 1990) and laboratory bench tests described in the methods chapter. The various hydrolysis products that Al forms serve to complicate its solubility. Since the column experiments were conducted at two different pH conditions, the amount of Al that could be designated as soluble varied between to the two pH conditions. At pH 6.3 the influent Al concentration was 12-16 ppb and 35-43 ppb at pH 7.2. In both cases the applied dose of Al could be considered nearly ‘saturated’, but the exact dosage of Al varied for each pH condition.

Experiments Applying Insoluble Al Species

After completing an extensive analysis of the way in which soluble Al species interact with the MnO_{x(s)} surface, it was important to conduct a similar study on how particulate species of Al(OH)_{3(s)} interact with the surface in order to characterize the interaction of all species of Al with the surface. Rather than contacting the MnO_{x(s)} surface with an under-saturated dose of Al, the dose of Al was increased in order to facilitate the creation of Al(OH)_{3(s)} colloids and particles in solution.

Ultimately, each column received a super-saturated dosage of Al (200- 220 ppb) that resulted in the formation of Al(OH)_{3(s)} colloidal materials in the bulk solution. A free chlorine residual was
also applied to the columns in order to oxidize the adsorbed Mn onto the surface of the coated media. The primary difference between each of the columns in the particulate Al experimental trials was the dosage of reduced Mn applied to each column.

Each column contained a bed of media that was six inches deep. The column media was a commercially produced MnO$_{x}$-coated sand that was donated by Siemens (Ames, IA). The sand grains had been previously sieved and were between 0.45 and 0.55 mm in diameter. Based on an extraction of the coated media prior to use in the columns, the measured Mn content of the coating was determined to be approximately 0.11 mg Mn/gram of dry media at the beginning of the experiment. The bed of coated sand media was supported inside of the glass column by a small (1/2”) plug of glass wool.

The materials used to construct the experimental apparatus were similar to those used in the soluble Al experiments, but the configuration of this series of experiments was different in several respects. While previously the entire system had been closed, the particulate loading to the columns made that approach impractical and would not have been representative of the behavior that the experiment was meant to replicate. Instead, in order to simulate the particulate loading in a typical filter, the head in the column was allowed to increase over time as particulate Al(OH)$_{3}$ deposition caused the head on the filter to increase. The range of experimental parameters applied during the insoluble Al column studies are summarized in Table 5.
Table 5 - Summary Table of Particulate Al Experimental Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Numerical Value</th>
<th>Notes / Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic Loading Rate</td>
<td>3.8 – 4.0 gpm/ft²</td>
<td>Loading rate was selected to simulate that of a conventional filtration plant</td>
</tr>
<tr>
<td>pH</td>
<td>6.9 – 7.2</td>
<td>Experimental pH condition</td>
</tr>
<tr>
<td>Mn Concentration</td>
<td>0 – 0.4 mg/L</td>
<td>Concentrations were selected to model seasonal Mn loadings in treatment plants</td>
</tr>
<tr>
<td>Al Concentration</td>
<td>200 – 220 µg/L</td>
<td>Saturated dosage of Al to produce amorphous Al(OH)₃(s) particles</td>
</tr>
<tr>
<td>Free Chlorine</td>
<td>&gt; 1.0 mg/L</td>
<td>Allowed for continuous surface oxidation of Mn</td>
</tr>
</tbody>
</table>
Two primary feed waters were applied to each of the columns shown in Figure 4. The bulk of the feed solution was prepared by combining 30 gallons of Blacksburg tap water with stock solutions of Al sulfate and chlorine in the form of sodium hypochlorite (NaOCl). This feed solution was common to each of the columns and the feed lines of all three columns drew from this feed solution at a rate of 13 mL/min per column. The secondary feed solution (13 mL/min) was prepared for each column and consisted of deionized water and a small amount of a stock solution of Mn chloride (MnCl₂). This feed water was prepared in batches inside of ten liter glass carboys and was added to each feed reservoir as needed during the experimental trial. The two solutions were pumped with peristaltic pumps and were combined using a PVC ‘tee’ fitting. This solution was then allowed to drip into the water above the column media bed. After filtering through the column media the effluent discharged into the sink where samples of the effluent could be taken. As in the previous experimental trial, the column effluent port was positioned above the column media bed in order to ensure that the head on the column was always higher than the top of the media bed.

Influent samples were collected from the 'tee' fitting near the air gap shown in Figure 4 and effluent samples were collected from the effluent tubing at the sink. All samples were collected in capped 16 mL polystyrene ICP analysis tubes. Periodic backwashing was necessary to remove solids accumulated in the filtration media in order to prevent excessive head from building up on the filters. This was accomplished by attaching a larger peristaltic pump to the effluent of each column and forcing Blacksburg tap water back through the column media at a backwash rate of 16 gpm/ft². Backwashing was performed when the head on the column exceeded 2 feet above the media bed and effluent port.

The experiments were allowed to continue for a much longer time period than the previous experiments in order to monitor the development of the MnOₓ(s) coating on the media over the course of the experiment (4 - 8 weeks). The development of the coating was tracked over time by removing a small amount (~0.2 grams) of media from each of the columns for extraction analysis. This analysis was performed every seven to fourteen days. The extraction analytical procedure is described later in this section.
Figure 4 - Schematic Showing Laboratory Setup for Experiments Applying Soluble and Insoluble Species of Al to MnO$_x$(s) - Coated Media
Feed Water Preparation

Figure 4 shows that the feed water for the columns was prepared in two different feed reservoirs and combined just before entering the small diameter column. Because the columns required both free chlorine and reduced Mn, it was necessary to have the Mn separated from the free chlorine to prevent premature oxidation of the Mn prior contact with the MnO$_x$(s) coated media. Though free chlorine has been shown to be a relatively poor oxidizer of Mn in bulk solution under the hydraulic retention times in a typical water treatment facility (Knocke et al., 1987), the hydraulic retention time of the prepared feed water would be much longer.

The Al and free chlorine feed solution was prepared by mixing 30 gallons of Blacksburg tap water with 25 mL of a stock solution of Al sulfate. A small volume (10 – 15 mL) of a NaOCl solution was also added to the feed solution. The necessary dosage of sodium hypochlorite was determined using a breakpoint chlorination trial. Blacksburg tap water was gradually dosed with a NaOCl stock solution. As the NaOCl was added, the concentration of free chlorine was measured in order to produce a breakpoint chlorination curve. The appropriate dosage of free chlorine was determined from the curve and the data was used to determine the appropriate dosage of NaOCl for the 30 gallon volume. The free chlorine content of the feed solution was verified each time feed solution was prepared. The amount of added NaOCl varied because the amount of free chlorine in the NaOCl stock solution diminished over time. The NaOCl solution was refrigerated at 6°C in an effort to slow this decay process, but the stock had to be replaced bi-weekly. In an effort to minimize variation resulting from differences in water temperature, the water taken from the tap was allowed to sit at room temperature for at least 24 hours before being mixed and added to the feed solution.

The Mn feed solution was prepared by combining ten liters of distilled water with a small volume (1.25 – 5 mL) of a Mn stock solution. This secondary feed solution was stored in 5 gallon buckets.

Particle Size Study

It was important to ensure that the prepared feed water that the column media was exposed to was comparable to the water found in a typical surface water treatment plant. It was therefore necessary to attempt to duplicate a similar size distribution Al species in the feed water. This was achieved by filtering the raw feed water through a number of different filters of varying pore sizes. By comparing the amount of Al that was captured by a filter of one pore size to the amount captured by a different filter pore size, a size distribution of Al particles could be generated. Typical results are shown in Figure 5. Three quantifications of the influent Al size species were conducted in the laboratory. The average concentration of Al passing through each of the pore sizes shown on the x-axis is indicated by the blue bar. The minimum and maximum
Figure 5 - Size Characterization of Influent Al for Insoluble Al Species Column Study
concentration passing through the filters are indicated by the upper and lower bounds of the error bars.

**Batch Studies of Al and Mn**

It was initially hypothesized that perhaps the particulate Al(OH)$_3(s)$ species themselves played a role in the oxidation of Mn. It seemed plausible that small particles of oxidized Mn were adsorbed by colloidal or particulate Al species and the Al(OH)$_3(s)$ flocs themselves provided a nucleation site for further reaction.

The experiment was conducted using Blacksburg tap water in order to effectively simulate the alkalinity typical of a mid-Atlantic surface water source. The alkalinity helped to stabilize the pH over the course of the experimental trial. A small volume of a stock solution of Al sulfate was added to the tap water in order to achieve an Al concentration of roughly 200 ppb as Al. After measuring the pH of the solution, the prepared solution of Al spiked tape water was distributed to eight different flasks. Each flask contained 250 mL of the water. Four of the flasks were then spiked with a stock solution of sodium hypochlorite until a free chlorine residual of 1.0 mg/L was present in each. The remaining four flasks did not receive chlorine.

Each set of four flasks, chlorinated and unchlorinated, were then spiked with a stock solution of Mn chloride (MnCl$_2$). Small volumes of the Mn stock were added in order to produce four different concentrations of Mn in the batch reactors. Each of the two sets of reactors contained Mn concentrations of 20, 50, 100, and 200 ppb of Mn.

The flasks were then sealed and placed on a shake table in order to gently mix the solutions for several hours. At two time intervals (four hours and ten hours) each of the eight batch reactors were sampled. For each sampling event, 10 mL of solution was collected from each reactor and another 10mL was collected and filtered through a 0.45 µm filter.

By comparing the raw sample to the filtered sample, it was then possible to measure the adsorption of Mn onto the alum. The difference in measured Mn concentration between the filtered and unfiltered sample was regarded as the concentration of Mn adsorbed to the surface of Al particles.

**Analytical Methods**

**Extraction Analysis**

Knocke et al. (1990) developed a method for the analysis of the extractable metals content of coated media. A small amount of MnO$_{3(s)}$-coated media was dried and weighed (~ 1 gram). The
weighed media was then placed into a 250 mL of nanopure water. Nitric acid was then added to this volume of water in order to create a 2% acid solution. Finally, 300 mg of a reducing agent called Hydroxyl Amine Sulfate was applied in order to reduce the oxidized metals in the coating and solubilize them into solution. A portion of the solution was then analyzed on an ICP-MS instrument (Thermo Electron Corp. X Series ICP-MS, X-0458) and the metals content was reported in mg/L. With a known volume of water and a known mass of dry media used in the extraction it was then possible to characterize the amount of each metal present in the coating in terms of mg of metal per dry gram of media. A complete description of the method can be found elsewhere (Knocke, 1990).

**Atomic Absorbance Spectroscopy**

An atomic absorbance spectrometer was utilized in order to measure Mn in some of the laboratory procedures according to Standard Methods 3111 B (21st ed. 2005). The instrument was manufactured by Perkin-Elmer and utilized both compressed air from the laboratory as well as acetylene gas.

Acidified precision Mn standards were obtained from Fisher Scientific and were diluted in order to produce a four-point calibration curve between 0.00 mg/L and 0.50 mg/L for the instrument. Once the calibration curve relating absorbance intensity to Mn concentration, samples were analyzed in the same manner as the calibration standards and the concentration of the samples was recorded by hand after the machine produced the result.

**Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)**

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was utilized for all of the reported Mn measurements and Al measurements. All measurements conformed to the ICP-MS method outlined in Standard Methods 3125-B (21st ed. 2005). All samples prepared for measurement on the ICP-MS were first collected in capped 16 mL polypropylene ICP tubes. Exactly 10 mL of sample was collected in the tubes and 200 μL of concentrated nitric acid was added to the sample in order to preserve the samples and to ensure that all of the metals present in the sample remained soluble.

**pH**

The solution pH was measured using a probe produced by Accumet© (Cat. No. 13-620-221) and a meter produced by Oakton© pH/mV/°C (110 Series, RS232). Two different calibration buffer standard solutions were used prior to each measurement and were used in accordance with the
instructions for the pH probe. Both the pH 4 and pH 7 buffer solutions were produced by Fisher Scientific (Cat. No. SB101-4 and SB107-4, respectively). The probe was stored in a pH 4 buffer solution and was rinsed between measurements with distilled water.

**Free Chlorine**

A Hach DR 2400 instrument was used to quantify free chlorine using the DPD method (Hach Method 8021 – DPD). The low-range detection of 0.02 – 2.00 mg/L was used to measure free chlorine throughout the laboratory experimental trials. In accordance with the method, 10mL of sample was collected and analyzed in the sample cell as a blank. After the instrument was zeroed, the reagent was added and mixed for 30 seconds. The sample was again placed in the sample cell and analyzed. The instrument then reported the free chlorine concentration in mg/L.

**Scanning Electron Microscope (SEM) Sample Preparation**

Sand media samples subjected to analysis by SEM were first allowed to air dry. A small silicon wafer was selected in order to provide a site on which to mount the media sample. A short length of double-sided carbon adhesive tape was placed on top of the silicon wafer. Then several grains of media were sprinkled on the surface of the tape. After carefully pressing the grains into the tape, canned compressed air was used to blow away any grains that were not properly attached to the surface. This was a precautionary measure to ensure that the sample would not fall off of the silicon wafer while the sample was in chamber of the SEM instrument. This method of preparation is one of several commonly applied methods for the analysis of mineral samples in SEM. A lengthier description of this and other sample preparation methods can be found in the literature (Goodhew, 1972, Goldstein et al., 1981).

After the sample was secured to the silicon wafer the sample was coated in order to minimize the effects of charging. Charging can distort the surface image and thus interfere with image generation. This conductive coating was applied in order to allow the sample to more effectively ground itself during the analysis and prevented a charge from building up on the surface. A coating composed of gold and platinum nanoparticles was applied for samples that were analyzed to produce images. Gold and platinum were most effective at reducing surface charge and were chosen in order to generate the sharpest possible image. The nanoparticles were applied to the surface using a procedure that is commonly referred to as 'sputter coating’. The sample was placed into an evacuated chamber and was subjected to bombardment by high energy nanoparticles. After several minutes, the thickness of the applied coating was several nanometers thick and the sample was ready for analysis. In some cases a coating of carbon nanoparticles was applied to the SEM samples rather than gold and platinum nanoparticles. Carbon was chosen as a coating medium for the chemical analysis of the surface because it was
thought that the introduction of a significant concentration of other metals onto the surface might interfere with the measurement of the metals of interest on the surface. A full description and discussion on sputter coating theory and methodology can be found elsewhere (Goldstein et al., 1981, Bozzola and Russell, 1992).

Finally the sample was ready to be placed into the instrument. Once the sample(s) were placed in the appropriate sample holder, the instrument was closed and a vacuum was applied. The voltage used for image generation was generally low (only 5-10 kV). The voltage used for chemical analysis however, was higher (20 kV or more). The reason for this is that the voltage must be adequate to excite an electron to produce a measurable response. The required voltage for a measurable backscatter response is different for each element, but it was higher than the voltage necessary to produce an image. A detailed guide on the use of an ESEM instrument and the theory of electron microscopy can be found elsewhere (Goldstein et al., 1981).

**Transmission Electron Microscope (TEM) Sample Preparation**

A sample of media was placed in a small glass vial. Once the vial was partially filled with water the vial was capped and the sample was vigorously shaken by hand. The intended result was to cause the MnO$_x$(s) coating to flake off of the sand grains. The resulting solution was a dark brown suspension of very small pieces of media. This sample was then allowed to settle for roughly one minute in order to allow the much larger particles to settle to the bottom of the vial. Then a small dropper was used to draw up less than a milliliter of the solution from the top of the vial.

A single drop of the suspension of pulverized media contained in the dropper was then placed onto a carbon coated copper TEM grid. The grid was placed inside of a desiccator for 24 hours in order to remove any residual moisture from the sample. The media was then placed into the TEM shown in Figure 6.
Figure 6 - Transmission Electron Microscope - Nanoscale Characterization and Fabrication Laboratory, Virginia Tech
Diffraction Pattern Analysis

Several samples of pulverized media were analyzed with a TEM in order to produce a Selected Area Diffraction Pattern (SADP). The specific crystal structure of a given solid is characteristic of that solid. Even solids that have the same chemical composition may have differing crystalline forms. Using TEM, an analysis of the way in which a solid interacts with an electron beam can be used to identify not only the chemical composition of a substance, but also its specific crystalline structure (Beeston et al., 1972).

When a beam of electrons penetrates a thin crystalline sample the beam is partially deflected by the crystal structure. This elastic scattering creates a pattern that is recorded by the instrument. This resulting image is called a diffraction pattern. Because the sample is so thin (often less than 50 nanometers) the majority of the beam penetrates the sample. However, a portion of the electron beam is deflected by the crystal lattice structure of the solid sample, much like a prism. The specific way in which the beam is deflected can be determined using Bragg’s Law. (Goldstein et al., 1981) Figure 7 shows both a profile view of the electron beam and a plan view of the resulting image on the detector film.

If the selected area (or spot size) is sufficiently small to cover only a single crystal, the structure of the crystal is uniform within the selected area. Thus, the beam is diffracted in several specific angles and a dotted pattern consisting of a series of spots in a regular array is produced on the detector film. However, if several smaller crystals of the same type are present in the selected area, the result is what is known as a polycrystalline diffraction pattern which appears as a series of rings. The ring pattern is the result of the electron beam interacting with crystals of the same type in many different orientations. (Beeston et al., 1972)

The distance from the sample to the detector film (or camera length) is a constant and is set by the operator of the instrument. The distances on the image produced by the detector are calibrated to a specific camera length. In the case of this analysis, gold nanoparticles of a known crystal structure were analyzed in order to calibrate the camera length.

The first step in the calibration procedure was to view the gold nanoparticles using the same camera length that was used for the analyzed sample. A pattern was produced for the gold nanoparticles. The ring pattern shown on the detector film was then analyzed by measuring the length from the center of the electron beam to the first ring.

This distance was recorded for each ring compared to a database of known values for gold nanoparticles. Using image processing software, the number of pixels from the center of the electron beam to the ring produced was established. This resulted in a correlation between the width of the ring on the detector and the number of pixels on the screen. The length of several rings was calibrated in this fashion.
Figure 7 - Formation of a Diffraction Pattern in Transmission Electron Microscopy (Plan and Profile views)
Adapted from a Figure Originally Generated by Mitsu Murayama
This distance from the center of the ring to the ring's edge corresponds to a d-spacing, each mineral structure has a series of d-spacings which arises based on the specific crystal structure of the mineral that can aid in the identification of the mineral structure. A screenshot of this process is shown in Figure 8. Utilizing basic trigonometry, the angle of each deflection can be determined. For a given diffraction pattern, the set of angles can then be compared against a database of values and the specific mineral can then be identified.

Energy Dispersive Spectroscopy (EDS) Line Scan Analysis

An analysis of the coated media surface was conducted using the SEM. The purpose was to determine how the composition of the MnO_{x(s)} surface varied with the depth of coating. Since the operating conditions of each of the columns had remained the same during the coating deposition it was initially hypothesized that the composition of the coating would be uniform regardless of depth. However, after considering the issue and the possibility of chemical reactions within the surface itself, it seemed possible that redox reactions and even chemical substitutions may have occurred within the MnO_{x(s)} surface on the media.

The media was prepared in two different ways in order to get a cross section of the media surface. One way was to prepare the media in exactly the same way as it had been for the initial analysis in the SEM, except that this time the sand grains would be cleaved in order to split the sand grain and hopefully create a clean cut of the coating as well. Sand grains were placed on a clean portion of the lab bench and were then pressed with a flat piece of steel until several sand grains were crushed. The resulting pulverized and cleaved grains were then placed onto silicon wafers with a carbon tape backing and placed into the SEM for analysis (Goodhew, 1972).

The second method aimed to create a thin cross-section of media suspended in an epoxy resin. This was accomplished by mixing two components of an epoxy resin together and combining that with several dozen grains of MnO_{x(s)}-coated sand. That mixture was then carefully inserted into a small diameter brass tube. The epoxy mixture was heated for 30 minutes at 135°C in order to harden the resin.

A small diamond saw was then used to cut the tube containing the hardened resin and coated media into several lengths that were 5 mm long or less. The sections were then ground down using several different types of sandpaper; beginning with a coarse grain and gradually decreasing to a finer grain. The result was a thin section 100 µm thick with a small section of coating clearly visible around each sand crystal. This provided a clear cross section of the coating that could then be viewed on the ESEM.

Once the two different types of samples were prepared they were placed into the ESEM instrument chamber and the sample chamber was placed in a vacuum prior to analysis. After
selecting a region of the media for analysis, a line scan of the chemical composition was conducted. The resulting output can be found in the results chapter.
Figure 8 - Computer Analysis of Selected Area Diffraction Pattern to Acquire d-Spacing Values
EXPERIMENTAL RESULTS

The primary purpose of this section is to present and to interpret the results of several different experiments and analyses that were conducted in the laboratory. The experiments were designed with the objective of discovering how Al interacts with the MnO₆ₓ(s) surface under carefully controlled and monitored conditions similar to those that would typically be present in a conventional surface water treatment plant. The conducted experiments were broken down into distinct categories, each attempting to identify and analyze the interaction of Al with the MnO₆ₓ(s) surface utilizing slightly varied experimental conditions. The first section details experiments that analyzed the adsorptive interaction of ‘soluble’ Al with the MnO₆ₓ(s) surface by varying the solution pH, the type of media, and the applied dosage of Mn. The next set of experiments sought to quantify the interaction of both soluble Al and particulate Al(OH)₃(s) species with the MnO₆ₓ(s) surface and to track the development of the MnO₆ₓ(s) surface over time. Finally, the MnO₆ₓ(s) surface was characterized using several different electron microscopy techniques. Selected imagery and analytical results from these analyses are presented in a later section of this chapter.

Adsorption of Soluble Mn and Al onto MnO₆ₓ(s)-Coated Media

As was described previously, the first set of bench-scale column experiments sought to explore the adsorption of soluble Mn and Al onto an MnO₆ₓ(s) coating. The purpose was to experimentally verify or refute that the primary mechanism of Al incorporation onto the MnO₆ₓ(s) surface was the adsorption of soluble Al species. The amount of soluble Al and Mn was quantified by comparing the concentration of the two metals in both the influent and effluent of the column. The two metals were dosed to the column media in their soluble forms; therefore any difference between the influent and the effluent concentration was presumed to be the result of adsorptive uptake of the metal by the MnO₆ₓ(s) surface.

Effect of Al on the Adsorption of Mn

All experimental trials that utilized an MnO₆ₓ(s)-coated media and soluble Mn showed absorptive uptake of Mn. The amount of Mn adsorption in a given experimental trial was dependent on two primary factors: the amount of MnO₆ₓ(s) coating on the media and the pH of the applied water. The quantity of MnO₆ₓ(s) coating present on the media determined the number of available adsorptive sites. The correlation between the level of MnO₆ₓ(s) coating and the potential for adsorptive uptake of Mn has already been well established by previous research efforts (Tobiason et al., 2008). When comparing two column trials using two different types of media,
the media with the greatest amount of MnO\textsubscript{x(s)} coating showed the greatest amount of Mn adsorption. The effect of pH on the adsorptive uptake of Mn on the MnO\textsubscript{x(s)} surface has been characterized in previous studies as well (Knocke et al., 1991a, Morgan and Stumm, 1964). These studies have demonstrated that the adsorptive capacity of the surface is largely a function of the solution pH. This is due to the adsorptive competition of Mn\textsuperscript{2+} with H\textsubscript{3}O\textsuperscript{+} (Morgan and Stumm, 1964).

In the case of Al, a change in the solution pH has an effect on the dominant form of Al present in solution. The dominant soluble Al species can vary from cationic, to neutral, to anionic (Srinivasan et al., 1999). If Al incorporation into the MnO\textsubscript{x(s)} surface is adsorptive, then it stands to reason that the behavior of that adsorption might be affected by the solution pH.

It was initially hypothesized that the potential adsorptive uptake of soluble Al onto the surface might compete with Mn adsorption. Therefore, experimental trials were conducted in order to compare the adsorptive uptake of Mn onto the MnO\textsubscript{x(s)} surface in the presence and absence of soluble Al. The effluent Mn concentrations shown in Figure 9 show minimal difference in the adsorption of soluble Mn whether soluble Al species are present or absent at pH 7.2. In the presence of soluble Al species, the adsorptive uptake of Mn was quantified to be 1.48 mg. In the absence of soluble Al species 1.47 mg absorbed to the surface. This demonstrates that the presence of soluble Al does not have any significant effect on the adsorptive uptake of soluble Mn onto the MnO\textsubscript{x(s)} surface.

The effluent data also seem to reveal an interesting phenomenon between the surface and the bulk solution. Data presented in Figure 10 show a measurable concentration of Al in the effluent of the column that did not receive any Al in the influent. With no significant Al in the influent feed water, it appears that Al is leaving the surface of the media gradually over time. Two possible explanations can be postulated for this behavior:

1. The MnO\textsubscript{x(s)} surface is behaving as a pseudo ion-exchange media and Al is being desorbed from the surface in favor of replacement by adsorbed Mn.
2. The MnO\textsubscript{x(s)} surface of this treatment plant media was formed in the presence of supersaturated concentrations of Al due to the practice of alum coagulation. Taking this media and exposing it to a feed water without any soluble Al may have caused the Al to leave the surface as the MnO\textsubscript{x(s)} surface attempted to establish a ‘new’ equilibrium between the soluble Al in the bulk solution and the surface Al.

The first explanation is implausible simply because there is no difference in the effluent behavior of Mn whether Al is present or not. If Mn was being adsorbed as Al was being desorbed, it would be expected that more Mn would be absorbed in the column that did not receive a soluble dosage of Al.

Data presented in Figure 11 and Figure 12 show the effluent concentrations of Mn and Al for columns that received an added dosage of soluble Al and columns that did not. During this
experiment the effluent concentrations of Mn in each column approached the influent concentration much faster at pH 6.3 than at pH 7.2. This indicated that the surface’s adsorptive capacity for Mn was saturated much more quickly at pH 6.3 than at 7.2 and led to a decrease in the total amount of Mn adsorbed to the surface during the experimental trial. This was most likely due to the increased cationic competition on the MnO_\text{(s)} surface between Mn and H_3O^+. A change in the solution pH also likely caused a change in the abundance of certain species of soluble Al. A decrease in pH would have increased the concentration of cationic soluble Al hydroxides, specifically Al(OH)_2^+. From these data sets alone it is difficult to saw what effect, if any, this change had on the adsorptive competition with Mn^{+2} on the MnO_\text{(s)} surface as the measured uptake of Al during the experimental trial was negligible. Data presented in Figure 12 show that the effluent concentration of Al was similar to the influent concentration of Al for most of the experimental trial. In the presence of soluble Al species at pH 6.3 the surface adsorbed 0.32 mg of Mn and adsorbed 0.60 mg in the absence of soluble Al species. In both cases the quantity of Mn taken up by the surface was very slight. The effluent behavior of the columns seems to again confirm that the presence or absence of soluble Al does not have any significant effect on the adsorption of soluble Mn onto the surface.

**Effect of Media Type on the Adsorption of Soluble Mn and Al**

The type of media used in the experiments was varied in order to quantify any variability in the potential for adsorptive uptake by the media. Most of the experimental trials utilized column media that was taken from treatment facilities that applied a free chlorine residual across their filtration media in order to achieve soluble Mn control. These media samples were selected because they already contained a significant MnO_\text{(s)} coating that could be used to quantify adsorptive uptake of soluble Mn during bench-scale column experimental trials. Not all of the experiments conducted used media from treatment facilities. Some experimental trials were conducted using either a synthetically coated media or commercially produced MnO_2\text{(s)} in the form of pyrolusite. The important distinction between these types media and the media taken from treatment facilities was the initial Al content already present in the media coating.

Unlike the media taken from treatment facilities, the pyrolusite media and the media possessing a synthetically prepared MnO_\text{(s)} coating did not contain a significant amount of Al. Analysis by chemical extraction showed that both the pyrolusite and the synthetically prepared MnO_\text{(s)} coating contained more than 100 times more Mn than Al by weight. This meant that the uptake on the media could be quantified and compared against the uptake onto media taken from water treatment facilities which did contain a significant amount of Al. The synthetically generated MnO_\text{(s)} coating on anthracite media was prepared in accordance with the method developed by Merkle (Merkle et al., 1997). The variation in the adsorptive behavior between the various types of media allowed for important inferences to be made about the interactions between soluble Mn, soluble Al and the MnO_\text{(s)} surface.
Figure 9 - Adsorptive Uptake of Mn onto Blacksburg MnO\textsubscript{x(s)}-Coated Anthracite Media (pH 7.2, HLR = 4.0 gpm/ft\textsuperscript{2}, No HOCl Added)

Figure 10 - Adsorptive Uptake of Al onto Blacksburg MnO\textsubscript{x(s)}-Coated Anthracite Media (pH 7.2, HLR = 4.0 gpm/ft\textsuperscript{2}, No HOCl Added)
Figure 11 - Adsorptive Uptake of Mn onto Blacksburg MnO$_{x(s)}$-Coated Anthracite Media (pH 6.3, HLR = 4.0 gpm/ft$^2$, No HOCl Added)

Figure 12 - Adsorptive Uptake of Al onto Blacksburg MnO$_{x(s)}$-Coated Anthracite Media (pH 6.3, HLR = 4.0 gpm/ft$^2$, No HOCl Added)
Data presented in Figure 13 show the adsorption of soluble Mn species onto synthetically coated anthracite coal at pH 7.2. The amount of MnO$_x$(s) coating present on the synthetic media (approximately 0.2 mg Mn per gram of dry media) was much less than the amount on the samples of media taken from treatment facilities which accounts for the lower adsorptive capacity for Mn.

Data presented in Figure 13 show that the uptake of Mn onto the synthetically generated MnO$_x$(s) surface is minimal compared to other column trials (0.42 mg for an influent [Mn] of 100 ppb and 0.74 mg for an influent [Mn] of 200 ppb). However, data presented in Figure 14 show that the uptake of Al during that same experimental trial is significant (0.47 mg for an influent [Mn] of 100 ppb and 0.57 mg for an influent [Mn] of 200 ppb). The uptake of Mn onto the media is quickly exhausted and the effluent concentrations of Mn become almost equivalent to the influent concentrations. Interestingly, the results show that the adsorption of soluble Al species continues even after the adsorptive capacity for Mn has been exhausted.

A similar result is observed when this experiment is repeated under a lower pH condition as is shown in Figure 15 and Figure 16. At pH 6.3 the uptake capacity for soluble Mn is again rapidly exhausted. The effluent concentration of Mn even appears to exceed the influent briefly. Thus no measurable adsorption of Mn was observed during the column trials at pH 6.3. Again the influent concentration seemed to have no effect on the amount of Al adsorbed by the column media. (0.41 mg for an influent [Mn] of 100 ppb and 0.43 mg for an influent [Mn] of 200 ppb).

It is important to note that for all of the experimental trials in which a synthetic MnO$_x$(s) coating was utilized soluble Al continued to adsorb onto the surface long after the Mn adsorption behavior has ceased. These results indicate that the mechanism for soluble Al incorporation may not be competitive with manganese. If the two were competitive then it would be expected that the adsorption of one would be accompanied by the release of the other.

Pure MnO$_2$(s) in the form of pyrolusite was also used in one set of the adsorption column studies. The fact that the media was pure MnO$_x$(s) rather than a coated media afforded the media surface a very large adsorptive capacity for Mn. Data presented in Figure 17 show the influent and effluent concentrations of Mn that flowed through the column media at pH 7.2. The data show a steady effluent concentration of Mn throughout the column trial. This suggests that the hydraulic loading rate and the short media bed allowed for only a portion of the influent Mn to be adsorbed during the time the media was in contact with the bed of media. The Mn in the effluent was not given enough contact time with the media bed to adsorb and the Mn that did not adsorb exited the column. Previous researchers studying the adsorption of Mn onto an MnO$_x$(s) surface generated concentration profiles within an filter containing MnO$_x$(s)-coated media. The researchers showed how the adsorptive behavior of Mn in a filter varied with filter media depth and the hydraulic loading rate (Knocke et al., 2010). Based on their results, it is likely that a deeper bed of filtration media would have yielded a lower effluent concentration of Mn.
By the end of the experimental trial the pyrolusite media was far from being saturated with soluble Mn. This is evidenced by the large and unchanging discrepancy between the influent and effluent concentrations. The Al data do not follow a similar pattern. Data in Figure 18 show the corresponding Al adsorptive behavior by presenting the influent and effluent concentration of Al. As the experimental trial progressed, the effluent Al concentrations appear to have gradually increased towards the influent concentration as the media approached its adsorptive capacity for Al. Similar behavior was observed when the experiment was repeated at the lower pH condition of 6.3. Data for this lower pH condition are presented in Figure 19 and Figure 20.

Despite the vast differences (orders of magnitude) in the amount of Mn present in the MnO\(_x\)(s) surface of the synthetically prepared MnO\(_x\)(s) coating and the pyrolusite, the capacity for the uptake of soluble Al was similar. Thus, the type of media (or more accurately, the level of MnO\(_x\)(s) coating) makes a significant difference in the adsorptive uptake of Mn, but makes almost no difference in the adsorptive uptake of Al.

**Effect of Mn on the Adsorption of Al**

The concentration of Mn in the feed water was varied in an effort to further explore the possibility of competitive adsorptive behavior between Mn and Al in solution. Figure 14 and Figure 16 show the performance of two columns containing a media with a synthetic MnO\(_x\)(s) coating at pH 7.2 and pH 6.3 respectively. In each of the paired columns shown in the figures the Mn concentration in one of the columns was twice that of the other. Despite the difference in the Mn fed to each column, the observed adsorption of Al was similar in both cases.

Figure 18 and Figure 20 summarize the data regarding the adsorption of Al by comparing columns containing pyrolusite media and feed water in which Mn was present and absent at pH 7.2 and 6.3 respectively. Table 6 and Table 7 summarize the mass of Al and Mn adsorbed during the experimental trials involving pyrolusite and a synthetically generated MnO\(_x\)(s) coating. Again, the adsorptive behavior of Al in each column was similar despite one column having a significant concentration of Mn in the feed while the other contained no added Mn.

**Particulate Al(OH)\(_3\)(s) Deposition onto MnO\(_x\)(s)-Coated Media**

The experimental procedures in which a soluble dosage of Al was applied confirmed the adsorptive uptake of ‘soluble’ species of Al onto MnO\(_x\)(s)-coated media. However, this quantity of Al alone was insufficient to account for the amount of Al present in MnO\(_x\)(s) coatings found on coated media from water treatment facilities (Tobiason et al., 2008). This meant that some other mechanism of Al deposition was at work in order to account for the remainder of the Al present in these MnO\(_x\)(s) coatings from full-scale treatment facilities.
Figure 13 - Adsorptive Uptake of Mn onto a Synthetic MnO\textsubscript{x(s)} Coating
(pH 7.2, HLR = 4.0 gpm/ft\textsuperscript{2}, No HOCl Added)

Figure 14 - Adsorptive Uptake of Al onto a Synthetic MnO\textsubscript{x(s)} Coating
(pH 7.2, HLR = 4.0 gpm/ft\textsuperscript{2}, No HOCl Added)
Figure 15 - Adsorptive Uptake of Mn onto a Synthetic MnO_x(s) Coating
(pH 6.3, HLR = 4.0 gpm/ft^2, No HOCl Added)

Figure 16 - Adsorptive Uptake of Al onto a Synthetic MnO_x(s) Coating
(pH 6.3, HLR = 4.0 gpm/ft^2, No HOCl Added)
Figure 17 - Adsorptive Uptake of Mn onto Pyrolusite Media  
(pH 7.2, HLR = 4.0 gpm/ft², No HOCl Added)

Figure 18 - Adsorptive Uptake of Al onto Pyrolusite Media  
(pH 7.2, HLR = 4.0 gpm/ft², No HOCl Added)
Figure 19 - Adsorptive Uptake of Mn onto Pyrolusite Media
(pH 6.3, HLR = 4.0 gpm/ft², No HOCl Added)

Figure 20 - Adsorptive Uptake of Al onto Pyrolusite Media
(pH 6.3, HLR = 4.0 gpm/ft², No HOCl Added)
Table 6 - Calculated Mass Uptake of Al and Mn onto a Synthetic MnO$_{x(s)}$ Coating - Varying pH, Mn Loading

<table>
<thead>
<tr>
<th>pH</th>
<th>Al Uptake (mg)</th>
<th>Mn Uptake (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 ppb Mn</td>
<td>0.47</td>
<td>0.42</td>
</tr>
<tr>
<td>200 ppb Mn</td>
<td>0.57</td>
<td>0.74</td>
</tr>
<tr>
<td>pH 6.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 ppb Mn</td>
<td>0.41</td>
<td>0.13</td>
</tr>
<tr>
<td>200 ppb Mn</td>
<td>0.43</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 7 - Calculated Mass Uptake of Al and Mn onto Pyrolusite Media - Varying pH, Mn Loading

<table>
<thead>
<tr>
<th>pH</th>
<th>Al Uptake (mg)</th>
<th>Mn Uptake (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No Added Mn</td>
<td>0.59</td>
<td>0.09</td>
</tr>
<tr>
<td>100 ppb Mn</td>
<td>0.65</td>
<td>5.16</td>
</tr>
<tr>
<td>pH 6.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No Added Mn</td>
<td>0.55</td>
<td>0.61</td>
</tr>
<tr>
<td>100 ppb Mn</td>
<td>0.51</td>
<td>5.15</td>
</tr>
</tbody>
</table>
A new set of bench-scale experimental trials involving columns with short beds of media was conducted. This study differed from the previous adsorptive study of soluble Al and Mn in two important ways. First, a supersaturated dosage of Al was applied to the column media in order to monitor the deposition of both soluble Al and particulate Al(OH)$_3$ onto the MnO$_x(s)$-coated media over time. Secondly, a free chlorine residual (~2-3 mg/L free chlorine) was applied in the feed water in order to continually regenerate the MnO$_x(s)$ surface.

**Al Size Study**

A characterization of the Al that comes into contact with the media surface was crucial to understanding how and why Al incorporates into the MnO$_x(s)$ surface. For a treatment plant that utilizes Al coagulation, the MnO$_x(s)$ surface of the filter media is undoubtedly in contact with Al in both insoluble and soluble forms. The size ranges of colloidal and particulate species of Al are diverse. Particles observed in treatment facilities range in size from several nanometers to several millimeters in diameter.

Measurements of Al in both the column feed water and the water upstream of the dual media filters at the BCVPIWTF were acquired in order to separate the Al into size fractions. The various species of Al were separated into different size ranges by filtering the water containing particles of Al through a series of different membrane filters and ultrafilters. In this way it was possible to separate the Al into different size ranges. The concentration of Al passing through one filter was subtracted from the concentration passing through the next smaller filter. The result is a visual representation of the Al species with respect to size.

Figure 21 shows the measured sizes of Al species taken directly upstream of the filters of the BCVPIWTF. The large concentration of Al species greater than 20 µm is due to the large particulates created by the coagulation process at the treatment facility; particulates that unfortunately did not settle out in the previous sedimentation processes. Figure 22 shows the typical Al species present in the column feed water sampled directly above the column filter media used in these laboratory studies. The purpose of comparing the two was simply to verify that the Al loadings in the laboratory columns successfully generated Al species in a wide range of sizes. It was not possible to load the columns with the same total concentration of Al that would be typical of a facility like the BCVPIWTF. Likewise, in a real-world treatment situation the particulate Al loading to the filters would be experience a certain amount of variation due to the changing effectiveness of upstream processes used to remove particulate Al species from one day to the next. Unlike the BCVPIWTF, the media bed of the laboratory columns was a composed of a single type of media. The higher loading of Al coupled with the small void spaces of the media bed would have rendered column operation impossible due to frequent backwashing.
**Figure 21 - Blacksburg Al Size Fractionation of Pre-Filter Al Species**

**Figure 22 - Size Fractionation of Influent Al for Particulate Al(OH)$_3$ Column Study**
**Effluent Mn and Al Data**

Effluent samples were taken during the experiment in order to track the Al and Mn capture performance of the MnO$_x$(s)-coated media over the entire course of the experiment. Data presented in Figure 23 show the effluent concentrations of Al varying as a function of the Mn loading. The data show the effluent concentrations of Al for a variety of different Mn loadings during the parallel column study in which short beds of MnO$_x$(s)-coated sand media were loaded with soluble Mn, free chlorine and particulate Al(OH)$_3$(s). The only significant difference in the effluent behavior in terms of Al species occurred in the column media loaded with background levels of Mn ([Mn] < 10 ppb). This column showed significant variation in the effluent Al concentration that was likely the result of particulate breakthrough of Al(OH)$_3$(s). Columns with applied dosages of Mn showed little variability in their effluent behavior with regard to Al. Whether this consistent capture of Al for columns loaded with Mn can be attributed to a property of the MnO$_x$(s) coating itself, an interaction with the entrained Al solids within the media bed, or a combination of both is difficult to say from this data set alone.

Effluent Mn data presented in Figure 24 indicate that the ability of the MnO$_x$(s) coated media to sequester Mn rapidly improved in just a few days. In each experimental trial, an effluent concentration of Mn of less than 5 ppb was achieved within 10 days of column operation. In a practical sense, these data seem to indicate that a filtration media seeded with a very modest initial MnO$_x$(s) coating can effectively capture soluble Mn within a few days.

**Media Extraction Data**

In their investigation of Mn uptake by filtration media, Tobiason et al. (2008) performed chemical extraction analyses of media coatings from a variety of different treatment facilities in order to characterize the metal content of the MnO$_x$(s) coating. A procedure developed by Knocke et al. (1990) was used to extract the MnO$_x$(s) coating from the media in order to measure the metals content. This was necessary in order to compare the results of the laboratory study of particulate Al(OH)$_3$(s) species to the results of the 2008 AWWARF study. The specific method can be found in the methods chapter of this document. Table 8 is a selection of the results obtained by Tobiason et al. (2008) showing an Al:Mn molar ratio typical of the plants included in the study. The data show how the amount of Mn and Al present in the MnO$_x$(s) coatings on filtration media taken from a core sample of a bed of filtration media. The authors also presented the calculated molar ratio of Al:Mn. While the data represented in Table 8 are taken from a single core sample from a single plant, data in Table 9 in the discussion chapter provide a summary of Al:Mn molar ratios from surface water treatment facilities surveyed in the 2008 AWWARF study.
Figure 23 - Effluent Al During Particulate Al Column Study - Varying Mn Loadings
(4.0 gpm/ft$^2$, pH 6.8-7.1, [HOCl] = 2-3 mg/L)
Figure 24 - Effluent Mn During Particulate Al Column Study - Varying Mn Loadings
(4.0 gpm/ft$^2$, pH 6.8-7.1, [HOCl] = 2-3 mg/L)
Table 8 - Molar Metal Ratios for Harwood's Mill WTP (Tobiason et. al. 2008)

<table>
<thead>
<tr>
<th>Average Depth (in)</th>
<th>Mn Coating (mg/g)</th>
<th>Al Coating (mg/g)</th>
<th>Al:Mn Molar Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>37.7</td>
<td>27.8</td>
<td>1.50</td>
</tr>
<tr>
<td>9</td>
<td>28.1</td>
<td>21.4</td>
<td>1.55</td>
</tr>
<tr>
<td>15</td>
<td>29.8</td>
<td>21.6</td>
<td>1.47</td>
</tr>
<tr>
<td>21</td>
<td>30.4</td>
<td>23.8</td>
<td>1.59</td>
</tr>
<tr>
<td>27</td>
<td>9.25</td>
<td>9.03</td>
<td>1.99</td>
</tr>
<tr>
<td>33</td>
<td>0.675</td>
<td>1.20</td>
<td>3.61</td>
</tr>
</tbody>
</table>
Figure 25 characterizes the molar ratio of Al to Mn within the MnO_x(s) coating during the experiment. All of the columns were exposed to a similar concentration of Al (200 - 220 ppb), but each column was loaded with feed water containing a different concentration of soluble Mn. The data show that the molar ratio of Al:Mn decreased as the amount of soluble Mn in the feed water increased. As the amount of Mn loaded to the columns decreases to 50 ppb, the ratio of Al:Mn increases to a value typical of MnO_x(s)-coated samples from surface water treatment facilities.

These results demonstrate that it is possible to produce a molar ratio of Al to Mn in the coating similar to that observed in the MnO_x(s)-coated media found on the media of surface water treatment plants presented in the 2008 AWWARF study. Unlike the Mn loadings that were applied in the laboratory, treatment plant filtration media is usually subjected to seasonally varied loadings of Mn. Additionally, treatment plants with very high Mn loadings will remove a significant fraction of the influent Mn by applying strong oxidants. In any case, the concentration of soluble Mn that reaches the filtration media is typically much lower than many of the experimental conditions tested in the laboratory.

The chemical extraction data presented in Figure 26 show the Al content of the MnO_x(s) coatings in each of the columns operated during the particulate Al experimental trials. The amount of Al is expressed in units of mg of Al per dry gram of filtration media. The data cover a variety of different Mn loadings (< 10 ppb – 400 ppb). In each of the columns in which added dosage of soluble Mn was applied, the column media did accumulate Al within the MnO_x(s) surface. The only column media that did not accumulate a significant amount of Al was the column which did not receive an added dosage of Mn (“< 10 ppb Mn”). The data show that in the Al deposition onto MnO_x(s)-coated media only occurs with the continued deposition of soluble Mn.

**Mn Loading and Al Capture**

A study was conducted in which the influent and effluent concentrations of Al were compared for three parallel columns with varying loadings of Mn in an effort to further quantify the capture of Al. The fraction of the influent Al for each size fraction that was captured as the feed water passed through the filtration media was quantified and the data are presented in Figure 27. Samples were collected of the influent feed water and were filtered through a series of filters of various pore sizes. The filtrate from each filter size was sampled and measured on the ICP-MS. This analysis was repeated three times; once for each of the three column influent waters. The resulting Al concentrations were then averaged (because the column feed waters were identical except for their added Mn concentrations) to produce a single value for each size filter size.
Figure 25 - Molar Ratio of Al:Mn In the MnO\textsubscript{x(s)}-Coated Media Over Time - Particulate Al(OH)\textsubscript{3(s)} Column Study, Varying Soluble Mn Loadings (50 ppb - 400 ppb)

Figure 26 - Al Content of MnO\textsubscript{x(s)}-Coated Media Over Time (mg Al / gram of Dry Media) - Particulate Al Column Study, Varying Soluble Mn Loadings (50 ppb - 400 ppb)
Figure 27 - Percentage of Influent Al Species Captured During Filtration as a Function of Mn Loading (50 ppb - 400 ppb)
Then two effluent samples were collected from each column and filtered through the same series of filter sizes that were applied to the influent samples. One effluent sample was taken near the beginning of the filter cycle and another was taken just prior to filter backwash in order to capture any variability that may have occurred during the filter cycle. These two values were then averaged to produce a single value. Finally, the difference between the concentration of Al passing through a filter of a given pore size in the influent sample and the concentration of Al pass through that same filter size in the effluent was computed for each column and each filter size.

Across every size category, the amount of Al captured increased as the soluble Mn loading to the MnO\textsubscript{x(s)}-coated media increased. It is impossible to say with certainty the specific reason why higher Mn loadings increase the Al capture efficiency. It cannot be stated whether this enhanced capture of Al occurs on the MnO\textsubscript{x(s)} surface, on the backwash solids present within the media bed, or a combination of both. However, what can be stated is the presence of a greater amount of Mn deposition the capture of particulate Al species is enhanced.

In addition, several detailed sampling trials were conducted during a single filter run cycle. Data presented in Figure 28 show the effluent Al concentrations from several columns beginning with the initial backwash of the media until the accumulated head on the column media exceeded the limits of the experimental apparatus and data collection ceased. The data suggest a relationship between the loading of Mn and the breakthrough of particulate Al.

The column loaded with only background levels of tap water Mn experiences a significant increase in Al particles larger than 0.45 μm near the end of the filter cycle. The two columns that contained additional dosages of Mn (100 ppb, 400 ppb) show little or no change between the filtered and unfiltered Al concentrations during the filter run. The discrepancy between the effluent samples that were unfiltered and the samples that were filtered through a 0.45 μm filter can be thought of as the ‘particulate’ fraction of Al in the effluent. The column with the highest loading of Mn (400 ppb) had to be ‘taken offline earlier than the other two columns because the head on the filter reached a level that was beyond the capacity of the apparatus.

The length of the filter run does not appear to have any impact on the capture of species of Al less than 0.45 μm. As the filter cycle progresses from time zero (filter backwash) to the end of the data collection, there appears to be little or no change in the effluent Al species less than 0.45 μm in any of the columns during the filter run.
Figure 28 - Measured Particle Breakthrough Behavior with Varying Mn Loading
Scanning Electron Microscopy Images

Several samples of filter media were prepared and analyzed using the ESEM instrument of the Nanoscale Characterization and Fabrication Laboratory (NCFL) at Virginia Tech. The analysis yielded both qualitative and quantitative information about the MnO$_x(s)$ surface composition. Several different analyses are presented in the following subsection.

*MnO$_x(s)$-Coated Media Surface Images*

Figure 29 shows a sample of sand media prior to being loaded into the bench scale column experiment in which soluble Mn and a mixture of soluble and insoluble Al species were applied to the media. The sand media was donated by Siemens (Ames, IA) and possessed a light MnO$_x(s)$ coating.

Figure 30 shows a sample of sand media that was used during the particulate Al loading column study. The original MnO$_x(s)$-coated sand grain was exposed to feed water containing a high concentration of Mn ([Mn] = 0.4 mg/L) and a supersatured dosage of Al. The resulting coating appeared rough in texture and covered the entire sand grain. An image of the surface of the same piece of media at a higher magnification is shown in Figure 31. The higher magnification revealed crevices and voids on the surface of the media that were only a few micrometers wide. In a qualitative sense this provided a physical representation of the enormous surface area of the MnO$_x(s)$ coating. Additionally, the multitude of small crevices suggested the potential for small insoluble particles of Al(OH)$_3(s)$ to bind to the surface and entrain themselves within the MnO$_x(s)$ surface.

*EDS Mapping*

Several different prepared samples of sand media were placed into the ESEM instrument and analyzed using EDS for a qualitative analysis of the elemental composition of the coating. This analysis helped to describe the composition of the samples and was utilized in selecting sections for further analysis using EDS line scans.

Results presented in Figure 32 and Figure 33 show a sample of MnO$_x(s)$-coated media (feed water [Mn] = 0.4 mg/L) suspended in a resin prepared by a method described in the EDS line scan analysis section of the methods chapter. Figure 32 is a presentation of the normal ESEM image of the sample combined with the backscatter response of the sample by element (each element is designated by a different color), whereas Figure 33 is the same image segregated by element. In both images, the silicon sand base of the media was clearly visible and was contrasted by the Mn and Al of the coating that compose of MnO$_x(s)$ coating. While this analysis did qualitatively demonstrate the elemental content of the coating, it could not be used to quantify the coating.
content. This sample was placed into the ESEM and a small corner was selected for analysis. The base material showed a very high silicon signal and was surrounded by the MnO_x(s) coating that was generated during the particulate Al column study. The image of the coating does not appear to show any silicon, but does show a strong presence of Mn and Al. Line scans of this sample are presented in the appendix.

The same sample of media was analyzed again at a lower magnification. At this magnification, the broken pieces of sand media contained in the resin can be observed. The sample was in the process of being prepared for TEM analysis, but it was abandoned for TEM analysis when a thin slice of sand media broke and fell out of the resin. The residual coating of that sand was left behind on the resin and can be identified by the strong signal of Mn and Al in the upper left corner of Figure 34. The individual signals produced by Mn and Al are shown in Figure 35. The image of Mn shown in the lower left portion of the figure clearly shows the outlines of the coated sand.
Figure 29 - SEM Image of Column Media Sand Grain With Minimal MnO$_x$(s) Coating Prior To Mn Loading - 150x
Figure 30 - SEM Image of Column Media Sand Grain, 500x
(Feed Water [Mn] = 0.4 mg/L)
Figure 31 - SEM Image of Column Media Sand Grain, 10,000x
(Feed Water [Mn] = 0.4 mg/L)
Figure 32 - EDS Map of Thin Section of MnO_x(s)-Coated Sand in Resin (Feed Water [Mn] = 0.4 mg/L) 
Blue Silicon Oxide Sand Particle Surrounded By An MnO_x(s) Coating Shown in Red and Green

Figure 33 - EDS Backscatter Images of Thin Section of MnO_x(s) Separated by Element
Figure 34 - EDS Map of Thin Section of MnO$_x$(s)-Coated Sand Particles in Resin (Feed Water [Mn] = 0.4 mg/L)
MnO$_x$(s) Surface Is Visible Along The Edges Of The Sand Particles

Figure 35 - Backscatter Images of Thin MnO$_x$(s)-Coated Particles Separated By Element EDS Line Scan Analysis
The ESEM was also used to apply EDS to line scans across sections of the coating that was produced during the laboratory analysis. The analysis was similar in concept to the previous EDS analyses, but instead of a map showing the elemental composition of a region, a short length was chosen for analysis. At several points along the defined length, the elemental composition was quantified by detecting the response of the surface to the applied electron beam.

This process was applied to several samples of column media that were used during the particulate Al study. Each media sample had been exposed to a different Mn loading (50, 200, and 400 ppb). The samples were prepared by cleaving samples of the MnO$_x(s)$-coated sand media and attempting to scan across the exposed cross section of the coating. Several plots showing the measured counts of Al and Mn across the length of the scan were compiled. Representative results are presented here, with others in the appendix.

Figure 36 shows the direction of the scan across the media MnO$_x(s)$ coating with the lowest feed water Mn concentration (50 ppb). The instrument was able to roughly quantify the abundance of each element by detecting the response of the media surface to a high energy electron beam. When the beam was focused on a specific area, an X-ray was produced. The intensity and energy of this X-ray can be interpreted by the detector to a specific element. Each time a characteristic X-ray of a certain element is detected, a single count is registered. The counts of both Al and Mn (shown in Figure 37) were lowest in the region of the scan covering the silicon oxide sand base of the coated media. In the portion of the scan covering the MnO$_x(s)$ coating the number of detected counts of Al consistently exceed that of Mn, but an increase in one was almost always matched by an increase in the other. Figure 38 shows another MnO$_x(s)$-coated media loaded with a higher concentration of Mn (200 ppb). The counts of Al still exceeded those of Mn in the scan of the MnO$_x(s)$ coating shown in Figure 39, but the discrepancy in the counts is less than was observed in Figure 37.

The EDS Map shown in Figure 40 shows how the topography of the MnO$_x(s)$ surface hinders the instrument’s ability to detect the counts of Mn and Al (Goldstein et al., 1981). The media shown was exposed to a feed water containing a high concentration of Mn (400 ppb). The backscatter response of both Mn and Al drop off in the crevices of the surface, evidenced by the darker regions of Figure 40. Figure 41 shows an EDS scan conducted across that same surface.

The limitations of this type of analysis make it difficult to make quantitative statements about the composition of the surface. In order to speculate about the composition of the surface in terms of mass, assumptions have to be made about the form of each element. The number of oxygen atoms assumed for each detected atom of Mn or Al can have a significant impact on the estimation of the mass composition of the surface.

However, the EDS line scans confirm that Al and Mn are present together throughout the media surface as opposed to existing in localized deposits. This yields important information about how the Mn and Al are deposited onto the MnO$_x(s)$ surface.
Figure 36 - ESEM Image - Coating Cross Section of Cleaved Sand Grain (Feed Water [Mn] = 0.05 mg/L)
Arrow Indicates the Line Scan Pathway

Figure 37 - EDS Line Scan of Coating - Mn and Al Counts (Feed Water [Mn] = 0.05 mg/L)
Figure 38 - ESEM Image of Coating Cross Section (Feed Water [Mn] = 0.2 mg/L) 
Arrow Indicates the Line Scan Pathway

Figure 39 - EDS Line Scan of Coating - Mn and Al Counts (Feed Water [Mn] = 0.2 mg/L)
Figure 40 - ESEM Map of MnO$_x$ Surface (Feed Water [Mn] = 0.4 mg/L)

Figure 41 - Line Scan of Coating Mn and Al Counts (Feed Water [Mn] = 0.4 mg/L) 
Variation in Detected Counts Is Likely The Result of Variation In Surface Topography
TEM Images

An analysis using a Transmission Electron Microscope (TEM) was completed in order to further characterize the MnO\textsubscript{x(s)} surface. Previous work conducted on MnO\textsubscript{x(s)} surfaces utilized a chemical extraction procedure to characterize the MnO\textsubscript{x(s)} coating (Knocke, 1990). Analysis of the media surface by chemical extraction does yield important about metals content of the surface, but does not provide any information beyond the total chemical composition of the MnO\textsubscript{x(s)} surface. As previously discussed, seasonal loadings of Mn in water treatment facilities result in the formation of layered depositions of Al and Mn. When a piece of coated media from a treatment plant is examined in cross section under an electron microscope the media coating structure resembles that of tree rings. Each layer embodies a deposition representative of the bulk water solution at a given time that the media was being used at the plant. When the MnO\textsubscript{x(s)} surface is fully extracted and averaged the information contained in the layered deposits is lost.

Though the cost and time investment for TEM analysis is much greater than simple chemical extractions, the information obtained is much greater. TEM analysis characterizes not only the chemical composition of the surface, but also yields the potential to determine the specific mineral composition of the surface.

The samples of media selected for analysis were pulverized using a method described in the TEM sample preparation section of the methods chapter. A visual inspection of cross section images of the MnO\textsubscript{x(s)} surface in Figure 42 shows a surface that is far from homogeneous. The surface appears to be composed of a mix of weakly crystalline and amorphous structures. Figure 42 and Figure 43 are images of the same sample of MnO\textsubscript{x(s)} coating. Both images show a heterogeneous mixture of particles. The sample appears to consist of a mixture of small, dense crystalline structures accompanied by less dense amorphous or weakly crystalline structures.

From these images alone it is not possible to say with certainty that the darker areas are necessarily Mn oxide crystals and that the lighter areas are amorphous Al. The contrast between light and dark in the image is not always indicative of differences in chemical composition or physical state. Contrast in the image can be caused by several factors including differences in the topography of the sample and variability in the thickness of the sample (Goldstein et al., 1981). Careful preparation of the sample and careful selection of the analyzed particle can reduce this variability. When the sample is relatively uniform in topography and thickness, the variability in image contrast can be attributed to differences in the sample composition(Goldstein et al., 1981).

The composition of the TEM samples was verified using SADP. Using the diffraction pattern analysis, a specific crystal structure can be analyzed in detail. When the electron beam was focused on the sample a ring pattern was produced.
Figure 42 - TEM Image of Pulverized MnO$_{x(s)}$ Coating (Scaled as Shown)
Figure 43 - TEM Image of Pulverized MnO$_x$(s) Coating (Scaled as Shown)
**High Resolution TEM**

One analysis was conducted using a different TEM than the one that was used in the laboratory at Virginia Tech. Several images were generated and scans for elemental composition were conducted. The image shown in Figure 44 is so sharp that the lattice structures of Mn oxide crystals a few nanometers wide can be observed. The crystalline structures appear as clusters of parallel lines within the image. Different clusters show different orientations of lattices indicating the presence of many different nano-sized crystals rather than a larger crystalline structure.

**TEM – Diffraction Pattern Analysis**

One of the key motivations for pursuing a TEM analysis of the coating was the potential to gather information about the specific mineral phase of the coating rather than simply its chemical composition. The TEM produces an image of the sample by illuminating the sample with a focused high energy (~120kV) electron beam. Alternatively, the beam can focus on a much smaller area of the sample in order to produce a diffraction pattern. The result in this case was a series of rings. Each ring’s distance from the center of the image was analyzed in order to measure a d-spacing.

Figure 45 represents a diffraction pattern that was typical of the analysis of several coated media surfaces. The collected diffraction patterns were analyzed using a computer in order to measure several d-spacings. After analyzing several diffraction patterns 3 or 4 values of d-spacings appeared consistent through many of the images. These values were then analyzed using a database in order to confirm the crystalline structure of the constituent phases in the TEM. Using a computer database and assuming that Mn was part of the chemical composition, the mineral was successfully identified as a weakly crystalline Mn oxide.

None of the d-spacings could be matched to known Al minerals or crystalline structures. This is likely because the Al on the MnO$_x$(s) surface was probably amorphous and lacked a lattice structure that would have produced a measurable response from this analytical method.
Figure 44 - High Resolution TEM Image of Nano-Size MnO$_x$(s) Crystals
Small Parallel Lines Bounded in White Show Lattice Structure of MnO$_x$(s)
Figure 45 - Diffraction Pattern of MnOx(s) Coating
(Feed Water [Mn] = 0.4 mg/L, 200-220 ppb Al)
DISCUSSION

Soluble Al Study

The results of the adsorptive bench-scale column studies demonstrated the potential of the MnO$_x$(s) surface to adsorb soluble Al species. This adsorptive behavior did not appear to be impacted by the concurrent adsorption of reduced Mn. Similarly, the presence or absence of soluble species of Al did not impact the adsorptive uptake of Mn onto the MnO$_x$(s) surface. This proved to be true under all of the experimental conditions tested. Experiments were conducted under two pH conditions (6.3 and 7.2) and with several different types of MnO$_x$(s)-coated filtration media. Comparative analysis of effluent data from the each of the experimental trials shows that the presence or absence of one species (Al or Mn) had no effect on the adsorption of the other onto an MnO$_x$(s)-coated surface.

One of the initial motivations for conducting this study of the interaction of Al with the MnO$_x$(s) surface was the molar ratios of Al to Mn observed in the MnO$_x$(s) coatings of filtration media in surface water treatment plants surveyed for the 2008 AWWARF study on Mn removal. The fact that the ratio was relatively consistent (1.0 - 2.0 Al:Mn) across several different water treatment facilities suggested some sort of functional relationship between the two metals (Tobiason et al., 2008). The measured molar ratio of Al:Mn within the MnO$_x$(s) coatings of several facilities that applied chlorine across their filtration media is presented in Table 9.

Interestingly, one facility (Cantref) showed a significant accumulation of Al on the MnO$_x$(s) media despite the fact that the facility did not apply Al-based coagulants. The Al present in the MnO$_x$(s) coatings of that media most likely came from low levels of Al present in the raw source water. Though the ratio of Al:Mn present in the MnO$_x$(s) coatings of that media is less than other MnO$_x$(s)-coated media, it seems to suggest that Al possesses a strong affinity for the MnO$_x$(s) surface.

Initial experiments conducted in the laboratory focused on the adsorption of soluble Al species onto the MnO$_x$(s) surface under a variety of different experimental conditions. In each case, the uptake of Al onto the MnO$_x$(s) surface was compared against the uptake of Mn onto the surface. Table 10 presents observed molar ratios of absorptive uptake (Al:Mn) for the experiments in which soluble Al species were applied to MnO$_x$(s)-coated media.

Comparing the experimentally generated data in Table 10 to the Al:Mn ratios observed in the 2008 AWWARF study presented in Table 9, excepting the facility that applied Fe-based coagulants, none of the experimental trials were successful in producing Al:Mn ratios to match those observed in water treatment facilities. This led to an important conclusion; namely that the Al content of the MnO$_x$(s) coating could not be explained solely by the uptake of soluble species of Al. Thus, some amount of particulate Al uptake by the surface must also occur.
Table 9 - Molar Ratio Ranges of Selected Treatment Facilities Surveyed in 2008 AWWARF Study (Tobiason et al, 2008)

<table>
<thead>
<tr>
<th>Facility Name</th>
<th>Observed Al:Mn Molar Ratio Range</th>
<th>Average MnO$_{x(s)}$ Coating (mg Mn/g Media)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cantref (UK)</td>
<td>0.14 - 0.37</td>
<td>3.41</td>
<td>Uses Fe-Based Coagulants</td>
</tr>
<tr>
<td>Carno (UK)</td>
<td>1.03 - 1.33</td>
<td>4.97</td>
<td>--</td>
</tr>
<tr>
<td>Warner (VA)</td>
<td>1.96 - 2.16</td>
<td>11.0</td>
<td>--</td>
</tr>
<tr>
<td>Harwood’s Mill (VA)</td>
<td>1.28 - 2.09</td>
<td>30.8</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 10 - Adsorptive Molar Ratios Generated During Laboratory Studies Applying Soluble Al to MnO$_{x(s)}$-Coated Media

<table>
<thead>
<tr>
<th></th>
<th>Pure MnO$_2(s)$</th>
<th>Blacksburg Treatment Plant Media</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average MnO$_{x(s)}$ Coating (mg Mn/g Media)</td>
<td>100% Mn</td>
<td>5.3</td>
</tr>
<tr>
<td>Molar Al:Mn in Original Coating</td>
<td>N/A (No Al Present)</td>
<td>1.3</td>
</tr>
<tr>
<td>Observed Molar Adsorption Ratio (Al:Mn)</td>
<td>0.20, 0.25</td>
<td>0.26, 0.49, 0.15, 0.18, 0.51</td>
</tr>
</tbody>
</table>
Insoluble Al Study

A second set of experimental trials was conducted in which a super-saturated dosage of Al was applied to MnO\(_{(x(s)}\)-coated column media in order to facilitate the formation of insoluble Al hydroxide (Al(OH)\(_3(s)\)). The MnO\(_{(x(s)}\)-coated media was exposed to a combination of soluble species of Al, insoluble species of Al, varying dosages of Mn, and free chlorine. This series of bench-scale experiments that monitored formation of an MnO\(_{(x(s)}\) coating under varying influent concentrations of Mn successfully demonstrated the incorporation of Al into an MnO\(_{(x(s)}\) coating. Effluent concentrations of Al species were monitored along with extraction data of the generated MnO\(_{(x(s)}\) surfaces themselves in order to characterize the phenomenon of Al incorporation onto the MnO\(_{(x(s)}\) surface.

Periodic chemical extraction of the surface showed that the molar ratio of Al:Mn decreased as the influent Mn increased. The measured molar ratio of Al:Mn in the coating was determined to be 1.3 when the Mn loading was 50 ppb. This ratio fell to 0.6 as the Mn loading increased to 400 ppb. Effluent Mn and Al concentrations were measured throughout the experiment.

Analysis of this effluent data demonstrated a relationship between the capture of Al species and the amount of Mn loaded to the column media. Data presented in Figure 28 show the breakthrough of particles larger than 0.45\(\mu\)m breaking through the bed of filtration media on the column with the lowest Mn loading. Another set of data shown in Figure 27 illustrates a comparative analysis of the influent and effluent Al species for columns loaded with varying amounts of Mn. Both sets of data indicate a relationship between the loading of Mn and the potential to capture Al species. When the loading of Mn was increased, the ability of the media to capture Al across every size range was improved. This result leads to the question of whether or not the MnO\(_{(x(s)}\) surface enhances the capture of other species as well.

A study published in 2011 surveyed several different treatment facilities applying a wide range of different treatment techniques and filter hydraulic loading rates in order to characterize the influent and effluent particle sizes. The authors tracked the capture of both organic and inorganic solids across the filters of each facility by separating the particles into size classifications. In one case, the researchers attempted to draw a correlation between the breakthrough of organic carbon and Al particles. Ultimately no such correlation could be determined (Brant et al., 2011). Several operational variables and varying treatment techniques of the treatment plants were considered in the study, but the authors did not consider the surface of the filtration media itself. In light of the results of this study which demonstrate enhanced Al capture with increased Mn loading, it would be interesting to study the effect of the measured MnO\(_{(x(s)}\) media surface area on the capture of sub-micron particles.

The SEM micrographs shown in Figure 46 and Figure 47 were generated by a previous researcher. These images of an MnO\(_{(x(s)}\) surface from a treatment facility in Durham, NC were
Figure 46 - Diatom Entrained in MnO$_{x(y)}$ Coating – Durham, NC (Merkle, 1995)

Figure 47 - Diatom Entrained in MnO$_{x(y)}$ Coating – Durham, NC (Merkle, 1995)
generated using an ESEM. Here we can observe several diatoms that became entrained into the MnO$_x$(s) surface.

**Comparison of Bench-Scale Experimental Results Against Observed Al:Mn Ratios**

Bench-scale experiments in which soluble Al species were applied confirmed that soluble Al alone was insufficient to account for the molar ratios observed in MnO$_x$(s)-coated media from treatment facilities. Bench-scale experiments in which both soluble and insoluble Al species were applied to MnO$_x$(s)-coated media produced MnO$_x$(s) coatings with a molar ratio of Al:Mn comparable to the treatment facilities. The varied Al:Mn molar ratios of the MnO$_x$(s) coatings produced in the laboratory study which applied insoluble Al species indicate that the extent of Al incorporation into the MnO$_x$(s) surface is primarily a function of the Mn loading.

The authors of the 2008 AWWARF study noted the relative consistency in the composition of the MnO$_x$(s) coating across a number of different facilities, but were unable to identify a reason for the presence of Al. The relative consistency of the molar ratio of Al:Mn in the coating suggested the possibility of a functional relationship between the two metals. This does not appear to be the case. Though the data from the 2008 AWWARF report showed molar ratios Al:Mn that generally ranged from 1.0 to 2.0, experimental trials successfully produced ratios well outside of this range. Data presented in Figure 26 from this new research effort seem to have succeeded in proving that Al incorporation depends on the concurrent deposition of Mn onto the MnO$_x$(s) coating. The data show that the column that did not receive an added dosage of Mn did not accumulate a significant amount of Al.

A supposition about the reason for the relative consistency in the ratios of Al:Mn in MnO$_x$(s)-coated media can be made based upon a combination of laboratory data and analysis of media samples taken from treatment facilities conducted by previous researchers. Laboratory data produced in this study show that under a constant loading of Mn, the molar ratio of Al:Mn in the coating remains relatively constant. In a real treatment plant this is not necessarily the case. Loadings of Mn, especially in plants that utilize a reservoir as a source water, are subject to significant seasonal variability.

In a water treatment plant setting when the loadings of Mn are high, the amount of Mn deposited onto the surface is high. Laboratory data confirm that when Mn loadings are higher that the Al:Mn ratio drops as the deposition of Mn outpaces the deposition of Al. During periods of lower Mn loadings however, the effect is reversed as the deposition of Al outpaces that of Mn. If these two processes occurred cyclically for years on end, the results would be a heterogeneous coating. The MnO$_x$(s) coating cross section of coated anthracite coal generated by Merkle et al in Figure 2 shows a ring pattern of deposition.
In effect, this seems to suggest that the relatively consistent ratio of Al:Mn in the coatings of plants surveyed in the 2008 AWWARF report is more likely a consequence of cyclical loadings of Mn rather than an indication of a functional relationship between the two elements.

**Electron Microscope Analysis of the MnO$_x$(s) Surface**

Several analyses of the MnO$_x$(s) surface were conducted using various electron microscopy techniques. The analyses provided insight into the physical and chemical composition of the surface. The analyses show that the surface is homogeneous in a macroscopic sense, but is heterogeneous on the nanoscale. In a qualitative sense, the ESEM images shown in Figure 30 and Figure 31 provide a visual explanation for why the MnO$_x$(s) surface possesses such a high surface area.

Analysis of the surface using an SEM and EDS shows a strong correlation between the observed counts of Al and Mn on the MnO$_x$(s) surface. The correlation varied depending on the Mn loading of the media sample. In Figure 48 it’s clear that the counts of Al are similar to the counts of Mn. Though the magnitude of the counts varied, an increase in the counts of Mn was generally accompanied by an increase in the counts of Al. In Figure 49 however, the sample analyzed experienced a lower loading of Mn. The red line in each of the figures is meant to show where a perfect 1:1 correlation in the counts of Mn and Al would occur.

Though the ratio of counts for Al and Mn shown here are different, the consistency of the ratio of counts seems to confirm that the sample is homogeneous on even a very small scale. Only when applying a much higher magnification during TEM analysis was it possible to see the heterogeneous nature of the surface.

When the MnO$_x$(s) surface was analyzed using a TEM, the resulting output showed a heterogeneous mixture of very small Mn oxide crystals (5-10 nanometers) along with amorphous materials (20-30 nanometers). These materials were presumed to be Al hydroxide species, but could not be verified using diffraction pattern analyses because they lacked a crystalline structure. Analysis of the diffraction patterns generated by the TEM showed that the crystalline structures observed in the TEM image to be Mn oxides.
Figure 48 - EDS Data - Mn Counts vs. Al Counts Measured for an Experimentally Produced MnO$_x(s)$ Coating ([Mn] = 0.4 mg/L)

\[ y = 0.7914x \]
\[ R^2 = 0.7822 \]

Figure 49 - EDS Data - Mn Counts vs. Al Counts Measured for an Experimentally Produced MnO$_x(s)$ Coating ([Mn] = 0.05 mg/L)

\[ y = 1.7822x \]
\[ R^2 = 0.9149 \]
CONCLUSIONS

The presence of Al within MnO\textsubscript{X(s)}-coated water treatment filtration media was analyzed in a laboratory research study that applied a number of analytical techniques in an effort to characterize the interaction of Al with the MnO\textsubscript{X(s)} surface. Small diameter glass columns loaded with short beds of MnO\textsubscript{X(s)}-coated media were used to study the interaction of Al and Mn on the MnO\textsubscript{X(s)} surface. The media produced in several of the column studies was then subjected to further analysis by electron microscopy techniques. By combining the work of many previous researchers with the results of this new research study several important conclusions regarding the presence of Al within the MnO\textsubscript{X(s)} surface can be stated:

1. The soluble adsorption of Al species onto the MnO\textsubscript{X(s)} surface was confirmed experimentally.
2. The ability of the MnO\textsubscript{X(s)} surface to take up Mn does not appear to be impacted in any way by the concurrent adsorptive uptake of Al. This was confirmed by bench-scale laboratory experiments under a variety of different experimental conditions. The uptake of Al by the surface does not appear to augment nor hinder the uptake of Mn by the surface.
3. The Al content of MnO\textsubscript{X(s)}-coated media observed in water treatment settings cannot be accounted for by the adsorption of soluble species of Al alone. Thus, the mechanism of Al incorporation must include the capture of insoluble or particulate species of Al as well as soluble species.
4. Column experiments applying both soluble Al and insoluble Al(OH)\textsubscript{3(s)} species demonstrated that the incorporation of Al into the MnO\textsubscript{X(s)} surface is highly dependent on the deposition of Mn. This was observed by comparing two different columns; one column was given a relatively high dose of Mn while the other received only trace amounts of Mn. Only the column media that continuously deposited Mn was able to incorporate a significant amount of Al into the MnO\textsubscript{X(s)} surface. This demonstrated that significant Al deposition only occurs with concurrent Mn deposition.
5. Analysis of the MnO\textsubscript{X(s)} surface using a TEM showed that the surface was composed of a mixture of both very small Mn oxide crystals (5-10 nanometers) and amorphous materials (20-30 nanometers) assumed to be Al(OH)\textsubscript{3(s)}.
6. In general, though the continued deposition of Mn does appear to reduce the amount of Al in the filtration effluent, the amount of Al removed is not enough to make a significant impact on the finished water Al. The high Mn loadings necessary to make a significant impact on finished water Al levels would make it completely impractical as a control strategy.
Future Research

It would be interesting to conduct a series of parallel column experiments in which all of the different columns deposited a similar Mn coating, but each MnO₅(s)-coated media sample would contain a different amount of Al. A comparison of the measured surface area of each of the various media coatings would effectively demonstrate how much of the media’s surface area could be attributed to the media’s Al content and how much could be attributed to the oxidized Mn. This information would undoubtedly lead to important conclusions about the coated media’s performance for particle capture.

Al may have an impact on the media coating's surface area, but there is also the potential for Al to play a role in the MnO₅(s) surface’s ability to capture charged particles. It has been well established that the slight negative charge of the MnO₅(s) surface gives the surface an affinity for metal cations, but could the Al contained in the media give that same surface the ability to attract anionic species?

Research work should be also be conducted on the MnO₅(s) surface to determine what effect, if any, the presence of Al in the MnO₅(s) coating may have on the performance of a filtration media possessing an MnO₅(s) coating in the capture of particles. The role of the MnO₅(s) surface in the enhanced capture of particulate and dissolved species has been studied in some detail in this research effort and in the literature but has generally not been given the consideration and attention it deserves in practice.
### Table of Abbreviations

<table>
<thead>
<tr>
<th>Abbr</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>Atomic Absorbance</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>AWWARF</td>
<td>American Water Works Association Research Foundation</td>
</tr>
<tr>
<td>BCVPIWTF</td>
<td>Blacksburg, Christiansburg, VPI Water Treatment Facility</td>
</tr>
<tr>
<td>CMD</td>
<td>Coal Mine Drainage</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscope/Microscopy</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma – Mass Spectrometry</td>
</tr>
<tr>
<td>L</td>
<td>Liter</td>
</tr>
<tr>
<td>MCL</td>
<td>Maximum Contaminant Level</td>
</tr>
<tr>
<td>mg</td>
<td>milligram</td>
</tr>
<tr>
<td>Mn</td>
<td>Manganese</td>
</tr>
<tr>
<td>MnO$x(s)$</td>
<td>Manganese Oxide (General Term for Various Oxide Species)</td>
</tr>
<tr>
<td>NCFL</td>
<td>Nanoscale Characterization and Fabrication Laboratory</td>
</tr>
<tr>
<td>SADP</td>
<td>Selected Area Diffraction Pattern</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope/Microscopy</td>
</tr>
<tr>
<td>SMCL</td>
<td>Secondary Maximum Contaminant Level</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope/Microscopy</td>
</tr>
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</table>
REFERENCES


KNOCKE, W. 1990. *Removal of Soluble Manganese from Water by Oxide-Coated Filter Media*, Denver, CO.


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