Optimizing Sequestration of Manganese (II) with Sodium Triphosphate

A Major Qualifying Project Report
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By

Jessica Coelho
____
Environmental Engineering

Katrina Kucher
____
Civil Engineering

Aaron Ting
____
Civil Engineering

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Approved

Professor John Bergendahl

Table of Contents

Table of Figures

Table of Tables

Executive Summary

Dissolved manganese (II) has become prevalent in many drinking water systems and is causing aesthetically displeasing issues for consumers. Due to this, many towns have received complaints from community members about the condition of their water. Many communities currently use a polyphosphate chemical to hold the manganese in solution, otherwise known as sequestration. This is not meant to solve the problem, but to prevent manganese from forming solids that leave residue on porcelains and clothing. This polyphosphate chemical has proven to resolve current issues, but how the chemical works is still unknown.

The goal of this project was to elucidate the mechanisms of manganese sequestration using a polyphosphate and suggest an efficient method toward producing water that will not form manganese precipitation. Experiments that were completed throughout the project included polyphosphate and ozone dose variations at varying pHs and detention times.

The results that were obtained from the completed experiments showed that sodium triphosphate, with sufficient contact time provided for effective sequestration of manganese and reduced the presence of precipitate. Several unknown proprietary chemical blends were also tested to determine the capability of manganese sequestration, but the results were found to be inconclusive. Although this study was unable to test the interference of competing ions with manganese sequestration, it is strongly suggested that further experiments be conducted with competing ions, and temperature in mind. Running these experiments using actual groundwater samples would also be beneficial.

MQP Design Requirement

The design section of an MQP is required to fulfill the Capstone design experience all WPI students need to graduate. This MQP team fulfilled the design requirement in two ways.

The first aspect of this project that encompassed design was through the design of our experiments. Before getting into the environmental lab, the team had to design tests that were to be performed. The team designed tests which included manganese precipitation and sequestration experiments, as well as resolving problems when these tests went wrong (redesign).

The second aspect of this project that included design, was the design of the polyphosphate injection system. Once the team had collected enough data to decide on effective dose, we designed a full scale system for the West Boylston, Massachusetts Water District By using this city's flow rates, the team was able to design a large scale model for dosage of a sodium triphosphate sequestering agent.

1 Introduction

Clean water is the desire for every drinking water facility. Drinking water discharged from the facility unclean leads to customer complaints and expensive counter treatment measures. One factor that affects the cleanliness of water is dissolved metals. Dissolved metals cause turbidity, color, and taste (American Chemistry Council, 2004). Metal precipitates also produce unsightly films on light colored surfaces and fabrics. Two common metal precipitates are manganese and iron. Removing these metals from the water solves issues pertaining to impure drinking water. The focus of this report is dissolved manganese (II).

Manganese contamination of drinking water originated as a groundwater problem. In the past to counteract manganese contamination, a new well was dug or the water source was diluted (American Water Works Association Research Foundation [AWWARF], 2006). For treatment facilities today, this is not a viable option. With the worldwide need for clean drinking water, manganese treatment has become a greater priority.

In order to remove metals from water, most drinking water facilities utilize simple gravity settling and filtration methods. Yet, this process can become expensive. Aeration, or bubbling oxygen/ozone through water, is required to generate oxidizing conditions. To expediate the precipitation process, drinking water facilities mix chemicals such as NaOH or KOH, pH adjusters, to the water. For small drinking water facilities, money can be in limited supply (Robinson, 1990).

An alternative to removing metal precipitates via filtration is containing the metals within solution. This type of treatment is known as sequestering. Three percent of drinking water facilities utilize sequestering to contain dissolved metals such as manganese and iron within solution (AWWARF, 2006). Sequestering simply involves a poly-anion bonding with the dissolved metal. In the case of this report, the anion will be a linear chain of phosphates, more commonly known as a polyphosphate.

Sequestering, however, does not have long lasting effects. Over time, the polyphosphate may disassociate, or release the metal ion back into solution.

Thereby allowing the metal to bond with other anions in water and produce precipitates. Under specific pH ranges, water characteristics, and a variety of polyphosphates, the sequestering potential varies.

While many communities face problems associated with manganese precipitation, our report utilizes one such example, West Boylston's drinking water facility located in West Boylston, MA. West Boylston has had problems with the precipitation of manganese. Currently, the drinking water facility employs sequestering using a sodium triphosphate blend. While the treatment seems to be working because of the reduced number of customer complaints, the facility does not know if the sodium triphosphate blend is the reason for the decline in manganese precipitation and if they are using the blend in an efficient manner. Thus, the drinking water facility of West Boylston, similar to several other facilities, would like to understand the potential of their polyphosphate, sodium triphosphate, towards manganese sequestration.

West Boylston seems to have resolved its problem of manganese precipitation by the use of a polyphosphate. Yet, what is the principle mechanism behind sequestration of dissolved manganese? If this is determined, West Boylston and other drinking water facilities can efficiently produce water that does not contain manganese precipitate. Experimentation of parameters such as polyphosphate dosage, pH, residence time, and competing ions will help expand the understanding of manganese sequestration mechanisms.

2 Background

The precipitation of manganese is a major concern for drinking water facilities. Manganese precipitate can form, under the right conditions, an aesthetically displeasing residue and promote corrosion of pipe work. The oxidation of the metal causes a brownish-black discoloration in contact with light colored surfaces. Oxidation occurs due to contact with oxygen from the air or ozone/oxidizing agents being utilized for treatment or disinfection purposes (MRWA, 2007).

The West Boylston drinking water facility has had problems with the precipitation of manganese. Polyphosphates sequester, or contain, the manganese before precipitation takes place in order to deter the development of residue produced by the manganese precipitate. Sequestering is a process where a chelating agent, the polyphosphate, combines with metal ions, such as manganese (II), to form soluble complexes. The West Boylston drinking water facility has used undetermined amounts of polyphosphate chemical to sequester the manganese. The desire for West Boylston's treatment facility and numerous other water treatment facilities is to quantify the effectiveness of its polyphosphate for sequestering manganese under a variety of conditions.

This background will clarify the basic characteristics of manganese and the dynamics of the manganese-polyphosphate relationship. Additionally, this background section provides information necessary for understanding the efficiency of sequestering manganese utilizing a polyphosphate and understanding the conditions that potentially could weaken polyphosphate effectiveness.

2.1 Water Chemistry

Before delving further into the issue surrounding West Boylston, it is necessary to gain an understanding of the reactions occurring within an aqueous solution and then examine the relationship between polyphosphates and manganese. The following chemistry sections will provide the reader with a necessary overview of aquatic chemistry and sequestering.

2.1.1 Ligands

All metals in solution are cations, having a positive charge. Ligands are electron donors that may form ionic or large covalent bonds with metal ions. In essence, a ligand is a negatively charged ion able to form a coordination compound (Morgan, 1996). Simple ligands form bonds with metal ions and produce monodentate ligands or bond at several different negative poles and generate multidentate ligands or chelates (Snoeyink, 1980). *Figure 2-1* illustrates the single bond of a ligand to a metal ion.

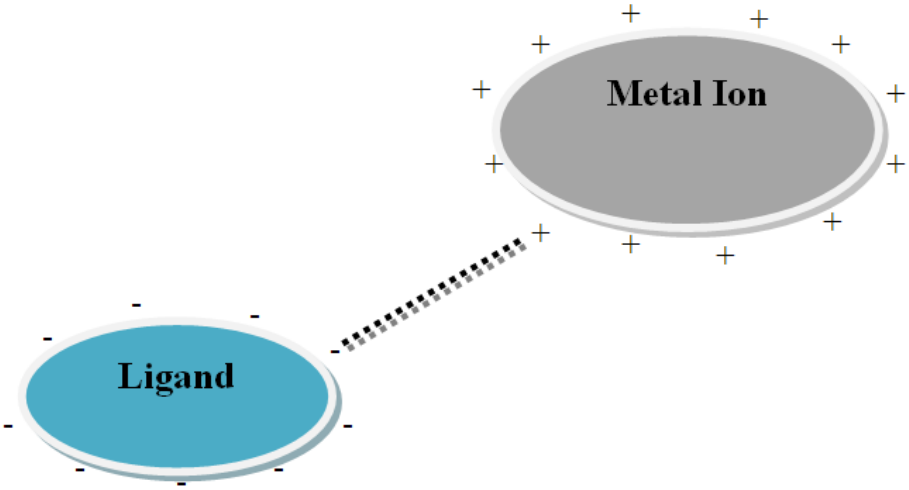

Figure 2-1. Simple Illustration of a Monodentate Ligand

Inorganic ligands commonly found in water include hydroxides [OH^-], fluorides [F^-], chlorides [Cl^-], sulfates [SO_4^{-2}], phosphates [PO_4^{-3}], carbonates [CO_3^{-2}], bromides [Br^-], and nitrates [NO_3^-].

2.1.1.1 Polyphosphates

One type of complex ligand is a polyphosphate. Polyphosphates are groupings of phosphate ions connected by single oxygen bonds. Vendors have created many different forms of polyphosphates in order to sequester, or contain, metals within solution. A discussion on sequestering will occur later in this report.

Appropriate dosing and selection of a polyphosphate for treatment is both variable and difficult. Linear chains are most appropriate for hard waters, where there are high levels of calcium and magnesium in the water. However, there are several varieties of linear chain polyphosphates, all with different capabilities to reduce metals in water.

There are three main types of linear chain polyphosphates: pyrophosphate, triphosphate, and hexametaphosphate. Each has a specific number of locations where the coordination of a soluble metal complex may form. Pyrophosphates have four locations, triphosphates have five, and hexametaphosphates have six. A figure of pyro-, tri- and metapolyphosphate, *Figure 2-2*, depicts all of the coordination bond locations for each.

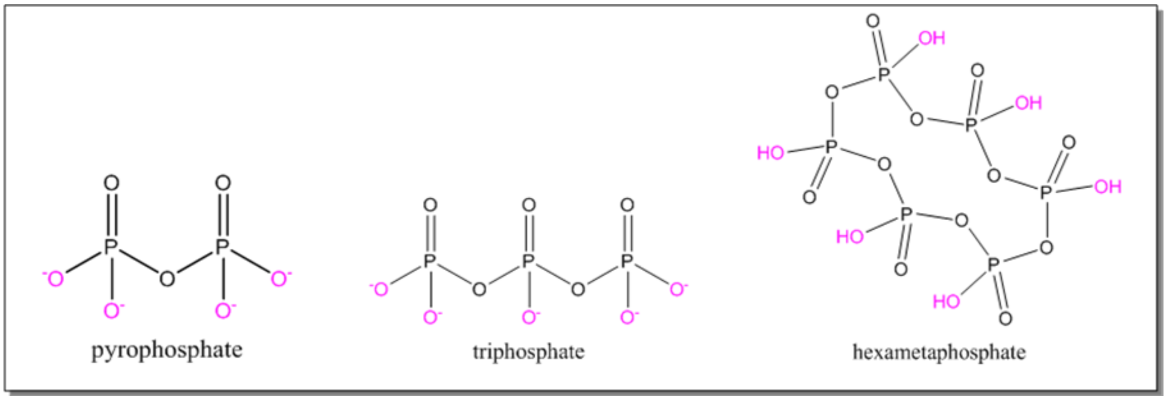

Figure 2-2. Three Main Types of Linear Chain Polyphosphates

For less aggressive water, drinking water with low concentrations of metals, water treatment facilities utilize a zinc polyphosphate for sequestering. In areas where zinc is questionable or prohibited, a silicate phosphate blend is employed. This mixture is conducive under low pH and high O_2 conditions. However, for both zinc and silicate blends, a higher dosage than linear chain polyphosphates is required for proper sequestering (Deblois, 2002).

2.1.2 Metal Complexes

Dissolved metals in water tend to form bonds with ligands. The relationship between the metal ions and the ligands are known as metal complexes. A formal definition of a metal complex is "a stable entity that results from the formation of a largely covalent bond between a metal ion and an electron – donating ligand" (Morgan, 1996).

2.1.3 Bonding Mechanisms

Metal complexes are not permanent structures in aqueous solutions. Several factors affect the association and disassociation of metal complexes: two most importantly are solubility and stability. The solubility of a certain reaction, such as the reaction between a metal and a ligand, determines how likely that bond will occur in solution. The stability of the reaction on the other hand relates to the direction of the reaction (i.e. association or dissociation). This report will discuss this concept in more detail later.

Precipitation is the main issue surrounding metals in water. Precipitation of manganese and iron produce a black or reddish film, respectively. In general chemistry, the solubility constant, K_{sp}, of a reaction dictates whether a metal will bond with a ligand and fall out of solution. The solubility of specific reactions further helps to determine the reactions occurring within solutions containing metal ions, polyphosphates, and ligands.

For example, reactions involving a dissolved metal Me^{+2} and two different inorganic ligands, L_1^- and L_2^- illustrate the importance of solubility.

$$Me^{+2} + 2L_1^- \leftrightarrow Me(L_1)_2\,(s) \qquad K_{sp} = \boldsymbol{3.40 \times 10^{-3}\ g/L}$$

$$Me^{+2} + 2L_2^- \leftrightarrow Me(L_2)_2\,(s) \qquad K_{sp} = \boldsymbol{773\ g/L}$$

Note: Arbitrary Ksp Values

Precipitation is more likely to take place, according to the corresponding K_{sp} values, with L_1^- than L_2^- in solution.

Nevertheless, the conditions displayed above are both ideal and general conditions. Water contains many ions and quantifying all the reactions within solution is virtually impossible. Additionally, the presence of oxygen in both cases would alter the states of both cations and produce different results (Robinson, 1990).

2.1.4 Precipitation versus Sequestration

Stability and more importantly solubility, as discussed in *section 2.1.3*, influence the bonds between dissolved metals and ligands. A more soluble ligand such as carbonate or hydroxide will react quick with the dissolved metal and produce a precipitate. Thus, drinking water facilities prevent precipitation by introducing polyphosphates into their water for sequestration purposes.

Sequestration follows the same principles of precipitation, except that sequestering a metal involves containing it within solution. For example, using *Table 2-1* displayed on the next page, the stability of triphosphate is much greater than most aqueous ligands. Thus, under normal conditions, triphosphate would prove effective for preventing precipitation. However, for ligands such as carbonates, once precipitation has occurred, the ability to force this bond to dissociate would be exceedingly difficult. Additionally, for both carbonate and hydroxide species, with K_{sp} values of 8.00×10^{-4} and 3.40×10^{-3} g/L respectively, precipitation occurs very rapidly. Therefore, triphosphate would need to bond even more readily with manganese in order to avoid precipitation.

Table 2-1. Dissolved Metal Solubility & Stability

Me^{+2}			
Ligand	**Complexes**	**Solubility**	**Stability**
Hydroxide (OH^-)	Me (II) Hydroxide	***3.40×10^{-3} g/L***	***3.4***
Carbonate (CO_3^-)	Me (II) Carbonate	***8.00×10^{-4} g/L***	***12.1***
Sulfate (SO_4^{-2})	Me (II) Sulfate	***637 g/L***	***2.3***
Phosphate (PO_4^{-3})	Me (II) Phosphate	**--**	**--**
Fluoride (F^-)	Me (II) Fluoride	***10.2 g/L***	***1.3***
Chloride (Cl^-)	Me (II) Chloride	***773 g/L***	***0.6***
Nitrate (NO_3^-)	Me (II) Nitrate	***1610 g/L***	**--**
Pyrophosphate ($P_2O_7^{-4}$)	Me (II) Pyrophosphate	**--**	**--**
Triphosphate ($P_3O_{10}^{-5}$)	Me (II) Triphosphate	**--**	***9.9***

Source: Handbook of Chemistry and Physics, 88th Edition (solubility),
Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters (stability).

2.2 Manganese

There are multiple valence states of ionic manganese. Therefore, manganese may bond in many ways with a ligand. The possible ionic forms of manganese are Mn^{+1}, Mn^{+2}, Mn^{+3}, Mn^{+4}, Mn^{+5}, Mn^{+6}, and Mn^{+7}. Chemical analysis of manganese has determined that the most common forms in water are the manganese (II) and manganese (IV) species (AWWARF, 2006). Therefore, the primary focus of this paper will be the complexes formed by the manganese (II) and (IV) ion.

Manganese (II) can react in various ways depending on the conditions present. *Figure 2-3* on the next page, illustrates the different reactions Mn^{+2} may undergo. As stated in the previously, oxygenated systems cause Mn^{+2} to oxidize to the Mn^{+4} state. Manganese (IV) ions are insoluble and precipitate out of solution. Mn^{+2} may also bond to primary ligands such as hydroxides or carbonates. These ligands have very low solubility constants [K_{sp}], meaning each will cause manganese to precipitate out of solution quickly. Polyphosphates sequester the Mn^{+2} before oxidation or ligand bonds produce precipitates.

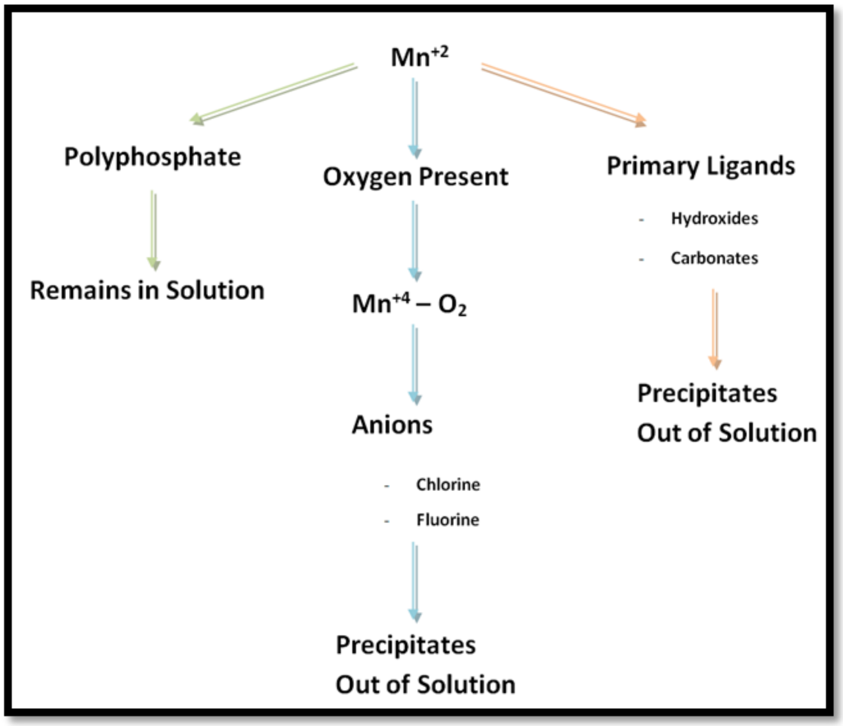

Figure 2-3. Diagram of Manganese (II) Reactions

2.2.1 Chemical Structure

In aqueous solutions, Mn^{+2}, Mn^{+4}, and Mn^{+7} are commonly found. Aquatically, Mn^{+2} and Mn^{+7} are soluble, while Mn^{+4} is insoluble. The production of Mn^{+4} transpires when Mn^{+2} is oxidized by air or other reagents (Deblois, 2002). The presence of either Mn^{+2} or Mn^{+4} varies by the aquatic conditions. Dissolved oxygen concentrations in the water system will establish the dominating valence state of the manganese ion. Studies conducted by the Environmental Protection Agency [EPA] and American Water Works Association Research Foundation [AWWARF] have shown that anaerobic conditions, no oxygen present, in water promoted a higher frequency of Mn (II) ions (AWWARF, 2006). The study has demonstrated that dissolved O_2 levels below 3 mg/L, Mn^{+2} levels were detected. At dissolved O_2 levels below 2 mg/L, Mn^{+2} levels increased. Conversely, aerobic conditions, the presence of oxygen, the prevalent form of manganese ions would be of the valance state +4.

In any case, over a wide range of acidities, manganese (II) is the most stable (AWWARF, 2006). If one observes the electron configuration between Mn^{+2} and Mn^{+4}, *Figure 2-4*, the reason for superior stability of Mn^{+2} becomes obvious.

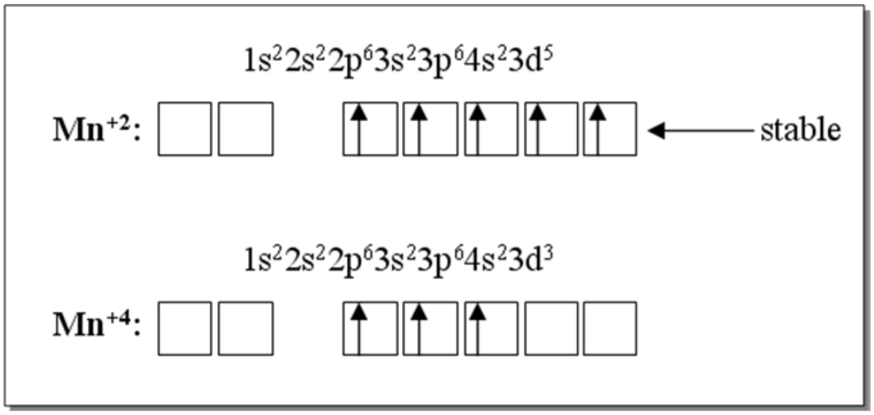

Figure 2-4. Electron configuration for manganese (II) & (IV)

Because the d-orbital is close in energy state to the fourth s-orbital, the electrons reconfigure to completely fill the d-orbital of manganese (II). Therefore, manganese (II) has a half-completed d-orbital creating a more stable outer shell structure than manganese (IV). Having a half filled valance shell constitutes a stable transition metal (Brewer, 1968). Thus, Mn^{+2} will remain unaffected by ions such as hydroxides or hydrides.

2.2.2 Environmental Concerns Associated with Manganese

Manganese naturally occurs in many surface and groundwater sources. Levels of manganese in freshwater typically range from 1 to 200 g/L. The United States Geological Survey's National Ambient Water Quality Assessment [NAWQA] gathered data since 1991 that indicates median manganese levels are 16 g/L in surface waters. Additionally, 70% of the sites tested had measurable manganese levels detected. However, the concentrations analyzed at each site were far below the point where human health is affected.

Manganese consumption poses no immediate human threat. Human consumption of some manganese is actually vital. *Table 2-2* displays the amount of manganese required per age group.

Table 2-2. Maximum Allowable Consumption of Manganese by Age

Age Group	Male	Female
Infants, 0 – 12 months	3 g/day	3 g/day
Children, 1 – 8 years	1.2 – 1.5 g/day	1.2 – 1.5 g/day
Young Adults, 9 – 18 years	1.9 – 2.2 g/day	1.6 g/day
Adults, 19+ years	2.3 g/day	1.8 g/day

Manganese at low doses is non-toxic. However, at higher concentrations chronic symptoms may occur. Patients who have inhaled manganese have presented with neurological effects. However, two studies involving ingesting manganese via water found no evidence that neurological effects occurred (U.S. EPA, 2004).

While the human health affects of manganese consumption may be in question, oxidized manganese produces aesthetically unappealing residue on pipes, household fixtures, dishes, and fabrics. Additionally, manganese can alter the taste of the drinking water. Although these are not serious effects, they are displeasing to the consumer.

The precipitation of manganese produces a brownish-blackish film on surfaces. Specialists call this discolored water "Black Water" (Deblois, 2002). Manganese oxides and ligand bonds make up the brownish-blackish precipitate. The manganese oxide discussed is of the manganese valance state +4.

2.2.3 Conventional Manganese Removal Methods

The most common form of treatment to remove manganese from water is oxidation and clarification by filtration. Typical oxidizers include chlorine, permanganate, and ozone (WSDH, 2001). Other methods currently employed are ion exchange, granulated activated carbon [GAC], membranes, and biological removal (City of Vernon, 2007). The following sections will only discuss oxidation/filtration treatment of drinking water.

Oxidation & Filtration

The removal of iron and manganese is most efficient when levels do not exceed 0.3 ppm iron and 0.5 ppm manganese. When such conditions are available, drinking water facilities most often utilize oxidation and filtration for treatment (Minnesota Rural Water Association [MRWA], 2007). Oxidation and filtration removal of manganese uses the agents to transform the soluble Mn (II) to the insoluble Mn (IV) oxidation state (City of Vernon, 2007). Oxidation usually occurs best at higher pH levels. Levels above pH 7.5 are desired, but not required. For example, permanganate can oxidize manganese under a wide range of pHs (WSDH, 2001).

Oxidation using Aeration

While atmospheric oxygen easily oxidizes iron, manganese requires a higher dosage of dissolved oxygen [DO]. Iron requires 0.14 ppm DO for effective oxidation of 1 ppm iron (II), but for 1 ppm manganese (II), 0.24 ppm DO is needed (MRWA, 2007). Oxidation using aeration can become difficult for municipal treatment facilities. In order for adequate dosing of DO to enter into the drinking water, treatment facilities need to maintain proper flow. Too much flow and the dissolved oxygen concentration will be too low, too little flow and the concentration could become so high that corrosion occurs in the pipe work.

Nevertheless, aeration is the most cost-effective process since no chemical additions are necessary. Most often municipal treatment facilities introduce air into solution by bubbling the water or dispersing the water into the air (MRWA, 2007).

Chlorine Oxidation

Chlorine in water oxidizes manganese [Mn^{+2}] to manganese dioxide [MnO_2], which is an insoluble form of manganese. The dosage of chlorine is proportional to the precipitation of manganese. More chlorine means a higher rate of precipitation of manganese. However, in some cases five times the stoichiometric ratio of chlorine to manganese is required in order for adequate oxidation to occur. A reasonable detention time for oxidation to take place is necessary as well (MRWA, 2007).

While chlorine is a widely accepted oxidizing agent, problems with its use have arisen. Natural organic matter can bind with chlorine to form trihalomethanes [THMs] and haloacetic acids [HAAs]. The Stage 2 Disinfectant & Disinfection By-Products contamination list regulates both constituents (City of Vernon, 2007).

Potassium Permanganate Oxidation

While oxidation occurs optimally at pH higher than 7.5, potassium permanganate oxidation of manganese is effective over a wide range of pHs (MRWA, 2007). Permanganate reactions with manganese are much faster than chlorine. Therefore, both reductions in detention time and tank size transpire. For municipal treatment facilities, space requirements are normally and issue. However, permanganate solutions are more expensive than chlorine (City of Vernon, 2007). Thus, water treatment facilities must consider a suitable balance between cost and plant size.

2.3 Sequestering using a Polyphosphate

Another approach for controlling manganese precipitation includes sequestering using a polyphosphate. The potential of sequestering using a polyphosphate depends upon the pH of the water. Polyphosphate reactions work best under alkaline, higher pH, conditions. Less hydrolysis, or breakdown of polyphosphates, will occur under alkaline conditions (American Chemistry Council, 2004). In addition, complete sequestering occurs typically before the metal ion and the polyphosphate reach the equilibrium stoichiometric ratio. This is because polyphosphates have low threshold activity levels.

Sequestering, however, is only a temporary measure to mitigate staining produced by metal precipitation. Polyphosphate chains are very stable by nature, but stability greatly depends upon the aquatic environment. Hydrolytic stability, similar to metal complex stability, determines the length of a polyphosphate chain. All polyphosphate chains will reduce to a single phosphate molecule (Robinson, 1990). Typically, under ideal conditions, hydrolysis is slow for polyphosphates. However, as pH decreases or temperature increases, a polyphosphate chain will begin to degrade faster (American Chemistry Council, 2004). Generally, this is why black or reddish film from manganese or iron deposits cover machines used for laundering clothes and the laundered clothes themselves.

2.3.1 Polyphosphate Reactions with Manganese (II)

Water treatment facilities utilize polyphosphates to sequester metals such as iron and manganese because of the chemicals stability when bonded to the dissolved metal ion. Stated earlier in this report, the stability of manganese – polyphosphate bonds is more superior to those of inorganic ligands. Thus, the ability for other constituents to reverse the bonding of manganese and a polyphosphate would require a great deal of energy.

In the case of a manganese-polyphosphate bond, the longer the phosphate chain the greater the sequestering capability of the polyphosphate due to coordination. *Figures 2-5 – 2-7* display the relationship of manganese (II) to the three types of linear chain polyphosphates. As exhibited, triphosphate sequesters the most Mn^{+2} even though hexametaphosphate has six locations where bonds may form. Pyrophosphate, a two-chain phosphate, sequesters the least Mn^{+2}.

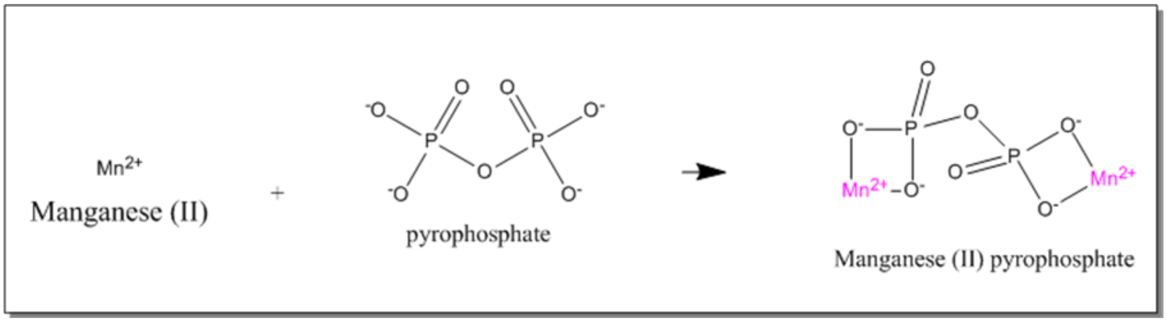

Figure 2-5. Manganese (II) Metal Complex with Pyrophosphate

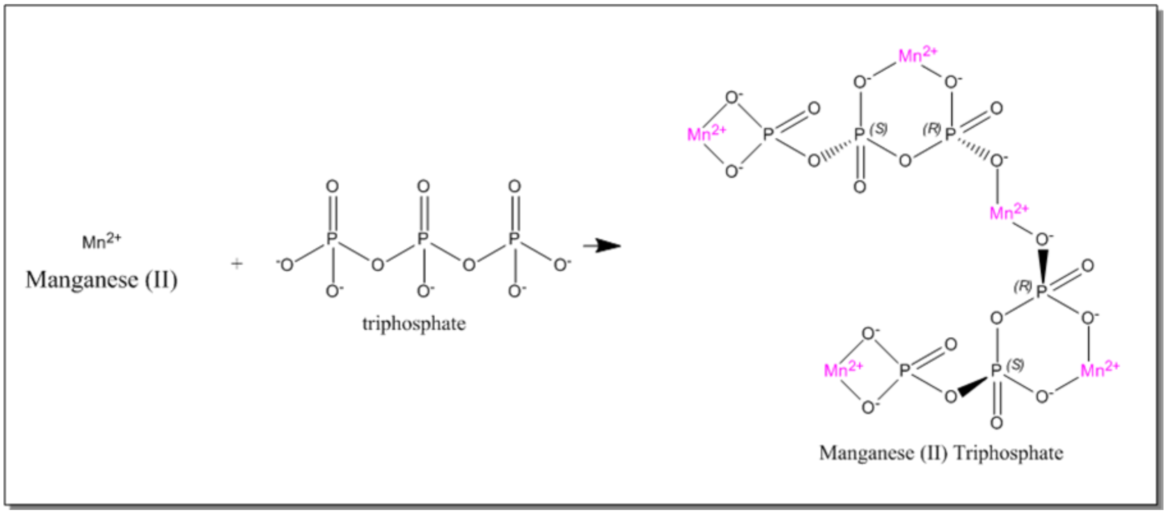

Figure 2-6. Manganese (II) Metal Complex with Triphosphate

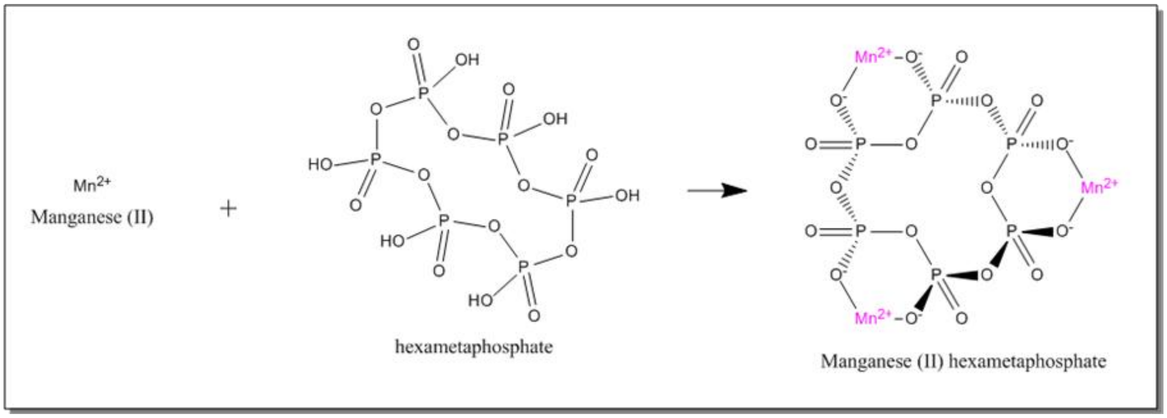

Figure 2-7. Manganese (II) Metal Complex with Hexametaphosphate

While the quantity of manganese removal is important, drinking water facilities equally observe the required cost for the removal of manganese. To examine the cost of implementation, facilities would note the amount of chemical necessary to meet federal standards. The reaction equations for pyro-, tri-, and hexametapolyphosphate illustrate the ideal stoichiometric ratio required to completely sequester manganese (II). As can be seen from the ideal reactions below, triphosphate requires 2 moles, but removes 5 moles of manganese. Pyro- and hexametaphosphate require only one mole for sequestration, but remove less manganese.

$$2Mn^{+2} + 1P_2O_7^{-4} \rightarrow Mn_2(P_2O_7)$$

$$5Mn^{+2} + 2P_3O_{10}^{-5} \rightarrow Mn_5(P_3O_{10})_2$$

$$3Mn^{+2} + 1P_6O_{18}^{-6} \rightarrow Mn_3(P_6O_{18})$$

Although, polyphosphates show great potential for the removal of manganese through the figures and ideal reactions, proper experimentation performed with the water utilized at the facility is necessary in order to compute the sequestering capability of a polyphosphate towards manganese (II).

2.3.2 Polyphosphate Reactions with Other Metals

Polyphosphates are not only conducive to sequestering manganese. Other metals compete to bond with polyphosphates. Iron (II), which originates from pipe work, is one main contributor to the difficulties of sequestering manganese. Additionally, other metals such as potassium, utilized as a pH adjustor in the form of potassium hydroxide [KOH], and magnesium and calcium, sources of hardness, add to the complexity of sequestering manganese.

Polyphosphates sequester iron more readily than manganese (AWWARF, 2006). A case study demonstrated that for an iron (II) dose of 2 mg/L at pH 7 and a 1 mg/L polyphosphate dosage, the iron (II) was effectively sequestered. A manganese dose of 1 mg/L under the same conditions as the iron (II) experiment relies on a range of polyphosphate between 1 mg/L and no more than 5 mg/L phosphate (Robinson, 1990). Therefore, iron (II) sequestered better than manganese under ideal conditions.

Under hard water conditions, the presence of calcium and magnesium bivalent cations, the effectiveness of sequestration was not as efficient for iron as for manganese. With 100 mg/L Ca as $CaCO_3$, the turbidity for the iron (II) tests generated levels above 0.6 NTUs after day 0. A suitable turbidity for the time scale would be less than 0.3 NTU. An explanation for the high turbidity levels originates from the low solubility of calcium phosphate. However, the filterability of iron was also low, determining that calcium and magnesium have affected the efficiency of iron sequestering.

Manganese under the same conditions as the iron (II) experimentation showed effective sequestration even with hardness present. 2 mg/L dosages of polyphosphates were added to a manganese solution containing 100 mg/L Ca as $CaCO_3$. The only downfall concluded from the experiments showed that overdosing with the polyphosphate could increase turbidity, but a reduction in the color of the water. Nevertheless, manganese sequestering still occurred with hardness constituents present. The causation for the high turbidity is from the hydrolysis of the polyphosphate to ortho- and phosphates and then the precipitation of insoluble calcium phosphate.

However, the potential for these other metals to be sequestered is similar to the circumstances that allow manganese to become sequestered. For example, while iron may be more likely to bond with a polyphosphate than manganese, iron may precipitate out of solution quicker than manganese; then the polyphosphate may not have an opportunity to bond with iron, leaving manganese to predominately form polyphosphate bonds. Again, experimentation with iron, manganese, and the water sample are required to determine the more likely metal-polyphosphate relationship.

2.3.3 Additional Issues Surrounding Polyphosphate Sequestering

Temperature and excess dissolved oxygen both pose problems for sequestering manganese. Adding polyphosphates to drinking water for sequestration should occur before oxidation can influence the manganese. Also, as discussed in *section 2.6*, the polyphosphate chain will break up under specific conditions. Though, this break down is typically long, higher water temperatures can produce faster rates of disassociation. This leads to sequestered manganese to be released back into the water (WSDH, 2001).

Even sequestering itself creates issues for customers who utilize internal treatment systems such as reverse osmosis [RO]. Sequestration does not remove manganese from solution and therefore, the membranes for the RO system could become fouled easier (City of Vernon, 2007).

Lastly, federal regulations do not permit polyphosphate use in excess of 10 mg/L as PO_4. This is the standard limit for drinking water.

2.4 West Boylston Drinking Water Facility

While many communities are affected by manganese precipitation, our report will closely relate design and treatment methods to those employed at the West Boylston's treatment facility. Prior to the sequestering of manganese, the West Boylston drinking water facility located in West Boylston, Massachusetts had had many customer complaints arise due to manganese deposits ending up on kitchen and bathroom surfaces. To hinder the formation of manganese oxide [MnO_2], the unwanted brownish-black manganese precipitate, West Boylston employed a sodium tripolyphosphate blend to sequester the manganese. However, the facility does not fully understand the mechanism of polyphosphate sequestration and how effective sodium tripolyphosphate is for sequestering dissolved manganese.

2.4.1 West Boylston Drinking Water Distribution

The West Boylston Water District supplies water, via groundwater, to almost 7,000 people in the City of West Boylston (City-Data, 2008). Approximately 72% of the water consumers are family households. The district is an independent government entity established in 1939. The district consists of three gravel packed wells, and four storage facilities. These three supply sources include one on Lee Street, which pumps at 250 gpm [gallons per minute]; one on Oakdale, which pumps 725 gpm and the final well is located on Pleasant Valley that pumps at a rate of 500 gpm. All of these pumping rates have been approved by the Massachusetts Department of Environmental Protection [MassDEP].

2.4.2 Common Constituents in West Boylston Drinking Water

West Boylston annually performs water quality testing to quantify organic and inorganic contaminants present in the water. The testing is necessary to ensure the safety of the city's drinking water, but also to abide by government set standards and regulations. The Annual Consumer Reports, which is a public document contains the results of these tests. *Table 2-3* provides data pertaining to constituents in West Boylston's water for a four-year period.

Table 2-3. Secondary Contaminants Found in West Boylston Drinking Water

	Cations	HQD*	Avg D*	SMCL*	ORSG*
2003	Manganese	0.12 – 1.0	0.45	0.05	n/a
	Iron	0 – 0.03	0.01	0.3	n/a
	Sodium	11.0 – 18.0	15.3	n/a	20
2004	Manganese	0.14 – 1.60	0.67	0.05	n/a
	Iron	0.00 – 0.03	0.01	0.3	n/a
	Sodium	11.0 – 18.0	15.3	n/a	20
2005	Manganese	1.40	0.48	0.05	n/a
	Iron	0.013	0.003	0.3	n/a
	Sodium	11.0-18.0	15.3	n/a	20
2006	Manganese	1.30	0.41	0.05	n/a
	Iron	0.024	0.002	0.3	n/a
	Sodium	13.0-26.0	19.6	n/a	20

HQD: Highest Quantity Detected
Avg D: Detected Average
SMCL: Secondary Maximum Contaminant Level
ORSG: Massachusetts Office of Research and Standard Guides
**quantities are in units of parts per million (ppm)*

Some common inorganic contaminants found in the West Boylston drinking supply include small concentrations of lead, copper, nitrate and barium. Lead most likely occurs in the water because of the corrosion of household plumbing, and/or the corrosion of natural deposits. Copper occurs because of these reasons as well as the leaching of wood preserves. Nitrate occurrences are due to fertilizers in runoff, septic tank leaching, sewage, and the erosion of natural deposits. Barium is most likely to occur from drilling wastes, metal refineries, and natural deposits. One site was declared to be above the Active Level of Lead in 2003, 2005 and 2006. This means that this site required treatment. None of the other inorganic contaminants were cause for concern (West Boylston Water District, 2007).

2.4.3 Federal & State Regulations for Water Quality at West Boylston

Manganese for West Boylston is categorized as a secondary contaminant. A secondary contaminant is one that does not pose an immediate threat to human health, but chronic exposure to the contaminant may lead to undesired health concerns. The city of West Boylston publishes qualitative data for contaminant levels in the drinking water via the annual water quality report.

According to the 2006 Water Quality Report of West Boylston, manganese is an unregulated contaminant. However, as

Table 2-3 shows, manganese has surpassed secondary maximum contaminant levels [SMCLs] in all four years. SMCLs are "standards developed to protect the aesthetic qualities of the drinking water and are not health based (West Boylston Water District, 2007). The number 0.05 ppm Mn is a standard regulated by both the state of Massachusetts and the U.S. EPA.

2.4.4 Water Treatment Methods Employed by West Boylston

In order to maintain contaminant levels within regulated limits and ensure standard water quality, the city mixes treatment additives into the drinking water. To elevate the pH of the water, potassium hydroxide is injected. Potassium hydroxide helps to control the corrosion of plumbing. For bacterial contaminants in the water, West Boylston adds disinfectants, such as chlorine. Typically, West Boylston does not incorporate disinfectants into its treatment. However, the facility did encounter a small coliform problem. During the months of January, May, and June of 2004, West Boylston found traces of coliform bacteria in the storage tanks. In 2004 and the beginning of 2005, West Boylston used chlorine and other disinfectants to clean the tanks.

Manganese and iron both occur naturally in West Boylston's drinking water. Unfortunately, they form precipitates, which produce an aesthetic problem. Both metals can discolor bathtubs, sinks, white clothing, and other light colored surfaces. The facility utilizes a sodium polyphosphate blend to sequester the iron and manganese to prevent the formation of a precipitate (West Boylston Water District, 2007).

2.5 Previous Experimentation to Alleviate Manganese Precipitation at the West Boylston Drinking Water Facility

A former Major Qualify Project [MQP] performed by Rebekka Sullivan at Worcester Polytechnic Institute tested parameters such as pH, iron-polyphosphate bonding, and polyphosphate dose variations. Ms. Sullivan performed experiments using E-pure water, dihydrous phosphate, and water samples from West Boylston's Oakdale well. From the results of Ms. Sullivan's work, she strongly suggested lengthening the times when mixing and settling and to consider the interference of other ions.

2.6 Background Summary

From the collection of research, manganese sequestering is variable, especially with polyphosphates. For example, research states that polyphosphates sequester more effectively under alkaline conditions. However, what is a suitable range for the alkaline conditions and is this range suitable for West Boylston? Additionally, other dissolved metals such as iron affect polyphosphate sequestering. However, how greatly does iron generate negative results toward the sequestering of manganese?

Manganese sequestering becomes difficult as additional constituents enter the water source. These constituents include both ligands such as hydroxides and carbonates and metals such as iron. Based on the research collected, West Boylston may temporarily prevent the precipitation of manganese in its drinking water using polyphosphates under optimum conditions.

3 Methodology

The purpose of this project was to observe and quantify the sequestering capabilities of a polyphosphate, namely sodium triphosphate. The hypothesis during our project was sodium triphosphate would be an effective sequestering agent for water treatment facilities to control manganese (II). We researched and analyzed conditions such as pH, residence time in both the distribution pipeline and the injection/mix system, and polyphosphate dosage for optimum sequestering potential. The outcome for this paper should allow water treatment facilities such as West Boylston and others to properly treat their water for manganese.

3.1 Stock Solutions

Stock solutions were created on a need basis. We refrigerated all stock solutions and labeled with chemical name and date of creation. The stock solutions required for experimentation included manganese (II), hydroxides, triphosphate, iron (II), and potassium. To produce the stock solutions our group used both solid based and liquid based solutes. The solids used include manganese chloride, sodium triphosphate, and potassium chloride. 1 N liquid sodium hydroxide was used to create the hydroxide solution. The environmental water quality laboratory had all of these chemicals in supply.

Listed below are additional apparatus used for preparing stock solutions:

- 250 mL volumetric flasks
- Micropipette
- Small and large beakers
- 250 mL clear glass bottles
- scale
- aluminum weighing dish
- Parafilm

Manganese (II)

A stock solution of manganese (II) ions is required for all experiments expressed in this report. To make the stock solution, a known amount of manganese (II) ions, from solid manganese chloride [$MnCl_2$], was added to E-pure water.

For our experiments, a 0.15 g/L stock solution of Mn^{+2} was created. To produce a stock solution of Mn^{+2}, we calculated the required amount of $MnCl_2$ necessary to produce 0.15 g of Mn^{+2}. Using the equation for the dissociation of $MnCl_2$, *reaction 1,* we could determine the proper dose of $MnCl_2$ to generate 0.15 g of Mn^{+2}.

$$MnCl_2\,(s) \rightarrow Mn^{+2} + 2Cl^{-}$$

Reaction 1

Therefore, 1 mole of $MnCl_2$ produces 1 mole of Mn^{+2}. The specific calculations for the stock solution can be found in the *appendix*. After calculating, 0.0850 g of $MnCl_2$ per 250 mL of E-pure was required to produce 0.15 g/L Mn^{+2}.

Triphosphate

The chemical used for sequestration in our experiments was triphosphate [$(P_3O_{10})^{-5}$]. Similar to the manganese (II) stock solution methodology, using the equation for the dissociation of $Na_5(P_3O_{10})$, *reaction 2*, we could determine the proper dose of $Na_5(P_3O_{10})$ to generate 1.0 g/L of $(P_3O_{10})^{-5}$.

$$Na_5(P_3O_{10})\,(s) \rightarrow 5Na^{+} + (P_3O_{10})^{-5}$$

Reaction 2

Therefore, 1 mole of $Na_5(P_3O_{10})$ produces 1 mole of $(P_3O_{10})^{-5}$. The *appendix* contains the calculations for the tripolyphosphate stock solution. After calculating, 0.2667 g of $Na_5(P_3O_{10})$ per 250 mL of E-pure was required to produce 1.0 g/L $(P_3O_{10})^{-5}$.

Hydrochloric Acid and Sodium Hydroxide

Our group used both hydrochloric acid, and sodium hydroxide, as pH adjusters to test how various pH levels affected manganese sequestration. While, hydrochloric acid would not produce a manganese precipitate, sodium hydroxide will form a precipitate. The following section will discuss making a suitable hydroxide [OH^-] solution.

From the ideal chemical reaction of sodium hydroxide and manganese hydroxide:

$$NaOH\ (l) \rightarrow Na^+ + OH^-$$

Reaction 3

The dissociation of sodium hydroxide produces one mol of hydroxide. To generate solid manganese hydroxide, the reaction requires two moles of hydroxide for every one mole of manganese. From the first reaction, our group quantified the necessary volume of 1 N NaOH to add to E-pure water to create a stock solution of 0.30 g/L OH^-. The calculations are shown in the *appendix*.

Iron [Fe^{+2}], Potassium [K^+], and Magnesium [Mg^{+2}]

For iron, potassium, and magnesium, the reactions for each are displayed below, but calculations were not performed due to limited time and research warranting no need for testing.

Ferrous chloride [$FeCl_2$] produced aqueous iron (II) for our experiments pertaining to competing metal influence. The dissociation of ferrous chloride generates one mol of iron (II).

$$FeCl_2\ (s) \rightarrow Fe^{+2} + 2Cl^-$$

Reaction 4

Potassium chloride [KCl] produced aqueous potassium ions. Ideal chemical reactions show that one mol of potassium is generated from one mol of potassium chloride.

$$KCl\ (s) \rightarrow K^{+} + Cl^{-}$$

Reaction 5

Magnesium chloride [$MgCl_2$] produced aqueous magnesium ions. Ideal chemical reactions show that one mol of magnesium is generated from one mol of magnesium chloride.

$$MgCl_2\ (s) \rightarrow Mg^{+2} + 2Cl^{-}$$

Reaction 6

3.2 Calibration of Analyzing Apparatuses

pH meter

The Accumet® Basic [AB15] pH meter, displayed in *Figure 3-1*, was used for regulating the pH in samples analyzed with sodium hydroxide additions.

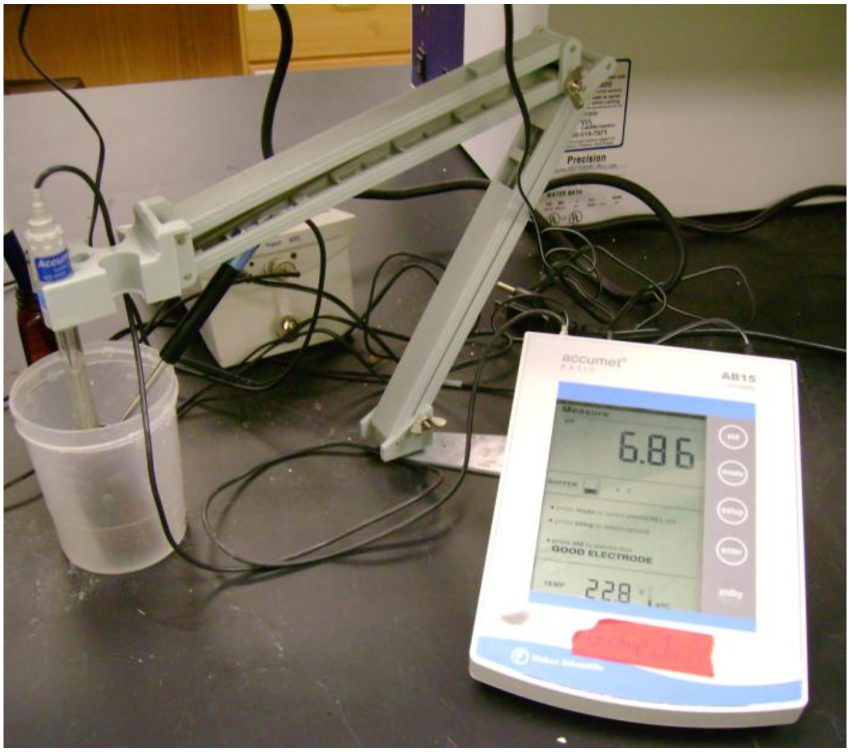

Figure 3-1. Accumet® Basic pH meter

In order to calibrate the pH meter, we created three solutions of 4, 7, and 10 pH from premade stock available in the environmental laboratory. We standardized the pH meter to each of these pH solutions until the meter read GOOD ELECTRODE. GOOD ELECTRODE presented if the pH meter's slope was between 90 – 100%.

AA spectrophotometer

To perform metal concentration analysis, an AA spectrophotometer is required. To calibrate, a standard curve using diluted stock solutions of Mn (II) were utilized. Calibration points observed through the absorbance readings produced a linear regression. Plotting the data points using Microsoft Excel enabled our group to generate equations to determine metal concentration.

3.3 Manganese Precipitation Using Ozone

In order to visualize sequestration, the manganese solution without polyphosphate additions should have a significant decrease in manganese (II) concentration. With our stock solution of 0.15 g/L Mn^{+2}, we produced a 3 ppm solution of manganese (II) in E-pure water by adding 10 mL of stock solution to a 500 mL beaker. Then we oxidized the soluble Mn^{+2} to insoluble Mn^{+4}. Using pure oxygen [O_2] and an ozone machine, we bubbled ozone [O_3] through the manganese solution for 6 hours. Ozone is a strong oxidant and is used in water treatment for disinfection and chemical oxidation. The solution settled for a 120-hour period [5-days] to allow for separation of the solids from water to occur. The newly formed Mn^{+4} combined with other anions in the water, formed solids and settled out of solution. Lastly, we filtered the sample using a 0.45 µm glass microfilter; a dark brown film was present on the white filter paper if precipitate had formed. The filtration process removed the manganese (IV) as precipitate. Thus, a reduction in concentration of Mn^{+2} remaining in solution theoretically should have occurred.

To quantify the reduction of manganese (II) concentration in solution, we analyzed the solution through atomic absorption spectrophotometry. The AA spectrophotometer uses light produced by a flame to measure the amount of a specified metal in solution. To begin, we prepared a standard curve, which is illustrated in the *appendix*, using the AA machine and standard solutions of 0.1, 0.5, 1.0, 3.0 ppm Mn^{+2}. Next, we tested our manganese (II) solutions and recorded the absorbance data into an excel spreadsheet. Using our standard curve, we could interpolate the unknown concentration of our ozoned solution.

3.4 Preliminary Sequestration experiments using Sodium Triphosphate

After having shown that manganese (II) can be oxidized to manganese (IV) and precipitate out of solution, we demonstrated that polyphosphate could be utilized to sequester the manganese (II) ions and prevent precipitation. From the reaction equation of manganese (II) and triphosphate, we can observe the theoretical behavior of the polyphosphate sequestration. The reaction for sequestration using a polyphosphate, *reaction 7,* is as follows:

$$5Mn^{+2} + 2(P_3O_{10})^{-5} + 2O_3\ (g) \dashrightarrow Mn_5(P_3O_{10})_2\ (aq) + O_3\ (aq)$$

Reaction 7

As shown above, stochiometrically, 2 moles of triphosphate are necessary to sequester 5 moles of manganese (II). Calculations, displayed in the *appendix*, show that a concentration of 5.55 ppm triphosphate is necessary to fully sequester a 3 ppm manganese (II) solution. However, as research has shown polyphosphates do not always require stoichiometric conditions for complete sequestration of manganese. Therefore, using our stock solution of 1.00 g/L $(P_3O_{10})^{-5}$, we added 0.000, 1.390, 2.100, 2.775, 4.165, and 5.550 mL to 6-500 mL volumetric flasks. This produced triphosphate concentrations of 0.000, 2.775, 4.163, 5.550, 8.325, and 11.100 ppm. Then we added 10 mL of the 0.15 g/L Mn^{+2} solution to each flask. Lastly, we filled the volumetric flasks up to the line for a total volume of 500 mL. For this test, we ran two sets of beakers, for a total of twelve solutions.

Our test is similar to the manganese precipitation test performed in *section 3.3*. The manganese-triphosphate solution mixed for two hours to promote a suitable contact time for the two chemicals. Next, we ozoned the solution for 2 hours to facilitate the oxidation of free Mn^{+2} to the insoluble Mn^{+4} state. Finally, with one set of beakers, we allowed the solution to settle for a 72-hour (3-day) period to allow solid/liquid separation. For the other set, we allowed the solution to settle for a 24-hour (1-day) period.

After each time period, we filtered the solution through a 0.45 μm filter and removed the precipitate. If precipitate is present, it presented as a light to dark brown film on the white filter paper. Following the filtration, we employed the AA spectrophotometer to analyze the sample for manganese (II).

3.5 Residence Time for Proper Sequestering of Mn using $Na_5(P_3O_{10})$

Our study of residence time and its affect on sequestering potential of a polyphosphate incorporated analysis of a distribution pipe configuration and a batch reactor configuration. The settling of a polyphosphate with manganese, from our study of the literature, has shown to affect the sequestering potential of the polyphosphate.

Water Distribution Analysis

Similar to the procedures outlined in *section 3.3 & 3.4*, we created samples of 3 ppm Mn^{+2} and different polyphosphate dosages. Four sets of six solutions were produced for this experiment. We mixed all solutions for 2 hours, then ozonated the solutions for either 3 or 6 hours, and allowed settling to occur for either 5, 3, or 1 day.

Table **3-1** summarizes the process of ozoning and settling.

Table 3-1. Water Distribution Method Summary

Set Number	Ozone Time (hours)	Mixing Time (hours)	Settling Time (days)
Set #1	6	2	5
Set #2	6	2	3
Set #3	3	2	3
Set #4	3	2	1

An analysis for remaining manganese (II) was performed on the AA spectrophotometer. Lastly, our group calculated and displayed the data in an excel spreadsheet and graph.

Mixing (via Batch Reactor)

This report analyzed the effects of mixing residence time in a batch reactor regarding the capacity of sequestered manganese. The only difference between the mixing method and the water distribution method is the time of mixing and the time of settling. Our group mixed solution sets for 0, 2, 4, and 6 hours. Standard ozoning of all solutions was executed. Lastly, settling of each solution set proceeded for only 24 hours (1-day) period.

Table 3-2 summarizes the procedure for ozoning and settling our solution sets.

Table 3-2. Summary of Batch Reactor Procedure

Set Number	Ozone Time (hours)	Mixing Time (hours)	Settling Time (days)
Set #1	3	0	1
Set #2	3	2	1
Set #3	3	4	1
Set #4	3	6	1

We employed the AA spectrophotometer to analyze the remaining manganese (II). Again, our group calculated and displayed the data in an excel spreadsheet and graph.

3.6 Optimizing pH for Sequestering Mn Using $Na_5(P_3O_{10})$

As previous literature states, manganese sequestration is affected by pH. Following similar guidelines to the manganese precipitation experiment, our group introduced sodium hydroxide or hydrochloric acid to the solution as pH adjusters. After ozoning, settling, and filtering the samples, we analyzed each solution for manganese losses. Our analysis showed a range for pH that would allow for effective sequestration of manganese (II).

3.7 Effect of Competing Metals on $Na_5(P_3O_{10})$ and Sequestering Mn

Unfortunately, due to time constraints experiments to evaluate the effect of competing metals in sequestration were not conducted.

Metals of interest included iron and potassium. As stated in *section 2.3.2*, incorporating these metals into the manganese-triphosphate solution should influence the sequestration potential of triphosphate towards manganese (II). Research, as stated in *section 2.3.2*, has shown that hardness does not effect manganese sequestration, so no calcium or magnesium testing occurred.

3.8 Alternative Sequestering Agents

Three alternative polyphosphate mixtures were analyzed for comparison to our laboratory created triphosphate solution. The three samples were unknown samples produced by vendors.

Our test is similar to the manganese precipitation test performed in *section 3.4*. The manganese-polyphosphate solution mixed for two hours to promote a suitable contact time for the two chemicals. Next, we ozoned the solutions, and finally, we allowed the solution to settle for a 24-hour (1-day) period to allow for any residual reactions to occur.

After the each time period, we filtered the solution through a .45 µm filter and removed the precipitate. If precipitate is present, it presented as a light to dark brown film on the white filter paper. Following the filtration, we employed the AA spectrophotometer to analyze the sample for manganese (II) losses. Evaluation of each chemical was made by a comparing µmol of remaining manganese (II) to the polyphosphate dose in mL. A Microsoft Excel graph plotted the results from the AA test.

4 Analysis & Results

This report begins to uncover the facts pertaining to sequestration using a polyphosphate by identifying the mechanisms and chemistry involved. Our findings in turn should help water treatment facilities determine the most appropriate course of action to mitigate manganese precipitation.

4.1 Manganese Precipitation

A variety of environments may lead to the precipitation of manganese. In our study, we chose to utilize ozone, a strong oxidant, to precipitate manganese (II) to the soluble manganese (IV) state. Largely, this preliminary step is required in order to properly visualize manganese sequestration.

For our first test, after having added ozone to our sample of 3 ppm manganese (II) with no triphosphate additions, only 15.73% of the manganese had precipitated. Our group had expected a much higher percentage of the 3 ppm manganese (II) solution to precipitate due to the length of ozonation and the strength of the oxidant. *Table 4-1* displays the data we extrapolated from our first test.

Table 4-1. Remaining Manganese after Ozone Addition

Analysis / Results			
AA Absorbance Reading	**Concentration of Sequestered Manganese (II) (mg/L)**	**Concentration of Precipitated Manganese (mg/L)**	**Percent Manganese (IV)**
0.182	2.528	0.472	15.73%

These results exhibited an inadequate precipitation of manganese. Reevaluating our method and apparatuses, we discovered that our ozone flow was insufficient to promote proper oxidation. Therefore, we increased airflow from 4 to 10 scfm [standard cubic feet per minute]. Two more tests were prepared following similar methods presented in *section 3.1* of the methodology.

As *Figure 4-1 & Figure 4-2* illustrates, manganese precipitation increased significantly from the last tests. Between 97.4 – 98.9%, manganese (IV) was present in the samples.

Figure 4-1. Manganese with and without Triphosphate Addition (left & right)

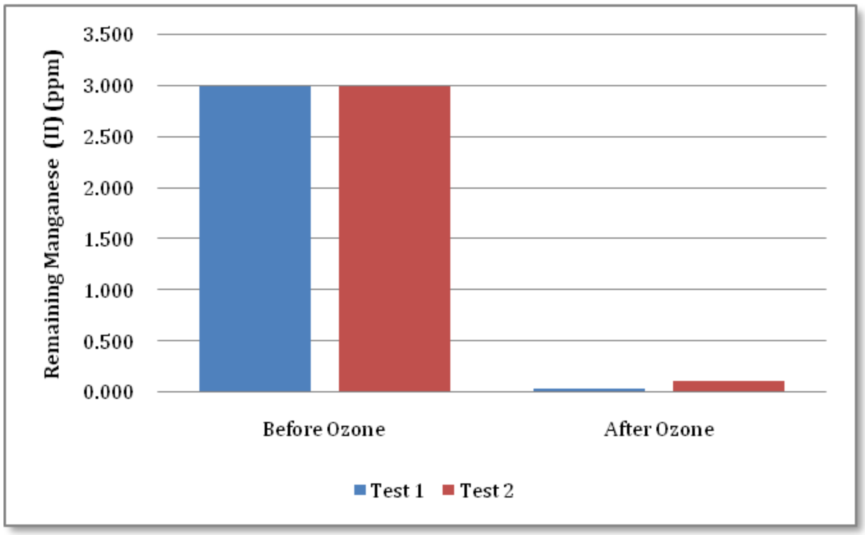

Figure 4-2. Sequestered Manganese after Ozone Addition

Thus, increasing the ozone flowrate amplified the manganese precipitation to levels that could allow us to properly visualize sequestration.

4.2 Sequestration

As mentioned in *section 2.3,* the use of polyphosphates has proven to be an adequate method of sequestering manganese in water. Sequestration holds the metal ions in solution instead of allowing them to precipitate out, leaving visible residue. Ideally, higher dosages of triphosphate should produce greater sequestration of manganese. For our experimental purposes, doses above the theoretical dose, 10 µmol triphosphate, precipitation of manganese should not occur.

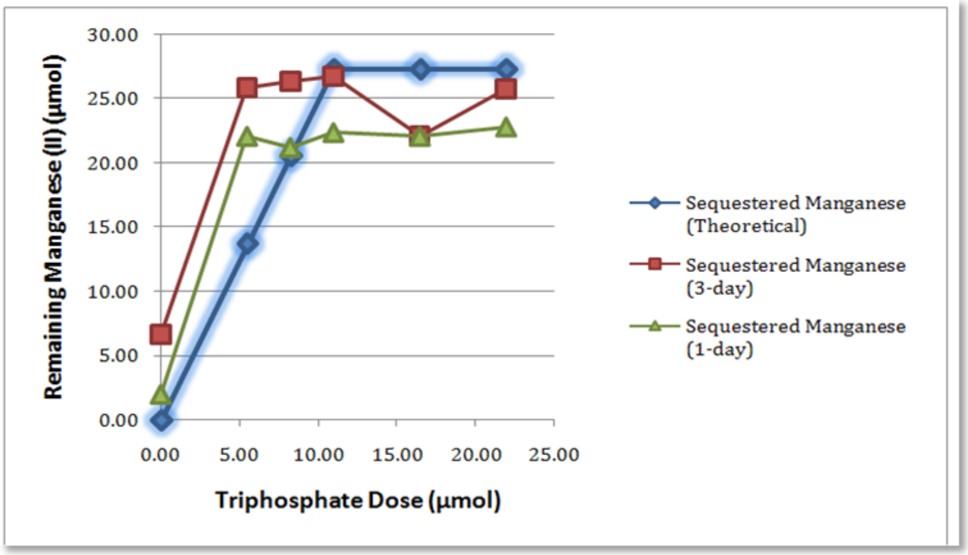

Figure 4-3. Sequestration of Manganese with 1- and 3- Day Settling

Our results, illustrated by *Figure 4-3*, indicated that all triphosphate doses administered successfully sequestered manganese for both the one and three day settling scenarios. The data also demonstrated the strength of sequestration by a triphosphate. Ozone as a strong oxidant did not allow manganese to be fully sequestered by the triphosphate.

$$5Mn^{+2} + 2(P_3O_{10})^{-5} \xrightarrow[ozone]{yields} Mn_5(P_3O_{10})_2$$

Fully Sequestered

$$5Mn^{+2} + 2(P_3O_{10})^{-5} \xrightarrow[ozone]{yields} Mn_5(P_3O_{10})_2 + Mn^{+4}(insoluable)$$

Partially Sequestered

This phenomenon is expressed entirely by the fact that none of the triphosphate doses completely sequestered the manganese. Manganese precipitation still arose between 4 – 22%.

Nevertheless, the precipitation of manganese did not occur fully with no triphosphate addition either. The one-day results exhibited 2.02 μmol and a lower precipitation reading of 25.30 μmol compared to the 27.30 μmol hypothetical precipitation for a one-day settling time. The three day results showed similar results where for the sample with no triphosphate, the sequestered manganese readings was higher at 6.65 μmol while the manganese precipitation readings was lower at 20.85 μmol.

After some consideration, we concluded that these readings were inaccurate for the samples with no tri-polyphosphate due to evaporation and the tested volume change. This was altered for the remaining tests that were run by covering the samples during settling and re-measuring the volume of solution back to 500 mL.

From the results we acquired, the optimum dose of triphosphate is between 8.00 and 11.00 μmol. Sequestered manganese utilizing these doses fell between 21.00 and 27.00 μmol for both the one and three day settling times. At any dose greater than 11.00 μmol, theoretically, all of our manganese should be sequestered. However, the actual readings of manganese sequestration were lower than the theoretical values illustrated in the previous figure. For drinking water facilities, this data outlines the conditions for sequestration and the practicality of sequestering using a polyphosphate.

4.3 Detention Time of Triphosphate & Manganese

Sequestering agents such as triphosphate and many other polyphosphates lose their “potency” in solution as time progresses. Research showed the life of a polyphosphate is typically on the order of years (American Chemistry Council, 2004). Two possible areas where time variations are a factor for sequestration are in the water distribution pipeline and the reactor where the polyphosphate mixes with the drinking water.

Batch Reactor System

Our analysis begins with the polyphosphate entering the reactor. A typical drinking water facility utilizes either a plug flow reactor or a batch system reactor to inject chemicals into the drinking water. A plug flow reactor injects the chemical of interest, in our case a polyphosphate, into the drinking water line and utilizes the movement of water to produce mixing. A batch reactor injects the chemical into a large tank that mixes both the water and the chemical together until the solution is well mixed. Our analysis examined both configurations.

Schematics of a plug flow reactor and a batch reactor can be seen below in *Figure 4-4*.

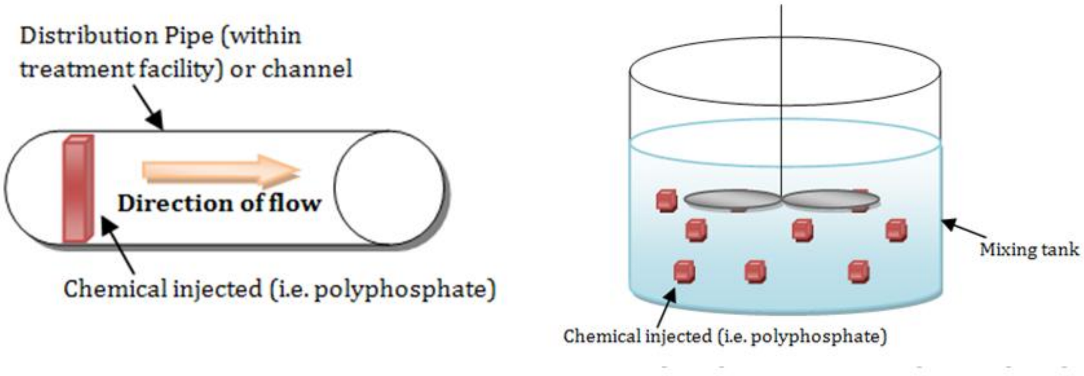

Figure 4-4. Schematics of Plug Flow (left) & Batch Reactor (right)

A plug flow reactor does not have a regulated mix time, as does a batch reactor. Contact by mixing, between the polyphosphate and the manganese, is dictated by the length of pipe/channel. The size of the tank and the flow rate can influence the contact time between polyphosphate and manganese. Whereby, residence time (contact time) is given by $= \frac{Volume\ [V]}{Flowrate\ [Q]}$ (Droste, 2004).

Data collected through our experimentation verifies facts stated in the literature pertaining to injection of polyphosphates into the drinking water for treatment purposes. Typically, treatment facilities introduce the polyphosphate directly into the water distribution line before pH adjusters or chlorine (Sullivan, 2007).

Theoretically, from the reaction of manganese (II) and triphosphate,

$$5Mn^{+2} + 2(P_3O_{10})^{-5} \xrightarrow{yields} Mn_5(P_3O_{10})_2$$

The stoichiometric molar ratio of manganese (II) to triphosphate is 5:2. Therefore, 27.3 µmol of manganese (II), approximately 10 µmol of triphosphate was required as a theoretical dose for complete sequestration of the manganese.

From *Figure 4-5* on the next page, the data showed that the no mix scenario sequesters the greatest quantity of manganese, while 2-, 4-, and 6-hour mix times proved to sequester the least amount of manganese. However, none of the samples showed complete sequestration. Most likely, complete sequestration did not occur for any of our samples because ozone is too strong of an oxidant.

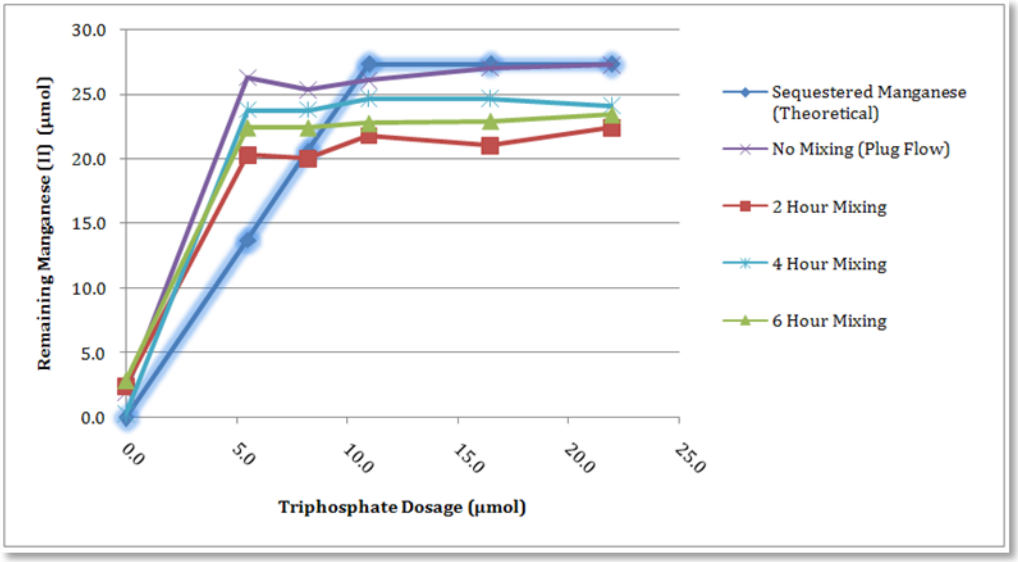

Figure 4-5. Mixing Results

Only the no mix completely sequestered the manganese (II), even with ozone present, but at 21.9 µmol of triphosphate. This dose is two times the theoretical dose needed to sequester our concentration of manganese. Still, for drinking water treatment purposes, the data clearly proved that no mixing presents the best results.

Pipeline Distribution System

During the distribution of water from the treatment plant to residents, polyphosphate reactions may occur with constituents, growths on the pipe walls, and general chemical reactions. Polyphosphates also degrade into simple phosphate molecules. The time of travel, or residence time, within a distribution pipe depends on the distance residents reside from the treatment facility. Generally, residence times are on the order of hours to days (Carallo Engineers, n.d.).

Our experimentation collected two sets of data to determine the effects of pipeline residence time. One data set utilized strong oxidation to simulate harsh, oxidative, conditions in the pipeline. The illustration of data in *Figure 4-6* is inconclusive as to whether triphosphate would destabilize within the pipe. Furthermore, for the 3-day residence time, the large drop in remaining manganese (II) should not occur due to the above stoichiometric addition of triphosphate to manganese. Additionally, for 5-days, the strength of ozone proved that triphosphate would not survive under such conditions. However, similar to the 3-day residence time, a large drop was present in remaining manganese at the higher triphosphate doses. The strength of the oxidant, ozone, could explain both drops in the data.

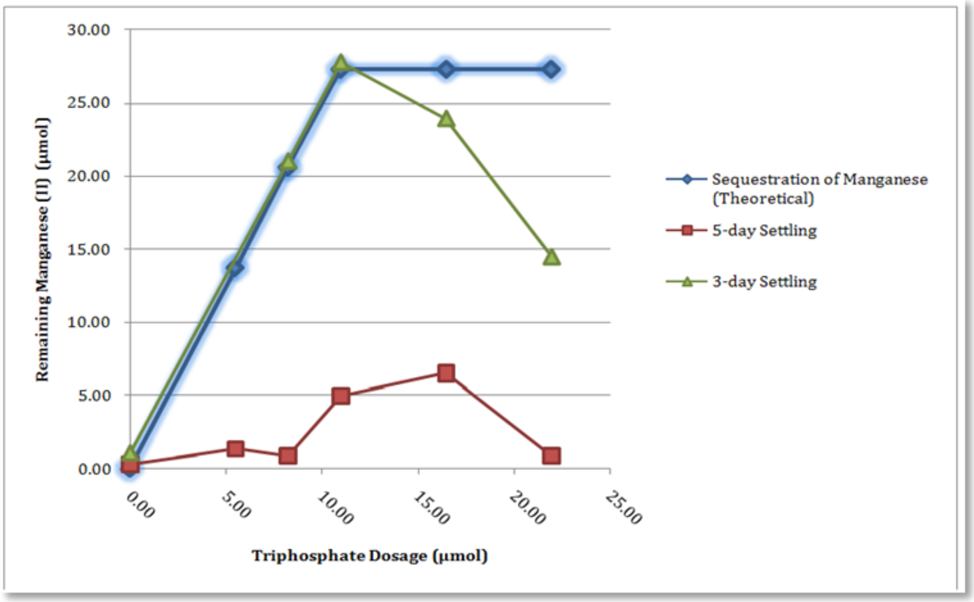

Figure 4-6. Results of 6-Hour Ozone & Settling

Under less severe conditions, the triphosphate remained bonded to the manganese. Remaining manganese (II) data presented in *Figure 4-7*, displayed steady sequestering of the manganese via triphosphate. Similar to the 6-hour ozone test, the 3-day settling data showed a drop in remaining manganese, but only for the 16.5 µmol dose. We later found a leak in the manifold used to distribute ozone evenly to the six beakers to cause the unsteady results.

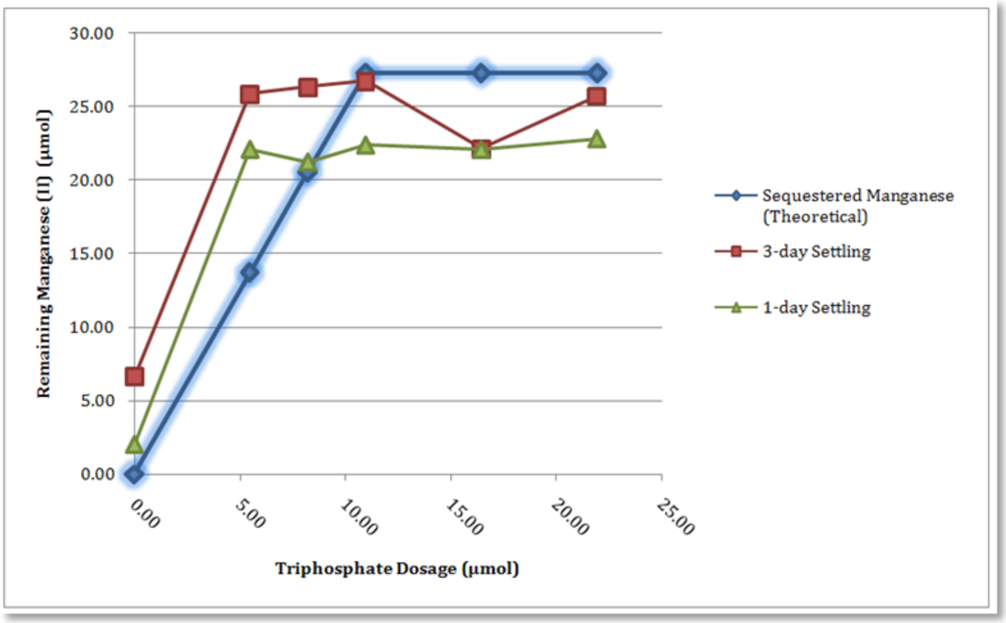

Figure 4-7. Results of 3-Hour Ozone & Settling

Clearly, both data sets provided evidence showing that triphosphate sequestering decreases under oxidizing conditions.

4.4 pH

High pH, as discussed in the background of this report, promotes precipitation of the manganese. The reaction that can occur is:

$$Mn^{+2} + 2OH^{-} \xrightarrow{yields} Mn(OH)_2$$

K_{sp} [Solubility Constant] = *3.40 x 10^{-3} g/L*
Source: Handbook of Chemistry and Physics, 88th Edition

As shown by the data in *Figure 4-8*, precipitation occurs readily even in the presence of a sequestering agent such as sodium triphosphate. With no triphosphate additions ozone and hydroxide removed manganese (II) by 97 – 99%. With triphosphate present to sequester the manganese, only 11 – 16% of the Mn^{+2} was oxidized. Still, these numbers are much higher than the 4 – 6% oxidized Mn^{+2} documented in *section 4.2*.

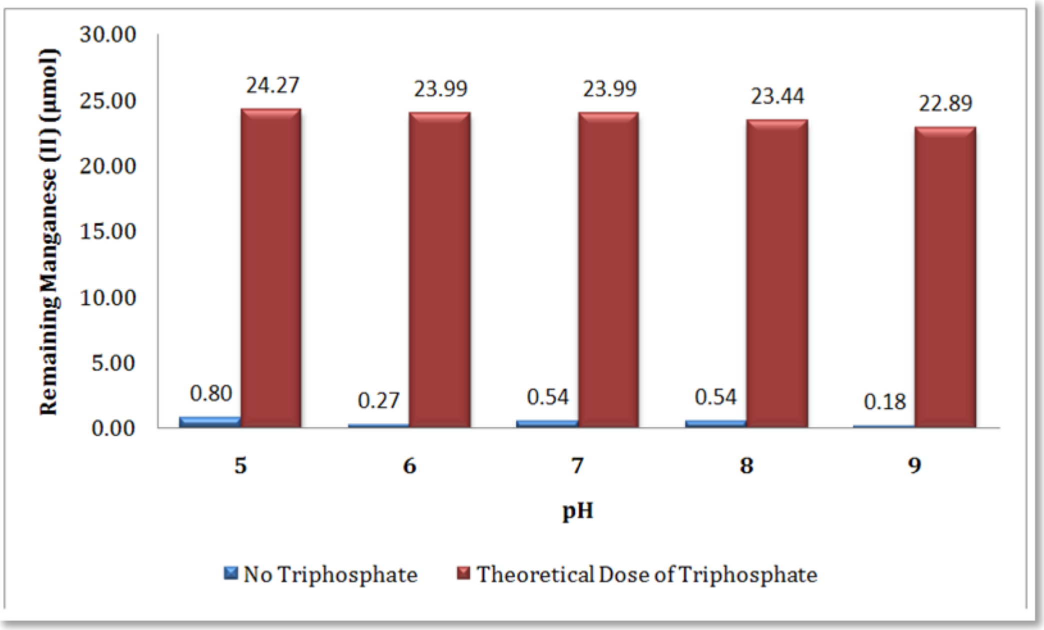

Figure 4-8. Effects of pH towards Sequestration of Manganese

The data visibly exhibited a decrease of sequestered manganese (II) as pH increased. From the reaction equations of manganese (II) in the presence of sodium hydroxide and sodium triphosphate,

$$6Mn^{+2} + 2OH^- + 2(P_3O_{10})^{-5} \xrightarrow{yields} Mn(OH)_2 + Mn_5(P_3O_{10})_2$$

Partially Sequestered

$$5Mn^{+2} + OH^- + 2(P_3O_{10})^{-5} \xrightarrow{yields} Mn_5(P_3O_{10})_2 + OH^-$$

Fully Sequestered

we can expect at higher pHs rather than lower pHs this decrease to occur. The latter reaction displayed below is unlikely due to the solubility of manganese hydroxide and is even more unlikely at higher pH levels due to the concentration of hydroxide ions. *Figure 4-9* physically displays the chemistry of hydroxide ions to the precipitation of manganese. As one can see, the darker, more precipitated manganese lies heavily towards higher pHs.

Figure 4-9. Manganese precipitation with Triphosphate for pH 5 - 9

In effect, water treatment facilities must monitor pH closely. Furthermore, the data affirms the reason why most facilities that utilize polyphosphates such as sodium triphosphate inject the chemical before pH adjusters.

4.5 *Alternative Polyphosphate Chemicals*

As the background of this report shows, many different polyphosphates and preciprietary polyphosphate solutions exist. Our final experiment tested several chemical blends with our manganese solution and compared these results with our results while using a laboratory-created triphosphate solution. Due to the unknown make-up of the phosphate blends, we were unable to compute the µmol of the solutions so they remained in mL readings. The results, given in *Figure 4-10*, showed that the SK-7699 (sodium triphosphate blend) closely correlated to the laboratory-created triphosphate. The SK-7691 (hexametaphosphate) had a slight decline in sequestered manganese at doses above 6.91 mL while the AquaMag (blended phosphate) had a sharp decline at only 2.775 mL. This indicated that at some point, the manganese is precipitating instead of remaining sequestered.

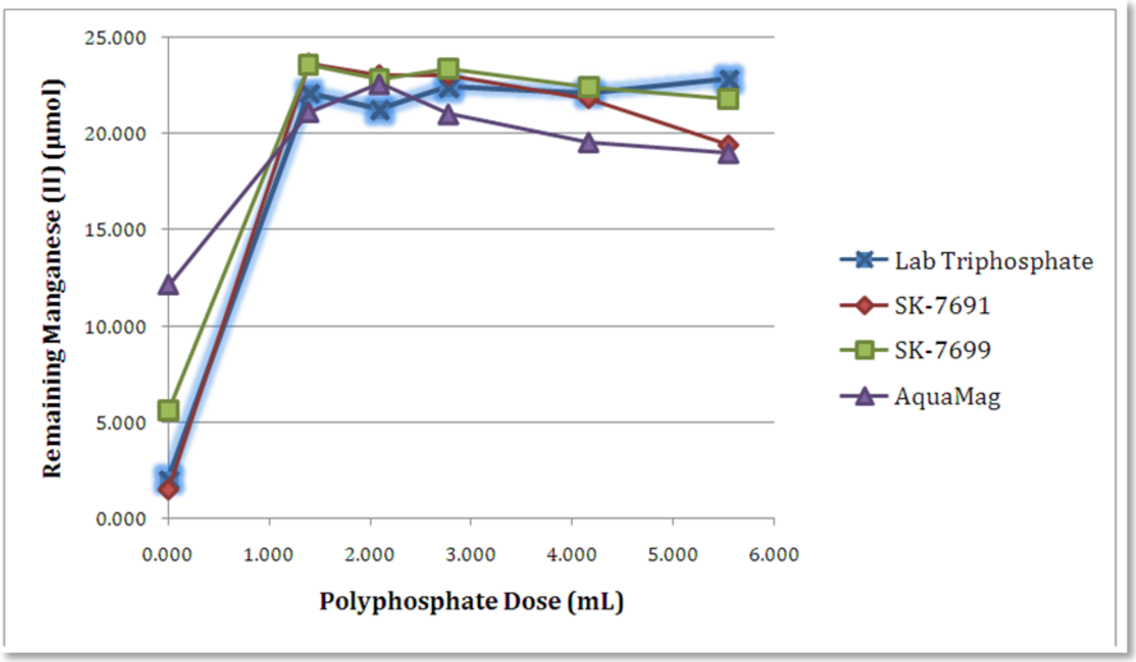

Figure 4-10. Alternative Polyphosphate Sequestering Data

The percentages found in *Table 4-2* indicated the quantity of manganese that precipitated.

Table 4-2. Percentages of Sequestered Manganese by Polyphosphate Dose

Polyphosphate Added [mL]	SK – 7691	SK – 7699	AquaMag
1.390	13%	14%	23%
2.090	16%	16%	17%
2.775	16%	14%	23%
4.165	20%	18%	28%
5.550	29%	20%	30%

The results showed that the alternative phosphate to produce the least amount of precipitate was SK-7691 (sodium triphosphate blend) at 13%.

This data allowed us to see how effective some of these phosphate blends are for sequestering manganese.

5 Triphosphate Dosing Design: West Boylston

From the results of our experimentation, a proposed design for distributing and properly dosing West Boylston's drinking water can be considered. This design procedure may also be utilized for other drinking water facilities. The following section discusses the most appropriate application of sodium triphosphate into West Boylston's drinking water. However, our discussion does not completely encompass every variable affecting sequestration.

5.1 Problem

The drinking water consumers of West Boylston, Massachusetts may complain of black stains on light colored surfaces caused by the water coming from their plumbing if manganese is not controlled. Although not a toxic material to humans, manganese becomes problematic when it can be seen. These stains, commonly found on the white porcelain of sinks, bathtubs, and toilets, can be attributed to the manganese in the water.

5.2 Laboratory Experimentation

A laboratory simulation was performed, using a 3 ppm solution of manganese and E-pure water. A series of tests were performed to determine the optimal polyphosphate dosage, mix time, and detention time to hold the manganese in solution. Also, a series of tests were conducted to determine whether outside factors such as pH levels or competing metal ions such as iron had any effect on the sequestration.

The group has concluded through performing testing in the laboratory that using a 500 mL solution containing 3 ppm [10 mL] of manganese, a dose of 5.550 ppm [2.775 mL] of triphosphate was optimal. This was combined with three hours of ozone to promote oxidation and therefore precipitation of the manganese (for testing purposes only), and finally, a settling time of one day. It was determined that better results came from not mixing the solution. Also, it is important to note that the triphosphate must be added prior to pH adjustment, if pH adjustment is done.

5.3 Application of Data

From our experimental concentration of 3 ppm manganese (II) and 5.550 ppm sodium triphosphate required, a simple ratio of experimental manganese to the actual manganese concentration at West Boylston Drinking Water facility established a sodium triphosphate dose for West Boylston.

$$\frac{\text{experimental concentration of manganese}}{\text{experimental dose of triphosphate}} = \frac{\text{actual concentration of manganese}}{\text{actual dose of triphosphate}}$$

Accordingly, an optimum dose for West Boylston was extrapolated from the data and results of our experiments. *Table 5-1*, presents the proper dose of sodium triphosphate.

Table 5-1. Sodium Triphosphate Dose Extrapolated from Experimentation

Manganese Concentration [ppm]	Sodium Triphosphate Dose [Current Dose] [ppm]	Sodium Triphosphate Dose [Analytical Dose] [ppm]
3.00	--	5.550
1.50	--	2.775
1.40	--	2.590

In addition to the proper dosage, this simulation was applied to West Boylston's actual flows and current manganese levels. As discussed in the background of this report, West Boylston uses three main wells, one on Lee Street, one on Pleasant Valley Street, and one on Oakdale. These wells supply water in flows of 250 gallons per minute, 500 gallons per minute, and 725 gallons per minute respectively (West Boylston Water District, 2007). Because the West Boylston Water District's latest consumer report showed a manganese level of 1.4 ppm in the water, the simulation can easily be applied by cutting the dose in half and recalculating all as gallon per minute flows.

If we consider a manganese concentration of 1.5 ppm, the 2.775 mL per 500 mL solution dose would then be cut in half to give a 1.3875 mL per 500 mL solution dose of triphosphate. A conversion factor of 0.132 gallon to 1 mL allowed the data to coincide with the flows coming from the wells. The calculations from the equations below showed an optimal dose of .69 gallons of sodium triphosphate per minute in the Lee Street well.

$$\frac{500mL}{0.132\ gal} = \frac{X\ mL}{250\ gal/min};\ X = 946352.95\ mL/min$$

$$\frac{1.3875mL}{500mL} = \frac{X}{946352.95mL/min};X = 2626.13\ mL/min\ =\ .69gal/min$$

Table 5-2 displays the appropriate dose of triphosphate required in order to properly sequester the manganese present for the Oakdale well and the Pleasant Valley well. The Oakdale well needs 2.01 gallons per minute to be injected, while the Pleasant Valley well would require 1.38 gallons per minute of sodium triphosphate dosing.

Table 5-2. Sodium Triphosphate Injection Rates for West Boylston Wells

Well	Average Manganese Concentration [ppm]	Average Flowrate [gpm]	Average Sodium Triphosphate Injection Rate [gpm]
Lee Street	1.40	250	0.69
Oakdale	1.40	725	2.01
Pleasant Valley	1.40	500	1.38

5.4 Barriers of Deployment

Barriers toward the deployment of sequestering agents such as sodium triphosphate relate to the cost of implementation. Cost factors not only include the injection pump and capital cost of the reagent itself, but the power consumption necessary to drive the pump. These factors are also predicated on the initial concentration of manganese present in the drinking water. Nevertheless, for some facilities, the cost of implementation may still be much less than other remediation methods (i.e. oxidation/filtration).

6 Recommendations

Table 6-1. Summary of Triphosphate Study

Experimental Variable	*Background*	*Method*	*Analysis/Results*	*Recommendation /Outcome*
P_3O_{10} sequestration under ideal conditions	Removes manganese effectively	Add specific dose of P_3O_{10} Standard Ozone, mix, settle, analyze	4 – 6% oxidized Mn^{+2} (3-day) 16 – 22% oxidized Mn^{+2} (1-day)	Sequestration using sodium triphosphate viable
Batch reactor τ	Residence time affects sequestering potential of polyphosphate	Add specific dose of P_3O_{10} 3-6 hour ozone, mix, (1,3,5) day settle, analyze	0-hour mix best (0% precipitation of Mn^{+2})	Inject as plug flow configuration
Pipeline τ	Residence time affects sequestering potential of polyphosphate	Add specific dose of P_3O_{10} Ozone, (0,2,4,6) hour mix, settle, analyze	Inconclusive, max 3 days under harsh conditions	3 days max before breakdown of triphosphate-manganese bond
pH	Manganese hydroxide precipitation more likely than sequestration	Add specific dose of P_3O_{10} and NaOH Standard Ozone, mix, settle, analyze	11 – 12% oxidized manganese (II) (high pH) 14 – 16% oxidized manganese (II) (low pH)	Must inject polyphosphate before oxidation chemicals Hydroxide ions (pH) affect sequestration
Alternative polyphosphates	Variety of polyphosphates utilized under multiple conditions	Add specific dose of alternative polyphosphate (mL) Standard Ozone, mix, settle, analyze	SK-7691: 13 – 29% oxidized Mn^{+2} SK-7699: 14 – 20% oxidized Mn^{+2} AquaMag: 17 – 30% oxidized Mn^{+2}	Lab triphosphate performed better than vendor mixtures Vendor blends sequestered 70 – 90% manganese (II)

6.1 Sequestration of Manganese

As stated multiple times throughout this report, polyphosphate sequestration is variable. The data in *section 4* verifies that certain variables can influence the sequestering capabilities of the sodium triphosphate. Through our laboratory studies sequestration has proven to be a successful measure for controlling manganese. Most often, manganese in drinking water would not reach levels as high as 3 ppm. Most often water treatment facilities utilize sequestering agents such as polyphosphates if manganese concentrations are below 0.1 ppm (MRWA, 2007). Although, we would propose based on our data that manganese levels around 1 – 2 ppm would be sequestered to the point where precipitation would be unrecognizable.

As for other variables such as residence time and pH, we recommend sequestering agents be injected immediately into drinking water and prior to oxidizing agents such as chlorine for disinfection purposes and pH adjusters. In addition, we suggest treatment facilities having pipelines distributing drinking water to residents monitor the delivery time. A maximum of three days is allowed for polyphosphates to remain bonded to manganese under any conditions. If the distribution time exceeds three days, more polyphosphate may be required.

Lastly, alternative polyphosphates provide drinking water facilities with alternatives to more expensive treatment processes. However, our group proposes that an extensive examination of these chemicals be completed. Using similar methods outlined in this report, the alternative polyphosphates should be studied to quantify their potential to sequester manganese under various conditions.

6.2 Future Work for West Boylston Drinking Water Facility

Examining the chemistry of West Boylston's drinking water must first occur before the data presented in this report can be useful. Our group proposes utilizing the data as a preliminary calculation for dosage of the sodium triphosphate. In addition, we suggest employing the data as conditions of the drinking water as it passes through the plant. Lastly, we recommend West Boylston perform a model evaluation of its processes and other possible courses of action to prevent manganese precipitation in order to find a reasonable solution to this problem.

6.3 Other Water Treatment Facilities

For drinking water facilities with manganese precipitation issues, we strongly recommend using this data as a basis for sequestering agent dose. Facilities utilizing other forms of treatment for removing manganese may find the data useful. These facilities may employ this report to determine the cost benefit of using a polyphosphate for sequestering manganese.

Furthermore, cost, plant size, and type of sequestering agent limits the applicability of sequestering manganese. Our group proposes that facilities utilize the data and our design methods to establish the proper sequestering agent and pump injection rate required for the polyphosphate. From this, plants can determine pump sizes, the outline for the apparatuses, and cost of the mechanism.

6.4 Future Analysis of Polyphosphate Sequestering

This report partially covered the factors necessary for water treatment facilities to make educated decisions pertaining to the required dose of polyphosphate. However, some crucial areas that future experiments should examine are temperature and competing metal ions.

Temperature can cause the polyphosphate to break down in solution, thereby releasing the manganese back into solution and allowing oxidation to occur. Once the water enters a household, water boilers and washing machines raise the temperature of the water, initiating the breakdown. Our group suggests studying the effects of temperature on polyphosphate sequestering. We also strongly suggest examining common household processes (i.e. doing dishes, laundry) to understand the extent of polyphosphate degradation from each of these processes.

Secondly, competing metal ions such as iron can prevent proper sequestration of manganese. Iron (II) has similar characteristics as manganese (II). Both are equally sequestered by sodium triphosphate.

$$5Mn^{+2} + 2P_3O_{10}{}^{-5} \xrightarrow{yields} Mn_5(P_3O_{10})_2$$

$$5Fe^{+2} + 2P_3O_{10}{}^{-5} \xrightarrow{yields} Fe_5(P_3O_{10})_2$$

In addition, iron itself causes aesthetic problems as a precipitate. Therefore, our group proposes observing the sequestration behavior of iron both in the presence of manganese and not in the presence of manganese. This type of scenario will allow the mechanism for iron sequestration to be better inspected.

6.4.1 Proposed Future West Boylston Drinking Water Experimentation

Due to the limited time to study polyphosphate sequestration, our group was unable to analyze the mechanisms discovered in this report using West Boylston's drinking water. For that reason, we propose using the methods outlined in this report to test West Boylston's drinking water with the sodium triphosphate.

In addition to employing our methods, we strongly suggest examining polyphosphate sequestration by observing a continuous pumping test. Whereby, the polyphosphate of interest would be injected into a continuous flow stream. This set up would simulate the conditions of West Boylston's water and its processes for treatment.

7 Conclusion

Metals that tend to precipitate in water, such as manganese, are problematic for many water treatment facilities and their consumers. Although the manganese is not harmful in low concentrations, the precipitate can discolor the water resulting in stained surfaces and clothing. Because of this, many municipalities have chosen to sequester manganese using a polyphosphate so that it will not precipitate. The manganese is present in the water, but is not visible.

This report evaluated the optimum dosage and conditions for keeping the manganese sequestered in solution. Despite the usage of a polyphosphate, municipalities do still receive complaints of staining from the precipitated manganese. Other conditions and factors such as the notion that iron within the water may be competing for the polyphosphate should be considered. The recommendation section of this text can be referred to for more tests that should be examined in the future.

In addition, polyphosphate use may not be the most appropriate option. One source stated that adding phosphate is not always the best method of dealing with manganese. It does not remove the manganese, which can result in a metallic taste. Also, using higher doses of phosphate may cause diarrhea. Polyphosphates may even cause corrosion in copper plumbing (Neb Guide, 2007). Because of this, and the possibility that despite a future completion of testing the manganese may continue to precipitate, perhaps treatment such as in-home basis would be a better option. In the end, treatment facilities will have to determine if polyphosphate sequestering is a cost effective measure for preventing the fouling of drinking water via manganese precipitation.

8 References

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Appendix

Stock Solutions

Table 8-1. Manganese Stock Solution Calculations

Base Solution for Mn+2

Solubility of Manganese Chloride (MnCl2): **773 g/L**
Mn+2 Stock Solution Utilized: **0.15 g/L**
Required MnCl2 salt for Making Mn+2 Stock: **0.34357 g**
Actual MnCl2 Salt Utilized: **0.08589 g per 250 mL**

Precipitation will not occur because conc. of stock solution utilized is below solubility constant

Determining Requirement of MnCl2 Salt (calculations):

Mn+2 + 2Cl- MnCl2 (s)

0.15 g Mn+2 * (1 mol Mn+2/54.94 g Mn+2) * (1 mol MnCl2/1 mol Mn+2) * (125.84 g MnCl2/1 mol MnCl2) = **0.34537 g MnCl2**

This makes a 150 ppm Mn+2 solution

Table 8-2. Sodium Triphosphate Stock Solution Calculations

Base Solution for Tripolyphosphate (P3O10)-5

Solubility of Sodium Tripolyphosphate ($Na_5(P_3O_{10})$): **150 g/L**
P_3O_{10} Stock Solution Utilized: **1.0 g/L**
Required $Na_5(P_3O_{10})$ for making $P_3O_{10}^{-5}$ Stock Solution: **1.067 g $Na_5(P_3O_{10})$**
Actual $Na_5(P_3O_{10})$ Utilized: **0.2667 g/250 mL E-Pure**

Determining Requirements of P3O10 (calculations):
H(+) + Mn+2 + (P3O10)-5 + O3(g) --> Mn5(P3O10)2 + O2(g) + H2O
Assuming complete sequestration of Mn+2
2H(+) + 5Mn+2 + 2(P3O10)-5 + O3(g) --> Mn5(P3O10)2 + O2(g) + H2O

Calculations:
3ppm Mn+2 = 3mg/L Mn+2 * (1 g/1000 mg) * (1 mol Mn+2/54.938 g Mn+2) * (2 mol (P3O10)-5/5 mol Mn+2) * (252.915g (P3O10)-5/1 mol (P3O10)-5) * (1000 mg/1 g) = 5.524 mg/L (P3O10)-5 = 5.55 mg/L (P3O10)-5

5Na+ + P3O10-5 Na(P3O10) (s)
1.0 g OH-* (1 mol P3O10-5/344.87 g P3O10-5) * (1 mol Na5(P3O10)/1 mol P3O10-5) * (367.86 g Na5(P3O10)/1 mol Na5(P3O10)) = **1.067 g Na5(P3O10)**
This makes a 1000 ppm P3O10-5 solution

Table 8-3. Sodium Hydroxide Stock Solution Calculations

Sodium Hydroxide Stock Solution

Base Solution for OH-

Solubility of Sodium Hydroxide (NaOH): **1000 g/L**
Solubility of Manganese Hydroxide (Mn(OH)2): **0.0008 g/L**
OH- Stock Solution Utilized: **0.30 g/L**
Required NaOH for making OH- Stock Solution: **17.65 mL NaOH/L E-Pure**
Actual NaOH Utilized: **4.415 mL per 250 mL E-Pure**

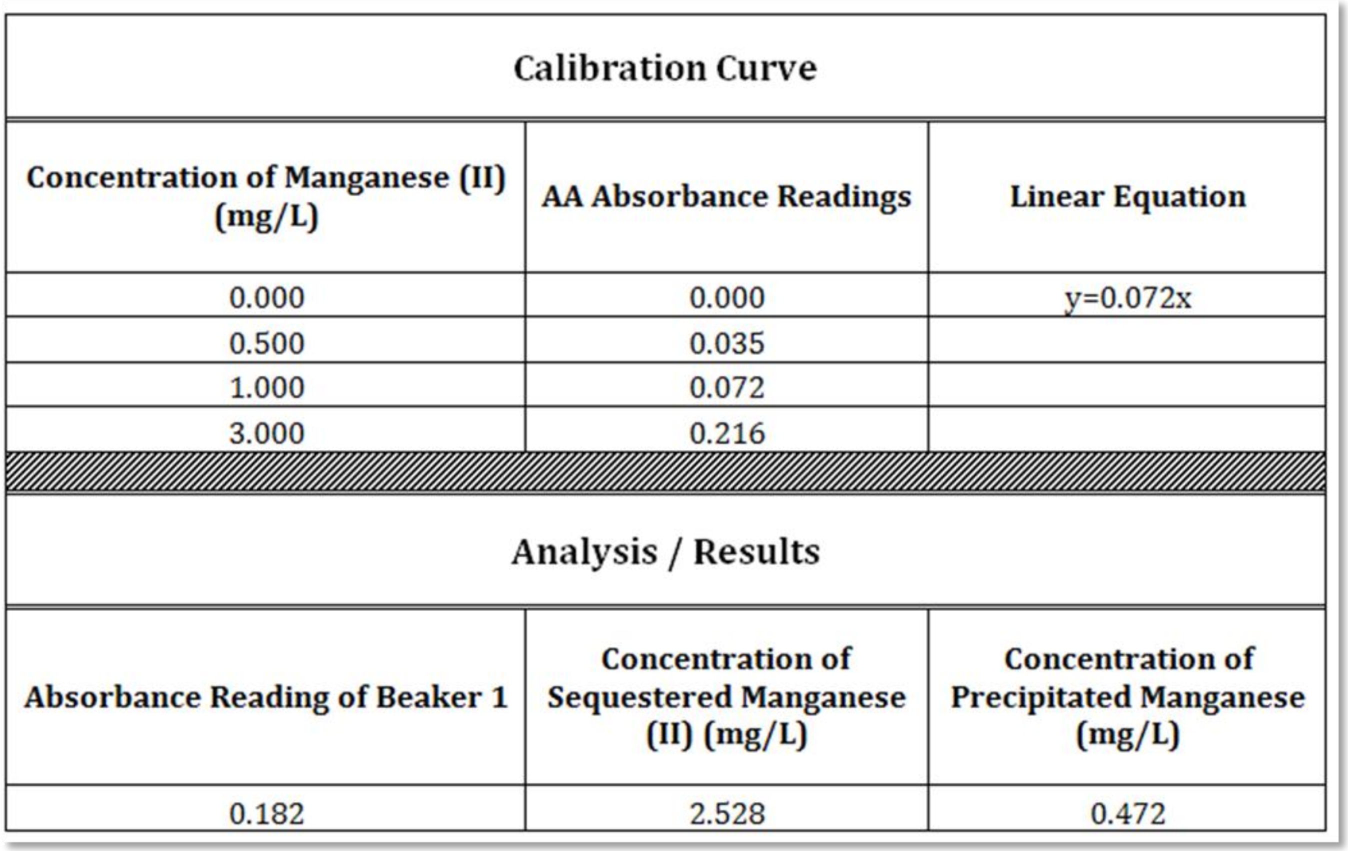
Determining Requirements of NaOH (calculations):

Na+ + OH- NaOH (l)
0.30 g OH-* (1 mol OH-/16.999 g OH-) * (1 mol NaOH/1 mol OH-) * (39.98 g NaOH/1 mol NaOH) = **0.7056 g NaOH**
Using 1 N NaOH Solution
1 N NaOH * (39.98 g NaOH/1 mol NaOH) **39.98 g/L NaOH**
0.7056 g NaOH/(39.98 g/L NaOH) * (1000 mL/1 L) **17.65 mL NaOH/L E-Pure**
This makes a 300 ppm OH- solution

Data

Precipitation

Table 8-4. Manganese Precipitation

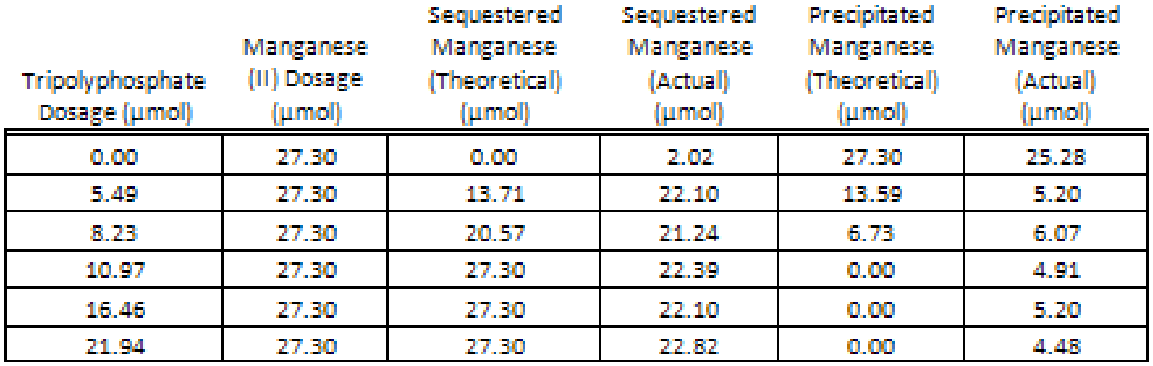


Calibration Curve		
Concentration of Manganese (II) (mg/L)	**AA Absorbance Readings**	**Linear Equation**
0.000	0.000	y=0.072x
0.500	0.035	
1.000	0.072	
3.000	0.216	

Analysis / Results		
Absorbance Reading of Beaker 1	**Concentration of Sequestered Manganese (II) (mg/L)**	**Concentration of Precipitated Manganese (mg/L)**
0.182	2.528	0.472

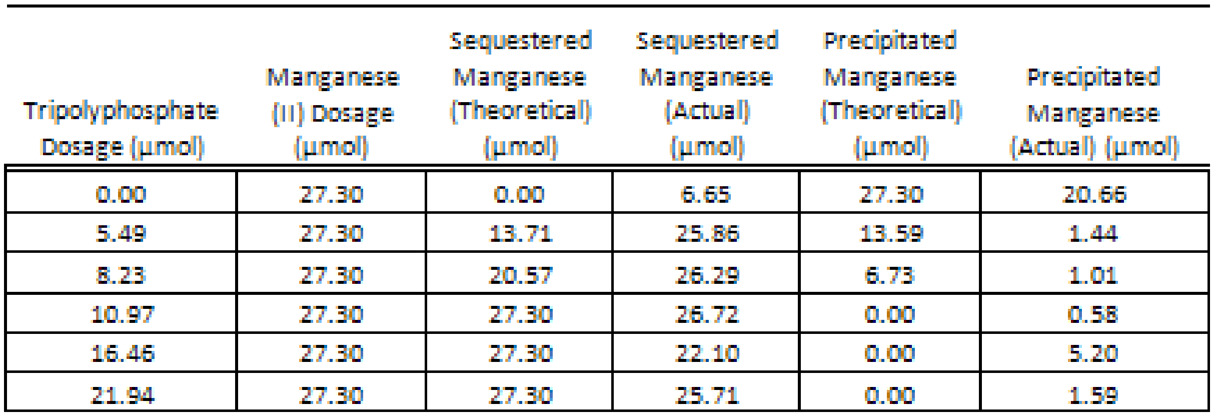
Sequestration

Table 8-5. 1-day Settling (Sequestration)



Tripolyphosphate Dosage (µmol)	Manganese (II) Dosage (µmol)	Sequestered Manganese (Theoretical) (µmol)	Sequestered Manganese (Actual) (µmol)	Precipitated Manganese (Theoretical) (µmol)	Precipitated Manganese (Actual) (µmol)
0.00	27.30	0.00	2.02	27.30	25.28
5.49	27.30	13.71	22.10	13.59	5.20
8.23	27.30	20.57	21.24	6.73	6.07
10.97	27.30	27.30	22.39	0.00	4.91
16.46	27.30	27.30	22.10	0.00	5.20
21.94	27.30	27.30	22.82	0.00	4.48

Table 8-6. 3-day Settling (Sequestration)



Tripolyphosphate Dosage (µmol)	Manganese (II) Dosage (µmol)	Sequestered Manganese (Theoretical) (µmol)	Sequestered Manganese (Actual) (µmol)	Precipitated Manganese (Theoretical) (µmol)	Precipitated Manganese (Actual) (µmol)
0.00	27.30	0.00	6.65	27.30	20.66
5.49	27.30	13.71	25.86	13.59	1.44
8.23	27.30	20.57	26.29	6.73	1.01
10.97	27.30	27.30	26.72	0.00	0.58
16.46	27.30	27.30	22.10	0.00	5.20
21.94	27.30	27.30	25.71	0.00	1.59

Detention Time in Pipe

Table 8-7. 3-Hour Ozone

Tripolyphosphate Dosage (µmol)	Manganese (II) Dosage (µmol)	Sequestered Manganese (Theoretical) (µmol)	Sequestered Manganese (Actual) (µmol)	Precipitated Manganese (Theoretical) (µmol)	Precipitated Manganese (Actual) (µmol)
0.00	27.30	0.00	6.65	27.30	20.85
5.49	27.30	13.71	25.86	13.59	2.34
8.23	27.30	20.57	26.29	6.73	1.92
10.97	27.30	27.30	26.72	0.00	1.50
16.46	27.30	27.30	22.10	0.00	5.96
21.94	27.30	27.30	25.71	0.00	2.48

3-day

Tripolyphosphate Dosage (μmol)	Manganese (II) Dosage (μmol)	Sequestered Manganese (Theoretical) (μmol)	Sequestered Manganese (Actual) (μmol)	Precipitated Manganese (Theoretical) (μmol)	Precipitated Manganese (Actual) (μmol)
0.00	27.30	0.00	2.02	27.30	25.30
5.49	27.30	13.71	22.10	13.59	5.96
8.23	27.30	20.57	21.24	6.73	6.79
10.97	27.30	27.30	22.39	0.00	5.68
16.46	27.30	27.30	22.10	0.00	5.96
21.94	27.30	27.30	22.82	0.00	5.26

1-day

Table 8-8. 6-Hour Ozone

Tripolyphosphate Dosage (μmol)	Manganese (II) Dosage (μmol)	Sequestered Manganese (Theoretical) (μmol)	Sequestered Manganese (Actual) (μmol)	Precipitated Manganese (Theoretical) (μmol)	Precipitated Manganese (Actual) (μmol)
0.00	27.30	0.00	0.30	27.30	27.00
5.49	27.30	13.71	1.37	13.59	25.94
8.23	27.30	20.57	0.91	6.73	26.39
10.97	27.30	27.30	5.01	0.00	22.30
16.46	27.30	27.30	6.52	0.00	20.78
21.94	27.30	27.30	0.91	0.00	26.39

5-day

Tripolyphosphate Dosage (µmol)	Manganese (II) Dosage (µmol)	Sequestered Manganese (Theoretical) (µmol)	Sequestered Manganese (Actual) (µmol)	Precipitated Manganese (Theoretical) (µmol)	Precipitated Manganese (Actual) (µmol)	
0.00	27.30	0.00	1.05	27.30	26.60	
8.23	27.30	20.57	21.00	6.73	2.66	
10.97	27.30	27.30	27.77	0.00	-5.46	
16.46	27.30	27.30	23.92	0.00	-0.84	
21.94	27.30	27.30	14.47	0.00	10.50	
5.49	27.30	13.71	0.00	13.59	0.00	dropped sample

3-day

Detention Time in Batch Reactor

Table 8-9. No Mixing

Tripolyphosphate Dosage (μmol)	Manganese (II) Dosage (μmol)	Sequestered Manganese (Theoretical) (μmol)	Sequestered Manganese (Actual) (μmol)	Precipitated Manganese (Theoretical) (μmol)	Precipitated Manganese (Actual) (μmol)
0.0	27.3	0.0	2.0	27.3	25.3
5.5	27.3	13.7	26.3	13.6	1.0
8.2	27.3	20.6	25.3	6.7	2.0
11.0	27.3	27.3	26.1	0.0	1.2
16.5	27.3	27.3	27.1	0.0	0.2
21.9	27.3	27.3	27.3	0.0	0.0

Table 8-10. 2-Hour Mix

Tripolyphosphate Dosage (μmol)	Manganese (II) Dosage (μmol)	Sequestered Manganese (Theoretical) (μmol)	Sequestered Manganese (Actual) (μmol)	Precipitated Manganese (Theoretical) (μmol)	Precipitated Manganese (Actual) (μmol)
0.0	27.3	0.0	2.4	27.3	24.9
5.5	27.3	13.7	20.3	13.6	7.0
8.2	27.3	20.6	20.0	6.7	7.3
11.0	27.3	27.3	21.8	0.0	5.5
16.5	27.3	27.3	21.1	0.0	6.2
21.9	27.3	27.3	22.4	0.0	4.9

Table 8-11. 4-Hour Mix

Tripolyphosphate Dosage (μmol)	Manganese (II) Dosage (μmol)	Sequestered Manganese (Theoretical) (μmol)	Sequestered Manganese (Actual) (μmol)	Precipitated Manganese (Theoretical) (μmol)	Precipitated Manganese (Actual) (μmol)
0.0	27.3	0.0	0.3	27.3	27.0
5.5	27.3	13.7	23.8	13.6	3.5
8.2	27.3	20.6	23.8	6.7	3.5
11.0	27.3	27.3	24.7	0.0	2.6
16.5	27.3	27.3	24.7	0.0	2.6
21.9	27.3	27.3	24.1	0.0	3.2

Table 8-12. 6-Hour Mix

Tripolyphosphate Dosage (μmol)	Manganese (II) Dosage (μmol)	Sequestered Manganese (Theoretical) (μmol)	Sequestered Manganese (Actual) (μmol)	Precipitated Manganese (Theoretical) (μmol)	Precipitated Manganese (Actual) (μmol)
0.0	27.3	0.0	2.9	27.3	24.4
5.5	27.3	13.7	22.4	13.6	4.9
8.2	27.3	20.6	22.4	6.7	4.9
11.0	27.3	27.3	22.8	0.0	4.6
16.5	27.3	27.3	22.9	0.0	4.4
21.9	27.3	27.3	23.4	0.0	3.9

pH

Table 8-13. No Triphosphate

Tripolyphosphate Dosage (µmol)	Manganese (II) Dosage (µmol)	Sequestered Manganese (Actual) (µmol)	Precipitated Manganese (Actual) (µmol)
0.00	27.30	0.80	26.50
0.00	27.30	0.27	27.03
0.00	27.30	0.54	26.77
0.00	27.30	0.54	26.77
0.00	27.30	0.17	27.14

Table 8-14. Theoretical Dose of Triphosphate

Tripolyphosphate Dosage (µmol)	Manganese (II) Dosage (µmol)	Sequestered Manganese (Actual) (µmol)	Precipitated Manganese (Actual) (µmol)
0.00	27.30	24.27	3.03
0.00	27.30	23.99	3.31
0.00	27.30	23.99	3.31
0.00	27.30	23.44	3.86
0.00	27.30	22.89	4.41

Alternative Polyphosphates

Table 8-15. SK-7691 Data

SK-7691 Dose (ml)	Initial Conc. of Mn+2 (micromol)	Conc. of Mn Remaining (micromol)
0.000	27.30	1.52
1.390	27.30	23.66
2.090	27.30	23.06
2.775	27.30	23.06
4.165	27.30	21.84
5.550	27.30	19.42

Table 8-16. SK-7699 Data

SK-7699 Dose (ml)	Initial Conc. of Mn+2 (micromol)	Conc. of Mn Remaining (micromol)
0.000	27.30	5.61
1.390	27.30	23.60
2.090	27.30	22.86
2.775	27.30	23.39
4.165	27.30	22.43
5.550	27.30	21.80

Table 8-17. AquaMag Data

AquaMag Dose (ml)	Initial Conc. of Mn+2 (micromol)	Conc. of Mn Remaining (micromol)
0.000	27.30	12.13
1.390	27.30	21.12
2.090	27.30	22.58
2.775	27.30	21.01
4.165	27.30	19.55
5.550	27.30	18.99