# THE OXIDATIVE PRECIPITATION OF THALLIUM IN MINING INFLUENCED WATER

by

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## ABSTRACT

Thallium (Tl) is an uncommon metal that may be found in concentrations that exceed regulatory limits in mining influenced water (MIW) associated with processing cadmium, copper, gold, lead, and zinc ores. It is a toxic metal that is soluble over a wide pH range, resulting in both persistence in the environment and poor removal by conventional lime precipitation. This study evaluated the effect of potassium permanganate ($KMnO_4$) at alkaline pH on Tl removal from MIW in batch experiments. The oxidation of $Tl^{+}$ to $Tl^{3+}$ by $KMnO_4$ and the subsequent Tl removal was explored at Tl concentrations ≤ 1ppm in synthetic MIW and real MIW. In addition to Tl, the synthetic MIW contained Mn near 5 mg/L while the real MIW contained Al, Cu, Fe, Mn, and Zn above 10 mg/L. Dissolved Tl of less than 2 ppb in synthetic MIW was achieved with the addition of CaO to pH ca. 9 and 5 mg/L $KMnO_4$. In the real MIW, dissolved Tl of less than 2 ppb was achieved with the addition of CaO to pH ca. 9 and 12.5 mg/L $KMnO_4$. The mechanism of Tl removal by $KMnO_4$ is complicated due to the presence of reduced Mn in the synthetic MIW and multiple metals in the real MIW. However, effective thallium removal is achievable by $KMnO_4$ addition to synthetic and real MIW.

TABLE OF CONTENTS

LIST OF FIGURES AND TABLES

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CHAPTER 1

# INTRODUCTION

Thallium (Tl) is an uncommon heavy metal. The maximum contaminant level (MCL) for drinking water set by the Environmental Protection Agency is 2 ppb and the maximum contaminant level goal is .5 ppb. Concentrations of Tl in the environment from sources that are not directly impacted by anthropogenic activities tend to be below the drinking water limit. For example, in the Great Lakes the concentrations of Tl range from sub ng/L to 50 ng/L (Cheam *et al.* 1995) and seawater concentrations range from 12-16 ng/kg (Flegal and Patterson 1985). However where concentrations exceed the regulatory limit, Tl is of major concern because of its toxicity and persistence in the environment. The aquatic toxicity of Tl is greater than that of Ni, Cu, and Zn (Borgmann *et al.* 1998). Borgmann *et al.* (1998) found that there was a 25% reduction in the survival rate of Hyalella azteca when they were exposed to 48 nmol/liter Tl for 4 weeks. The toxicity of Tl is comparable to Pb, but Tl is not as toxic as Hg or Cd (Borgmann *et al.* 1998).

Thallium concentrations from the ppb to ppm range have been observed in industrial effluents associated with metal mining, coal mining, tailings and smelters. Tl is predominantly associated with sulfide ores, but it can also be found in oxides (Ikramuddin, Besse, and Nordstrom 1986). Zitko *et al.* (1975) reported thallium concentrations of 1-80 ppb in two rivers draining base-metal mining properties in Canada. Cheam *et al.* (2000) surveyed Tl concentrations at a coal mine and coal power plants in Canada. Tl concentrations were less than 2 ppb at all the coal mines surveyed.

However, Tl concentrations up to 24 ppb were observed in an ash lagoon discharge at a coal power plant in Nova Scotia. A tailings pond at a base-metal site in eastern Canada contained 1,600 ppb of Tl (Cheam 2001). In Lanmuchang, China, some of the surface and ground waters are impacted by Tl leaching from both naturally occurring sources and localized areas of past mining (Xiao *et al.* 2003). Streams under base flow regimes in the region had concentrations up to 33 ppb (Xiao *et al.* 2003). The authors found that the concentration of Tl in acid mine drainage from an abandoned adit was 59 ppb and in deep mine groundwater was up to 1,100 ppb (Xiao *et al.* 2003). In summary, in mining influenced water, thallium concentrations surveyed ranged from a high of 1.6 ppm to below 2 ppb.

## 1.1 Chemical Properties of Tl

The chemical properties of thallium can be used to predict its behavior in the environment. Thallium has a molecular weight of 204.4 making it the heaviest of the IIIa subgroup in the periodic table. It is bracketed between mercury and lead on the periodic table and it behaves similarly to $K^+$, $Ag^+$, and rubidium (Kaplan and Mattigod 1998). Thallium is persistent in the environment because the predominant species, $Tl^+$, is soluble at a wide pH range and for most redox conditions present in the environment. As seen in Figure 1, only under high oxidizing conditions can $Tl^+$ be oxidized to $Tl^{3+}$. However, once oxidized $Tl^{3+}$ readily forms the solid phase $Tl(OH)_3$ at a pH range between 2 and 12. The low log Ksp value for the formation of $Tl(OH)_3$, -45.2, suggests that $Tl(OH)_3$ is very insoluble. As expected from the Eh-pH diagram, $Tl^+$ is not removed in conventional lime precipitation treatment, which utilizes an increase in pH of 10 to 11 in order to precipitate metals. $Tl^{+}$ must be oxidized to $Tl^{3+}$ to remove Tl from mining influenced water during alkaline precipitation.

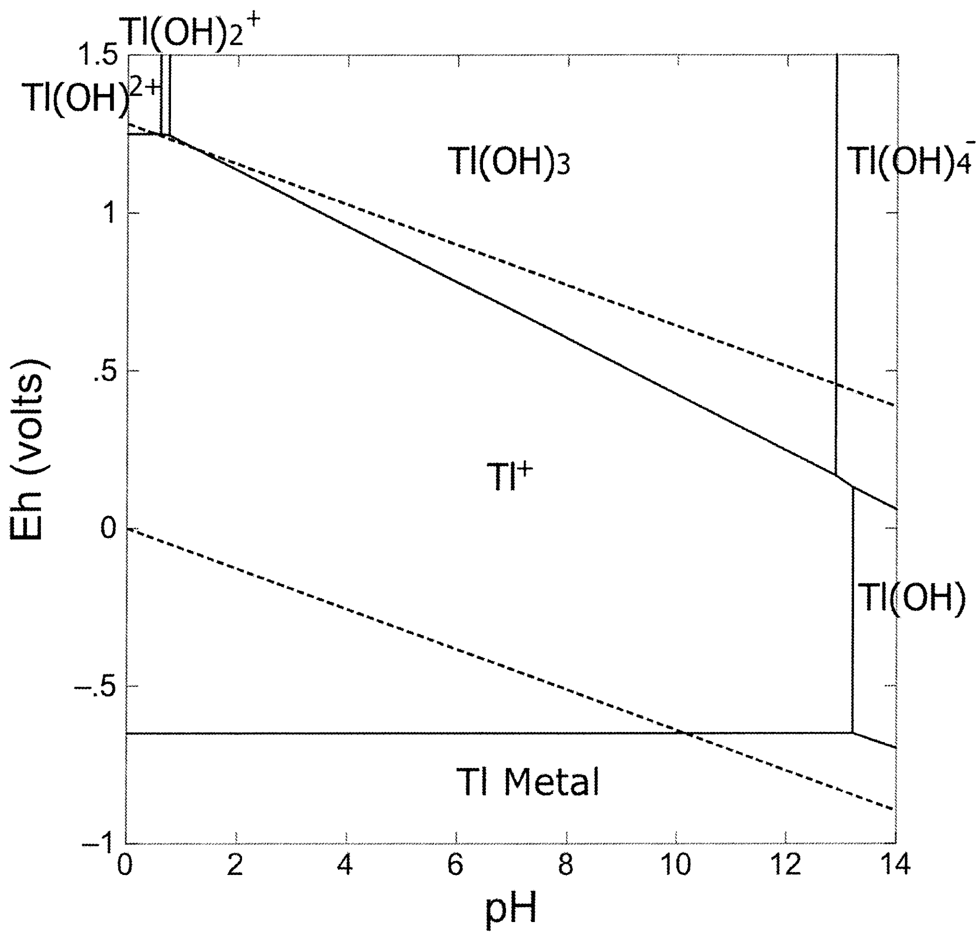


Figure 1.1 Eh-pH diagram of Tl, 1 ppm, 25°C. The diagram was generated using the Minteq thermodynamic database in Geochemist Workbench. Dashed lines indicate the stability of water.

## 1.2 Tl Transport in the Environment

Thallium is more mobile from anthropogenic sources because the metal is no longer bound in a mineral structure. In a study of soils influenced by Zn-Pb mining, Tl was determined to be of high risk to the aquatic environment because of its solubility in water and the significant percent, (12.4%), of Tl released from sediments as a result of ion exchange (Lis et al. 2003). Similarly, Kaplan and Mattigod (1998) found that although, thallium does sorb as a result of cation exchange reactions, it is not bound strongly and thus it is mobile in groundwater and surface water.

Vanek et al. (2010) performed experiments on three types of soils to better understand the adsorption and mobility of $Tl^+$ on soils with varying mineralogy and with low molecular weight organic acids (LMWOA). Initially, the authors spiked 200 g of soil (Leptosol, Arenosol, and Cambisol) with $Tl_2SO_4$ solution to obtain a concentration of 25 mg/kg Tl. The first experiments were to compare thallium transport in the three types of soil with varying mineralogy: leptosol, arenosol, and cambisol. A leptosol is a shallow soil over calcaresous rock or unconsolidated gravelly material. An arenosol is a sandy soil with little to weak or no soil development. And a cambisol is a weakly to moderately developed soil. In the second set of experiments, citric, oxalic, and acetic acids were applied to each type of soil. To fully assess the adsorption capacity of the soils, a modified BCR (Community of Bureau Reference) technique was used to measure the fraction of Tl in the soils. The soils were digested in four steps. First, a .11 M $CH_3COOH$ acid was applied to determine the exchangeable/acid-extractable fraction. Second, a .5 M $NH_2OH$*HCl solution was applied to determine the reducible fraction. Third, the oxidisable fraction was measured after the application of both 8.8 M $H_2O_2$ and

1M $CH_3COONH_4$ solutions. Finally, a total digestion was completed using a combination of concentrated $HF/HClO_4/HNO_3$.

The study by Vanek et al. (2010) found that thallium was most available in the exchangeable-acid extractable fraction in the arenosol. The low adsorption capacity of the arenosol was likely the cause of the increased mobility in this soil. The majority of the thallium measured was associated with the reducible fractions of the soils. The authors attribute most of the thallium sorption to unspecific exchange reactions with manganese oxides, illite, and amorphous aluminosilicates. The structure of illite or aluminosilicates may increase the sorption capacity of the soil. In the study by Vanek et al. (2010), only a small portion of thallium was observed in the oxidisable fractions of the soil. The amount of thallium measured in the residual fraction of the soils was relatively low, but increased over time indicating that the thallium was incorporated into the mineral structures of the soils. The greatest concentration of thallium in the residual fraction was found in the leptosol; Vanek et al. (2010) propose that thallium may coprecipitate with newly formed carbonates.

The application of low molecular weight organic acids increased the concentrations of water-soluble thallium. Vanek et al. (2010) observed that although there was a significant increase in water-soluble thallium with LMWOA, there was no significant difference between the effectiveness of citric, oxalic, or acetic acids on the concentration of water-soluble thallium. The authors determined the speciation of thallium using PHREEQC-2 and Visual MINTEQ. They estimate that 97.6-99.7% of the thallium is $Tl^+$ and predict that up to 1.8% may be $TlNO_3$ and less than 1% Tl-oxalate$^-$. The formation of strong organic complexes with thallium is unlikely (Vanek et al. 2010).

The authors suggest that in contrast to the experiments that showed increasing thallium concentrations in the residual fraction, that the application of LMWOA shifts the concentration of thallium from the residual fractions to more labile fractions.

The sorption capacity of Tl is important to predict its fate and transport in the environment. An EPA study by Allison and Allison (2005) estimated the partition coefficients for thallium in soil/soil water, sediment/porewater, suspended matter/water, and dissolved organic carbon(DOC)/inorganic solution species. The study used six Kd values for the sediment/water interface to estimate Kd values for the media of concern. The median log Kd for thallium in the sediment/water interface was 3.2 with a range of 3.0-3.5. The mean log $K_{DOC}$ value for $Tl^{+}$ was derived from a linear free energy relationship using the first hydrolysis constant and the binding constant for acetate. Next, MINTEQA2 was used to estimate the log Kd values for soil/soil water, sediment/porewater, suspended matter/water, DOC/inorganic solution species. The results were as follows:

Table 1.1: log Kd values from Allison and Allison (2005).

| | Mean | Standard Deviation | Min | Max |
|---|---|---|---|---|
| Soil/Soil Water | .5 | .9 | -1.2 | 1.5 |
| Sediment/Porewater | 1.3 | 1.1 | -.5 | 3.5 |
| Suspended Matter/Water | 4.1 | 1.0 | 3.0 | 4.5 |
| DOC/Inorganic Solution | 1.6 | 1.0 | 0 | 3.0 |

This data was derived from models with limited data sets, but are comparable to the Kd derived experimentally from Twiss et al. (2003), who determined a Kd for suspended particulate matter/water of 1164 +/- 241 (log Kd of 3.065).

One particular concern in regards to the mobility of Tl in the subsurface is its potential for bioaccumulation. A study by LaCoste, Robinson, and Brooks (2001) showed that thallium will hyperaccumulate in vegetables and crops. The authors dosed Manawatu Silt Loam with thallium sulphate. Most vegetables showed a lower degree of adsorption to thallium, however there was hyperaccumulation in beetroot, green cabbage, lettuce, onions, peas, radish, spinach, turnips, and watercress. Pavlickova (2005) confirmed Tl hyperaccumulation in brassicaceous plants such as kale, spring rape, winter rape, and kohlrabi. LaCoste, Robinson, and Brooks (2001) suggest a maximum level of 2 mg/kg (dry mass) thallium in human food. The authors point out that if a thallium concentration of 1 mg/kg was applied to the soil, the concentration of Tl in spinach, beetroot, green cabbage and turnip could exceed the suggested maximum level of 2 mg/kg dry mass. Their study also indicated that phytoremediation could be a viable method for Tl removal.

The ion $Tl^{+}$ is an unusually soluble metal. It does adsorb to soils, sediments, suspended matter, and dissolved organic carbon, but it tends to remain mobile and is not incorporated in the mineral structure of the sediments. Tl may hyperaccumulate in certain plants.

# CHAPTER 2

## THALLIUM REMOVAL

A number of methods for thallium removal have been reported including zinc cementation, reductive precipitation, oxidative precipitation, sorption to manganese oxides, and sorption to organic matter (MWTP 1999, Jibiki 1995, Rissman and Schwartz 1989, Bidoglio *et al.* 1993, Gadde and Laitinen 1974, and Memon *et al.* 2008). However, few methods demonstrated the ability to remove thallium to below the regulatory limit of 2 ppb anticipated for mining influenced water (MWTP 1999). This research focused on discovering a robust method for the oxidative precipitation of thallium that could be integrated into an alkaline precipitation treatment scheme, which is the most common process for metals removal from mining influenced water.

The EPA has approved Activated Alumina and Ion Exchange for removal of thallium from drinking waters. However, using this approach for removing Tl from MIW requires a separate post-lime precipitation treatment system. The EPA (Rosengrant and Craig 1990) inferred from the work of Mellor, 1946, that chemical oxidation followed by precipitation is the Best Demonstrated Available Technology (BDAT) for thallium removal from Resource Conservation and Recovery Act (RCRA) hazardous wastewaters. The treatment goal for RCRA wastewaters is removal of Tl to less than 140 ppb, much higher than the drinking water MCL. Recommended oxidants include hydrogen peroxide, potassium permanganate, and sodium hypochlorite. However, no data is presented in the EPA supporting document for the RCRA thallium BDAT and so the efficacy of chemical oxidation and precipitation to remove thallium to below the drinking water MCL of 2 ppb cannot be assumed. More recent research has demonstrated that very high oxidizing conditions are necessary for the formation of $Tl(OH)_3$ from waters containing $Tl^+$ (Gao *et al.* 2007, MWTP 1999, Lin and Nriagu 1998). As a result, it is important to explore in greater depth the reactants that can be used to oxidatively precipitate Tl.

## 2.1 Oxidative Precipitation of Tl

The oxidation of $Tl^+$ to $Tl^{3+}$ is energetically favorable based on standard reduction potentials for oxidants typically used for wastewater treatment processes. Table 1 is a list of the standard free energies for the oxidation of one mole of $Tl^+$ to $Tl^{+3}$ at a pH of zero. Examination of the Eh-pH diagram (Figure 1) shows that the addition of oxidant under alkaline conditions, will result in the subsequent formation of $Tl(OH)_3$ precipitate, and the formation of this precipitate makes the oxidation reaction much more favorable. A comparison of the standard free energies for the oxidation reactions suggests that permanganate, hydrogen peroxide and ozone are most energetically favorable.

Table 1.2 Standard Gibbs Free Energy for the reaction of 1 mole Tl with potential oxidants at pH 0.

| Reagent | $\Delta G^0$ (kJ/mole Tl) |
|---|---|
| $O_2$ | -1.9 |
| $ClO^-$ | -17.4 |
| $KMnO_4$ | -91.0 |
| $H_2O_2$ | -108.0 |
| $O_3$ | -164.0 |

However, oxidants for Tl removal from MIW, must meet certain criteria. An ideal oxidant must be inexpensive, manageable, and nontoxic. The chemical must be commercially available. Managing the oxidant should not require a significant investment in infrastructure. The oxidant itself, as well as its by-products, must be removed from solution or rendered nontoxic before discharge. Furthermore, for an ideal removal process, the oxidation and precipitation should be as rapid as possible, though not all redox reactions are instantaneous. Bearing these screening criteria in mind, the efficacy of the oxidants is discussed below.

Rissman and Schwartz (1989) suggest sodium hypochlorite is a viable oxidant based on the work of Mellor (1946) for pretreatment of thallous salts. They suggest that either lime or sodium hydroxide subsequently can be used to increase the pH to between 8 and 10 and then thallium hydroxide will be precipitated with other metal hydroxides (Rissman and Schwartz 1989). However, sodium hypochlorite is a corrosive hazard and reacts with ammonia (sometimes a component of MIW) to form hazardous chlorine gas. Oxygen, though nontoxic, does not appear to oxidize thallium rapidly, which is consistent with its relatively low free energy shown in Table 1. One reason may be the low solubility of oxygen in water and the relative slow mass transfer unless high pressure and fine bubbles are used. Hydrogen peroxide is another potential oxidant based on energetics. However, Twiss, Twining, and Fisher (2003) were unable to form $Tl^{3+}$ using hydrogen peroxide alone. The oxidation of thallium with hydrogen peroxide in the presence of iron powder was effective (Kikuchi *et al.* 1990), but high peroxide (100 mL/L of 30% $H_2O_2$) and iron (12.5 g/L) concentrations were required. Another drawback of hydrogen peroxide is that bubbles form that can adhere to sludge particles, preventing settling. Ozone must be generated on-site to be effective and so would require the development of infrastructure for its use. Potassium permanganate ($KMnO_4$) is a viable reagent because it is easy to acquire and manage on-site. $KMnO_4$ oxidizes $Mn^{2+}$ and $Fe^{2+}$ and will precipitate as $MnO_2$ at neutral to high pH (Pontius 1990). Oxidative precipitation of thallium using $KMnO_4$, $K_2Cr_2O_7$, or $K_2CrO_4$ has been used to remove thallium from zinc concentrates (Jibiki 1995). However, the addition of chromium in the form of $K_2Cr_2O_7$, $K_2CrO_4$ is undesirable due to the toxicity of Cr. Hiremath *et al.* (1996) have demonstrated $Tl^+$ oxidation by $KMnO_4$. In their experiments, the concentration of Tl was very high compared to typical environmental concentrations, ranging from 81-810 mg/L Tl. The study by Hiremath *et al.* (1996) shows potential, however their conditions seemed to require high chloride concentration and low pH, and thus does not directly support the removal of Tl at low concentrations (less than 1 mg/L) in MIW and at alkaline pH. The study by Hiremath *et al.* (1996) is promising; however, it is not necessarily indicative of whether Tl removal will be effective from 1 mg/L to below 2 μg/L in MIW. Our objective is to develop a method that can be integrated into a lime precipitation treatment system that requires a short hydraulic residence time (minutes). Thus, the reaction of Tl with the oxidant must not only be energetically favorable, but the kinetics of the reaction must be relatively fast (on the order of minutes). $KMnO_4$ was chosen for further evaluation as a result of the above oxidant screening.

## 2.2 Tl Sorption to Manganese (hydr)oxide

The production of manganese (hydr)oxides, byproducts of the reaction of $KMnO_4$ with $Mn^{2+}$ and $Tl^+$ may also be advantageous because Tl has been associated with different manganese precipitates in the environment. Thallium in deep-sea sediments has been associated with hydrous manganese dioxide (Matthews and Riley 1970) and manganese nodules (Willis and Ahrens 1962). Jacobson *et al.* (2005) and Vanek *et al.* (2010) found Tl sorption to manganese (hydr)oxides in soils. (It should be noted that at basic pHs, manganese forms a number of solid phases of +2, +3, and +4 oxidation states. Figure 2 shows some of these complexities. If it is known what specific species of manganese solid has been formed, it will be stated. If the phases or oxidation states are uncertain, then, the generic term manganese (hydr)oxides will be used.

Dahal and Lawrance (1995) and MWTP (2003) demonstrated Tl sorption to electrolytically produced manganese dioxide (EMD). EMD is a non-stoichiometric material with a composition of $MnO_{1.96}H_{0.08}$. EMD is particularly effective at adsorbing metal ions and incorporating foreign ions. Dahal and Lawrance (1995) found that the adsorption of Tl to EMD fit a Langmuir adsorption isotherm and proposed exchange reactions that did not oxidize $Tl^+$. MWTP (2003) also demonstrated Tl adsorption to EMD. In the experiments described in MWTP (2003) the adsorption of 2 mg/L Tl to 20 g/L EMD was studied at pH 4, 150 rpm, over the course of 30 minutes. Given these conditions the concentration of Tl was reduced from 2 mg/L to below 2 μg/L. It is not clear if the mechanism in these experiments is solely sorption or if there is some oxidation of the $Tl^+$ in solution.

Experiments examining Tl sorption to manganese dioxide by Gadde and Laitinen (1974) and Bidoglio *et al.* (1993) demonstrated that $Tl^+$ sorbs to the manganese precipitate and oxidizes to $Tl^{3+}$. Bidoglio *et al.* (1993) observed that there was significant adsorption of $Tl^+$, at concentrations between 24 to 40 ppb to $\delta$-$MnO_2$ from a pH of 4.7 to 8.5. Bidoglio *et al.* (1993) were able to demonstrate that the $Tl^+$ sorbed to the surface of the $\delta$-$MnO_2$ had a similar XANES spectrum as thallium oxide ($Tl_2O_3$) and hypothesized that $Tl^{+}$ oxidized to $Tl^{3+}$ on the surface of the $MnO_2$. The surface oxidation of $Tl^{+}$ to $Tl^{3+}$ on manganese precipitates could be a significant method of Tl removal in MIW because the water usually contains significant concentrations of Mn(II), which will precipitate as manganese (hydr)oxides at high pHs.

**2.3 Current Study**

This paper summarizes our study of the removal of thallium from synthetic and real MIW. Rather than conduct experiments where equilibrium conditions were sought in simple systems, a balance between constructed and actual removal conditions was attempted (Miller *et al.* 2011). The synthetic MIW was formulated to contain manganese and sulfate, which usually persist in mine waters at basic pHs. Experiments were aimed to mimic actual removal conditions, given some limitations of laboratory experiments, and to indicate the viability of oxidative precipitation in the presence of potentially competing constituents, which may consume $KMnO_4$ or otherwise inhibit Tl oxidation. Both the synthetic MIW and real MIW experiments emphasized what occurred in the first hour and rarely extended beyond 2 days. Tl concentrations may exceed 1.0 mg/L in mining influenced water (MWTP 1999); however, in order to best understand actual removal conditions at low concentrations, the starting thallium concentration in synthetic MIW samples was always 1.0 mg/L. Trace concentrations of thallium meant that the formulation of some precipitates and complexes could be impaired. Also, at trace concentrations, the amount of the thallium in the precipitates may be too low to be able to detect phases by scanning electron microscopy (Gill 1997), x-ray diffraction (Dutrow and Clark 2011), or x-ray fluorescence (Fitton 1997). However, at concentrations high enough for spectroscopic detection, thallium would act as a major constituent in solution and its chemical behavior could be quite different. Nevertheless, even under these experimental restrictions, by careful observation of experimental conditions, strong inferences can be made of the fundamental processes involved in thallium removal.

### 2.3.1 Experimental Procedures

The method used was developed with the intention of identifying the removal of Tl and Mn from aqueous solution.

#### 2.3.1.1 Materials

To make up the synthetic MIW solutions, dilute $Tl^{+}$- $Mn^{2+}$ solutions were prepared from trace-metal grade solutions used for ICP-AES. In addition, nanopure water, trace metal grade sulfuric acid; High Purity Standards CaO; and 'Baker Analyzed' Reagent $KMnO_4$ were used.

The makeup of the real mining influenced water is presented in Table 2.

Table 2.1 Major constituents of the real mining influenced water (mg/L except for pH).

| Al | As | Ca | Cd | Co | Cu | Fe | K | Mg | |
|---|---|---|---|---|---|---|---|---|---|
| 66.2 | 1.106 | 108 | 0.8253 | 0.551 | 46.2 | 263 | 4.03 | 18.3 | |
| Mn | Na | Ni | P | Pb | S | Si | Tl | Zn | pH |
| 13 | 11.4 | 0.177 | 0.53 | 0.1133 | 383 | 26.9 | 0.0316 | 16.4 | 2.49 |

#### 2.3.1.2 Methods

Not all of the typical constituents of mining influenced water were included in synthetic MIW solutions in order to isolate the effects between Tl, Mn, and $KMnO_4$. In the oxidative precipitation of Tl by $KMnO_4$, a decision on the dose of permanganate was developed as follows. The solutions have been adjusted to about pH 7 or above, and, according to the Mn Eh-pH diagram (Figure 2), the product of permanganate reduction should theoretically be $MnO_2$ solid. Also, the products of $Tl^+$ oxidation should be $Tl(OH)_3$; $Mn^{2+}$ should oxidize to $MnO_2$. In both cases, two electrons would be gained during reduction. Consequently, a stoichiometric dose of permanganate added would theoretically be such that all the permanganate would be consumed, oxidizing all the $Tl^+$ and $Mn^{2+}$ in a 3 to 2 ratio based on the following equations:

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+ \tag{2.1}$$

$$3Tl^+ + 2MnO_4^- + 5H_2O \rightarrow 3Tl(OH)_3 + 2MnO_2 + H^+ \tag{2.2}$$

The effect of $KMnO_4$ on Tl removal from synthetic solutions at alkaline pH was determined using the following procedure. In the case of the synthetic MIW solutions, 500 mL of solution containing 1 ppm Tl, 5 ppm Mn, 100 ppm sulfate was placed in a 1 L beaker and the required dose of $KMnO_4$ was added. In the control sample, no $KMnO_4$ was added. Based on the above equations, the stoichiometric addition of $KMnO_4$ was determined to be .005 g and the half stoichiometric was .0025 g. Shortly after the potassium permanganate was added, .055 g calcium oxide (CaO) was also added to increase the pH to $9 \pm 0.5$. The pH was monitored continuously and the solution was agitated using a magnetic stir bar. Nominal 10 ml samples were taken at 10-minute intervals for 30 minutes and the solution was filtered using a 0.45 μm nylon filter. Post-filtration, all samples were acidified using concentrated nitric acid in order to prepare the samples for measurement on the ICP-OES and ICP-MS. Also post-filtration, four drops of 30% hydrogen peroxide ($H_2O_2$) was added to all samples containing residual permanganate to prevent the formation of manganese precipitates. At acidic pH, hydrogen peroxide reduces the permanganate to $Mn^{2+}$ and prevents the formation of manganese precipitates prior to analysis. The removal efficiencies of Tl and Mn were determined by analyzing the initial and final concentrations using a Perkin Elmer 5300 ICP-OES or Perkin Elmer Elan DRC-e ICP-MS. Each experiment was performed in triplicate.

A procedure meant to mimic a two-stage lime precipitation was developed for the mining influenced water. A 500 ml sample of solution was taken. The pH was raised to $7.2 \pm .4$, after the addition of 0.487 g CaO, at which point Fe and Al oxyhydroxides formed. The precipitates were allowed to settle for a minimum of one hour. Taking care not to disturb the precipitate, 400 ml of solution was pipetted from the initial sample. A stoichiometric, half-stoichiometric, or quarter stoichiometric amount of solid $KMnO_4$ was added based on the concentration of Mn (13 ppm) in the 400 mL solution. Shortly after the $KMnO_4$ was added, .01 g calcium oxide was added to increase the pH to $9.6 \pm .5$. Again, nominal 10 ml samples were taken at 10-minute intervals for 30 minutes and the solution was filtered using a 0.45 μm nylon filter. Post-filtration, all samples were acidified using concentrated nitric acid. Also post-filtration, four drops of 30% hydrogen peroxide ($H_2O_2$) was added to all samples containing residual permanganate to prevent the formation of manganese precipitates. The removal efficiencies were determined by analyzing the initial and final Mn and Tl concentrations using a Perkin Elmer 5300 ICP-OES or Perkin Elmer Elan DRC-e ICP-MS. Each experiment was performed in triplicate.

### 2.3.2 Results

Tables 3 and 4 present the results for the removal studies using synthetic and real MIW. For Tl and Mn, the averages of experiments performed in triplicate are given along with the standard deviation (S.D.). Ranges in pH are given so that an assessment can be made of the stability of the solutions during the removal reactions.

Table 2.2 Changes in Tl (ppb), Mn (ppb), and pH with time for synthetic MIW under three $KMnO_4$ conditions: none, half stoichiometric, and stoichiometric. S.D. is the standard deviation for the triplicate analyses.

| Synthetic Solutions | | | | | |
|---|---|---|---|---|---|
| No $KMnO_4$ | | | | | |
| | Tl (ppb) | | Mn (ppb) | | pH |
| | AVG | S. D. | AVG | S. D. | Range |
| Initial | 1113 | 32 | 5375 | 92 | 2.5-2.9 |
| 10 mins | 1066 | 18 | 94 | 79 | 9.0-9.4 |
| 20 mins | 944 | 82 | 58 | 33 | 8.9-9.4 |
| 30 mins | 913 | 131 | 63 | 38 | n/a |
| 1 day | 581 | 155 | 8 | 0 | 8.1-8.3 |
| 2 days | 553 | 156 | 36 | 9 | 6.5-7.6 |
| Half Stoichiometric (5 mg/L) $KMnO_4$ | | | | | |
| | Tl (ppb) | | Mn (ppb) | | pH |
| | AVG | S. D. | AVG | S.D. | Range |
| Initial | 951.4 | 64.5 | 5054 | 29 | 2.6 - 3.0 |
| 10 mins | 0.4 | 0.4 | 2317 | 802 | 8.9-9.6 |
| 20 mins | 0.3 | 0.1 | 2308 | 843 | 9.0-9.6 |
| 30 mins | 0.3 | 0.1 | 2300 | 836 | 8.9-9.5 |
| 1 day | 0.3 | 0.1 | 2142 | 860 | 8.1-8.3 |
| 2 days | 0.2 | 0.1 | no data | no data | 7.3-7.7 |
| 1 x Stoichiometric (10 mg/L) $KMnO_4$ | | | | | |
| | Tl (ppb) | | Mn (ppb) | | pH |
| | AVG | S.D. | AVG | S.D. | Range |
| Initial | 999.7 | 25.19 | 4921 | 57 | 2.5-2.8 |
| 10 mins | 0.2 | 0.1 | 3468 | 1165 | 8.8-9.2 |
| 20 mins | 0.2 | 0.1 | 3435 | 1156 | 8.8-9.2 |
| 30 mins | 0.1 | 0.1 | 3453 | 1187 | 8.7-9.1 |
| 1 day | 0.2 | 0.1 | 3265 | 1124 | 7.6-8.3 |
| 2 days | 0.2 | 0.1 | 3185 | 1111 | 7.1-7.7 |

Table 2.3 Presents Tl (ppb), Mn (ppb), and pH with time for real MIW under three $KMnO_4$ conditions: quarter stoichiometric, half stoichiometric, and stoichiometric. S.D. is the standard deviation for the triplicate analyses.

| **Mining Influenced Water** | | | | | |
|---|---|---|---|---|---|
| Quarter Stoichiometric $KMnO_4$ | | | | | |
| | Tl (ppb) | | Mn (ppb) | | pH |
| | AVG | S. D. | AVG | S. D. | Range |
| Initial | 31.0 | 0.7 | 13629 | 342 | 2.4-2.6 |
| 10 mins | 23.8 | 0.8 | 18 | 3 | 9.7-10.1 |
| 20 mins | 24.9 | 1.2 | 13 | 6 | 9.7-10.1 |
| 30 mins | 24.2 | 1.6 | 8 | 3 | 9.5-10.1 |
| 1 day | 22.8 | 0.5 | 32 | 21 | 8.3-8.7 |
| 2 days | 21.9 | 0.5 | 145 | 53 | 7.7-8.0 |
| Half Stoichiometric $KMnO_4$ | | | | | |
| | Tl (ppb) | | Mn (ppb) | | pH |
| | AVG | S. D. | AVG | S. D. | Range |
| Initial | 31.5 | 0.33 | 12234 | 502 | 2.4-2.6 |
| 10 mins | <.3 | 0.00 | 1162 | 326 | 9.1-9.3 |
| 20 mins | <.3 | 0.00 | 1027 | 312 | 9.1-9.2 |
| 30 mins | <.3 | 0.00 | 971 | 299 | 9.0-9.2 |
| 1 day | <.3 | 0.00 | 452 | 290 | 7.9-8.1 |
| 2 days | <.3 | 0.00 | 326 | 277 | 7.6-7.8 |
| 1 x Stoichiometric $KMnO_4$ | | | | | |
| | Tl (ppb) | | Mn (ppb) | | pH |
| | AVG | S. D. | AVG | S. D. | Range |
| Initial | 32.0 | 0.80 | 11961 | 240 | 2.3-2.4 |
| 10 mins | <.3 | 0.00 | 4333 | 1266 | 9.2-9.5 |
| 20 mins | <.3 | 0.00 | 4291 | 1216 | 9.3-9.5 |
| 30 mins | <.3 | 0.00 | 4275 | 1255 | 9.2-9.5 |
| 1 day | 0.1 | 0.04 | 3584 | 1488 | 8.2-8.3 |
| 2 days | 0.0 | 0.02 | 3140 | 1425 | 7.7-7.9 |

## 2.4 Discussion

The concentration of Tl was effectively reduced from 1 ppm to below 2 ppb in synthetic MIW and from 30 ppb to below 2 ppb in real mining influenced water.

### 2.4.1 General Observations

In the control synthetic MIW, when the pH was increased to 9, there was near complete removal of Mn. However, Tl was reduced by only 20% after 30 minutes of reaction time (Table 3). Interestingly, the reduction in Tl increased to 50% after 1 day of contact time and the pH dropped by one unit. This change in Tl concentration and concurrent decrease in pH suggests that the reactions were not at equilibrium at the end of 30 minutes.

In the synthetic MIW, Tl was reduced to below the 2 ppb EPA MCL at both the half and full stoichiometric addition of $KMnO_4$ at alkaline pH within 10 minutes. However, as seen in Table 3, the manganese concentration was above the regulatory limit of 50 ppb when $KMnO_4$ was added. According to reaction 2, for stoichiometric addition, all of the $Mn^{2+}$ should have been oxidized to $MnO_2$ and the permanganate reduced to $MnO_2$. In fact, the final solutions were noticeably purple from the 10 minute through the 2 day mark, and, as seen in Table 3, the manganese concentration was relatively the same after 10 minutes. The lower concentration of permanganate resulted in a somewhat lower manganese concentrations (2.3 mg/L vs 3.5 mg/L after 10 minutes). However, it was still above the regulatory limit of 50 ppb and the final color of the solution was purple.

The results using the synthetic MIW met the objective of removing thallium to below the regulatory concentration of 2 ppb. However, the proposed stoichiometry of permanganate oxidation of $Mn^{2+}$, shown in equations 1 and 2, was not supported by the data. The presence of residual manganese in solution and the purple color suggests that the permanganate was in excess of the actual oxidant demand for $Mn^{2+}$ and $Tl^{+}$ in the basic solution.

Similar to the synthetic solution results, the addition of half stoichiometric and stoichiometric $KMnO_4$ to the real MIW resulted in a decrease in the Tl concentration to below the regulatory limit. However, again the Mn concentration remained above the regulatory limit of 50 ppb, and there was a persistent purple color to the final solutions suggesting that not all of the $MnO_4^-$ was consumed. Experiments using quarter stoichiometric $KMnO_4$ proved interesting. The concentration of Tl was not significantly reduced even after 2 days. However the concentration of Mn was reduced to below the regulatory limit within 10 minutes.

### 2.4.2 Manganese Oxidation and Removal

Based on the stoichiometric reaction (Equation 1) of $Mn^{2+}$ with $MnO_4^-$, 1 mg/L of $KMnO_4$ should oxidize 0.52 mg/L of soluble manganese (Sanks 1978). However, it has been observed that a stoichiometric addition of $KMnO_4$ is not necessary to remove metals from solution (US EPA 1999, Roccaro *et al.* 2007, Phatai *et al.* 2010). Roccaro *et al.* (2007) found that a pH adjustment to 8.5 coupled with the addition of half the stoichiometric amount of $KMnO_4$ was sufficient in order to reduce the dissolved concentration of Mn from about 1.5 mg/L to below 50 μg/L. Phatai *et al.* (2010) also demonstrated that the half stoichiometric dose of $KMnO_4$ successfully reduced the dissolved concentration of Mn from 0.5 mg/L to below 50 μg/L at pH 9.0. The observation that less than the stoichiometric amount of $KMnO_4$ was necessary to oxidize the metals in solution can be attributed to: 1) the oxidation of $Mn^{2+}$ to manganese (hydr)oxides of lower oxidation state than $MnO_2$ at increased pH, 2) $Mn^{2+}$ sorption to manganese (hydr)oxides, 3) and the autocatalytic effect of manganese (hydr)oxides on the oxidation of $Mn^{2+}$. These mechanisms likely attributed to the finding that less than the stoichiometric amount of $KMnO_4$ was required to oxidize the $Mn^{2+}$ and $Tl^+$ in solution. Figure 2, the Eh-pH diagram below, suggests that an increase in pH may promote the oxidation of $Mn^{2+}$ to form oxides of mixed Mn oxidation states, $Mn_3O_4$ and $Mn_2O_3$, or the fully oxidized $MnO_2$ in aqueous waters depending on the redox conditions and whether equilibrium has been attained.

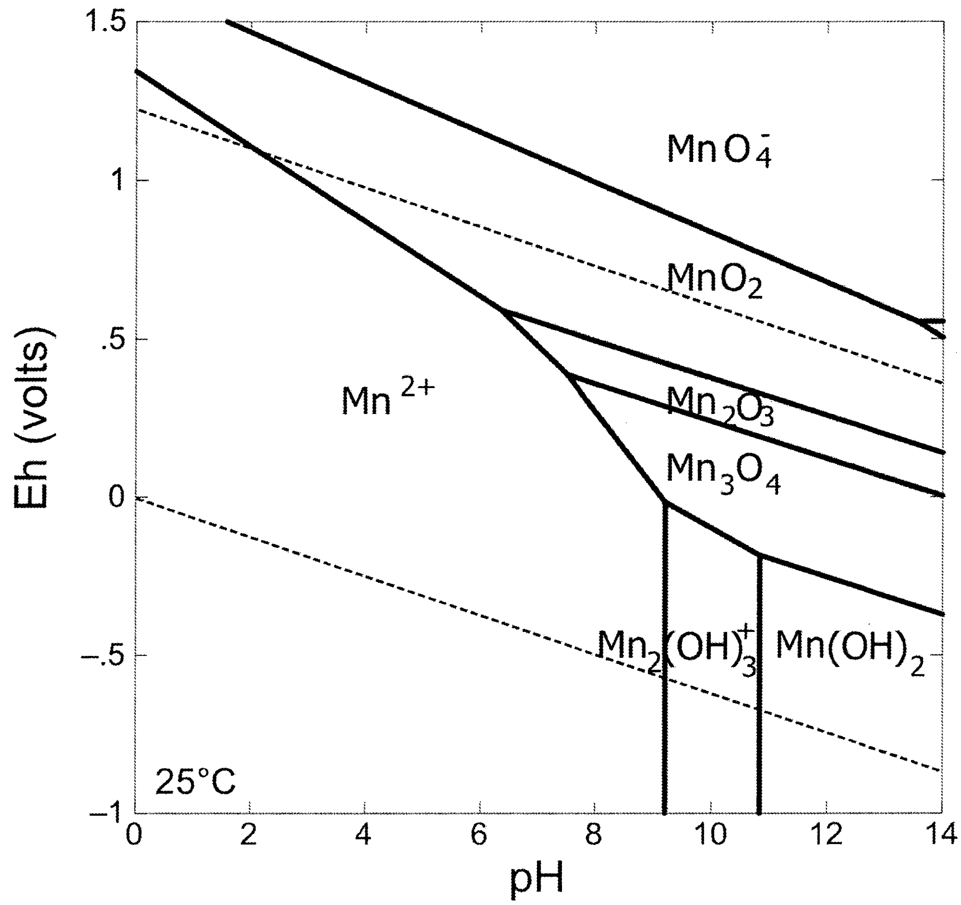


Figure 2. Eh-pH diagram of Mn, 5 ppm, 25°C. The diagram was generated using the Minteq thermodynamic database in Geochemist Workbench. Dashed lines indicated the stability of water.

When oxygen is the oxidizing agent, it is postulated that $Mn^{2+}$ initially oxidizes to MnOOH(s) and then may oxidize to $MnO_2$ (Morgan 2005). MnOOH(s) (manganese oxyhydroxide) tends to be a hydrated nonstoichiometric manganese oxide with an empiric oxidation state formula of $MnO_{1.51}$ to $MnO_{1.54}$.

$$4Mn^{2+}(aq) + O_2(aq) + 6H_2O = 4\ MnOOH(s) + 8H^+ \qquad (2.3)$$

In oxic conditions, $Mn(OH)_2(s)$ may oxidize to $Mn_3O_4(s)$ (Morgan 1964). Formation of the lower oxidation state species of $Mn_2O_3$ and $Mn_3O_4$ instead of $MnO_2$ would require lower doses of $KMnO_4$ than suggested in equation 2. A high rate of $Mn^{2+}$ oxidation is essential for cost-effective integration into a MIW treatment scheme. However, the rate of $Mn^{2+}$ oxidation is highly dependent on the pH (Hem 1963). The rate of oxidation changes dramatically between a pH of 8.5 and 9: at a pH of 8.5 the half-time of reaction in aerated distilled water is 30 minutes and at pH 9 it is 1.5 minutes (Hem 1963). The extent of oxidation is also dependent on the concentration of manganese in solution. Morgan (2005) presents the following experimental rate law for the oxidation of $Mn^{2+}$ in a homogeneous solution:

$$-d[Mn(II)]/dt = k_{app}[O_2][Mn^{2+}] \tag{2.4}$$

The term $k_{app}$ is dependent on the temperature, pH, complexing ligands, and ionic strength. The equation shows the rate of $Mn^{2+}$ oxidation is dependent on the oxidant (oxygen) concentration as well as the $Mn^{2+}$ concentration.

Concerning $KMnO_4$ as the oxidizing agent, the amount necessary to fully oxidize the manganese in solution could also be reduced as a result of manganese sorption to the manganese (hydr)oxides formed. Manganese has been shown to sorb to the surface of hydrous manganese dioxide (Murray 1975, Posselt *et al.* 1968, Morgan and Stumm 1964). The specific crystalline form of $MnO_2$ is important to its sorption capacity. Kanungo *et al.* (1984) and Coughlin and Matsui (1976) observed that the sorption capacity of $MnO_2$ is much higher for the $\delta$ form than the $\beta$ form. The sorptive capacity of hydrous manganese dioxide is pH dependent; more Mn is sorbed at higher pH (Murray 1975). Posselt *et al.* 1968 found that the sorptive capacity of $\delta$-$MnO_2$ was 0.284 moles of

$Mn^{2+}$ per mol of hydrous $MnO_2$ at a pH of 5. At a pH of 7.5, the sorptive capacity of $MnO_2$ was 0.5 moles $Mn^{2+}$ per mole $MnO_2$. And at a pH of 9, 2 moles of $Mn^{2+}$ were sorbed per mole of $MnO_2$ (Morgan and Stumm 1964). As a result of the sorptive capacity of $MnO_2$, $Mn^{2+}$ may sorb to the surface of the precipitate reducing the amount of oxidant, in this case $MnO_4^-$, necessary to oxidatively precipitate the manganese in solution.

Another mechanism that could have influenced the amount of oxidant necessary to remove the metals in solution is the autocatalytic nature of manganese precipitate. A number of studies have demonstrated that the rate of oxidation of manganese using oxygen is dependent on the formation of manganese oxide precipitate (Hem 1963, Morgan and Stumm 1963, Morgan 1964, Coughlin and Matsui 1976). In the presence of oxygen, the $Mn^{2+}$ oxidizes to form manganese oxide precipitate and the negative surface charge of the precipitate attracts more cations, which react with oxygen on the surface to form manganese (hydr)oxide (Coughlin and Matsui 1975). Morgan (1964) proposed the following rate law for the autocatalytic oxidation of Mn(II) to Mn(III) manganese oxyhydroxide:

$$-d[Mn(II)/dt = k_1[Mn(II)] + k_2[MnO_x][Mn(II)] \qquad (2.5)$$

As a result, the oxidation of Mn(II) is dependent on both the concentration of Mn(II) in solution and also the concentration of manganese (hydr)oxide. The sorptive and autocatalytic properties of manganese (hydr)oxide have clear implications for the amount of oxidant necessary to oxidize the metals in solution, but may also play key roles in thallium removal.

### 2.4.3 Thallium Oxidation and Removal

The mechanisms for thallium removal in the experiments described are unclear. Four potential mechanisms are as follows: 1) sorption to manganese (hydr)oxide (Jacobson *et al.* 2005, Vanek *et al.* 2010), 2) sorption to manganese (hydr)oxide followed by surface oxidation to $Tl^{3+}$ and then formation of $Tl(OH)_3$ (Gadde and Laitinen 1974, Bidoglio *et al.* 1993, Dahal and Lawrance 1995), 3) permanganate oxidation of $Tl^{+}$, formation of $Tl^{3+}$ and subsequent formation of $Tl(OH)_3$ and 4) oxidation of $Tl^{+}$ to $Tl^{3+}$ followed by sorption to manganese (hydr)oxide.

One of the challenges in determining the mechanisms responsible for Tl removal is that the form of the manganese precipitate may not have been the same in all of the experiments. For example, from the above discussion, it appears that in the control experiment, MnOOH likely formed (Morgan 2005). However, MnOOH may not be the predominant form after the addition of $KMnO_4$. Instead, a result of using a more powerful oxidant, could be that the Mn precipitates were further oxidized to $MnO_2$. As a result, it is not possible to completely compare the control synthetic MIW experiments with the other experiments that used the addition of $KMnO_4$, except to note that Tl was not adequately removed in the presence of manganese precipitates without the addition of $KMnO_4$ in amounts that exceeded a quarter of the assumed stoichiometry.

Nevertheless, some strong inferences can be made concerning thallium removal that might be able to be substantiated using modern spectroscopic methods, if the amount of thallium in the solids formed is in high enough amounts to be detected. First, the poor removal of $Tl^{+}$ in the control experiment and in the real MIW experiment using the quarter stoichiometric amount of $MnO_4^{-}$ strongly suggests that the thallium has to be oxidized and form $Tl(OH)_3$ to be removed. Also, because the experiments using an adequate amount of $MnO_4^-$ demonstrated thallium removal within the first ten minutes, the mechanism of $Tl^+$ adsorption and then oxidation does not seem reasonable because the rate of this two-step mechanism should be slower. The experiments do not clearly indicate whether or not the presence of manganese precipitate is necessary for thallium removal. In our study, preliminary experiments leading up to the use of permanganate as the oxidizing agent for thallium removal found that all attempts to use other oxidizing agents in basic solutions were unsuccessful (Davies 2011). Furthermore, mechanisms 3 and 4 stated above would not be able to be distinguished using spectroscopic methods, such as XANES, because XANES can identify the oxidation state, but not the specific structure.

CHAPTER 3

CONCLUSIONS

$KMnO_4$ was an effective oxidant for removing Tl to below the MCL (2 ppb) from MIW at alkaline pH. Extensive experiments revealed that Tl removal ranging from partial to below the MCL was a function of pH and permanganate dosage. Increasing pH using lime resulted in partial Tl removal, but was not effective at removing Tl from mining influenced water to below the MCL. The addition of an oxidant was necessary for thallium removal to below the MCL. The hypothesized stoichiometry for oxidant addition over-estimated the required $KMnO_4$ dose to oxidize both the $Mn^{2+}$ and $Tl^+$ in solution. Unreacted $KMnO_4$ remained in solution at the full and half stoichiometry doses at the assumed stoichiometry given in reaction 2. The removal mechanisms of $Mn^{2+}$ and $Tl^+$ by $KMnO_4$ addition appeared to be complex and most likely include formation and reaction with manganese hydr(oxide) species other than $MnO_2$. One quarter stoichiometric addition of $KMnO_4$ removed Mn to below the target of 200 ppb but was relatively ineffective at Tl removal even after incubation for two days. In contrast, addition of half stoichiometric or stoichiometric $KMnO_4$ promoted the rapid removal of Tl to below the MCL of 2 ppb, but Mn in solution was above 1000 ppb.

Although the actual mechanisms of oxidation and removal of both Tl and Mn are complex, it is still the case that rapid removal of Tl to below 2 ppb has been achieved. This is an important finding because thallium will probably become a contaminant of increasing concern now that modern analytical methods are capable of more easily detecting it in low concentrations.

## 3.1 Implications

The MCL for drinking water is 2 ppb, however few methods have been developed for Tl removal to this low concentration. Not only is the research on Tl removal in the ppb range inadequate, but it is also particularly lacking for methods that could be applicable to large scale mine operations. The existing methods are principally designed for lower volumes and flows than that at large operating mine sites. Some methods would require a longer residence time than that which would be feasible for a mine site, while others would produce a large volume of sludge This study furthered the understanding of Tl removal from MIW. The method is potentially applicable to an operating mine site-- using relatively low cost, non-proprietary reagents. The addition of $KMnO_4$ to a two-stage lime precipitation treatment process caused the removal of Tl within 10 minutes. This method would generate some sludge, but the production would not exceed the capacity of an operating mine site.

## 3.2 Further Research

This study has demonstrated that the addition of KMnO4 to two-stage lime precipitation treatment is an effective method for Tl removal from 1 ppm to below 2 ppb in synthetic MIW and from 30 ppb to below 2 ppb in real MIW. However, further analysis of the solutions and the precipitates is necessary to demonstrate the mechanism for Tl removal. The amount of $KMnO_4$ necessary for Tl removal remains unclear. This research demonstrated that between a quarter stoichiometric to half stoiciometric addtition of $KMnO_4$ to oxidisable metals is necessary. Further research should use a spectrophotometer to monitor the change in the amount of $KMnO_4$ consumed as the reactions progress. A better understanding of the amount of $KMnO_4$ consumed within the first ten minutes of reactions would enable the researcher to better estimate the amount of $KMnO_4$ necessary for Tl removal.

In order to better understand the mechanism at work, SEM analysis of the manganese precipitates would be extremely advantageous. Although a SEM analysis would not likely definitively show the Tl minerals formed (because the Tl minerals are such a low percentage of the total sludge), the SEM should identify the manganese minerals. Some understanding of the manganese precipitates formed could provide insight to the amount of permanganate necessary for effective Tl removal.

Finally, an analysis of the precipitates using XANES/XAFS could help determine the mechanism of Tl removal. XANES could provide a further understanding of the mechanism of Tl removal by determining the oxidation state of the Tl in the precipitate. If the oxidation state of Tl was +1, that would provide support for mechanism 1 presented, $Tl^+$ sorption to manganese oxy(hydroxides). However if $Tl^{3+}$ was detected, that would support the idea that Tl must be oxidized to be effectively removed. XAFS would be particularly interesting if it provided information in regards to the binding energy of Tl to the atoms in its immediate vicinity and could indicate if $Tl^{3+}$ is adsorbed to the manganese oxyhydroxides or if the oxidizing conditions in the solution have caused the formation of $Tl_2O_3$ or the incorporation of $Tl^{3+}$ into a Mn oxide mineral structure.

Not only is further analysis of the solutions and precipitates necessary to better understand the mechanism for Tl removal after the addition of $KMnO_4$ to two-stage lime precipitation treatment, but the method must be improved before it can be applied at the mine scale. Excess manganese exists after the addition of the $KMnO_4$. One idea that should be explored in more depth is the use of green sand for removal of residual manganese concentrations. Further optimization of the method could also encompass the removal of other contaminants of concern such as nickel. Also pilot studies to determine the optimal mixing rate and the effect of flocculants on the removal of thallium are necessary before the method is implemented.

Finally, preliminary experiments were performed to determine an effective reagent for Tl removal. Fully evaluating the mechanisms at work in the preliminary experiments is beyond the scope of this work, however there were perplexing results that should be studied more thoroughly. One case was Tl adsorption to glass fiber prefilters on 0.45 μm nylon filters. Tl did not adsorb to the 0.45 μm nylon filter, but the concentration was reduced when the filter had a glass fiber prefilter. Also, preliminary experiments demonstrated that Tl was not effectively removed using $H_2O_2$. Research on the use of $H_2O_2$ and other viable oxidants should be performed to identify cost-effective methods for Tl removal to the MCL of 2 ppb.

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APPENDIX

Figure A-1. Pertinent log K values for Tl. (Gustafsson 2005)

| Species | Log K |
|---|---|
| Tl(OH) | 13.2070 |
| $Tl(OH)^{2+}$ | -2.6940 |
| $Tl(OH)_2^{+}$ | -1.897 |
| $Tl(OH)_3$ | -5.4410 |
| $Tl(OH)_4^{-}$ | 11.697 |
| $Tl^{3+}$ | -3.2910 |
| $Tl^{+}$ | -2.510 |
| Tl metal | 27.1962 |