The Effects of Aluminum, Iron, Manganese and Hydrogen Peroxide on Thallium Removal

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Abstract
Thallium is not significantly removed from mining influenced water (MIW) in hydroxide precipitation plants. Thallium removal methods from MIW that can be cost effectively integrated into existing hydroxide precipitation schemes are lacking. Our goal was to evaluate thallium removal methods that would require minimal modifications to the hydroxide precipitation process. Strategies targeted either sorption/ion exchange and/or oxidation of monovalent thallium. Batch tests using synthetic MIW with 1 mg/L thallium were conducted with the addition or presence of iron, aluminum, manganese, hydrogen peroxide and hydroxide. Partial thallium removal varying from 10 to 90% was achieved. The highest amount of thallium was removed in the presence of iron and manganese precipitates at alkaline pH. This paper reports and discusses the potential to remove thallium with minor modifications to the hydroxide precipitation process.

Key Words: oxidation, sorption, lime precipitation, mining influenced water, co-precipitation

Introduction
Thallium is an uncommon, yet very toxic, naturally occurring metal. Exposure for mammals is considered to be more dangerous than that of mercury, cadmium, lead, copper or zinc (Xiao 2003). Naturally occurring concentrations of thallium are normally below regulatory limits, but anthropogenic influences may introduce higher levels of thallium into the surrounding environment, most often as a by-product of smelting and mining operations (Gao 2007).

Thallium occurs mainly in two oxidation states. The species most often found in nature is monovalent thallium (Tl□); the second oxidation state is trivalent thallium (Tl³□) (Twidwell and Beam 2002). Monovalent thallium persists in groundwater. Thallium sorption to sediments is weak and thus the metal is very soluble and mobile once in an aqueous system (Kaplan and Mattigod 1998). Trivalent thallium is much more insoluble and forms stronger complexes than its monovalent counterpart (Kaplan and Mattigod 1998). Thus, the formation of the oxidized trivalent thallium form is the goal when targeting thallium removal.

Until recently, thallium concentrations were difficult to determine because the level of Tl was below detection limits (Peter and Viraraghavan 2005). Now that more advanced analytical techniques have been developed, it has become apparent that methods for thallium removal need to be developed as well.

The EPA has denoted the Best Demonstrated Available Technology (BDAT) for thallium removal as chemical oxidation of thallium followed by chemical precipitation with hydroxide compounds, settling, and filtration (U.S. EPA 1999). This BDAT given by the EPA for RCRA wastes is taken from a single study done in 1946 (Rosengrant and Craig 1990). Details on reagent doses and specific conditions required are not given.

The EPA also recommends activated alumina and ion exchange (MTWP, 2003) as effective processes for thallium removal in a drinking water treatment context. However, the ion types and concentrations are different between MIW and most drinking water sources. In addition, these processes need to be implemented as stand alone processes post-precipitation.

Thallium removal has been investigated previously using aluminum oxides (Bidoglio *et al.* 1993, Zhang *et al.* 2008), iron oxyhydroxides (Kikuchi *et al.* 1990) and manganese oxyhydroxides (Bidoglio *et al.* 1993). These investigations were not constrained by feasible integration into conventional metal precipitation processes. Thus, while insight was gained on potential thallium removal mechanisms, explicit integration of specific reagents and concentrations used is impractical.

In summary, there is a need to develop information on the reagent doses and required conditions for thallium removal from MIW. The approach taken here embraces the complexities of mixed precipitate formation.

This investigation into potential thallium removal techniques is framed around modifications to a lime precipitation treatment already in place. Lime precipitation is the most widely used method to concurrently remove multiple metals from MIW. The challenge was to explore previous thallium removal methods and modify procedures to fit into the lime precipitation framework for a specific set of conditions. Specific mechanisms were not targeted per se. Oxidation occurs to some extent during reagent addition and mixing. The precipitates formed in the treatment plant will tend to be of mixed ligand form (e.g., hydroxide and carbonate) and mixed oxidation state (e.g., MnOOH). These constraints eventually lead to the decision to test the removal of thallium in the presences of aluminum, iron and manganese precipitates as a function of pH. The addition of hydrogen peroxide with iron and manganese was also investigated.

Experimental Procedures

Materials

To make up the synthetic MIW solutions, Tl^{+}, Mn^{2+}, Al^{3+} and Fe^{2+} were provided from trace-metal grade solutions used for ICP-AES. In addition, nanopure water, trace metal grade sulfuric acid; High Purity Standards CaO; reagent grade NaOH, and 'Baker Analyzed' Reagent H_2O_2 were used.

Methods

The batch tests were conducted with a volume of 500 mL in 1-liter beakers. The baseline test condition was 1 mg/L thallium at pH 2.5. This represented our minimum MIW condition. Sulfate addition was at 100 mg/L. Metal additions to the MIW included iron at 5.5 and 250 mg/L, aluminum at 250 mg/L and manganese at 5 and 25 mg/L. Hydrogen peroxide additions were 1 ml or 5 mL of a 30% solution. The specific conditions are noted with the data presentation in the results. Table 1 demonstrates the concentrations of the different solutions used for MIW.

Experiments were conducted at ambient conditions on a magnetic stirrer and were open to the atmosphere. NaOH or CaO was added in increments to acheive the target pH. Four to twelve samples were taken over time as the pH increased. Each sample for metal analysis was filtered through a 0.45-micron nylon filter and acidified with concentrated HNO_3. The metals were then determined on a Perkin Elmer 3000 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) for the constituents of concern.

Table 1. Experimental conditions

Experiment		Constituent concentrations in mg/L					
Name	pH	SO_4^{2-}	Al^{3+}	Fe^{2+}	Mn^{2+}	Tl^{+}	
Thallium only	2±0.5	0	0	0	0	1.0	
Aluminum	2±0.5	100	250	0	0	1.0	
Iron	2±0.5	100	0	250	0	1.0	
Manganese	2±0.5	100	0	0	25	1.0	
Manganese+H_2O_2	2±0.5	100	0	0	25	1.0	
Fenton's	2±0.5	100	0	5.5	5	1.0	

Results

The experimental data is primarily presented in plots of relevant metals with respect to pH. In all of the cases experiments were run in at least duplicate and individual results are shown in Figures 1 through 5.

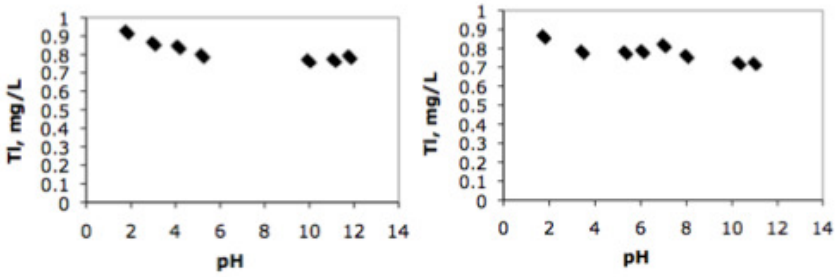

Figure 1. Thallium concentration versus pH. Initial Tl = 1 mg/L and pH = 2.5. pH adjusted using 0.01N NaOH.

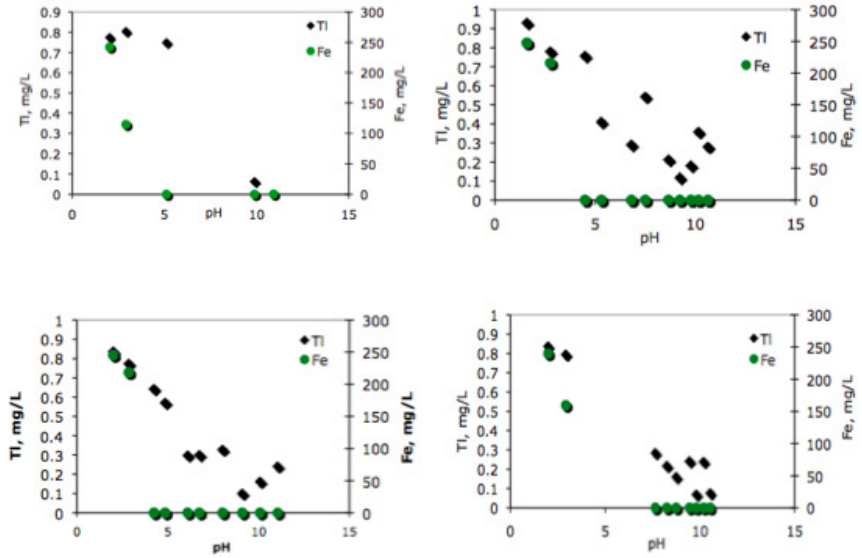

Figure 2. Thallium and iron concentration versus pH. Initial Tl = 1 mg/L, Fe = 250 mg/L, sulfate = 100 mg/L, pH = 2.5. pH adjusted using solid CaO.

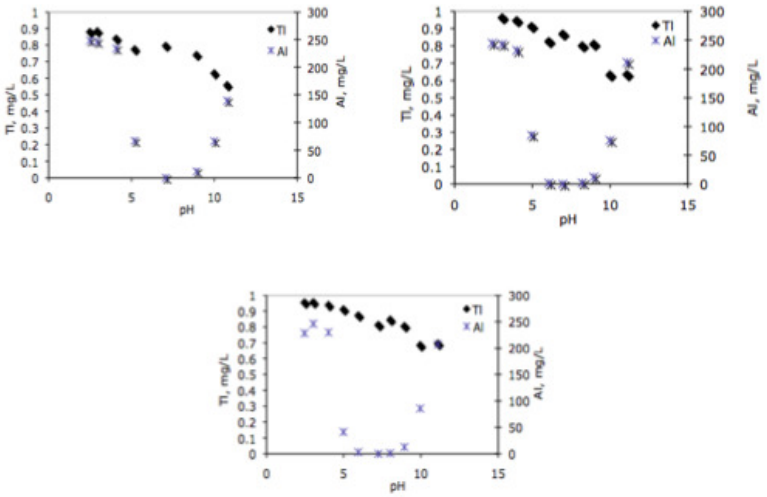

Figure 3. Thallium and aluminum concentration versus pH. Initial Tl = 1 mg/L, Al = 250 mg/L, sulfate = 100 mg/L, pH = 2.5. pH adjusted using solid CaO.

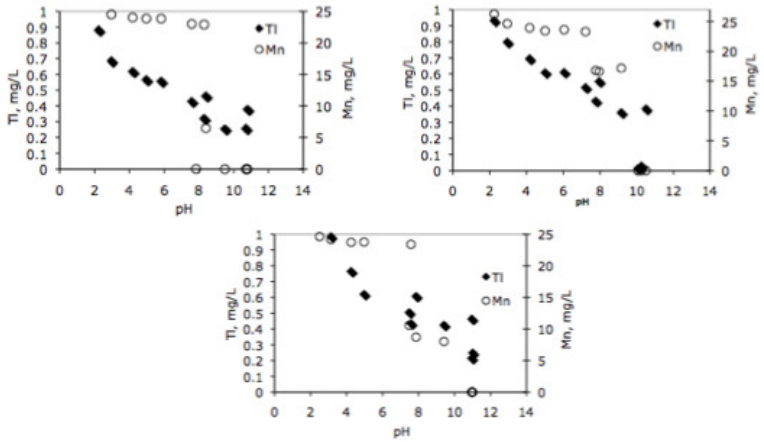

Figure 4. Thallium and manganese concentration versus pH. Initial Tl = 1 mg/L, Mn = 25 mg/L, sulfate = 100 mg/L, pH = 2.5. pH adjusted using solid CaO.

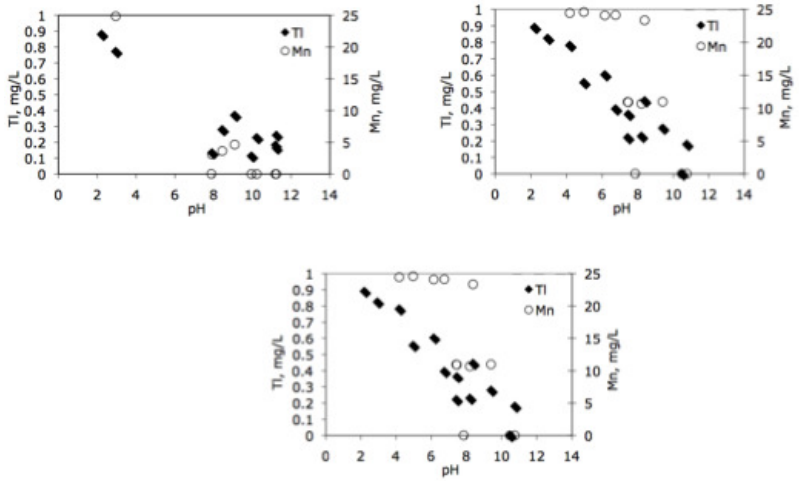

Figure 5. Thallium and manganese concentration versus pH. Initial Tl = 1 mg/L, Mn = 25 mg/L, sulfate = 100 mg/L, pH = 2.5. pH adjusted using solid CaO and 1 mL of 30% H_2O_2 added.

Discussion

The baseline case of thallium concentration in solution with increasing pH shows some removal (10%) at relatively low pH values (4 to 6) and the most thallium removal (20%) above pH 10 (Figure 1). Thallium was removed along with iron precipitation at the concentrations examined. Thallium removal lagged iron precipitation. Thallium concentrations as low as 0.1 mg/L were achieved in the pH 9 to 11 range (Figure 2). Thallium removal in the presence of aluminum precipitation was not related to the removal of aluminum from solution. The lowest thallium concentration observed was at the highest pH where aluminum had returned to solution to near the initial value (Figure 3). Thallium was also removed in the presence of manganese precipitation. The highest removal was observed in the pH 9 to 11 range (Figure 4). The addition of hydrogen peroxide improved the extent of thallium removal (Figure 5). In one of the replicates, thallium was below detection limit. The addition of ferrous iron and hydrogen peroxide was investigated at iron concentrations of 5.5 mg/L and 5 mL of 30% peroxide. No change in thallium removal above the baseline case was observed (data not shown).

Thallium is removed to some extent at alkaline pH. The Eh-pH from Davies *et. al* (2011) shows thallium (I) is soluble at pH values up to 13 (Figure 6). Thallium removal in a pH range of 6 to 11 is consistent with the partial oxidation of monovalent thallium to trivalent thallium and the subsequent precipitation as $Tl(OH)_{3(S)}$. The magnetic stirrer used for mixing is able to transfer oxygen to the water and apparently provided for some oxidation of thallium. Some of the apparent variation in the thallium removal with pH was related to the variation in time taken for the titration with base. In general, longer titration times produced more thallium removal, which is consistent with more time for oxidation.

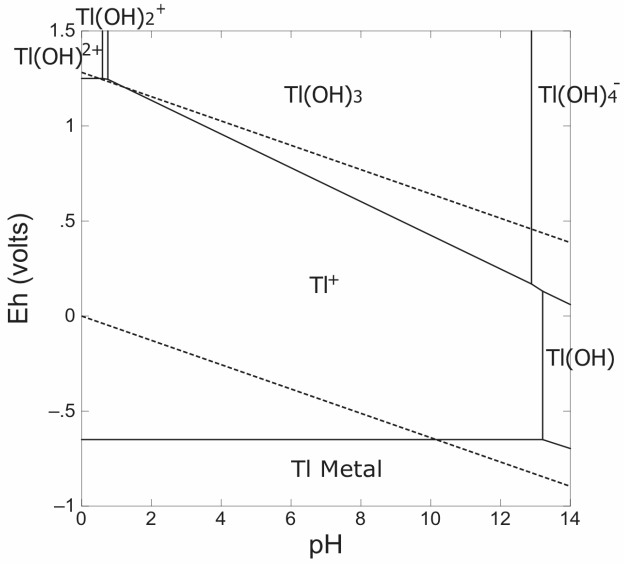

Figure 6. Thallium Eh-pH diagram for initial Tl = 1 mg/L (from Davies *et al.* 2011)

Aluminum interactions

Aluminum showed the lowest removal promise of all the metal precipitates examined. Aluminum exhibited its amphoteric qualities, precipitating out of solution completely at pH 6 and increasing in concentration again at pH near 10. The observed thallium concentration was not affected by

the behavior of aluminum. However, in the presence of the aluminum, the amount of thallium removed (40%) in the pH 9 to 11 range was higher than the baseline case.

Manganese interactions

Manganese had a significant effect on thallium removal even in the absence of a solid manganese phase at pH less than 8. Thallium removal was 50% in the pH 6 to 8 range in the presence of manganese in solution. Higher removal of thallium occurred in once a solid phase of manganese was formed. One possible explanation for manganese precipitation is the formation of $MnCO_3$. If the alkalinity of the water is sufficient and considering the K_{sp} of $2.2x10^{-11}$ for manganese carbonate, $MnCO_3$ will likely precipitate at pH of 8. Manganese oxyhydroxides will not precipitate unless it is at a pH 13. The addition of 1 mL of hydrogen peroxide to the 500 mL test solution resulted in thallium removal to less than 0.1 mg/L. The presence of manganese is an important factor in how thallium behaves in solution. It is a co-contaminant in most MIWs , and is capable of different oxidation states, the higher oxidation states can affect the precipitation and/or adsorption of thallium.

Iron interactions

Iron by itself produced the highest removal of thallium, from 1 mg/L to 0.1 mg/L. The removal of the iron in solution by pH 5 suggests the formation of ferric oxyhydroxide from the initial ferrous sulfate in solution. The mixing conditions of the magnetic stirrer appear to be sufficient for oxidation of all of the iron initially in solution. Ferric iron can participate in redox reactions and also be reduced to ferrous iron in anoxic environments. Thallium removal during iron redox cycling is not well understood. However, the evidence is clear that thallium removal is improved in the presence of ferric iron precipitates.

Fenton's Reagent was also tested. It was found that thallium was not removed over a wide range of pH. It was added at an acidic or circumneutral pH, then titrated to an alkaline pH. In all the various trials, the Fenton's reagent was ineffective at thallium removal. Using the Fenton's Reagent is also a test on the effect of hydrogen peroxide. Fenton's Reagent addition used 0.1 mmoles of iron and 44 mmoles of peroxide. The peroxide was 440 times the molar ratio of the iron. This shows the peroxide addition was well in excess of the Fenton's Reagent need. The excess peroxide was available to react with the thallium, yet there was no removal of thallium above the baseline case of simple pH increase (data not shown).

Implications for treatment

All the metal precipitates examined had a positive effect on thallium removal from MIW. Thallium removal from solution ranged from 0.1 to 0.9 mg/L from an initial thallium concentration of 1 mg/L. However, encountering thallium concentrations above 1.0 mg/L in MIW is rare and the lower initial concentrations of thallium should also be examined. It is not clear how a lower initial concentration of thallium would respond to the treatment conditions examined. A lower initial thallium concentration may have resulted in a lower final concentration if the removal mechanism is based on total mass in solution.

The results of these experiments show promise for thallium removal in the presence of metal precipitates but the more work is needed to elucidate the mechanism and/or the relation between thallium removal and the other metals. For example, high thallium removal was observed in the presence of iron precipitates, yet while iron concentration was ten times higher than manganese the thallium removal was not ten times better. Two questions that remain unanswered are: 1) Is there a concentration dependence of thallium removal?, and 2) Is the removal a function of thallium mass to co-precipitated metals? Addition investigations are needed using the site-specific metal concentrations to refine the treatment modifications.

A lime precipitation treatment system may have one or more mixing tanks prior to the clarifier. The simplest system will contain only one mixing tank to increase pH to 10 – 11. However, multiple mixing tanks are common in order to separate reagent addition and to provide for flocculation. Multiple mixing points offer possibility to add oxidants or other reagents at different pH values. It allows for multiple reactions to take place before the water reaches the clarifier. The mixing tanks that precede a hydroxide precipitation clarifier could be optimized to provide oxidation of thallium and co-contaminant metals. Also, in a high-density sludge treatment system, the recycle of sludge from the clarifier is used to generate higher concentrations of metal precipitates than a traditional single pass through system. The higher concentration of metal precipitates formed for reaction in the mixing tanks provides another opportunity to target thallium removal. Relationships that need to be explored are the ratio between the mass of other metals to thallium in solution, the concentration of metals in the reaction/mixing tanks (varied by sludge recycle), the mixing/aeration time and the explicit use of oxidants. The reaction time will be key in sizing the mixing tanks than precede the clarifier.

Conclusion

Mine water complexity requires empirical study to understand combined effects of the co-constituents. The presence of the many other metals in the MIW increases the removal of thallium at alkaline pH. Manganese appears to be the most effective on a concentration basis for thallium removal in comparison to aluminum and iron, the other oxyhydroxide precipitates that form in a lime treatment process. Oxidation of thallium in basic solution using hydrogen peroxide is an ineffective removal process. Metal co-contaminants may be leveraged to promote thallium removal from MIW.

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