Thallium removal strategies through modification of conventional metal hydroxide precipitation plants

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Objective

- To find a cost effective and efficient method for thallium removal
- Implement the thallium removal procedure into an existing lime treatment system
Outline

1) Thallium Background
2) HDS Metal Hydroxide Precipitation Process
3) Removal Strategies
   - Sorption
   - Oxidative Precipitation
4) Implementation in HDS Treatment System
Background

• Thallium is a toxic, naturally occurring metal
• Thallium exists principally in two oxidation states, Tl\(^+\) and Tl\(^{3+}\)

• Found in selected Mining Influenced Waters (MIW)
• Major constituents in the MIW include Al, Mn, Fe

• Thallium (Tl\(^+\)) is extremely soluble and persists in water, even in basic solutions
• Current MCL is 2 ppb
Eh-pH Stability Diagram

Small stability region for Tl$^{3+}$ in water
Simple HDS Lime Precipitation System

Influent MIW  CaO

Air

Tank 1

Air

Tank 2

Recycled sludge

Effluent

Waste

Lime added to raise pH to 10 -11
Air added to oxidize ferrous iron
Strategies for Thallium Removal

1) Sorption to oxyhydroxides
   - Aluminum
   - Iron
   - Manganese

2) Oxidative Precipitation
   - Oxygen
   - Hydrogen Peroxide
   - Potassium Permanganate

• Kinetics must be rapid enough to achieve removal within typical HDS system hydraulic residence times
Sorption

- Activated alumina is one EPA BDAT for thallium removal
- Sorption the main removal mechanism for activated alumina
- High levels of aluminum, iron and manganese have the potential to form sorptive oxyhydroxides during HDS process
- Sorption to metal oxyhydroxides during formation may include multiple mechanisms (adsorption, ion exchange, co-precipitation, sweep floc)
- Complex MIW chemistry requires experimental evaluation
Oxidative Precipitation

Eh-pH stability diagram for thallium suggests oxidative precipitation a is viable strategy for thallium removal

- Thallium exists principally in two oxidation states, Tl\(^+\) and Tl\(^{3+}\)
- Tl\(^+\) is highly soluble like potassium
- Tl\(^{3+}\) forms Tl (OH)\(_3\), an insoluble precipitate
- Difficult to oxidize Tl\(^+\) to Tl\(^{3+}\), but stable once oxidized
- Oxidation by the addition of a chemical oxidant should lead to the precipitation of Tl(OH)\(_3\)
Methods: Sorption Experiments

Synthetic MIW used (initial concentrations presented with results)

Experimental matrix

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<th></th>
<th>Ti</th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
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Procedure

1) 500 mL of MIW titrated from pH ~2 to ~11 with lime
2) Periodic sampling as pH increased (incremental pH by 1)
3) Filter sample through 0.45 micron filter, submit for ICP analysis
Sorption Experiment Results

Filtered thallium concentration versus pH

Initial $\text{Tl} = 1 \text{ ppm}$, pH adjusted using 0.01N NaOH.

Negligible thallium removal
Thallium sorption to iron oxyhydroxides

Filtered thallium and iron concentration versus pH

Initial $\text{Tl} = 1 \text{ ppm}, \text{Fe} = 250 \text{ ppm}, \text{SO}_4^{2-} = 100 \text{ ppm}$, pH adjusted with solid CaO

Removal of up to 0.9 ppm of Tl from solution
Thallium sorption to manganese oxyhydroxides

Filtered thallium and manganese concentration versus pH

Initial Tl = 1 ppm, Mn = 25 ppm, SO$_4^{2-}$ = 100 ppm; pH adjusted using solid CaO

Removal of up to 0.8 to > 0.95 ppm of Tl from solution
Sorption experiment findings

• Negligible Tl removal with pH only
• Al precipitates not effective for Tl removal
• Mn and Fe precipitates promoted the removal of Tl
• Sorption alone was not sufficient to reduce Tl to 2ppb for the conditions tested
Oxidative Precipitation

**Oxidative Precipitation** was pursued to reach 2 ppb MCL

- Tl$^{3+}$ forms Tl (OH)$_3$, an insoluble precipitate
- Difficult to oxidize Tl$^+$ to Tl$^{3+}$, but stable once oxidized
- The addition of a chemical oxidant should lead to the precipitation of insoluble Tl(OH)$_3$

Oxidants screened with synthetic MIW included: oxygen, hydrogen peroxide, Fenton’s reagent and permanganate

**Permanganate** able to achieve 2ppb target in synthetic and actual MIW (Davies et al., 2011). *However, residual permanganate remained and method used did not simulate HDS process.*
Simulated HDS Experiments with Actual MIW

- Major Constituents (>100 ppm)

<table>
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<tr>
<th>Major Constituents</th>
<th>Real MIW (avg.)</th>
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<tr>
<td>Iron</td>
<td>585 ppm</td>
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<td>Manganese</td>
<td>105 ppm</td>
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<td>Aluminum</td>
<td>400 ppm</td>
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<td>Sulfate</td>
<td>1690 ppm</td>
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<td>Thallium</td>
<td>66 ppb</td>
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Oxidative Precipitation Simulated HDS Method

1) In 500 mL of Real Mine Water, raise pH from ~2 to 10.5 with lime
2) Sparge and mix for 30 min, monitoring pH (10.5)
3) Test Mn and dose KMnO₄
4) Continue to monitor pH (kept at 10.5 with 1M NaOH), and sample every 10 min for 30 min for ICP analysis
The color change shown above begins just after the dosage of lime. A 30 minute time frame is shown:

- First, lime is added and ferrous iron precipitate is formed (green)
- Second, oxidation begins 10-12 min. into mixing and aeration
- Third, ferric iron precipitate forms, turning the sludge reddish-brown
- Finally, KMnO₄ is added and initially turns the solution purple. Once the permanganate oxidizes the Mn and Ti, the precipitates become red/brown
Simulated HDS oxidative precipitation findings

Important observations from these tests:

1) Aeration is a critical part of the process
2) Solids (sludge) are important
3) Dosage of KMnO$_4$ at 20 mg/L effective at TI (< 2 pbb) without residual permanganate
Proposed Implementation Into Simple HDS Lime Precipitation System

Influent MIW  CaO

Air

Air

Proposed oxidant addition

Tank 1

Tank 2

Recycled sludge

Waste

Effluent

Lime added to raise pH to 10-11
Air added to oxidize ferrous iron
Implementation:
Operational variables

Operational variables must be evaluated with actual water and in continuous flow mode

Important variables include:
• Oxidant type and dose
• Reaction tanks
• Location of Dosing
• Recycle of settled precipitates
• Aeration
Conclusion

- Thallium removal can be achieved in a typical HDS system
- Multiple strategies can affect thallium removal from MIW. However, the selected strategy will depend on the MIW chemistry and the effluent target
- Although sorption promotes thallium removal, it appears that the addition of an oxidant is critical to achieving thallium concentrations below 2ppb
- Batch experiments are valuable in screening viable oxidant types and doses
- Pilot-scale investigations are an important follow up to batch investigations
Thallium removal is achievable in a HDS system

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