

Thallium removal strategies through modification of conventional metal hydroxide precipitation plants

Katie Vatterrodt¹, Morgan Davies², Linda Figueroa¹,
Thomas Wildeman¹ and Charles Bucknam³

¹Colorado School of Mines,² Geomega and ³Newmont

Presented at the U.S. EPA Hardrock Mining Conference

April 4, 2012

Objective

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

Outline

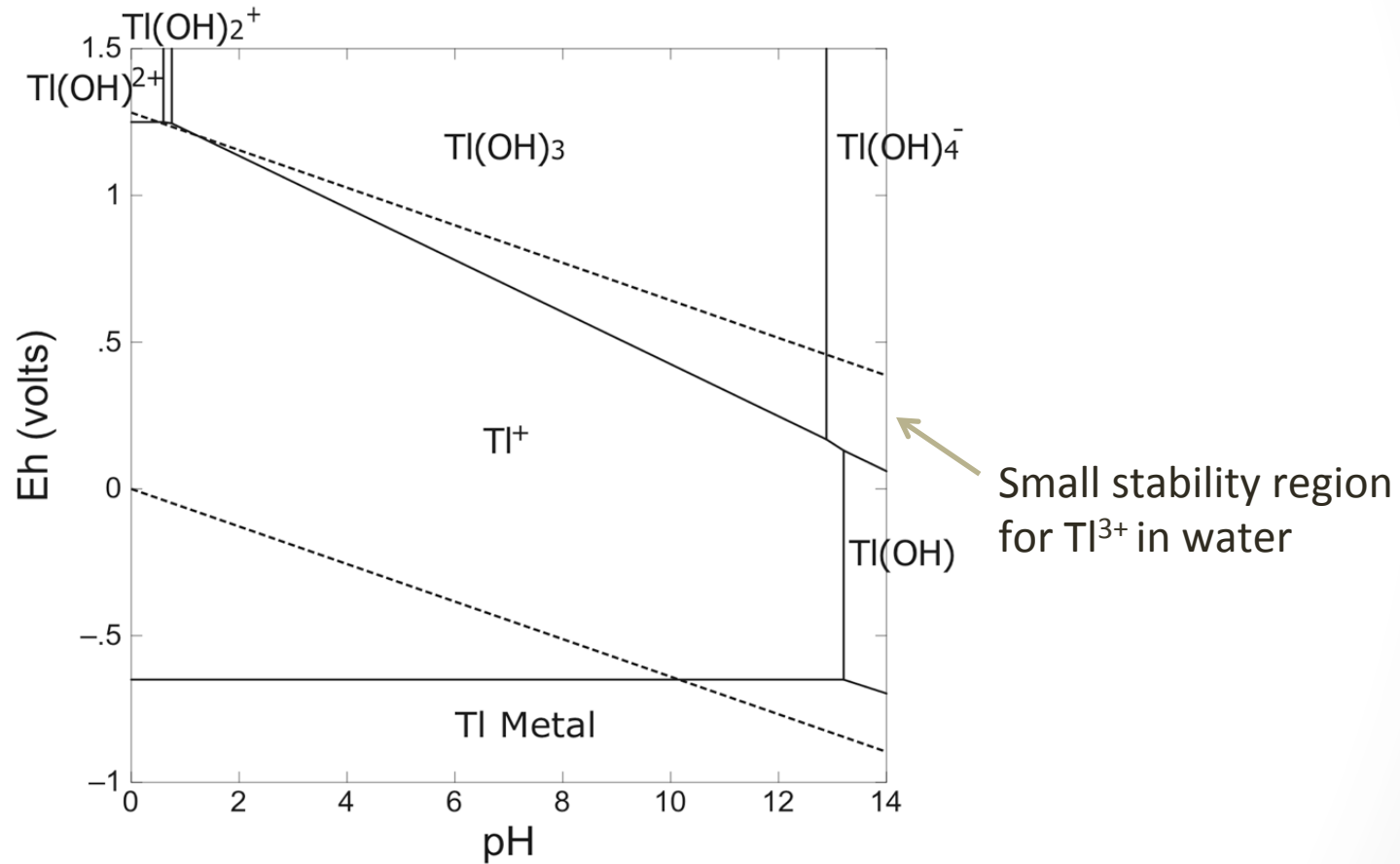
- 1) Thallium Background
- 2) HDS Metal Hydroxide Precipitation Process
- 3) Removal Strategies
 - Sorption
 - Oxidative Precipitation
- 4) Implementation in HDS Treatment System

Background

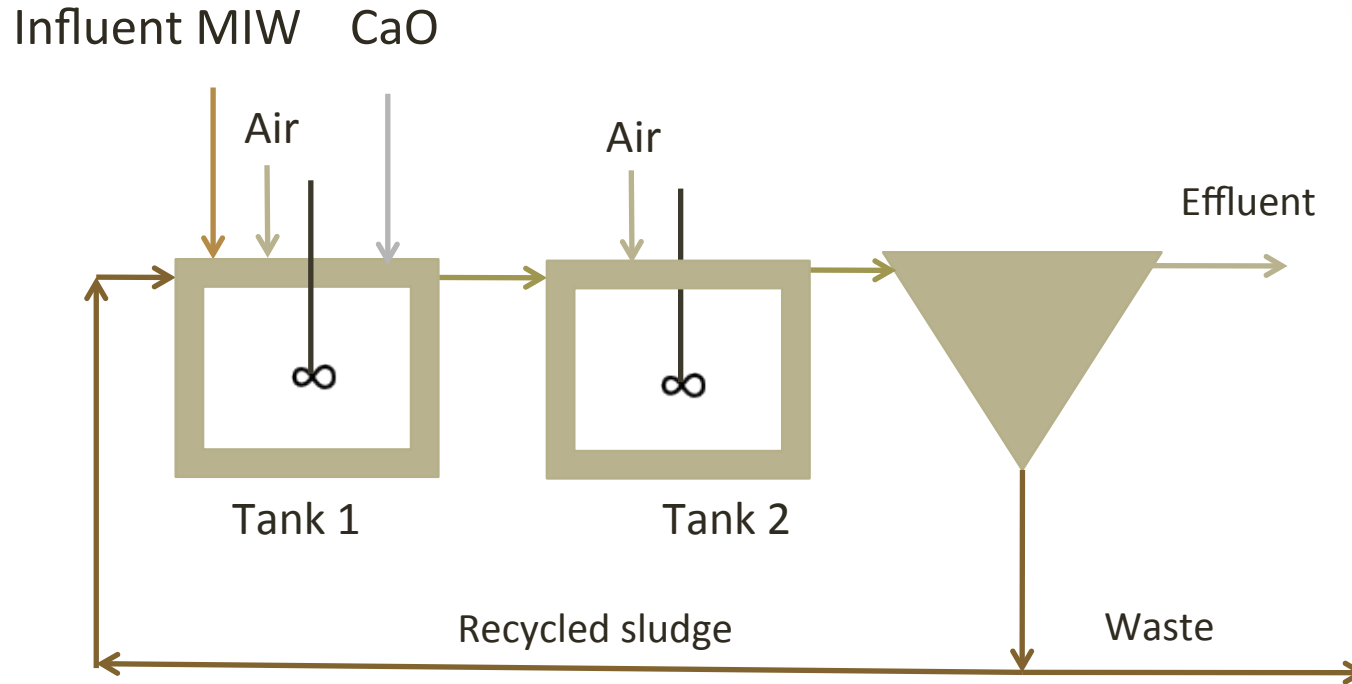
- Thallium is a toxic, naturally occurring metal
- Thallium exists principally in two oxidation states, Tl^+ and Tl^{3+}
- Found in selected Mining Influenced Waters (MIW)
- Major constituents in the MIW include Al, Mn, Fe
- Thallium (Tl^+) is extremely soluble and persists in water, even in basic solutions
- Current MCL is 2 ppb



Eh-pH Stability Diagram



Simple HDS Lime Precipitation System



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 is a 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

Tl	Fe	Mn	Al
X			
X	X		
X		X	
X			X

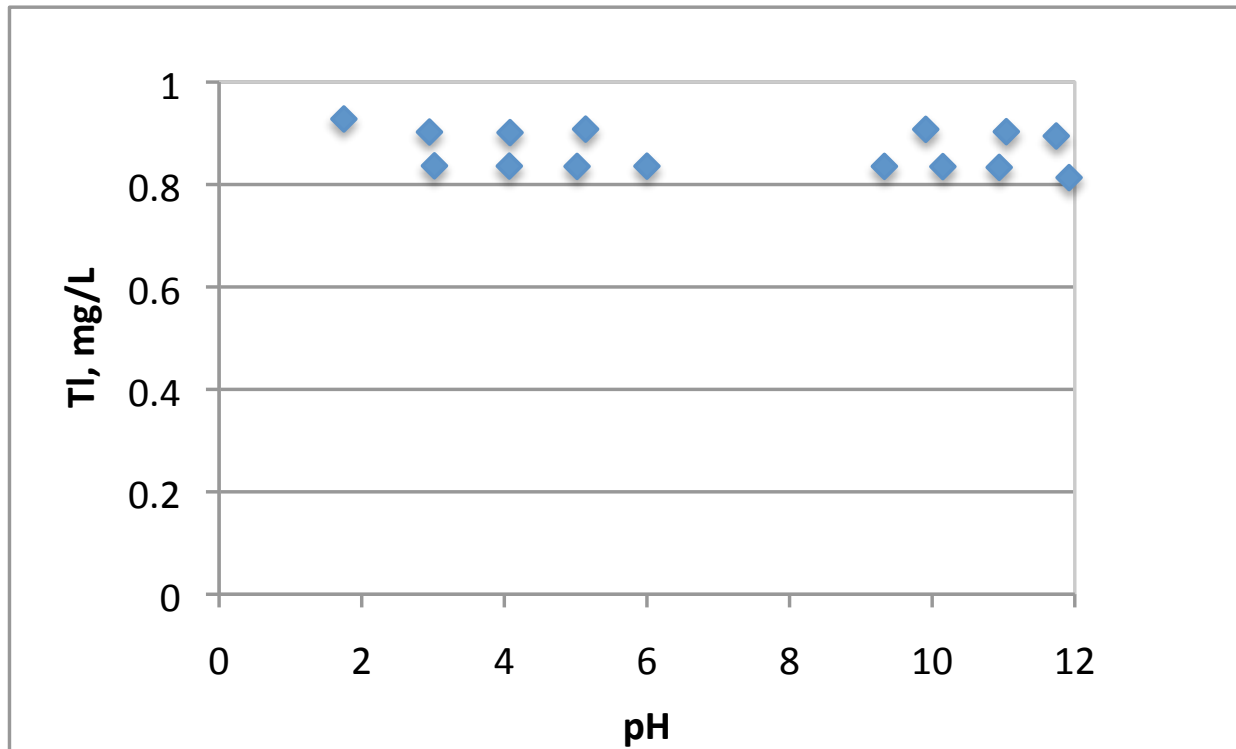
Procedure

- 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 Tl = 1 ppm, pH adjusted using 0.01N NaOH.

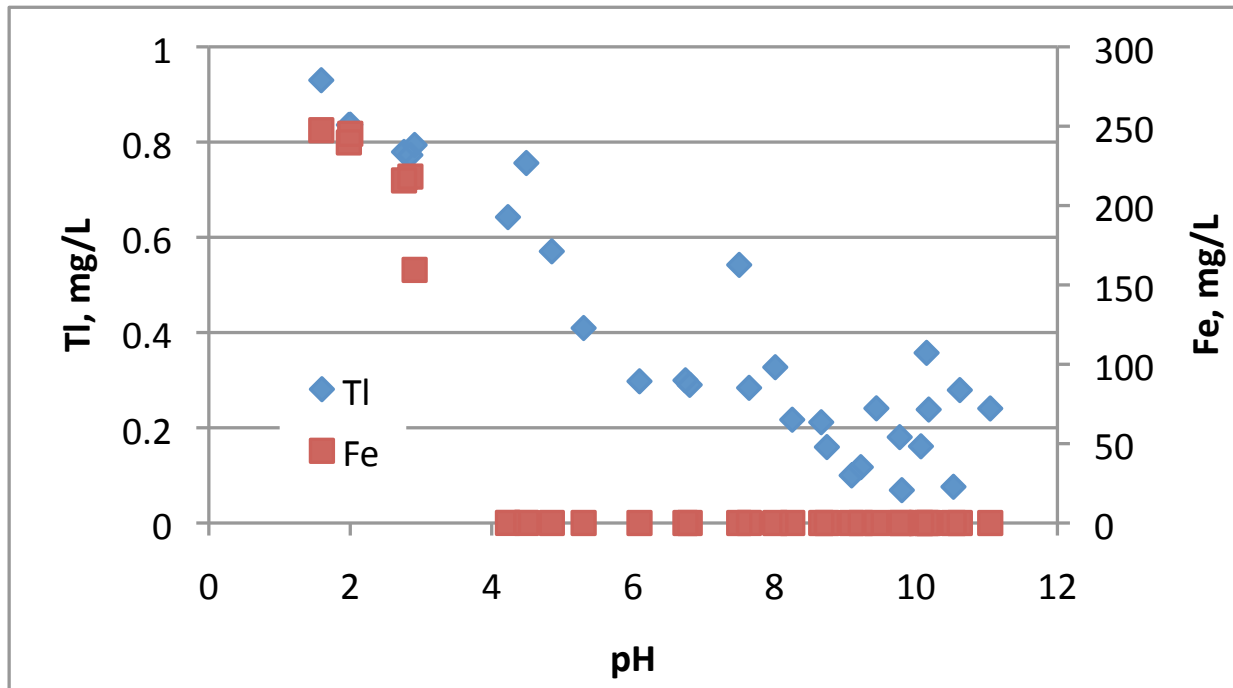


Negligible thallium removal

Thallium sorption to iron oxyhydroxides

Filtered thallium and iron concentration versus pH

Initial Tl = 1 ppm, Fe = 250 ppm, SO_4^{2-} = 100 ppm, pH adjusted with solid CaO

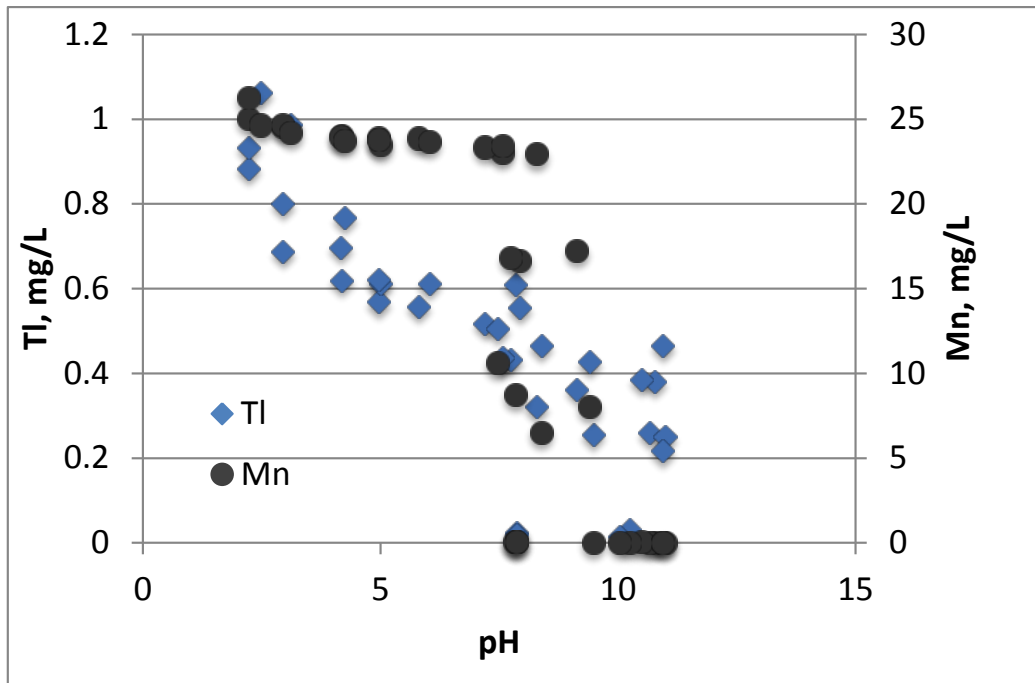


Removal of up to 0.9 ppm of Tl from solution

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.*

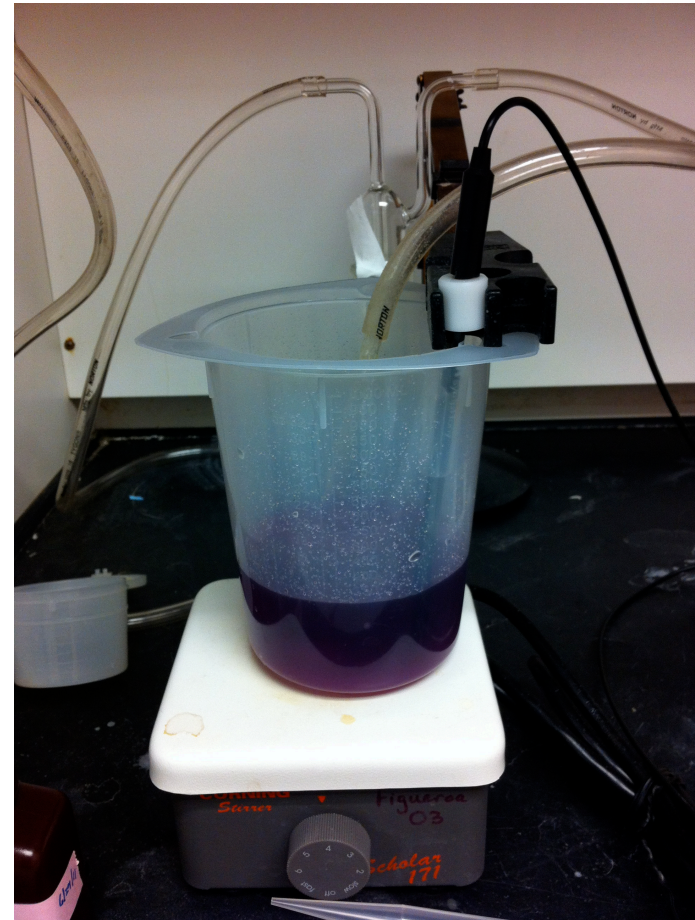
Simulated HDS Experiments with Actual MIW

- Major Constituents (>100 ppm)

Major Constituents	Real MIW (avg.)
Iron	585 ppm
Manganese	105ppm
Aluminum	400 ppm
Sulfate	1690 ppm
Thallium	66 ppb

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 KMnO_4
- 4) Continue to monitor pH (kept at 10.5 with 1M NaOH), and sample every 10 min for 30 min for ICP analysis



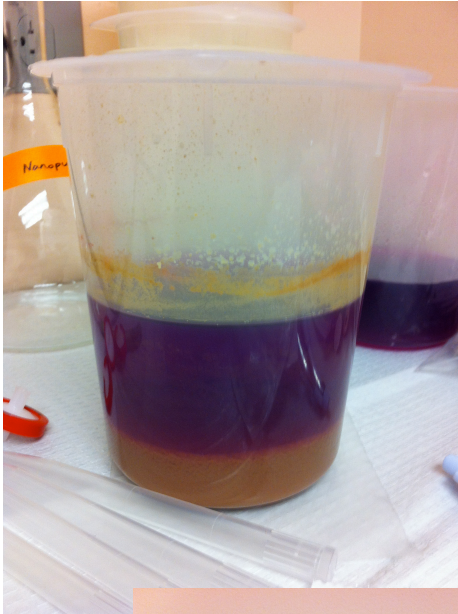
Time series of experimental process



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, KMnO_4 is added and initially turns the solution purple. Once the permanganate oxidizes the Mn and Tl, the precipitates become red/brown

Simulated HDS oxidative precipitation findings

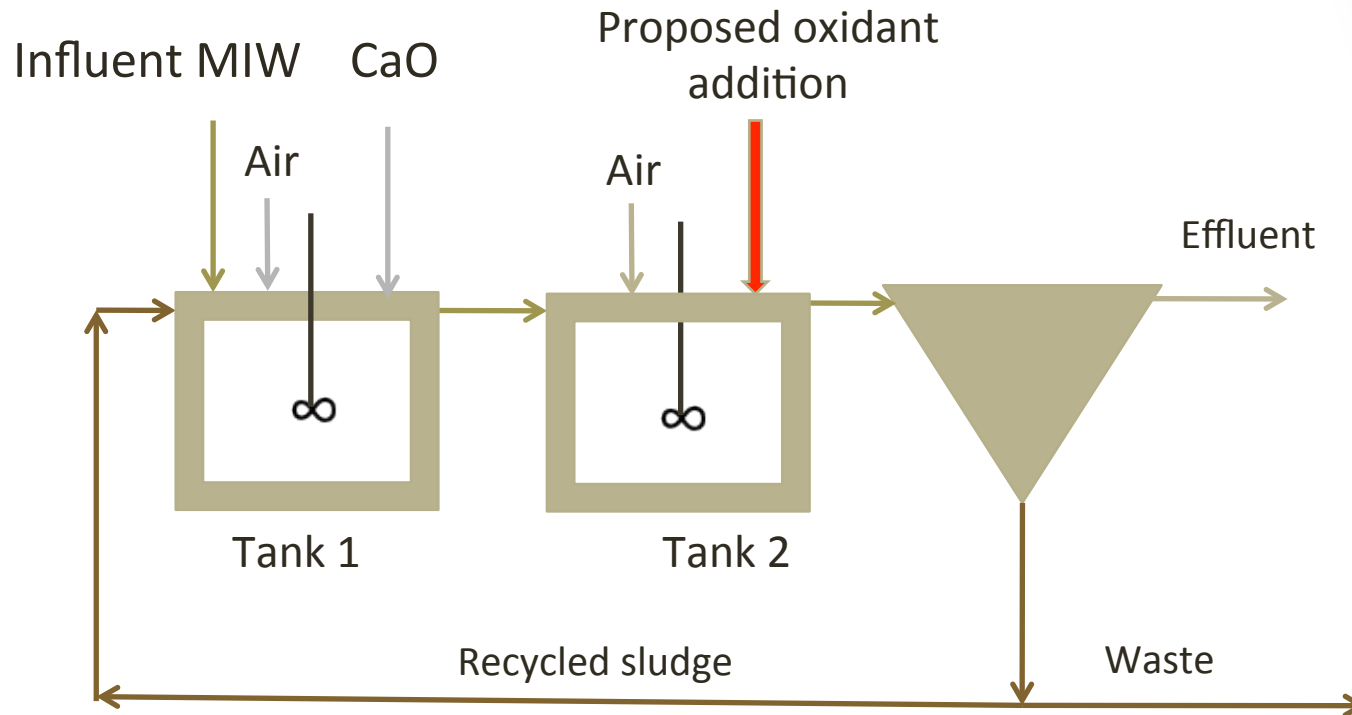


Important observations from these tests:

- 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



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

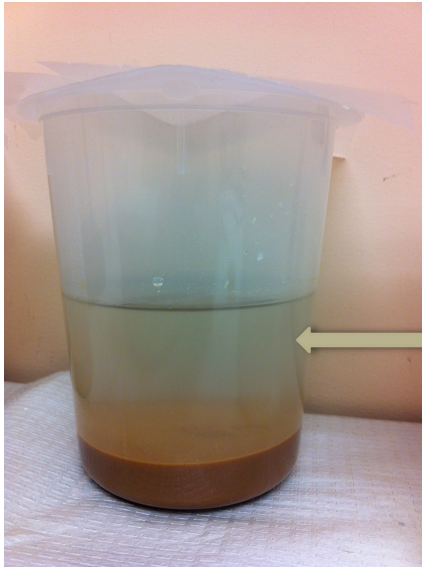
Important variables include:

- **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

Questions



Thallium removal is
achievable in a HDS system

For more information on this project contact:

Dr. Linda Figueroa
lfiguero@mines.edu