Active Alkaline Addition Schemes for Removal of Diverse Contaminants in ARD

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Aggressive ARD

Metals	WATER 1	WATER 2	Targets
	mg/L	mg/L	mg/L
Al	66.2	458	0.087
As	1.106	0.062	0.01
Cd	0.862	0.363	0.005
Fe	263	608	1
Mn	13	101	0.88
Tl	0.032	0.001	0.002
Zn	16.4	32.4	0.38
SO4	1818	5435	
Cu	46.2	19.7	0.03
Ni	0.204	0.586	0.17
pH		2.61	6.5-8.4

Passive treatment is most problematic

Objective

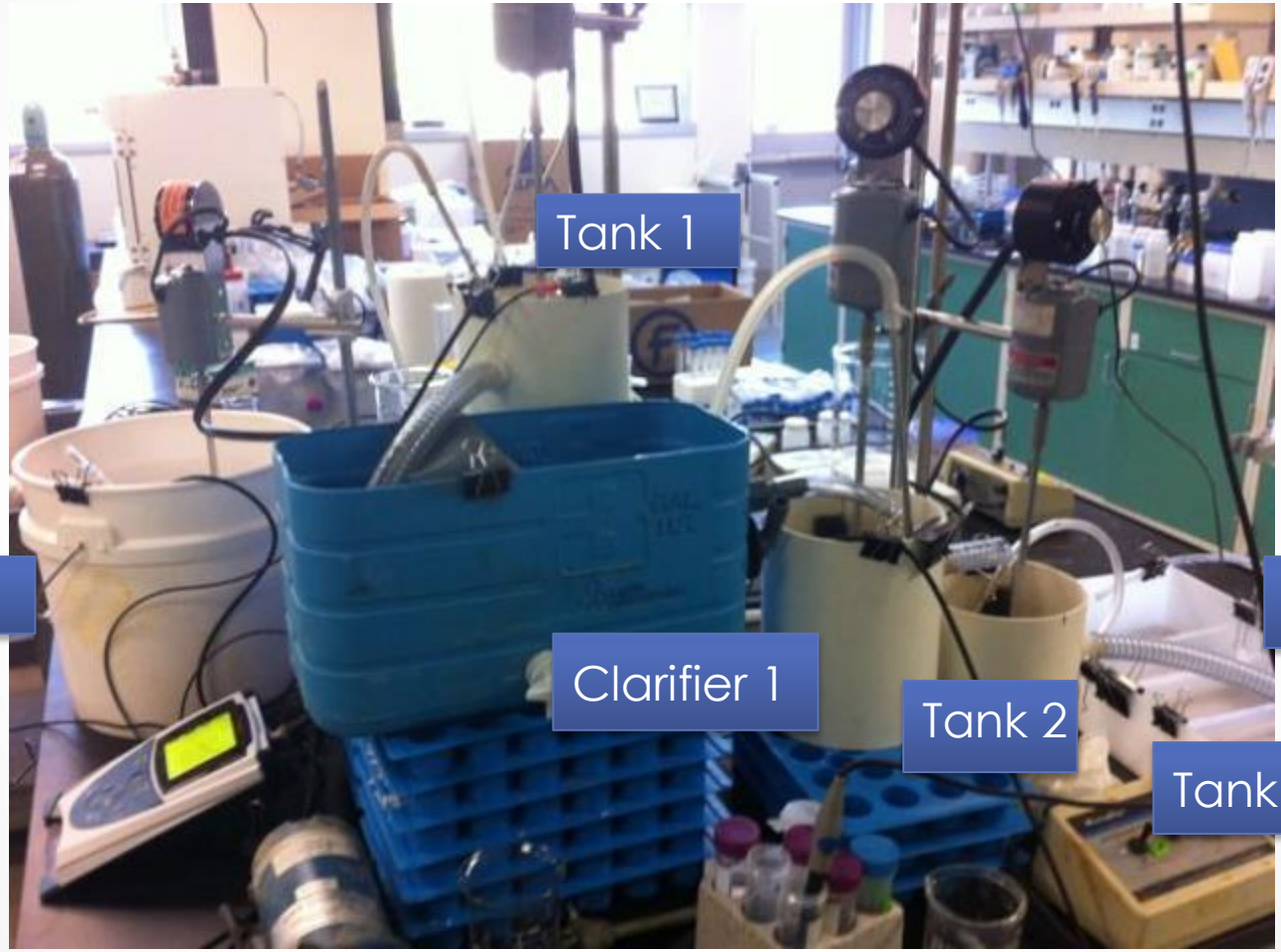
Try various methods of active alkaline addition to determine the best removal scheme.

Concentrate on effective arsenic and thallium removal

Chemicals Used

- Hydrated CaO for pH increase in a 10% soln, variable flow
- Mn soln at 3000 ppm (used $MnSO_4$) at 2.5mL/min (75ppm)
- Fe soln at 1000 ppm (used $FeCl_3$) in at 2.5 mL/min (25 ppm)
- Nalco 8872 polymer (nonionic surfactant) added in Tank 2 (1% solution)
- Air added to all mixing tanks

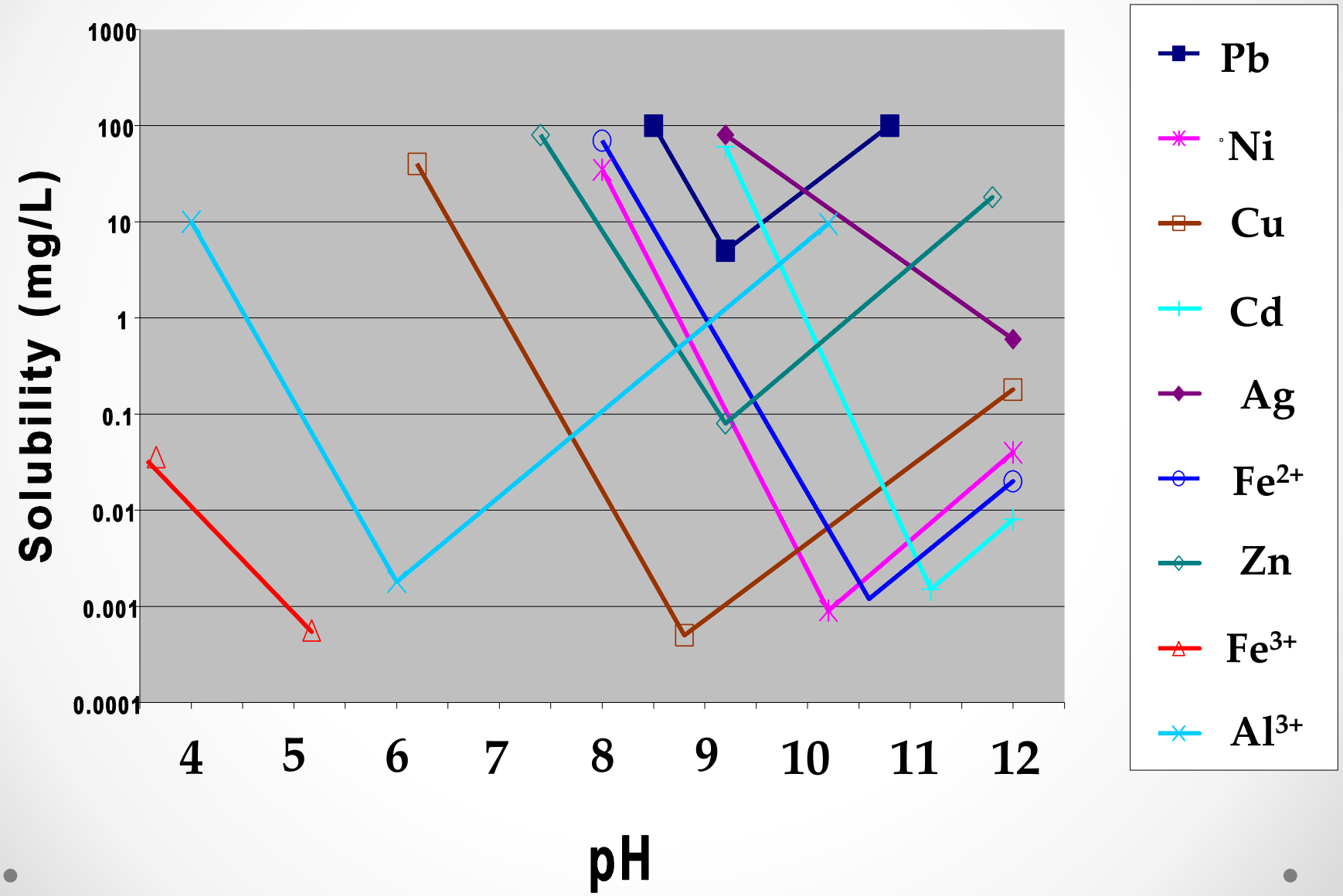
Configuration 1



Bench Scale Plant Specifications

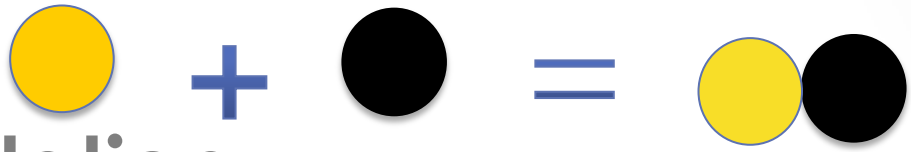
- Reaction tanks=1.9L
- Clarifier 1 = 9L; Clarifier 2 = 7L
- Flow rate = 100mL/min
- Rapid mix in Tank 1, Slow mix in Tank 2, Rapid mix in Tank 3

HYDROXIDE SOLUBILITY

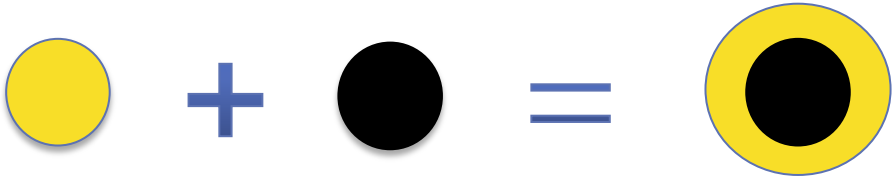


Mechanisms for Removal

- Sorption - Occlusion

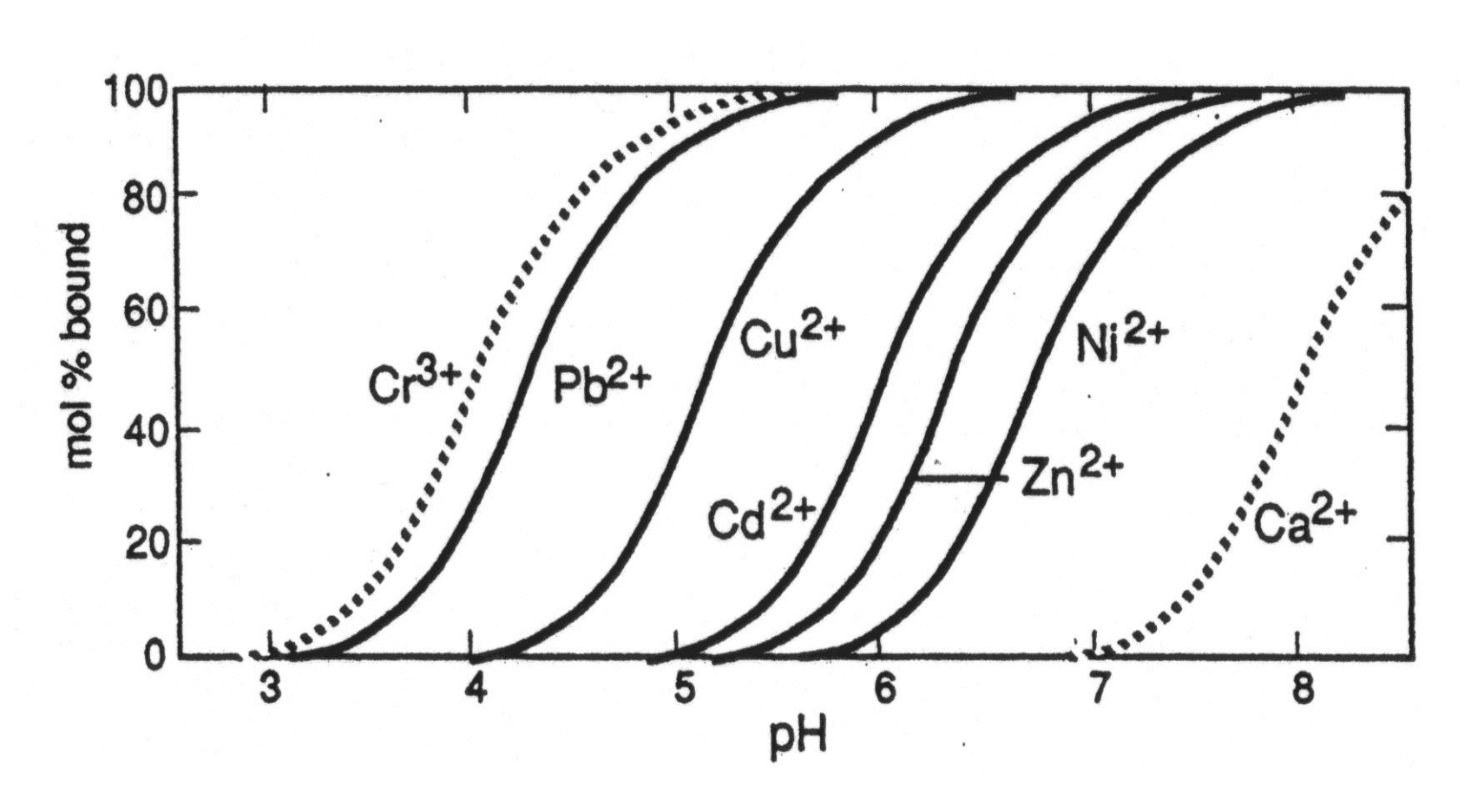


Co-precipitation



- Oxidative- Precipitation

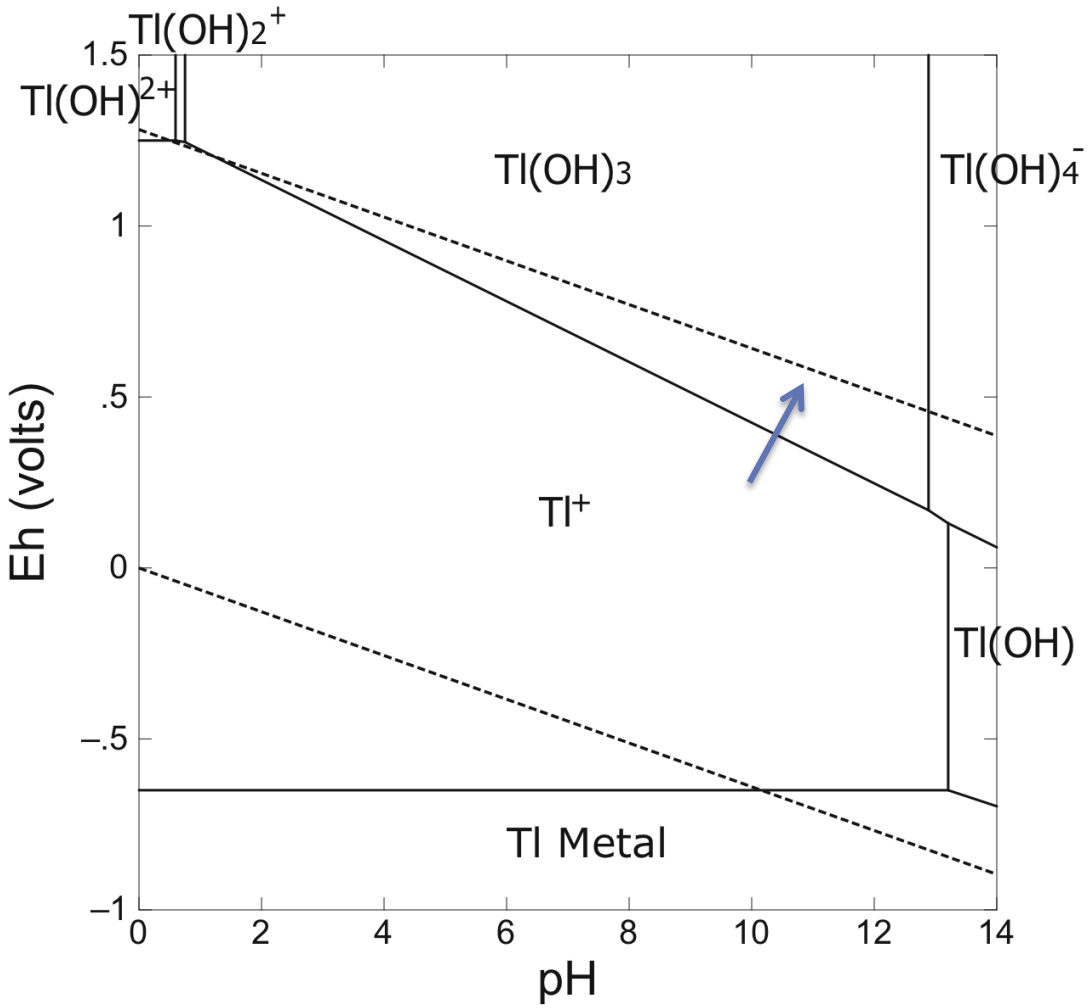
ADSORPTION ONTO $Al(OH)_3$



Hydroxide precipitation & adsorption sequence are comparable but adsorption is ~ 2 pH units lower

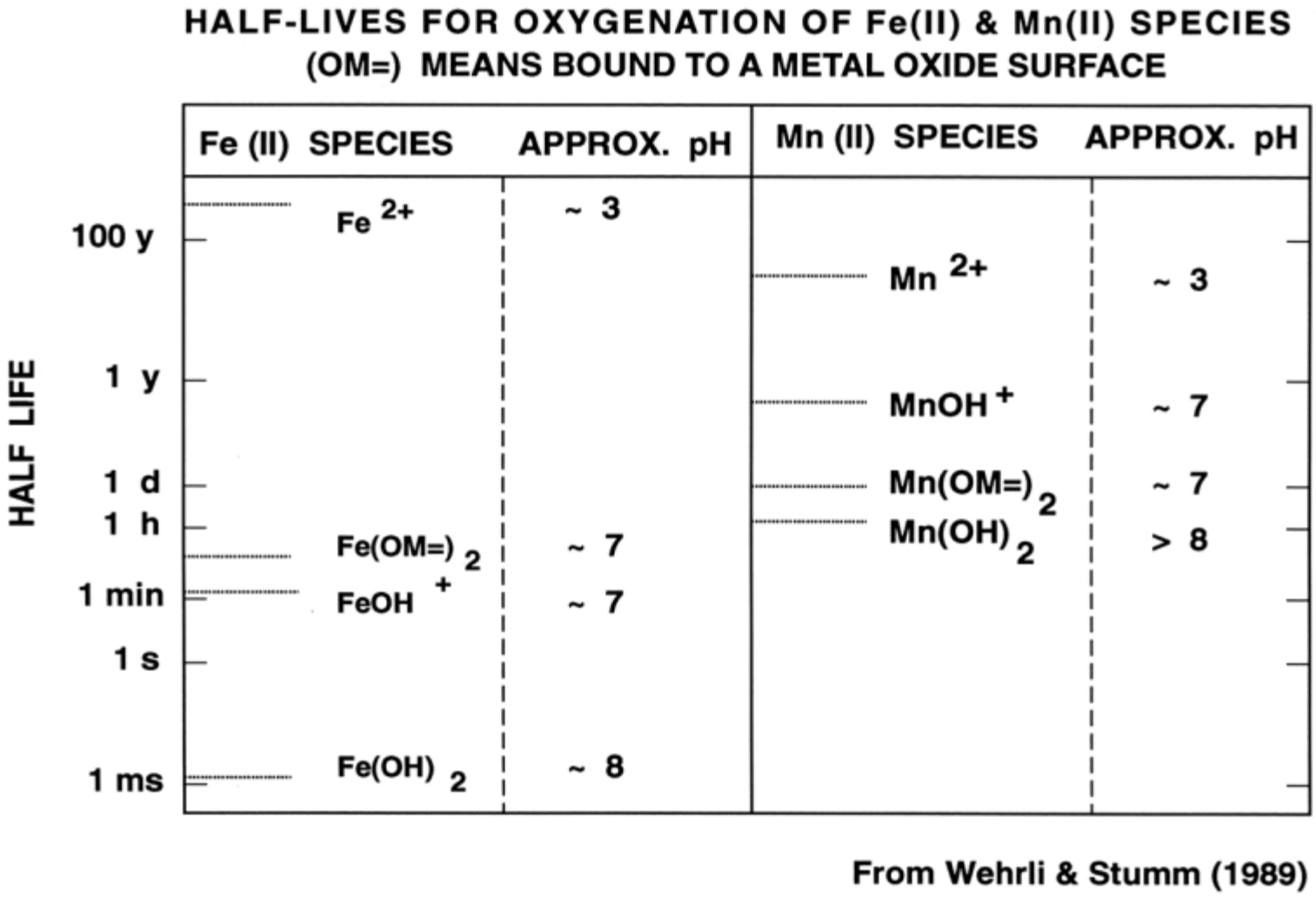
Thallium Oxidation & Precipitation

- Thallium (Tl) is a very toxic, naturally occurring trace metal present in a range of metal sulfide minerals.
- The dominant ion is Tl^{+}. It is very difficult to oxidize to the insoluble species of Tl^{3+}
- Try oxidation & precipitation at high pH.



****Small stability region for Tl^{3+} in water**

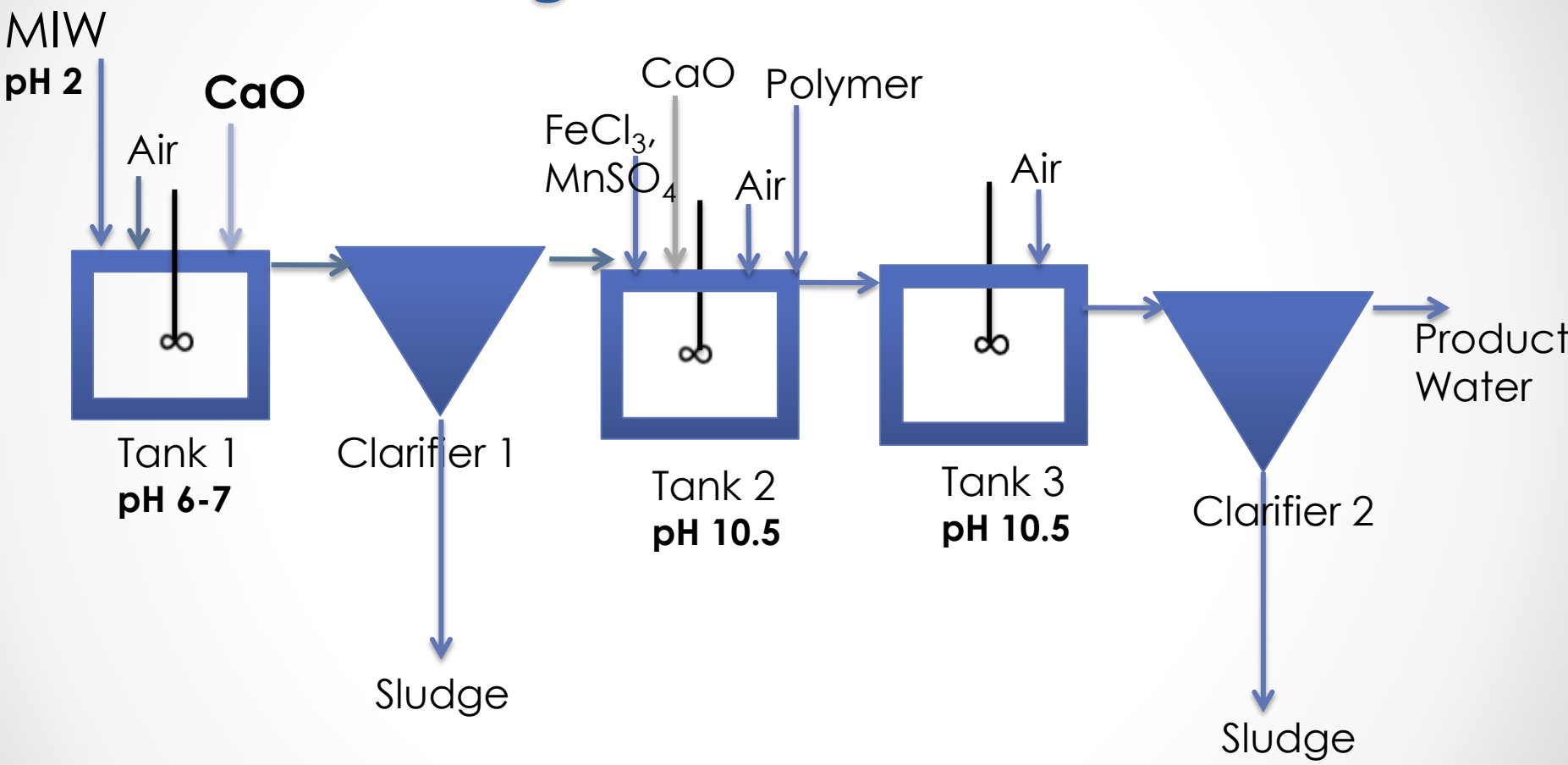
Mn & Fe OXIDATION KINETICS



Configuration 1

- **Goal: Two-stage Precipitation, low to high**
  - **Stage 1 at pH 7**
    - Aluminum, Iron, Selenium, Arsenic removal expected
    - Removal of Cadmium, Copper, Nickel, and Zinc??
    - Only CaO and O_2 addition
  - **Stage 2 at pH 10.5**
    - Removal of Cadmium, Copper, Nickel, and Zinc??
    - Oxidation of Manganese co-precipitation/sorption of Thallium
    - Chemical addition: iron, manganese, polymer
    - Longer HRT (2 reaction tanks)

Small Scale Lime Precipitation System Configuration 1 (N1-N4)



Experimental Runs

- N1: Configuration 1 - Polymer
- N2: Configuration 1 - $FeCl_3$
- N3: Configuration 1 - $FeCl_3$ and Polymer
- N4: Configuration 1 - $FeCl_3$, $MnSO_4$ and Polymer

Removal of COCs

Cd, Cu, Co, Ni, and Zn not completely removed at pH 7 but all met targets at pH 10.5

**Red values on the following tables indicate the metal is above the target.

Results: Run N1

- **Polymer addition, 3hr run time. *All values in (mg/L)***

COC	Initial	Clarifier 1 (pH 7)	Clarifier 2 (pH 10.5)
Arsenic	0.39	6.1	0.052
Thallium	0.131	0.118	0.069
Iron	197	0.003	0.011
Manganese	14.4	8.2	0.056
Aluminum	73	0.052	6.08

Results: Run N2

- $FeCl_3$ addition, 3.5 hr run time.

COC	Initial	Clarifier 1 (pH 7)	Clarifier 2 (pH 10.5)
Arsenic	0.424	0.006	0.012
Thallium	0.225	0.173	0.140
Iron	212	0.049	0.060
Manganese	17	7.4	0.018
Aluminum	85	0.083	0.23

Results: Run N3

- Polymer and $FeCl_3$ addition, 3hr run time.

COC	Initial	Clarifier 1 pH 7	Clarifier 2 pH 10.5
Arsenic	0.036	0.0051	0.0052
Thallium	0.143	0.150	0.099
Iron	193	0.0003	0.0001
Manganese	14.5	10.97	0.495
Aluminum	72	0.022	0.22

Results: Run N4

- $FeCl_3$, $MnSO_4$ and Polymer addition, 3hr run time

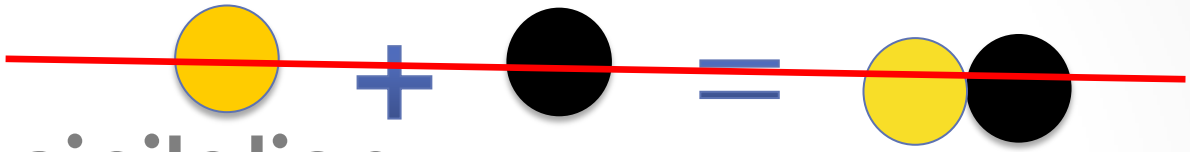
COC	Initial	Clarifier 1 (pH 7)	Clarifier 2 (pH 10.5)
Arsenic	0.35	0.0069	0.0047
Thallium	0.112	0.110	0.048
Iron	187.6	0.021	0.018
Manganese	14.3	9.32	0.007
Aluminum	69.9	0.026	0.160

Conclusions: Configuration 1

- ***All COCs removed to below targets except thallium, arsenic and aluminum***
- **For Cu, Cd, Co, Ni, and Zn, in all 4 experiments, removal was not below targets until stage 2 (pH 10.5)**
- **Mn addition resulted in higher thallium removal.**
- **Iron is important for arsenic removal**

Mechanisms for Removal

- Sorption - Occlusion



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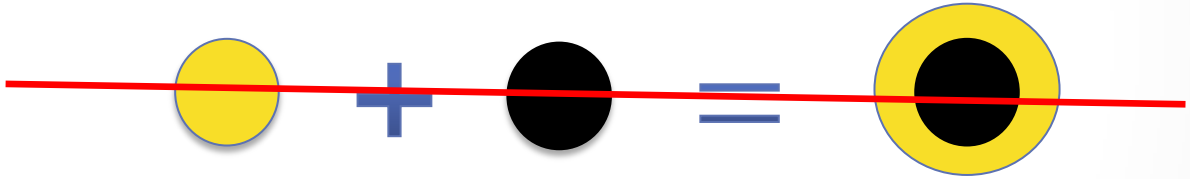
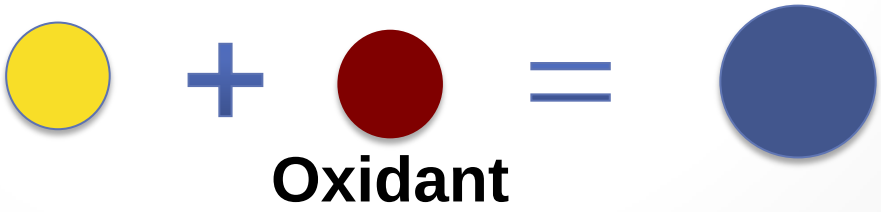


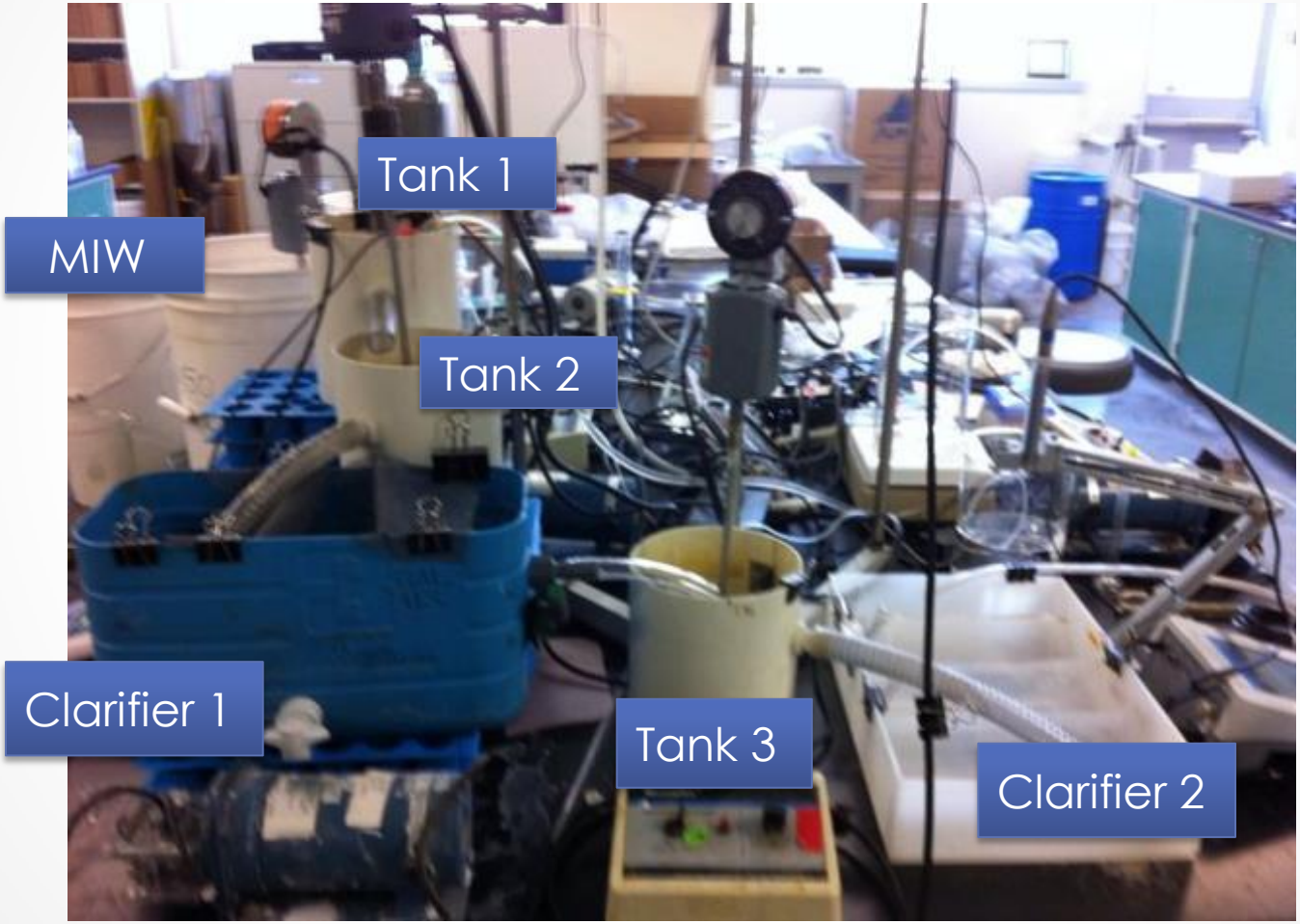
- Oxidative- Precipitation



Configuration 2: Jake Croal's Method

- **Goal: Two-stage Precipitation, high to low**
  - **Stage 1 at pH 11**
    - **Addition of CaO and O2**
    - **Oxidation/removal of most COCs**
    - **Chemical addition variables: Manganese, Polymer**
  - **Stage 2 at pH 6-8**
    - **Targeting aluminum and arsenic removal**
    - **Chemical addition variables: Iron, HCl**

Configuration 2



Specifications: Configuration 2

Volumes And Flow

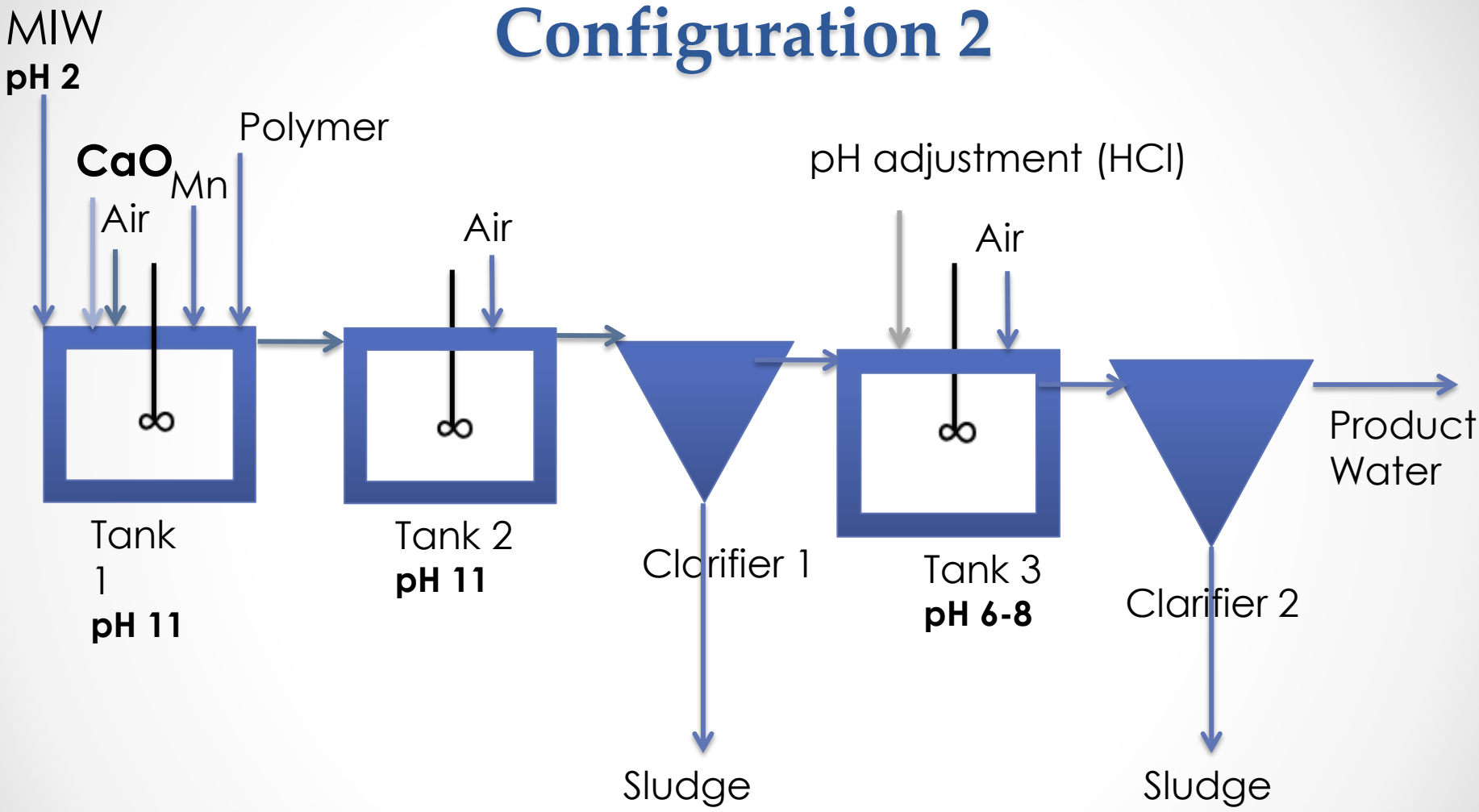
- Reaction tanks=1.9L
- Clarifier1= 9L; Clarifier2 = 7L
- Flow rate = 100mL/min
- Rapid mix in Tank 1, Slow mix in Tank 2, Rapid mix in Tank 3

Chemical additions

- CaO for pH increase in a 10% soln, variable flow
- Mn soln at 3000ppm (used $MnSO_4$) in at 2.5mL/min (75ppm)
- Fe soln at 1000 ppm (used FeCl3) in at 2.5 mL/min (25ppm)
- Polymer (Nalco 8872 nonionic surfactant) added in Tank 2 (1% solution)
- Air added to all mixing tanks
- HCl added for pH decrease

Small Scale Lime Precipitation System

Configuration 2



Configuration 2 Experiments

- **N5: Configuration 2 - $MnSO_4$, Polymer and HCl**
- **N6: Configuration 2 - $MnSO_4$, Polymer and HCl**
- **N7: Configuration 2 - $MnSO_4$, Polymer, $FeCl_3$ and HCl**

Results: Run N5

- $MnSO_4$ and Polymer addition. 3hr run time.

COC	Initial	Clarifier 1 (pH 11)	Clarifier 2 (pH 6-8)
Arsenic	0.37	0.005	0.004
Thallium	0.055	0.010	0.0017
Iron	204	0.020	0.008
Manganese	15.6	0.006	0.104
Aluminum	79	13.7	0.037

Results: Run N6

Duplicate of N5

COC	Initial	Clarifier 1 (pH 11)	Clarifier 2 (pH 6-8)
Arsenic	0.36	<0.004	<0.004
Thallium	0.005	<0.002	<0.002
Iron	189	0.028	0.014
Manganese	15	0.012	0.143
Aluminum	65	1.1	0.92

Results: Run N7

- $MnSO_4$, Polymer and $FeCl_3$ addition. 3 hr run time.

COC	Initial	Clarifier 1 (pH 11)	Clarifier 2 (pH 6-8)
Arsenic	0.385	<0.004	0.004
Thallium	0.0425	0.0047	0.006
Iron	222	0.03	0.014
Manganese	16.1	0.008	0.50
Aluminum	81	10.5	0.14

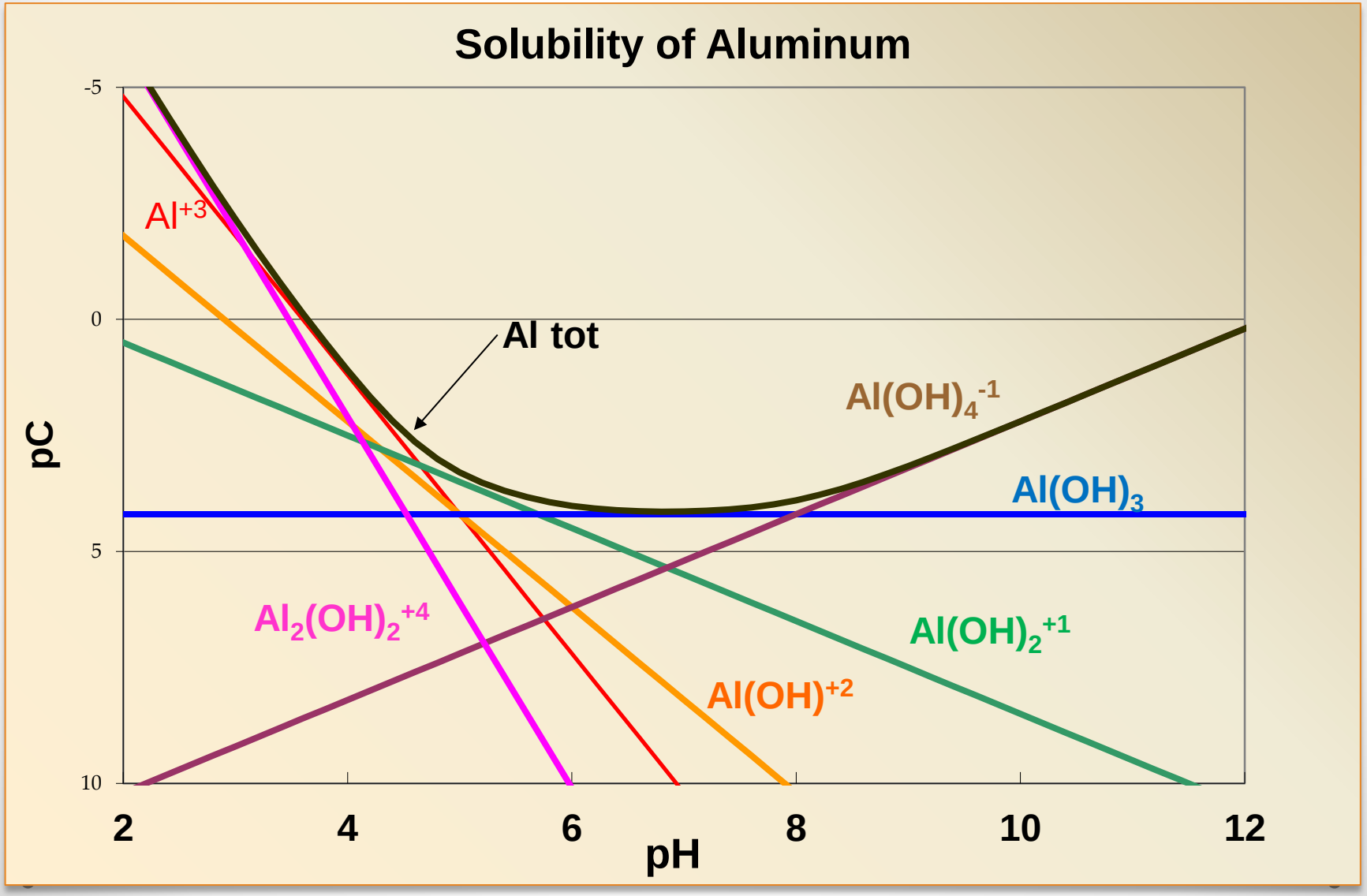
Conclusions Configuration 2

- Thallium removed at pH 11 with the addition of manganese. Need that oxidation – precipitation.
- Arsenic removed at pH 11 with no iron addition.
- Aluminum removal is possible.

Further Work

- Pilot high density sludge study
- How much Mn and Fe are necessary?
- Is aluminum problem a result of ineffective clarification, or is there a chemical issue?
- What would happen to selenium in these schemes?

Aqueous Aluminum Chemistry



Questions - Comments