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EM-31 Alternative and Enhanced Chemical Cleaning Program

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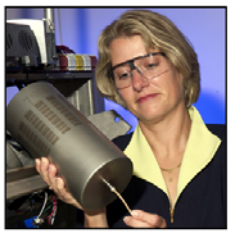
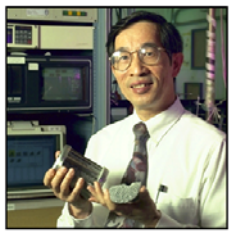

EM Waste Processing Technical Exchange Meeting

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

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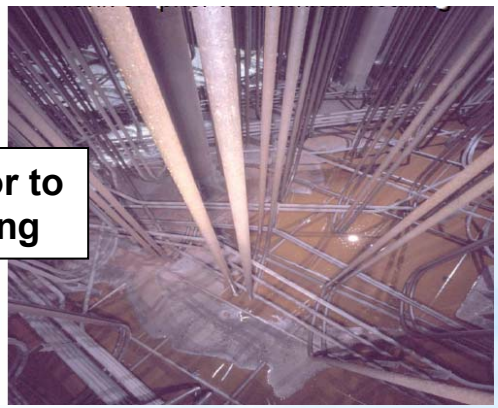
Introduction

- Numerous SRS tanks scheduled for closure (contract commitments)
- Cannot remove all sludge by mechanical means due to obstructions
- Chemical removal technology needed (likely oxalic acid)
- Post-dissolution neutralization required prior to transfer to compliant tanks
- Sodium oxalate salts precipitate on neutralization and have negative downstream impacts
- Currently three SRS chemical cleaning programs
  - **Baseline: 8 wt. % OA batch contact (Tanks 5 and 6)**
  - **ECC: 1-3 wt. % OA with oxalate destruction**
  - **Alternative/Enhanced Chemical Cleaning (EM-31)**



SRS Tank 5F prior to chemical cleaning

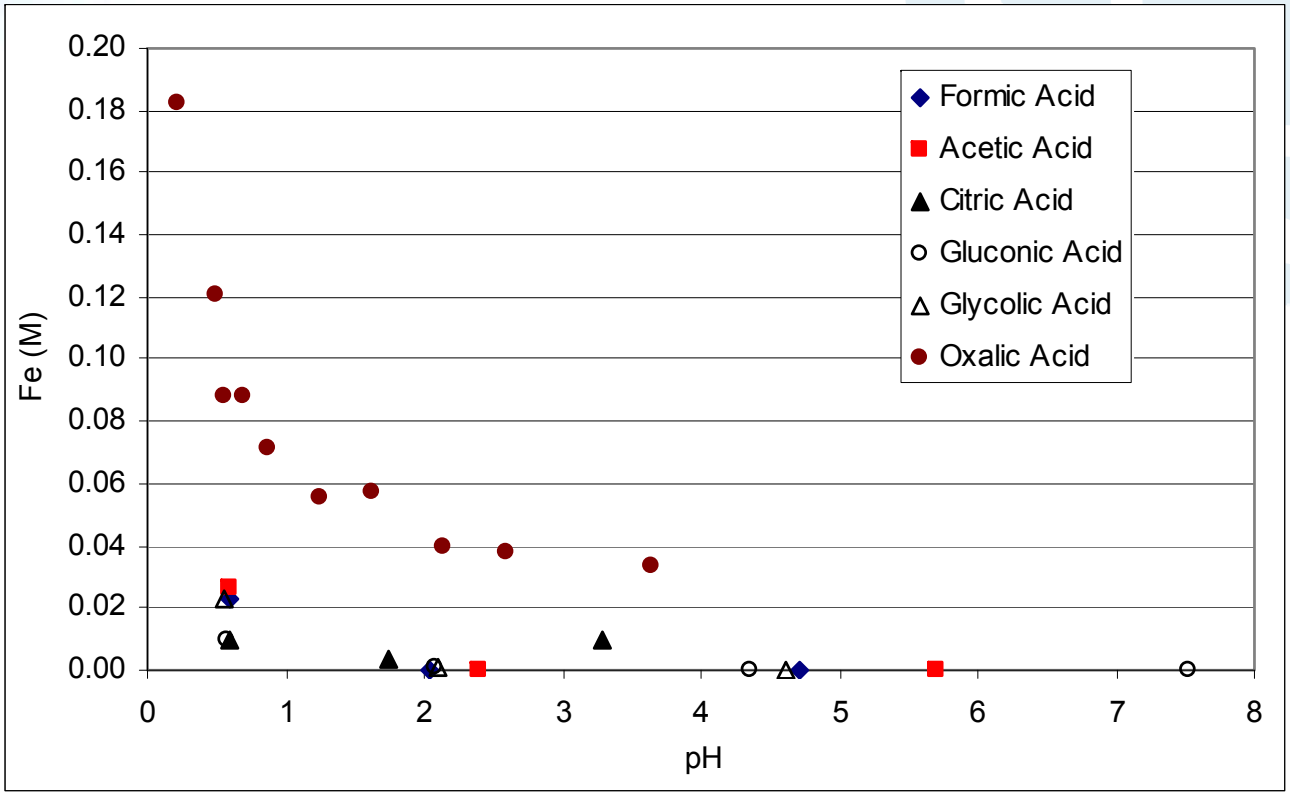
EM-31 Chemical Cleaning Program

- **Focus**
  - Alternative technologies
  - Optimization and oxalate minimization
  - Increased chemical understanding to supplement other programs
  - Broader application and longer-term view
- **Initial Approach and Results**
  - Identified primary metal phases
  - Pure phase dissolution testing
  - Identified need for supplemental acid based on literature and modeling
  - pH control using nitric or sulfuric acids proven effective for oxalate minimization
- **Issues/Questions**
  - Will other complexing acids work well with pH control?
  - Is hematite a conservative standard phase?
  - What is dissolution timescale?
  - Can optimized conditions be identified with acceptable corrosion rates?

Dissolution Test Conditions

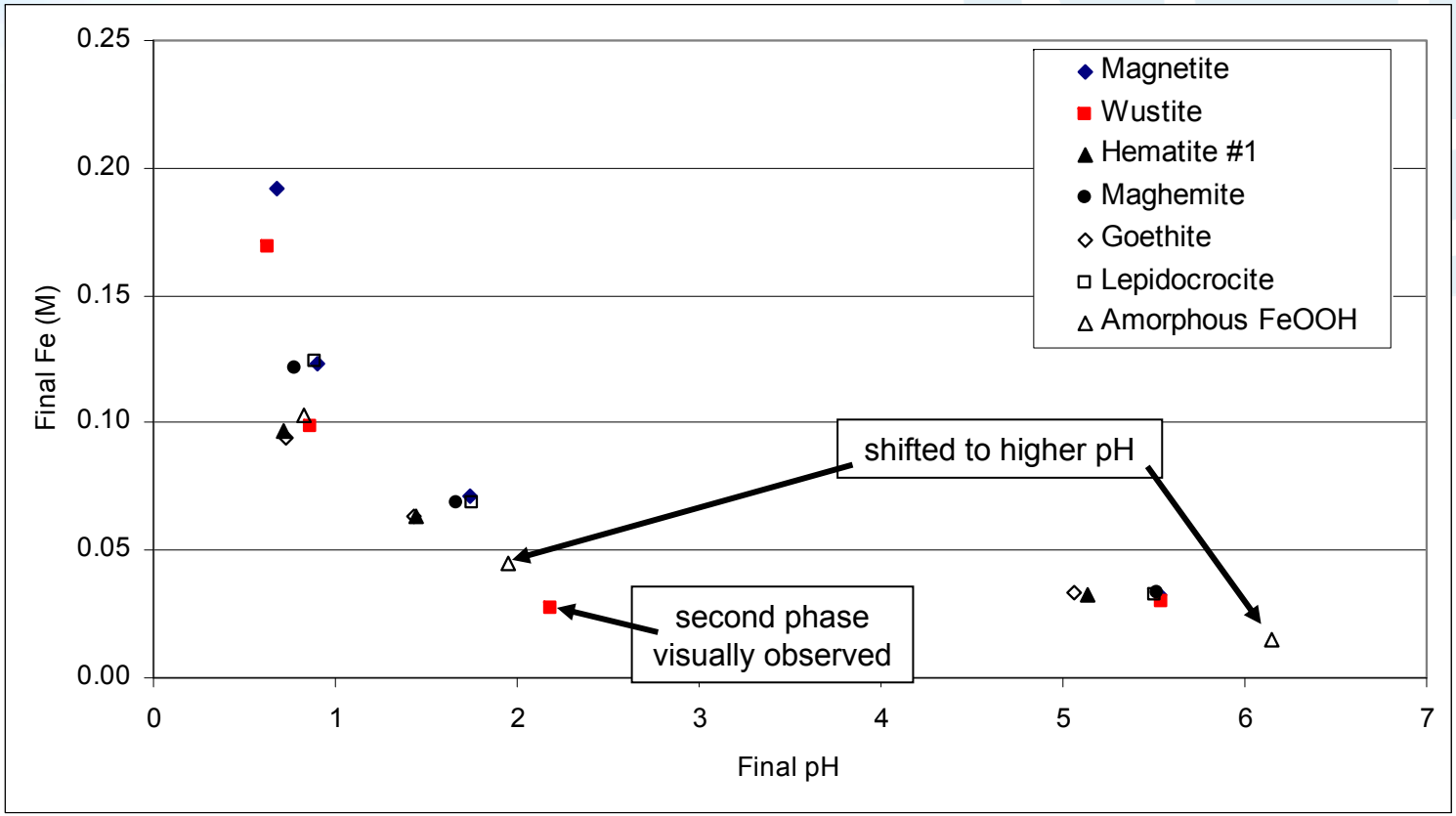
- **0.11 M complexing acids (1 wt. % OA) unless otherwise indicated**
- **0-1.0 M HNO_3, 0-1.0 M H_2SO_4, 0-0.1 M NaOH (mixtures with complexing acids)**
- **Primary solid phases studied: hematite (Fe_2O_3) and gibbsite ($Al(OH)_3$)**
- **Liquid:solid mass ratios**
  - 1 wt. % OA and other 0.11 M complexing acids - 50:1
  - 4 wt. % OA - 10:1
  - 8 wt. % OA - 5:1
- **Teflon bottles**
- **Temperature: 50 ºC (25 and 70 ºC tested previously)**
- **Orbital rotation at 250 RPM**
- **Contact time: 5-6 weeks**
- **Samples maintained in dark throughout testing and during analysis transport**
- **Analysis sub-samples filtered at temperature directly into 3 M HNO_3**

Hematite Solubility in Various Complexing Acids



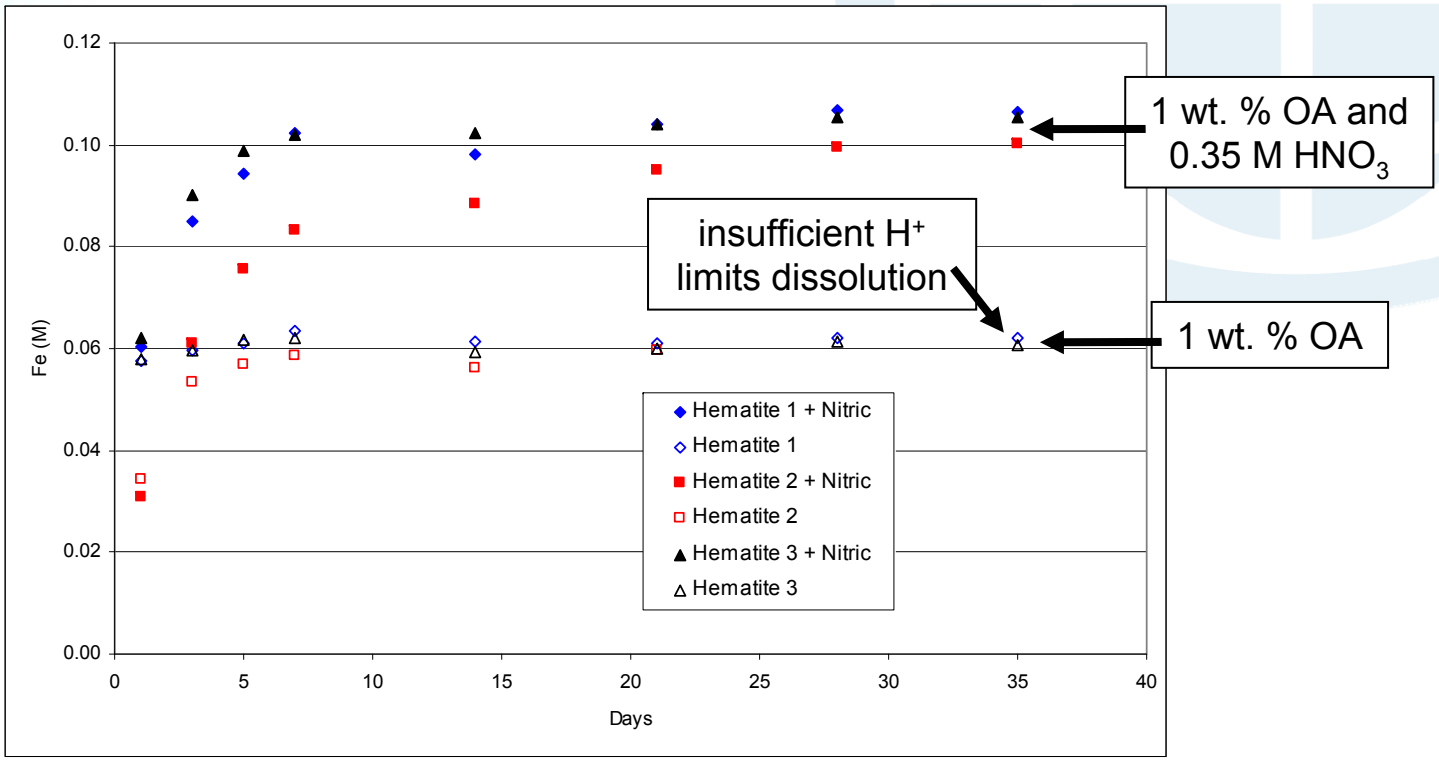
- **Oxalic acid strongest acid of group**
- **Conjugate base salts more soluble for alternative acids**
- **Needed direct comparison of various complexing acids at similar pH**
- **Oxalic acid clearly best acid across pH range**

Solubility of Various Iron Phases in 1 wt. % Oxalic Acid



- **Generally comparable trends for all phases**
- **Wustite (FeO) solubility in pure OA limited by ferrous oxalate solubility**
- **Hematite least soluble phase in oxalic/nitric mixtures**

Hematite Dissolution Kinetics in OA and OA/Nitric Mixtures

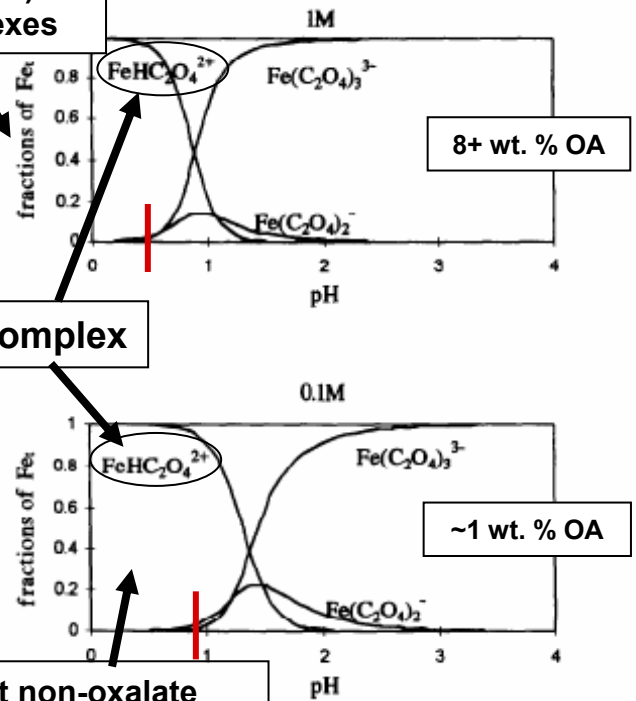


- 90% dissolution observed within 2 to 3 weeks
- Slower kinetics with largest particle size (#2)
- Final iron concentration nearly 50% lower with OA only
- Hematite dissolution kinetics slower than other iron phases (not shown)
- Dissolution kinetics acceptable for tank cleaning applications

Optimal pH for Iron (III) Phases in Various Oxalic Acid Concentrations

optimal pH (indicated by red line) shifts to higher pH with lower OA

fraction of iron (III) as oxalate complexes



8+ wt. % OA

preferred 1:1 complex

~1 wt. % OA

models predict non-oxalate complexes contribute at lower pH

Thermodynamic modeling
Panias, 1996

- Fe:oxalate stoichiometry changes from 3:1 to 1:1 across narrow pH range
- Goal: Provide sufficient H^+ to form $FeHC_2O_4^{2+}$ while promoting acceptable tank corrosion
- Optimal pH decreases from ~1.5 to 0.5 when [OA] increases from 0.01 to 1 M
- need supplemental H^+ source, cannot optimize with pure OA
- 3 fold efficiency increase by controlling pH with supplemental acid

Expected Fe Concentrations at Low pH

$$Fe_2O_3\,(s) + 2H_2C_2O_4\,(aq) + 4H^+\,(aq) \rightarrow 2FeHC_2O_4^{2+}\,(aq) + 3H_2O$$

hematite — mono-bioxalate

preferred 1:1 complex

Fe:oxalate:H = 1:1:2 (excluding OA protons)

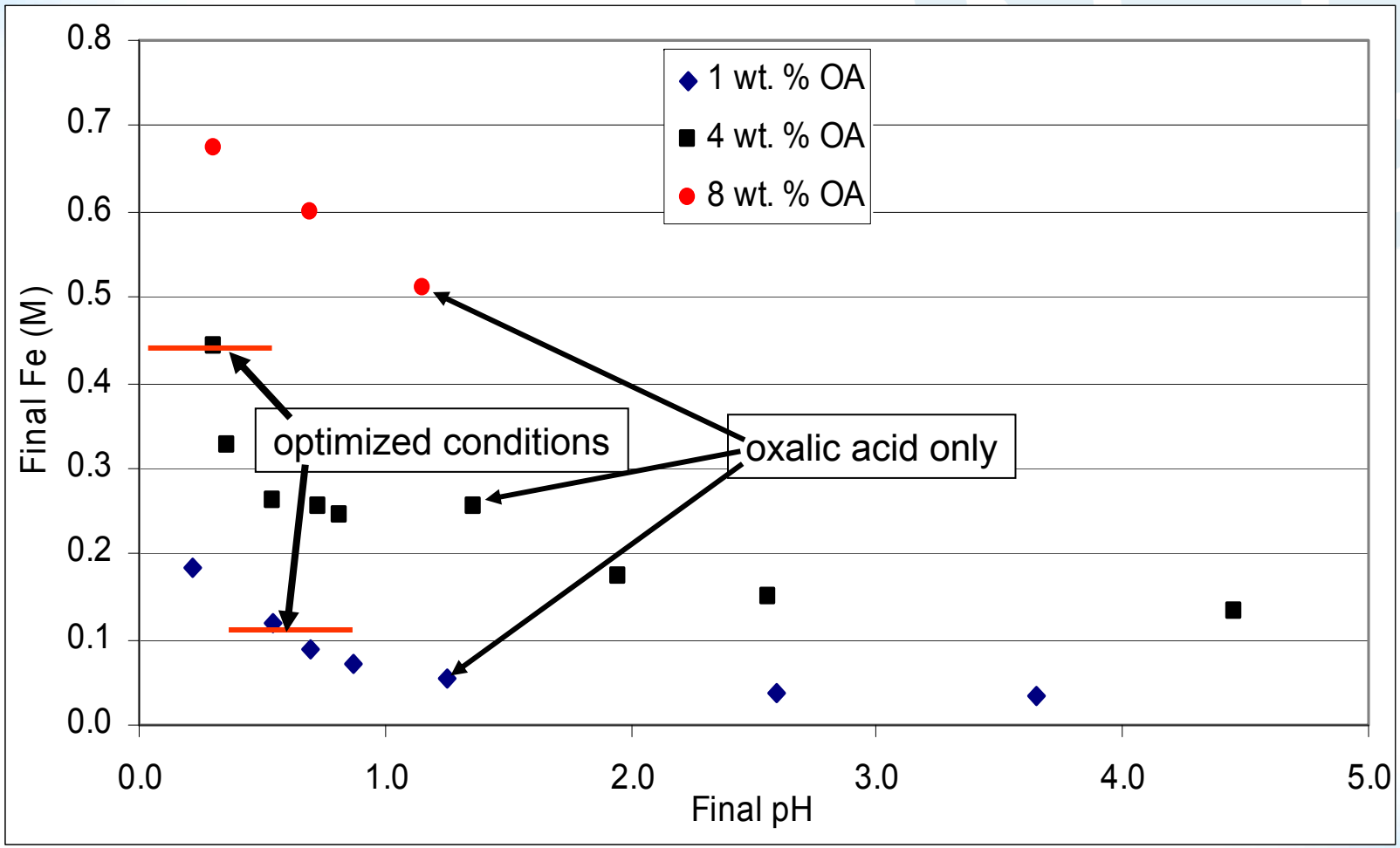
assuming 1:1 molar ratio

OA (wt. %)	OA (M)	Fe (M)	Supplemental H^+ (M)
8	0.92	0.92	2.16
4	0.45	0.45	1.10
1	0.11	0.11	0.32

2 x [OA] + 0.1 M

to maintain pH 1

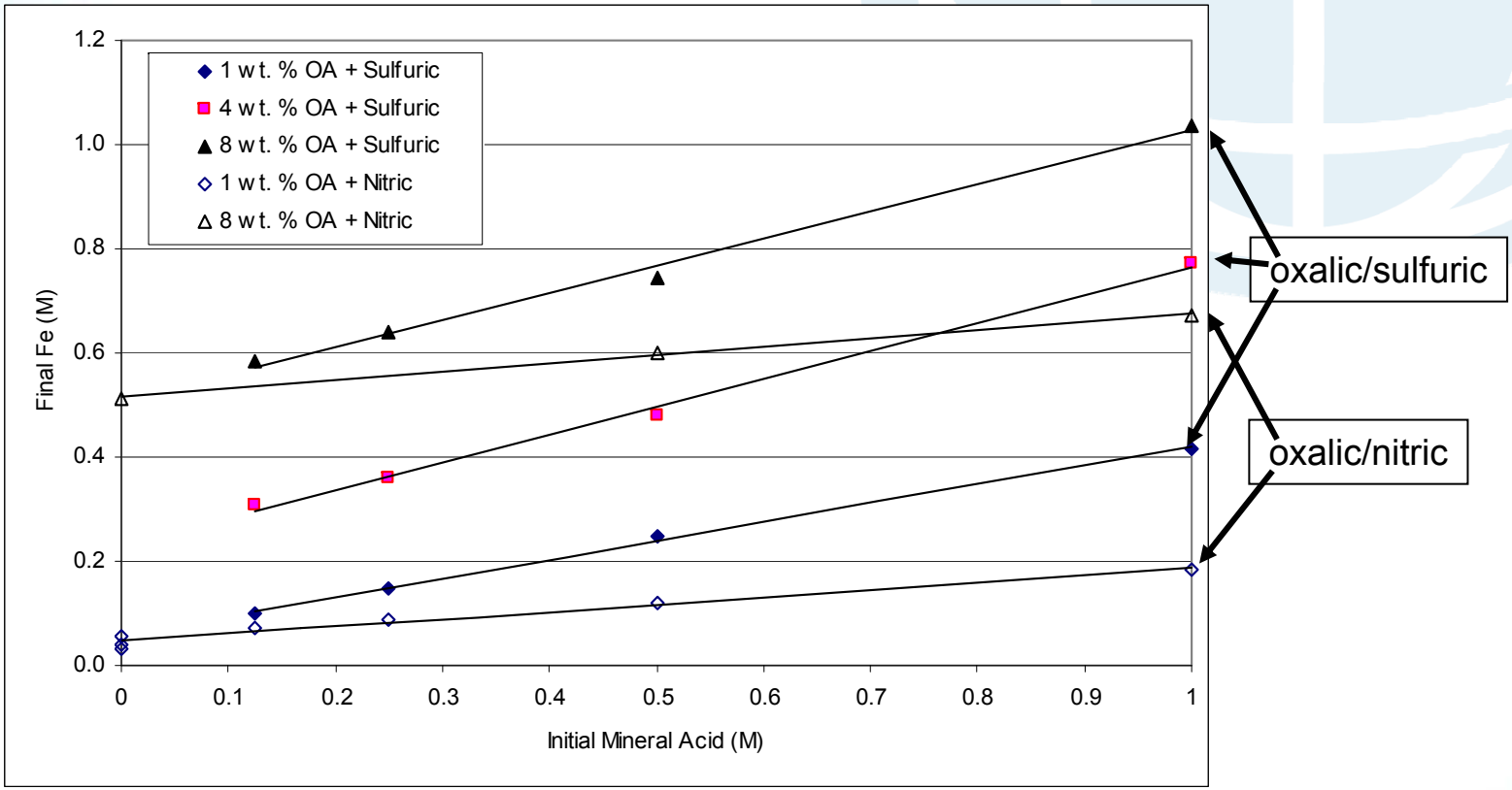
Hematite Dissolution Versus pH in Various OA Conc.



Comments on pH Control Tests with Hematite and OA

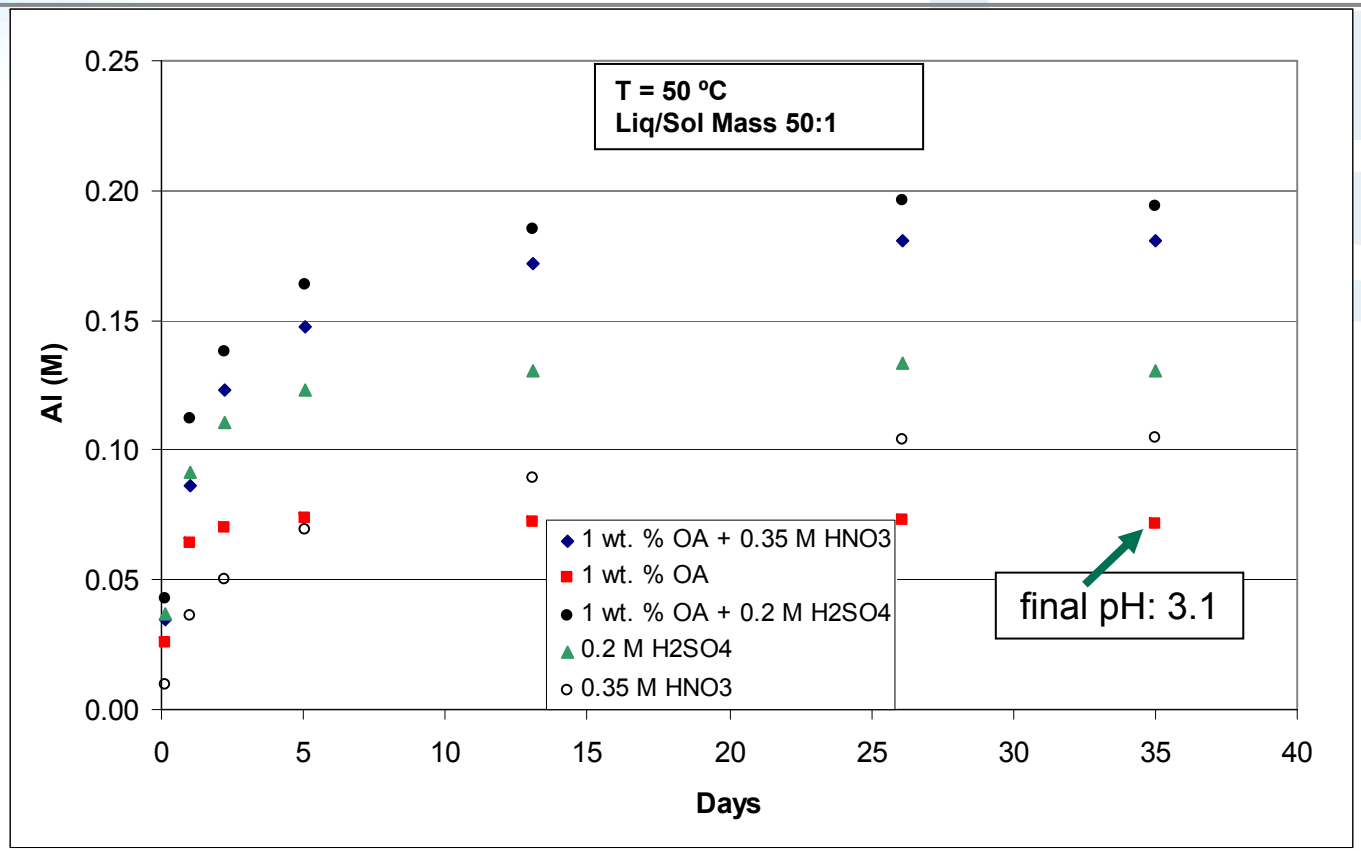
- 1.0 M nitric acid insufficient for optimization in 8 wt. % OA, but sufficient for 4 wt. % OA
- 0.25-0.5 M nitric acid needed to maximize oxalate usage in 1 wt. % OA
- Results consistent with calculations
- Nitric acid concentrations required to maximize oxalate usage in 4 and 8 wt. % OA likely to promote unacceptable corrosion - dilute OA needed
- 51-57% of optimized iron concentrations observed in pure oxalic acids - supplemental acid needed
- OLI model predictions generally consistent with trends observed
  - **Over predicts solubility in oxalic/nitric acid mixtures**
  - **pH dependence slightly off at low pH**
  - **Accurate predictions with oxalic/sulfuric acid mixtures**

Hematite Dissolution - Nitric Versus Sulfuric Acid



- **Sulfuric acid approximately twice as effective as nitric acid on molar basis**
- **Solubility in acid mixtures greater than sum of individual acids (synergistic effect)**
- **For 1 wt. % OA, 0.35 M HNO_3 or 0.2 M H_2SO_4 selected for optimization**

Gibbsite Dissolution Kinetics in Various Acid Mixtures



- **Sulfuric outperforms nitric even though nearly half concentration**
- **≥95% dissolution within 2 weeks except for nitric only (85%)**
- **Solubility in mixtures approximately sum of individual acids**

Aluminum Phase Dissolution

- Oxalic acid and oxalic/mineral acid mixtures effectively dissolve gibbsite
- Boehmite dissolution in dilute/moderate acid concentrations only practical at elevated temperatures (70 ºC) where tank corrosion rates high
- Dissolution of more refractory Al phases probably requires caustic wash

Gibbsite: $Al(OH)_3$
Boehmite: AlOOH

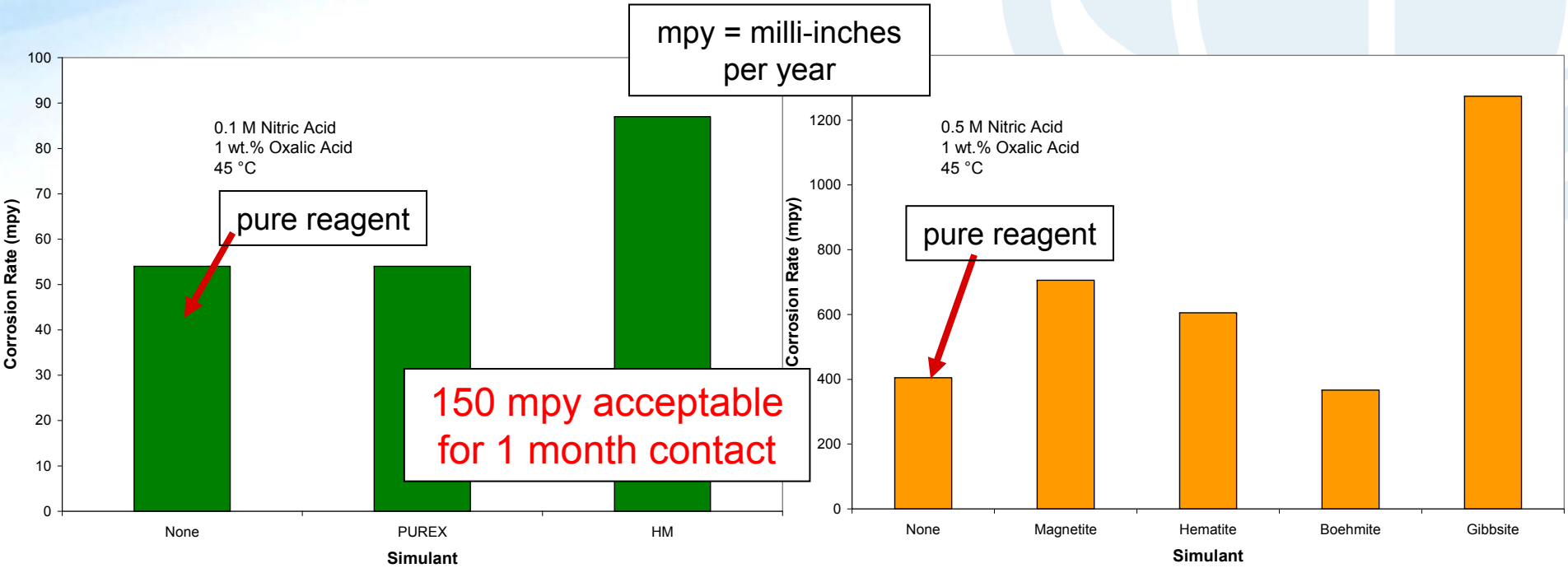
Potential Advantages of Using OA/Mineral Acid Mixtures

- Easier pH control
- Not using OA for base neutralization and pH control
- Optimization and oxalate minimization
- Several metals exist as free ions at low pH rather than oxalate complexes at low pH: Fe^{2+}, Fe^{3+} (partial), Al^{3+}
- Increased solubility of ferrous oxalate, $Fe(C_2O_4)$
- Solubility of Mn and Ni in actual Tank 5 residuals (post OA strike) observed to increase in 0.25 M HNO_3

Corrosion Test Conditions

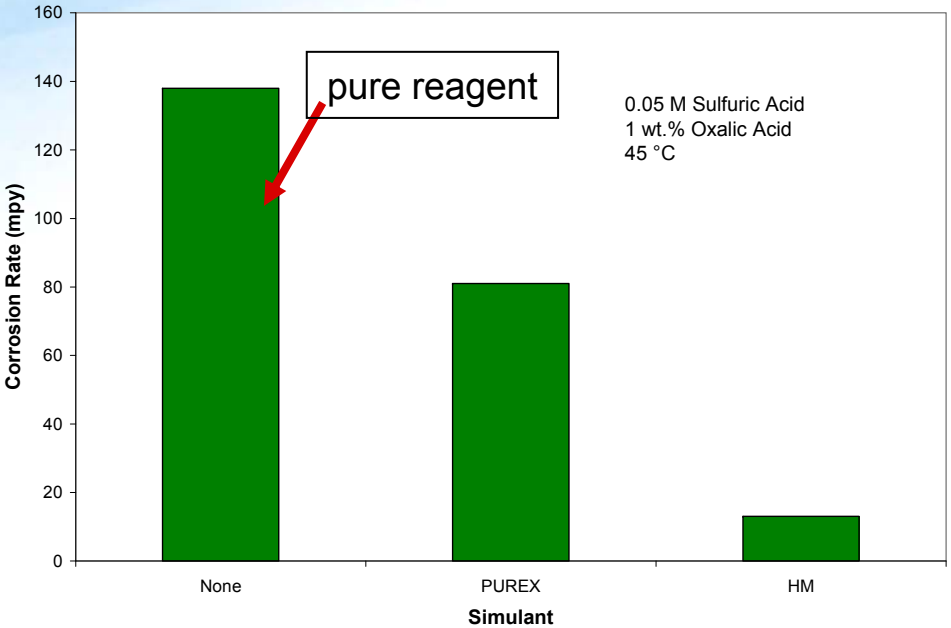
- **Acid mixtures evaluated:**
  - 1 wt. % OA with 0.1 and 0.5 M HNO_3
  - 1 wt. % OA with 0.05 and 0.25 M H_2SO_4
- **Pure reagent solutions and solutions pre-equilibrated with solid phases**
- **Solid phases: hematite, gibbsite, PUREX and HM sludge simulants**
- **Liquid:solid mass ratio 50:1**
- **Temperature: 45 and 75 ºC**
- **Stirred**
- **Light excluded**
- **Linear Polarization Resistance (LPR) following ASTM G59-97**
- **Electrodes: ASTM A285, Grade C carbon steel similar to tank wall material**

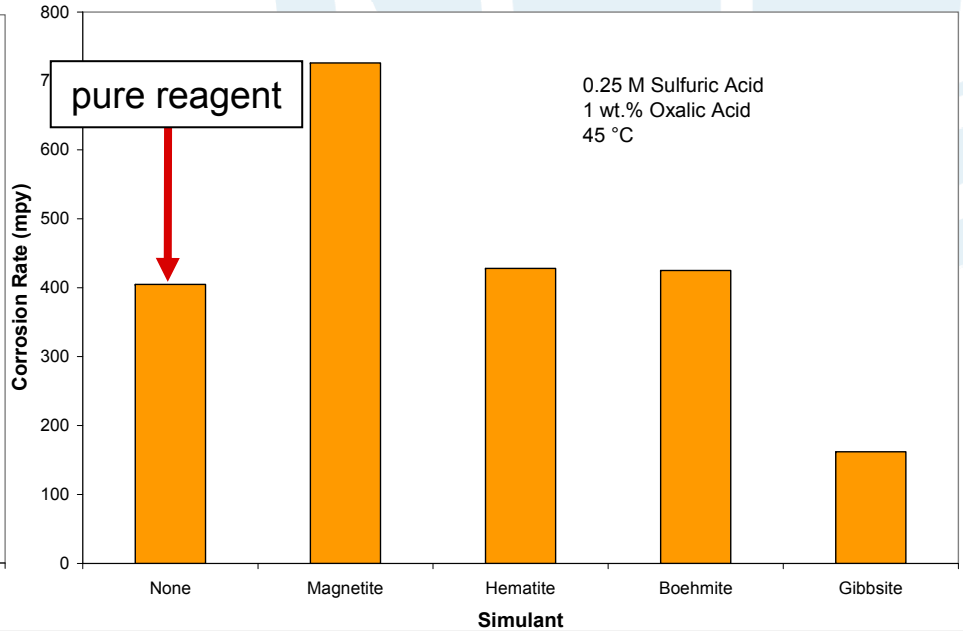
Electrochemical Corrosion Studies - OA/Nitric Mixtures



- Manageable corrosion rates with 0.1 M HNO_3 at 45 ºC
- High corrosion rates at 75 ºC (not shown) and with 0.5 M HNO_3 at 45 ºC
- Solid phases impacted results
- Hydrogen generation rates appear low

Electrochemical Corrosion Studies - OA/Sulfuric Mixtures





- Manageable corrosion rates and mild localized pitting with 0.05 M H_2SO_4 at 45 ºC
- High corrosion rates at 75 ºC (not shown) and with 0.25 M H_2SO_4 at 45 ºC
- Solid phases impacted results
- Hydrogen generation rates appear low

Conclusions

- Oxalic acid preferred cleaning reagent
- Hematite most challenging iron phase, but dissolution occurs within acceptable time scale
- pH control with mineral acids can be used to optimize iron phase dissolution in OA, but dilute conditions required to minimize corrosion
- Manageable corrosion with low mineral acid concentrations at 45 ºC
- Optimization should lead to significant reductions in total oxalate required
- Recommend preliminary heel washing with dilute mineral acid to neutralize base equivalents and dissolve some metals (such as Al)
- Proposed optimized conditions: 0.055 M OA (0.5 wt. %) with 0.18 M HNO_3 or 0.09 M H_2SO_4 (initial focus on nitric)
- General trends consistent with OLI model predictions, but model improvements recommended

Path Forward

- Solubility and corrosion testing of dilute optimized conditions (0.055 M OA)
- Dissolution testing of mixed pure phases (gibbsite/hematite)
- Real waste dissolution testing
- Pure phase testing of secondary metals
- Dissolution methods for unique heel compositions and problematic metals
- Hanford white paper and simulant testing

Reports

- Systems Engineering Evaluation - Martino, C. J. SRNL-L3100-2009-00118, June 2009.
- Literature Review - Hay, M. S.; *et. al.* SRNL-STI-2009-00500, August 2009.
- FY09 Experimental Results - King, W. D.; *et. al.* SRNL-STI-2009-00791, February 2010.
- 2010 WM Proceedings manuscript - Hay, M. S., *et. al.* SRNL-STI-2009-00510, March 2010.
- FY2010 Corrosion Study Results - Wiersma, B. J. SRNL-STI-2010-00555, September 2010.
- FY2010 Basic Studies Results - King, W. D.; *et. al.* SRNL-STI-2010-00541, under review.