EM-21 Alternative Enhanced Chemical Cleaning Program for Sludge Heel Removal - 10308

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ABSTRACT

Preliminary studies in the EM-21 Alternative Chemical Cleaning Program have focused on understanding the dissolution of Hematite (a primary sludge heel phase) in oxalic acid, with a focus on minimizing oxalic acid usage. Literature reviews, thermodynamic modeling, and experimental results have all confirmed that pH control, preferably using a supplemental proton source, is critical to oxalate minimization. With pH control, iron concentrations as high as 0.103 M have been obtained in 0.11 M oxalic acid. This is consistent with the formation of a 1:1 (iron:oxalate) complex. The solubility of Hematite in oxalic acid has been confirmed to increase by a factor of 3 when the final solution pH decreases from 5 to below 1. This is consistent with literature predictions of a shift in speciation from a 1:3 to 1:1 as the pH is lowered. Above a solution pH of 6, little Hematite dissolves. These results emphasize the importance of pH control in optimizing Hematite dissolution in oxalic acid.

INTRODUCTION

As efforts continue at US Department of Energy Sites (primarily in Hanford, WA and Aiken, SC) to treat and dispose of millions of gallons of legacy radioactive materials from the production of nuclear weapons, non-compliant waste storage tanks will gradually be emptied of the bulk waste volume leaving heel materials requiring removal prior to tank closure. The waste heel slurries are distributed on the floor of large tanks which frequently contain numerous obstructions that limit the effectiveness of mechanical removal methods. As a result, chemical dissolution methods are needed for the effective removal of the heels. Oxalic acid has been considered as the preferred cleaning reagent for heel dissolution, particularly for iron-based sludges, due to the strong complexing strength of oxalate and the lower corrosion rates with carbon steel compared to mineral acids. Several recent literature reviews [1-3] and a Systems Engineering Evaluation [4] have considered the various known methods for sludge dissolution, and oxalic acid remains the chemical dissolution reagent of choice. Oxalic acid is an industry standard used for the cleaning and maintenance of nuclear power plants, although these operations often involve the removal of chemical scales with dilute acid and regeneration of the acid.[5] Waste tanks at the Savannah River Site (SRS) in Aiken, SC can contain sludge and salt heel volumes approaching 5,000 gallons at the conclusion of bulk waste removal and heel washing campaigns. The addition of oxalic acid and the subsequent

addition of sodium hydroxide (required after heel removal to make the waste stream compatible with interim storage vessels) has significant impacts on downstream waste processing facilities. The current baseline chemical cleaning process for heel removal at SRS involves the addition of concentrated (8 wt. %) oxalic acid directly to the waste tanks in several treatment cycles. Concentrated oxalic acid is preferred because available tank farm volume is limited and evaporation to remove excess liquid is expensive. The large mass of waste requiring treatment makes the utilization of traditional techniques such as ion exchange for acid regeneration impractical. As a result, sludge dissolution with oxalic acid using the baseline technology involves the addition of large amounts of oxalate to the tank farm inventory, although the process has not been optimized to minimize oxalate usage.

The baseline chemical cleaning method was recently used for heel removal in two SRS waste tanks with limited success.[6] Lower than expected amounts of solids were removed from the tanks in each case. The results indicate that a better understanding of sludge dissolution chemistry with oxalic acid is needed in order to achieve more consistent and effective results. It is also known that the baseline process cannot be implemented in all waste tanks planned for closure because of the large additions of oxalate and sodium involved. Given that numerous waste tanks are targeted for closure within the next decade, there is an urgent need to understand and optimize the chemical cleaning process for heel removal. Although much information has been reported in the literature regarding the dissolution of iron oxide materials using oxalic acid [7], the work typically involves mechanistic studies under dilute conditions rather than the concentrated and possibly saturated conditions expected in SRS waste tanks. A chemical cleaning process for sludge heel removal involving an oxalate destruction technology is currently being designed for implementation at SRS. In a separate effort, the Savannah River National Laboratory (SRNL) is working to refine the baseline chemical cleaning process to optimize sludge dissolution. This effort involves evaluations of various acids and combinations of acids for sludge dissolution with an emphasis on oxalic acid. The work is being conducted as part of the EM-21 Alternative Enhanced Chemical Cleaning Program which is focused on developing technologies for sludge heel removal.

Iron and aluminum are two of the most common chemical constituents of SRS waste tank heels, although numerous other insoluble metal oxides are also present to varying degrees depending on the tank history. The residual liquid portion of the sludge is dilute alkaline solution remaining after washing campaigns intended to remove soluble waste components. Most of the metals present in the heels exist as oxides, hydroxides, and oxy-hydroxides. In many cases these materials have been stored and aged for many years in an alkaline environment at elevated temperatures in the presence of concentrated sodium salt solutions. The metal oxidation states and phases vary. The effectiveness of sludge dissolution methods is dependent upon the crystalline phases present in the waste. The body of XRD data for waste tank sludge is limited, but efforts are underway to obtain additional data. Common aluminum phases observed thus far include Gibbsite ($AlOH_3$) and Boehmite ($AlOOH$). Common iron phases include Hematite (Fe_2O_3) and Magnetite (Fe_3O_4) and it is believed that iron exists primarily as Fe^{3+}, with Fe^{2+} contributing to a minor degree. Hematite is a primary iron phase observed in SRS sludge
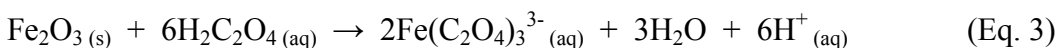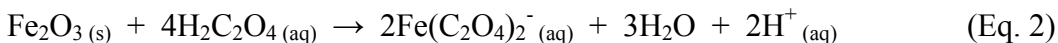
that is known to be refractory. Solubility testing reported herein focuses on Hematite dissolution in nitric acid, oxalic acid, and acid mixtures. For aluminum, a dissolution method has already been developed involving sludge contact with highly alkaline solutions.[8] The dissolution of aluminum in acid is limited in effectiveness due to concentration limits imposed as a result of tank corrosion concerns. Results of testing focused on the acid-side dissolution of aluminum phases have been reported separately.[9]

Waste sludge heels contain significant base equivalents contributed by residual hydroxide as well as various undissolved salts which must be neutralized prior to or during waste treatment with oxalic acid. Under conditions where there is a need to minimize oxalate additions it is likely important to ensure that oxalic acid is being utilized primarily for metal complexation rather than as a proton source. Other acids with minimal downstream effects should be used for sludge neutralization. As a result, Hematite dissolution in nitric acid was also evaluated at mild to moderate concentrations ($\leq$1 M). Concentrations exceeding 1 M were considered impractical due to tank corrosion concerns. It is not known at this time what concentration limits will be imposed for nitric acid during sludge heel removal operations from noncompliant waste tanks scheduled for closure. Besides providing acid equivalents for sludge neutralization, there is a need for an additional proton source to assist in and optimize sludge dissolution with oxalic acid. The Hematite dissolution reaction shown in Equation 1 reveals the importance of providing sufficient H^+ to promote dissolution and oxalate complex formation. The monobioxalate iron dication complex, $FeHC_2O_4^{2+}$, is believed to be a primary species present in the Fe^{3+}-oxalate system at low pH.[10] Two equivalents of protons are needed for every oxalic acid molecule and every iron atom to promote complex formation and iron dissolution. Note that these protons are needed in addition to those provided by oxalic acid. For the formation of this complex, these protons must be provided by excess oxalic acid, or by an alternative acid source. Alternatively, the mono-oxalate complex, $FeC_2O_4^+$, could form, which requires only one equivalent of additional H^+ for the dissolution of each iron atom. Regardless of which species is involved, the most efficient dissolution of iron-based sludge heels, requires a supplemental proton source such as nitric acid.

$$Fe_2O_{3\,(s)} + 2H_2C_2O_{4\,(aq)} + 4H^+_{\,(aq)} \rightarrow 2FeHC_2O_4^{2+}_{\,(aq)} + 3H_2O \qquad \text{(Eq. 1)}$$
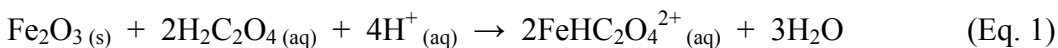
Based on the dissertation of Lee [10], iron speciation in solution may also be manipulated by controlling the pH. For the Fe^{3+}-oxalate system with 1 wt. % oxalic acid, it is believed that the iron exists almost entirely as the monobioxalate complex, $FeHC_2O_4^{2+}$, at a pH below 0.9. Above pH 2, the iron exists almost exclusively as the trioxalate, trianion complex, $Fe(C_2O_4)_3^{3-}$. At intermediate pH values between 1 and 2, the iron exists as a mixture of the monobioxalate, the trioxalate, and the dioxalate complex, $Fe(C_2O_4)_2^-$. Therefore it is expected that the mole ratio of iron: oxalate in solution changes from 1:3 to 1:1 as the pH is lowered from 2 to below 1. Obviously the 1:1 complex is preferred in the case where the goal is to minimize oxalate usage. The formation of the dioxalate and trioxalate complexes from Hematite do not require the addition of excess acid, since more than enough protons are provided by the oxalic acid needed for complexation, as shown

below (Eqs. 2 and 3). These observations indicate that lower pH is preferred for iron dissolution with oxalic acid and pH monitoring and control may be important for process optimization. These features of iron-oxalate chemistry were not fully appreciated during previous chemical cleaning efforts at SRS with oxalic acid.

$$Fe_2O_{3\,(s)}\ +\ 4H_2C_2O_{4\,(aq)}\ \rightarrow\ 2Fe(C_2O_4)_2^-{}_{(aq)}\ +\ 3H_2O\ +\ 2H^+{}_{(aq)} \qquad (Eq.\ 2)$$

$$Fe_2O_{3\,(s)}\ +\ 6H_2C_2O_{4\,(aq)}\ \rightarrow\ 2Fe(C_2O_4)_3^{3-}{}_{(aq)}\ +\ 3H_2O\ +\ 6H^+{}_{(aq)} \qquad (Eq.\ 3)$$

EXPERIMENTAL DETAILS AND MODELING APPROACH

Hematite (Fe_2O_3) and oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$) solid reagents and concentrated nitric acid solutions were purchased commercially and confirmed to be pure by analysis. The Hematite was phase pure by XRD and contained 65.4 wt. % Fe (theoretical: 69.9 wt. %) with trace amounts (<0.5 wt. % for each element) of Si, S, Ca, and Cr. The mass of Hematite reagent used for individual tests was corrected for sorbed water, although the water content was typically small (<1 wt. %). Solubility testing involved simple batch contacts with known amounts of liquid and solid. Samples were continuously maintained in incubator shaker ovens at the target temperatures (25-70 ºC) and agitated at 250 RPM. Prior to sample manipulations (sampling or pH adjustment) the agitation was stopped so that the solids could settle. Sampling and pH monitoring and adjustment were conducted out of the oven in a chemical hood. All sample manipulations were conducted quickly (within 2-3 minutes) prior to sample cooling. Solution pH was monitored using calibrated pH probes. Sample pH adjustments were conducted using 1 or 3 M nitric acid solutions. Tests were continued for several weeks, while the pH was monitored and adjusted (as needed). No tests were stopped or analytical sub-samples collected until the test samples were observed during inspection and measurement to have remained stable for at least a week. Characteristics of stable samples included no visual changes in the amount of solids present or the solution color and minimal changes in the measured pH. Analytical sample bottles were prepared by the addition of known masses (typically 6 g) of 3 M nitric acid. Sub-samples of solution from each test sample were then collected and filtered through a 0.45 μm nylon syringe filter at temperature directly into the bottles containing nitric acid. The mass of each filtered sub-sample added to the bottles (typically 2 g) was determined by difference and recorded for the calculation of dilution factors. Visual inspection of each acidified sample confirmed that no precipitates had formed upon dilution. Analytical samples were transported and stored in closed buckets to avoid light exposure.

In order to evaluate the effects of pH on Hematite dissolution with oxalic acid, solutions were prepared with varying initial pH values. For most samples the ionic strength was held constant by the addition of either sodium chloride or sodium nitrate background salt. Both nitrate and chloride salts were tested due to concerns that the chloride salt used for initial tests could promote iron dissolution via halide complexation and impact the results. Background nitrate is also more representative of SRS waste tank conditions. The total sodium concentration for all samples was 0.22 M. Sodium hydroxide was used to generate solutions with the target pH in all cases but one, where it was necessary to use

0.5 M nitric acid. The nitric acid based solution therefore had a different ionic strength than the other solutions due to the presence of the added acid.

A model was developed using the OLI Systems Inc, Environmental Simulation Program (ESP) version 8.1 to evaluate the ability of the software to predict the experimental results. The model contained two sequential Mix blocks with the first block combining an acid solution stream with a solids only stream of the mineral phase of interest. The output of this first Mix block became an input to the second Mix block. The second Mix block allowed addition of an acid or base solution to adjust pH of the mixture from the first Mix block. This model construct seemed the most direct way to simulate the methodology used in the experiments. The chemistry model for the simulations included the GEOCHEM database as the source for the iron compounds hematite and magnetite.

RESULTS AND DISCUSSION

Initial evaluations of Hematite dissolution in acid involved solubility tests at 50 ºC using oxalic and nitric acids at concentrations ranging from 0.1 to 1 M. Results are provided in Figure 1. Oxalic acid is clearly superior to nitric acid for Hematite dissolution, as expected. In 0.92 M oxalic acid the equilibrium iron concentration approaches 0.5 M, while the iron concentration in 1 M nitric was less than 0.1 M. For both acids the equilibrium iron concentrations increased nearly linearly versus the acid molarity, with the slope being significantly higher for oxalic acid. A nitric acid concentration of 0.125 M results in very little hematite dissolution (equilibrium [Fe]: 0.002 M). Using nitric acid to control the pH to near 1 during oxalic acid dissolution of Hematite is therefore expected to increase the equilibrium iron concentration primarily by providing additional protons and thereby shifting the speciation toward the 1:1 complex (as shown in Eq. 1).

The ESP model predictions of the equilibrium iron concentrations expected for Hematite versus pH in 1 wt. % (0.11 M) oxalic acid are provided in Figure 2 along with the predicted iron speciation at various pH values. The speciation is similar to that predicted by Lee [10] except that the 1:1 complex is assumed to be the oxalate complex, $Fe(C_2O_4)^+$, rather than the bioxalate complex. The pH dependence predicted by the model differs from the predictions of Lee, with the model predictions being offset to about 1 pH unit higher. The model predicts that the 1:3 complex dominates at a pH ≥ 3.5 and the 1:1 complex dominates at a pH ≤ 1.8. The model predicts that the equilibrium iron concentrations increases by a factor of three as the pH is decreased from 4 to near 1.5 due to shifts in the iron-oxalate speciation from the 1:3 complex to the 1:1 complex. Near pH 1, iron concentrations near 0.11 M (assuming stoichiometric reaction with the available oxalate) are expected. At a pH near 0.8 the model predicts that 33% of the soluble iron exists as uncomplexed Fe^{3+}. The solubility predictions at pH <1 assume that nitric acid has been used to lower the pH. Separate modeling evaluations of Hematite solubility in nitric acid have revealed that the model over predicts equilibrium iron concentrations in nitric acid by a factor of about 2. As a result, the dramatic increase in soluble iron below pH 1 is believed to be incorrect. Regardless of these discrepancies, there is agreement between the model and experimental data that dramatic increases in solubility are expected at lower pH.

Solubility studies were conducted using 1 wt. % (0.11 M) oxalic acid and 0.22 M NaNO$_3$ background salt at various final pH values to determine the impact of pH on Hematite solubility. Results are provided in Figure 3 along with the model predictions. At a constant oxalate concentration the equilibrium iron molarity increased from 0.001 to 0.09 M as the final solution pH was decreased from 6.6 to 0.5. Based on these results, pH dramatically impacts the effectiveness of oxalic acid for Hematite dissolution, as expected. A pH below 6 is necessary to promote significant dissolution. Approximately a 3 fold increase in the equilibrium iron concentration was observed when the pH was decreased from 5 to below 1. The calculated oxalate to dissolved iron molar ratios for various experimental data points are provided in Figure 4 versus the final measured pH. It is apparent from this plot that a mono-oxalate or mono-bioxalate complex is dominant below pH 1 while a trioxalate complex dominates near pH 3.5. At pH 5 and above, significant uncomplexed oxalate is present as indicated by molar ratios exceeding 3. At a final pH of 6.6 the calculated molar ratio is 84, indicating that most of the oxalate in solution exists as the free anion and is ineffective at dissolving Hematite. This observation is not surprising given Eqs. 1 through 3.

The model predictions shown in Figure 3 are quite consistent with the experimental data above pH 3, but are much higher than the data below pH 3. It is believed that the discrepancy at low pH results from several factors. Separate tests have shown that experimental results which are more consistent with model predictions can be obtained at lower pH if lower phase ratios (oxalic acid:Hematite) are used. This could be a consequence of the presence of small amounts of more refractory phases in the Hematite reagent. The low pH data (≤2.5) used for Figure 2 involved >70% solids dissolution. In separate tests using excess solids involving only 37 wt. % solids dissolution the predicted final iron concentration was 0.106 M versus the observed value of 0.103 M. The predicted final pH for this test was 1.0 and the measured value was 0.9. This iron concentration approaches stoichiometric levels expected for the formation of a 1:1 complex. At lower phase ratios, where excess iron is available for complexation, higher iron concentrations (near stoichiometric) may result due to the presence of excess soluble Fe$_2$O$_3$. As discussed previously, the model also appears to over-predict Hematite solubility in nitric acid and these test solutions contained sodium nitrate background salt in acid. Both of these factors likely contributed to the high predicted values for the model at low pH. Additional testing is planned to resolve the discrepancies between the predicted and observed values at low pH and determined whether the predictions of Lee or those generated with the OLI model are more accurate.

CONCLUSIONS

Based on these results the following conclusions can be drawn:

- Hematite dissolution in oxalic acid is a stoichiometric process dependant upon the provision of sufficient oxalate molar equivalents to complex the iron and H$^+$ to react with the oxide (O^{2-})

- optimal utilization of oxalic acid for Hematite (a primary sludge phase) dissolution requires an additional proton source at low pH, such as nitric acid, in the absence of a supplemental proton source, greater than stoichiometric amounts of oxalate are required
- solution pH control dramatically effects the efficiency of Hematite dissolution in oxalic acid with pH values ≤1 being preferred due to the formation of a 1:1 iron:oxalate complex, above pH 6 little iron complexation or Hematite dissolution occurs
- the OLI Thermodynamic Model is a useful tool for the prediction of equilibrium iron concentrations, but predictions must be experimentally verified
- minimization of oxalate consumption during sludge heel chemical cleaning is possible through the use of other acids for neutralization and pH control
- dissolution of other Fe^{3+} phases in oxalic acid should behave similarly, although supplemental acid requirements should be lower for mixed oxy/hydroxide phases such as $Fe(O)OH$
- pH control should be considered in future chemical cleaning efforts for the removal of sludge heels

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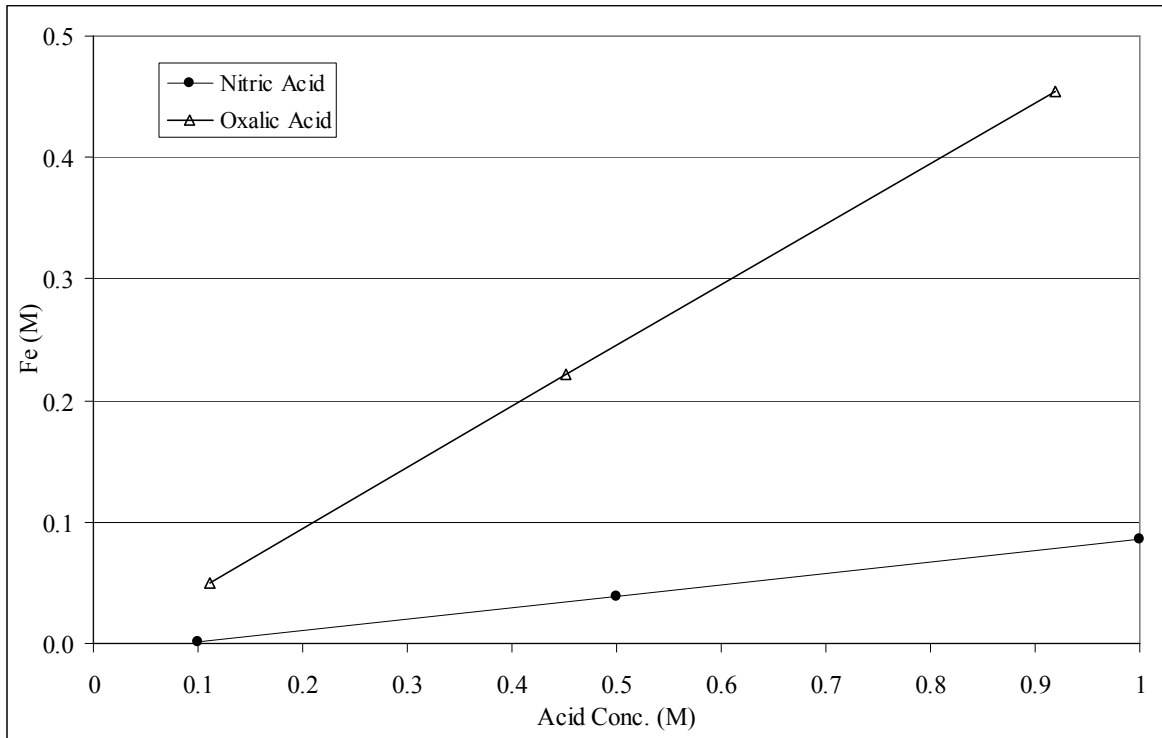
Figure 1. Hematite Solubility Versus Concentration in Nitric and Oxalic Acids at 50 ℃ (pH ~1).
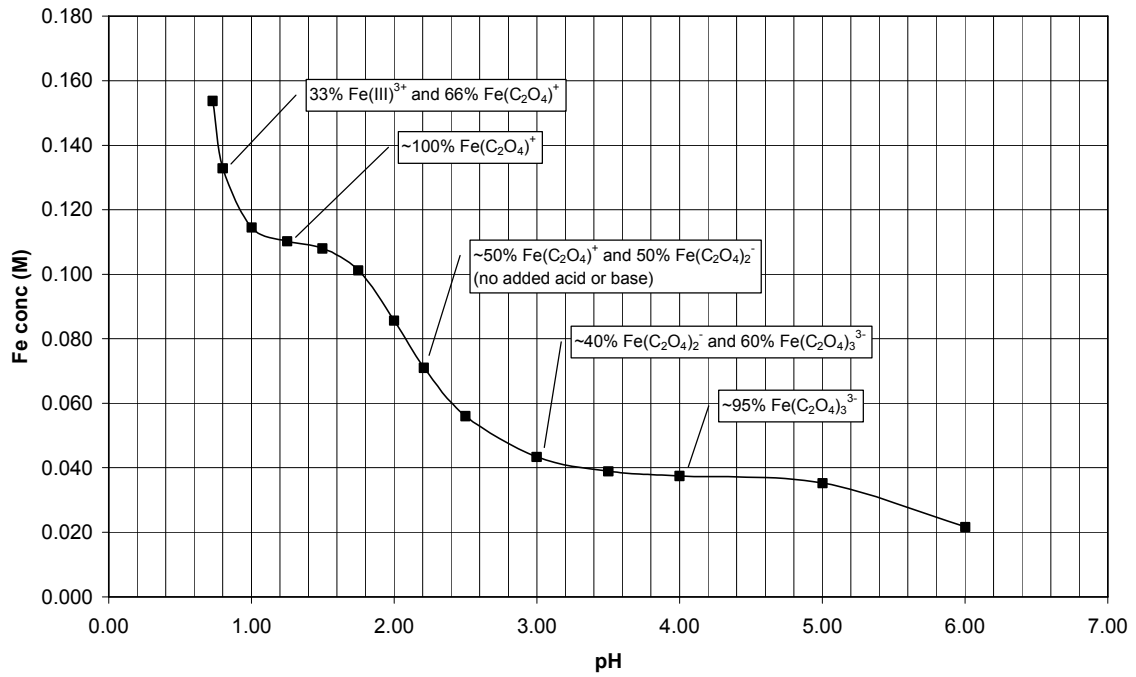
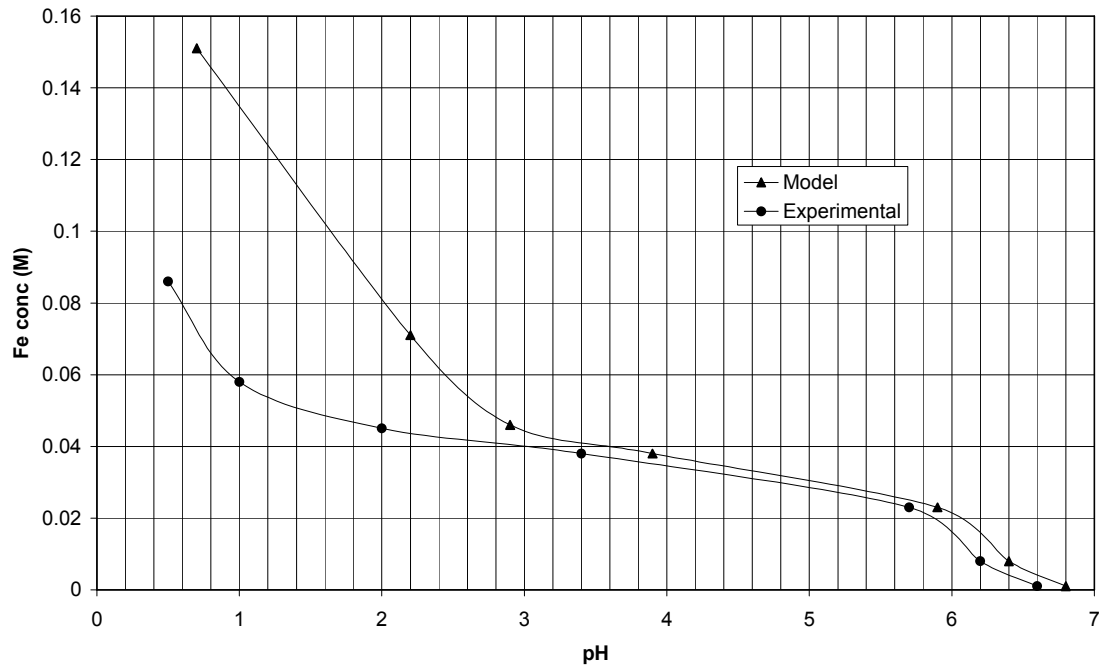Figure 2. Model Predictions of Hematite Solubility versus pH in 1 wt. % Oxalic Acid at 50 ºC.

Figure 3. Hematite Solubility Versus pH in 1 wt. % Oxalic Acid at 50 ºC (0.22 M Na$^+$ background).

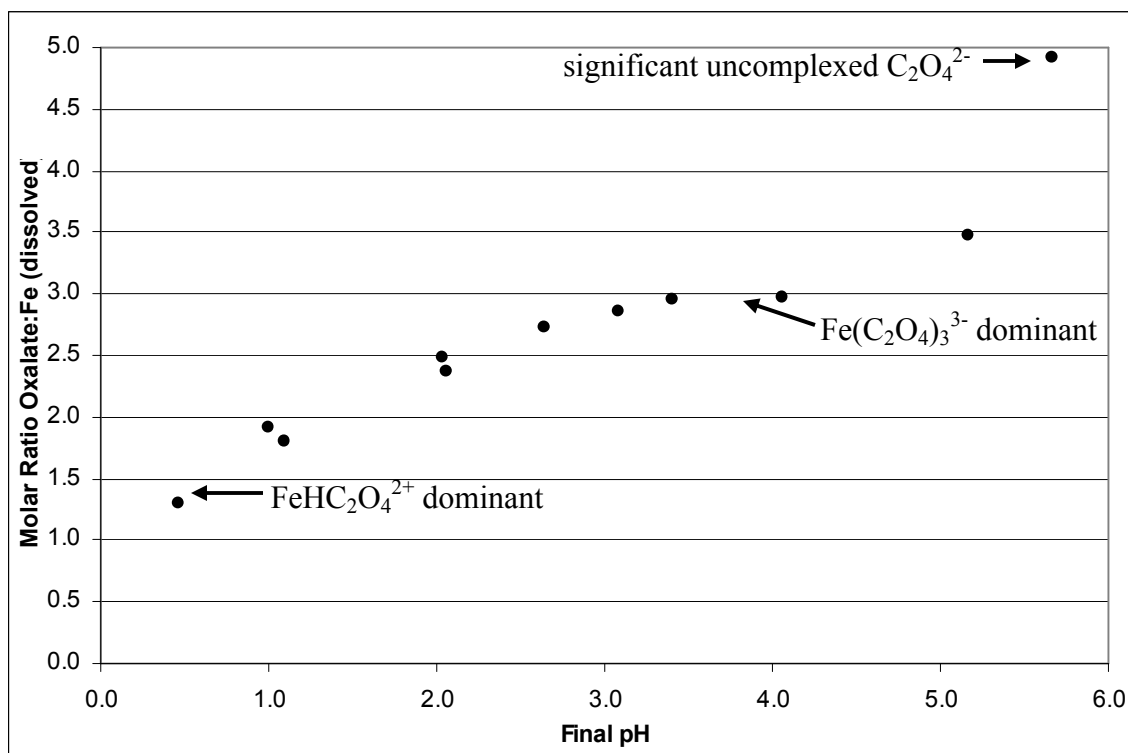Figure 4. Oxalate:Iron Molar Ratios in Solution Versus pH at 50 ºC (0.22 M Na^+ background).