ALTERNATIVE AND ENHANCED CHEMICAL CLEANING: BASIC STUDIES RESULTS FY2010

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ALTERNATIVE AND ENHANCED CHEMICAL CLEANING: BASIC STUDIES RESULTS FY2010

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LIST OF ACRONYMS

AECC	Alternative Enhanced Chemical Cleaning
DOE	Department of Energy
ESP	Environmental Simulation Program
HLW	High Level Waste
ICP-ES	Inductively Coupled Plasma-Emission Spectroscopy
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
XRD	X-ray Diffraction

1.0 SUMMARY

In an effort to develop and optimize chemical cleaning methods for the removal of sludge heels from High Level Waste tanks, solubility tests have been conducted using non-radioactive, pure metal phases. The metal phases studied included the aluminum phase gibbsite and the iron phases hematite, maghemite, goethite, lepidocrocite, magnetite, and wustite. Many of these mineral phases have been identified in radioactive, High Level Waste sludge at the Savannah River and Hanford Sites. Acids evaluated for dissolution included oxalic, nitric, and sulfuric acids and a variety of other complexing organic acids. The results of the solubility tests indicate that mixtures of oxalic acid with either nitric or sulfuric acid are the most effective cleaning solutions for the dissolution of the primary metal phases in sludge waste. Based on the results, optimized conditions for hematite dissolution in oxalic acid were selected using nitric or sulfuric acid as a supplemental proton source. Electrochemical corrosion studies were also conducted (reported separately; Wiersma, 2010) with oxalic/mineral acid mixtures to evaluate the effects of these solutions on waste tank integrity.

The following specific conclusions can be drawn from the test results.

- Oxalic acid was shown to be superior to all of the other organic acids evaluated in promoting the dissolution of the primary sludge phases.
- All iron phases showed similar solubility trends in oxalic acid versus pH, with hematite exhibiting the lowest solubility and the slowest dissolution.
- Greater than 90% hematite dissolution occurred in oxalic/nitric acid mixtures within one week for two hematite sources and within three weeks for a third hematite sample with a larger average particle size. This dissolution rate appears acceptable for waste tank cleaning applications.
- Stoichiometric dissolution of iron phases in oxalic acid (based on the oxalate concentration) and the formation of the preferred 1:1 Fe to oxalate complex is possible with the addition of a supplemental hydrogen ion source (HNO_3 or H_2SO_4) and pH control.
- Sulfuric acid is nearly twice as effective as nitric acid (on a molar basis) at promoting hematite dissolution in oxalic acid solutions, most likely due to the fact that it is diprotic.
- The greater the oxalic acid concentration, the greater the demand for supplemental H^+ to promote optimal dissolution. Minimum mineral acid concentrations required for optimal oxalic acid utilization based on hematite solubility tests are provided in the table below.

	Supplemental Acid	
Oxalic Acid (wt. %)	HNO_3 (M)	H_2SO_4 (M)
1	0.25 to 0.5	0.125 to 0.25
4	1.0	0.5
8	>1	1.0

- Corrosion studies conducted (reported elsewhere) with 1 wt. % oxalic acid revealed that carbon steel corrosion rates are manageable at lower mineral acid concentrations (0.1 M HNO_3 and 0.05 M H_2SO_4) and lower temperatures (45 ºC).
- Proposed conditions for waste tank heel dissolution based on the solubility and corrosion test results are 0.5 wt. % oxalic acid and 0.18 M HNO_3 or 0.09 M H_2SO_4 at 50 ºC.
- The OLI Thermodynamic Model appears to over-predict the solubility of the iron phases studied in oxalic acid and oxalic/nitric acid mixtures. The predictions show better agreement with experimental results at higher pH and in sulfuric/oxalic acid mixtures.
- Oxalic, nitric, and sulfuric acids are effective at quickly dissolving gibbsite ($\geq$86% dissolution in 2 weeks), with oxalic/sulfuric acid mixtures being particularly effective.
- Limited dissolution tests conducted with carbon steel coupons revealed that the presence of metallic iron can, in some cases, result in dramatically different results. Additional studies in this area are recommended.

Based on the current results, the optimal approach for the removal of sludge heels for HLW tanks would include the following steps:

1) removal of the maximum possible amount of heel materials by mechanical means
2) neutralization and acidification of the heel using dilute mineral acid (This step should promote significant dissolution of certain metal hydroxides and salts, including gibbsite.)
3) dissolution of the residual heel material at 50 ºC using an acid mixture containing 0.5 wt. % oxalic acid and 0.18 M nitric acid (This step should dissolve the iron phases.)

2.0 BACKGROUND AND INTRODUCTION

As efforts continue to treat and dispose of millions of gallons of legacy radioactive materials from the production of nuclear weapons, non-compliant High Level Waste (HLW) 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 (~1 million gallon) tanks which frequently contain numerous obstructions that limit the effectiveness of mechanical removal methods. As a result, chemical cleaning methods are needed for the effective removal of the heels as well as chemical scales that are present on the tank walls and other interior surfaces. Oxalic acid is the preferred cleaning reagent for heel dissolution, particularly for iron-based sludge. Several recent literature reviews (Adu-Wusu, 2003; Ketusky, 2007; Hay, 2009) and a Systems Engineering Evaluation (Martino, 2009) 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 relatively small volumes of chemical scale materials with dilute acid followed by regeneration of the acid for reuse (Bertholdt, 1999).

Numerous HLW tanks at two DOE sites in Hanford, WA and Aiken, SC (Savannah River Site - SRS) contain large volumes of sludge and salt slurries which have been stored for years under highly alkaline conditions. At the conclusion of bulk waste removal and heel washing campaigns at SRS, residual chemical heel volumes typically approach 5000 gallons per tank. The current baseline chemical cleaning process for SRS heel removal involves the addition of 8 wt. % oxalic acid to the waste tanks in several treatment cycles. More concentrated oxalic acid is preferred in this case because available tank farm volume is limited and evaporation to remove excess liquid is expensive. The large amount 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 involves the addition of large amounts of oxalate to the tank farm inventory. 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) have significant impacts on downstream processes.

The baseline chemical cleaning method was recently used for heel removal in two SRS waste tanks, and lower than expected amounts of solids were removed from the tanks (Poirier, 2009 and 2010). The baseline method has not been optimized to minimize the use of oxalic acid and the results indicate that better understanding of sludge dissolution chemistry in oxalic acid is needed in order to achieve more consistent and effective results. 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. SRS operations is currently developing a chemical cleaning process for heel removal involving an oxalate destruction technology. In a separate effort, as part of the EM-31 Alternative Enhanced Chemical Cleaning (AECC) program, the Savannah River National Laboratory (SRNL) is working to refine the baseline chemical cleaning process to optimize sludge dissolution. This

effort includes the evaluation of various acids (including oxalic) and combinations of acids for sludge dissolution and the measurement of tank corrosion rates for the most promising acids. The latest dissolution test results are the subject of this report. The corrosion test results are provided in a separate report (Wiersma, 2010).

Iron and aluminum oxides and hydroxides are the most abundant chemical constituents of SRS waste tank heels. Variable amounts of sodium, calcium, uranium, manganese, nickel, and silicon are also present as secondary metal ions along with numerous other trace metal ions and radioactive isotopes. Dissolution methods focus on the removal of iron and aluminum and it is assumed that removal of these primary sludge constituents is necessary for the effective removal of the hazardous metals and radionuclides. The liquid portion of the sludge is dilute alkaline solution remaining after waste removal campaigns and sludge washing with water to remove soluble waste components. Except for certain tanks containing high levels of residual and moderately soluble salts, 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 a highly alkaline environment in the presence of concentrated sodium salt solutions. Common crystalline aluminum phases in sludge include gibbsite ($AlOH_3$) and boehmite ($AlOOH$) (King, 2010a). Common crystalline iron phases include hematite (Fe_2O_3), magnetite (Fe_3O_4), and lepidocrocite ($FeOOH$). It is believed that iron exists primarily as Fe(III), with Fe(II) contributing to a minor degree and being present in phases such as magnetite. The metal phases present in the sludge heels may significantly impact the effectiveness of dissolution methods. For aluminum, a dissolution method has already been developed involving contact with highly alkaline solutions (Reboul, 2004; Adu-Wusu, 2008). Gibbsite is also effectively dissolved in dilute acids at moderate temperatures. However, acid dissolution of more refractory aluminum phases (boehmite, alumina, and aluminosilicates) is limited in effectiveness at low acid concentrations and tank corrosion concerns prohibit the use of more concentrated acids. Alkaline dissolution remains the preferred method for removing these refractory aluminum phases.

Thus far, the focus of the EM-31 program has been on determining the solubility of the primary iron and aluminum phases in various acid systems. Oxalic acid has received the greatest attention, but mineral acids have also been evaluated with regard to dissolution strength and ability to assist with oxalic acid based dissolution. Under conditions where there is a need to minimize oxalate additions, it is important to ensure that oxalic acid is being utilized only for metal complexation and not as a proton source. Mineral acids that have minimal downstream impacts could be used for sludge neutralization and to provide the protons needed for dissolution. The hematite dissolution reaction in Eq. 2-1 reveals the importance of providing sufficient protons to promote dissolution and oxalate complex formation. The monobioxalate iron dication complex ion, $FeHC_2O_4^{2+}$, is believed to be the primary species present in Fe(III)-oxalate solutions at low pH, as indicated by Lee (1995), Panias (1996), and Christodoulou (2001). Two molar equivalents of additional protons (excluding H^+ from oxalic acid) are needed for every oxalic acid molecule and every iron atom to promote the preferred complex formation and iron dissolution. For the formation of this complex, these protons must be provided by an alternative acid source. For the

dissolution of sludge heels, where there is a need to minimize oxalic acid, a supplemental proton source is required for optimization.

$$Fe_2O_{3\,(s)} + 2H_2C_2O_{4\,(aq)} + 4H^+_{\,(aq)} \rightarrow 2FeHC_2O_4^{2+}_{\,(aq)} + 3H_2O \qquad \text{(Eq. 2-1)}$$

Iron speciation in solution can be manipulated in oxalic acid solutions by controlling the pH. For the Fe(III)-oxalate system with 1 wt. % oxalic acid, the iron is believed to exist almost entirely as the monobioxalate complex, $FeHC_2O_4^{2+}$, at a pH below 1. Above pH 2, the iron exists almost exclusively as the trioxalate, trianion complex ion, $Fe(C_2O_4)_3^{3-}$.   At intermediate pH values between 1 and 2, the iron exists as a mixture of the monobioxalate, the trioxalate, and the dioxalate complex ion, $Fe(C_2O_4)_2^-$. Therefore, under saturated conditions (based on iron) it is expected that the mole ratio of oxalate:iron in solution changes from 3:1 to 1:1 as the pH is decreased from above 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 does not require the addition of a supplemental acid, since more than enough protons are provided by the oxalic acid. At solution pH values below one, the dissolution of ferric ions can also occur without the formation of oxalate complexes. However, these conditions also tend to promote excessive corrosion of carbon steel vessels and are typically avoided. Since magnetite (Fe_3O_4) can be formally viewed as a mixture of hematite (Fe_2O_3) and wustite (FeO), the above discussion likely applies to the dissolution of this phase as well. At low pH values the dissolution of Fe(II) in oxalic acid is believed to result in the formation of uncomplexed Fe^{2+} ion in solution, which does not consume oxalate ion, but does consume H^+ (Panias, 1996).

The selection of optimal conditions for sludge dissolution in oxalic/mineral acid mixtures involves the identification of mineral acid concentrations that promote the formation of the preferred 1:1 complex, but do not cause excessive carbon steel corrosion. Careful review of the literature (Christodoulou, 2001) has revealed that the optimal pH for the dissolution of iron phases increases as the oxalic acid concentration decreases. The iron(III) oxalate species distribution is expected to contain 90% $FeHC_2O_4^{2+}$ near pH 0.5 in 8 wt. % oxalic acid. In 1 wt. % oxalic acid, 90% $FeHC_2O_4^{2+}$ is observed near pH 1.0. This pH dependence in the species distribution for the oxalate complexes may allow for the selection of an oxalic acid concentration where the optimum pH gives manageable carbon steel corrosion rates.   More dilute oxalic acid solutions can be optimized at higher pH values, but operation under dilute conditions requires the handling of greater water volume. Therefore, the optimization of sludge dissolution in oxalic acid involves a balance between tank corrosion and waste volume.

Nitric and sulfuric acids were evaluated in this testing as supplemental proton sources to promote the formation of the monobioxalate iron complex. In contrast to previous testing where mineral acids were added dropwise to adjust the pH, this testing involved the use of oxalic/mineral acid mixtures. This approach is considered more suitable to large scale waste processing operations. Minimal downstream impacts are expected from the addition of nitrate, since SRS waste streams already contain significant sodium nitrate salts. Sulfate

could potentially have negative downstream impacts associated with the formation of separate phases during waste vitrification. However, based on the solubility of sodium sulfate, it is expected that the sulfate salts would be washed away from the re-precipitated sludge and might be disposed of in the low activity grout (saltstone) waste stream. Hydrochloric and hydrofluoric acids are also expected to be somewhat effective at dissolving sludge solids. However, these acids have not been considered at this point, since they are currently present only at low levels in SRS waste.

The waste tanks at SRS and Hanford are constructed of carbon steel. Carbon steel corrodes rapidly in most acidic environments. For example, carbon steel corrosion rates at 25 °C in 1 M and 6 M nitric acid are 2 and 13 inches/yr, respectively (Uhlig, 1948). The corrosion rate for carbon steel in 0.75 M sulfuric acid at 45 °C is approximately 0.8 inches year (Craig, 1989). One of the reasons for selecting oxalic acid for chemical cleaning is that carbon steel corrodes at a relatively low general corrosion rate of approximately 0.06 inches per year (Herman, 2007). For a short contact time between the oxalic acid and the steel tank, on the order of two months, this corrosion rate results in a loss of approximately 0.01 inches from the tank wall. This amount of corrosion does not significantly impact the structural integrity of the tank (McKeel, 2008) or the performance assessment analysis (Garcia-Diaz, 2010). Previous testing in oxalic/nitric acid mixtures suggested that the corrosion rate for carbon steel in dilute acid mixtures (i.e., 0.3 M nitric acid) would result in a "manageable" amount of degradation over a short period of time (Wiersma, 2002). These expectations were confirmed during recent corrosion evaluations performed in support of the EM-31 chemical cleaning program (Wiersma, 2010). Corrosion studies conducted with acid mixtures containing 1 wt. % oxalic acid and either 0.1 M HNO_3 or 0.05 M H_2SO_4 at 45 ºC revealed that corrosion rates are manageable under these conditions. In some cases with sulfuric acid, localized pitting was observed at minimal levels.

3.0 EXPERIMENTAL METHODS, MATERIALS, AND EQUIPMENT

All testing was conducted according to the applicable Technical Task and Quality Assurance Plan for this work (King, 2010b).

3.1 REAGENTS AND MATERIALS

Nitric and sulfuric acid solutions were prepared from concentrated, commercial reagents. Oxalic acid dihydrate reagent was used for the preparation of all oxalic acid solutions. The densities of all solutions were measured to allow for the calculation of sample volumes. Selected reagent solutions were analyzed to confirm that the nitrate, sulfate, and oxalate anion concentrations were near the targeted values. Teflon bottles were used for all batch contact solubility tests. These bottles were proven during previous testing to perform well at elevated temperature for extended time periods without significant liquid loss by evaporation.

Pure metal phases were purchased from Aldrich, Strem Chemicals, Inc. (Newburyport, MA), and Almatis, Inc. (Bauxite, AK). Elemental analysis results for all of the metal phases are provided in Table 3-1. For the iron phases, all metals other than iron were present at concentrations lower than 1 wt. %. The measured iron content was lower than the theoretical value for every sample. For the Fe_2O_3 phases, the measured iron content was 4 to 8 wt. % lower than the theoretical values. For the FeO(OH), Fe_3O_4, and FeO phases, the measured iron content was 13 to 17 wt. % lower than the theoretical values. For the gibbsite sample, all metals other than aluminum were present at concentrations lower than 1 wt. %. In this case, the measured aluminum content was higher than theoretical. Correction for water content does not explain the magnitude of the differences between measured and theoretical values, since the water content of all samples was ≤2.5 wt. %. Presumably, analysis error such as incomplete acid digestion caused this discrepancy. As-received and sonicated particle size analysis results (Microtrac) are also provided in Table 3-1. Sample sonication was conducted due to the observation of large particle agglomerates in some samples. Sonication resulted in the reduction of the mean particle diameters to ≤10.5 μm, except for the amorphous iron oxide and wustite samples. The size distributions after sonication may be more representative of the solid phase after agitation during batch contact testing. Caution should be taken in comparing the volume-based mean particle size distributions for the as-received samples, since many of the distributions were polymodal in nature. In contrast, the particle size distributions for the sonicated samples were typically more monomodal in shape. X-ray diffraction analysis results for most of the phases tested are provided in Figures 3-1 through 3-8. XRD data for the hematite #1 and magnetite reagents were provided in a previous report (King, 2010a). XRD results indicate a high degree of purity for all crystalline phases. A trace amount of magnetite was observed in hematite reagent #3 (Figure 3-2). A trace amount of goethite was observed in the lepidocrocite sample (Figure 3-5). Broad hematite peaks were observed for the hydrated iron(III) oxide sample, but the material was largely amorphous (Figure 3-6). Trace elemental iron was observed in the wustite sample (Figure 3-7).

The carboxylic acids were obtained from commercial vendors as pure reagents, except for gluconic acid, which was received as a 50 wt. % aqueous solution. Commercially-purchased, reagent grade sodium nitrate and sodium hydroxide solids were used for the preparation of selected test solutions.

3.2 TEST METHOD

Solubility testing involved simple batch contacts with known masses of liquid and solid. All sample and bottle weights were obtained using analytical balances that were calibrated annually in the SRNL Standards Laboratory and checked on a daily basis with a calibrated weight set. Mass phase ratios varied from 20:1 (liquid to solid) to 100:1 depending upon the test. Unless otherwise indicated, a mass ratio of 50:1 was used for all tests with 1 wt. % oxalic acid. Masses of solid phases ranged from 0.5 to 5 g per test. The mass of solid used in each test was corrected for measured absorbed water as determined by sample drying at 50-70 ºC under vacuum. Teflon bottles used for testing were confirmed to be essentially leak

tight by the periodic monitoring of liquid levels and sample masses. Samples were maintained in temperature-controlled incubator shaker ovens (Innova Models 4230 and 42 from New Brunswick Scientific) at 50 ºC and agitated continuously at 250 RPM. Prior to sampling or pH measurement, sample agitation was stopped so that the solids could settle. Sampling and pH measurement were conducted out of the oven in a chemical hood within 2-3 minutes after removal from the oven to minimize sample cooling. All tests were continued for 5-6 weeks (unless otherwise indicated) with periodic pH monitoring. Based on liquid phase analysis, the amount of residual solids remaining in each sample was calculated for all tests and confirmed to be >0.5 g, except for the high phase ratio kinetics tests (where almost the entire solid sample dissolved) and one test with 1 wt. % OA, as indicated in the results section.

Analysis sample bottles were prepared by the addition of a known mass (3 or 6 g) of 3 M nitric acid. Sub-samples of solutions from each test sample were collected and immediately filtered through a 0.45 μm nylon syringe filter directly into the analysis bottles containing nitric acid. The mass of each filtered sub-sample added to the bottles (1 or 2 g) was determined by difference and recorded for the calculation of dilution factors (approximately 4 for all samples). Dilution in 3 M nitric acid serves to avoid the precipitation of insoluble phases. Visual inspection of each acidified sample confirmed that no precipitates had formed upon dilution. In order to avoid the light-promoted reduction of Fe(III) to Fe(II) and the subsequent precipitation of ferrous oxalate, samples were maintained in closed buckets during transport and storage to avoid light exposure. The shaker oven windows were also covered and the oven lights were turned off to exclude light from the test samples.

Solution pH values were measured using Oakton pH 110 Series probes. Each time that the pH probes were used, the instruments were calibrated using four standard buffer solutions. Calibration involved sequential use of pH 7.0, 1.68, 4.0, and 10.0 standard buffer solutions following the recommendations of the probe manufacturer for these test solutions. Each pH measurement was conducted with two separate probes. The probes were rinsed, lightly wiped, and briefly stored in de-ionized water between measurements. Prior to and after the measurement of the pH for a given sample set, the pH was measured and recorded for the four buffer solutions. Reported pH values are the averaged data recorded for the two probes. Generally, good agreement was observed between the two probes, although occasionally the repeated utilization of the probes in low pH solutions with moderate dissolved metal ion concentrations resulted in a slight drifting ($\leq$0.5 pH units) of the measured pH to higher values. When a probe was observed to drift to higher pH values, the probe was replaced.

Table 3-1. Elemental Analysis and Particle Size Data for Metal Phases Tested

Phase	Source and Catalogue #	Al Wt. %	Fe Wt. %	Theoretical Wt. %[a]	As-received Volume-Based Mean Particle Diameter (μm)	Sonicated Volume-Based Mean Particle Diameter (μm)[b]
Hematite #1 (Fe_2O_3)	Strem 93-2617	---	65.40	69.9	2.94	0.99
Hematite #2 (Fe_2O_3)	Aldrich 20,351-3	---	64.30	69.9	48.81	6.65
Hematite #3 (Fe_2O_3)	Aldrich 31,005-0	---	67.20	69.9	53.47	0.74
Maghemite (Fe_2O_3)	Aldrich 48,066-5	---	66.30	69.9	5.75	2.51
Goethite (FeOOH)	Strem 93-2618	---	54.40	62.9	260.00	0.39
Lepidocrocite (FeOOH)	Strem (special order)	---	52.80	62.9	55.30	1.30
Iron(III) Oxide, hydrated	Aldrich 37,125-4	---	54.40	62.9[c]	554.90	436.80
Magnetite (Fe_3O_4)	Strem 93-2616	---	62.20	72.4	5.71	0.90
Wustite (FeO)	Aldrich 40,086-6	---	64.20	77.7	429.90	539.00
Gibbsite ($Al(OH)_3$)	Almatis	42.60	0.04	34.6 (Al)	13.54	10.38

[a]theoretical values for iron based on the formula weight unless otherwise indicated
[b]particle size analysis following 6 minute sonication
[c]assumed composition: FeOOH
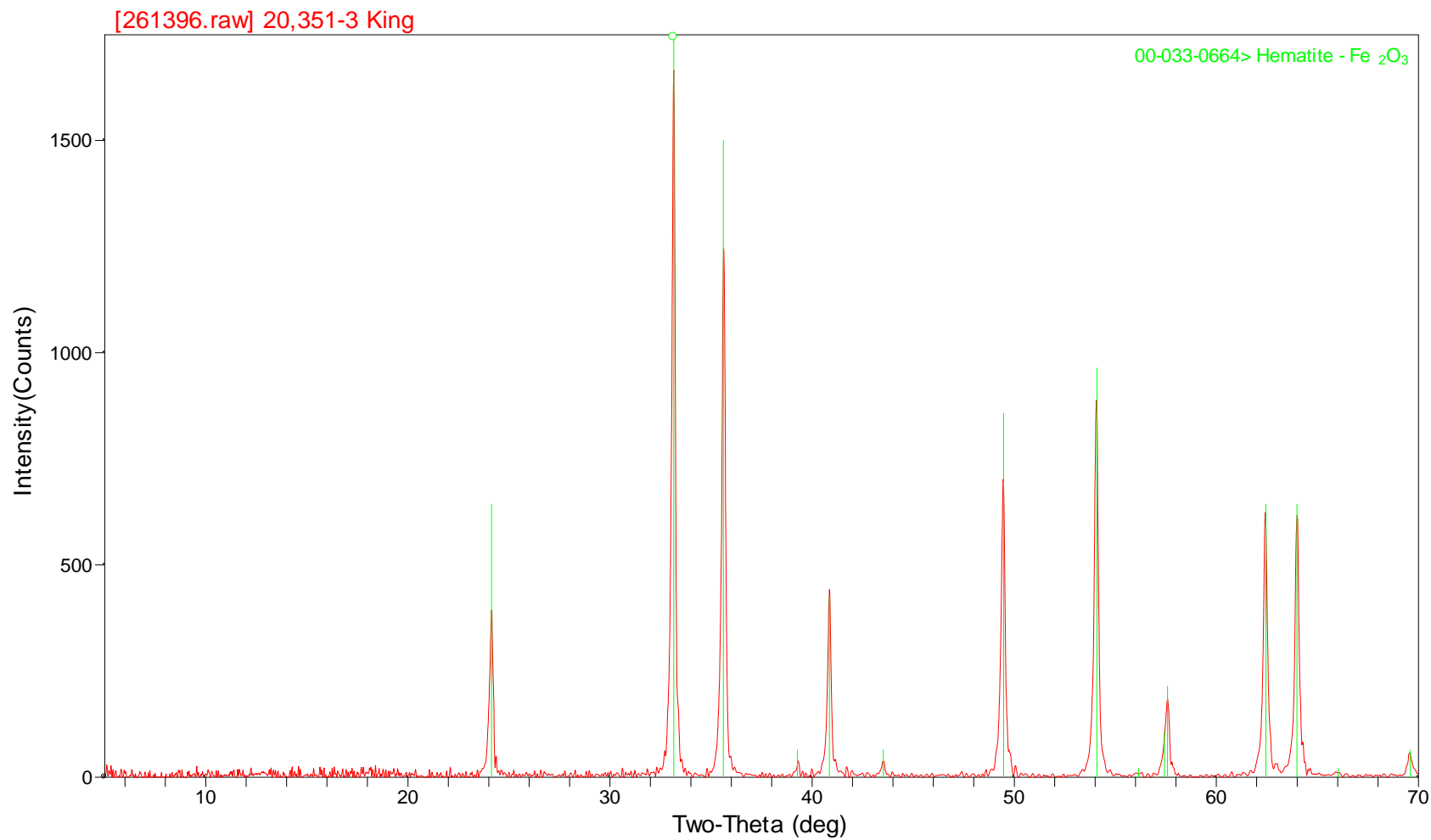
Figure 3-1. XRD analysis results for hematite reagent #2.
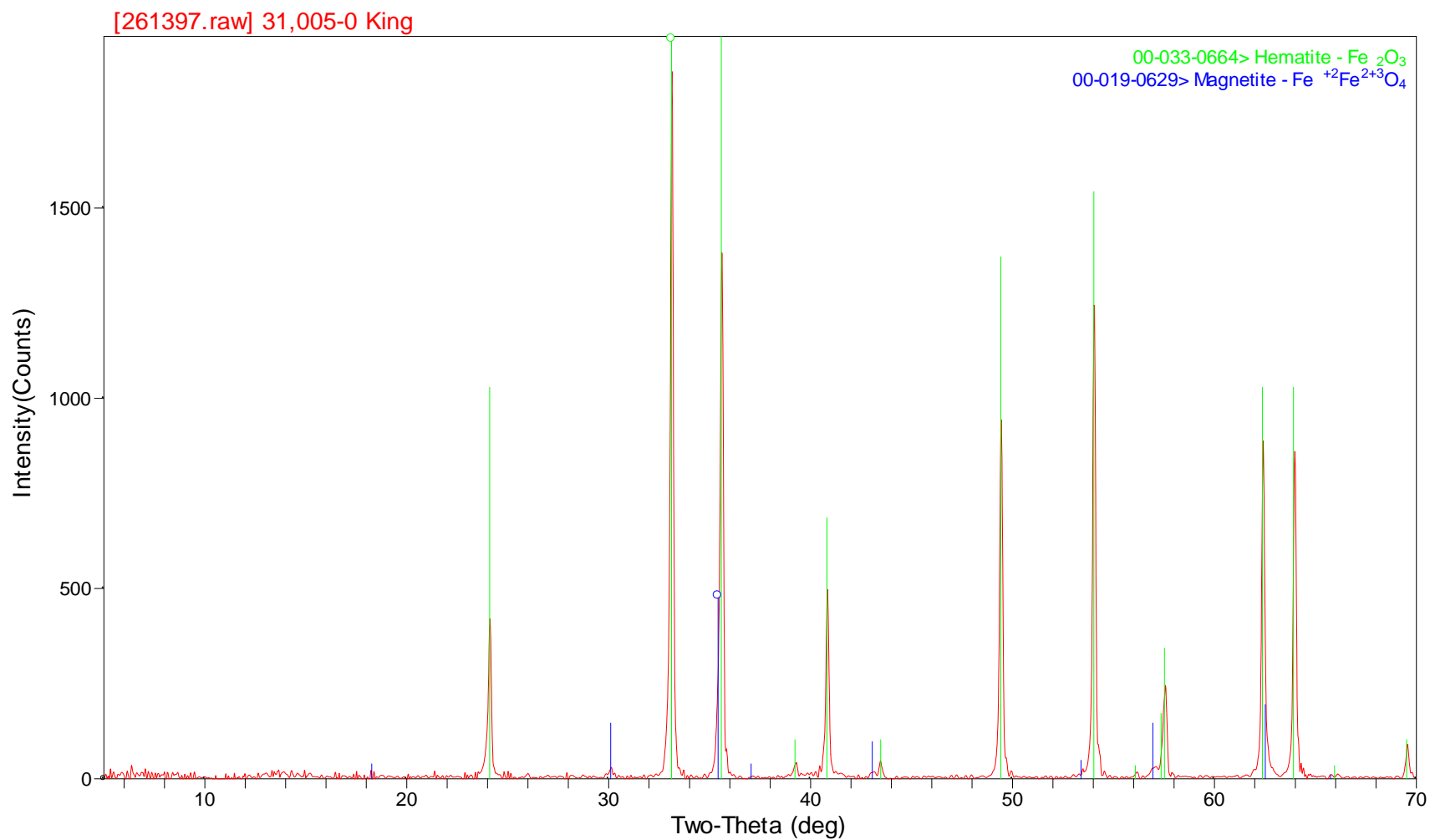
Figure 3-2. XRD analysis results for hematite reagent #3.
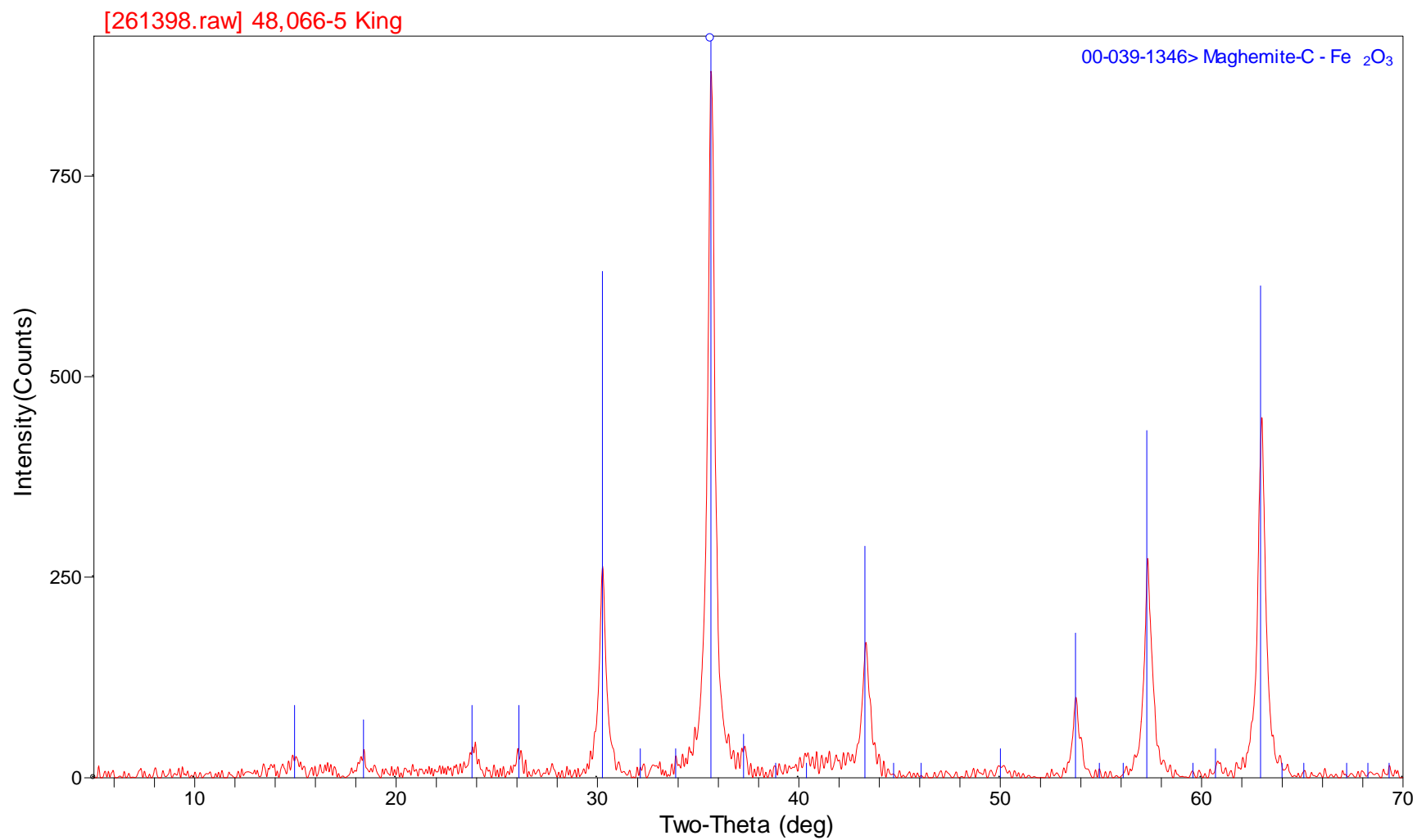
Figure 3-3. XRD analysis results for maghemite reagent.
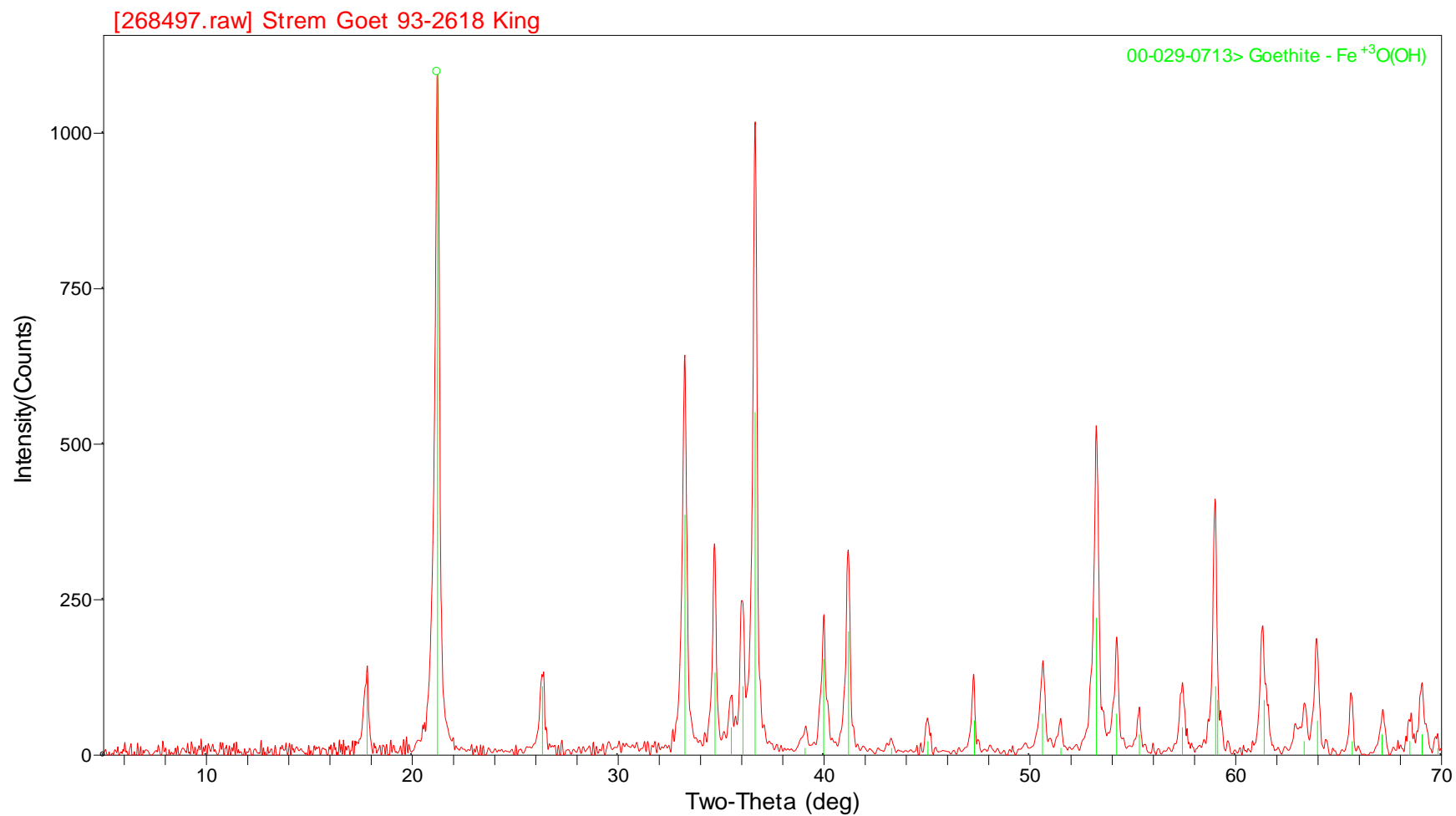
Figure 3-4. XRD analysis results for goethite reagent.
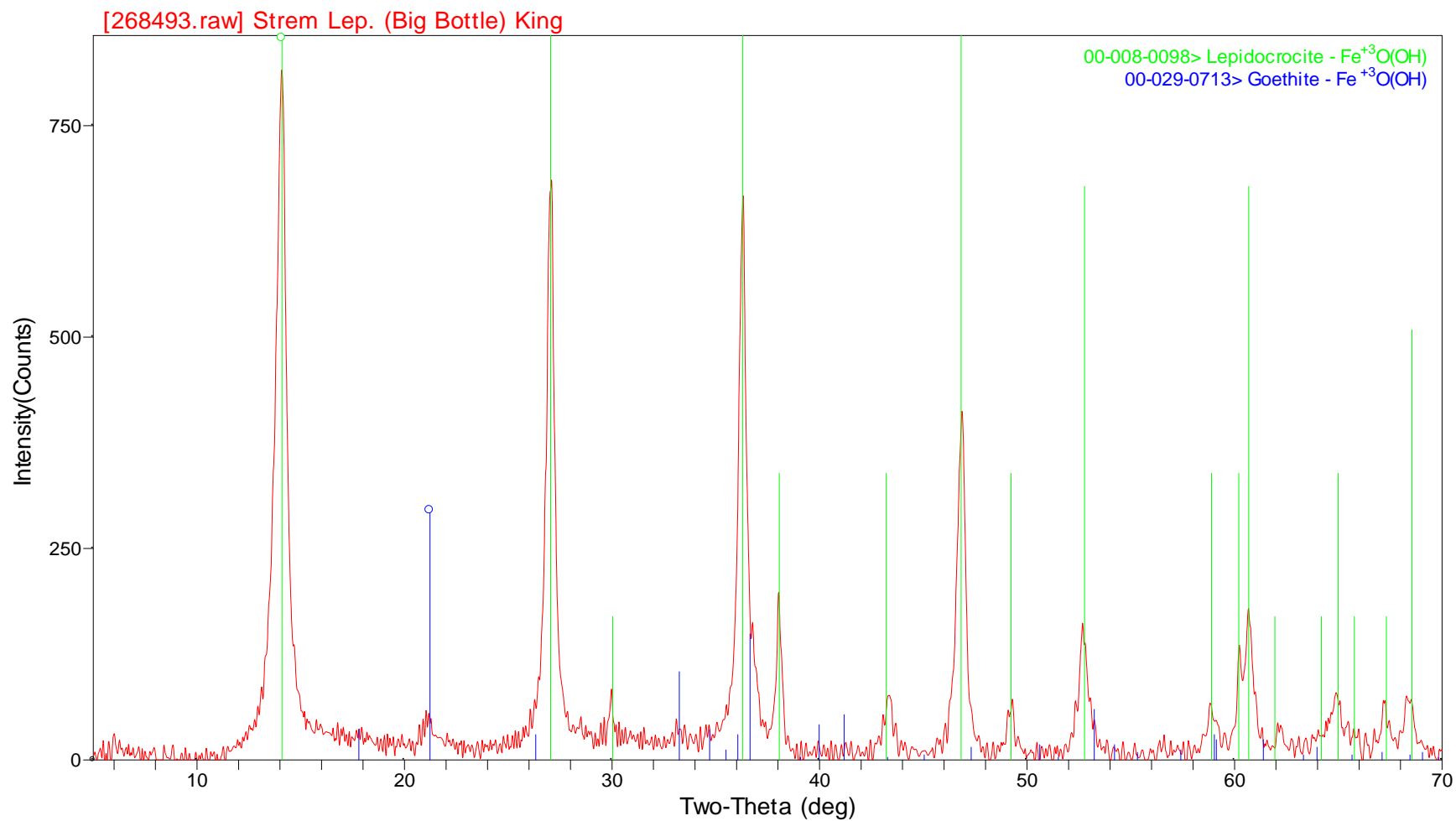
Figure 3-5. XRD analysis results for lepidocrocite reagent.
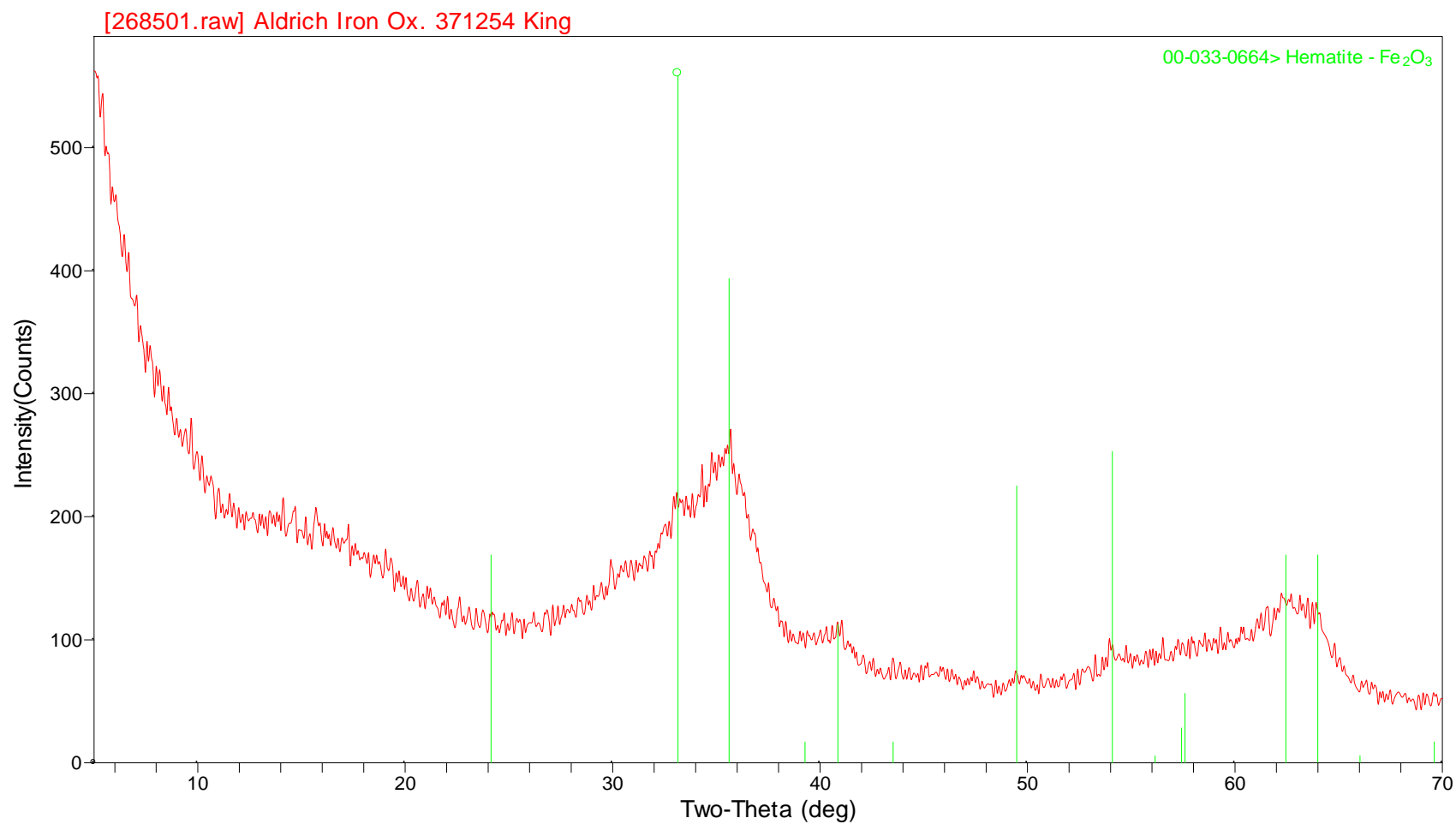
Figure 3-6. XRD analysis results for hydrated, iron(III) oxide reagent.
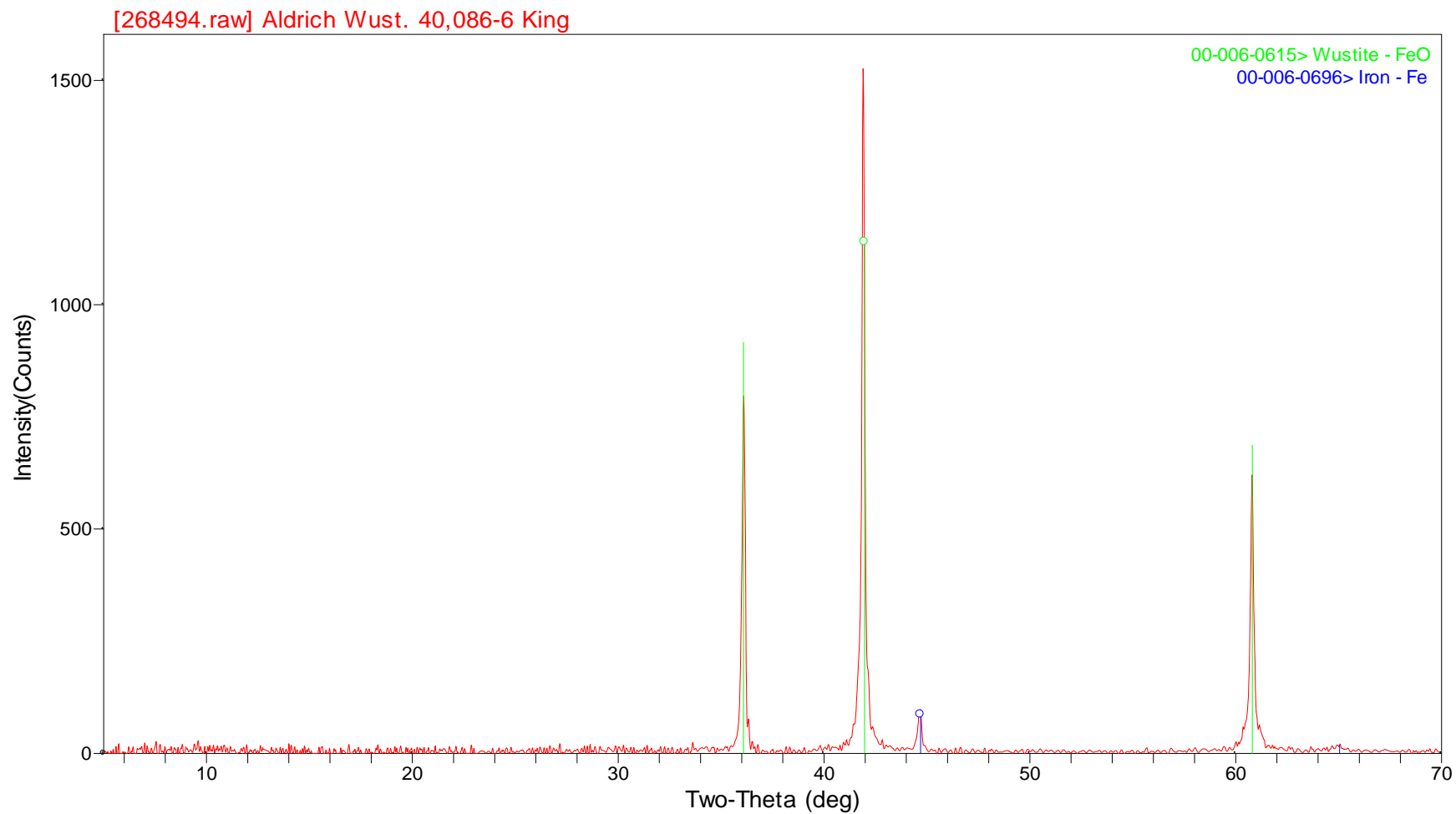
Figure 3-7. XRD analysis results for wustite reagent.
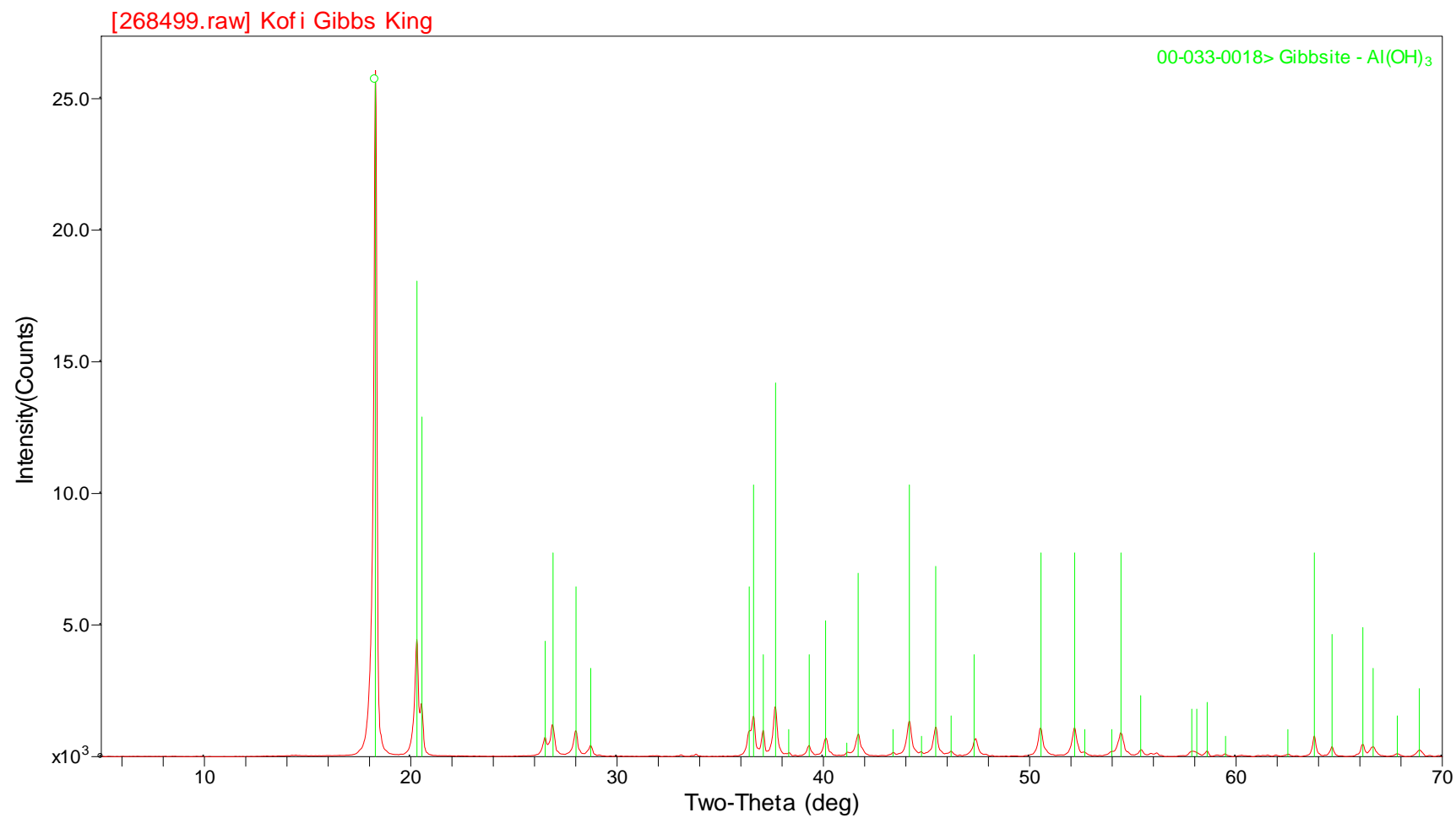
Figure 3-8. XRD analysis results for gibbsite reagent.

4.0 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 SOLUBILITY TESTING WITH PURE IRON PHASES

Various solubility tests were conducted using pure iron and aluminum phases with oxalic acid, as well as with oxalic/mineral acid mixtures and oxalic/NaOH mixtures. Tests were conducted to evaluate the effects of pH, oxalic acid concentration, mineral acid, phase ratio, complexing acid, iron phase, and ionic strength. Dissolution kinetics tests were also conducted for several phases using pure oxalic acid and oxalic/mineral acid mixtures. Hematite (Fe_2O_3) was the most commonly used solid phase since it was believed to be one of the most difficult iron phases to dissolve. In all tests, the solution pH was monitored, but no reagent additions were made to control the pH after the initial sample preparation. A mass phase ratio of 50:1 and a temperature of 50 ºC were used for most tests. These conditions typically resulted in only partial dissolution of the solid phase. Initial mineral acid concentrations and test conditions were selected such that the pH ranges of interest could be evaluated. Except for the kinetics tests, where analysis sub-samples were collected periodically, tests typically involved five to six weeks of contact time prior to sampling and analysis.

4.1.1 Hematite Solubility Versus pH

Hematite solubility tests were conducted using 1, 4, and 8 weight percent oxalic acid solutions containing various amounts of nitric acid or sodium hydroxide. Tests were conducted with and without sodium nitrate background salt to evaluate ionic strength effects. One goal of this testing was to determine the amount of supplemental acid required to fully utilize the oxalate anion for hematite dissolution with the goal of confirming the molar stoichiometries given in Eq. 2-1. In addition, hematite solubility across the pH range of 0.5 to 6 was determined to confirm model and literature predictions which indicated lower solubility at higher pH. Results are provided in Table 4-1 and Figure 4-1. As expected, iron solubility increased at lower pH. For 1 wt. % oxalic acid, the final iron concentration increased from near 0.03 M to 0.18 M as the final pH decreased from 3.7 to 0.2. This solubility increase is believed to be partially due to the provision of the needed protons to support the oxalic acid-based dissolution reactions and partially due to proton-induced dissolution of the iron phase that does not involve oxalate complexation. Previously reported hematite dissolution results in nitric acid solutions revealed that significant hematite dissolution occurs in ≥0.5 M nitric acid (King, 2010a). Hematite solubility in pure acids must be considered when interpreting the results for acid mixtures.

0.5 M nitric acid with 1 wt. % oxalic acid has recently been shown to promote very high carbon steel corrosion rates (Wiersma, 2010). Based on these results, it will likely be necessary to use an oxalic acid concentration between 0.5 and 1 wt. % to promote sludge dissolution while simultaneously maintaining steel corrosion rates at manageable levels. 1 wt. % oxalic acid corresponds to 0.111 M oxalate, so optimal iron phase dissolution involves iron concentrations of 0.111 M, based on the formation of a 1:1 Fe:oxalate complex ion. The dissolution test results shown in Table 4-1 and Figure 4-1 indicate that 0.111 M Fe is reached

when the initial nitric acid concentration is between 0.25 and 0.5 M. This result is consistent with Eqn. 2-1 involving the formation of the mono-bioxalate iron complex, $Fe(HC_2O_4)^{2+}$. The reaction requires that two molar equivalents of additional protons be provided by a supplemental acid source. Additional hydrogen ion at a concentration near 0.1 M is required to maintain the pH near 1 where the mono-bioxalate complex is the thermodynamically preferred species. Therefore, for 1 wt. % oxalic acid, a nitric acid concentration of 0.322 M (2 x 0.111 M + 0.1 M) should be needed to promote optimal dissolution and minimize oxalate usage.

The solubility data for the oxalic/nitric acid mixtures with and without added background sodium salts is plotted in a different manner in Figure 4-2, where a linear dependence is observed for the final iron concentration versus the initial nitric acid concentration. It should be pointed out that the sample involving 1 wt. % oxalic acid with 0.5 M HNO_3 and no background salt contained only 0.3 g of residual solids at the conclusion of the test, based on ICP-ES analysis of the liquid. Despite the lower residual solids level for this sample, the measured iron concentration is consistent with the other samples. The slopes of the least squares linear fits to the data for each oxalic acid concentration are similar. The data point for 4 wt. % oxalic acid with no background sodium salt and 0.5 M nitric acid appears to be an outlier. There is no evidence that the presence of background sodium nitrate salts significantly affects the solubility results. For the tests conducted with 4 and 8 wt. % oxalic acid, iron concentrations near 0.452 and 0.92 M, respectively, should be possible under optimized conditions. An iron concentration of 0.443 M was observed with 4 wt. % oxalic acid at a nitric acid concentration of 1.0 M. The maximum iron concentration observed with 8 wt % oxalic acid was only 0.67 M (1 M nitric acid result). These results are generally consistent with the nitric acid concentrations predicted based on the formation of the mono-bioxalate complex using the formula provided above for 1 wt. % acid (1.00 and 1.94 M nitric acid for 4 and 8 wt. % oxalic acid, respectively). The results also indicate that optimization of iron phase dissolution is not possible within a carbon steel waste tank at oxalic acid concentrations greater than 1 wt. %, because the nitric acid requirements lead to unacceptable corrosion rates. Based on these results, a more dilute oxalic concentration of 0.5 wt. % has been recommended for real waste dissolution testing (King, 2010c).

At a mass phase ratio of 50:1 the final iron concentration observed for 1 wt. % oxalic acid with no added nitric acid was near 0.05 M, whereas in the 1 wt. % oxalic/0.5 M nitric acid mixture the final iron concentration was near 0.12 M. This two-fold increase in the iron solubility is greater than the sum of the hematite solubilities measured for pure oxalic and nitric acids of 0.09 M (0.04 M Fe in 0.5 M HNO_3 King, 2010a; 0.05 M in 1 wt. % oxalic acid). The enhanced solubility is due to the hydrogen ions contributed by the nitric acid which drive the dissolution reaction in Eq. 2-1 to the right, resulting in complete utilization of the oxalate anion for the formation of the 1:1 Fe:oxalate complex. Actual waste sludge includes many base equivalents which tend to raise the pH above the optimal range, especially for oxalic acid solutions without added nitric. This effect was observed during the cleaning of SRS Tanks 5F and 6F, as discussed previously. As a result, a 2 fold increase in oxalate usage efficiency should probably be viewed as the minimum impact of adding a supplemental acid.

4.1.2 Hematite Solubility in Other Complexing Acids

Hematite dissolution tests were also conducted using other complexing acids to confirm that oxalic acid (HOOCCOOH) was the superior and preferred acid for sludge dissolution. Although studies have been conducted previously to compare the effectiveness of these complexing acids (Hay, 2009), the recent discovery of the importance of pH control was sufficient cause for additional evaluations. Since oxalic acid is a particularly strong organic acid (pK_{a1} = 1.3, pK_{a2} = 4.3), it was possible that it was the acidity of the acid that lead to the superior performance in previous comparisons. Alternative complexing acids evaluated in this study included formic (HCOOH), acetic (H_3CCOOH), citric (HOOC-COH-($CH_2COOH)_2$), gluconic ($HOCH_2(CHOH)_4COOH$), and glycolic ($HOCH_2COOH$) acids. The first dissociation constants (pK_{a1}) for these acids are all ≥ 3.2. The fact that these solubility tests were conducted using pure hematite rather than the complicated mixture of components used for previous tests increased the likelihood that conclusive results could be obtained and pH effects for the various acids could be directly compared. The sodium salts of all of these alternative acids are significantly more soluble than sodium oxalate (Lide, 1990), making it likely that sludge washing, following caustic neutralization, could be used to effectively remove these salts from the other HLW sludge components. Tests were conducted using 0.111 M complexing acids with 0.35 M nitric acid, with no nitric acid, and with 0.1 M NaOH. An additional test was conducted using 0.111 M gluconic acid with 0.12 M NaOH, since gluconate ion is known to complex iron well above pH 7 relative to other complexants.

Hematite solubility test results for the alternative complexing acids are provided in Table 4-2 and Figure 4-3. Solubility results for hematite with 1 wt. % (0.111 M) oxalic acid are included in the figure for comparison. The results confirm that oxalic acid is superior for hematite dissolution under these conditions relative to the alternative acids evaluated across the pH range 0 to 8. Generally greater iron solubility was observed for the alternative acids at lower pH, but the acids were not effective at dissolving hematite since the highest iron concentration observed for any sample was 0.026 M (acetic acid result in 0.35 M nitric). For the samples containing 0.35 M nitric acid, where the final measured pH remained at a relatively constant value of 0.6, equilibrium iron concentrations were near 0.024 M for 3 of the 5 alternative acids tested. These results are very near the value that would be expected based on previous hematite solubility tests conducted in pure nitric acid solutions (King, 2010a), where a linear dependence in the iron concentration was observed versus the nitric acid concentration. Extrapolating from the earlier data, the iron concentration in 0.35 M nitric acid is expected to be 0.025 M. This indicates that the hematite dissolution observed for these alternative complexing acids is almost entirely the result of the nitric acid. Interestingly, for the two remaining alternative acids (citric and gluconic), the iron solubility in the oxalic/nitric mixture was near 0.01 M, indicating that the presence of these complexing acids actually suppresses iron dissolution. Trends in the measured pH values of the final solutions without added nitric acid are generally consistent with the acidities of the various complexing acids. Based on these results, oxalic acid is still considered the preferred acid for iron dissolution and all subsequent testing focused on this acid.

4.1.3 Solubility of Various Iron Phases in Oxalic Acid and Oxalic/Nitric Acid Mixtures

In order to confirm that hematite represented the most difficult iron phase to dissolve, solubility tests were performed on various iron oxide phases obtained from several commercial vendors. Besides hematite (Fe_2O_3), the iron phases studied included maghemite (Fe_2O_3), lepidocrocite (FeOOH), goethite (FeOOH), magnetite (Fe_3O_4), wustite (FeO), and an amorphous iron(III) oxide sample described by the vendor as hydrated FeOOH. Magnetite formally contains 33% Fe(II) and wustite contains only Fe(II), while all of the other phases contain only Fe(III). Phases which include Fe(II) might be expected to form insoluble ferrous oxalate (FeC_2O_4) salts under some conditions, while the Fe(III) phases are not believed to form significant Fe(II) in the absence of light. Tests were conducted using 1 wt. % oxalic acid with initial nitric acid concentrations of 0.0, 0.25, and 0.5 M and initial NaOH concentrations of 0.0 and 0.1 M.

Solubility test results are provided in Table 4-3 and Figure 4-4. In the figure, the final iron concentrations are plotted versus the final measured pH. For all phases, the iron solubility increased as the pH decreased and the data trends for all phases are similar. For all phases, nearly stoichiometric iron dissolution (0.11 M) was observed at a final pH just below 1, which occurred with an initial nitric acid concentration of 0.25 M. In general, the results indicate that the solubilities of the various phases are similar in oxalic acid and oxalic/nitric acid mixtures and that the acid demand for the dissolution reactions is similar. This result is consistent with the chemical equations for the various dissolution reactions for Fe(III) phases, which indicate that two hydrogen ions are required for the dissolution of each iron atom. For the dissolution of Fe(II) atoms in the magnetite and wustite phases, it is believed that no oxalate is required to promote dissolution, since uncomplexed Fe^{2+} ions are thought to exist in solution. Interestingly, wustite does not dissolve as well as the other phases in pure oxalic acid, where the measured iron solubility was only 0.028 M. This is approximately half of the iron concentration observed for the other phases in 1 wt. % oxalic acid. A second solid phase was visually observed in this sample within a day after initial contact that was yellow in color. Furthermore, the observed iron concentration is very near the solubility (0.024 M Fe) reported previously for ferrous oxalate (FeC_2O_4) in 1 wt. % oxalic acid (King, 2010a). Based on these observations, it appears that ferrous oxalate may limit the solubility of Fe(II) in pure oxalic acid solutions. A second phase was also observed to form for wustite in oxalic/nitric acid mixtures, although the soluble iron concentrations were comparable to other phases. In pure oxalic acid, the magnetite solubility was measured to be 0.071 M Fe, which corresponds to 0.024 M Fe(II), assuming 33.3% Fe(II) in solution. This indicates that the dissolution of magnetite may also be limited in pure oxalic acid by the solubility of ferrous oxalate. No second phase was visually observed to form for the magnetite sample in pure oxalic acid. Results for hematite tended to be near the low end of the data, which indicates that this is one of the more difficult phases to dissolve. It was expected that the difficulty of dissolving hematite relative to other phases would be more evident during dissolution kinetics tests (discussed in Section 4.1.4).

4.1.4 Dissolution Kinetics in Oxalic Acid and Oxalic/Nitric Acid Mixtures

Dissolution kinetics tests were conducted for several iron phases to determine the timescale of iron dissolution. This information is important for process development and is needed to calculate acceptable carbon steel corrosion rates in the solutions of interest. Three different hematite samples (numbers 1, 2, and 3) were obtained for kinetics testing to evaluate the range of dissolution rates that might be observed with this phase. The dissolution kinetics may be impacted by such things as the sample history (including heat treatments), the level of purity, or the degree of hydration, but a primary characteristic that impacts the rate of dissolution is the particle size. The solid phases used for testing appeared during initial particle size analysis to be composed of significant amounts of agglomerated particles, as indicated by polymodal size dsitributions. Since the dissolution testing involved sample agitation during solid/liquid contact, particle size analysis was also conducted on sub-samples of the solid phases which had been briefly sonicated. Samples were sonicated in an effort to create a particle size distribution that might be representative of the distribution created *in-situ* during sample agitation. Differences were observed between the as-received and sonicated hematite samples as shown in Table 3-1. Size distributions for the sonicated samples were more nearly monomodal. The as-received mean particle diameters (volume-based) were near 50 μm for sample #2 and sample #3, but only 3 μm for sample #1. However, after sonication, the mean particle diameters for sample #1 and sample #3 were both near 1 μm, while the mean diameter for sample #2 was near 7 μm. These results indicate that sample #2 may represent a larger size distribution under the test conditions. The particle size distributions of two actual SRS sludge samples have been measured and the volume-based mean particle diameter ranged from 3.8 to 4.3 μm in water and from 5 to 23 μm in waste supernate (Click, 2005). For the hematite samples tested, the particle size distributions of the sonicated samples are more similar to actual tank sludge. Nonetheless, only as-received samples were used for solubility testing.

Dissolution kinetics test results for the three hematite samples in 1 wt. % oxalic acid and a mixture of 1 wt. % oxalic acid and 0.35 M nitric acid at a phase ratio of 50:1 are provided in Table 4-4 and Figure 4-5. The measured solution pH values stabilized for all three samples within 7 days to near 0.58 for the samples containing the oxalic/nitric acid mixture and 1.39 for the samples containing pure oxalic acid. As expected based on earlier results, the maximum iron concentrations for the samples that did not contain nitric acid all converged near 0.06 M, while the maximum iron concentrations for the samples with nitric acid appeared to converge at just above 0.1 M. This result was also expected since the final iron concentration under optimized conditions in 1 wt. % oxalic acid should be 0.111 M. Percent dissolution values for each data point normalized to the final measured maximum iron concentration for each sample are also provided in Table 4-5. Greater than or equal to 90% dissolution was observed in ≤7 days for all samples except for hematite sample #2 in the oxalic/nitric acid mixture, where 90% dissolution was observed after 21 days. This is consistent with the observation of a larger average particle size for this material (Table 3-1, sonicated results).

The effect of the liquid:solid phase ratio on the dissolution of hematite (#1) was evaluated by conducting two additional kinetics tests at mass phase ratios of 100:1 and 20:1 (Table 4-4 and Figure 4-6). The phase ratios were above and below the baseline phase ratio of 50:1 used in all other tests. A phase ratio of 100:1 was expected to result in complete dissolution of the solid phase based on previous testing. Nearly complete solid phase dissolution (>95%) was observed for the high phase ratio samples containing either oxalic acid alone or an oxalic/nitric acid mixture within one week based on the measured iron concentrations and the known reagent amounts. In this case, the presence of the supplemental acid had little effect on the final iron concentration (0.055 to 0.061 M), since the solid phase was the limiting reagent rather than the hydrogen ion. The tests conducted at a low mass phase ratio of 20:1 exhibited the fastest dissolution rate of all of the hematite tests conducted. Greater than 90% dissolution was observed for the low phase ratio tests with and without nitric acid within 3 days. The fact that the final measured iron concentrations observed at 20:1 and 50:1 mass ratios were similar (0.114 versus 0.106, respectively) is an indication that hematite sample #1 is nearly homogeneous in composition and phase. The final solution pH values for the tests conducted at high and low phase ratios were similar to the values measured for the tests at a phase ratio of 50:1.

Dissolution kinetics tests were also conducted for magnetite and lepidocrocite samples with 1 wt. % oxalic acid with and without 0.35 M nitric acid. The results are shown in Table 4-5 and Figure 4-7. Results observed for hematite under these conditions are also provided for comparison. In oxalic acid and oxalic/nitric acid mixtures, the dissolution of the lepidocrocite and magnetite phases is fast, with greater than 90% dissolution observed within 1 day. These results confirm that non-hematite phases dissolve more quickly. As was the case for hematite in the absence of nitric acid, the maximum iron concentrations are in the range 0.06 to 0.07 M, while higher concentrations are observed with the oxalic/nitric acid mixture. The maximum iron concentrations observed for both magnetite and lepidocrocite in 0.35 M nitric acid and 1 wt. % oxalic acid are consistent with the values reported in Table 4-3 for these phases in 0.25 and 0.5 M nitric acids with 1 wt. % oxalic acid. The results for magnetite and lepidocrocite in the oxalic/nitric acid mixture are significantly higher than was observed for hematite under the same conditions and higher (28-38% higher, respectively) than would be expected based on complete utilization of the oxalate anion to form the 1:1 Fe(III)-oxalate complex. The higher solubility indicates that these phases are more susceptible to direct dissolution in acid without oxalate complexation than is hematite. This is expected for magnetite based on the fact that it contains 33% Fe(II), which is not believed to require oxalate complexation for dissolution.

4.1.5 Hematite and Magnetite Solubility in Oxalic/Sulfuric Acid Mixtures

Solubility tests were also conducted using sulfuric acid as a supplemental acid to promote oxalic acid based dissolution of hematite. Dissolution tests were conducted with oxalic/sulfuric acid mixtures at oxalic acid concentrations ranging from 1 to 8 wt. % and sulfuric acid concentrations ranging from 0.125 to 1.0 M. No background sodium salts were included in these test solutions. Results are provided in Table 4-6 and Figure 4-8. In the figure, the final iron concentration is plotted versus the initial sulfuric acid concentration to show the linear dependence of the solubility. The slopes of the least squares linear fits to the

data for each oxalic acid concentration are similar for all oxalic acid concentrations. Comparison of the results with sulfuric acid to the data obtained using nitric acid as a supplemental proton source, reveals that sulfuric acid is approximately twice as effective as nitric acid at promoting hematite dissolution in oxalic acid. While a nitric acid concentration of approximately 0.35 M is needed to fully utilize 1 wt. % oxalic acid and promote complete utilization of the oxalate ion, between 0.125 and 0.25 M sulfuric acid is required. Similarly, for 4 and 8 wt. % oxalic acid solutions, 0.5 and 1.0 M sulfuric acid solutions (respectively) are sufficient to obtain iron solutions at nearly stoichiometric concentrations based on the added oxalate ion. Presumably the effectiveness of sulfuric acid is due to the fact that this is a diprotic acid.

Dissolution kinetics tests were also conducted for hematite and magnetite using solutions containing 1 wt. % oxalic acid and 0.2 M sulfuric acid. Based on the data above it was believed that 0.2 M sulfuric acid was sufficient to promote full utilization of the oxalate ion in 1 wt. % oxalic acid. Results are provided in Table 4-5 and Figure 4-9. No data was collected between 7 and 35 days of contact time. After 7 days of contact, 86% hematite dissolution and 97% magnetite dissolution were observed. These kinetics results are on the same timescale as the previously discussed data for oxalic/nitric acid mixtures, and it is anticipated that these dissolution rates are acceptable for tank cleaning applications. The maximum iron concentration observed for hematite of 0.134 M in the oxalic/sulfuric acid mixture during kinetics tests was consistent with the data in Figure 4-8 for 1 wt. % oxalic/sulfuric acid mixtures. The predicted iron concentration in the 1 wt. % oxalic/0.2 M sulfuric acid mixture based on the least squares fit to the data in Figure 4-8 was 0.131 M. As was observed with nitric acid, the maximum iron concentration in the oxalic/sulfuric acid mixture is greater than the sum of the hematite solubilities determined for the individual acids. The hematite solubility in pure oxalic acid is 0.06 M, while the solubility in 0.2 M sulfuric acid is 0.05 M, giving a total solubility of 0.11 M. The maximum iron concentration observed for magnetite in the oxalic/sulfuric acid mixture of nearly 0.2 M was especially high compared to other phases.

4.1.6 Hematite Solubility in the Presence of Other Iron Oxidation States

Short-term (7 days) hematite dissolution kinetics tests were also conducted using oxalic acid and oxalic/nitric acid mixtures with various other iron sources added. The purpose of these tests was to evaluate the impact of the presence of iron in other oxidation states upon the Fe(III)-oxalic acid system. 1 wt. % oxalic acid was used for all tests and the nitric acid concentration for tests involving acid mixtures was 0.35 M. Other iron sources included $FeCl_2 \cdot 4H_2O$, wustite (FeO), and carbon steel coupons. Ferrous chloride and wustite were added at levels that would generate 0.01 M Fe(II) if the solids dissolved entirely. Small carbon steel coupons with a total surface area of 7.2 cm^2 were added to the test bottles which contained approximately 100 mL of solution. This corresponds to a steel surface area to solution volume ratio of 2.2 ft^2/ft^3, which is near the range expected during tank chemical cleaning operations. The addition of ferrous chloride and wustite had minimal effects upon hematite dissolution in oxalic acid and oxalic/nitric acid mixtures. Iron solubility after 7 days of contact was similar to that observed with pure hematite in these solutions. Slightly

higher iron concentrations were observed for the solutions containing ferrous chloride, most likely due to the fact that this reagent is more soluble than wustite in oxalic acid.

Results observed for samples containing carbon steel coupons were quite different. These tests involved placement of the coupon into the Teflon sample bottles, which were continually agitated at 250 RPM. The coupons were positioned such that they laid flat on the bottom of the bottle. Therefore, as the bottles were agitated, the coupon surface was likely continually rubbed against the bottom of the bottle. This may have resulted in the continual presentation of a fresh carbon steel surface with little surface passivation from ferrous oxalate. For the sample containing hematite in the oxalic/nitric acid mixture with a carbon steel coupon, sample self heating and off-gassing were observed within one hour after contact and the solution color became dark brown. Off-gassing subsided after a few hours, but the bottle was observed to be pressurized prior to the 1-day sampling event and a yellow gas (presumably NO_x) was observed when the cap was removed. Interestingly, no off-gassing was observed for the sample containing a coupon and ferrous chloride in the oxalic/nitric acid mixture. During the 2-day sampling event, samples that contained hematite, a coupon, and pure oxalic acid (no added nitric acid) were observed to have nearly clear solutions. The measured iron concentrations for these samples confirmed the visual observations. Iron concentrations for the samples containing hematite, a coupon, and oxalic/nitric mixtures were particularly high (0.16 M) after 2 days. All four samples that contained coupons exhibited a maximum in iron solubility at 1 or 2 days follow by a decrease from 2 to 7 days. This effect was much more pronounced for the samples that did not contain nitric acid, where the soluble iron decreased to 0.01 M within 5 days. Iron solubility remained relatively high for the samples that contained nitric acid. The results observed with the coupons are consistent with the formation of a less soluble iron phase (perhaps ferrous oxalate) associated with the steel corrosion reactions, which is significantly more soluble in oxalic/nitric acid mixtures than in oxalic acid alone. The observation that carbon steel coupons cause such dramatic decreases in iron solubility in pure oxalic acid indicates that this may be area of concern for tank chemical cleaning. At a minimum, these observations should be taken into consideration when determining the method of agitation to use during cleaning operations.

4.2 SOLUBILITY TESTING WITH GIBBSITE

Dissolution kinetics tests were conducted with pure phase gibbsite reagent using oxalic, nitric, and sulfuric acid solutions and acid mixtures. The mineral acid reagent concentrations used (0.35 M nitric acid and 0.2 M sulfuric acid) were selected based on the results described in previous sections, which indicated that these were the concentrations required for complete utilization of the oxalate ion to promote iron dissolution in 1 wt. % oxalic acid. Results are provided in Table 4-7 and Figure 4-11. Greater than 90% dissolution was observed within 13 days for every sample except for the test involving 0.2 M sulfuric acid, where 86% dissolution was observed. Oxalic acid was effective at dissolving gibbsite (final Al: 0.07 M). Sulfuric acid was the most effective pure acid at dissolving gibbsite (final Al: 0.13 M), with nitric acid giving intermediate results. Based on the results, it is believed that gibbsite dissolution primarily involves acid-base chemistry, rather than oxalate complexation. For the acid mixtures, the overall solubility was essentially the sum of the

solubilities observed with the pure acids. For the oxalic/nitric acid mixture, the sum of the solubilities measured for the pure acids was 0.175 M and the observed solubility for the mixture was 0.181 M. For the oxalic/sulfuric acid mixture, the sum of the solubilities measured for the pure acids was 0.201 M and the observed solubility for the mixture was 0.194 M. In general, gibbsite dissolution in dilute acids is effective at 50 ºC. For actual sludge waste, which includes both iron and aluminum phases, it is believed that aluminum dissolution will primarily consume hydrogen rather than oxalate ions. Optimal sludge dissolution might involve preliminary contact with dilute mineral acid to neutralize residual base equivalents in the sludge and to promote aluminum dissolution prior to oxalate addition. Aluminum dissolution could also be accomplished using caustic wash methods (Reboul, 2004). Iron dissolution could then be accomplished by the addition of oxalic/mineral acid mixtures. Without preliminary acid washes, higher mineral acid concentrations may be needed to promote iron phase dissolution for a given oxalic acid concentration.

Table 4-1. Dissolution Test Results for Hematite #1 Versus pH in Various Oxalic Acid Concentrations

Oxalic Acid (M)	HNO₃ (M)	NaOH (M)	Total Na (M)	Final Fe (M)	Final pH
1 wt. % oxalic acid					
0.111	1.000	0.000	0.000	0.182	0.22
0.111	0.500	0.000	0.000	0.126	0.70
0.111	0.500	0.000	0.220	0.121	0.50
0.111	0.500	0.000	1.150	0.088	0.55
0.111	0.250	0.000	0.220	0.088	0.70
0.111	0.125	0.000	0.220	0.071	0.87
0.111	0.000	0.000	0.000	0.057	1.62
0.111	0.000	0.000	0.220	0.055	1.25
0.111	0.000	0.094	1.244	0.040	2.15
0.111	0.000	0.094	0.220	0.038	2.60
0.111	0.000	0.108	0.220	0.033	3.65
4 wt. % oxalic acid					
0.452	1.000	0.000	0.000	0.443	0.31
0.452	0.500	0.000	0.452	0.327	0.36
0.452	0.500	0.000	0.000	0.256	0.73
0.452	0.250	0.000	0.452	0.262	0.55
0.452	0.000	0.000	0.452	0.245	0.82
0.452	0.000	0.000	0.000	0.256	1.37
0.452	0.000	0.338	0.451	0.174	1.95
0.452	0.000	0.406	0.451	0.151	2.57
0.452	0.000	0.451	0.451	0.134	4.46
8 wt. % oxalic acid					
0.920	1.0	0.00	0.00	0.673	0.31
0.920	0.5	0.00	0.00	0.601	0.70
0.920	0.0	0.00	0.00	0.511	1.16

Conditions: 50:1 liquid/solid mass ratio, 42 day contact time, 50 ºC

Table 4-2 Dissolution Test Results for Hematite #1 Versus pH with Various Other Acids and at a Complexant Concentration of 0.111 M

Acid	HNO$_3$ (M)	Initial NaOH (M)	Final Fe (M)	Final pH
formic	0.35	0.00	0.0228	0.60
formic	0.00	0.00	0.0002	2.04
formic	0.00	0.10	<1.68E-6	4.71
acetic	0.35	0.00	0.0260	0.59
acetic	0.00	0.00	2.32E-05	2.39
acetic	0.00	0.10	<1.68E-6	5.71
citric	0.35	0.00	0.0100	0.59
citric	0.00	0.00	0.0036	1.74
citric	0.00	0.10	0.0098	3.29
gluconic	0.35	0.00	0.0093	0.58
gluconic	0.00	0.00	0.0005	2.08
gluconic	0.00	0.10	0.0002	4.36
gluconic	0.00	0.12	2.03E-05	7.53
glycolic	0.35	0.00	0.0225	0.56
glycolic	0.00	0.00	0.0004	2.09
glycolic	0.00	0.10	1.14E-05	4.61

Conditions: 50:1 liquid/solid mass ratio, 46 day contact time, 50 ºC

Table 4-3 Dissolution Test Results Versus pH for Multiple Iron Phases in 1 Weight Percent Oxalic Acid

Reagent	HNO₃ (M)	Initial NaOH (M)	Final Fe (M)	Final pH
magnetite	0.50	0.00	0.192	0.68
magnetite	0.25	0.00	0.124	0.91
magnetite	0.00	0.00	0.071	1.75
magnetite	0.00	0.12	0.032	5.53
wustite	0.50	0.00	0.169	0.63
wustite	0.25	0.00	0.099	0.87
wustite	0.00	0.00	0.028	2.19
wustite	0.00	0.12	0.030	5.54
hematite #1	0.25	0.00	0.097	0.71
hematite #1	0.00	0.00	0.064	1.45
hematite #1	0.00	0.12	0.033	5.14
maghemite	0.25	0.00	0.122	0.78
maghemite	0.00	0.00	0.068	1.67
maghemite	0.00	0.12	0.033	5.55
goethite	0.25	0.00	0.094	0.73
goethite	0.00	0.00	0.063	1.43
goethite	0.00	0.12	0.033	5.06
lepidicrocite	0.25	0.00	0.124	0.89
lepidicrocite	0.00	0.00	0.068	1.76
lepidicrocite	0.00	0.12	0.033	5.51
amorphous iron oxide	0.25	0.00	0.103	0.83
amorphous iron oxide	0.00	0.00	0.045	1.96
amorphous iron oxide	0.00	0.12	0.015	6.15

Conditions: 50:1 liquid/solid mass ratio, 41 day contact time, 50 ºC

Table 4-4. Dissolution Kinetics Results for Various Hematite Samples in 1 Weight Percent Oxalic Acid With and Without 0.35 M HNO₃ at 50 ºC

HNO₃ (M)	Days	Fe (M)	pH	% Dissolved
hematite #1 (20:1 mass ratio)				
0.35	1	0.085	0.31	74.7
0.00	1	0.060	1.21	97.5
0.35	3	0.103	---	90.0
0.00	3	0.062	---	100.0
0.35	5	0.111	---	97.2
0.00	5	0.063	---	101.4
0.35	7	0.113	---	98.9
0.00	7	0.063	---	101.1
0.35	14	0.109	0.64	95.5
0.00	14	0.059	1.43	95.3
0.35	21	0.111	---	97.7
0.00	21	0.061	---	99.2
0.35	28	0.114	0.51	100.1
0.00	28	0.063	1.37	101.6
0.35	35	0.114	---	100.0
0.00	35	0.062	---	100.0
0.35	52	---	0.60	---
0.00	52	---	1.48	---
hematite #1 (50:1 mass ratio)				
0.35	1	0.060	0.29	56.8
0.00	1	0.057	1.20	92.4
0.35	3	0.085	---	79.7
0.00	3	0.060	---	96.2
0.35	5	0.094	---	88.6
0.00	5	0.061	---	98.2
0.35	7	0.102	---	96.2
0.00	7	0.064	---	102.4
0.35	14	0.098	0.63	92.2
0.00	14	0.061	1.44	98.6
0.35	21	0.104	---	97.6
0.00	21	0.061	---	98.2
0.35	28	0.107	0.53	100.3
0.00	28	0.062	1.32	100.0
0.35	35	0.106	---	100.0
0.00	35	0.062	---	100.0
0.35	52	---	0.65	---
0.00	52	---	1.44	---

Table 4-4 (continued)

HNO$_3$ (M)	Days	Fe (M)	pH	%Dissolved
hematite #1 (100:1 mass ratio)				
0.35	1	0.021	0.26	34.9
0.00	1	0.038	0.99	67.8
0.35	3	0.045	---	73.9
0.00	3	0.049	---	88.0
0.35	5	0.053	---	87.4
0.00	5	0.051	---	92.5
0.35	7	0.058	---	95.3
0.00	7	0.054	---	96.7
0.35	14	0.058	0.54	95.1
0.00	14	0.053	1.29	94.6
0.35	21	0.060	---	98.1
0.00	21	0.053	---	96.0
0.35	28	0.061	0.43	100.0
0.00	28	0.055	1.22	100.0
0.35	35	---	---	---
0.00	35	0.055	---	99.9
0.35	52	---	0.58	---
0.00	52	---	1.37	---
hematite #2 (50:1 mass ratio)				
0.35	1	0.031	0.28	30.7
0.00	1	0.034	0.97	56.7
0.35	3	0.061	---	60.7
0.00	3	0.053	---	88.3
0.35	5	0.076	---	75.5
0.00	5	0.057	---	94.4
0.35	7	0.083	---	83.1
0.00	7	0.058	---	96.9
0.35	14	0.089	0.57	88.3
0.00	14	0.056	1.39	93.3
0.35	21	0.095	---	94.9
0.00	21	0.059	---	98.6
0.35	28	0.100	0.48	99.3
0.00	28	0.060	1.28	100.0
0.35	35	0.100	---	100.0
0.00	35	0.060	---	100.0
0.35	52	---	0.60	---
0.00	52	---	1.41	---

Table 4-4 (continued)

HNO$_3$ (M)	Days	Final Fe (M)	pH	% Dissolved
hematite #3 (50:1 mass ratio)				
0.35	1	0.062	0.30	59.0
0.00	1	0.058	1.18	95.4
0.35	3	0.090	---	85.3
0.00	3	0.060	---	98.6
0.35	5	0.099	---	93.8
0.00	5	0.062	---	102.1
0.35	7	0.102	---	96.6
0.00	7	0.062	---	102.3
0.35	14	0.102	0.66	97.1
0.00	14	0.059	1.43	97.5
0.35	21	0.104	---	98.8
0.00	21	0.060	---	99.2
0.35	28	0.105	0.52	100.0
0.00	28	0.061	1.32	101.1
0.35	35	0.105	---	100.0
0.00	35	0.061	---	100.0
0.35	52	---	0.59	---
0.00	52	---	1.46	---

Table 4-5. Dissolution Kinetics Results for Other Iron Phases and Conditions in 1 Wt. % Oxalic Acid with and Without 0.35 M HNO₃ and 0.2 M H₂SO₄ at 50 ºC

HNO₃ (M)	H₂SO₄ (M)	Days	Final Fe (M)	pH	% Dissolved
magnetite (50:1 mass ratio)					
0.35	0.00	0.15	0.075	---	55.3
0.00	0.00	0.15	0.068	---	91.7
0.00	0.20	0.15	0.112	---	58.9
0.35	0.00	1.0	0.125	---	92.0
0.00	0.00	1.0	0.073	---	98.0
0.00	0.20	1.0	0.159	---	84.2
0.35	0.00	2.2	0.130	---	95.8
0.00	0.00	2.2	0.073	---	98.1
0.00	0.20	2.2	0.187	---	98.9
0.35	0.00	5.1	0.140	---	102.8
0.00	0.00	5.1	0.075	---	100.9
0.00	0.20	5.1	0.183	---	96.7
0.35	0.00	7.1	0.136	0.64	95.6
0.00	0.00	7.1	0.074	1.80	101.5
0.00	0.20	7.1	0.189	1.20	97.1
0.35	0.00	28.0	---	0.71	---
0.00	0.00	28.0	---	1.91	---
0.00	0.20	28.0	---	1.23	---
0.35	0.00	35.0	0.142	0.71	100.0
0.00	0.00	35.0	0.073	1.91	100.0
0.00	0.20	35.0	0.195	1.23	100.0
lepidocrocite (50:1 mass ratio)					
0.35	0.00	0.15	0.134	---	87.6
0.00	0.00	0.15	0.067	---	98.6
0.35	0.00	1.0	0.166	---	108.8
0.00	0.00	1.0	0.074	---	109.2
0.35	0.00	2.2	0.149	---	97.6
0.00	0.00	2.2	0.058	---	85.6
0.35	0.00	5.1	0.166	---	108.7
0.00	0.00	5.1	0.068	---	100.5
0.35	0.00	7.1	0.159	0.74	104.2
0.00	0.00	7.1	0.068	1.78	100.3
0.35	0.00	28.0	---	0.79	---
0.00	0.00	28.0	---	1.75	---
0.35	0.00	35.0	0.153	---	100.0
0.00	0.00	35.0	0.068	---	100.0

Table 4-5 (continued)

HNO$_3$ (M)	H$_2$SO$_4$ (M)	Days	Final Fe (M)	pH	% Dissolved
hematite #1 (50:1 mass ratio)					
0.00	0.20	0.15	0.011	---	8.2
0.00	0.20	1.0	0.065	---	48.7
0.00	0.20	2.2	0.076	---	57.0
0.00	0.20	5.1	0.110	---	82.2
0.00	0.20	7.1	0.116	0.88	86.3
0.00	0.20	28.0	---	0.92	---
0.00	0.20	35.0	0.134	---	100.0

Table 4-6. Dissolution Test Results for Hematite #1 in Various Oxalic and Sulfuric Acid Mixtures (no added sodium or hydroxide)

Oxalic Acid (M)	H$_2$SO$_4$ (M)	Final Fe (M)	Final pH
1 wt. % oxalic acid			
0.111	1.000	0.417	0.745
0.111	0.500	0.249	0.905
0.111	0.250	0.146	1.040
0.111	0.125	0.101	1.190
4 wt. % oxalic acid			
0.452	1.000	0.770	---*
0.452	0.500	0.482	---
0.452	0.250	0.359	---
0.452	0.125	0.307	---
8 wt. % oxalic acid			
0.920	1.000	1.037	---*
0.920	0.500	0.746	---
0.920	0.250	0.641	---
0.920	0.125	0.583	---

Conditions: 50:1 liquid/solid mass ratio, 42 day contact time, 50 ºC
*final pH not measured, solution pH outside probe range

Table 4-7. Dissolution Test Results for Gibbsite in 1 Weight Percent Oxalic Acid, 0.35 M Nitric and 0.2 M Sulfuric Acids and Mixtures

Oxalic Acid (M)	HNO₃ (M)	H₂SO₄ (M)	Days	Al (M)	pH	% Dissolved
0.111	0.00	0.00	0.15	0.026	---	19.0
0.111	0.35	0.00	0.15	0.034	---	36.3
0.111	0.00	0.20	0.15	0.043	---	22.2
0.00	0.35	0.00	0.15	0.010	---	28.5
0.00	0.00	0.20	0.15	0.037	---	9.3
0.111	0.00	0.00	1.0	0.064	---	47.6
0.111	0.35	0.00	1.0	0.086	---	89.5
0.111	0.00	0.20	1.0	0.112	---	57.9
0.00	0.35	0.00	1.0	0.036	---	70.1
0.00	0.00	0.20	1.0	0.091	---	34.4
0.111	0.00	0.00	2.2	0.070	---	68.2
0.111	0.35	0.00	2.2	0.123	---	98.1
0.111	0.00	0.20	2.2	0.138	---	71.0
0.00	0.35	0.00	2.2	0.050	---	84.6
0.00	0.00	0.20	2.2	0.110	---	48.0
0.111	0.00	0.00	5.1	0.074	---	81.5
0.111	0.35	0.00	5.1	0.147	---	103.7
0.111	0.00	0.20	5.1	0.164	---	84.3
0.00	0.35	0.00	5.1	0.069	---	94.5
0.00	0.00	0.20	5.1	0.123	---	66.3
0.111	0.00	0.00	7.0	---	2.78	---
0.111	0.35	0.00	7.0	---	0.81	---
0.111	0.00	0.20	7.0	---	1.45	---
0.00	0.35	0.00	7.0	---	0.82	---
0.00	0.00	0.20	7.0	---	---	---
0.111	0.00	0.00	13.1	0.172	---	94.9
0.111	0.35	0.00	13.1	0.073	---	101.7
0.111	0.00	0.20	13.1	0.185	---	95.3
0.00	0.35	0.00	13.1	0.130	---	99.9
0.00	0.00	0.20	13.1	0.089	---	85.7
0.111	0.00	0.00	26.1	0.181	3.05	99.8
0.111	0.35	0.00	26.1	0.073	1.30	102.2
0.111	0.00	0.20	26.1	0.197	2.08	101.2
0.00	0.35	0.00	26.1	0.133	1.07	102.2
0.00	0.00	0.20	26.1	0.104	2.60	99.9
0.111	0.00	0.00	35.0	0.071	---	100.0
0.111	0.35	0.00	35.0	0.181	---	100.0
0.111	0.00	0.20	35.0	0.194	---	100.0
0.00	0.35	0.00	35.0	0.104	---	100.0
0.00	0.00	0.20	35.0	0.130	---	100.0

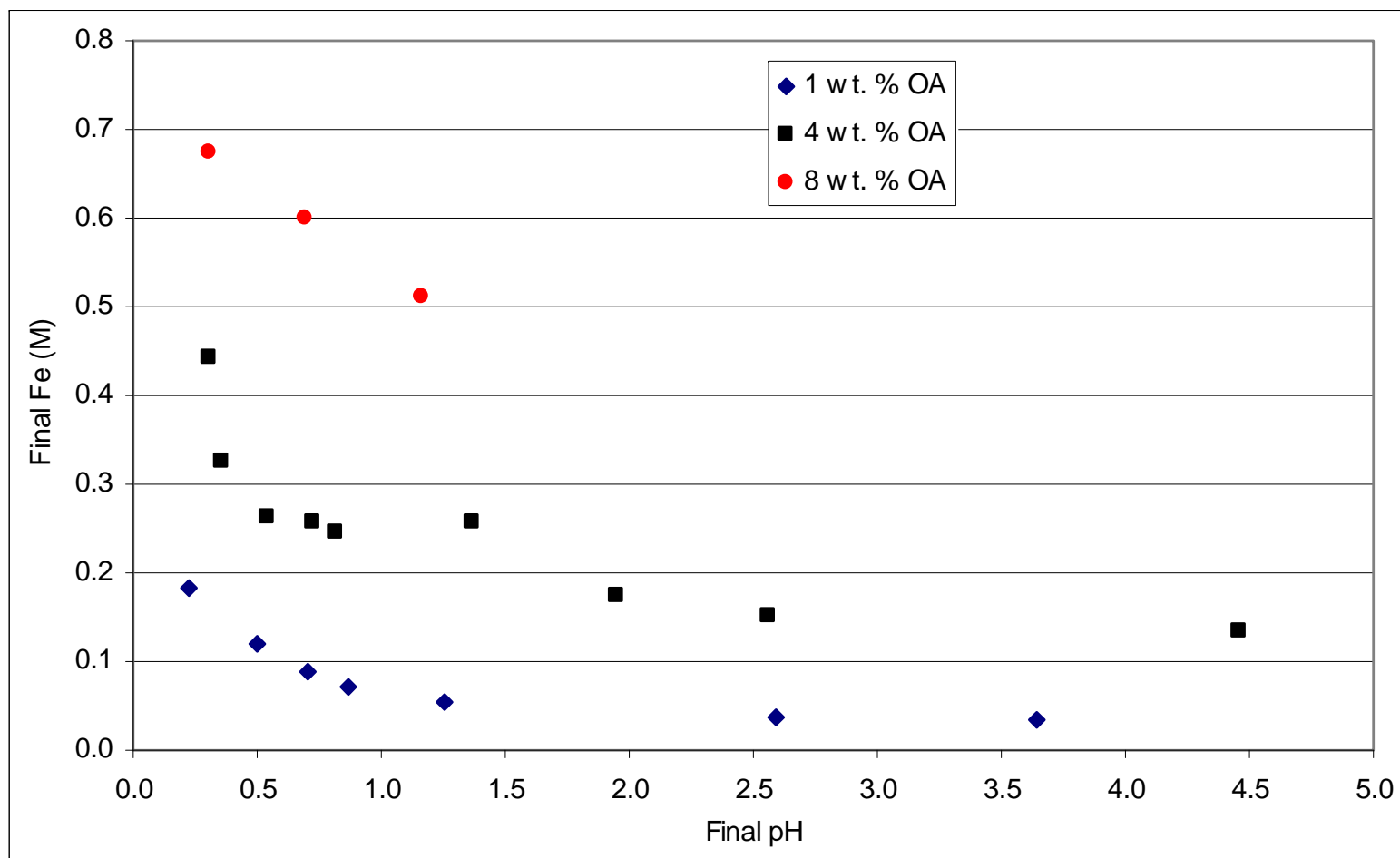Conditions: 50:1 liquid/solid mass ratio, 50 ºC

Figure 4-1. Dissolution results for hematite #1 versus pH with various oxalic acid concentrations at 50 ºC.
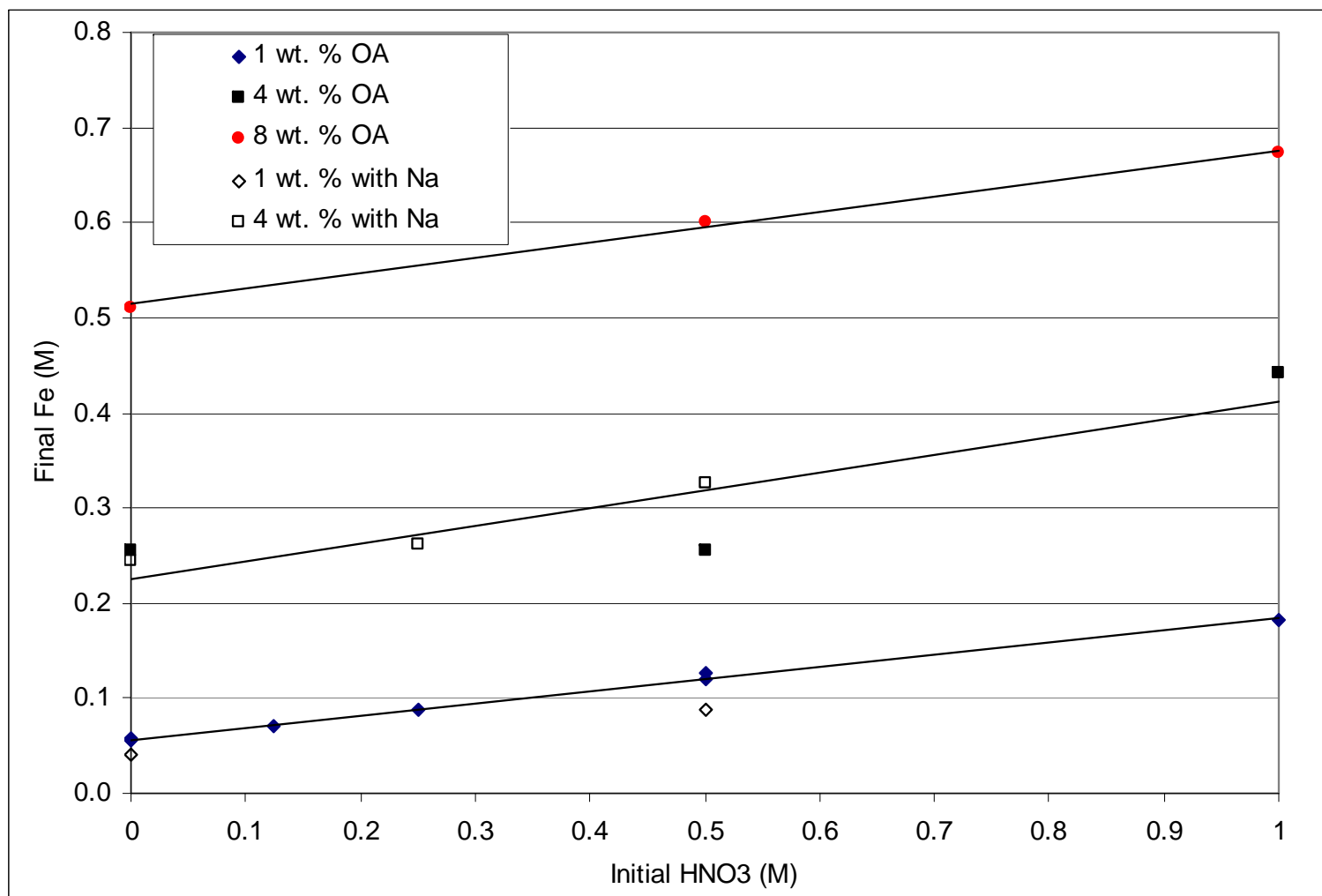
Figure 4-2. Dissolution results for hematite #1 versus initial HNO_3 with various oxalic acid concentrations at 50 ºC (least squares linear fits shown for data points with no added sodium salts).
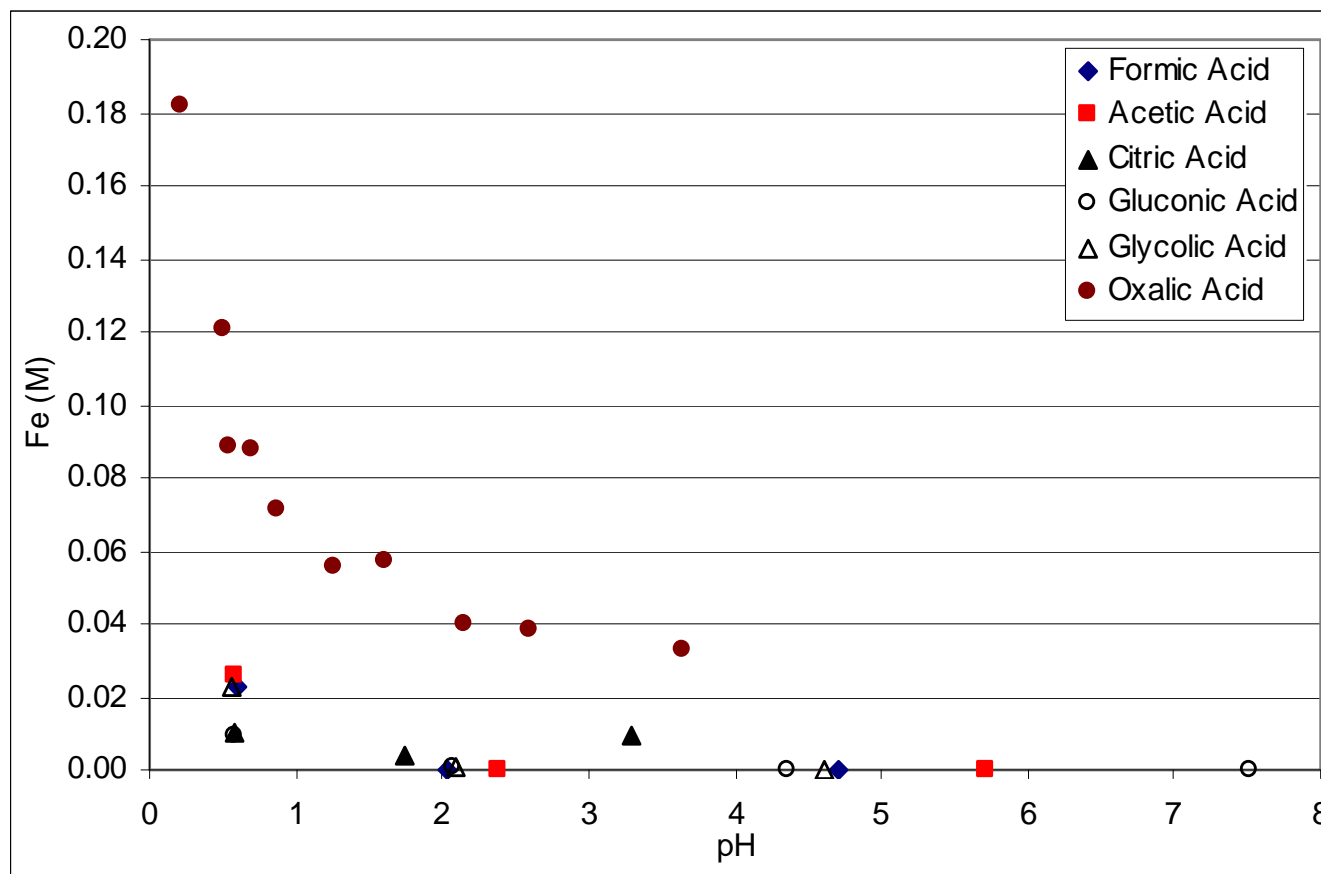
Figure 4-3. Dissolution results for hematite #1 versus pH in various complexing acids (0.11 M) at 50 ºC.

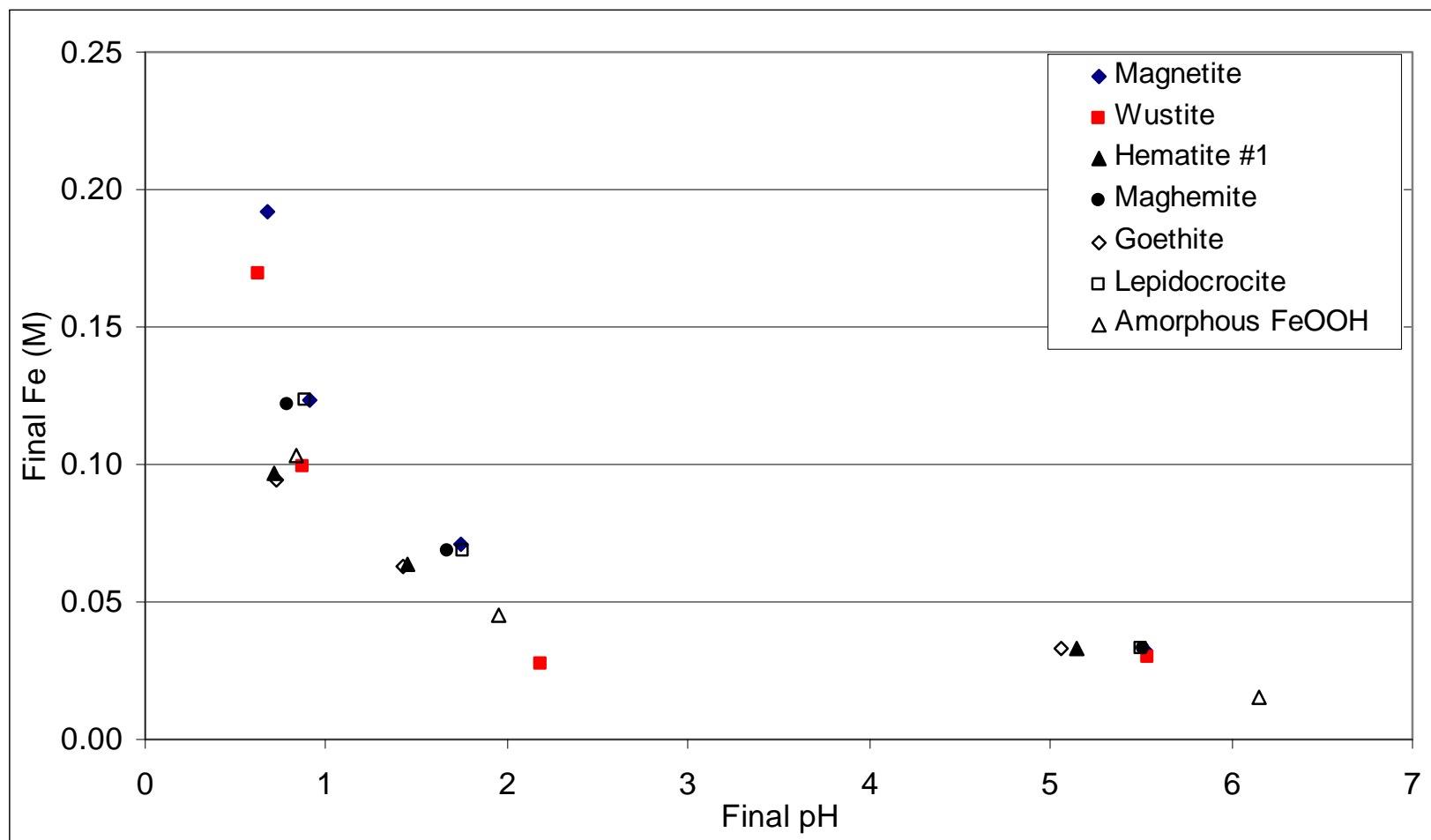**Figure 4-4.** Dissolution results for various iron phases versus pH in 1 wt. % oxalic acid at 50 ºC.
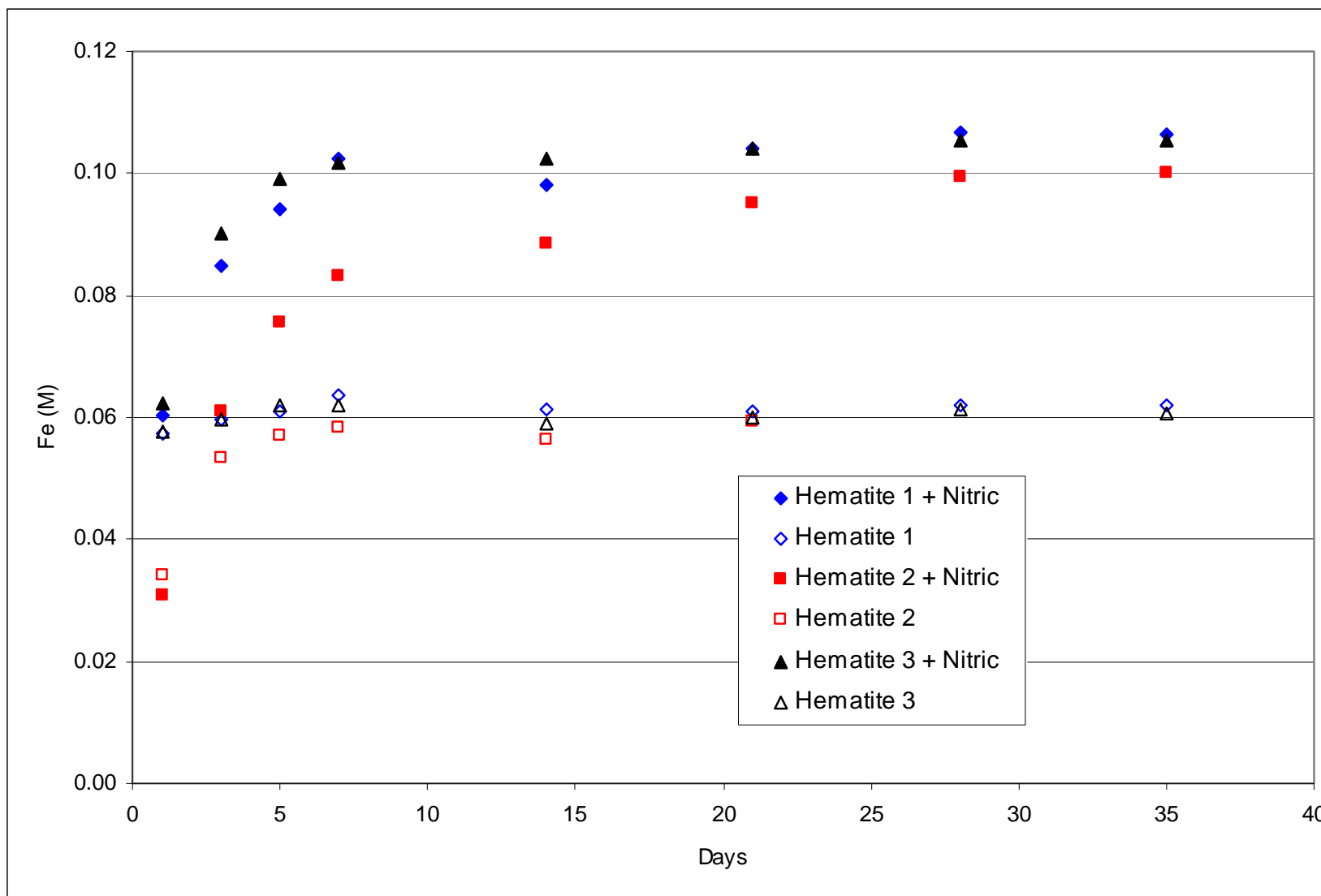
Figure 4-5. Dissolution results for hematite phases versus time in 1 wt. % oxalic acid with and without 0.35 M HNO_3 at 50 ºC.
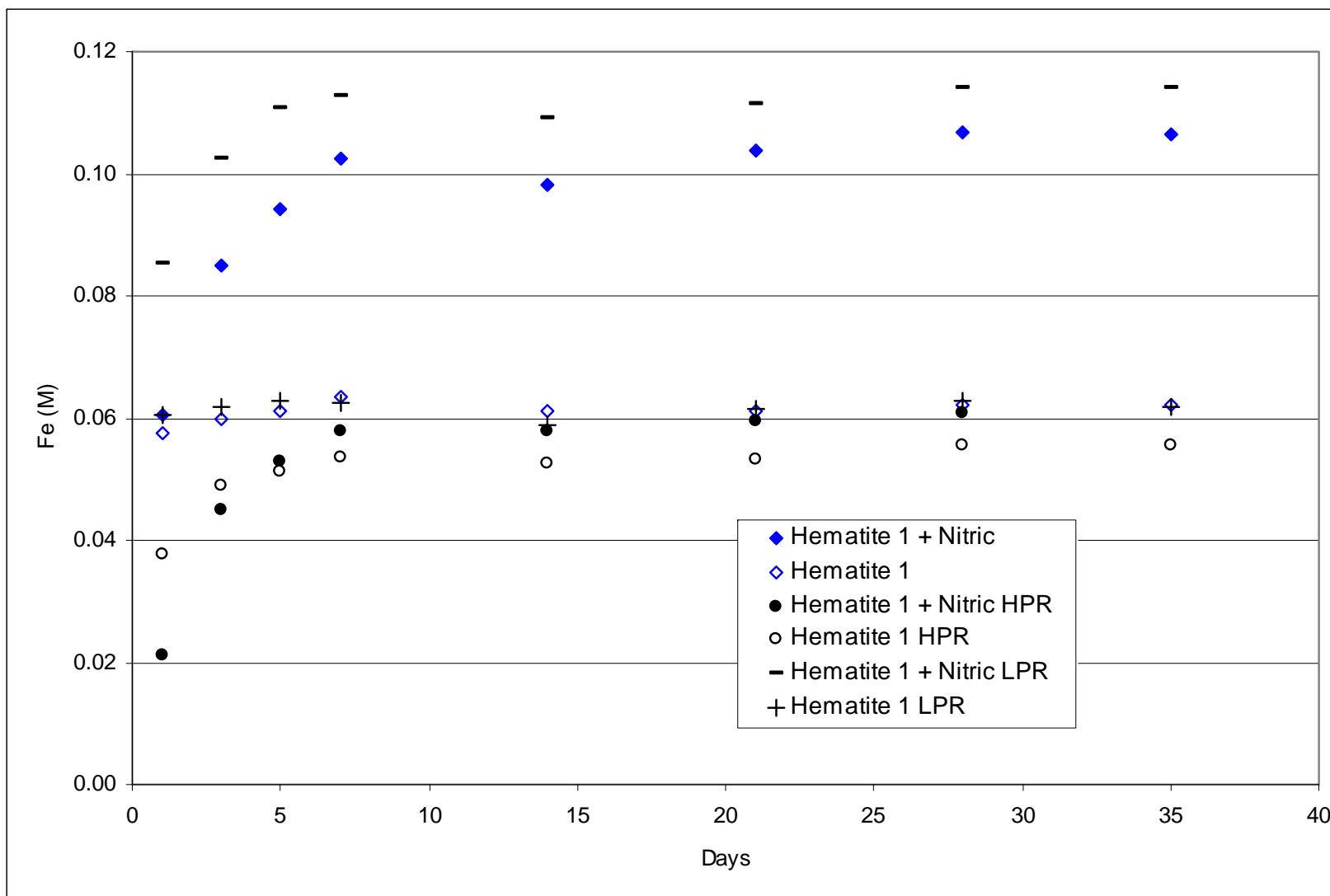
Figure 4-6. Dissolution results for hematite #1 versus time in 1 wt. % oxalic acid with and without 0.35 M HNO_3 at phase ratios of 100:1 (HPR), 50:1, and 20:1 (LPR) at 50 ºC.
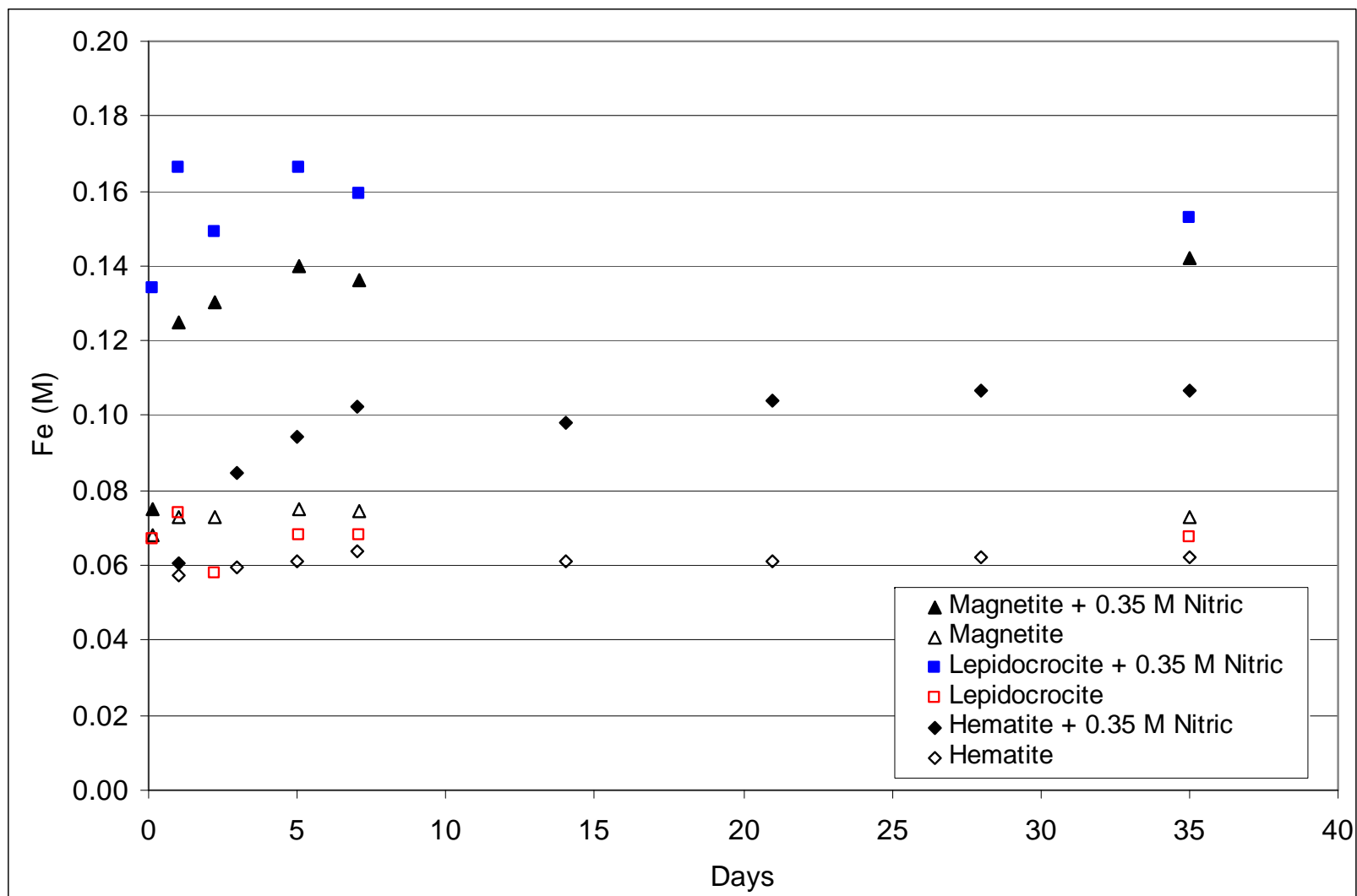
Figure 4-7. Dissolution results for hematite #1, magnetite, and lepidocrocite versus time in 1 wt. % oxalic acid with and without 0.35 M HNO_3 at 50 ºC.
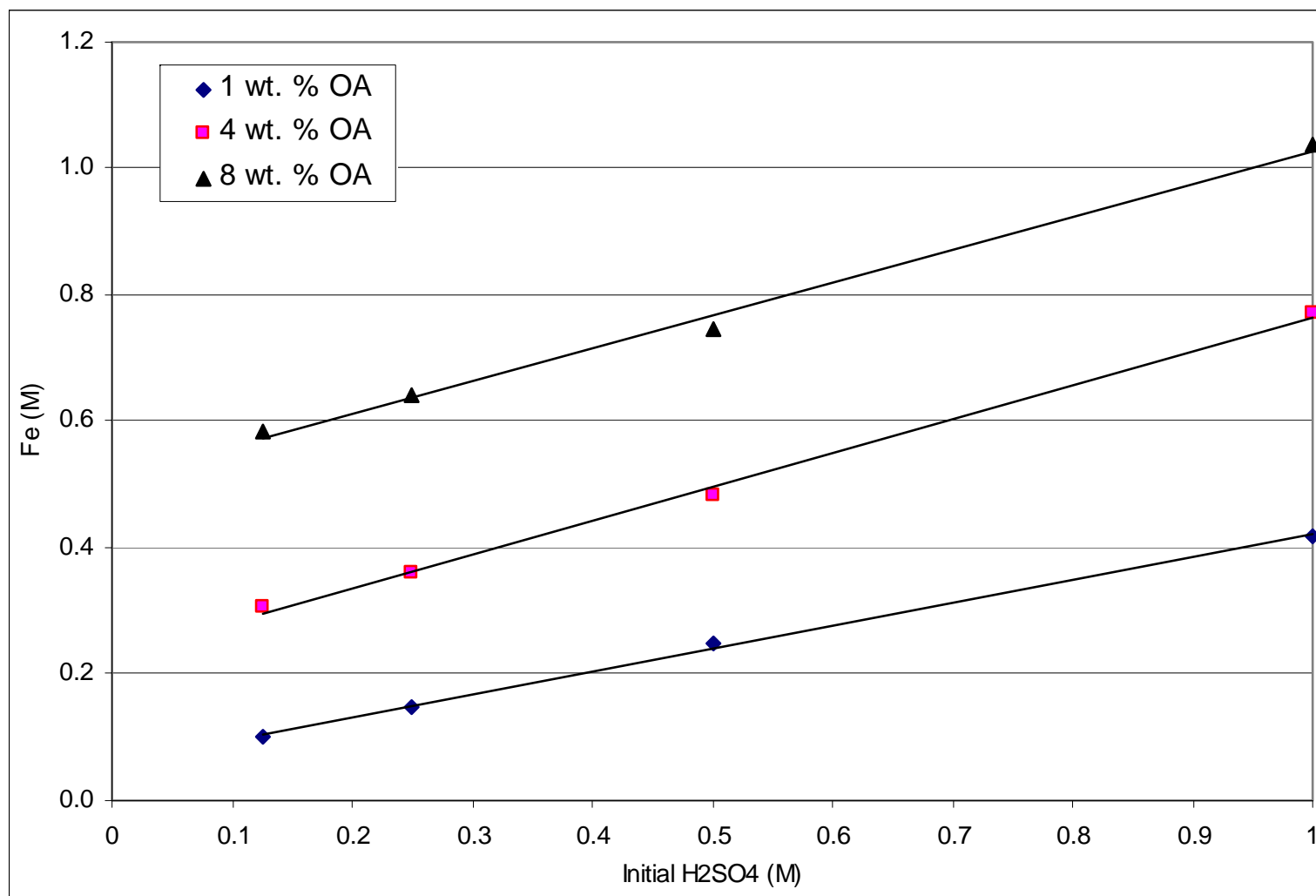
Figure 4-8. Dissolution results for hematite #1 in sulfuric/oxalic acid mixtures at 50 ºC.
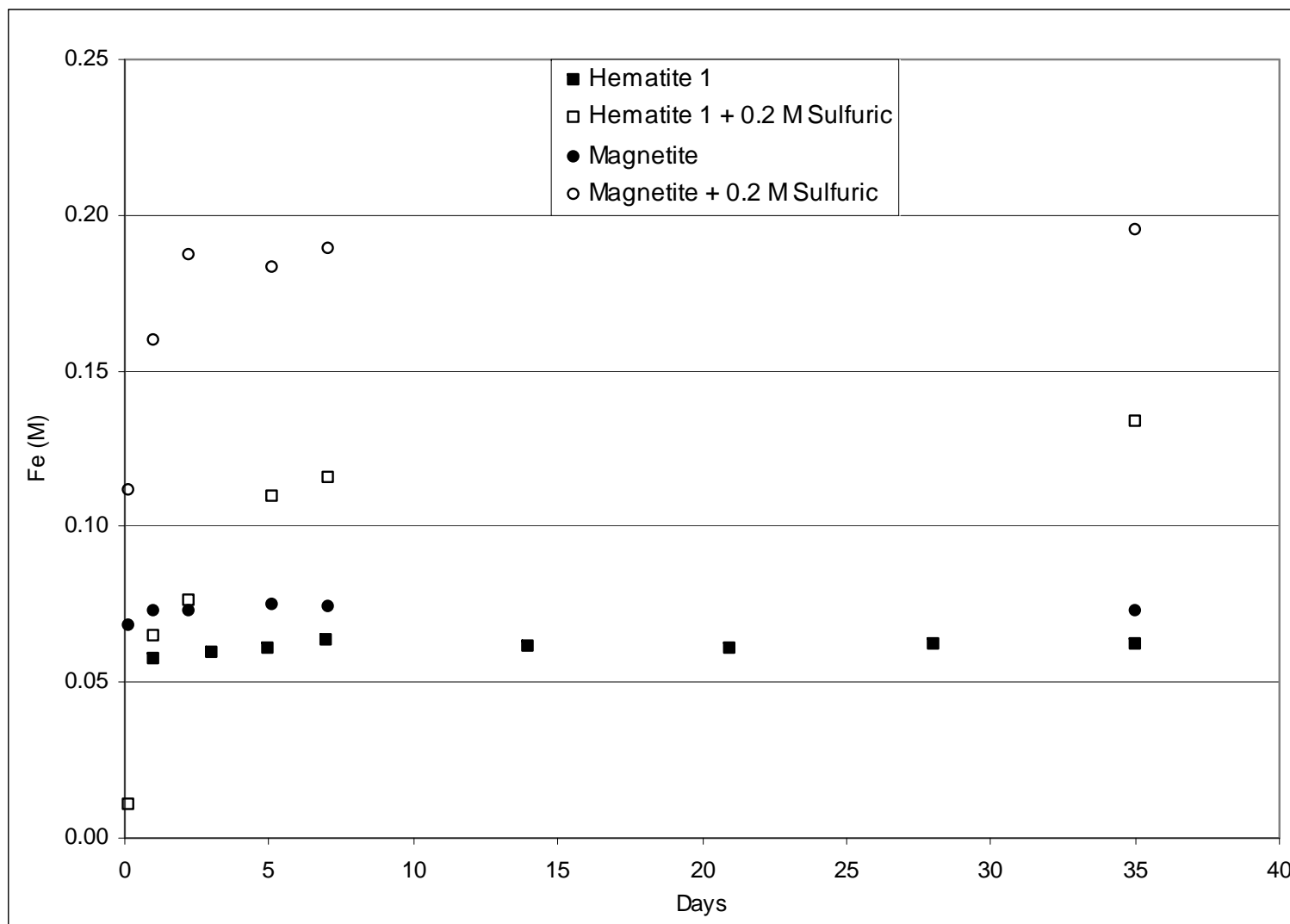
Figure 4-9. Dissolution results for hematite #1 and magnetite versus time in 1 wt. % oxalic acid with and without 0.2 M H_2SO_4 at 50 ºC.

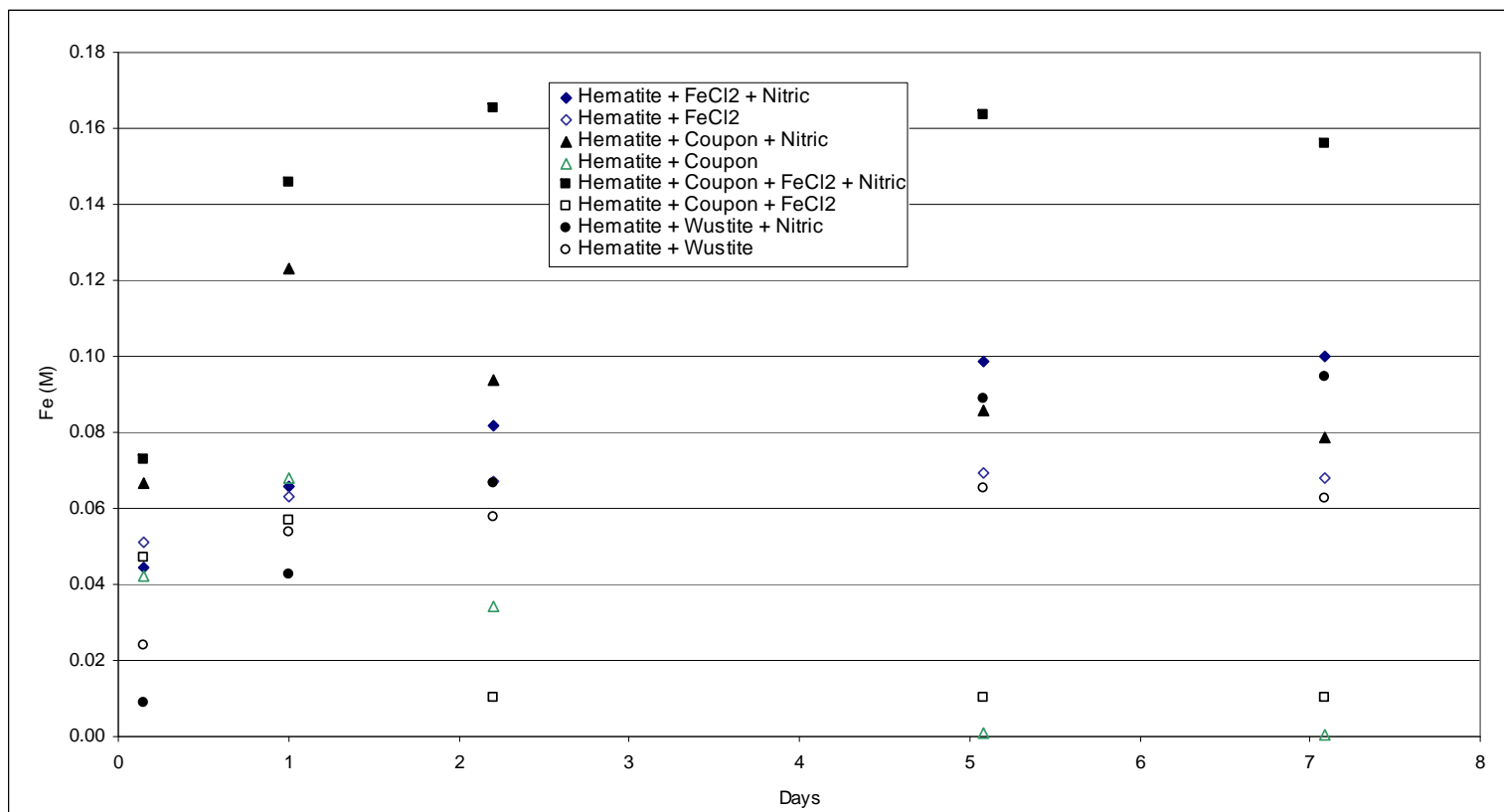**Figure 4-10.** Dissolution results for hematite #1 in 1 wt. % oxalic acid with and without nitric acid and various other iron sources added at 50 ºC.
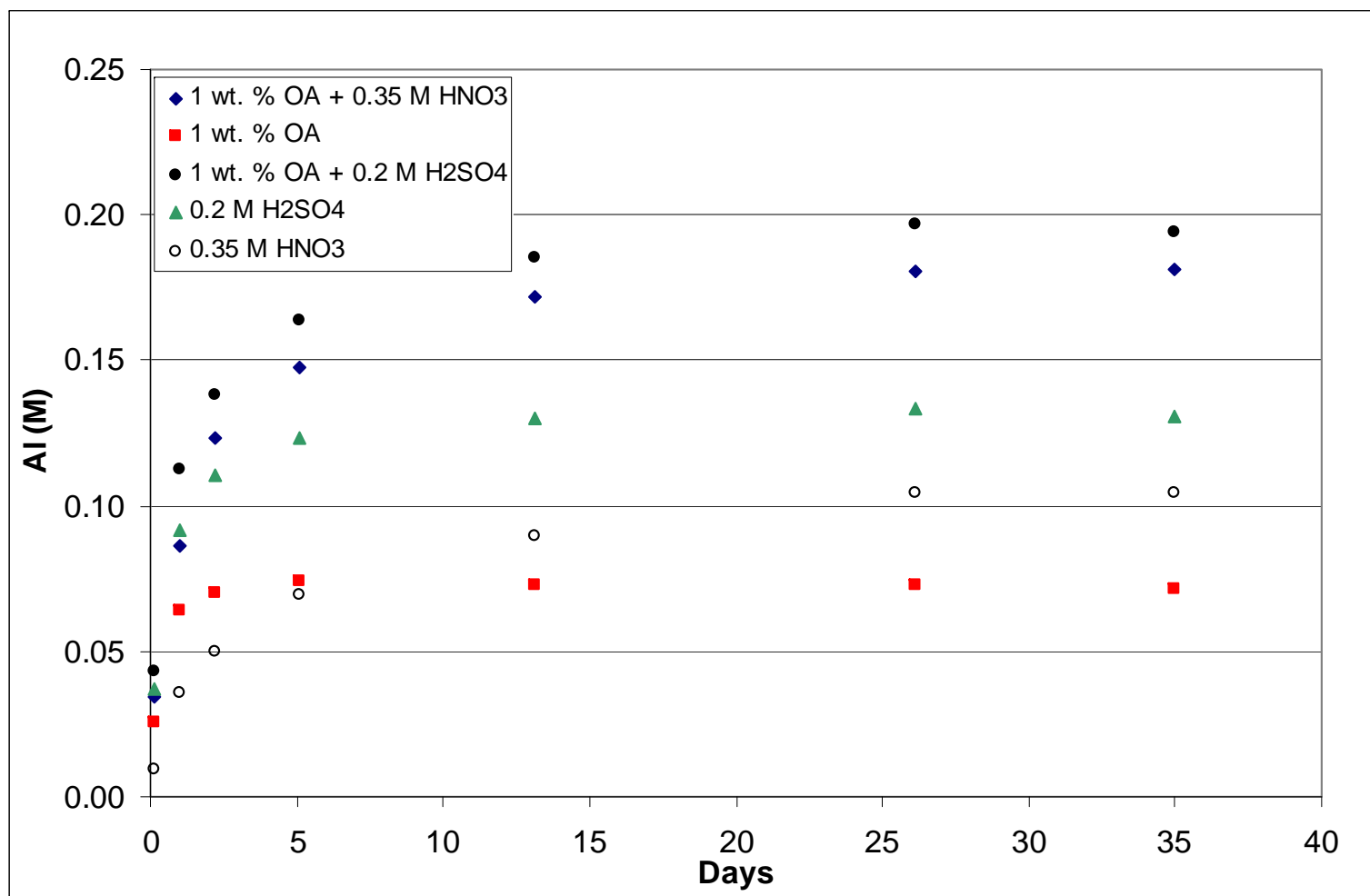
Figure 4-11. Dissolution results for gibbsite versus time in various combinations of oxalic, nitric, and sulfuric acids at 50 ºC.

5.0 THERMODYNAMIC MODELING OF TESTS

As part of the AECC program, a model was developed using the OLI Systems Inc, Environmental Simulation Program (ESP), version 8.1. The purpose of the model was to aid in the experimental design and 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 the pH of the mixture from the first Mix block. Figure 5.1 shows a schematic of the ESP model. The chemistry model for the simulations included the GEOCHEM database as the source for the iron compounds hematite (Fe_2O_3), magnetite (Fe_3O_4), lepidocrocite (FeO(OH)), and wustite (FeO).
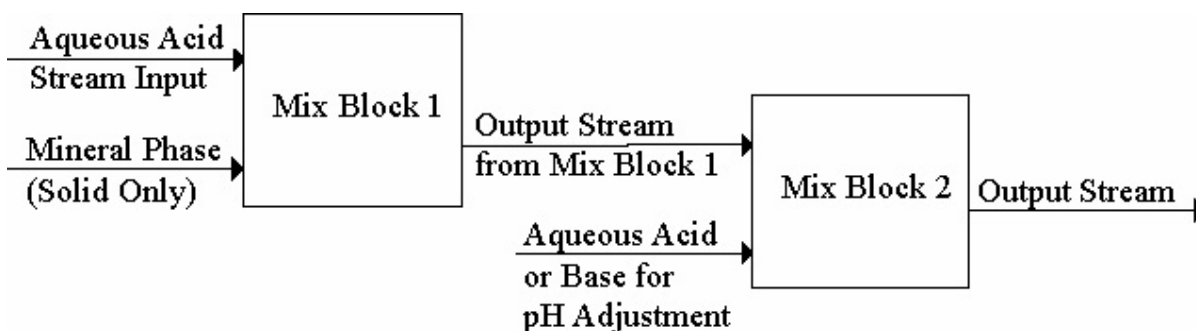
Figure 5.1 Schematic of ESP Model

5.1 MODEL PREDICTIONS COMPARED TO EXPERIMENTAL DATA

The model was used prior to the initiation of experiments to help determine appropriate phase ratios and total acid consumption to eliminate problems with the experimental methodology that lead to some inconsistency in the data from previous testing. In previous testing, the need to add additional solids and acid periodically during each test was thought to be the cause of some of the uncertainty and inconsistency in the resulting data. In this application the absolute accuracy of the model is not as important as the ability of the software to correctly predict trends in the underlying chemistry. The results of the modeling effort led to changes in the experimental methodology and greater consistency in the resulting data.

The model was also used after the completion of the experiments to evaluate how accurately the software predicts the final composition of the individual experiments. The simplified experimental methodology of adding all the required acid at the start of the test, and using appropriate phase ratios so that no additional solids needed to be added during the test, made modeling the tests more straight forward.

Table 5-1 compares the experimental results of hematite (Fe_2O_3) dissolution in various oxalic/nitric acid mixtures at 50 °C with the model predictions. The column labeled "% Diff" shows the percent difference between the iron concentrations measured in the test solutions versus the OLI predicted iron concentration. Positive "% Diff." values correspond to cases where the predicted iron solubility was greater than the observed value. The last two columns show the measured pH of the final test solutions and the OLI predicted pH at the end of the test. In general, the model predicts higher concentrations of iron in the final test solutions than was measured. The higher predicted dissolution of hematite should also result in higher predicted final pH which is also the case. The model does better at predicting the final iron concentration (and pH) when the final pH of the test is above 2.

These modeling results are consistent with the determination from the previous years modeling results that the OLI software over predicts the solubility of hematite in acids. The model predicts that the iron concentration from the dissolution of hematite is governed by three iron-oxalate complexes, $[Fe(C_2O_4)]^+$, $[Fe(C_2O_4)_2]^-$, $[Fe(C_2O_4)_3]^{3-}$, and free Fe^{3+}. At pH$\geq$2 the tri-oxalate complex, $[Fe(C_2O_4)_3]^{3-}$, predominates. As the pH decreases to $\leq$1 the mono-oxalate complex, $[Fe(C_2O_4)]^+$, predominates. This generally agrees with the accepted theory (Lee (1995), Panias (1996), and Christodoulou (2001)), however, the accepted form of the mono-oxalate species thought to be involved is $[Fe(HC_2O_4)]^{2+}$. This difference in the model would affect the predicted pH and therefore the predicted solubility of the iron. This speciation difference might be responsible for some of the differences between the model predictions and the measured experimental results, especially for tests with only oxalic acid. However, for the nitric acid/oxalic acid mixtures, the over prediction of the solubility of Fe^{3+} in nitric acid seems to be the biggest contributor to the over prediction of iron solubility.

Table 5-2 compares the experimental results of hematite dissolution in various oxalic/sulfuric acid mixtures at 50 °C with the model predictions. The model predictions appear much closer to the measured values relative to predictions in oxalic/nitric acid mixtures. Because the predicted iron concentrations are much closer to the measured values, the predicted final pH is also in much better agreement, since the free hydrogen ion concentration is directly affected by the degree of metal phase dissolution. The higher iron concentrations predicted by the model when sulfuric acid is substituted for nitric acid are not the result of sulfate complexation of the iron. The iron sulfate species in solution remain at very low concentrations. The higher iron concentrations are achieved due to the diprotic nature of sulfuric acid. The second proton from the sulfuric acid is not quite as effective as the first proton. Therefore, under the same conditions, the iron concentration resulting from sulfuric /oxalic acid mixtures versus a nitric/oxalic acid mixtures will be something less than 2X higher.

Table 5-3 shows a comparison of the experimental results with the model predictions for the dissolution of various iron phases in oxalic/nitric acid mixtures at 50 °C. The OLI/ESP database does not contain maghemite (γ-Fe_2O_3) or goethite (α-FeO(OH)), so these phases were not included in Table 5-3. The model predictions for hematite (α-Fe_2O_3) and lepidocrocite (γ-FeO(OH)) dissolution appear to be identical. Presumably, the predictions for maghemite and goethite would be the same as for hematite and lepidocrocite. The model

appears to generate the same speciation in solution for all Fe(III) phases. This agrees with the experimental results as discussed in section 4.1.3.

The model over predicts the solubility of Fe(II) phases, as shown in the results for wustite (FeO). This over prediction of Fe(II) was observed in all three acids examined, oxalic acid, nitric acid, and sulfuric acid. There also does not appear to be a solid phase for Fe(II) oxalate, FeC_2O_4, included in the model, so no precipitation of this compound is observed. This same problem was encountered with magnetite (Fe_3O_4), formally a mixture of one Fe(II) and two Fe(III) atoms per molecule. At low phase ratios, the Fe(II) of magnetite was predicted to completely dissolve resulting in a very high iron concentration in solution. However, as the phase ratio increases, the two Fe(III) atoms start to dissolve and the dilution resulting from the higher phase ratio causes the iron concentration to drop, even though some of the iron is still dissolving. The predictions of the iron concentration shown in Table 5-3 for magnetite were obtained by taking the dissolution to 99% of the magnetite dissolved regardless of the phase ratio required. For modeling purposes, the amorphous iron(III) oxide, $Fe(OH)_3$ was chosen from the OLI/ESP database. Again, the modeling results for $Fe(OH)_3$ containing Fe(III) are identical to the results for hematite and lepidocrocite.

Table 5-4 shows a comparison of the experimental results with the model predictions for the dissolution of gibbsite ($Al(OH)_3$) in oxalic acid, nitric acid, sulfuric acid, and oxalic/nitric acid and oxalic/sulfuric acid mixtures at 50 °C. The model does a good job of predicting the solubility of gibbsite in pure nitric and sulfuric acid solutions, but under predicts the solubility in oxalic acid. The model does not predict any oxalate complexation of the aluminum.

The OLI/ESP model appears to be a useful tool for helping to develop an experimental design. The accuracy of the predictions vary widely depending on the metal phase being dissolved, the pH, and the acid system employed. For the accuracy of the model to increase, changes in the Fe-oxalate speciation need to be made, the predicted Fe solubility in nitric acid needs to be adjusted, and the addition of an Fe(II) oxalate solid phase is needed.

Table 5-1. Dissolution Test Results for Hematite #1 in Various Oxalic and Nitric Acid Mixtures at 50 ºC Compared with OLI/ESP Predictions for Final Iron Concentrations and pH.

Initial Oxalic Acid (M)	Initial HNO₃ (M)	Initial NaOH (M)	Final Fe (M)	OLI Fe (M)	% Diff	Final pH	OLI pH
1 wt% Oxalic Acid							
0.111	1.000	0.000	0.182	0.257	41%	0.22	0.53
0.111	0.500	0.000	0.088	0.114	29%	0.55	1.05
0.111	0.500	0.000	0.121	0.150	25%	0.50	0.74
0.111	0.500	0.000	0.126	0.152	21%	0.70	0.75
0.111	0.250	0.000	0.088	0.114	29%	0.70	1.05
0.111	0.125	0.000	0.071	0.105	47%	0.87	1.66
0.111	0.000	0.094	0.040	0.042	5.9%	2.15	2.96
0.111	0.000	0.000	0.055	0.071	28%	1.25	2.21
0.111	0.000	0.000	0.057	0.071	25%	1.62	2.22
0.111	0.000	0.094	0.038	0.042	11%	2.60	3.08
0.111	0.000	0.108	0.033	0.038	14%	3.65	3.79
4 wt% Oxalic Acid							
0.452	1.000	0.000	0.443	0.512	16%	0.31	0.66
0.452	0.500	0.000	0.327	0.434	33%	0.36	1.31
0.452	0.500	0.000	0.256	0.434	69%	0.73	1.31
0.452	0.250	0.000	0.262	0.369	41%	0.55	1.72
0.452	0.000	0.000	0.245	0.293	20%	0.82	1.95
0.452	0.000	0.000	0.256	0.294	15%	1.37	1.99
0.452	0.000	0.406	0.151	0.164	8.6%	2.57	2.80
0.452	0.000	0.451	0.134	0.150	12%	4.46	4.19
8 wt% Oxalic Acid							
0.920	1.0	0.00	0.673	0.868	29%	0.31	1.15
0.920	0.5	0.00	0.601	0.742	24%	0.70	1.63
0.920	0.0	0.00	0.511	0.596	17%	1.16	1.87

Table 5-2. Dissolution Test Results for Hematite #1 in Various Oxalic and Sulfuric Acid Mixtures at 50 ºC Compared with OLI/ESP Predictions for Final Iron Concentration and pH.

Initial Oxalic Acid (M)	Initial H_2SO_4 (M)	Final Fe (M)	OLI Fe (M)	% Diff	Final pH	OLI pH
1 wt% Oxalic Acid						
0.111	1.000	0.417	0.471	13%	0.75	0.99
0.111	0.500	0.249	0.229	-8.2%	0.91	0.97
0.111	0.250	0.146	0.130	-11%	1.04	1.04
0.111	0.125	0.101	0.101	8.8%	1.19	1.41
4 wt% Oxalic Acid						
0.452	1.000	0.770	0.690	-10%	---	1.02
0.452	0.500	0.482	0.470	-2.4%	---	1.13
0.452	0.250	0.359	0.404	13%	---	1.59
0.452	0.125	0.307	0.353	15%	---	1.78
8 wt% Oxalic Acid						
0.920	1.000	1.037	0.988	-4.7%	---	1.10
0.920	0.500	0.746	0.816	9.3%	---	1.48
0.920	0.250	0.641	0.713	11%	---	1.68
0.920	0.125	0.583	0.656	13%	---	1.77

Table 5-3. Dissolution Test Results Versus pH for Multiple Iron Phases in 1 Weight Percent Oxalic Acid at 50 ºC Compared with OLI/ESP Predictions for Final Iron Concentrations and pH.

Reagent	Initial HNO$_3$ (M)	Initial NaOH (M)	Final Fe (M)	OLI Fe (M)	% Diff	Final pH	OLI pH
magnetite	0.50	0.00	0.192	0.194	1.1%	0.68	0.87
magnetite	0.25	0.00	0.124	0.161	30%	0.91	1.56
magnetite	0.00	0.00	0.071	0.082	16%	1.75	2.61
magnetite	0.00	0.12	0.032	0.038	19%	5.53	5.39
wustite	0.50	0.00	0.169	0.361	113%	0.63	6.82
wustite	0.25	0.00	0.099	0.236	138%	0.87	6.83
wustite	0.00	0.00	0.028	0.111	297%	2.19	7.17
wustite	0.00	0.12	0.030	0.051	70%	5.54	8.14
hematite #1	0.25	0.00	0.097	0.114	8.1%	0.71	1.03
hematite #1	0.00	0.00	0.064	0.071	4.7%	1.45	2.22
hematite #1	0.00	0.12	0.033	0.034	3.0%	5.14	5.24
lepidocrocite	0.25	0.00	0.124	0.114	-8.1%	0.89	1.03
lepidocrocite	0.00	0.00	0.068	0.071	4.7%	1.76	2.22
lepidocrocite	0.00	0.12	0.033	0.034	3.0%	5.51	5.24
amorphous iron oxide	0.25	0.00	0.103	0.113	9.6%	0.83	1.04
amorphous iron oxide	0.00	0.00	0.045	0.071	58%	1.96	2.22
amorphous iron oxide	0.00	0.12	0.015	0.034	124%	6.15	5.24

Table 5-4. Dissolution Test Results for Gibbsite in 1 Weight Percent Oxalic Acid, 0.35 M Nitric and 0.2 M Sulfuric Acids and Mixtures at 50 ºC Compared with OLI/ESP Predictions for Final Iron Concentrations and pH.

Initial Oxalic Acid (M)	Initial HNO₃ (M)	Initial H₂SO₄ (M)	Final Fe (M)	OLI Fe (M)	% Diff	Final pH	OLI pH
0.111	0.00	0.00	0.071	0.041	-41.7%	1.30	2.91
0.111	0.35	0.00	0.181	0.160	-11.6%	3.05	2.81
0.111	0.00	0.20	0.194	0.176	-9.3%	2.08	2.91
0.000	0.35	0.00	0.104	0.116	11.2%	1.07	2.77
0.000	0.00	0.20	0.130	0.131	1.0%	2.60	2.89

6.0 CONCLUSIONS

The conditions required to promote optimal dissolution of iron-based HLW sludge in oxalic acid have been determined. Mixtures of nitric and sulfuric acids with oxalic acid proved to be suitable solutions to promote optimal dissolution of iron phases. The oxalic and mineral acid concentrations required to give acceptable and manageable carbon steel corrosion rates were determined separately (Wiersma, 2010). Based on the combined dissolution and corrosion test results, conditions for real waste dissolution testing using oxalic/nitric acid mixtures were recommended (King, 2010c). Based on the current results, the optimal approach for the removal of sludge heels for HLW tanks would include the following steps:

1) removal of the maximum possible amount of heel materials by mechanical means
2) neutralization and acidification of the heel using dilute mineral acid (This step should promote significant dissolution of certain metal hydroxides and salts, including gibbsite.)
3) dissolution of the residual heel material at 50 ºC using an acid mixture containing 0.5 wt. % oxalic acid and 0.18 M nitric acid (This step should dissolve the iron phases.)

The above conditions were developed with a focus on promoting the dissolution of the major metal species (iron oxides and oxy-hydroxides and gibbsite). The dissolution of more refractory aluminum phases (boehmite and alumina) is believed to be impractical at this temperature. There is evidence that acid solutions might be used to remove boehmite at 70 ºC (King, 2010a), but tank corrosion rates are likely too high at this temperature. Therefore, elevated temperature caustic wash is recommended for the removal of refractory aluminum phases (Reboul, 2004). This would likely be conducted between steps 1 and 2 above. Impacts upon the dissolution chemistry of the various minor metals present in the sludge have yet to be determined. The dissolution of other metal phases may consume acid equivalents and adjustments to the above approach may be necessary. In addition, certain minor metals may not be sufficiently soluble in the above solutions and additional approaches may need to be developed for their removal. Evidence suggests that the utilization of oxalic/nitric acid mixtures enhances the dissolution of certain species (manganese and nickel) known to have low solubility in pure oxalic acid solutions (Poirier, 2010).

7.0 PATH FORWARD

Additional recommended testing includes:
- hematite dissolution evaluations in 0.5 wt. % oxalic acid and 0.18 M nitric acid
- corrosion evaluations in 0.5 wt. % oxalic acid and 0.18 M nitric acid
- real waste dissolution evaluations in 0.5 wt. % oxalic acid and 0.18 M nitric acid

- development of methods to dissolve problematic metals not highly soluble in oxalic acid or oxalic/mineral acid mixtures
- OLI model refinements

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