EM-31 Alternative and Enhanced Chemical Cleaning Program for Sludge Heel Removal - 11220

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ABSTRACT

Mixtures of oxalic acid with nitric acid have been shown to be superior to oxalic acid alone for the dissolution of iron-rich High Level Waste sludge heels. Optimized conditions resulting in minimal oxalate usage and stoichiometric iron dissolution (based on added oxalate ion) have been determined for hematite (a primary sludge iron phase) in oxalic/nitric acid mixtures. The acid mixtures performed better than expected based on the solubility of hematite in the individual acids through a synergistic effect in which the preferred 1:1 Fe:oxalate complex is formed. This allows for the minimization of oxalate additions to the waste stream. Carbon steel corrosion rates were measured in oxalic/nitric acid mixtures to evaluate the impacts of chemical cleaning with these solutions on waste tank integrity. Manageable corrosion rates were observed in the concentration ranges of interest for an acid contact timescale of 1 month. Kinetics tests involving hematite and gibbsite (a primary sludge aluminum phase) have confirmed that ≥90% solids dissolution occurs within 3 weeks. Based on these results, the chemical cleaning conditions recommended to promote minimal oxalate usage and manageable corrosion include: 0.5 wt. % oxalic acid/0.175 M nitric acid mixture, 50 ºC, 2-3 week contact time with agitation.

INTRODUCTION

As efforts continue at US Department of Energy Sites to treat and dispose of millions of gallons of legacy radioactive materials from the production of nuclear weapons, non-compliant storage tanks will gradually be emptied of the bulk waste volume leaving heel materials requiring removal prior to tank closure. The waste is primarily located within tanks at Hanford, WA and Aiken, SC (Savannah River Site). The waste heel slurries and scales are distributed on the floor, walls, and other surfaces of large (~1 million gallon) carbon steel storage tanks which frequently contain numerous obstructions that limit the effectiveness of mechanical cleaning methods. As a result, chemical cleaning methods are needed for the effective removal of the sludge heels and scales. Oxalic acid is considered the preferred cleaning reagent for sludge dissolution, particularly for iron-based sludge, due to the strong complexing strength of oxalate ion for iron and the fact that substantially lower tank corrosion rates are observed with oxalic acid relative to other acids. Oxalic acid is an industry standard 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 and subsequent acid regeneration [1]. Waste tanks at the Savannah River Site (SRS) can contain residual heel volumes approaching 5,000 gallons at the conclusion of bulk waste removal and heel washing campaigns. The amount of material involved makes acid regeneration by traditional methods such as ion exchange impractical. Furthermore, 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 waste processing facilities.

The current baseline chemical cleaning process for heel removal at SRS involves the addition of 8 wt. % oxalic acid directly to the waste tank in several treatment cycles. The process has not been optimized to minimize oxalate usage and cannot be used in all waste tanks planned for closure because of the large amounts of oxalate and sodium ions involved. The baseline method was recently used for heel removal in two SRS waste tanks with limited success [2]. 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. Given that numerous tanks are targeted for closure within the next decade, there is an urgent need to develop alternative or enhanced heel removal methods. Although much information has been reported in the literature regarding the dissolution of iron oxide materials using oxalic acid [3-5], the work typically involves mechanistic studies under dilute conditions rather than the concentrated and possibly saturated conditions expected in High Level Waste (HLW) tanks. The Savannah River National Laboratory (SRNL) is working to refine the baseline chemical cleaning process to optimize sludge heel dissolution [6-9]. Financial support for this effort has been provided by EM-31. The work thus far has focused on understanding the oxalic acid based dissolution chemistry of iron and aluminum phases and developing conditions that allow for the minimization of oxalic acid additions while simultaneously promoting manageable carbon steel corrosion rates.

Iron and aluminum are two of the most abundant chemical constituents in SRS waste sludge, although numerous other metals are also present to varying degrees depending on the tank history. The liquid portions of the sludge heel slurries are dilute basic solutions which remain after washing campaigns intended to remove soluble waste components. Most of the metals present in the heels exist as oxides, hydroxides, and oxy-hydroxides. These materials have typically been stored for many years in a highly alkaline environment at elevated temperatures in the presence of concentrated sodium salt solutions. The metal oxidation states and phases vary between tanks. The effectiveness of sludge dissolution methods is dependent upon the crystalline phases present in the waste, but the body of XRD data for waste tank sludge is limited. Common metal phases observed in HLW sludge include hematite (Fe_2O_3) and gibbsite ($Al(OH)_3$). Hematite is believed to be one of the most difficult iron phases to dissolve, but is quite soluble in oxalic acid solutions. Gibbsite is the most susceptible aluminum phase to acid dissolution. Another common aluminum phase, boehmite (AlOOH), has been shown to dissolve in dilute or moderate acid concentrations only at elevated temperatures (70 ºC) where tank corrosion rates are high [7-8]. Chemical dissolution of more refractory aluminum phases such as boehmite or alumina from the tanks is probably best accomplished using caustic wash methods developed in other programs [10-11]. Based on this information, dissolution testing and corrosion evaluations have focused on the use of pure phase hematite and gibbsite.

The dissolution of hematite in oxalic acid solutions has been studied extensively under dilute conditions [3-5]. Iron speciation in solution is believed to vary with the solution pH and with the oxalic acid concentration. In 1 wt. % oxalic acid, the mono-bioxalate complex, $FeHC_2O_4^{2+}$, is the dominant complex 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 mono-bioxalate, the trioxalate, and the dioxalate complex, $Fe(C_2O_4)_2^{-}$. The mole ratio of iron:oxalate in solution is therefore believed to change from 1:3 to 1:1 as the pH is lowered from 2 to 1. Obviously, the 1:1 complex is preferred in the case where the goal is to minimize oxalate usage, but optimization of oxalate usage must be balanced against tank corrosion, which increases at lower pH. The chemical reaction for the formation of the mono-bioxalate complex is provided in Eq. 1. Two molar equivalents of hydrogen ions are required for every oxalic acid molecule and every iron atom to promote the formation of the mono-bioxalate complex. These hydrogen ions are needed in addition to those provided by the oxalic acid. Since the pH of 1 wt. % oxalic acid is near 1.4, the mono-bioxalate complex is not expected to be the primary species in pure oxalic acid solution. Increasing the oxalic acid concentration results in a shift in the region of stability for the mono-bioxalate complex toward lower pH, such that it is not possible to produce the optimal pH for the formation of the mono-bioxalate complex in pure oxalic acid. Therefore, a supplemental proton source is needed to drive the system toward the preferred complex and minimize oxalate usage.

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

Based on the above information, testing has focused on the solubility of pure hematite in oxalic/nitric acid mixtures. The optimal concentrations of each acid required to minimize oxalate additions during hematite dissolution without promoting excessive carbon steel corrosion were determined. Gibbsite solubility testing was also conducted using the same solutions. Mixtures of mineral acids with oxalic acid are known to promote higher tank corrosion rates than pure oxalic acid solutions. Therefore electrochemical corrosion studies were conducted in the solutions of interest using carbon steel coupon electrodes which were representative of SRS tank wall materials [8].

EXPERIMENTAL DETAILS

Hematite, gibbsite, 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. X-ray Diffraction analysis confirmed that the hematite and gibbsite reagents were phase pure, except for one hematite sample (#3) which contained trace amounts of magnetite (Fe_3O_4). Upon acid digestion and analysis, the hematite and gibbsite samples were found to contain no metals other than the primary metal (Fe or Al, respectively) at concentrations greater than 1 wt. %. Oxalic acid solution, oxalic/nitric acid mixtures, and oxalic acid/sodium hydroxide mixtures were prepared to generate a range of solutions to allow for the evaluation of pH effects and determine the optimum acid ratios to promote full utilization of the oxalate ion for hematite dissolution.

Solubility testing involved simple batch contacts with known amounts of liquid and solid. Preliminary testing indicated that liquid:solid mass phase ratios of 50:1, 10:1, and 5:1 resulted in excess residual solids in 1, 4, and 8 wt. % oxalic acid solutions at test conclusion and these phase ratios were used for all tests. The hematite and gibbsite reagents were essentially dry ($\leq$2.5 wt. % water), but sample masses were corrected for water content when calculating the phase ratios. Test samples contained 1-2 g of solid and 10-50 g of liquid, depending on the oxalic acid concentration. Samples were continuously agitated in an orbital shaker oven at 250 RPM and maintained at 50 ºC throughout the testing. Samples were agitated for 5 to 6 weeks in sealed Teflon bottles known to be leak tight. Prior to sampling, agitation was stopped so that the solids could settle, and liquid sub-samples were collected, filtered, and diluted into known amounts of 3

M nitric acid (dilution factor ~4 for all samples) prior to cooling. Samples were analyzed for iron content by Inductively Couple Plasma Emission Spectroscopy (ICP-ES). All samples were confirmed to contain ≥0.25 g of residual solids at test conclusion based on the liquid phase iron analysis results. Samples were maintained in the dark throughout testing and during storage and transport to avoid the light-induced reduction of dissolved Fe(III) to Fe(II), which can lead to the precipitation of ferrous oxalate solids.

Electrochemical surveys of oxalic/nitric acid mixtures were conducted to evaluate the tendency of the solutions of interest to promote carbon steel corrosion. The Linear Polarization Resistance (LPR) technique was used to measure general corrosion rates for carbon steel electrodes typical of tank wall material which were immersed in the solutions of interest. Tests were conducted in oxalic/nitric acid mixtures with no added solids and in acid mixtures which had been pre-equilibrated for two weeks with various solid phases of interest. Data from these two test types may be representative of the initial and final corrosion rates (respectively) observed under these conditions, since the timescale of solids dissolution is approximately two weeks for these solid phases. All solutions contained 1 wt. % oxalic acid and either 0.1 or 0.5 M nitric acid. Electrodes were fabricated from ASTM A285, Grade C carbon steel (UNS K02200). Based on the hematite dissolution test results, these nitric acid concentrations were thought to bracket the nitric acid concentration required to maximize oxalate usage efficiency in 1 wt. % oxalic acid. Tests were conducted at both 45 and 75 ºC. Solid phases used for testing included hematite and gibbsite, as well as two sludge simulants (PUREX and HM) containing a wide range of chemical constituents typical of actual waste sludge materials. Details regarding the composition and preparation of these simulants are provided in a separate report [12]. The PUREX sludge simulant contained a high iron content and a relatively low Al content, while the HM simulant contained higher Al. The simulants included various iron and aluminum phases. Both sludge simulants contained moderately soluble sodium salts and numerous other metals, including RCRA hazardous components known to be present in HLW tank sludge. All tests were conducted with stirring and test slurries were maintained in the dark.

The LPR technique provides a quick, non-destructive, *in-situ* estimate of the uniform of general corrosion rate. The tests were conducted following a standard ASTM method [13]. This method is based on the observation that when the electrical potential at the metal surface is polarized anodically or cathodically within 15 mV of the Open Circuit Potential (OCP, measured separately) the measured current density at the metal surface increases linearly with potential. The system corrosion current density, which can be derived from the slope of the measured current density versus the applied potential, is related to the corrosion rate, which is generally reported in units of milli-inches per year (mpy). The corrosion rates reported are the average results for two replicate tests at each condition.

RESULTS AND DISCUSSION

Stoichiometric iron concentrations based on the added oxalate ion can be achieved in oxalic/nitric acid solutions with hematite. Solubility results are provided in Table I for three different oxalic acid concentrations. Equilibrium iron concentrations observed in 1 wt. % oxalic acid versus the final measured solution pH are plotted in Figure 1. In 1 wt. % oxalic acid (0.11 M), an iron concentration of 0.11 M represents stoichiometric iron dissolution assuming the

Table I. Equilibrium Iron Concentrations and pH Observed for Hematite (#1) in 1, 4, and 8 Wt. % Oxalic Acid Solutions.

$H_2C_2O_4$ (M)	NaOH Added (M)	Initial HNO_3 (M)	Final Fe (M)	Final pH
1 wt. % Oxalic Acid				
0.111	0.108	0.000	0.033	3.65
0.111	0.094	0.000	0.038	2.60
0.111	0.000	0.000	0.055	1.25
0.111	0.000	0.125	0.071	0.87
0.111	0.000	0.250	0.088	0.70
0.111	0.000	0.500	0.121	0.50
0.111	0.000	1.000	0.182	0.22
4 wt. % Oxalic Acid				
0.452	0.000	0.000	0.256	1.37
0.452	0.000	0.500	0.256	0.73
0.452	0.000	1.000	0.443	0.31
8 wt. % Oxalic Acid				
0.920	0.000	0.000	0.511	1.16
0.920	0.000	0.500	0.601	0.70
0.920	0.000	1.000	0.673	0.31

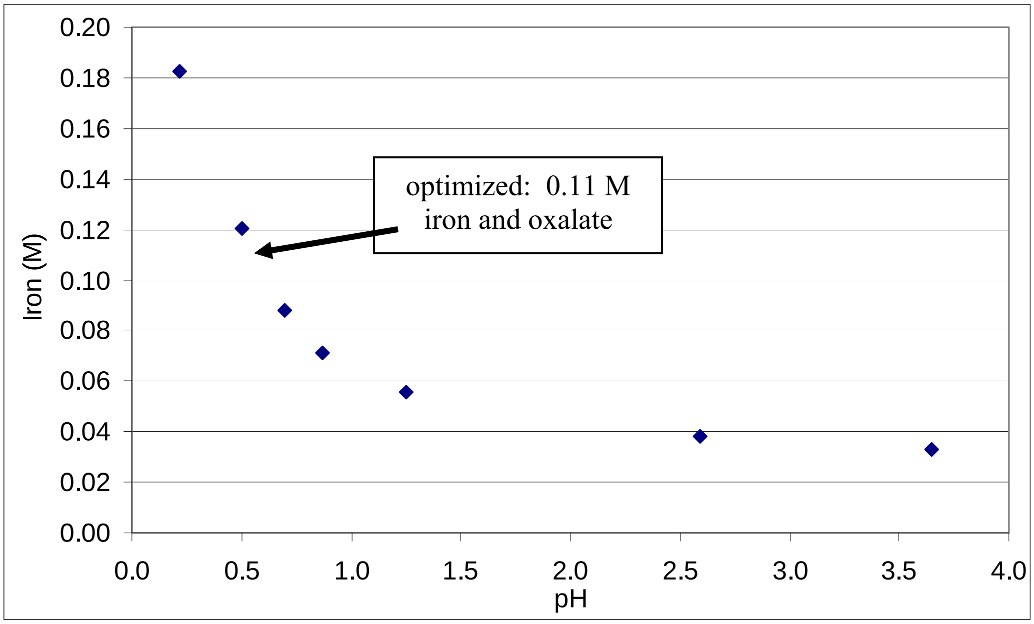

Fig. 1. Hematite (#1) solubility in 1 wt. % oxalic acid versus pH at 50 ºC (HNO_3 and NaOH added for pH control).

formation of a 1:1 Fe:oxalate complex. The measured iron concentrations in the oxalic/nitric acid mixtures are greater than the sum of the hematite solubilities measured for the pure acids, indicating a synergistic effect consistent with Eq. 1. Greater than stoichiometric iron solubility (>0.11 M) based on the added oxalate was observed with the 1 weight percent oxalic/1 M nitric acid mixture. This indicates that acid-based dissolution mechanisms are operative at this nitric acid concentration. Based on the results, it appears that a nitric acid concentration between 0.25 and 0.5 M promotes stoichiometric iron dissolution in 1 wt. % oxalic acid. This result is consistent with Eq. 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 also required to maintain the pH near 1, where the mono-bioxalate complex is the thermodynamically preferred species in 1 wt. % oxalic acid. Therefore, a nitric acid concentration of ~0.32 M (2 x 0.11 M + 0.1 M) should be needed to promote optimal iron phase dissolution and minimize oxalate usage in 1 wt. % oxalic acid solution.

For the tests conducted with 4 and 8 wt. % oxalic acid, iron concentrations near 0.45 and 0.92 M, respectively, are theoretically possible based on the oxalate ion concentrations in these solutions. An iron concentration of 0.44 M was observed with 4 wt. % oxalic acid at a nitric acid concentration of 1.0 M, while the maximum iron concentration observed with 8 wt % oxalic acid in 1 M nitric acid was only 0.67 M. These results are consistent with the nitric acid concentrations expected based on the formation of the mono-bioxalate complex using the formula provided above for 1 wt. % acid (1.10 and 2.16 M nitric acid for 4 and 8 wt. % oxalic acid, respectively). Final solution pH values near 0.5 and 0.7 are necessary to promote formation of the mono-bioxalate complex in 4 and 8 wt. % oxalic acid, respectively [5]. The results also indicate that optimization of iron phase dissolution may not be not possible within a carbon steel waste tank at oxalic acid concentrations greater than 1 wt. %, because the nitric acid requirements would likely lead to unacceptable tank corrosion rates. It is important to note that the iron concentrations observed in the pure oxalic acid solutions (1, 4, and 8 wt. %) are only 50 to 57% of the maximum theoretical values possible based on the oxalate ion concentrations and assuming the formation of the 1:1 complex. This indicates that it is not possible to maximize oxalate usage efficiency in pure oxalic acid solutions and a supplemental acid source is needed. This is a consequence of the fact that the pH at which the mono-bioxalate complex is thermodynamically preferred shifts to lower values as the oxalate ion concentration increases. Based on these results, subsequent solubility testing focused on a mixture containing 1 wt. % oxalic acid and 0.35 M nitric acid.

Dissolution kinetics tests were conducted on three different hematite samples (numbers 1, 2, and 3) to evaluate the range of dissolution rates that might be observed with this phase. The solid phases used for testing were all dry materials and appeared during initial particle size analysis to be composed of significant amounts of agglomerated particles. Since the dissolution testing involved sample agitation during solid/liquid contact, particle size analysis was conducted on sub-samples of the solid phases which had been briefly sonicated, as well as the as-received samples. 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. 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. 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 was near 4.0 μm in water and ranged from 5 to 23 μm in waste supernate. For the hematite samples tested, the particle size distributions of the sonicated samples are more similar to actual tank sludge.

Dissolution kinetics test results for the three hematite samples in 1 wt. % oxalic acid and a mixture containing 1 wt. % oxalic acid and 0.35 M nitric acid are provided in Figure 2. 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. 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 were just above 0.1 M. These results are consistent with the data in Figure 1. 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 sample #2 (after sonication). These results indicate that the timescale of hematite dissolution in oxalic acid based solutions and oxalic/nitric acid mixtures is suitable for tank cleaning operations.

Dissolution kinetics tests were also conducted with pure phase gibbsite reagent using 1 wt. % oxalic acid, 0.35 M nitric acid, and a 1 wt. % oxalic/0.35 M nitric acid mixture. Results are provided in Figure 3. Greater than 90% dissolution was observed within 2 weeks for each sample. The final measured solution pH values in the oxalic acid, nitric acid, and oxalic/nitric acid mixtures were 3.1, 1.1, and 1.3, respectively. Pure oxalic and nitric acid solutions were effective at dissolving gibbsite (final Al: 0.071 M and 0.104 M, respectively). The sum of the solubilities measured for the individual acids (oxalic and nitric) was 0.175 M Al and the observed solubility for the oxalic/nitric acid mixture was 0.181 M Al, indicating that the acids promote gibbsite dissolution independently. Gibbsite dissolution in dilute acids is effective at 50 ºC. Optimal sludge dissolution might involve preliminary contact with dilute mineral acid to neutralize residual base equivalents in the sludge and promote gibbsite dissolution prior to oxalic acid addition. Aluminum dissolution could also be accomplished using the caustic wash methods mentioned previously [10-11]. Iron dissolution could then be accomplished by the addition of oxalic/mineral acid mixtures. Without preliminary acid washes, higher mineral acid concentrations than the optimized values for a given oxalic acid concentration may be needed to promote stoichiometric iron phase dissolution.

Electrochemical corrosion tests were conducted using LPR for oxalic/nitric acid mixtures using an oxalic acid concentration of 1 wt. % and nitric acid concentrations of 0.1 and 0.5 M. Tests were conducted at 45 and 75 ºC using oxalic/nitric acid mixtures containing no solids, as well as oxalic/nitric acid solutions that had been contacted with hematite, gibbsite, and full sludge simulants (PUREX and HM). Results are provided in Table II. Interestingly, the presence of solid reagents significantly impacted the measured corrosion rates in many cases. For a reagent to be considered for use in the chemical cleaning of HLW tanks, corrosion rates less than 150 mpy are preferred [8]. If the chemical cleaning process were performed over a 1 month time period, this corrosion rate would result in a tank wall loss of 0.0125 inches. As seen in the table,

Table II. Linear Polarization Resistance Data for Oxalic/Nitric Acid Mixtures With and Without Solid Phases Added.

$H_2C_2O_4$ (M)	HNO_3 (M)	T (ºC)	Solid Phase	General Corrosion Rate (mpy)
0.111	0.1	45	none	54
0.111	0.1	45	HM	87
0.111	0.1	45	PUREX	54
0.111	0.5	45	none	405
0.111	0.5	45	hematite	605
0.111	0.5	45	gibbsite	1274
0.111	0.1	75	none	289
0.111	0.1	75	hematite	163
0.111	0.1	75	gibbsite	426
0.111	0.1	75	HM	724
0.111	0.1	75	PUREX	85
0.111	0.5	75	none	1848
0.111	0.5	75	hematite	999
0.111	0.5	75	gibbsite	1685
0.111	0.5	75	HM	1724
0.111	0.5	75	PUREX	4313

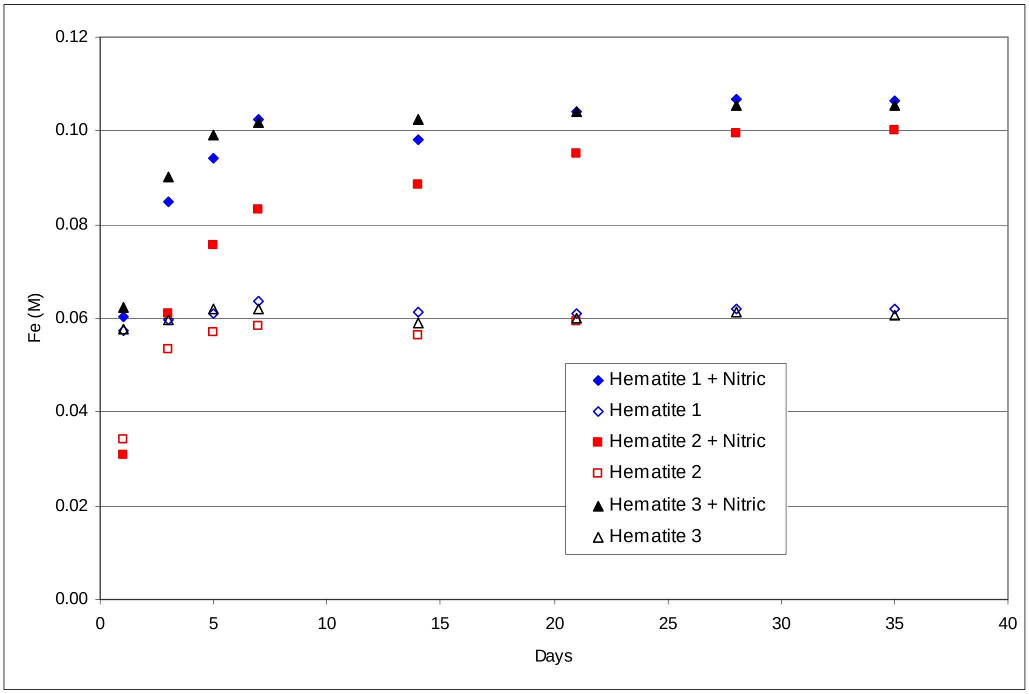

Fig. 2. Dissolution kinetics for three hematite samples in 1 wt. % oxalic acid and 1 wt. % oxalic/0.35 M nitric acid mixtures at 50 ºC.

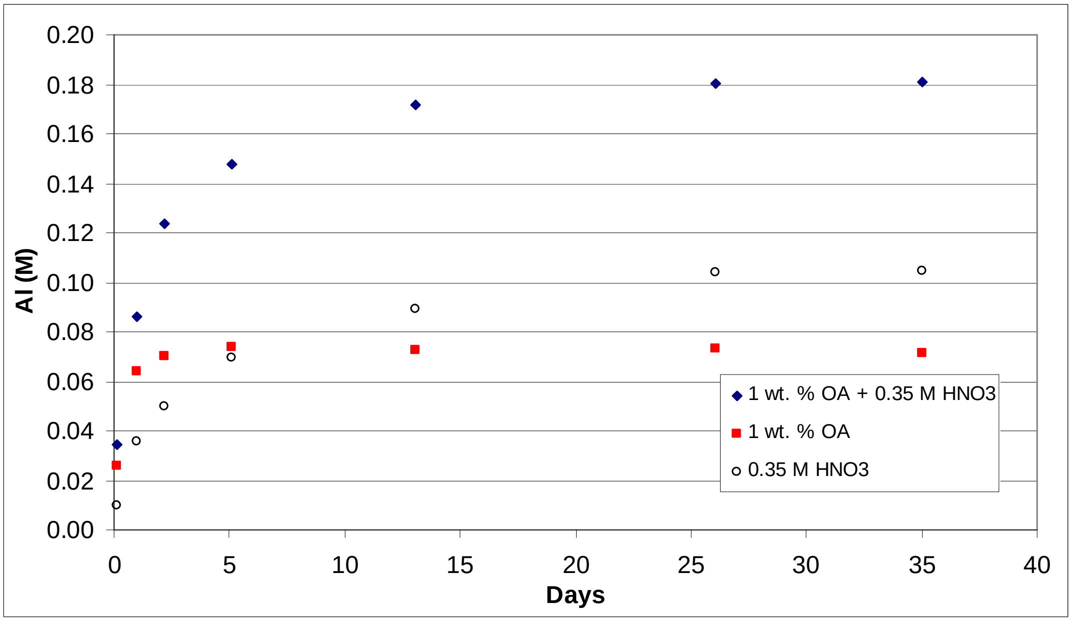

Fig. 3. Dissolution kinetics for gibbsite in oxalic acid, nitric acid, and oxalic/nitric acid mixtures at 50 ºC.

unacceptably high corrosion rates were observed in nearly every test conducted at 75 ºC. Unacceptably high corrosion rates were also observed at 45 ºC with 0.5 M nitric acid. However, relatively low corrosion rates (<90 mpy) were observed for all three tests conducted with 0.1 M nitric acid at 45 ºC. As indicated above, a nitric acid concentration of 0.35 M is needed to promote stoichiometric (based on added oxalate ion) hematite dissolution in 1 wt. % oxalic acid at 50 ºC. This nitric acid concentration is intermediate between the nitric acid concentrations tested. Based on the combined solubility and corrosion results, a mixture containing 0.5 wt. % (0.055 M) oxalic acid and 0.175 M nitric acid has been recommended for real sludge dissolution testing planned for 2011. This acid mixture is expected to promote optimal dissolution of iron phases with manageable carbon steel corrosion rates. Using more dilute oxalic acid for chemical cleaning than the baseline method under the optimized conditions will require the management and handling of greater water volume, but should add less oxalate to tank farm inventories.

CONCLUSIONS

The conditions required to promote optimal dissolution of iron-based HLW sludge in oxalic acid have been determined. Oxalic/nitric acid mixtures proved to be suitable solutions to maximize oxalate usage efficiency during the dissolution of iron phases. These acid mixtures are also effective at dissolving gibbsite, a common sludge aluminum phase. Based on the combined dissolution and corrosion test results, conditions for real waste dissolution testing using oxalic/nitric acid mixtures were 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) acidification of the heel using dilute mineral acid at 50 ºC (This step will promote significant dissolution of some metal hydroxides and salts, such as gibbsite.)
3) dissolution of the residual heel material using an acid mixture containing 0.5 wt. % oxalic acid and 0.175 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). Acid-based dissolution of more refractory aluminum phases (boehmite and alumina) is believed to be impractical at this temperature. There is evidence that these types of solutions might be used to remove boehmite at 70 ºC, but corrosion rates at elevated temperature have been shown to be unacceptably high. Caustic wash techniques could likely be used to remove the refractory aluminum phases. 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 methods may need to be developed for their removal. Preliminary evidence with actual HLW sludge suggests that the utilization of oxalic/nitric acid mixtures enhances the solubility of manganese and nickel relative to oxalic acid alone. In addition, the utilization of oxalic/nitric acid mixtures rather than pure oxalic acid has been shown to significantly increase the solubility of ferrous oxalate, which is known to limit the solubility of Fe(II) phases during oxalic acid based sludge dissolution. It is expected that oxalic/nitric acid mixtures will prove superior to oxalic acid for the dissolution of a number of metal species present in HLW sludge.

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