PNNL-14378

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Candidate Reagents for Dissolution of Hanford Site Tank Sludges—Scoping Studies with Simulants Using Single Reagents and Their Mixtures

S. Sinkov

August 2003

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-ACO6-76RLO183O

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Richland, Washington 99352

Summary

Chemical agents were investigated for their efficacies in dissolving metal compound phases known to be present in Hanford tank waste sludges. The phases included $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, MnO_2, and $Na_2U_2O_7$. In conjunction with the laboratory testing, a survey of the technical literature also was performed to identify candidate reagents. The tests were conducted in three campaigns. The first scoping tests investigated individual agents identified in the literature review along with other candidate agents. Based on the scoping test results, follow-up testing was performed to investigate the efficacies of mixed citric/oxalic acids (CITROX) and mixed nitric/oxalic acids (NITROX). Overall, oxalic acid is the most effective single reagent, dissolving all of the solid phases to some extent. However, for MnO_2 and $Na_2U_2O_7$, reprecipitation soon followed dissolution. The MnO_2 also oxidized at least two of organic acids tested, oxalic acid and citric acid, as shown by the evolution of gas during the tests with these reagents. The CITROX and NITROX tests failed to show beneficial synergistic effects in dissolving sludge phases. Instead, the findings suggest that the sequential addition of individual pure reagents (e.g., first citric acid to dissolve MnO_2 and $Na_2U_2O_7$ and removal of the solution followed by oxalic acid to dissolve the Fe, Cr, and Al hydroxides) may be more effective than individual or blended reagents.

Acronyms and Abbreviations

CITROX	mixture of citric and oxalic acids
EDTA	ethylenedinitrilotetraacetic acid
HEDTA	N-(2-Hydroxyethyl)ethylenedinitrilo-N,N’,N’-triacetic acid
HySS2	Hyperquad Speciation and Simulation utility program
IDA	iminodiacetic acid
NITROX	mixture of nitric and oxalic acids
NTA	nitrilotriacetic acid
Tiron	4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt
UV-Vis	optical absorbance spectroscopy in the ultraviolet and visible range of the optical spectrum

Acknowledgments

This work was funded by the CH2M HILL Hanford Group's S-112 Saltcake Waste Retrieval Technology Demonstration Project.

The author gratefully acknowledges fruitful technical and scientific discussions of the data obtained in the course of this project with Cal Delegard. Mr. Delegard's careful revision of the initial version of the report has substantially improved its quality and readability. James Huckaby managed the project and invited the author's participation in the C-106 sludge dissolution work.

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1.0 Introduction

High-level radioactive tank wastes have been generated at Hanford since 1944 as a result of chemical processes for plutonium recovery (by irradiated uranium metal fuel reprocessing), plutonium purification, radioisotope recovery, equipment decontamination, and laboratory and other smaller operations. Most operations were conducted in nitric acid (HNO_3); however, the waste solutions were made alkaline with sodium hydroxide (NaOH) so they would be compatible with the mild steel-lined underground waste storage tanks in which they were disposed. Thus, water and sodium nitrate ($NaNO_3$) compose 75 to 80 wt% of the disposed wastes.

The wastes are generally classified into three constituents: saltcakes comprising relatively soluble sodium salts [e.g., $NaNO_3$, $Na_3PO_4\cdot 12H_2O$, and $Na_2CO_3\cdot H_2O$], low solubility sludges [e.g., $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, $ZrO_2\cdot xH_2O$, and sodium aluminosilicates from alkaline precipitation of multicharged metals], and supernatant and interstitial solutions of sodium salts [e.g., NaOH, $NaNO_3$, $NaNO_2$, and $NaAl(OH)_4$ at higher NaOH concentrations].

Retrieval of the tank wastes for their immobilization and long-term disposal is being accomplished by dissolution in water and NaOH solution and by mechanical (mixing, slurrying, and pumping) methods. To a large extent, the completeness of waste removal from the tanks will be limited by the ability to move the sludge phases, where much of the radioactivity (e.g., ^{90}Sr, ^{154}Eu, Pu, and Am) resides. Means to chemically dissolve the sludge phases without unduly attacking the mild steel tank liners are therefore desired. To this end, investigations were undertaken to identify and test chemical agents that can dissolve sludge phases. Though the work reported in this document focused on phases known or suspected to be present in the sludge of Tank 241-S-112, similar or perhaps identical phases are present in other waste tanks.

2.0 Review of Technical Literature on Candidate Dissolution Agents

Sludge phases identified directly or suspected to be present in Tank 241-S-112 (designated S-112) include aluminum hydroxide [$Al(OH)_3$ and AlOOH], ferric hydroxide [$Fe(OH)_3$ and FeOOH], chromium hydroxide [$Cr(OH)_3$ and CrOOH], manganese dioxide [MnO_2], and sodium diuranate [$Na_2U_2O_7$]. These and other sludge phases have been identified in Hanford tank wastes (Rapko and Lumetta 2000).

Technical literature on candidate chemical agents potentially useful for sludge phase dissolution was reviewed with the valuable early guidance of Dan Reynolds of CH2M HILL Hanford Group (CH2M HILL). In addition to technical journals, the literature resources included reports from testing of alkaline sludge dissolution (Scientific Technology Center of the Mining and Chemical Combine, Zheleznogorsk, Krasnoyarsk, Russia; work performed under sponsorship of Sandia National Laboratory) and the book *Chemical Dissolution of Metal Oxides* (Blesa et al. 1994). Most agents were found to be carboxylic acids of several types—pure carboxylic acids, hydroxycarboxylic acids, and aminocarboxylic acids. Full results of the literature review are presented in the appendix at the end of this report.

To summarize the results of the review, none of the agents discussed in the literature were found to be capable of dissolving all five major types of sludge components (Al, Fe, Cr, Mn, and U) with a high efficiency. In addition, most of the metal hydroxide dissolution tests described in the literature were performed at elevated temperatures. Extrapolation of the observed dissolution rates to room temperature is not possible without a reliable knowledge of the activation energy for these processes. It was concluded, based on the review, that the widest possible number of organic chelators of different denticity and basicity should be tested by contact with the individual sludge hydroxides, hydrated oxides, or low solubility salts. By such experimentation, data can be acquired under similar and reproducible experimental conditions (equilibration time, temperature, agitation efficiency, reagent concentration). The effect of acidity for the same chelating moieties can be tested best by equilibration of hydroxides with the fully protonated form of the chelator and its salt in parallel experiments (for example, oxalic acid versus the alkali metal oxalate or citric acid versus sodium citrate). The effects of combining the most efficient agents also should be investigated.

3.0 Experimental Materials and Methods

The laboratory testing involved preparing the five sludge phases and candidate sludge dissolution reagents and testing the individual and combined reagents for their efficacy in sludge dissolution. The extent of sludge dissolution was monitored by changes in weight of the separated and dried solid phases after contact with the selected agents. Characterization of the sludge dissolution reactions was aided by spectrophotometric analyses. The laboratory testing and techniques are described in this section.

3.1 Simulant Phase Preparation

Fluor Hanford scientists determined the composition and characteristics of the residual solids phases remaining following water dissolution testing of S-112 saltcake materials (Cooke et al. 2002). Based on this characterization work and knowledge of the composition of sludge arising from the REDOX process (which supplied the waste to Tank S-112), the primary sludge phases of interest were identified to be chromium(III) hydroxide, iron(III) hydroxide, a calcium-chromium mixed hydroxide [postulated by Cooke et al. to be $Ca_3Cr_2(OH)_{12}$ based on its similarity to $Ca_3Al_2(OH)_{12}$], sodium diuranate ($Na_2U_2O_7$), boehmite (AlOOH), gibbsite [$Al(OH)_3$, with partial isomorphous substitution of Cr for Al], and MnO_2 in X-ray diffraction (XRD) pattern.

The constituents of most interest for removal from the S-112 "heel" for tank closure are technetium-99 (^{99}Tc), uranium, and chromium. The sludge characterization and process chemistry knowledge would indicate that chromium primarily is found separately or mixed with iron and aluminum in hydroxide phases [e.g., $(Cr,Fe,Al)(OH)_3$] and in the postulated $Ca_3Cr_2(OH)_{12}$ phase. The uranium is found as the compound sodium diuranate ($Na_2U_2O_7$). The disposition of ^{99}Tc in the solid phases present in the S-112 sludge, however, is not known. Therefore, to guarantee that ^{99}Tc is removed from the tank, it would be most beneficial to identify agents that dissolve all of the sludge phases.

Based on the sludge characterization and simulant preparation work, the tests were performed using the prepared compound phases $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, MnO_2, and $Na_2U_2O_7$.

The separate iron(III) hydroxide, chromium(III) hydroxide, aluminum hydroxide, and sodium diuranate compounds were prepared in 30 millimole amounts by precipitation of the corresponding metal nitrate salt solutions with sodium hydroxide, stirring, and overnight aging at 85°C. Manganese dioxide was prepared by reduction of potassium permanganate solution by hydrogen peroxide followed by the same overnight 85°C aging. The precipitates were washed with water to remove the accompanying $NaNO_3$ salt (in the cases of the iron, chromium, aluminum, and uranium solids) or potassium hydroxide (in the case of MnO_2).

Two batches of each of the $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, MnO_2, and $Na_2U_2O_7$ sludge constituent compounds were prepared. The first batch was used in the screening tests of the individual dissolution agents. The second batch was used in the tests of the mixed dissolution agents of nitric acid with oxalic acid or citric acid. The only difference in the hydroxide preparation procedure between the first and the second batches was the use of carbonate-free sodium hydroxide in the metal precipitation stage. It was noted that, in the preparation of the hydrated manganese(IV) dioxide for the second batch, a residual pinkish coloration was present due to unreacted permanganate. Introduction of even a large excess of hydrogen peroxide (H_2O_2) into the $KMnO_4$ (potassium permanganate) solution did not completely eliminate the pink color. In the end, addition of 6.0 M nitric acid (HNO_3) completed the reaction by eliminating the excess alkalinity. Like the first batch, precipitates in the second batch were digested under their respective mother liquors by overnight aging at 85°C. The $Fe(OH)_3$ precipitate from the second batch appeared more brick red than the first-batch product, while the MnO_2 from the second batch was blacker and more compact than the product from the first batch, which had a dark brown tint. The other precipitates prepared in the second batch were visually indistinguishable from their first-batch analogues.

Efforts to prepare the calcium-chromium mixed hydroxide were unsuccessful. In one attempt, a stoichiometric solution of the mixed calcium and chromium(III) nitrate salts was precipitated with sodium hydroxide and aged at 85°C overnight. In another attempt, the same mixed nitrate salt solution was precipitated homogeneously by hydrolytic decomposition of urea (H_2NCONH_2; decomposition produces ammonia and carbon dioxide). In the latter attempt, calcium carbonate precipitated separately, precluding formation of the Ca-Cr mixed compound. Product from the sodium hydroxide neutralization was washed of accompanying sodium nitrate salt and analyzed by XRD. The product was crystalline, but its pattern was not similar to that of $Ca_3Al_2(OH)_{12}$. A third attempt to prepare $Ca_3Al_2(OH)_{12}$ involved direct strike (alkali-to-nitrate salt) precipitation of a mixed solution of $Ca(NO_3)_2$ and $Cr(NO_3)_3$ with ~40 wt% NaOH solution. The light-green slurry was aged for two days at 150°C in a Parr Model 4744 acid digestion bomb with a 46-mL Teflon cup. The solids were washed in distilled water and then analyzed by XRD. Only peaks attributable to $CaCO_3$ could be assigned.

3.2 Dissolution Agents Selected for Scoping Tests

The dissolution agents selected for testing were identified based on review of the technical literature. Some related compounds also were tested. The agents may be chemically classified according to their functional groups. To dissolve the metal oxide/hydroxide sludge phases, agents generally combine acidity to neutralize the oxide/hydroxide with complexing ability to solubilize the resulting metal ions (Fe^{3+}, Cr^{3+}, Al^{3+}, Mn^{2+} or other Mn oxidation state, and UO_2^{2+}). The following classes of dissolution agents were included:

- carboxylic acids (containing the $–CO_2H$ functional group) and their salts (containing the $–CO_2^-$ group with K^+ or Na^+)
- hydroxycarboxylic acids and salts (containing both the –OH and $–CO_2H$ or $–CO_2^-$ groups)
- alcohols (containing the –OH group)
- aminocarboxylic acids (containing both $–CO_2H$ and –N⟨ groups)
- a hydroxamic acid (acetohydroxamic acid, $CH_3CONHOH$, known as AHA)
- a sulfonic acid (Tiron; 4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt, containing alcohol and $-SO_3H$ groups; the active complexing occurs through the *ortho* hydroxy groups)
- inorganic mineral acids.

The specific agents selected for initial testing are listed in Table 1.

Table 1. Dissolution Agents Selected for Testing

Chemical Class	Agent	Formula
Carboxylic acids	Acetic acid	CH_3CO_2H
	Oxalic acid	$(HO_2C)_2$
	Malonic acid	$HO_2CCH_2CO_2H$
	Phthalic acid	$o\text{-}C_6H_4(CO_2H)_2$
Hydroxy-carboxylic acids	Glycolic acid	CH_2OHCO_2H
	Lactic acid	$HO_2CCHOHCH_3$
	Tartaric acid	$HO_2C(CHOH)_2CO_2H$
	Gluconic acid	$HO_2C(CHOH)_4CH_2OH$
	Citric acid	$HO_2CCH_2C(OH)CO_2HCH_2CO_2H$
	Salicylic acid	$o\text{-}C_6H_4(OH)COOH$
Alcohol	Catechol	$o\text{-}C_6H_4(OH)_2$
	Tiron	4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt
Carboxylate salts	K_2Oxalate	$(KO_2C)_2$
	Na_3Citrate	$NaO_2CCH_2C(OH)CO_2NaCH_2CO_2Na$
Aminocarboxylic acids/salts	Glycine	$HO_2CCH_2NH_2$
	Na_2IDA	$(NaO_2CCH_2)_2NH$
	Na_3NTA	$(NaO_2CCH_2)_3N$
	H_2Na_2EDTA	$(NaO_2CCH_2)_2N(CH_2)_2N(CH_2CO_2H)_2$
	Na_3HEDTA	$(NaO_2CCH_2)_2N(CH_2)_2N(CH_2CH_2OH)CH_2CO_2Na$
Hydroxamic acid	Acetohydroxamic acid	$CH_3CONHOH$
Mineral acids	Nitric acid	HNO_3
	Hydrofluoric acid	HF

All agents were tested at 0.5-M concentrations except for H_2Na_2EDTA and Na_3HEDTA, which were tested at 0.25 M because of limited solubility. At these concentrations, all agents were completely in solution except phthalic and salicylic acids, which were introduced as aqueous suspensions of the respective crystalline compounds in amounts sufficient to achieve 0.5-M concentrations if completely dissolved.

Based on the results of the first scoping test series, a second test series was conducted using mixtures of citric and oxalic acid (sometimes called CITROX). The nine citric/oxalic acid mixtures were prepared for this series from 0.5 M stock solutions of the separate pure citric and oxalic acids by varying the ratios of the volumes being mixed. The citric/oxalic acid molar concentration combinations tested were 0/0.5, 0.0625/0.4375, 0.125/0.375, 0.1875/0.3125, 0.25/0.25, 0.3125/0.1875, 0.375/0.125, 0.4375/0.0625, and 0.5/0. The first and last (single component) members of this test series thus served as replicates of the prior scoping tests for oxalic and citric acid.

A third test series was performed using mixtures of nitric and oxalic acid (abbreviated here as NITROX). Combined nitric/oxalic acid mixtures had been considered, but not used, at the Savannah River Site to remove residual tank sludge (Hill and Bradley 1977) and were strongly endorsed for testing

Hanford tank sludge (Schulz and Kupfer 1991). The molar ratios of the nitric/oxalic acid components and their concentrations in the stock solution were chosen to be the same as in the CITROX test.

3.3 Scoping and Oxalic/Citric and Oxalic/Nitric Test Experimental Methods

The dissolution efficiencies for each of the five S-112 sludge components [$Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, MnO_2, and $Na_2U_2O_7$] were tested separately with each agent. In each test, 4.5 mL of the agent solution was mixed with the particular sludge phase for 40 hours at room temperature using a reciprocal shaker. A 3-fold molar excess of each dissolving agent was used with respect to amount of sludge phase metal hydroxide, MnO_2, or $Na_2U_2O_7$. The sludge phase solids were added as an aqueous suspension by pipetting. This method of addition permitted controlled accurate amounts to be used but also caused a little dilution (less than 10%) in the agent concentration. Control samples of each kind of precipitate were equilibrated with deionized water to serve as experimental blanks for determining the fraction of undissolved solids remaining after phase separation, washing, and vacuum drying of the solid residues.

After the 40-hour contact time, the residual solids were separated by centrifugation, rinsed, and vacuum-dried at room temperature in the contact vial. The weights of the residual solids were then determined. In cases where small amounts of residual solids were suspended by peptization during washing, the solids were collected by syringe filtration, dried, and weighed.

In certain instances, chemical reactions beyond simple sludge dissolution were observed. Phenomena included gassing and dissolution followed by reprecipitation. These observations were noted as they occurred.

Leachate pH measurements were done using an Accumet Research AR15 pH meter equipped with a Corning Semi-Micro Combo Electrode. The pH electrode and meter were calibrated using standard buffers before each measurement.

3.4 Spectrophotometric Analysis of the Sludge Dissolution Samples

Ultraviolet-visible (UV-vis) spectroscopic measurements were made on a 400-series charge-coupled device (CCD) array UV-vis spectrophotometer (Spectral Instruments Inc., Tucson AZ). The solutions were held in cuvettes with an optical transparency range from 220 to 900 nm (PLASTIBRAND®).

4.0 Results and Discussion

The testing was performed in three series. The first series was a set of scoping studies to evaluate individual agents for their efficacies in dissolving the five sludge phases. Based on the scoping test results, the second and third test series investigated the performances of reagents mixed at various ratios. The second series investigated citric/oxalic acids (CITROX), and the third experimental phase tested nitric/oxalic acids (NITROX) for their effectiveness in dissolving the five sludge phases.

4.1 Scoping Test Results

Results for the scoping tests are presented in Table 2 in the order of the three groupings in which they were performed (oxalic acid through HNO_3, malonic acid through Na_3HEDTA, and catechol through acetic acid). The sample results presented graphically in Figure 1 are grouped according to their respective dissolving agent class (e.g., carboxylic acid, hydroxycarboxylic acid) as given in Table 1. Several general observations can be made from these findings:

- No agent dissolved all solids completely; indeed, no agent dissolved $Fe(OH)_3$ completely.
- $Fe(OH)_3$ is the phase most difficult to dissolve, dissolving to 40% or more only with oxalic acid and HF.
- $Na_2U_2O_7$ is the most readily dissolved phase, dissolving to 80% or more for 10 of the 22 agents.
- Oxalic acid and HF are the best overall dissolving agents, though neither is completely effective for $Fe(OH)_3$ or for MnO_2.
- Agents ineffective for all five solid phases are acetic acid, tartaric acid, dipotassium oxalate, trisodium citrate, glycine, disodium IDA, trisodium NTA, and trisodium HEDTA. Many of these ineffective agents are salts, confirming that acidity likely is necessary for any agent to be successful. This is borne out by the fact that oxalic and citric acids are effective to some degree for certain phases, whereas their salts are not effective for any phase.
- The efficacies of phthalic and salicylic acids were difficult to judge because the acids, introduced as their respective solid crystals, did not dissolve completely. However, neither of these white crystalline acids completely dissolved any metal phase, as judged by the colored solids remaining in each test. Of the two, phthalic acid appeared to be slightly more effective.

Overall, oxalic acid is the most effective reagent, dissolving all the solid phases to some extent, including MnO_2. However, in the case of MnO_2, reprecipitation [probably as the white Mn(II) oxalate] soon followed dissolution. The MnO_2 also oxidized at least two of organic acids tested, oxalic acid and citric acid, as indicated by the evolution of gas that occurred during the tests with these reagents.

Dissolution followed by reprecipitation also was observed for $Na_2U_2O_7$ in its tests with oxalic acid, malonic acid, and acetic acid. The solubility of uranyl oxalate ($UO_2C_2O_4 \cdot 3H_2O$) in water is about 3 g U/L (~0.013 M), and the solubility roughly doubles in 0.5-M HNO_3 (Chernyaev 1966, p. 117). The total concentration of uranium available in these tests is ~0.087 M, above the amount expected to be dissolved based on the published solubilities. The complex sodium uranyl acetate compound $Na[UO_2(CH_3CO_2)_3]$

has a solubility (~0.1 M uranium in water) (Chernyaev 1966, p. 97) somewhat higher than the uranyl oxalate. The sodium uranyl acetate salt is plausibly the precipitate found in the acetic acid test. The presence of sodium uranyl malonate may explain the reprecipitation found in the test with malonic acid based on the observed behavior with the chemically related acetic acid.

The dissolution efficacy of acetohydroxamic acid and Tiron with respect to iron(III) hydroxide is much lower in this study than reported previously (Lumetta 1997) for cold simulant samples and genuine Hanford tank sludge. The differences most likely are associated with differing ratios of more- and less-soluble aged $Fe(OH)_3$ fractions prepared for the dissolution experiments. By transmission electron microscopy analysis, Lumetta (1997) showed evidence of at least two solid species in the aged material. Two particle types were identified—needle-like particles (most likely goethite) and round particles (most likely hematite). The ratio between these two components is expected to depend on preparation and aging techniques. In the present tests, the $Fe(OH)_3$ solids were prepared by NaOH addition to $Fe(NO_3)_3$ followed by aging under the hot supernatant $NaNO_3$ solution. In comparison, Lumetta (1997) prepared the $Fe(OH)_3$ solids by precipitating $FeCl_3$ with KOH, washing the solids with water, and drying the washed solids at 105ºC for several days.

Hydrofluoric acid was one of the more effective dissolving agents but was judged to be unacceptable in this application because of its chemical hazard, its corrosiveness on steel, and its deleterious effects in glass formation in subsequent waste vitrification.

Table 2. Scoping Dissolution Test Results

Dissolving medium, 0.5 M	Fe(III) hydroxide			Cr(III) hydroxide			Aluminum hydroxide			Mn(IV) dioxide			Sodium diuranate		
	Residue after 40 h, g	Starting amt, g (avg 2)	% undiss.	Residue after 40 h, g	Starting amt, g (avg 4)	% undiss.	Residue after 40 h, g	Starting amt, g (avg 4)	% undiss.	Residue after 40 h, g	Starting amt, g (avg 2)	% undiss.	Residue after 40 h, g	Starting amt, g (avg 4)	% undiss.
Oxalic acid	0.0443	0.07145	62	0.0049	0.09245	5	0.0271	0.05685	48	0.1399(a)	0.0984	142(a)	0.0637(b)	0.2429	26
K_2Oxalate	0.0779	0.07145	109	0.1070	0.09245	116	0.0593	0.05685	104	0.1275	0.0984	130	0.2573	0.2429	106
Citric acid	0.0771	0.07145	108	0.1146	0.09245	124	0.0569	0.05685	100	CD(c,d)	0.0984	CD(d)	CD	0.2429	CD
Na_3Citrate	0.0796	0.07145	111	0.1156	0.09245	125	0.0585	0.05685	103	0.1383	0.0984	141	0.2582	0.2429	106
Tiron	0.0708	0.07145	99	0.1046	0.09245	113	0.0573	0.05685	101	CD	0.0984	CD	CD	0.2429	CD
HNO_3	0.0711	0.07145	100	0.0375	0.09245	41	0.0482	0.05685	85	0.0811	0.0984	82	CD	0.2429	CD
Malonic acid	0.0699	0.07145	98	0.0892	0.09245	96	0.0480	0.05685	84	CD	0.0984	CD	RPR(e)	0.2429	RPR
Glycolic acid	0.0690	0.07145	97	0.0666	0.09245	72	0.0441	0.05685	78(f)	CD	0.0984	CD	CD	0.2429	CD
Gluconic acid	0.0738	0.07145	103	0.095	0.09245	103	0.0567	0.05685	100	0.0776	0.0984	79	0.2646	0.2429	109
Na_2IDA	0.0739	0.07145	103	0.0936	0.09245	101	0.0565	0.05685	99	0.1098	0.0984	112	0.2549	0.2429	105
AHA	0.0705	0.07145	99	0.0708	0.09245	77	0.0397	0.05685	91(f)	CD	0.0984	CD	0.0211	0.2429	9(f)
Na_3NTA	0.0763	0.07145	107	0.1022	0.09245	111	0.0577	0.05685	101	0.1221	0.0984	124	0.2493	0.2429	103
H_2Na_2EDTA(g)	0.0729	0.07145	102	0.0808	0.09245	87	0.0576	0.05685	101	0.0076	0.0984	8	0.0105	0.2429	4(f)
Na_3HEDTA(g)	0.0738	0.07145	103	0.0944	0.09245	102	0.054	0.05685	95	0.1382	0.0984	140	0.2491	0.2429	103
Catechol	0.0746	0.07145	104	0.0979	0.09245	106	0.0568	0.05685	100	0.1413	0.0984	144	CD	0.2429	CD
Salicylic acid(h)		0.07145			0.09245			0.05685			0.0984			0.2429	
Phthalic acid(h)		0.07145			0.09245			0.05685			0.0984			0.2429	
Tartaric acid	0.0753	0.07145	105	0.1026	0.09245	111	0.0559	0.05685	98	RPR	0.0984	RPR	CD	0.2429	CD
Lactic acid	0.0698	0.07145	98	0.0920	0.09245	100	0.0519	0.05685	91	0.0113	0.0984	11	CD	0.2429	CD
Glycine	0.0732	0.07145	102	0.0929	0.09245	100	0.0583	0.05685	103	0.0915	0.0984	93	0.2428	0.2429	100
HF	0.0141	0.050015	28	0.0137	0.064715	21	CD	0.039795	CD	0.0625	0.06888	91	CD	0.17003	CD
Acetic acid	0.0692	0.07145	97	0.0865	0.09245	94	0.0451	0.05685	79	0.0858	0.0984	87	RPR	0.2429	RPR

(a) Complete dissolution in less than 1 minute (solution color is greenish-brown), reprecipitation as a white crystalline compound (observed 16 hr after equilibration started). Significant pressure buildup inside the vial; pressure was released periodically to prevent the vial's rupture.

(b) Complete dissolution in 10–15 seconds followed by almost instant reprecipitation as uranyl oxalate.

(c) CD = Complete dissolution in less than 16 hr; solution remains homogeneous.

(d) Complete dissolution; significant pressure buildup inside the vial; pressure was released periodically to prevent the vial's rupture.

(e) RPR = Dissolution then reprecipitation occurred.

(f) Actual undissolved fraction should be higher than reported due to unaccounted loss of fine fraction of precipitate during phase separation.

(g) 0.25 M H_2Na_2EDTA and Na_3HEDTA used.

(h) Salicylic and phthalic acids were introduced as aqueous suspensions of the respective crystalline compounds in amounts sufficient to achieve 0.5 M concentrations if completely dissolved in 4.5 mL of water. In none of the 5 runs with these compounds was the complete dissolution of the sludge components observed. The resulting solid phases represent mixtures of the metal hydroxide and undissolved organic acid crystals, making estimation of dissolution efficiency by weighing the amount of the residue impossible. Qualitatively, phthalic acid appears to be a more efficient dissolving agent than salicylic acid.

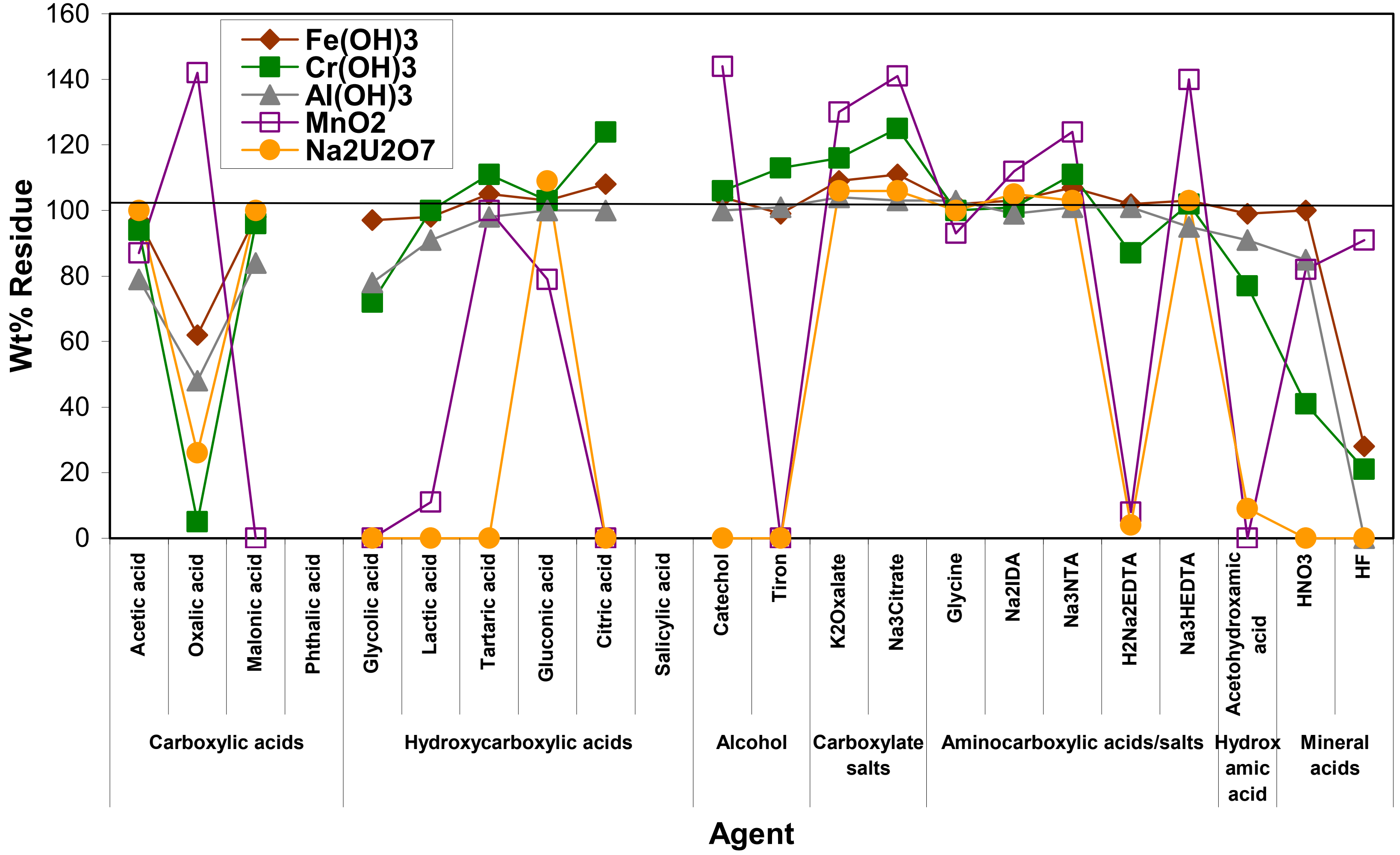

Figure 1. Sludge Phase Dissolution Performance for Various Agents

4.2 Mixed Citric/Oxalic Acid Test Results

The scoping tests showed that non-acidic reagents were not effective in dissolving the sludge phases. Therefore, acid consumption, as measured by increase in pH, was determined in testing of the citric/oxalic acid (CITROX) mixed reagent. The acidity change between the initial CITROX solutions and respective leachates after contact with the sludge components are shown in Table 3.

It is seen that pH increases in some cases (e.g., all MnO_2 tests and most $Na_2U_2O_7$ tests), decreases in some cases [the $H_2C_2O_4$-rich tests with $Fe(OH)_3$], and is virtually unchanged in some tests [the $H_2C_2O_4$-poor tests with $Fe(OH)_3$ and most $Cr(OH)_3$ and $Al(OH)_3$ tests]. The pH change results might be explained by the occurrence of the following reactions:

- Consumes acid (pH increases)

  For MnO_2 with $H_2C_2O_4$: $MnO_2 + 2\ H_2C_2O_4 \rightarrow MnC_2O_4 + 2\ CO_2 + 2\ H_2O$

  For MnO_2 with $C_6H_8O_7$: $9\ MnO_2 + 18\ H^+ + C_6H_8O_7 \rightarrow 9\ Mn^{2+} + 6\ CO_2 + 13\ H_2O$

  For $Na_2U_2O_7$ with $H_2C_2O_4$: $Na_2U_2O_7 + 2\ H^+ + 2\ H_2C_2O_4 \rightarrow 2\ UO_2C_2O_4 + 2\ Na^+ + 3\ H_2O$

- Produces acid (pH decreases)

  For $Fe(OH)_3$ with $H_2C_2O_4$: $Fe(OH)_3 + 2\ H_2C_2O_4 \rightarrow Fe(C_2O_4)_2^- + 3\ H_2O + H^+$

The absence of a pH change suggests, but does not prove, a lack of reaction. The bases for the postulated reactions are discussed in this section.

Table 3. CITROX Solution pH Before and After Contact with Sludge Components

Test	**Citric/Oxalic Acid Conc., M**	**pH Before Contact**	**pH After Contact**				
			$Fe(OH)_3$	**$Cr(OH)_3$**	**$Al(OH)_3$**	**MnO_2**	**$Na_2U_2O_7$**
1	0/0.5	0.63	0.49	0.61	0.58	1.07	0.94
2	0.0625/0.4375	0.68	0.57	0.64	0.61	1.28	0.91
3	0.125/0.375	0.71	0.59	0.69	0.64	1.43	0.90
4	0.1875/0.3125	0.73	0.63	0.75	0.69	1.90	0.84
5	0.25/0.25	0.78	0.70	0.84	0.75	2.36	0.83
6	0.3125/0.1875	0.84	0.75	0.98	0.84	2.69	0.79
7	0.375/0.125	0.93	0.95	1.18	0.95	2.84	0.92
8	0.4375/0.0625	1.09	1.28	1.49	1.18	2.97	1.23
9	0.5/0	1.41	1.51	1.74	1.44	2.91	2.60

Table 4 shows the results of the mixed oxalic/citric acid test series based on weights of the residual solids and visual observations. The weight results are depicted in Figure 2. Results are described individually for each sludge phase.

Table 4. Mixed Citric/Oxalic Acid Dissolution Test Results

Test Number	**Concentration citric/oxalic acids, M**	**Fe(III) hydroxide**			**Cr(III) hydroxide**			**Aluminum hydroxide**			**Mn(IV) dioxide**			**Sodium diuranate**		
		Residue after 40 h, g	**Starting amt, g (avg 3)**	**% undiss.**	**Residue after 40 h, g**	**Starting amt, g (avg 3)**	**% undiss.**	**Residue after 40 h, g**	**Starting amt, g (avg 3)**	**% undiss.**	**Residue after 40 h, g [a]**	**Starting amt, g (avg 3)**	**% undiss.**	**Residue after 40 h, g [a]**	**Starting amt, g (avg 3)**	**% undiss.**
1	0/0.5	0.0372	0.0727	51	0.0353	0.1033	34	0.0295	0.0568	52	0.0958	0.0635	151	0.0687	0.2423	28
2	0.0625/0.4375	0.0404	0.0727	56	0.0430	0.1033	42	0.0309	0.0568	54	0.0960	0.0635	151	0.0795	0.2423	33
3	0.125/0.375	0.0432	0.0727	59	0.0488	0.1033	47	0.0317	0.0568	56	0.1117	0.0635	176	0.0851	0.2423	35
4	0.1875/0.3125	0.0472	0.0727	65	0.0550	0.1033	53	0.0342	0.0568	60	0.1017	0.0635	160	0.0940	0.2423	39
5	0.25/0.25	0.0516	0.0727	71	0.0644	0.1033	62	0.0360	0.0568	63	0.0828	0.0635	130	0.1108	0.2423	46
6	0.3125/0.1875	0.0558	0.0727	77	0.0742	0.1033	72	0.0387	0.0568	68	0.0575	0.0635	91	0.1220	0.2423	50
7	0.375/0.125	0.0605	0.0727	83	0.0879	0.1033	85	0.0416	0.0568	73	0.0281	0.0635	44	0.0831	0.2423	34
8	0.4375/0.0625	0.0652	0.0727	90	0.1019	0.1033	99	0.0473	0.0568	83	0.0012	0.0635	2	CD [b]	0.2423	CD
9	0.5/0	0.0685	0.0727	94	0.1067	0.1033	103	0.0553	0.0568	97	0.0005	0.0635	1	CD	0.2423	CD
	Scoping Tests															
--	Oxalic acid	0.0443	0.07145	62	0.0049	0.09245	5	0.0271	0.05685	48	0.1399	0.0984	142	0.0637	0.2429	26
--	Citric acid	0.0771	0.07145	108	0.1146	0.09245	124	0.0569	0.05685	100	CD	0.0984	CD	CD	0.2429	CD

(a) The solid phases MnO_2 and $Na_2U_2O_7$ separated from solution after equilibration do not represent the initial solid phase taken for dissolution but rather oxalate salts of Mn(II) and U(VI) reprecipitated from the initially homogeneous solution over the time of equilibration.

(b) CD means complete dissolution solution is clear end of equilibration.

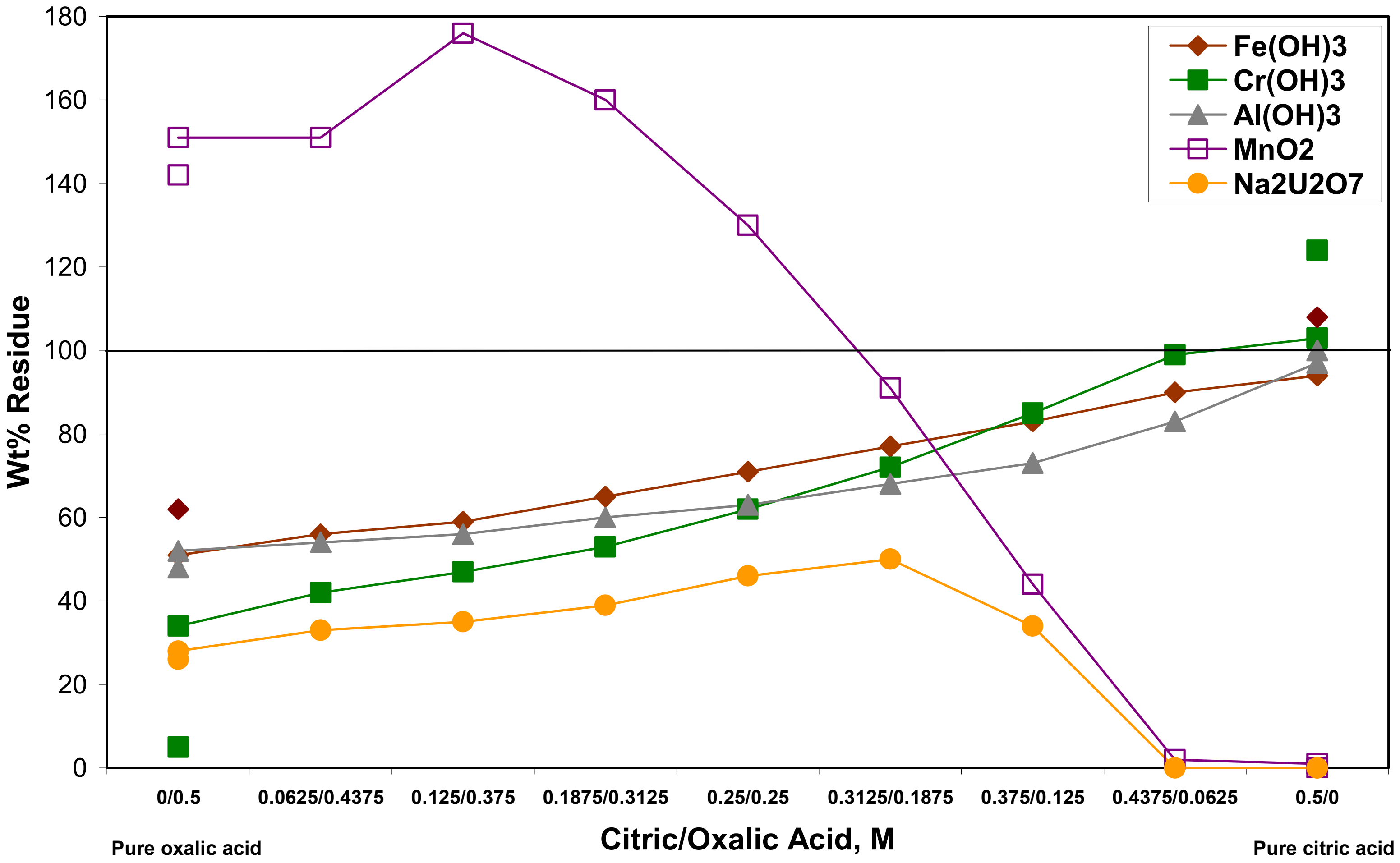

Figure 2. Sludge Phase Dissolution Performance for Mixed and Pure Citric/Oxalic Acids ($C_{\text{acid total}} = 0.5$ M)

$Fe(OH)_3$

Pure 0.5 M oxalic acid dissolves about 50% of the $Fe(OH)_3$. As shown in Figure 2, this finding closely reproduces the prior result for oxalic acid. Increasing the citric acid fraction in the oxalic/citric acid mixture decreases the dissolution. This reason for this result may be that citric acid is weaker (pK_{a1} ~3.1) than oxalic acid (pK_{a1} ~1.2). With protons less available to react with the hydroxide in the metal, less Fe^{3+} is available for citrate complexation. The test results also give no evidence for the formation of ternary Fe(III)-oxalate-citrate complexes judging by the continuous decrease in dissolution efficiency as the oxalic/citric acid ratio decreases. The observation that 0.5-M citric acid practically does not dissolve $Fe(OH)_3$ confirms the result from the scoping tests with 0.5-M citric acid.

$Cr(OH)_3$

The dissolution efficiency of $Cr(OH)_3$ in pure oxalic acid is significantly lower than that in the previous test (35% undissolved residue versus 5% in the scoping test). The reason for this discrepancy is not known; however, one plausible explanation is the higher purity of the Cr(III) hydroxide prepared in the present tests for the mixed oxalic/citric acid reagents compared with the $Cr(OH)_3$ in the prior test prepared using carbonate-contaminated NaOH. If carbonate is present in the alkali, mixed hydroxo-carbonates of Cr(III) may have formed, which in turn may have had a lower resistance to dissolution by oxalic acid. In all other respects, the dissolution trends for $Cr(OH)_3$ resemble those for $Fe(OH)_3$ in that citric acid does not promote the dissolution of either of these transition metal hydroxides.

$Al(OH)_3$

The dissolution of $Al(OH)_3$ in mixed oxalic/citric acids of various ratios is the same as for $Fe(OH)_3$ and $Cr(OH)_3$. Both 100% oxalic acid and 100% citric acid dissolution results are consistent with the prior results for these reagents. The intermediate oxalic/citric acid solution combinations show a continuous monotonic trend of increasing dissolution with increasing fraction of oxalic acid.

MnO_2

In the scoping experiments, MnO_2 was found to produce gas in the presence of either oxalic or citric acid. The gas, likely carbon dioxide, accumulated as the tests proceeded and required frequent venting of the test vials. In each case, rapid initial dissolution of the Mn(IV) dioxide was observed. However, after 40 hours of equilibration, a white precipitate (presumably hydrated MnC_2O_4) was found in the test with oxalic acid, while in the citric acid test the solution remained homogeneous (without solids). The pure constituent experiments were repeated in the present tests with mixed oxalic/citric acids. The results confirmed the prior observations both qualitatively and quantitatively. For the mixed oxalic/citric solutions, the highest amount of precipitate was found in contact with the 0.125 M citric acid/0.375 M oxalic acid solution. With further increase in citric acid concentration, the amount of precipitation decreased, first slowly and then abruptly, such that for pure citric acid practically all manganese was dissolved.

$Na_2U_2O_7$

The results of the scoping tests showed that oxalic acid quickly dissolved sodium diuranate ($Na_2U_2O_7$), but another compound subsequently precipitated. The lemon yellow crystals evidently were uranyl oxalate trihydrate. The CITROX tests with $Na_2U_2O_7$ showed a non-monotonic trend in the dissolution/precipitation efficiency of oxalic acid as its concentration decreased, such that no reprecipitation occurred for the tests richest in citric acid.

This observation can be understood as the result of several competing processes. On one hand, increasing oxalic acid concentration precipitated uranyl oxalate trihydrate. However, with further increased oxalate concentration, the system formed soluble U(VI) dioxalato and trisoxalato complexes, thereby dissolving the uranyl oxalate trihydrate. Speciation diagrams confirm this behavior and show that, at weakly acidic conditions, a low stoichiometric excess of oxalate leaves more uranium in the precipitate than would occur with a higher oxalate excess. In the absence of citrate, suppression of U(VI) reprecipitation by the action of oxalic acid also can be achieved by strong acidification.

Approximately five months after the CITROX dissolution test was completed, the leachates stored in separate vials were assayed by spectrophotometry. Minor amounts of newly formed precipitate were observed in some of the initially homogeneous uranium samples. The solids most likely are uranyl oxalate precipitated from slightly supersaturated solutions. The leachate spectra are shown in Figure 3. The main peak intensities correspond reasonably to the uranium concentration remaining in solution as derived by accounting for the amount of uranyl oxalate solid formed from the initially homogeneous solution. Unexpectedly, some samples exhibited an unusually intense peak at 665 nm. It was found that this peak represents a complexed form of tetravalent uranium. Uncomplexed U(IV) has its main absorption peak in 0.5 M HNO_3 at 648 nm and a molar absorptivity of ~40 $M^{-1}cm^{-1}$. The peak shift to 665 nm suggests complexation.

The U(IV) evidently is formed by reduction of uranyl(VI) by oxalic or/and citric acid. An interesting feature of the reduction process is its sensitivity to the ratio of the two dissolving components in the mixture. Thus, the 648-nm peak intensity [an indication of U(IV) concentration] is greatest for the sample with 1:3 oxalic-to-citric ratio (initial pH 0.93, final pH 0.92). However, the peak intensity is practically negligible at the 1:1 acid ratio (initial pH 0.78, final pH 0.83). The total ligand concentrations are identical and pHs similar in the two tests. These observations are consistent with the formation of mixed complexes of U(VI) and/or U(IV) with oxalate and citrate. The reduction kinetics must be slow because spectral monitoring of leachates from the NITROX series conducted one week after the NITROX dissolution test was completed does not reveal any U(IV) in the 0.5-M oxalic acid sample, a virtual duplicate of the 0.5-M oxalic acid test from the CITROX series.

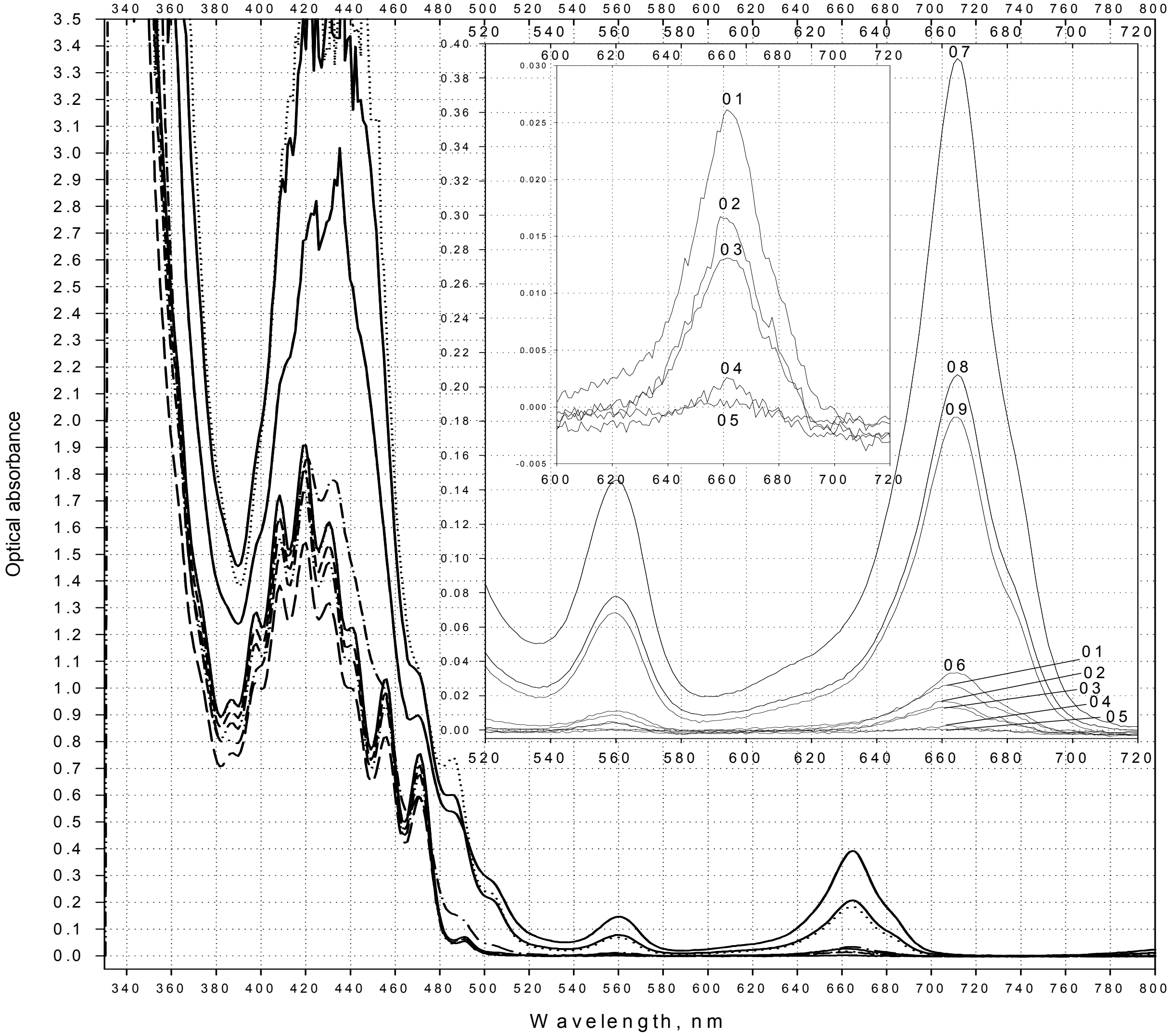

Figure 3. Spectra of Sodium Diuranate Leachates in the CITROX Mixtures. Spectra numbers correspond to sample numbers indicated in Table 3. The peak at 664 nm is due to U(IV).

4.3 Mixed Nitric/Oxalic Acid Test Results

Based on the effectiveness of oxalic acid and the known presence of sodium oxalate in the less-soluble saltcake heels of Tank S-112 and other waste tanks, addition of nitric acid to the tank residues is a possible means to generate oxalic acid in situ. As found in the scoping test results, acid is chemically required to dissolve the oxide and hydroxide phases. Thus, one promising avenue of work is to investigate the effectiveness of combined nitric/oxalic acid (NITROX) mixtures to dissolve sludge phases.

The remaining portions of hydroxides prepared for the CITROX experiment and stored under the respective mother liquids for about five months were used for the NITROX dissolution study. Some evaporation of mother liquids, which occurred during storage, was compensated for by adding deionized water to attain the original slurry concentration several hours prior to preparation of the standard 0.75-mmole slurry portions.

Table 5 compares pH values of the dissolving solutions before after their contact with the hydroxides. For the NITROX tests, it is seen that pH increases for nearly all tests except those of $Fe(OH)_3$, $Cr(OH)_3$, and $Al(OH)_3$ that are richer in $H_2C_2O_4$. In those cases, the pH remained virtually unchanged. The pH increases may be explained by the occurrence of the following reactions:

- Consumes acid (pH increases)
  For $M(OH)_3$ with HNO_3: $M(OH)_3 + 3\ HNO_3 \rightarrow M^{3+} + 3\ NO_3^- + 3\ H_2O$ (M=Fe, Cr, Al)
  For MnO_2 with HNO_3: $MnO_2 + 4\ HNO_3 \rightarrow Mn^{4+} + 4\ NO_3^- + 2\ H_2O$
  For MnO_2 with $H_2C_2O_4$: $MnO_2 + 2\ H_2C_2O_4 \rightarrow MnC_2O_4 + 2\ CO_2 + 2\ H_2O$
  For $Na_2U_2O_7$ with HNO_3: $Na_2U_2O_7 + 6\ HNO_3 \rightarrow 2\ UO_2(NO_3)_2 + 2\ NaNO_3 + 3\ H_2O$
  For $Na_2U_2O_7$ with $H_2C_2O_4$: $Na_2U_2O_7 + 2\ H^+ + 2\ H_2C_2O_4 \rightarrow 2\ UO_2C_2O_4 + 2\ Na^+ + 3\ H_2O$
- Produces acid (pH decreases)
  For $Fe(OH)_3$ with $H_2C_2O_4$: $Fe(OH)_3 + 2\ H_2C_2O_4 \rightarrow Fe(C_2O_4)_2^- + 3\ H_2O + H^+$

The absence of a pH change suggests, but does not prove, a lack of reaction. The bases for the postulated reactions are discussed in this section.

Table 5. NITROX Solution pH Before and After Contact with Sludge Components

Test	Nitric/Oxalic acid conc, M	pH before contact	pH after contact				
			$Fe(OH)_3$	$Cr(OH)_3$	$Al(OH)_3$	MnO_2	$Na_2U_2O_7$
1	0/0.5	0.62	0.65	0.65	0.59	0.98	0.94
2	0.0625/0.4375	0.57	0.58	0.60	0.55	0.95	0.91
3	0.125/0.375	0.52	0.52	0.58	0.51	0.89	0.90
4	0.1875/0.3125	0.44	0.46	0.54	0.46	0.88	0.84
5	0.25/0.25	0.39	0.40	0.50	0.42	0.91	0.83
6	0.3125/0.1875	0.33	0.37	0.46	0.38	1.05	0.79
7	0.375/0.125	0.31	0.32	0.44	0.35	1.22	0.92
8	0.4375/0.0625	0.24	0.28	0.41	0.33	0.51	1.23
9	0.5/0	0.17	0.26	0.39	0.25	0.29	2.60

Table 6 shows the results of the mixed nitric/citric acid test series based on weights of the residual solids and visual observations. The weight results are depicted in Figure 4. Results are described individually for each sludge phase.

Table 6. Mixed Nitric/Oxalic Acid Dissolution Test Results

Test Number	Concentration Nitric/Oxalic Acids, M	Fe(III) hydroxide			Cr(III) hydroxide			Aluminum hydroxide			Mn(IV) dioxide			Sodium diuranate		
		Residue after 40 h, g	Starting amt, g (avg 3)	% undiss.	Residue after 40 h, g	Starting amt, g (avg 3)	% undiss.	Residue after 40 h, g	Starting amt, g (avg 3)	% undiss.	Residue after 40 h, g [a]	Starting amt, g (avg 3)	% undiss.	Residue after 40 h, g [a]	Starting amt, g (avg. 3)	% Undiss.
1	0/0.5	0.0652	0.0705	93	0.0406	0.0807	50	0.0330	0.0593	56	0.0874	0.0603	145	0.0758	0.2347	32
2	0.0625/0.4375	0.0631	0.0705	90	0.0510	0.0807	63	0.0363	0.0593	61	0.0848	0.0603	141	0.1104	0.2347	47
3	0.125/0.375	0.0628	0.0705	89	0.0452	0.0807	56	0.0345	0.0593	58	0.0783	0.0603	130	0.1376	0.2347	59
4	0.1875/0.3125	0.0640	0.0705	91	0.0572	0.0807	71	0.0356	0.0593	60	0.0643	0.0603	107	0.1654	0.2347	70
5	0.25/0.25	0.0643	0.0705	91	0.0574	0.0807	71	0.0366	0.0593	62	0.0453	0.0603	75	0.1934	0.2347	82
6	0.3125/0.1875	0.0645	0.0705	92	0.0610	0.0807	76	0.0381	0.0593	64	0.0224	0.0603	37	0.2156	0.2347	92
7	0.375/0.125	0.0642	0.0705	91	0.0666	0.0807	83	0.0377	0.0593	64	0.0030	0.0603	5	0.1430	0.2347	61
8	0.4375/0.0625	0.0646	0.0705	92	0.0771	0.0807	96	0.0419	0.0593	71	0.0290	0.0603	48	0.0503	0.2347	21
9	0.5/0	0.0670	0.0705	95	0.0852	0.0807	106	0.0552	0.0593	93	0.0570	0.0603	94	CD	0.2347	CD
	Scoping Tests															
--	Oxalic acid	0.0443	0.07145	62	0.0049	0.09245	5	0.0271	0.05685	48	0.1399	0.0984	142	0.0637	0.2429	26
--	Nitric acid	0.0711	0.07145	100	0.0375	0.09245	41	0.0482	0.05685	85	0.0811	0.0984	82	CD	0.2429	0

(a) The solid phases MnO_2 and $Na_2U_2O_7$ separated from solution after equilibration do not represent the initial solid phase taken for dissolution but rather oxalate salts of Mn(II) and U(VI) reprecipitated from the initially homogeneous solution over the time of equilibration.

(b) CD means complete dissolution; solution is clear at the end of equilibration.

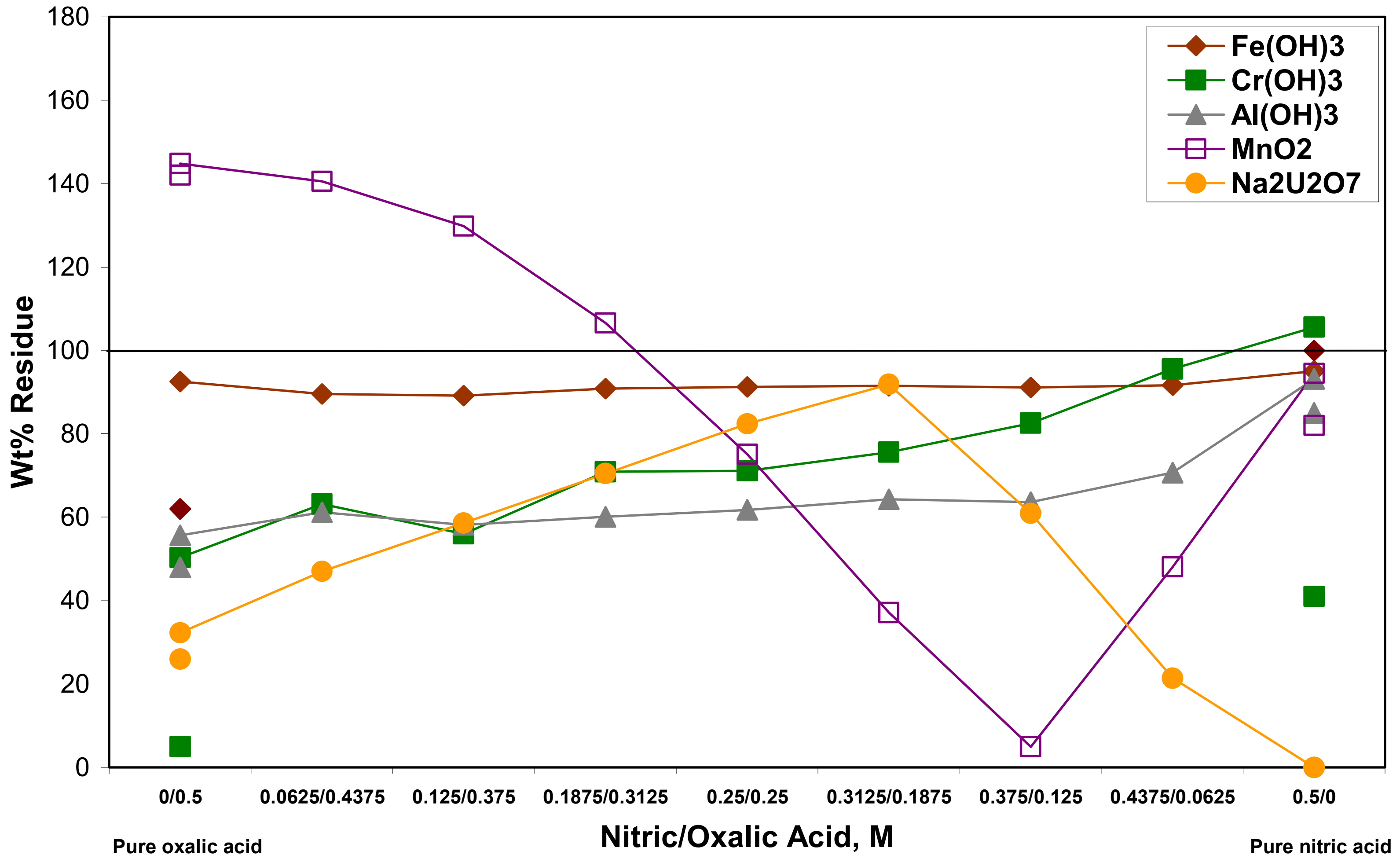

Figure 4. Sludge Phase Dissolution Performance for Mixed and Pure Nitric/Oxalic Acid Mixtures at 0.5 M Total Reagent

$Fe(OH)_3$

Much less dissolution of $Fe(OH)_3$ in 0.5 M oxalic acid was observed (7% of the precipitate dissolved) than was found with the 0.5 M oxalic acid sample from the CITROX series (~50% dissolved). This finding was attributed to the effects of precipitate aging in which dehydration of the bridging hydroxo-bonds with time forms stronger oxo-bonds and converts the largely amorphous $Fe(OH)_3$ precipitate to a more crystalline form such as FeOOH. Thus, even the overnight digestion of the hydroxide at 85°C was not sufficient to produce the aged precipitate formed at room temperature with five months of storage time.

No clear tendency emerged on the effect on dissolution efficiency of varying the nitric:oxalic acid ratio. The percentage of undissolved fraction remains the same within experimental uncertainty for any of the eight tests containing oxalic acid. The pure 0.5-M nitric acid solution showed some minor dissolution but still with 95% undissolved residue. The presence of Fe(III) in the nitric acid leachate (5.60 mM concentration) was confirmed by spectrophotometric assay ($A_{340} = 0.071$, $\varepsilon_{340} = 12.7\ M^{-1}\ cm^{-1}$). This concentration is equivalent to 3.4% dissolution (96.6% undissolved residue), consistent with the 5% weight loss observed by comparing weights before and after dissolution. Though spectra of the yellow-colored leachates were measured from the remaining samples containing oxalic acid, the quantities of dissolved iron were not determined because calibration measurements of the Fe(III)-$H_2C_2O_4$-HNO_3 system was not done. Nevertheless, based on optical density of the solutions, tests richer in nitric acid were more efficient in dissolving iron(III) hydroxide.

$Cr(OH)_3$

The extent of chromium(III) hydroxide dissolution in pure 0.5-M oxalic acid was 50% in the NITROX series, 1.3 times less than had been observed previously for 0.5-M oxalic acid in the CITROX series (65% dissolved). The decrease in $Cr(OH)_3$ dissolution efficiency after prolonged storage at room temperature is attributed to gradual crystallization (ripening) of the $Cr(OH)_3$ in a manner similar to that of $Fe(OH)_3$.

The decrease in leachate color intensity as the oxalic acid concentration in the NITROX mixture decreased suggested the corresponding decrease in $Cr(OH)_3$ dissolution. The dark violet color in the $H_2C_2O_4$-rich test solutions of the series is so intense that the optical absorbance could be measured only after six-fold dilution of the leachate. The increase of color intensity in solutions containing oxalic acid compared with that observed in oxalate-free solution indicates the formation of complexes between oxalate and chromium. Spectral analysis reveals information about the relative chromium concentration in the oxalate-containing solution and also shows the appearance of a third relatively weak but unusually sharp absorption band in the Cr(III) spectrum. This peak shifts from 690 nm to 699 nm as the oxalate:Cr ratio increases (and acidity decreases). Spectra of the six leachates highest in oxalic acid concentration in this series are shown in Figure 5. A control experiment performed by adding $Cr(NO_3)_3$ to a high excess of potassium oxalate solution shows that the absorption band at 699 nm can be attributed to the Cr(III) trisoxalato complex [i.e., $Cr(C_2O_4)_3^{3-}$]. The predominance of the dissolved Cr(III) trisoxalato complex in solution containing an excess of potassium oxalate was inferred from speciation diagrams based on magnitudes of the formation constants for Cr^{3+} and oxalate ($\log\beta_1 = 5.34$, $\log\beta_2 = 10.51$, $\log\beta_3 = 15.44$) (Nagata et al. 1965) at near-neutral pH.

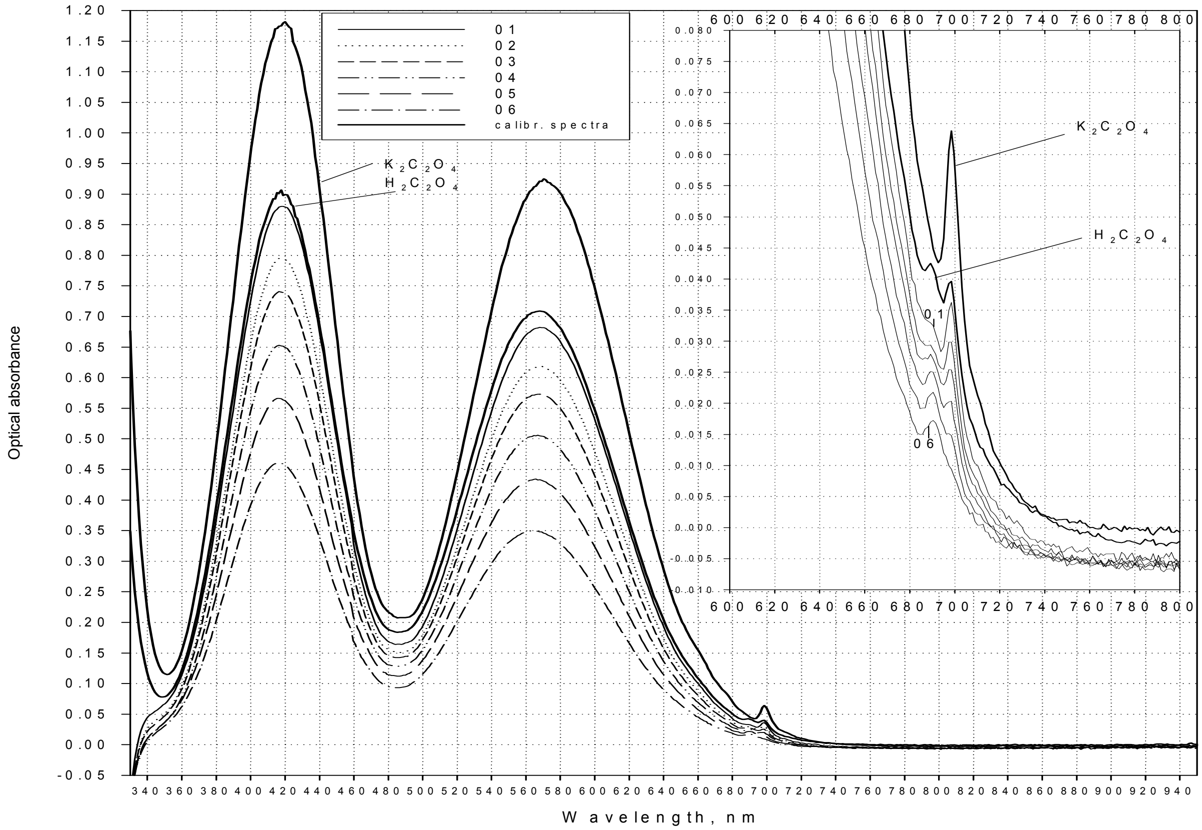

Figure 5. Spectra of Cr(III) Hydroxide Leachates in the NITROX Dissolution Series. Solutions are six-fold dilutions of the respective initial solutions from tests 1 to 6 plus $Cr(NO_3)_3$ spectra in 0.5-M oxalic acid and 0.5-M potassium oxalate.

$Al(OH)_3$

The dissolutions of $Al(OH)_3$ in mixed nitric/oxalic acids of various ratios are similar to those of $Cr(OH)_3$ for the $H_2C_2O_4$-rich tests (1–3) but are more efficient for the HNO_3-rich tests 4–8. In contrast to the behaviors shown by $Fe(OH)_3$ and $Cr(OH)_3$, the degree of crystallinity of $Al(OH)_3$ and its resistance to dissolution apparently do not increase after prolonged storage in nitrate solution at room temperature. This behavior is shown by the practically identical extents of dissolution observed for the pure oxalic acid samples in the CITROX and NITROX series.

MnO_2

The $H_2C_2O_4$-rich part of the NITROX dissolution series with MnO_2 behaved in a manner qualitatively similar to the CITROX tests. In both series, large amounts of white precipitate, presumably hydrated Mn(II) oxalate, formed by complete reductive dissolution of the black dioxide. The postulated reductive dissolution is supported by the observation of gas evolution and pressurization in the contact vial.

In contrast to the CITROX series, in which increasing concentrations of citric acid increased the fraction of dissolved manganese, increasing the HNO_3 fraction in the NITROX series failed to dissolve the Mn(II) oxalate in the $H_2C_2O_4$-rich experiments and failed to dissolve the MnO_2 in the HNO_3-rich experiments (tests 7–9). This behavior was observed qualitatively in the color of the undissolved residue—white in tests 1–6 (with oxalic acid) and black in tests 7–9 (little or no oxalic acid).

Results from the NITROX series are more amenable to quantitative interpretation and understanding of the reduction/oxidation (redox) behavior than the CITROX series. Because both oxalic acid and citric acid were present in the CITROX series, their relative contributions to the process of reductive dissolution of MnO_2 were difficult to assess. In the NITROX series, only oxalic acid can participate in the reductive dissolution. As a result, the reaction stoichiometry was determined based on analyses of the residual amounts of MnO_2 found in tests 7 and 8.

In sample 7, 5% of the MnO_2 remained in the solid residue, and no MnC_2O_4 precipitate formed. In contrast, 0.684 mmoles of MnO_2 were oxidized by 0.56 mmoles of oxalic acid, a 0.684:0.56 = 1.22:1 $Mn:H_2C_2O_4$ mole ratio. In test 8, 48% of the MnO_2 remained undissolved, and the $Mn:H_2C_2O_4$ mole ratio is 1.34:1. If the final product of MnO_2 reductive dissolution is Mn^{2+} and CO_2, the balanced chemical reaction indicates a 1:1 $Mn:H_2C_2O_4$ mole ratio:

$$MnO_2 + 2\ H^+ + H_2C_2O_4 \rightarrow Mn^{2+} + 2\ CO_2 + 2\ H_2O$$

This reaction can be seen as a superposition of two steps:

$$2\ MnO_2 + 6\ H^+ + H_2C_2O_4 \rightarrow 2\ Mn^{3+} + 2\ CO_2 + 4\ H_2O$$

and

$$2\ Mn^{3+} + H_2C_2O_4 \rightarrow 2\ Mn^{2+} + 2\ CO_2 + 2\ H^+$$

Deviation from the simple 1:1 stoichiometry can be understood by recognizing that, in addition to the Mn^{3+} reduced by the action of oxalic acid, some of the Mn^{3+} is reduced by water. The ability of Mn^{3+} to oxidize water is described in the literature (Lingane 1966). It is also possible that the starting MnO_2 is not stoichiometric; i.e., it is present as an oxide of composition MnO_{2-x} with manganese formal oxidation state less than +4. Stoichimetrically deficient ratios between oxygen and Mn are frequently observed for manganese dioxide samples of both natural and synthetic origin (Katz et al. 1956). Additional experiments are needed to prove the validity of either of these explanations.

The experimentally observed average stoichiometry of MnO_2 reduction by oxalic acid of (1.28 ± 0.06):1 was used to calculate the remaining oxalic acid concentration and account for the total proton concentration change in the NITROX series of samples. The results are shown in Table 7.

The data from Table 7 were used to produce a speciation diagram of Mn^{2+} in the nitric/oxalic acid mixtures after accounting for partial destruction of oxalic acid using HySS, the Hyperquad Simulation and Speciation utility program (Alderighi et al. 1999). The chemical model used to generate the diagram included protonation constants of oxalate, formation constants of the Mn^{2+} mono- and dioxalate complexes (corrected to 0.5 M ionic strength), and the MnC_2O_4 solid solubility product. The solubility product for MnC_2O_4 [K_{sp} (MnC_2O_4)] was used as an adjustable parameter because its published value, 1.7×10^{-7} (Lide 2001), is at zero ionic strength and appears to be unrealistically low for the conditions of

Table 7. Material Balance in MnO_2 Reductive Dissolution and Reprecipitation in NITROX Test Mixtures

Test	Nitric/Oxalic Acid Conc, M	pH		Ppt Color	% wt Change (w.r.t. initial 60.3 mg MnO_2)	Initial MnO_2, mmol	Initial $H_2C_2O_4$, mmol	Mn^{2+} after $H_2C_2O_4$ Contact	$H_2C_2O_4$ Left after 1:1.28 MnO_2 Dest'n.	MnC_2O_4 Pptd, mmol	Mn^{2+} Dissolved	
		Initial	Final								mmol	%
1	0/0.5	0.62	0.98	White	145	0.666	2.00	0.666	1.48	0.59	0.076	11
2	0.0625/0.4375	0.57	0.95	White	141	0.666	1.75	0.666	1.23	0.57	0.096	14
3	0.125/0.375	0.52	0.89	White	130	0.666	1.50	0.666	0.98	0.53	0.136	20
4	0.1875/0.3125	0.44	0.88	White	107	0.666	1.25	0.666	0.73	0.43	0.236	35
5	0.25/0.25	0.39	0.91	White	75	0.666	1.00	0.666	0.48	0.30	0.366	55
6	0.3125/0.1875	0.33	1.05	White	37	0.666	0.75	0.666	0.23	0.15	0.516	77
7	0.375/0.125	0.31	1.22	Black	5	0.666	0.50	0.633	0	0.00	0.633	95
8	0.4375/0.0625	0.24	0.51	Black	48	0.666	0.25	0.346	0	0.00	0.346	52
9	0.5/0	0.17	0.28	Black	94	0.666	0.00	0.040	0	0.00	0.040	6

the NITROX experiment conducted at approximately 0.5 M ionic strength. The total Mn^{2+} concentration was set to 160 mM, the range of oxalic acid concentration was varied from 58 mM (test 6) to 370 mM (test 1), and the respective total proton concentration range was set from 120 mM to 430 mM. The results of the simulation are shown in Figure 6.

It follows from the simulation data that the fraction of reprecipitated Mn^{2+} versus total divalent manganese can be reliably predicted using the ionic strength-adjusted thermodynamic data for the MnC_2O_4 solubility product and the Mn^{2+}-oxalate complex formation constants. The systematically lower actual pH readings compared with the calculated pH are attributed to ionic strength effects. The negatively biased pH reading is evident for test 9 (pure 0.5 M HNO_3); the theoretical pH [-log(0.5)] is 0.30, but the measured pH is 0.17.

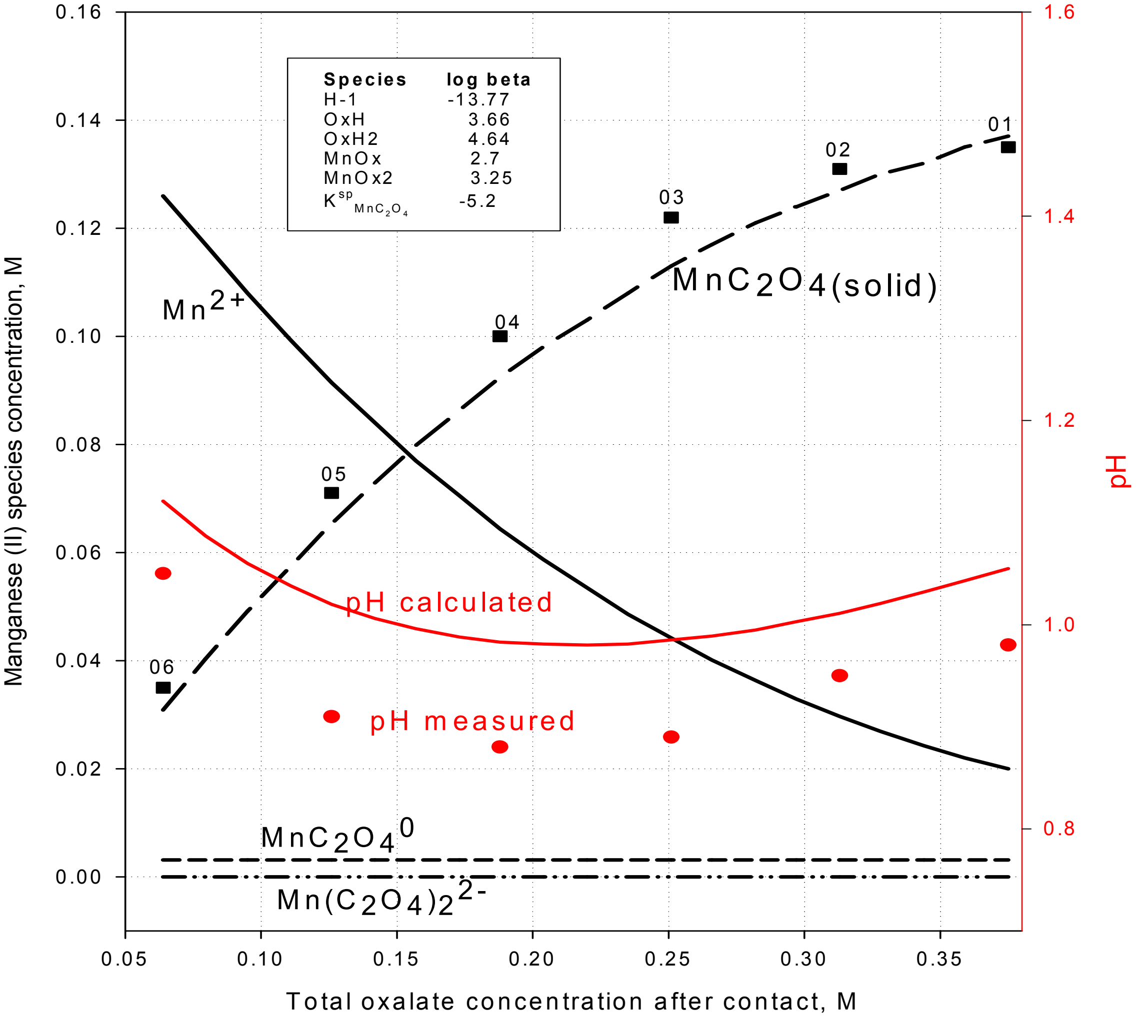

Figure 6. Mn^{2+} Speciation in $HNO_3/H_2C_2O_4$ Mixtures after Complete Reductive Dissolution of MnO_2 Based on a 1.28:1 MnO_2;$H_2C_2O_4$ Reaction Stoichiometry. Square and round points represent experimental data and lines represent predictions based on published ionic strength-adjusted thermodynamic quantities (see text).

A recent report describes the use of oxalic acid to dissolve genuine Hanford tank waste sludge from Tanks C-106 and AY-102 (Bechtold et al. 2003). The only manganese-containing phase tentatively identified in the water-washed starting material is $Na_3MnPO_4CO_3$ (sidorenkite) found in Tank C-106. This compound can be seen formally as an equimolar mixture of trisodium phosphate and manganese(II) carbonate salts, both of which should be practically colorless. On the other hand, the authors describe the C-106 sludge used in the dissolution experiment as "large, hard chunks of a very dark brown color with some white streaks and inclusions."

Among other mineral phases identified in the starting C-106 sample, only hematite (Fe_2O_3) is known to be colored, but its color varies from light brown to brick red and cannot explain the very dark brown appearance of the sludge taken for the dissolution test. Furthermore, the weight ratio of Mn:P in $Na_3MnPO_4CO_3$ is 1.77, whereas the Mn:P weight ratios in the water-washed C-106 sludge are 2.43 and 2.20 (Bechtold et al. 2003, Table 7-1) indicating an excess of Mn in the sludge above that needed to form sidorenkite. Based on these observations, the sludge may contain a substantial amount of amorphous MnO_2, undetectable by XRD analysis, as the second manganese-bearing solid phase. Using energy dispersive spectrometry of the scanning electron microscopic images, the authors also find some Mn in the Fe_2O_3 phase (Bechtold et al. 2003, Table 7-7).

If present, the MnO_2 also may account for some of the CO_2 observed in the gas products above that due to acidification of the dawsonite [$NaAlCO_3(OH)_2$] carbonate phase, also found in the C-106 sludge (Bechtold et al. 2003). The Mn^{2+}-catalyzed decomposition of oxalic acid in acid media (Gray et al. 1981), though it proceeds with a significant speed only in fairly concentrated nitric acid solutions and at elevated temperature, also should not be overlooked as a possible source of CO_2.

$Na_2U_2O_7$

Results for pure oxalic acid (test 1; 0.5 M $H_2C_2O_4$) and pure nitric acid (test 9; 0.5 M HNO_3) in the NITROX series for $Na_2U_2O_7$ closely resemble the respective points in the CITROX series and, in contrast to the findings for $Cr(OH)_3$ and $Fe(OH)_3$, show no effects by solids aging. The NITROX tests with $Na_2U_2O_7$ also confirm results of the scoping studies that show complete dissolution can be achieved either with a strong noncomplexing acid or by contact with an appropriate multiprotic organic acid. As the $HNO_3/H_2C_2O_4$ ratio increases, however, uranyl oxalate reprecipitation occurs, with maximum extent at the 0.3125 M HNO_3 / 0.1875 M $H_2C_2O_4$ ratio (test 6). At this point, as much as 81% of the total uranium is present as uranyl oxalate.

Chemical modeling of the uranyl-oxalate system with variation of total oxalate concentration from 0 to 0.5 M and total proton concentration from 1.0 M to 0.5 M (Figure 7) shows reasonable correspondence between the calculated $UO_2C_2O_4$ yield and the observed data. The modeling suggests that the decrease in uranyl oxalate precipitation as the oxalic acid concentration increases may be attributed to the increasing contribution of the uranyl dioxalato complex to the total dissolved uranium concentration.

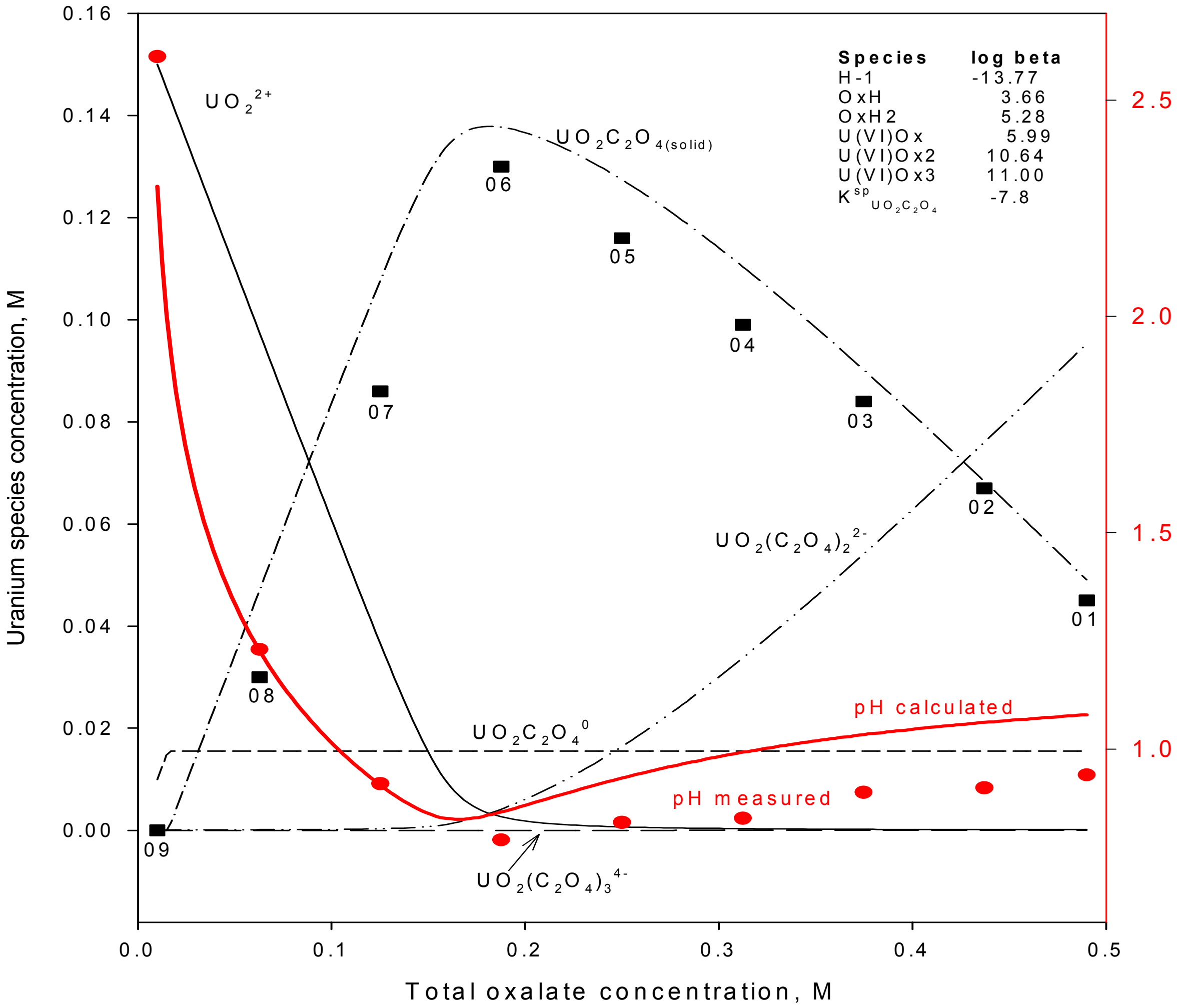

Figure 7. U(VI) Speciation in $HNO_3/H_2C_2O_4$ Mixtures after Complete Dissolution of Sodium Diuranate (C_U =160 mM; C_{HNO3} + C_{H2C2O4} = 0.5 M). Square and round points represent experimental data, and lines represent predictions based on published ionic strength-adjusted thermodynamic quantities.

The dissolved uranium species in equilibrium with uranyl oxalate precipitate were assayed by spectrophotometry. The results are shown in Figure 8. It is seen that for the $H_2C_2O_4$-rich part of the series, (tests 1–4), the dominant peak is at 420 nm, corresponding to the dioxalato complex. For test 5, the concentrations of the mono- and dioxalato complexes are nearly equal. The peak maximum shifts to 419 nm and on to 418 nm for the spectrum in test 6. This is the only test point in the speciation diagram (Figure 7) where the monoxalato complex is the dominant aqueous species. Further shift of the peak maximum position to 414 nm for the $H_2C_2O_4$-deficient tests in the series is associated with the increasing prevalence of the uncomplexed UO_2^{2+} species. These spectral shifts are consistent with findings reported in a recent publication by Havel et al. (2002).

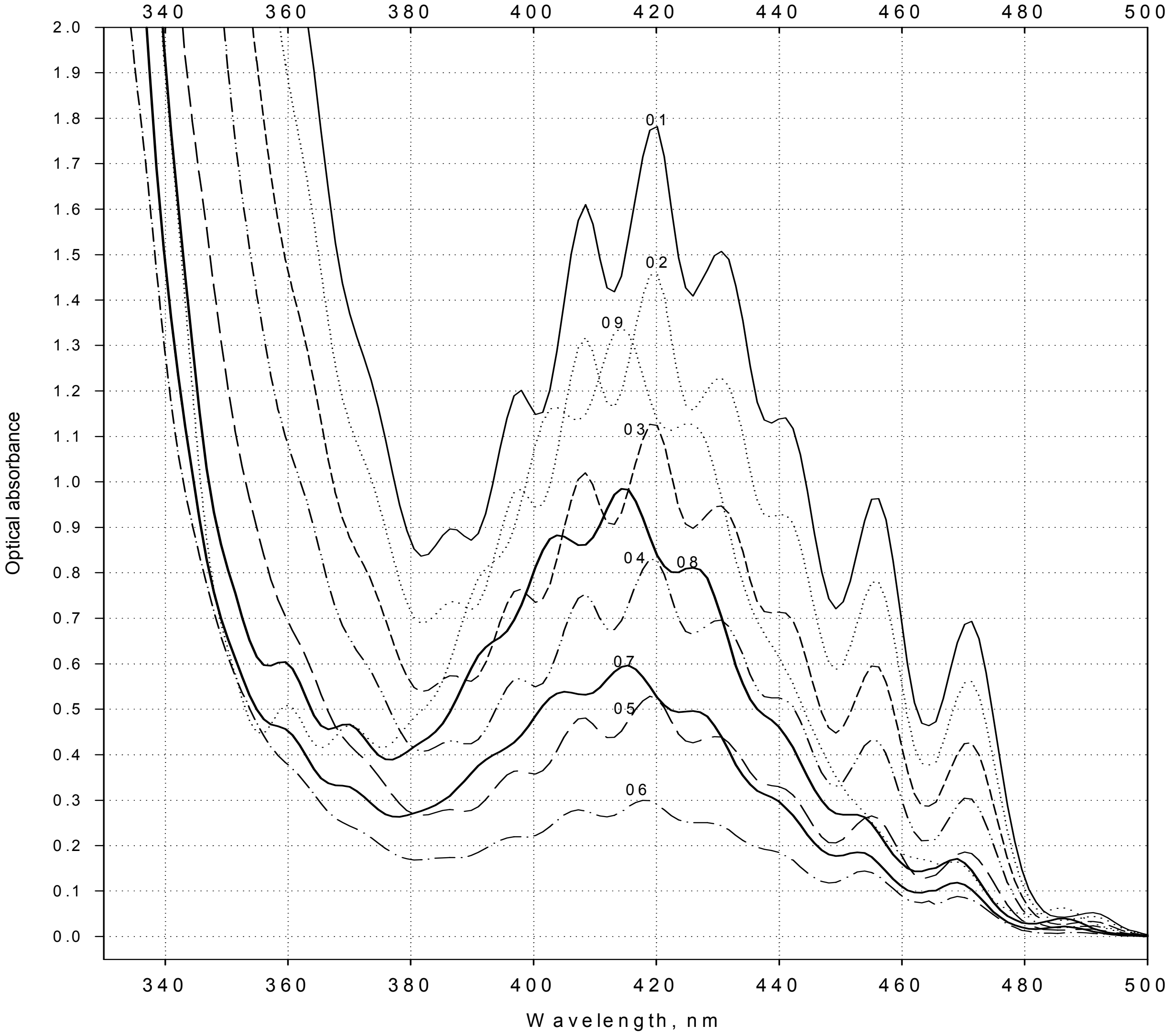

Figure 8. Spectra of Solutions from the $Na_2U_2O_7$ Dissolution Series in NITROX Mixtures

5.0 Conclusions

Chemical agents were investigated for their efficacies in dissolving metal compound phases known to be present in Hanford tank waste sludges. The phases included $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, MnO_2, and $Na_2U_2O_7$. The tests were conducted in three campaigns. In conjunction with the laboratory testing, a survey of the technical literature also was performed to identify candidate reagents. The first scoping tests investigated individual agents identified in the literature review along with other candidate agents. Based on the scoping test results, follow-up testing was performed to investigate the efficacies of mixed citric/oxalic acids (CITROX) and mixed nitric/oxalic acids (NITROX). Results of the literature survey are presented in the appendix. The results of the scoping tests and tests with the CITROX and NITROX mixed agents are summarized in this section.

5.1 Scoping Tests

Several general observations can be made from results of scoping experiments:

- No agent dissolved all solids completely; indeed, at the concentrations tested, no agent dissolved $Fe(OH)_3$ completely.
- $Fe(OH)_3$ is the phase hardest to dissolve, with dissolution of solids being more than 40% only for oxalic acid and HF.
- $Na_2U_2O_7$ is the most readily dissolved phase, dissolving to 80% or more for 10 of the 22 agents.
- Oxalic acid and HF are the best overall dissolving agents, though neither is completely effective for MnO_2 or $Fe(OH)_3$.
- Agents ineffective for all five solid phases are acetic acid, tartaric acid, dipotassium oxalate, trisodium citrate, glycine, disodium IDA, trisodium NTA, and trisodium HEDTA. Many of these ineffective agents are salts, suggesting that acidity is necessary for any agent to be successful. This is borne out by the fact that oxalic and citric acids are effective to some degree for certain phases whereas their salts are not effective for any phase.
- The effectiveness of phthalic acid and salicylic acid were difficult to judge because the acids, introduced as their respective solid crystals, did not dissolve completely. However, neither of these white crystalline acids completely dissolved any metal phase, judging from the colored solids remaining in each test. Of the two, phthalic acid appeared to be slightly more effective.

Overall, oxalic acid is the most effective reagent, dissolving all the solid phases to some extent, including MnO_2. However, in the case of MnO_2, reprecipitation [probably as the white Mn(II) oxalate] soon followed dissolution. The MnO_2 oxidized at least two of the organic acids tested, oxalic acid and citric acid, as shown by the evolution of gas during the tests with these reagents. Hydrofluoric acid was an effective dissolving agent but is judged to be unacceptable in this application due to its chemical hazard, its corrosiveness on steel, and its deleterious effects in glass formation in subsequent waste vitrification.

5.2 Tests with Mixed Citric and Oxalic Acids—CITROX

The tests with the mixed citric and oxalic acids (CITROX) for $Fe(OH)_3$, $Cr(OH)_3$, and $Al(OH)_3$ showed results that could be considered linear combinations of the effects of the individual agents. Thus, the highest dissolutions were observed for the pure 0.5 M oxalic acid test, the lowest dissolution for the pure 0.5 M citric acid test, and nearly linear dissolution behavior for combinations of these two acids.

All CITROX tests with MnO_2 produced gas consistent with the oxidation, by Mn(IV) oxide, of the organic acids to produce CO_2. The Mn^{2+} reduction product evidently reacted with excess oxalic acid to precipitate Mn(II) oxalate, as shown by the presence of a white solid and a residue weighing ~1.5- to 1.8 times the weight of the starting MnO_2 ($MnC_2O_4{\cdot}2H_2O$ weighs 2.06-times as much as an equivalent amount of MnO_2). As the fraction of citric acid in the test sequence increased at the expense of the oxalic acid, the quantity of MnC_2O_4 precipitate decreased such that the test with pure 0.5 M citric acid had no solid residue.

The CITROX reagent mixtures richer in oxalic acid dissolved the $Na_2U_2O_7$ only to have it reprecipitate as the lemon-yellow $UO_2C_2O_4{\cdot}3H_2O$. With increasing citric acid, however, dissolution increased such that no solid phase remained in the pure 0.5 M citric acid solution. The CITROX uranium leachate solutions, left standing for five months, showed that partial chemical reduction of the uranium occurred to form U(IV) in solution.

The CITROX dissolution test findings show that the combined citric/oxalic acid reagents have no particular efficacy or synergistic effects beyond those of the pure citric or oxalic acid solutions in dissolving any of the sludge phases.

5.3 Tests with Mixed Nitric and Oxalic Acids—NITROX

The results of the NITROX tests for $Fe(OH)_3$, $Cr(OH)_3$, and $Al(OH)_3$ were analogous with the findings obtained in the CITROX tests in that they exhibited nearly linear dissolution behavior from pure 0.5 M oxalic acid (showing the highest dissolution) to pure 0.5 M HNO_3 (showing least dissolution). The intermediate mixtures showed intermediate dissolution. However, the $Fe(OH)_3$ and $Cr(OH)_3$ solids dissolutions in the pure 0.5 M oxalic acid test were markedly lower than those observed in prior testing under similar leaching conditions [$Cr(OH)_3$ dissolution in the pure 0.5 M HNO_3 test also was sharply lower than in the prior analogous scoping test]. The decreased efficacy in the latter NITROX tests, not noted for $Al(OH)_3$, was attributed to aging and dehydration of the Fe(III) and Cr(III) hydroxides to form more refractory oxyhydroxides such as FeOOH or CrOOH or other species.

The dissolution of MnO_2 in the NITROX reagents was found to be greatest at 0.375 M oxalic acid/ 0.125 M HNO_3 with white solids (likely manganous oxalate) present in the tests richer in $H_2C_2O_4$ and the black original MnO_2 solids present in the three tests highest in HNO_3 concentration. The stoichiometry of reductive dissolution of MnO_2 by oxalic acid differed, however, from that expected. The difference was attributed to either parasitic oxidation of water by the Mn^{3+} intermediate or by non-stoichiometric MnO_2 (i.e., MnO_{2-x}).

Results for the pure 0.5 M oxalic acid and 0.5 M nitric acid tests for $Na_2U_2O_7$ closely resemble the respective points in the CITROX series and show no effects by solids aging. The NITROX tests with $Na_2U_2O_7$ confirm results of the scoping studies that show complete dissolution can be achieved either with a strong noncomplexing acid or by contact with an appropriate multiprotic organic acid. As the $H_2C_2O_4/HNO_3$ ratio decreases, however, uranyl oxalate reprecipitation occurs, with maximum precipitation (81%) at 0.1875 M $H_2C_2O_4$ / 0.3125 M HNO_3.

Chemical modeling was performed for the manganese and uranium test systems to help explain the observed findings. The influences of Mn(II) and U(VI) oxalate complexes and solid phases on the test observations could be discerned by this method. The quantity of the dissolved Cr(III) trisoxalato complex $[Cr(C_2O_4)_3^{3-}]$ also was observed to increase as oxalic acid concentration increased over the NITROX test series.

In summary, CITROX and NITROX tests failed to show beneficial synergistic effects in dissolving sludge phases. Instead, the tests do suggest that the sequential addition of individual pure reagents (e.g., first citric acid to dissolve MnO_2 and $Na_2U_2O_7$ followed by oxalic acid to dissolve the Fe, Cr, and Al hydroxides) may be more effective than individual or blended reagents.

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Appendix

Review of the Technical Literature

Appendix

Review of the Technical Literature

The technical literature was reviewed to determine the phases requiring dissolution from the Tank 241-S-112 (S-112) waste heel and to identify agents that might be effective to dissolve those phases.

A.1 Tank S-112 Sludge Characterization and Key Constituents

Cooke et al. (2002) described the composition of S-112 solids phases and some initial concepts for synthetic steps to be used for their preparation as sludge simulants. Based on their findings and knowledge of tank waste chemistry, the sludge phases of interest are chromium(III) hydroxide, iron(III) hydroxide, calcium-chromium mixed hydroxide, sodium diuranate ($Na_2U_2O_7$), boehmite (AlOOH), gibbsite [$Al(OH)_3$], and MnO_2. The key constituents for dissolution and removal from the S-112 heel for tank closure are uranium, chromium, and technetium-99 (^{99}Tc). If ^{99}Tc is present in the sludge as an insoluble component, it likely occurs in one of its lower and less soluble oxidation states and most probably as Tc(IV) in the form of the hydrated dioxide, $TcO_2{\cdot}xH_2O$. Speculatively, the behavior of MnO_2 in the dissolution tests might serve as a chemical analogue of TcO_2 behavior. However, such analogies are weakened by the significant differences in redox chemistry of these two neighbors in the group VIIB of the Periodical Table of the Elements.

A.2 Candidate Dissolution Agents

Despite a wealth of technical literature on the use of chemical agents to dissolve metal oxides, most are not related directly to dissolution of the above listed sludge components stored under long-term, high-temperature, alkaline conditions in high-radiation fields. The results of our survey of the technical literature on the dissolutions of the various metal oxides and hydroxides are examined in this appendix.

A.2.1 Chromium and Aluminum

The dissolutions of $Cr(OH)_3$ and $Al(OH)_3$ are among the most thoroughly examined of all Hanford sludge components, with methods centering on oxidative dissolution and alkaline leaching, respectively (Lumetta et al. 1998; Rapko and Vienna 2002).(a) Much less information is available on Cr and Al mobilization from their hydroxides by the actions of multidentate organic complexing agents in weakly acidic or moderately alkaline media without perturbing the oxidation state of Cr(III). However, stable oxalic acid complexes of Al^{3+} and Fe^{3+} are known (Christodoulou et al. 2001).

Moreover, chromium and aluminum may substitute isomorphously for one-another in their hydroxides. The dissolution resistance of these mixed hydroxide phases is practically unexplored. The presence of both calcium and chromium in certain particles observed in the S-112 tank sludge has been

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(a) Also reported in *Acid Dissolution of Hanford Tank Sludges: A Status Report*, by GJ Lumetta, 1994. Internal letter report TWRSPP-94-082, Pacific Northwest National Laboratory, Richland, WA.

postulated to be due to the presence of the mixed calcium-chromium hydroxide tentatively identified as $Ca_3Cr_2(OH)_{12}$, a variety of the mineral katoite (Cooke et al. 2002). Dissolution of chromium from this phase likewise is unexamined.

A.2.2 Iron

Iron(III) hydroxide is much less amphoteric than the corresponding Al(III) and Cr(III) hydroxides. At the same time, the Fe^{3+} cation hydrolyzes to form polymeric aggregates at notably lower pH than any of the other trivalent sludge metals. As summarized in a recent book by Blesa and co-authors (1994), conditions to dissolve Fe(III) oxides are best established by combining reducing conditions (low E values), acidic media, and chelating agents. Though the authors assert that an adequate choice of any of these three variables will guarantee appropriate thermodynamic conditions for dissolution, in practice, kinetic considerations are overriding, and all three variables must be optimized to achieve reasonably fast dissolution kinetics. One of the interesting features of Fe(III) oxide dissolution is the rate acceleration caused by dissolved ferrous ion (Fe^{2+}). This autocatalytic character is illustrated by magnetite, Fe_3O_4, dissolution in oxalic acid, $H_2C_2O_4$ (Panias et al. 1996; Baumgartner et al. 1983). Countering the acceleration due to Fe^{2+} is the action of oxalate, which forms low-solubility Fe(II) salts, scavenging Fe^{2+} from solution and decreasing the dissolution rate. The dissolution of hematite (Fe_2O_3) by oxalic acid is reported to occur only at higher temperatures and involves a redox reaction. More powerful complexing agents such as ethylenediaminetetraacetic acid (EDTA) and iminodiacetic acid (IDA) do not increase magnetite and hematite dissolution rates until temperatures reach 80°C or higher (Torres et al. 1989).

Lumetta (1997) studied selective leaching of iron from Hanford tank sludge by the action of acetohydroxamic acid (AHA) and disodium 4,5-dihydroxy1,3-benzenesulfonate (Tiron). Both aged Fe(III) hydroxide and freshly precipitated hydroxide as nonradioactive sludge simulants were examined. It was found that the both reagents dissolve $Fe(OH)_3$ over a wide range of pH, but the dissolution efficiency appears to depend on the history of the hydroxide such that it was more difficult to dissolve aged $Fe(OH)_3$ (as would be expected to be found in Hanford storage tanks). For AHA, Fe dissolution decreases upon increasing the pH from 9 to 13, but the opposite is true for Tiron. At pH 13, Tiron is the most promising of the systems examined for leaching Fe from tank sludges. However, heating up to 100°C had no effect on the amount of Fe dissolved. Several other elements (Bi, Cr, Mn and Si) also dissolved to a certain extent in experiments with genuine sludge from Tank U-110. A combination of caustic and Tiron leaching decreased the sludge solids mass by 97%. On the other hand, the transuranium elements (Pu and Am) remained largely in the solids. An approach was proposed to add Tiron to the caustic leaching solution to dissolve Al and Fe (along with other elements) in a single step.

A.2.3 Manganese

Like the case for Fe(III) oxides, manganese dioxide, MnO_2, is known for its reductive dissolution in aqueous systems (Blesa et al. 1994). Therefore, introduction of organic anions capable of reducing Mn(IV) is expected to promote dissolution of MnO_2. Proper choice of organic reductant also should consider the possible reprecipitation of Mn^{2+} with an excess of the reductant or its oxidation products. Carbon dioxide release and a pressure buildup if the system is closed may result from oxidation of the organic reagent.

A.2.4 Uranium

The chemical form of U(VI) identified in the S-112 sludge is sodium diuranate, $Na_2U_2O_7$. Under alkaline conditions, $Na_2U_2O_7$ readily precipitates from uranyl nitrate, $UO_2(NO_3)_2$. In acid, this compound is expected to dissolve according to thermodynamics, but again the kinetics of dissolution of an aged precipitate might be slow. The dissolution efficiency might be enhanced by the combined action of acid and chelate-forming organic anions, suggesting that multiprotic organic acids should be tested first in the search for the most efficient dissolving agents for sodium diuranate.

A.2.5 Plutonium

Plutonium(IV) hydrous oxide, $PuO_2 \cdot xH_2O$, is an S-112 sludge component of major concern. In light of its ionic radius, complexation ability, hydrolytic behavior, and redox properties, Pu(IV) is expected to associate predominantly with Fe(III) hydroxide. Indeed, such preferential association with $Fe(OH)_3$, as well as with $Cr(OH)_3$ and $Na_2U_2O_7$, has been found during alkaline precipitation of mixed acidic nitrate solutions and subsequent dissolution of the coprecipitated phases in hydrochloric acid (HCl) (Fedoseev et al. 1998). At the same time, little association with $Al(OH)_3$ was found. Plutonium(IV) hydrous oxide's resistance to dissolution depends strongly on its preparation history and degree of crystallinity. However, even the freshly prepared amorphous hydroxide of Pu(IV) strongly resists dissolution even by concentrated mineral acids due to extensive polymerization. A recent study by Ruggiero and colleagues (2002), in which a number trihydroxamate siderophores and simple organic chelators were tested for $PuO_2 \cdot xH_2O$ dissolution, showed that the ligands promoting dissolution at room temperature were very slow with the dissolved amount of Pu still increasing after four months of contact. Ruggiero and co-workers found that of the chelators studied (EDTA, Tiron, citrate), EDTA is the most efficient at solubilizing Pu(IV) hydrous oxide. They also found that the solution stability constants (thermodynamic quantities) for a number of ligands with different chelating moieties do not correlate with their dissolution efficiencies (kinetic values). Finally, they observed that addition of Fe(III) to the heterogeneous reaction mixture decreased the Pu dissolution rate, presumably due to chelator competition. One of the difficulties in using EDTA as a dissolution agent at higher concentration is its poor solubility as the fully protonated form in acidic and near neutral solutions (Pokrovski 2000).

Ermolaev et al. (2002) studied depolymerization of Pu(IV) hydrous oxide in 0.5 to 3 M nitric acid in the presence of reductants [hydroquinone, H_2O_2, hydroxylamine, U(IV)] and oxidants [permanganate, H_2O_2 + Fe(III), persulfate + catalysts, Co(III)]. Of the methods studied, they found that the most efficient agent for Pu(IV) polymer dissolution at room temperature is sodium persulfate ($Na_2S_2O_8$) in 1 M HNO_3 using Co(II) nitrate as a catalyst.

A.2.6 Effects of Combined Agents

Once the most efficient two or three dissolution agents are identified, the efficiencies of their combined mixtures with different concentration ratios should be tested. In favorable cases, when the complexation equilibria are strongly shifted to form ternary complexes with high binding constants, one might expect an enhanced dissolution efficiency of the sludge components compared with the case when a single complex forming agent is present.

Fundamental aspects of ternary complex formation are still poorly developed, and few formation constants of mixed complexes are measured. Thus, no reliable prediction of a possible synergistic effect can be made in the case where two or more chelators are simultaneously present in solution unless the system is examined experimentally. One recent example of application of double mixtures of oxalic and citric acid for dissolution of the PUREX-high-activity waste (HAW) sludge is reported in the literature (Kudinov 2001). In these tests, a solution containing 5 g/L each of citric and oxalic acid was used, but it is not clear whether this mixture represents the optimum ratio of the components and to what extent the dissolution efficiency of the sludge was enhanced using this double mixture because no comparison with the single chelator results is given.

A number of other multicomponent decontamination solutions comprising double and triple mixtures of organic chelating/complexing agents have been developed and tested over the last two decades for removing the buildup of activated metals and other radioactive components in the cooling systems of nuclear power plants and other applications. One investigated malonic and oxalic acids (Borghi et al. 1996). Others include:

- formic acid + picolinic acid (know as LOMI)
- citric acid + EDTA (called CAN-DEREM)
- citric acid + oxalic acid + DTPA (diethylenetriaminepentaacetic acid) + EDTA (called DOW NS-1).

A recent report by Serne et al. (2002) provides plentiful data on the behaviors many metals, including Ni^{2+}, Co^{2+},Cr^{3+} Sm^{3+} Th^{4+}, NpO_2^+ UO_2^{2+} and PuO_2^{2+} in batch and flow-through adsorption experiments, with solutions containing one or several of the above-listed complexants. Even though these results are not directly applicable to the sludge dissolution project, the speciation calculations conducted in the report might serve as a useful reference to better understand the potential significance of the selected organic agents in facilitating transport of transition metals and actinides from the waste forms through soil and aquifer materials.

A.3 Summary of Literature Review

In summary, no particular classes of solubilizing agents were found that might be capable of dissolving all five major sludge components with high efficiency. Most of the metal hydroxide dissolution tests described in the literature were performed at elevated temperatures. Extrapolation of the observed dissolution rates to room temperature is not possible without a reliable knowledge of activation energy for these processes. This suggests that the widest possible number of organic chelators of different denticity and basicity should be tested by contact with the individual hydroxides/hydrated oxides. By such experimentation, data will be acquired under similar and reproducible experimental conditions (equilibration time, temperature, agitation efficiency, reagent concentration). The effect of acidity for the same chelating moieties can be best tested by equilibration of hydroxides with the fully protonated form of the chelator and its salt in parallel experiments (for example, oxalic acid versus the alkaline metal oxalate or citric acid versus sodium citrate). The effects of combining the most efficient agents also should be investigated.

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