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Pacific Northwest
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Richland, Washington 99352

QA Level

This work was performed to satisfy WVSP FY 1997 milestone number 0605B and was conducted in accordance with Impact Level II quality assurance requirements as defined by the WVSP Quality Assurance Plan ETD-007 and the PNNL *Quality Assurance Manual* PNNL-MA-70.

Summary

These tests were designed and conducted to simulate the West Valley (WV) tank heel removal flowsheet in which oxalic acid solution is used to elute cesium from zeolite in tank 8D-1 over a period of 28 hours. The eluent from tank 8D-1 is then transferred to tank 8D-2, where it is used to dissolve the waste sludge heel. The process sequence used for these tests was as follows:

- Elute 10 g of cesium-loaded zeolite for 28 hours at 50°C at 40 L/kg-zeolite, using an 8 wt% oxalic acid solution.
- Decant used 8 wt% oxalic acid solution to a separate container and add 240 g of waste slurry simulant, which was washed to <2 g/L dissolved solids and containing 120-140 gTO/L.
- Let the three test combinations and a control test age at 50°C for 50 hours. Sample at 0.25, 0.5, 1, 2, 4, 10, 20, 28, and 50 hours. The three tests investigated the following conditions: added Fe_2O_3, no added Fe_2O_3, and added Fe_2O_3 with no agitation. Fe_2O_3 was added to simulate tank corrosion products. The control was a repeat of the first test.
- Following the oxalic acid digestion, the two identical tests were adjusted from pH 2.5 to pH 5 using 10 M NaOH solution added at a rate of 2% by weight of the calculated total necessary per minute. After pH adjustment, sampling occurred at 0.25, 0.5, 1, 2, and 16 hours.

Results include visual observations, IC analyses for oxalate, and ICP-MS for the dissolved elements and the washed slurry composition. The accompanying data tables include the composition of the oxalic acid solutions after contact with the cesium-loaded zeolite for 28 hours, the amount of cesium eluted, the composition of the supernate oxalic acid solution in contact with sludge for up to 50 hours, and that from the neutralized tests for up to 16 hours. The appropriate data have also been graphed for each element as a function of contact time. The cesium elution data was consistent with previously obtained results of greater than 90% eluted.

The oxalic acid concentration after cesium elution was also consistent with previously obtained values, i.e., essentially no acid consumed.

During the contact with the oxalic acid solution at pH ~ 2.5, the solution appears to have come into equilibrium with the sludge solid almost immediately. The presence of additional iron oxide appears to have decreased the relative solubility of transition elements chromium, nickel, and manganese.

After neutralization, elements that form more insoluble hydroxides such as iron, nickel, manganese, calcium, and strontium show a significantly lower concentration in the supernatant. Silicon may also have been removed from solution, precipitating along with the hydroxides.

Flowsheet testing confirms earlier data indicating that oxalic acid is an efficient method for eluting cesium from zeolite and promotes the dissolution of sludge heels in the WV tanks. Additional testing is still needed to evaluate the corrosive impact of this process on the tank's structural materials.

Acronyms

DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
FY	Fiscal Year
HLW	High Level Waste
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
PNNL	Pacific Northwest National Laboratory
PUREX	Plutonium and Uranium Extraction
QA	Quality Assurance
STS	Supernatant Treatment System
THOREX	Thorium Extraction Process
WVDP	West Valley Demonstration Project
WVNS	West Valley Nuclear Services
WVSP	West Valley Support Project
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
gTO/L	grams total oxide per liter

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1.0 Introduction

The work performed and reported here is part of the West Valley Support Project (WVSP) conducted by the Pacific Northwest National Laboratory (PNNL)[a] and is in support of residual waste removal during high-level waste (HLW) transition activities to be performed by the West Valley Demonstration Project (WVDP). The HLW, approximately 2 million liters, was generated by a former commercial nuclear fuel reprocessing plant at West Valley, New York, and was originally stored in three tanks at the site of WVDP (Cadoff 1991). The waste consists of an alkaline sludge, supernatant liquid, an acidic THOREX solution, and cesium-loaded zeolite.

The largest volume fraction of waste was generated during reprocessing of spent uranium fuel by the PUREX process. Waste from the PUREX process was neutralized with NaOH for storage in a carbon steel tank, designated tank 8D-2. Neutralization resulted in a precipitated hydroxide sludge, which settled to the bottom of the tank and was covered by a supernatant salt solution. The acidic THOREX waste originated from the processing of thorium fuel from the Indian Point I reactor by the THOREX process. This waste, approximately 55,000 L, was first stored in a stainless-steel tank and then added to the PUREX waste in tank 8D-2. The supernatant from tank 8D-2 was passed over zeolite before being grouted. The loaded zeolite was stored in tank 8D-1. The zeolite was retrieved from tank 8D-1 and added to the other wastes in tank 8D-2 in preparation for the current vitrification campaign. During vitrification, the waste will be incorporated, according to West Valley's flowsheet, into a borosilicate glass. It is estimated that the vitrification process will yield 4.54×10^4 kg (500 tons) of glass, which will be stored in stainless-steel canisters at a waste repository (Cadoff 1991).

In preparation of the vitrification phase of the WVDP waste remediation, a major portion of the zeolite was removed from tank 8D-1 and transferred to tank 8D-2, leaving a cesium-loaded zeolite residual waste (heel) behind, which may require treatment to remove the cesium in preparation for site closure.[b] Tank 8D-2 will have residual waste remaining after vitrification consisting of waste from the PUREX and THOREX process and spent cesium-loaded zeolite. The residual waste remaining in tank 8D-2 may also require treatment to dissolve the waste and transfer the radionuclides to the vitrification plant.

Substantial work has been completed at PNNL to evaluate processes for cesium elution from the zeolite in tank 8D-1 and sludge dissolution in tank 8D-2. This work was designed to develop treatment processes and give information on process limits, conditions, and controls for the individual treatment steps for removal of tank 8D-1 and tank 8D-2 tank residual wastes as an interim step to decontamination and decommissioning of the West Valley nuclear processing facility. The results of this non-radioactive work are thoroughly described by Sills et al. 1996 and Russell et al. 1996. The work performed for the FY 1996 0605 subtask focused on testing an integrated "Cs Elution/ Sludge Dissolution flowsheet," i.e., a series of individual processing steps to produce a final result, the tank residual waste remediation. Several factors such as the presence of Fe_2O_3, the lack of slurry agitation, and the results of in-tank neutralization of oxalic acid after the sludge dissolution step were evaluated as part of this integrated flowsheet.

(a) Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

(b) Schiffhauer MA. "Review of Zeolite Transfer Operation and Estimated Duration," Internal West Valley Demonstration Project Memo dated March 24, 1994. West Valley Nuclear Services Co., West Valley, New York.

2.0 Conclusions and Recommendations

2.1 Conclusions

The results of the FY 1996 tests provided the basis for the following conclusions.

2.1.1 Effect of Iron Addition

During zeolite treatment with oxalic acid, when no iron was added, the zeolite was completely stripped of iron (100% based on the supernate analysis and the reported iron content of the zeolite). Also, the measured cesium eluted was 100 wt% (again based on the supernate analysis and the reported loading of the zeolite). When additional iron was added, 90 wt% of the cesium was eluted, which was consistent with past testing results. The iron analytical values for the cesium elution solutions to which iron additions were made displayed considerable scatter, but averaged to a value a little higher but similar to that reported by Russell et al. 1996 (34% to 39% dissolved).

During sludge treatment, added iron appeared to reduce the solubility of iron and other transition elements. The reason might be that the equilibrium solubility of the added iron phase is lower than that of the iron phases contained in the slurry simulant. The reduced solubility of the other transition elements is assumed to be due to coprecipitation with iron, substituting for iron in the phase precipitated.

2.1.2 Effect of Agitation

The amount of agitation provided during these tests was not vigorous enough to completely suspend the zeolite and slurry solids. Agitation did not appear to make any difference in how the system behaved other than the samples removed from the test with no agitation contained less suspended solids than the samples from the other tests. One possible difference, due to lack of agitation, was that the pH of the oxalic acid plus sludge simulant reached a stable state slower in the unagitated test than for the other tests (≈ 20 % longer than the next longest equilibrating test).

2.1.3 pH Adjustment

Adjusting the pH from ≈ 2.5 to 5.0 with 10 M NaOH over a period of about one hour decreased the solubility of iron, nickel, manganese, strontium, and calcium significantly (50% to 80%) but did not increase the solubility of any of the other sludge components. Equilibrium concentrations of all of the elements appeared to have been attained by the end of the pH adjustment period.

2.1.4 Concerns

Several concerns have come up as the test results have been evaluated. Because of economy of scale both from the test performers' side and the analytical chemistry side, samples were accumulated as a batch of samples before being analyzed. Thus samples sat under ambient conditions for up to several days with the supernate in contact with sludge solids unintentionally pulled during sampling prior to being analyzed. What effects this had on the final results is not known. The possibilities range from none to producing a distortion of the real compositional changes with time. The apparent rapid equilibration of the sludge-oxalic acid system might be an example of this. The lack of differences between agitated and non-agitated tests might be another. In previous testing, suspended solids were not a problem because there was more supernatant volume. Previous tests also showed that lack of agitation resulted in no difference from the control tests after 50 hours of contact (Sills et al. 1996). A post-test scoping experiment indicated that the level of agitation used in these tests was inadequate to suspend all of the solids.

Another concern was the lack of agreement between the standard Test 1a and Test 4a, which was supposed to be the exact duplicate. The main differences were the amount of iron in solution and the condition of the zeolite at the end of cesium elution. Test 1a had almost twice as much iron in solution as Test 4a and the zeolite had degraded to a finer-grained material in Test 1a than in Test 4a. There is no apparent explanation for this observation.

2.2 Recommendation to West Valley on Increasing pH

After treating with oxalic acid, it is recommended that the acidic contents of 8D-2 be transferred to the stainless-steel tank 8D-4 and the hastalloy Concentrator Feed Makeup Tank (CFMT). This will minimize the amount of caustic that needs to be added. The sludge remaining in 8D-2 will need to be neutralized. Neutralizing to a pH of 5 will minimize the amount of solid precipitation when compared to neutralizing to a pH of 12. Any solid that precipitates will most likely have different characteristics than the original solid that dissolved with respect to particle size and mobility. The drift to lower pH will need to be monitored and additional caustic may periodically need to be added to adjust the pH to 5. The extent of the pH drift was not studied as part of these experiments but may be included in future work.

2.3 Recommendations for Future Laboratory Work

2.3.1 Purify Supernate of Suspended Solids as Soon as Sample is Taken

For future tests of this kind, samples should be isolated from any suspended solids as soon as possible by filtration or by centrifuging. This would remove any possibility of continued reactions with the solids or precipitation due to decreasing temperature.

2.3.2 Standardize Zeolite Grain Size Distribution

The differences in the zeolite from test vessel to test vessel observed after the cesium elution stage of the tests suggest that a standardized homogeneous form of the zeolite is needed for laboratory testing to eliminate this variable from testing. It would be ideal to mimic the particle size of the zeolite in 8D-1; however this information is not available. Another possibility is the use of a pressed pellet; this, however, is not representative of the zeolite in the tank.

2.3.3 Test Effects of Agitation Rate (agitate vigorously)

Agitation rate needs to be quantified and verified. Unless the agitation action fully mobilizes the solids, one is working with an unknown mixture of diffusion and reaction rates. The unclear differences between the agitated and non-agitated tests in this study may illustrate this point. Ideally, one should mimic the agitation in the tanks, but this is not possible on a laboratory scale because of the complex internal structure of the West Valley tanks. However, by looking at agitation that completely suspends the slurry solids and comparing with no agitation, one should be able to bracket the expected tank conditions.

2.3.4 Test Effects of Large Localized pH Differences

Repeatability of the effect of NaOH (or other caustics like KOH, LiOH, or CsOH - in the case of zeolite) addition rate, solids loading, and alternate final pH levels are recommended for future study.

3.0 Experimental Procedures

The WVNS baseline flowsheet for residual zeolite/sludge oxalic acid washing is as understood in 1996:

1) The zeolite in contact with a 0.045 M NaOH heel at 4 L/ kg in tank 8D-1 will be contacted with an 8 wt% oxalic acid solution under ambient (50°C) conditions at a solution volume to zeolite ratio of 40 L/kg. The contact time, during which the mixture will be agitated, is set at 20 hours because previous testing (Sills et al. 1996) has shown that this contact time is well past the saturation time for Cs elution under these conditions.
2) Solids-free supernate will be transferred from tank 8D-1 to tank 8D-2, which contains sludge wastes (i.e., PUREX sludge, THOREX, and zeolite) having an approximate 12 wt% solids loading. The supernate/sludge mixture will be agitated for 20 hours under 50°C conditions. The ratio of 8D-1-eluent-to-8D-2-sludge will be about 1.5 L eluent/kg sludge based on the total sludge (supernate plus suspended solids).

The laboratory sludge dissolution/pH adjustment/agitation experiments (shown schematically in Figure 3.1 and summarized in Table 3.1) used the following nominal test conditions: 8 wt% oxalic acid at 40 L/kg zeolite, a bath temperature of 50°C, an oxalic acid addition temperature of 25°C, and continuous stirring. These tests followed the basic two-stage flowsheet with the following exceptions besides system size: the zeolite elution period was 28 hours, one test was not agitated (sludge), the ratio of eluent-to-sludge was about 1.5 L eluent/kg sludge, again based on the total sludge, the sludge was washed so that the dissolved solids were less than 2 wt% of the supernate, and a pH adjustment step was added to the flowsheet following the oxalic acid-sludge contact period.

A total of four experiments were conducted: 1) control; 2) no iron compound; 3) no agitation during sludge dissolution; 4) neutralization. The experiments were performed in sealed 500 mL or 2000 mL vessels depending on the required volume (Figure 3.2). To maintain the presence of iron oxide solids representing tank steel corrosion products, 2 grams of ferric oxide were added to the tests along with the sludge for Tests 1, 3, and 4. The only iron in Test 2 came from the initial zeolite elution and subsequently from added washed sludge. Sampling times were: 28 hours. for the cesium elution stage, 15 minute, 30 minute, 1 hour, 2 hours, 4 hours, 10 hours, 20 hours, 28 hours, and 50 hours for the oxalic acid-sludge contact step, and 15 minute, 30 minute, 1 hour, 2 hours, and 16 hours for the adjusted pH stage. These conditions and sampling times were found to be most favorable based on previous testing experience (Sills et al. 1996).

During the tests, the temperature was maintained at 50°C in sealed vessels, as shown in Figure 3.2. Each of the agitated tests was stirred with a propeller stirrer on a stainless-steel shaft at a stirrer setting of "two," which was thought to be enough to maintain the solids in a suspended condition. Each test was sampled through a port in the vessel lid using a pipette with a rubber suction bulb on the end. Attempts to sample just the supernate from each test were not very successful because it was difficult to control the depth of penetration of the pipette tip and the small degree of sludge solids settling after five minutes of non-agitation. Also, the liquid level was below the top of the heating mantle controlling the vessel temperature and could not be directly observed. Two samples were taken at each sample time; one for oxalate analysis by ion chromatography (IC) and one for multi-element analysis by inductively coupled plasma-mass spectroscopy (ICP-MS).

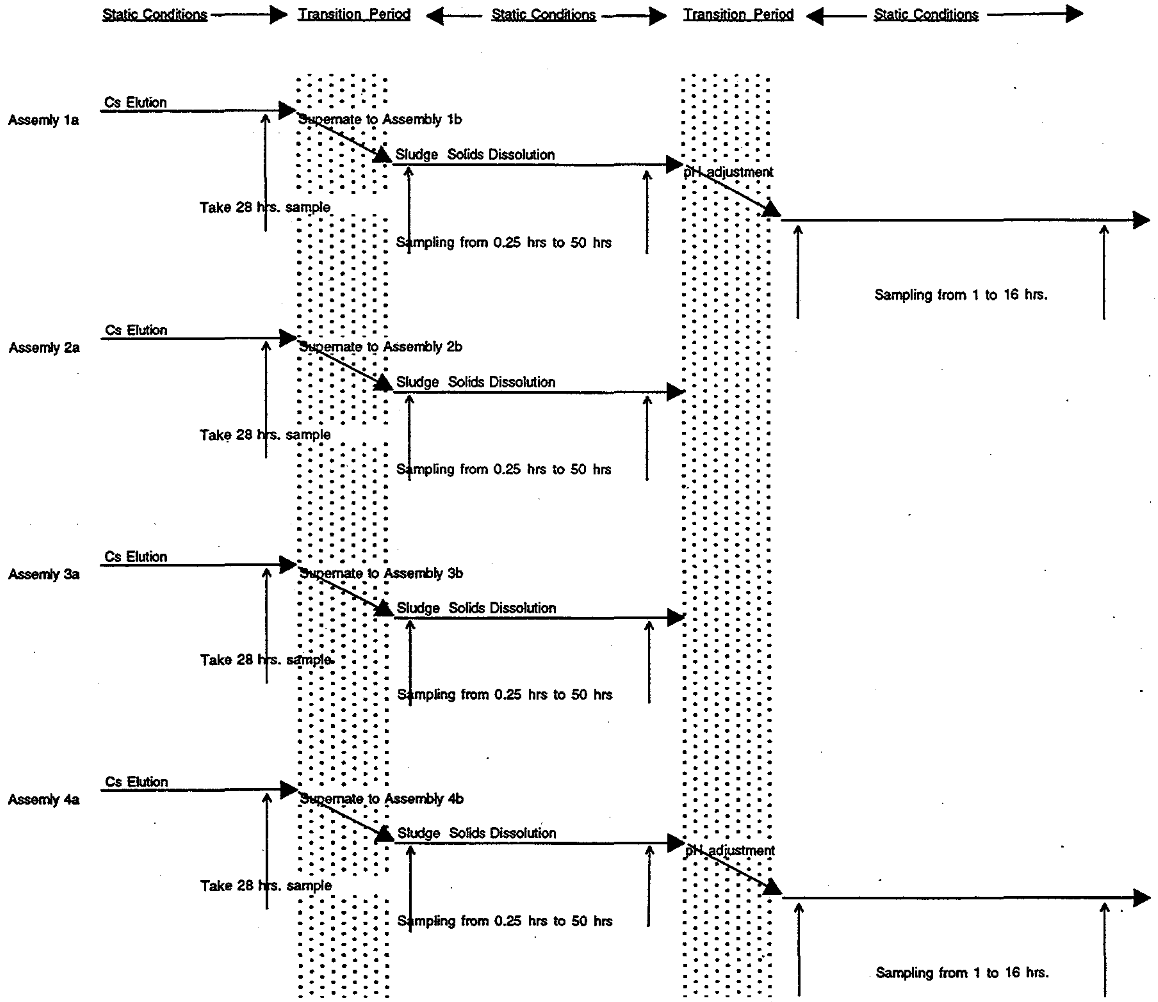

Figure 3.1. Flowsheet Used for Studying the Effects of Iron Addition, Agitation, and pH Adjustment for West Valley Tank Heel Remediation

The pH adjustment step was tested as a modification of the WVNS baseline flowsheet. It would be included after the sludge dissolution in tank 8D–2. It was performed as follows: First a small quantity of slurry (22 g) was removed from Test 4b to be pH adjusted. This slurry was titrated from pH ~2 to pH 8.0 in small steps using 10 M NaOH solution. The titration data is shown in Table 3.2. Based on the amount of 10 M NaOH used to adjust the slurry plus oxalic acid eluent sample pH to 5, the amount of 10 M NaOH needed to adjust the full laboratory-scale quantity was calculated. The oxalic acid-containing mixture of sludge and supernate for Test 1b and Test 4b was adjusted to a pH of about 5 ± 0.5 using 10 M NaOH solution at a rate of approximately 2% per minute of the calculated total (8.7 g) needed to accomplish the pH adjustment. The calculation of the amount of 10M NaOH needed to reach pH 5 ± 0.5 was based on a titration performed at ≈ 23°C. The error incurred by not performing the titration at test temperature (50°C)

Table 3.1. Experimental Test Matrix

	Test 1	Test 2	Test 3	Test 4
	Control	No Iron	No Agitation Sludge	pH Adjust
Standard Conditions - Cs Elution(a)				
Added ferric oxide with 10 g zeolite	4 g	0 g	4 g	4 g
Standard Conditions - Oxalic acid/Sludge Slurry(b)				
Added ferric oxide with 240 g sludge	2 g	0 g	2 g	2 g
Adjustment to pH 5	•			•
No agitation - Sludge			•	
Analyses				
ICP-MS for Cs during elution step	•	•	•	•
ICP-MS for Al	•	•	•	•
ICP-MS for Fe	•	•	•	•
ICP-MS for Sludge elements	•	•	•	•

was ≈ 0.18 pH units (Omega Handbook, p Z-11, 1992). Hence the Table 3.2 data is a good approximation for making the estimate. After the pH adjustment step, samples were taken at 15 minute, 30 minute, 1 hour, 2 hours, and 16 hours.

Sludge dissolution and oxalate salt formation were evaluated by analyzing the supernate and the sludge using ICP-MS and IC. The amount of zeolite remaining after contact with the oxalic acid solution was determined by retrieving, drying, and weighing the zeolite. Oxalate content was determined in the supernate using IC. The amount of simulated waste dissolved was determined by elemental analysis of the simulant and supernate using ICP-MS. Visual observations of the mixture containing sludge, supernate, and oxalic acid were made after the pH adjustment. Data reproducibility was tested by running Tests 1 and 4 in parallel and comparing test results.

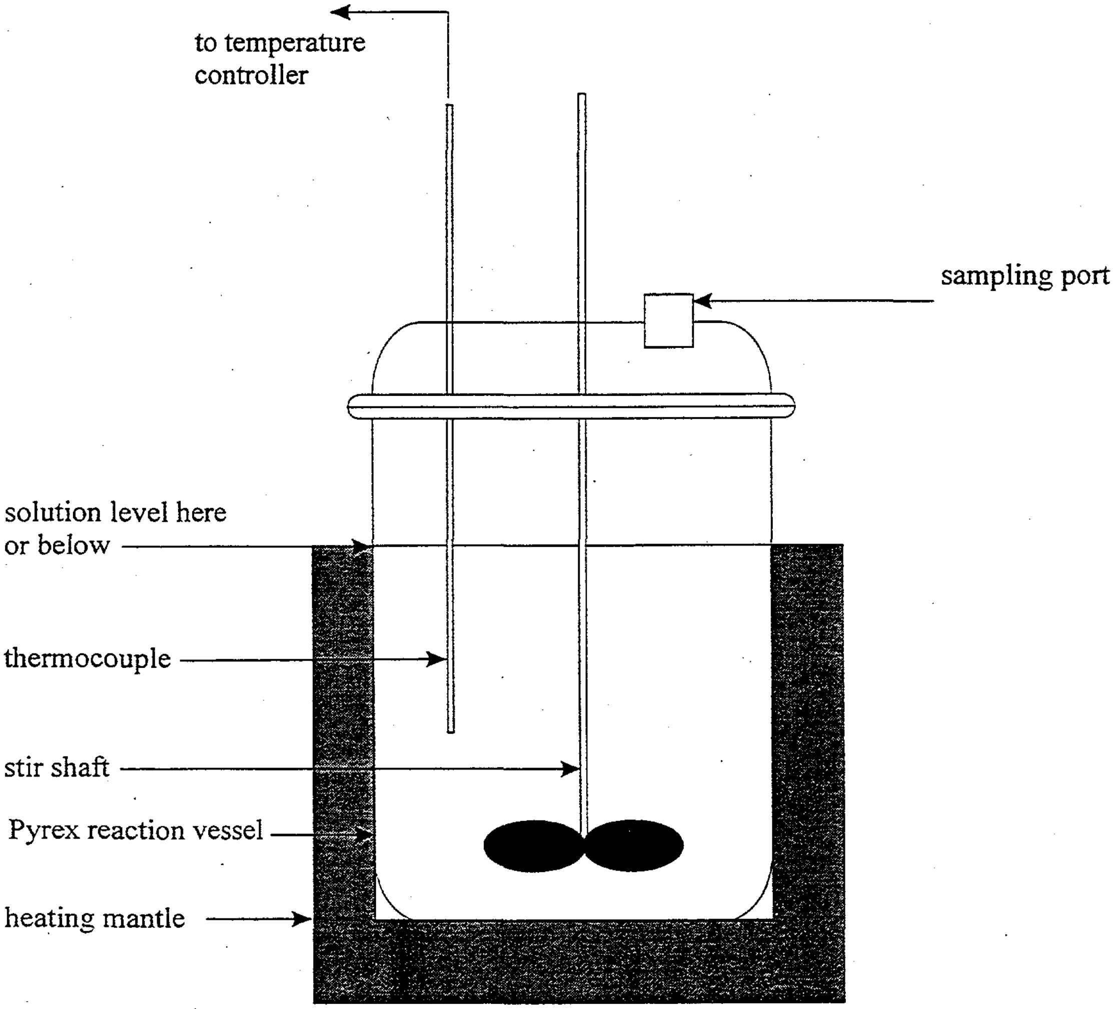

Figure 3.2. Five-Hundred ml Reaction Vessel Assembly Used in Cs-Elution and Sludge Dissolution Tests

Table 3.2. Test Solution Titration Data

Test 4b Slurry after 50 hours - 22.1g sample	
Measured pH @ 23±2°C	Amount 10 M NaOH solution added (grams)
3.05	0
4.21	0.20
5.15	0.40
5.95	0.60
7.10	0.80
8.01	1.00

4.0 Results and Discussion

Results include visual observations, IC analyses for oxalate, ICP-MS for the dissolved elements and the washed slurry composition. The data tables (Appendix A) include the composition of the oxalic acid solutions after contact with the cesium-loaded zeolite for 28 hours, the amount of cesium eluted, the composition of the supernate oxalic acid solution in contact with sludge for up to 50 hours and that from the neutralized tests for up to 16 hours. The appropriate data have also been graphed for each element as a function of contact time. Error bars have not been assigned to the data because the data scatter may be related to both analytical error and actual concentration fluctuations. The most accurate analytical results are probably ± 5 wt% with an average ±10-20 wt%, the error increasing as the detection limit is approached. Some elements such as silicon are difficult to accurately analyze because of poor dissolution during analytical sample preparation. Some elements such as iron and potassium can be a problem but difficulties can be detected by unexpected scatter in the results when a number of samples are analyzed at the same time. (Note that some of the analytical results show extremes which we have chosen to call "fliers" and are excluded from data plots. Some outliers that are less extreme may also be in the same category, but we have chosen to plot them and not flag them as "fliers.")

4.1 Visual Observations and pH

The visual observations and pH are summarized in Figure 4.1 and Table A.3, Appendix A. In Figure 4.1, the pH of the supernate for each test system is shown at each sampling stage. The final pH of the cesium elution solution for Tests 1a through 4a was taken at time zero. An arbitrary time interval of one hour was included between the final pH reading of the cesium elution solution and the initial pH measurement of the mixture of the cesium elution solution and sludge simulant so that the initial data points would not overlap on the Y-axis. The caption "Sludge Added to Cs Elution Solution" indicates the beginning of the time line for sludge mixed with the elution solution (Tests 1b through 4b), which continued for 50 hours at a pH that resulted from the mixing of 240 g sludge simulant described in Section 3 and about 360 g of the supernate solution each from Tests 1a through 4a. At the end of 50 hours Tests 1b and 4b were adjusted with NaOH to pH 5 over a period of about one hour (This hour is not included in Figure 4.1). After pH 5 was achieved, testing continued another 16 hours.

No dramatic changes in appearance were observed during these tests. Even though it was not possible to view the acid-slurry mixture directly, every time a sample was pipetted out of the reaction vessel, it was easy to see color and clarity. Most samples contained solids (a few appeared to be clear) and therefore most supernate samples were in constant contact with solids. The presence of solids in the samples *is a concern* because this condition allows the supernate and solids to continue to react after removal from the test system. This might be the reason for the consistency of concentrations of species between long- and short-term samples, as observed later. This possibility should be checked by repeating some of the tests and immediately isolating (such as by centrifuging the sample to quickly settle the solids) the supernate from any solids.

The pH of the cesium elution solution was uniformly acidic for all of the tests. When the sludge simulant was added, all of the systems except Test 2b (no iron added) displayed a pH maximum before settling down to equilibrium values. Test 3b, the non-agitated system, took the longest to come to a "constant" value, which might be expected. These initial variations might relate to the relative rate of reactions involving oxalic acid and the various metal hydroxides in the sludge simulant. The only difference known between Test 2b and the other tests was the lack of added iron oxide, hence the conclusion that the iron oxide addition was influencing the pH. In Tests 1b and 4b the pH was increased to 5 with the addition of 10 M NaOH solution at a rate of about 2 wt% of the estimated total per minute until a pH of 5 was attained. Almost immediately it was noticed that the pH began to decrease with time. It may be a similar phenomenon to the pH variation observed when the sludge simulant was added to the oxalic acid solution. As shown in Figure 4.1 below, the pH stabilization time was not determined because a sequence of constant values was not observed. The trend suggests that the pH will stabilize, but additional data points before and after 16 hours are needed to establish this.

4.2 Cesium Elution and Zeolite Mass Change

The cesium elution data are consistent with previously obtained values for eluting cesium-loaded zeolite. The comparison in Table 4.1 illustrates this fact. In this case, loading the zeolite to even higher levels has apparently improved the elution percentage. However, results of other tests with high versus low cesium-loaded zeolite conducted this year indicates that loading has a small effect, if any, on the percent of cesium that is elutable (Russell et al. 1996).

During the cesium elution, iron was dissolved into solution. Table 4.2 presents the iron mass balance for each test system during the 28-hour cesium elution. The iron has been recalculated as elemental iron and consists of 0.245 g per 10 g of zeolite and 2.798 g per 4 g of iron oxide. (The control was a sample of the zeolite material exposed to water for 24 hours and then dried, which illustrates that wetting and drying is not the reason for weight loss observed for the test solids.)

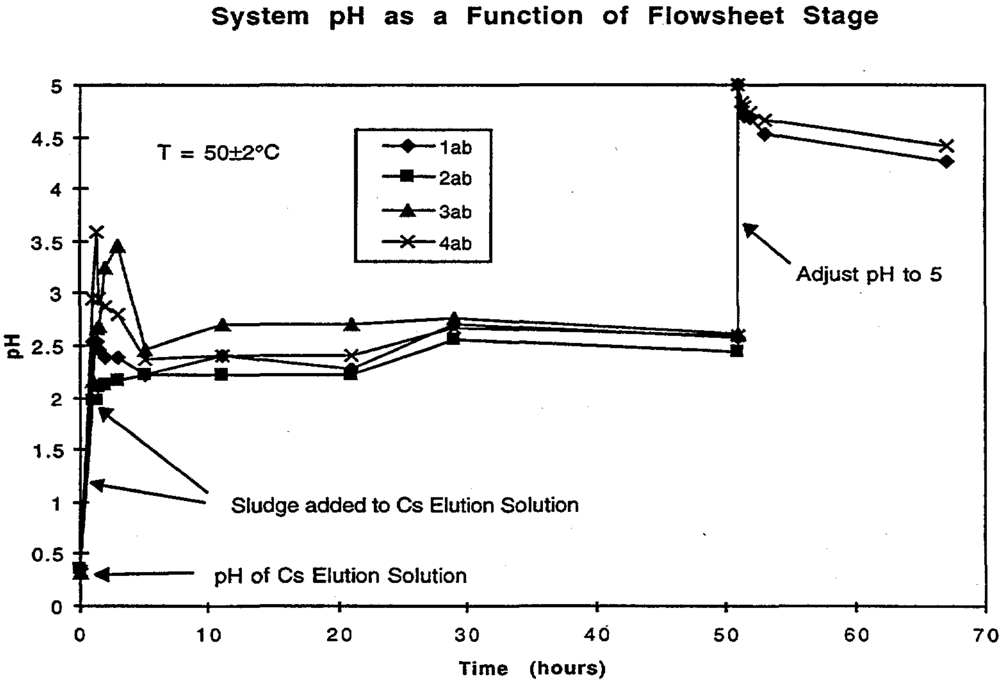

Figure 4.1. System pH as a Function of Flowsheet Stage as Reproduced by this Study

Table 4.1. Cesium Elution Data

Test	μg Cs/g dry zeolite	Percent eluted
1a-control	2910	91.98
2a-no Fe	2910	111.05
3a-no agitation	2910	94.19
4a-same as 1a	2910	91.98
30- control 1996(a)	922	87.8
31-Low Fe(a)	922	92.3
37- no Fe(a)	922	81.8
17- control 1995 (a)	957	91

(a) Russell et al. 1996.

Table 4.2. Solids Mass Changes During the 28-Hour Cesium Elution from Zeolite

Test Identification	1a	2a	3a	4a	control
Amount of Cs Loaded Zeolite IE-96 (grams)	10	10	10	10	5
Finely Divided Iron Oxide (grams)	4	0	4	4	0
Final dried weight solids (grams)	7.74	6.88	8.91	9.59	4.94
Net weight loss (grams)	6.26	3.12	5.09	4.42	0.06
Total elemental iron in test (grams)	3.043	0.245	3.043	3.043	-
Total elemental iron in solution (grams)	1.838	0.262	1.450	1.051	-
Percent total elemental iron in solution	60.4	106.9	47.7	34.5	-
Final pH of eluent	0.358	0.360	0.319	0.341	-

Considering Test 2a first, it is observed that all of the iron has been removed out of the zeolite and resides in solution. The same thing could be true of the other tests but no measurements have been made to determine this.

Considering next Tests 1a, 3a, and 4a, it is observed that though they all had the same amount of zeolitic iron plus added iron, they displayed considerable differences in the amount of iron in solution. It was expected that Tests 1a and 4a would give the same result and that Test 3a would be lower, because it was not stirred. It is not known why there is a discrepancy in the results but there are two factors that may have influenced these results. First, it is not clear that the stirring action used for these tests was energetic enough to agitate all of the solids into a suspended state. (This is a point to be addressed before performing additional tests of this kind.) Hence, iron oxide and other sludge components could have partially caked on the bottom of the vessels and not be in a condition to rapidly equilibrate with the supernate. Because only final iron concentrations were determined, it is not known if the measured values were equilibrium values or if the system was still approaching equilibrium. Second, it was observed after the cesium elution solution was removed that the zeolite grain size for Test 1a was considerably finer than that for Test 4a. Because they appeared to be the same at the time the tests were started, it must be concluded that something happened during Test 1a to cause the zeolite particles to break down or, despite initial observations, a lot of fines were contained in Test 1a from the beginning. Since the agitation was gentle, it is believed that the fines were there all along. The opinion is that the agitation was too weak to establish a clear difference between the agitated and non-agitated tests.

4.3 Oxalic Acid Concentration

The oxalic acid concentration after cesium elution was also consistent with previously obtained values (Sills et al. 1996). The samples needed to be filtered because most of them contained entrained sludge simulant solids. This was not by design, but due to the difficulty of positioning the sampling pipette so that only clear supernate was drawn into it. The percentage of the total oxalic acid in solution measured by IC is given in Table 4.3. Considering the scatter that is observed in these numbers (± 15%), it is difficult to say that two specific values are really different. However, the 28-hour cesium elution samples where the samples containing iron consistently indicate less oxalic acid in solution suggests some precipitated iron oxalate. Again during the sludge digestion stage, the test containing less total iron generally had the most oxalic acid in solution. The last five samples listed in Table 4.3 were taken after the pH of Tests 1 and 4 was raised to about 5. For these samples there appears to be about a 15% drop in oxalic acid concentration,

Table 4.3. Weight Percent of System Total Oxalic Acid in Solution

Test	1a	2a	3a	4a
hours	control	no Fe	no agit.	pH adj.
28	81.31	93.94	82.32	83.33
0.25	90.03	86.59	84.53	94.84
0.5	97.59	107.21	92.44	93.81
1	94.84	105.15	100.68	99.31
2	98.28	110.99	96.56	86.59
4	85.91	91.41	96.56	89.69
10	81.44	109.27	98.97	97.93
20	95.87	105.84	95.19	92.44
28	91.41	97.93	101.71	96.22
50	103.43	113.05	103.78	98.28
0.25	86.65			83.60
0.5	83.26			83.26
1	86.65			82.25
2	86.31			76.16
16	92.06			83.94

suggesting that some oxalate precipitated as a result of the pH adjustment. As discussed in Section 4.5, several elements could have precipitated as oxalates accounting for this concentration change. Sodium showed a drop in concentration with increased pH (see Appendix B) and it is not expected to precipitate as a hydroxide. Therefore it is concluded that sodium oxalate precipitated.

4.4 Supernate Concentrations of Sludge Components in the Presence of Oxalic Acid

During the contact with the oxalic acid solution at pH ~ 2.5, the solution appears to have come into equilibrium with the sludge solid almost immediately because the analytical values change little from the 15 minute sample to the 50 hour sample such as is indicated in the Tables 4.4, 4.5, 4.6, and 4.7 below. Considering the fine grain size of the sludge, this may not be surprising. However, the concern with respect to suspended solids in the samples needs to be considered here because continued contact with suspended solids in the sample bottle may have allowed the supernate composition to be altered by continuing reaction.

The presence of additional iron oxide appears to have decreased the relative solubility of transition elements chromium, nickel, and manganese as well as iron itself. As shown in Tables 4.4 through 4.6, these elements have a distinctly higher percentage in solution in the system with the lowest iron content (Test 2b). This trend is also true for iron where Test 2b has the highest supernate iron content of all the test supernates.

As indicated in Figure 4.2 and Table 4.7, a higher percentage of iron is in solution in Test 2b than for the other tests. Iron is also more concentrated in the supernate of Test 2b ≈ 4500 µg/mL versus ≈3700 µg/mL for each of the other tests (see Figure 4.3 below). Figure 4.4 presents the

Table 4.4. Percent Element Dissolved - Cr

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	30.41	54.95	36.24	35.45
0.5	27.47	52.99	33.69	40.70
1	28.00	50.05	29.75	40.55
2	31.78	52.12	31.08	39.29
4	31.20	38.93	29.41	38.06
10	32.03	104.57*	62.55*	100.10*
20	31.82	53.71	32.81	42.64
28	36.53	59.04	37.63	48.10
50	38.14	59.43	40.36	46.40
Adjusted to pH 5.0				
50.25	34.94			41.11
50.5	36.87			43.40
51	33.84			41.20
52	32.96			43.62
66	35.89			44.19
* believed to be analytical flier				

Table 4.5. Percent Element Dissolved - Mn

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	46.0	64.1	50.5	47.8
0.5	43.8	63.1	47.8	55.2
1	46.2	60.4	47.2	55.4
2	49.1	63.2	46.7	55.2
4	50	51	46	53
10	49.40	64.03	47.05	57.95
20	51.46	63.25	48.63	55.32
28	55.44	66.27	51.43	57.07
50	56.17	66.80	53.20	55.97
Adjusted to pH 5.0				
50.25	24.68			25.47
50.5	25.31			27.68
51	25.14			27.25
52	25.30			28.05
66	26.42			28.65

Table 4.6. Percent Element Dissolved - Ni

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	41.86	61.96	48.67	46.61
0.5	39.64	63.34	46.45	54.49
1	39.24	61.03	42.28	52.11
2	43.90	63.09	43.25	53.28
4	46.17	49.49	41.53	50.81
10	38.84	68.49	41.33	59.79
20	47.58	59.23	45.28	49.35
28	53.48	60.49	48.52	48.14
50	51.79	53.32	52.16	37.32
Adjusted to pH 5.0				
50.25	12.28			11.24
50.5	12.23			12.18
51	12.31			12.27
52	12.01			12.20
66	12.06			12.20

Table 4.7. Weight Percent of Total Iron in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	pH adj.
0.25	20.65	43.17	26.49	26.56
0.5	22.98	40.87	24.77	27.02
1	24.48	38.16	22.90	25.92
2	23.13	41.68	23.02	20.55
4	22.38	38.92	24.81	23.40
10	23.26	43.56	24.57	24.06
20	23.31	42.22	24.13	21.98
28	22.15	44.28	23.79	27.36
50	20.82	42.35	22.21	23.89
Adjust to pH 5.0				
50.25	12.38			9.75
50.5	11.03			12.05
51	10.07			11.35
52	11.51			12.10
66	12.35			10.99

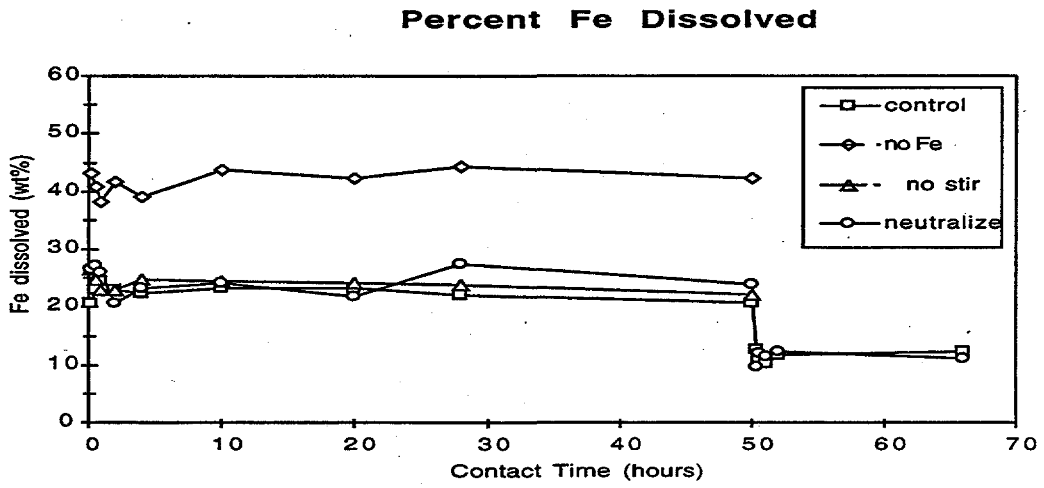

Figure 4.2. Weight Percent of Fe Dissolved in Each of the Four Test Systems as a Function of Contact Time

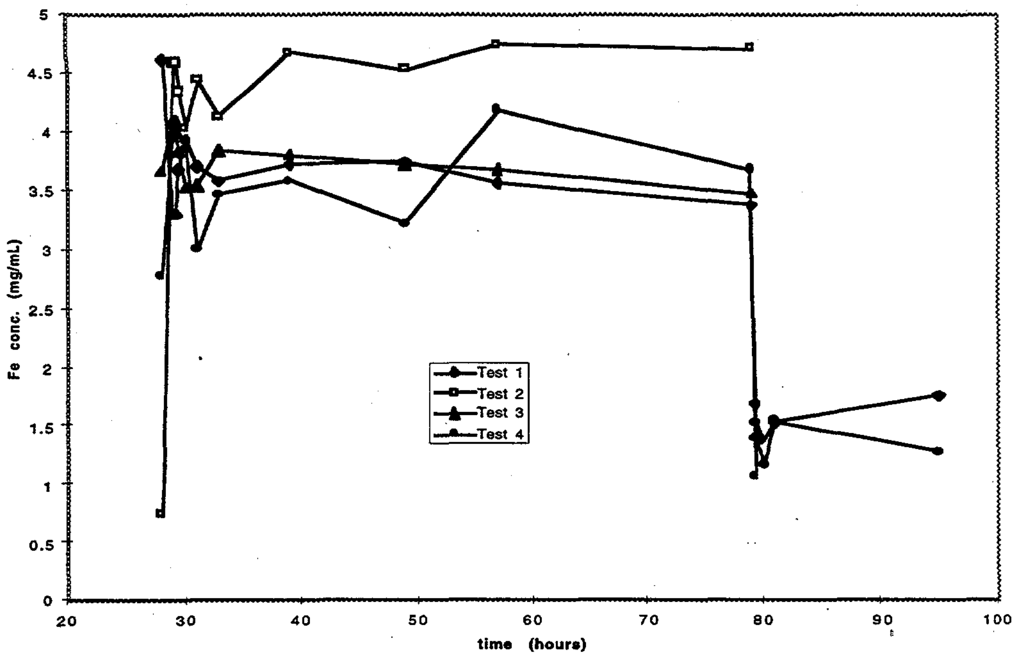

Figure 4.3. Measured Iron Concentration in the Supernate of Each Test as a Function of Time

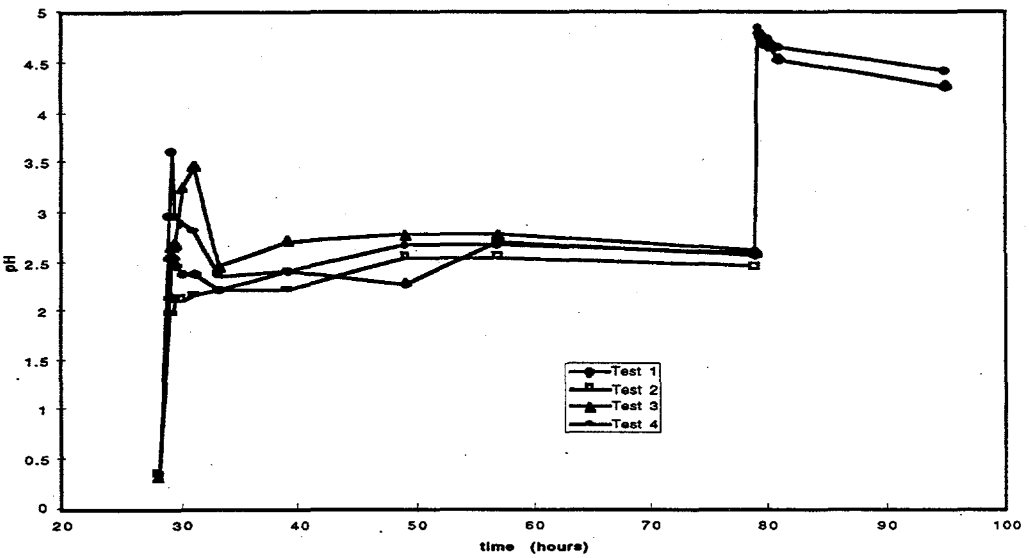

Figure 4.4. Test pH as a Function of Time Corresponding to Sample Times Analyzed for Iron and the Values Plotted in Figure 4.3

test pH for each test corresponding to each time the test was sampled and subsequently analyzed for iron, as reported in Figure 4.2. It appears that each test except Test 2 experienced some degree of pH maximum over the final equilibrium values when the sludge component was first added to the oxalic acid eluent solution. The pH peak lasted over an hour and was over a pH unit higher than the equilibrium range at its maximum extent. Because it was subsequently found that increased pH lowered the iron concentration in Tests 1 and 4 (see following section), it is possible that the lowered iron concentrations were related to the pH peaking; the mechanism is not clear, however, since the test pH values become equal again. The only difference known between Test 2 and the other three tests was that Test 2 did not contain additional iron (2 grams ferric oxide added in addition to 240 grams of sludge). It is possible that the 2 g ferric oxide could affect the iron concentration because it is a stable iron-containing phase that is already nucleated, allowing iron in solution to equilibrate at a lower concentration. Conversely, the higher supernate iron concentration alone was not enough to cause ferric oxide to nucleate under the conditions of Test 2. The mechanism causing the pH maximum is not understood but is suggested to be due to the presence of the red ferric oxide phase.

4.5 Supernate Concentrations of Sludge Components after System Neutralization

After adjusting the pH to 5.0, elements that form more insoluble hydroxides such as iron, nickel, manganese, calcium, and strontium show a significantly reduced concentration. Aluminum concentration has been reduced to a smaller but still detectable amount. It probably also precipitates as a hydroxide. Silicon concentration may also have been reduced in solution, precipitating along with the hydroxides (see silicon data in the appendices, which show a lot of scatter because of the difficulty in analyzing for silicon). An example of this change in concentration is shown in Figure 4.5 and in Table 4.8 (for strontium). Sodium, which can precipitate as sodium oxalate, also shows a step-like decrease in concentration. (See Appendix B data and plots of the elements in solution. The diminution in concentration of these elements appears to be complete by the time the first sample has been taken because the concentration (wt% dissolved) does not change significantly over a period of 16 hours. Again the concern of "supernate in contact with sludge solids re-equilibrating in the sample bottle waiting for analysis" potentially affecting the results needs to be considered here because the pH was observed to shift over the 16-hour period suggesting that the chemical environment was changing during that period (see Figure 4.1).

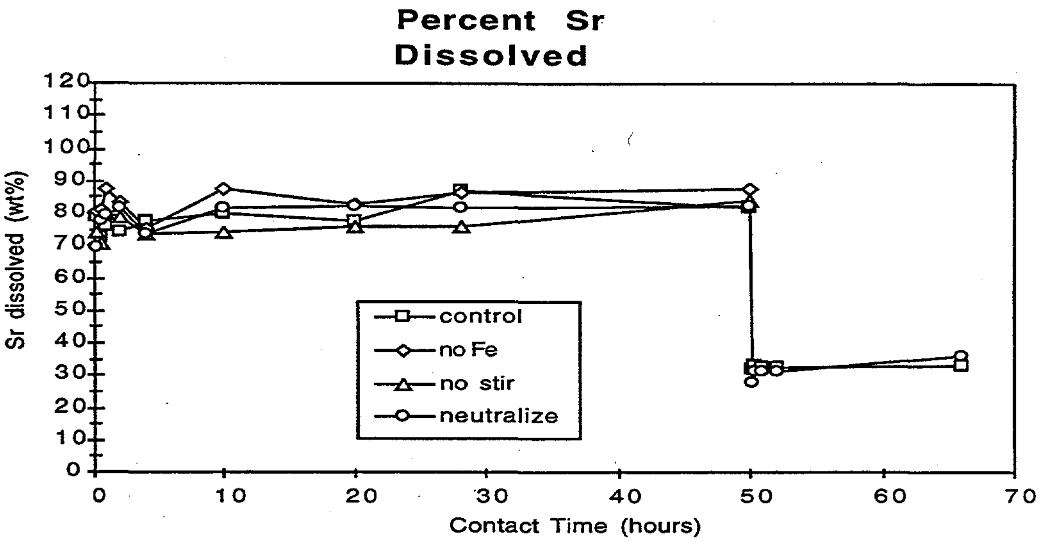

Figure 4.5. Percent Strontium Dissolved as a Function of Time

Table 4.8. Weight Percent of Strontium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	79.09	80.44	74.20	69.60
0.5	72.48	81.02	70.89	77.72
1	75.72	87.31	80.02	79.19
2	74.27	83.39	78.57	81.78
4	77.65	75.46	73.76	73.88
10	79.81	87.32	74.28	81.51
20	77.96	82.86	75.98	82.30
28	86.79	86.45	76.21	81.84
50	81.83	87.29	83.91	82.53
Adjusted to pH 5.0				
50.25	32.00			27.79
50.5	32.84			31.03
51	32.24			31.14
52	32.26			31.34
66	33.04			35.91

5.0 References

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Appendix A

Test Data Tables

Table A.1. Oxalate Concentrations in Test Samples and Weight Percent Suspended Solids

		Oxalate Concentration mg/g (supernate)				
		Wt% suspended solids in parentheses				
	test #	1	2	3	4	
sample /stage						
Cs elution-28hrs		48.3(0.27)	55.8(na)	48.9(na)	49.5(na)	
Sludge Dissolution						
0.25hrs		26.2(0.24)	25.2(0.27)	24.6(0.26)	27.6(0.33)	
0.5hrs		28.4(0.12)	31.2(0.19)	26.9(0.20)	27.3(0.23)	
1.0hr		27.6(5.80)	30.6(2.38)	29.3(1.79)	28.9(3.43)	
2.0hrs		28.6(4.26)	32.3(2.92)	28.1(0.18)	25.2(4.30)	
4.0hrs		25(3.71)	26.6(2.81)	28.1(0.12)	26.1(3.18)	
10.0hrs		23.7(2.21)	31.8(0.15)	28.8(0.10)	28.5(0.15)	
20.0hrs		27.9(3.39)	30.8(2.25)	27.7(0.08)	26.9(3.45)	
28.0hrs		26.6(4.30)	28.5(2.34)	29.6(0.08)	28(3.50)	
50.0hrs		30.1(4.53)	32.9(2.94)	30.2(0.12)	28.6(3.80)	
Adjusted to pH 5.0						
0.25hrs		25.6(5.18)	na	na	24.7(1.78)	
0.5hrs		24.6(6.12)	na	na	24.6(5.37)	
1.0hr		25.6(5.10)	na	na	24.3(3.08)	
2.0hrs		25.5(9.06)	na	na	22.5(5.35)	
16.0hrs		27.2(0.19)	na	na	24.8(0.09)	
LX-1 slurry						<0.01 (14.90)
LX-2 oxalic acid solution						59.4 (na)

Table A.2. Summary of Measured pH and Visual Observations

Test	pH(50°C)	Visual Observations
1a	0.358	Supernate -yellow/green, red Fe oxide, fine white zeolite solids
2a	0.360	Supernate -yellow/green , white zeolite solids
3a	0.319	Supernate -yellow/green, red Fe oxide, white zeolite solids
4a	0.341	Supernate -yellow/green, red Fe oxide, white zeolite solids
1b-0 min.	2.54	NR (none reported)
2b-0 min.	1.98	NR
3b-0 min.	2.16	NR
4b-0 min.	2.96	NR
1b-15 min.	2.54	NR
2b-15 min.	1.98	NR
3b-15 min.	2.66	NR
4b-15 min.	3.59	NR
1b-30 min.	2.47	NR
2b-30 min.	2.11	NR
3b-30 min.	2.68	NR
4b-30 min.	2.96	NR
1b-1hr.	2.38	NR
2b-1hr.	2.12	Some supernate
3b-1hr.	3.25	Some supernate
4b-1hr.	2.88	NR
1b-2hr.	2.38	NR
2b-2hr.	2.17	NR
3b-2hr.	3.46	Turgid yellow
4b-2hr.	2.81	NR
1b-4hr.	2.22	NR
2b-4hr.	2.22	NR
3b-4hr.	2.46	NR
4b-4hr.	2.36	NR
1b-10hr.	2.41	Some supernate with ten minute settling time

Table A.2. (contd)

Test	pH(50°C)	Visual Observations
2b-10hr.	2.21	Some supernate with ten minute settling time
3b-10hr.	2.71	Some supernate with ten minute settling time
4b-10hr.	2.41	Some supernate with ten minute settling time
1b-20hr.	2.28	NR
2b-20hr.	na	none - pH probe problem
3b-20hr.	na	none - pH probe problem
4b-20hr.	na	none - pH probe problem
1b-28hr.	2.71	NR
2b-28hr.	2.55	NR
3b-28hr.	2.77	NR
4b-28hr.	2.67	NR
1b-50hr.	2.57	NR
2b-50hr.	2.45	Some yellowish precipitate thought to be Fe oxalate
3b-50hr.	2.62	NR
4b-50hr	2.60	NR
1b-50+0.25hr.	4.79	NR
4b-50+0.25hr	4.84	NR
1b-50+0.5hr.	4.69	NR
4b-50+0.5hr	4.80	NR
1b-50+1.0hr.	4.68	NR
4b-50+1.0hr	4.73	NR
1b-50+2.0hr.	4.53	NR
4b-50+2.0hr	4.66	NR
1b-50+16.0hr.	4.26	Supernate light red brown with 20 minutes settling time.
4b-50+16.0hr.	4.42	As above and towards brownish yellow

Table A.3. Test 1 ICP-MS Data in μg (element) per g Solution

Element sample	Na	Mg	Al	Si	K	Ca	Ti	Cr	Mn	Fe	Ni	Sr	Zr	Cs
1a-28	1290	125	2000	<200	<200	<200	13.8	<4	9.68	4610	<4	9.6	5.6	59.8
1b-025	3610	143	2180	537	594	2830	<4	38.6	376	3300	203	2580	5	6.1
1b-05	3280	104	2140	<200	776	2640	<4	34.8	358	3680	192	2360	<4	<4
1b-1	3580	104	2060	531	619	3240	<4	35.5	378	3930	190	2470	4.1	<4
1b-2	3660	134	2650	451	564	3150	<4	40.6	404	3700	214	2420	<4	<4
1b-4	3740	181	2300	497	602	2960	<4	39.8	416	3570	226	2540	<4	4.4
1b-10	3580	114	2080	<200	824	3110	<4	41	406	3730	186	2620	4	4
1b-20	3560	112	2150	520	728	2920	<4	40.7	426	3740	236	2550	<4	<4
1b-28	3835	181	2280	342	653	3180	4.6	48.2	468	3560	270	2920	<4	4.5
1b-50	3890	158	2860	277	621	3620	<4	52.5	474	3380	261	2700	4.2	4.3
1b-N1	7170	102	1900	<200	592	411	<4	48.1	132	1690	8.3	547	<4	<4
1b-N2	7620	153	2070	<200	580	684	<4	51.4	139	1400	8	584	<4	4.7
1b-N4	7320	161	1925	<200	734	690	<4	45.9	137	1180	8.5	556	<4	4
1b-NX	7210	163	1920	<200	633	590	<4	44.2	139	1530	6.3	557	<4	<4
1b-NY	7800	111	2100	<200	698	561	<4	50.3	154	1750	6.7	599	<4	6.8

Table A.4. Test 2 ICP-MS Data in μg (element) per g solution

Element sample	Na	Mg	Al	Si	K	Ca	Ti	Cr	Mn	Fe	Ni	Sr	Zr	Cs
2a-28	1540	176	2095	<200	<200	381	18	<4	9.3	754	<4	10.5	7.5	72.2
2b-025	3880	130	2510	833	660	3610	<4	71.5	537	4590	308	2690	6	7.5
2b-05	3650	179	2250	660	722	2910	<4	68.9	529	4340	315	2710	<4	6.3
2b-1	3830	166	2420	820	590	3240	<4	64.9	505	4040	303	2930	>4	9.5
2b-2	3810	127	2510	740	733	3180	<4	67.8	530	4440	314	2790	5	6.9
2b-4	3700	123	2120	360	720	3380	<4	49	420	4120	240	2500	<4	7.1
2b-10	3790	203	2470	680	780	3340	<4	72	542	4680	347	2950	5	9.5
2b-20	3800	145	2570	470	670	3010	<4	74.3	535	4520	294	2780	4.9	6.1
2b-28	3820	150	2660	660	817	3220	<4	78.2	560	4740	300	2900	4.6	7.4
2b-50	4040	149	2650	381	727	3310	<4	82.7	573	4710	258	2970	5	6.9

Table A.5. Test 3 ICP-MS Data in μg (element) per g solution

Element sample	Na	Mg	Al	Si	K	Ca	Ti	Cr	Mn	Fe	Ni	Sr	Zr	Cs
3a-28	1250	103	1770	<200	<200	<200	<4	<4	7.1	3660	<4	9	6.2	61.3
3b-025	3530	118	2230	<200	839	2740	<4	46	412	4090	236	2420	<4	4
3b-05	3420	107	2020	<200	698	2590	<4	42.7	390	3820	225	2310	4.9	4
3b-1	3780	105	2250	830	849	3040	<4	37.5	385	3520	204	2620	5.3	6
3b-2	3820	120	2270	822	642	3460	<4	39.3	380	3540	209	2570	6	6.9
3b-4	3410	111	2140	<200	838	2740	<4	37	370	3840	200	2400	<4	7.5
3b-10	3500	123	2040	630	767	2860	<4	41.8	384	3800	199	2420	5	7.6
3b-20	3500	116	2220	391	853	2791	<4	43.6	399	3725	221	2485	<4	7.2
3b-28	3650	122	2170	<200	768	2710	<4	48.9	426	3680	239	2500	5	6
3b-50	3670	162	2160	527	1010	2960	<4	54.4	444	3470	261	2800	13	7.5

Table A-6. Test 4 ICP-MS Data in μg (element) per g solution

Element sample	Na	Mg	Al	Si	K	Ca	Ti	Cr	Mn	Fe	Ni	Sr	Zr	Cs
4a-28	1230	107	1760	<200	<200	<200	5	<4	7.26	2770	<4	8.3	6.3	59.8
4b-025	3240	110	2020	648	681	3020	<4	45	390	3950	226	2270	4.5	4.1
4b-05	3820	123	2320	<200	866	2900	<4	51.8	452	4020	265	2540	4.2	5
4b-1	3700	114	2280	850	787	2950	<4	51.6	454	3850	253	2590	<4	4.3
4b-2	3730	172	2240	527	536	3050	<4	49.9	452	3000	259	2680	<4	5
4b-4	3300	116	2120	<200	800	2680	<4	48.2	428	3460	246	2400	<4	<4
4b-10	3750	189	4160	569	661	3420	<4	78.9	478	3570	295	2680	5	6
4b-20	3670	180	2200	428	585	3140	<4	55.6	453	3210	236	2710	<4	4.7
4b-28	3840	129	2340	565	773	3580	<4	63	472	4170	232	2700	4.3	5.8
4b-50	3870	143	2460	<200	890	3070	<4	61.7	459	3680	163	2720	<4	5
4b-N1	6660	153	1010	<200	486	643	<4	54.1	149	1060	4.5	489	<4	<4
4b-N2	7050	107	1950	<200	636	390	<4	58	157	1520	4.9	535	<4	4
4b-N4	6900	114	2040	<200	784	462	<4	54	152	1370	5.5	540	<4	4.2
4b-NX	7420	134	2060	<200	694	491	<4	58.7	162	1540	5	550	<4	4.4
4b-NY	7250	168	2000	<200	716		<4	59.9	170	1270	5	795	<4	6.3

Appendix B

Tables and Plots of the Percent Dissolved for Each Sludge Element for Each Test as a Function of Time

Table B.1. Percent Aluminum in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	75.63	84.57	81.27	73.78
0.5	74.27	74.27	73.77	84.52
1	71.60	81.48	81.83	83.12
2	90.85	84.30	82.51	81.74
4	79.68	72.29	78.13	77.71
10	72.89	82.68	74.81	143.95@
20	74.93	85.52	80.52	82.53
28	78.18	88.83	78.84	84.46
50	94.34	87.54	78.50	90.25
	Adjusted to pH 5.0			
50.25	70.02			47.56
50.5	74.39			75.45
51	70.88			77.74
52	70.77			78.22
66	74.56			76.89

@ Believed to be an analytical flier.

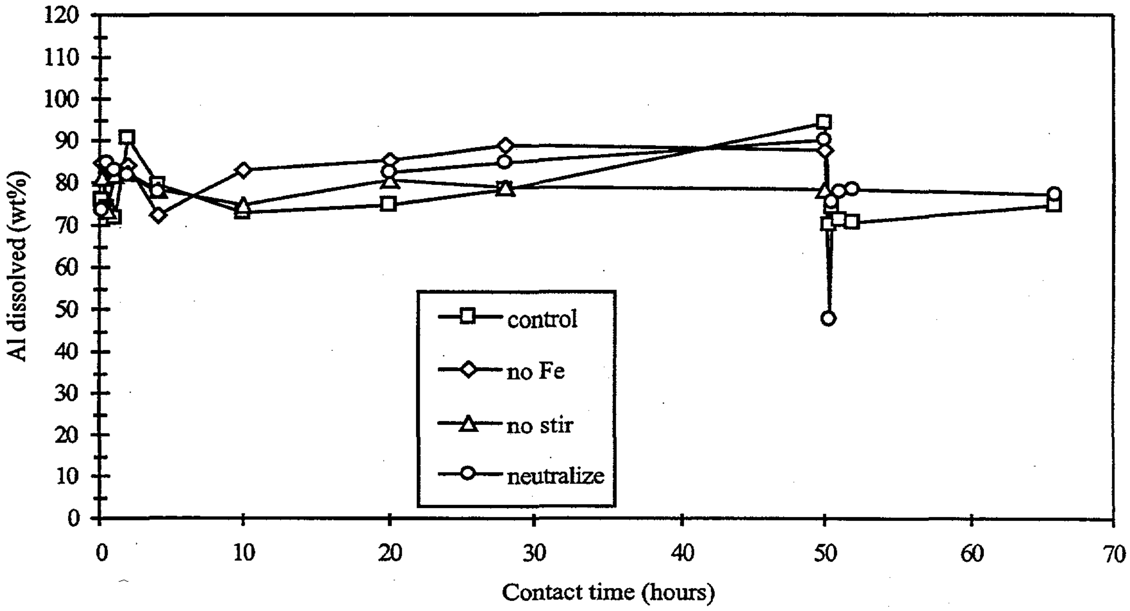

Figure B.1. Percent of Total System Aluminum in Solution

Table B.2. Percent Calcium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	96.30	114.72	93.24	102.77
0.5	89.96	92.95	88.24	98.77
1	109.57	102.98	102.96	100.40
2	106.69	101.19	116.41	103.60
4	100.74	106.98	93.80	92.00
10	105.25	105.80	97.44	114.39
20	99.72	96.66	95.29	106.21
28	106.09	102.89	92.57	118.42
50	118.60	104.23	99.88	104.74
	Adjusted to pH 5.0			
50.25	35.96			38.60
50.5	42.86			34.95
51	43.00			36.66
52	40.77			37.31
66	40.15			44.71

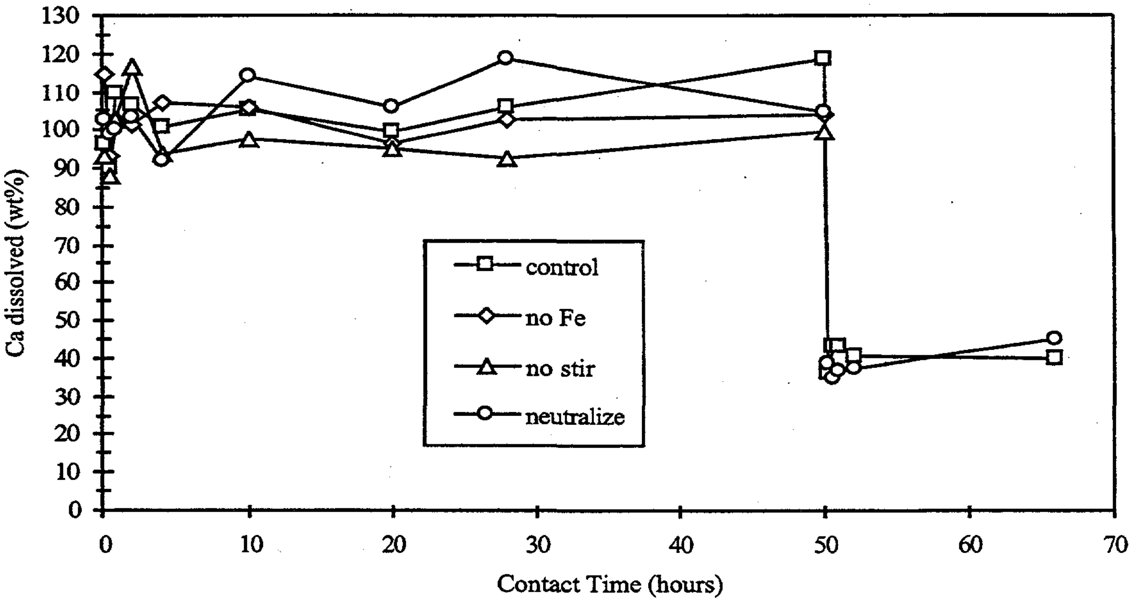

Figure B.2. Percent of Total System Calcium in Solution

Table B.3. Percent Chromium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	30.41	54.95	36.24	35.45
0.5	27.47	52.99	33.69	40.70
1	28.00	50.05	29.75	40.55
2	31.78	52.12	31.08	39.29
4	31.20	38.93	29.41	38.06
10	32.03	104.57	62.55	100.10
20	31.82	53.71	32.81	42.64
28	36.53	59.04	37.63	48.10
50	38.14	59.43	40.36	46.40
Adjusted to pH 5.0				
50.25	34.94			41.11
50.5	36.87			43.40
51	33.84			41.20
52	32.96			43.62

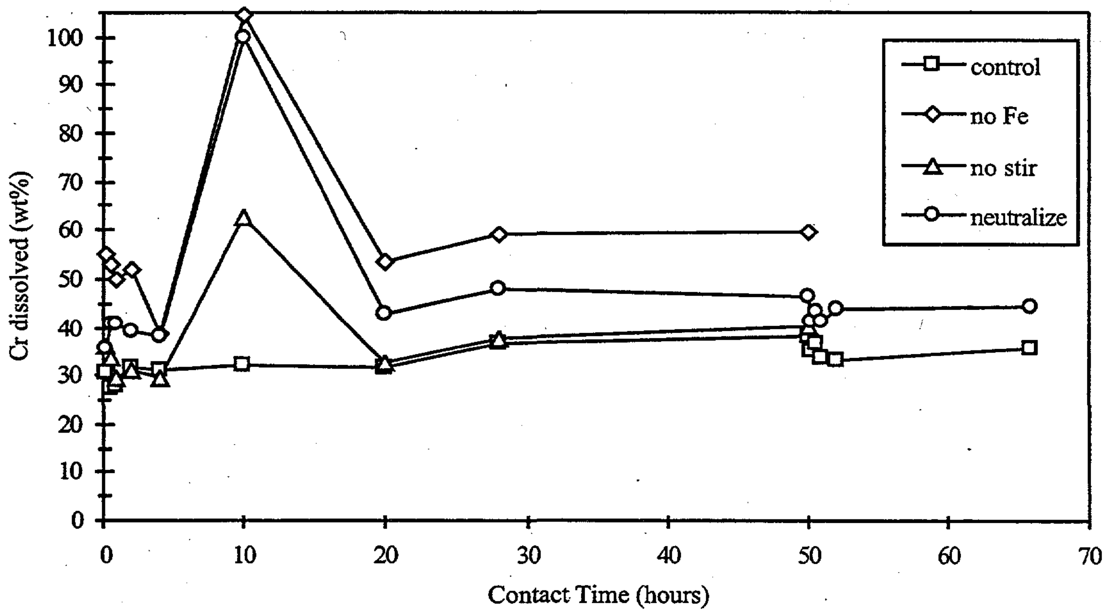

Figure B.3. Percent of Total System Chromium in Solution

Table B.4. Percent Cesium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	16.87	17.48	10.88	11.34
0.5	11.18	14.74	10.88	13.78
1	11.18	21.88	16.12	11.92
2	11.18	16.22	18.42	13.74
4	12.20	16.64	19.92	11.19
10	11.21	21.57	20.16	16.11
20	11.21	14.72	19.19	13.03
28	12.28	17.26	16.25	15.48
50	11.89	16.26	19.77	13.77
	Adjusted to pH 5.0			
50.25	11.42			11.43
50.5	12.86			11.80
51	11.50			12.19
52	11.50			12.55
66	16.25			15.74

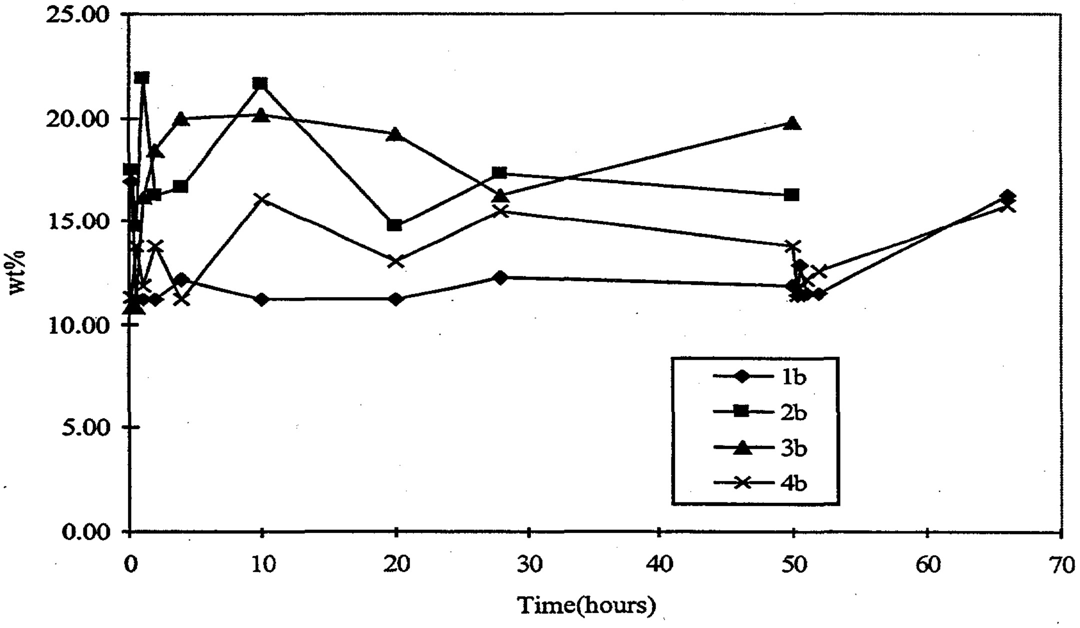

Figure B.4. Percent of Total System in Cesium in Solution

Table B.5. Percent Iron in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	20.65	43.17	26.49	26.56
0.5	22.98	40.87	24.77	27.02
1	24.48	38.16	22.90	25.92
2	23.13	41.68	23.02	20.55
4	22.38	38.92	24.81	23.40
10	23.26	43.56	24.57	24.06
20	23.31	42.22	24.13	21.98
28	22.15	44.28	23.79	27.36
50	20.82	42.35	22.21	23.89
Adjusted to pH 5.0				
50.25	12.38			9.75
50.5	11.03			12.05
51	10.07			11.35
52	11.51			12.10

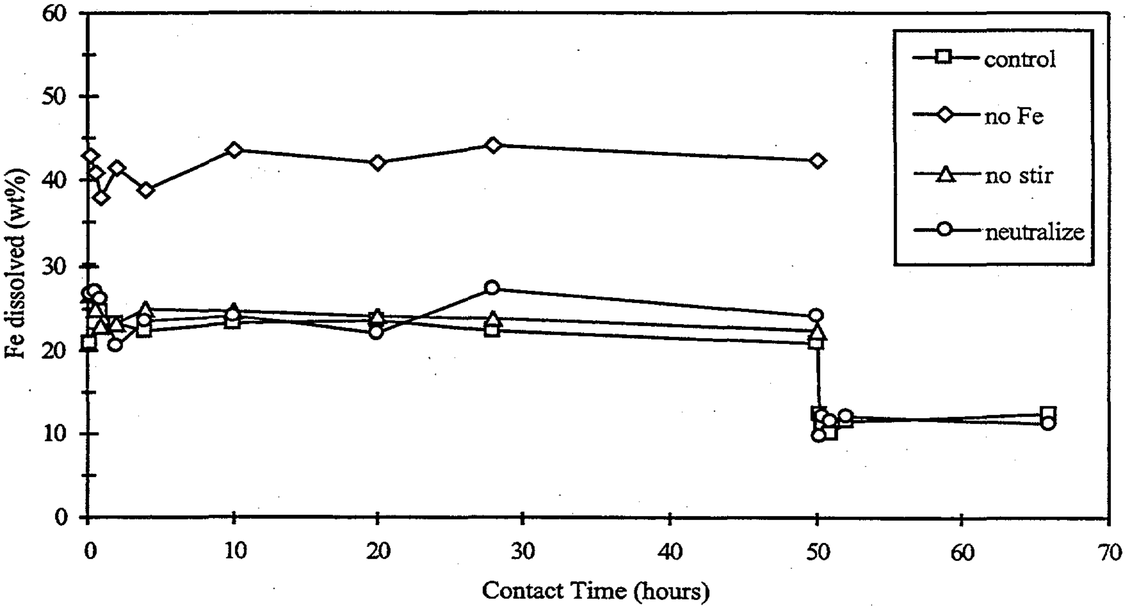

Figure B.5. Percent of Total System Iron in Solution

Table B.6. Percent Magnesium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	95.20	71.56	86.16	78.93
0.5	69.74	97.96	78.28	88.07
1	69.74	91.10	76.88	81.87
2	88.52	71.03	87.19	120.96
4	117.28	69.00	81.11	83.96
10	77.67	107.89	88.98	130.52
20	76.51	80.24	84.43	124.98
28	114.65	82.56	87.92	93.17
50	101.86	81.88	112.40	102.77
Adjusted to pH 5.0				
50.25	74.54			107.17
50.5	99.76			85.33
51	103.47			88.84
52	104.34			98.23
66	83.07			113.05

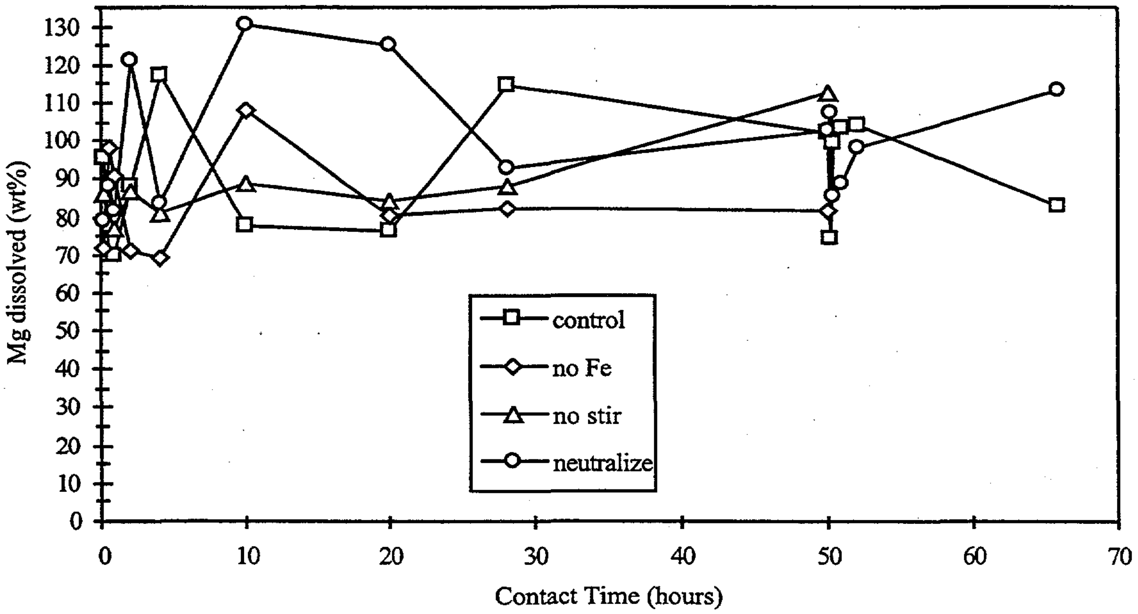

Figure B.6. Percent of Total System Magnesium in Solution

Table B.7. Percent Manganese in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	45.97	64.08	50.47	47.76
0.50	43.81	63.14	47.82	55.21
1.00	46.16	60.40	47.23	55.44
2.00	49.15	63.18	46.65	55.21
4.00	50.49	51.19	45.52	52.50
10.00	49.40	64.03	47.05	57.95
20.00	51.46	63.25	48.63	55.32
28.00	55.44	66.27	51.43	57.07
50.00	56.17	66.80	53.20	55.97
	Adjusted to pH 5.0			
50.25	24.68			25.47
50.50	25.31			27.68
51.00	25.14			27.25
52.00	25.30			28.05
66.00	26.42			28.65

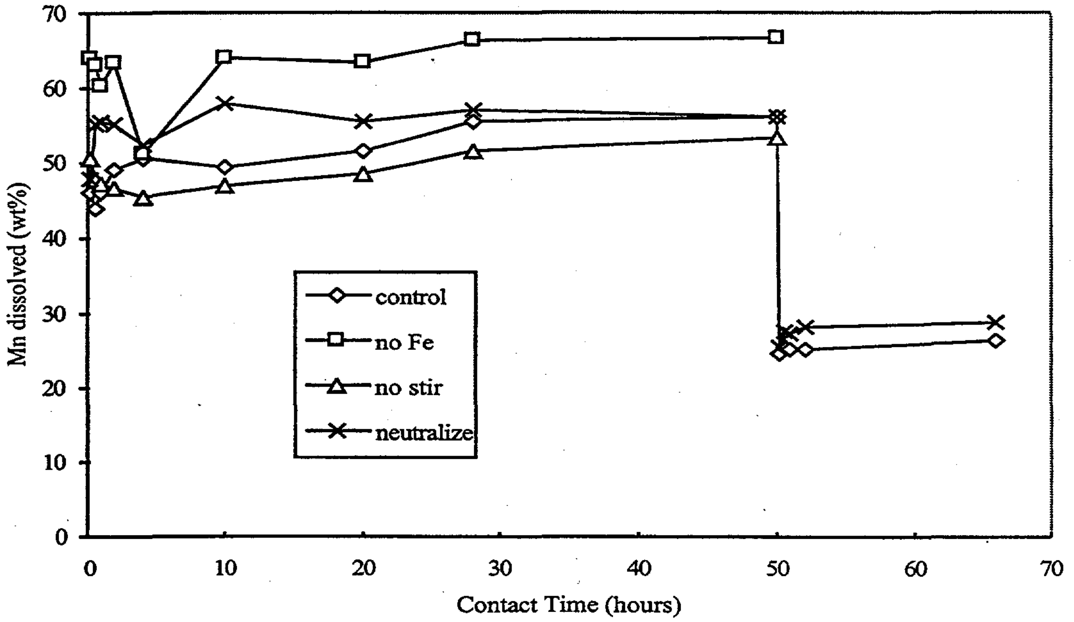

Figure B.7. Percent of Total System Manganese in Solution

Table B.8. Percent Nickel in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	41.86	61.96	48.67	46.61
0.5	39.64	63.34	46.45	54.49
1	39.24	61.03	42.28	52.11
2	43.90	63.09	43.25	53.28
4	46.17	49.49	41.53	50.81
10	38.84	68.49	41.33	59.79
20	47.58	59.23	45.28	49.35
28	53.48	60.49	48.52	48.14
50	51.79	53.32	52.16	37.32
	Adjusted to pH 5.0			
50.5	12.23			12.18
50.5	12.23			12.18
51	12.31			12.27
52	12.01			12.20
66	12.06			12.20

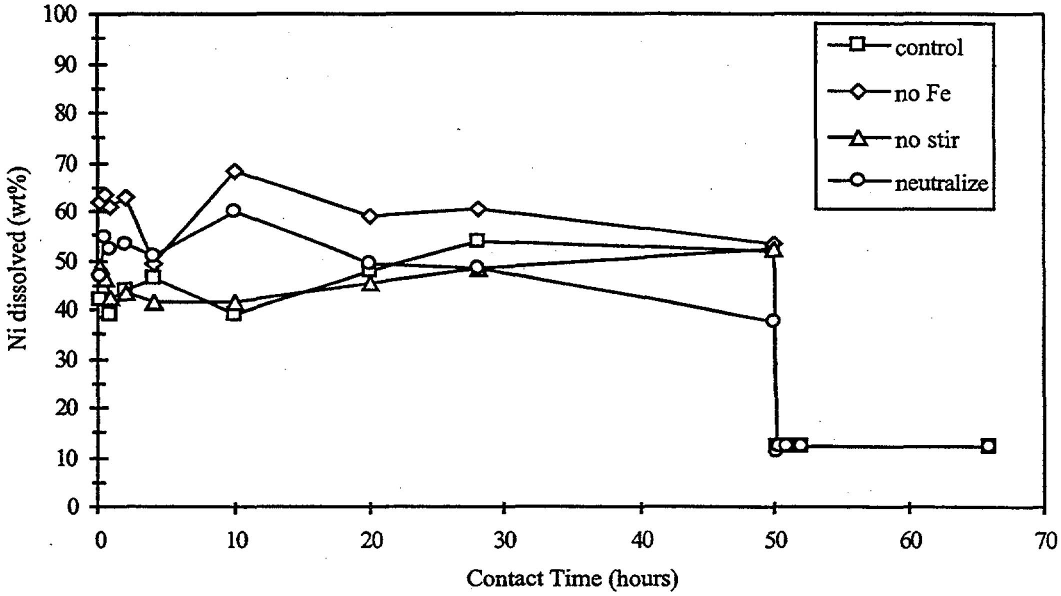

Figure B.8. Percent of Total System Nickel in Solution

Table B.9. Percent Potassium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	53.80	58.54	75.99	61.68
0.5	69.96	63.92	63.47	78.10
1	56.30	52.71	76.62	71.23
2	51.61	64.56	58.95	49.87
4	54.77	63.50	75.32	71.89
10	72.61	68.17	69.49	60.70
20	65.20	59.69	76.28	54.79
28	58.55	71.13	69.48	68.99
50	57.32	63.95	87.85	77.31
Adjusted to pH 5.0				
50.25	56.09			47.60
50.5	55.29			59.82
51	65.02			69.17
52	59.01			63.84
66	62.60			65.05

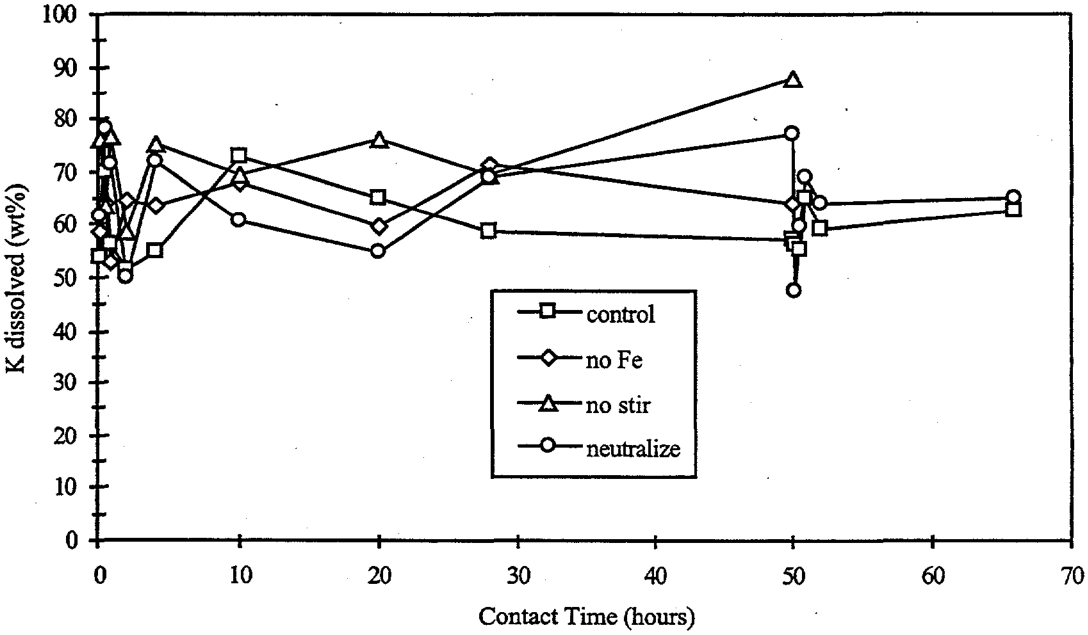

Figure B.9. Percent of Total System Potassium in Solution

Table B.10. Percent Silicon in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	85.90	130.88	31.99	103.66
0.5	33.06	104.28	31.99	33.43
1	83.92	128.34	128.89	133.29
2	71.88	116.58	127.67	84.75
4	78.64	62.06	35.90	36.58
10	36.45	106.46	97.88	89.06
20	79.92	77.89	64.25	69.71
28	57.06	103.40	36.38	87.55
50	48.45	67.35	81.67	41.24
Adjusted to pH 5.0				
50.25	39.56			40.85
50.5	39.56			41.69
51	39.56			41.69
52	39.56		41.69	
66	39.55			41.69

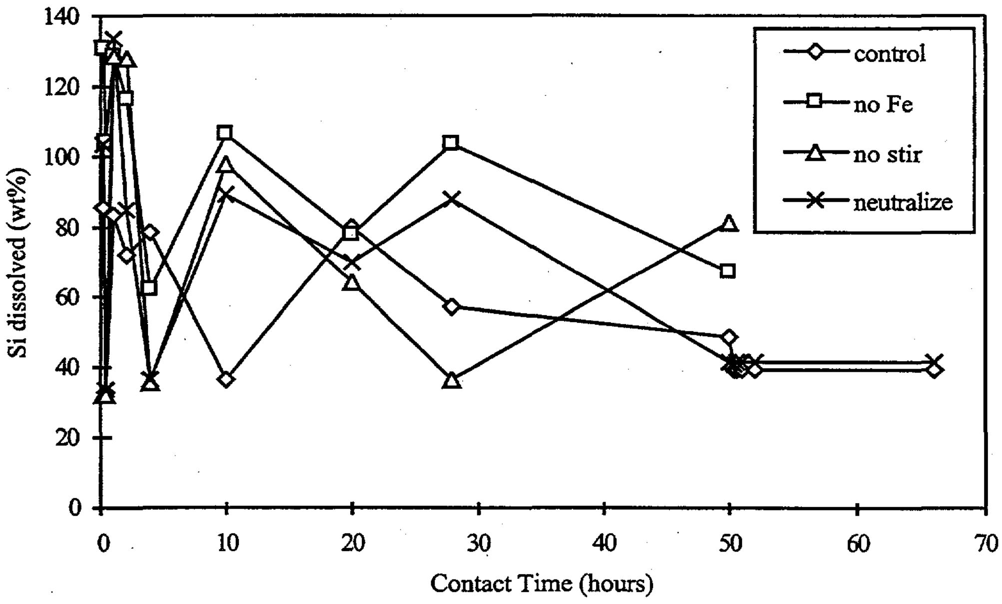

Figure B.10. Percent of Total System Silicon in Solution. The scatter of data points is believed to be due to the difficulty in analyzing for silicon by ICP-MS.

Table B.11. Percent Sodium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	152.58	152.38	150.74	139.07
0.5	138.91	143.54	146.13	163.46
1	151.08	150.30	160.90	158.52
2	154.26	149.55	162.50	159.73
4	157.36	145.58	146.34	142.73
10	151.32	148.63	149.74	159.90
20	150.56	148.85	149.64	156.96
28	159.04	150.64	154.84	162.66
50	161.71	156.03	155.54	164.01
	Adjusted to pH 5.0			
50.25	132.70			124.32
50.5	139.61			132.48
51	135.28			130.30
52	133.78			137.39
66	141.19			135.23

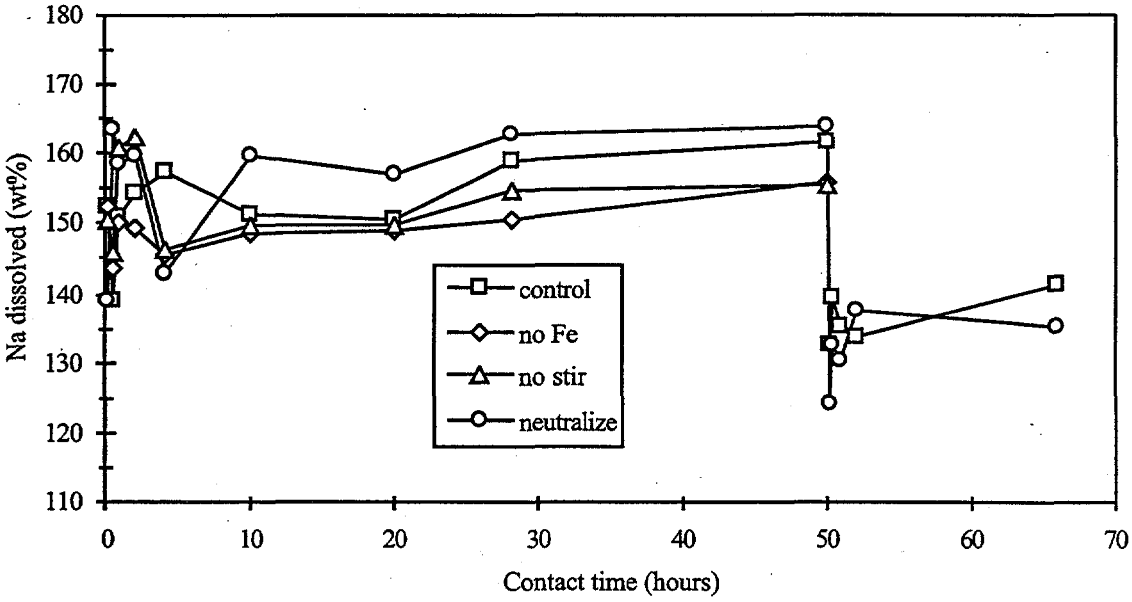

Figure B.11. Percent of Total System Sodium in Solution

Table B.12. Percent Strontium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	79.09	80.44	74.20	69.60
0.5	72.48	81.02	70.89	77.72
1	75.72	87.31	80.02	79.19
2	74.27	83.39	78.57	81.78
4	77.65	75.46	73.76	73.88
10	79.81	87.32	74.28	81.51
20	77.96	82.86	75.98	82.30
28	86.79	86.45	76.21	81.84
50	81.83	87.29	83.91	82.53
Adjusted to pH 5.0				
50.25	32.00			27.79
50.5	32.84			31.03
51	32.24			31.14
52	32.26			31.34
66	33.04			35.91

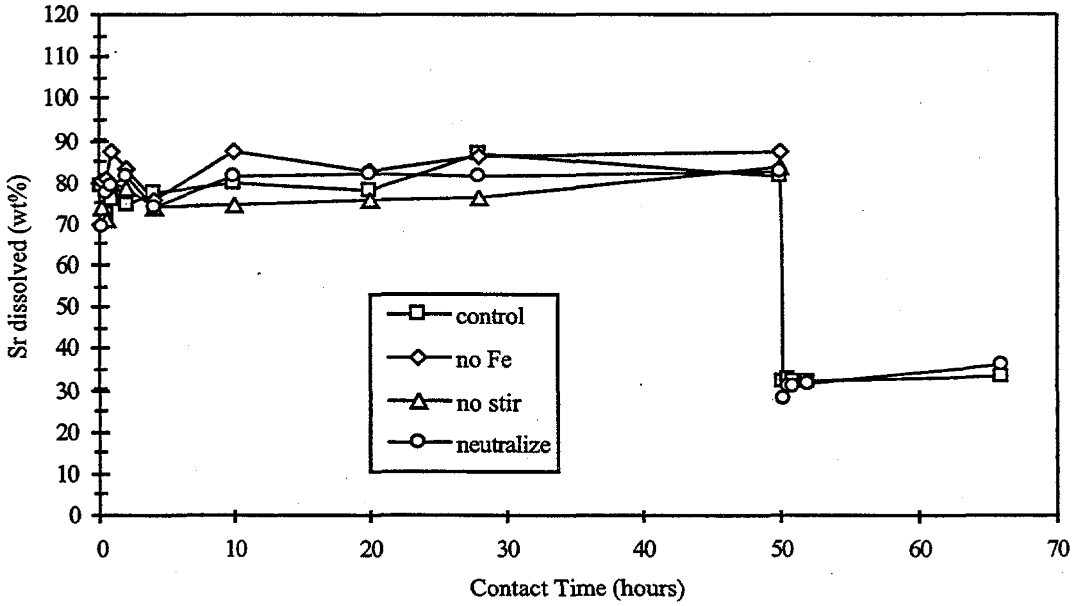

Figure B.12. Percent of Total System Strontium in Solution

Table B.13. Percent Titanium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	13.80	14.85	19.47	18.92
0.5	13.80	14.85	19.47	18.92
1	13.80	14.85	19.47	18.92
2	13.80	14.85	19.47	18.92
4	13.80	14.85	19.47	18.92
10	13.80	14.84	19.46	18.92
20	13.79	14.83	19.45	18.92
28	15.42	14.94	19.39	18.86
50	13.84	14.79	19.41	18.92
Adjusted to pH 5.0				
50.25	14.04			18.69
50.5	14.04			19.19
51	14.04			19.19
52	14.04			19.19
66	14.03			19.19

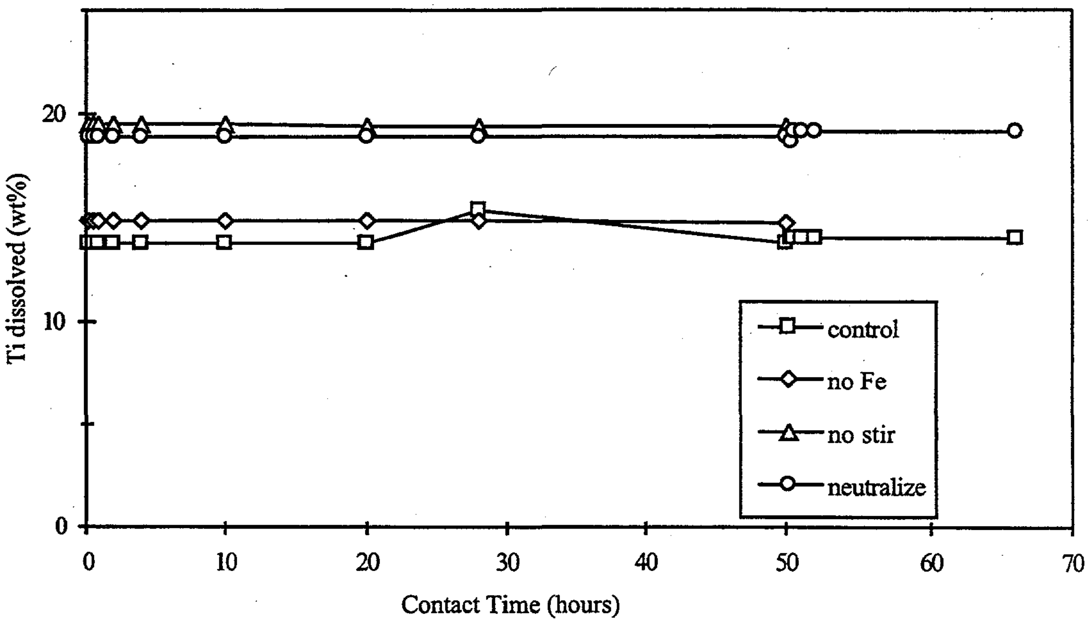

Figure B.13. Percent of Total System Titanium in Solution

Table B.14. Percent Zirconium in Solution

time (hours)	1b	2b	3b	4b
	control	no Fe	no stir	neutral.
0.25	52.72	55.90	40.63	45.43
0.5	42.38	37.66	49.59	42.46
1	43.39	37.66	53.49	40.52
2	42.40	46.37	60.18	40.52
4	42.40	37.86	41.44	40.52
10	42.39	46.07	50.58	49.49
20	42.38	45.23	41.63	40.83
28	42.01	43.15	50.20	43.00
50	43.99	45.78		40.92
Adjusted to pH 5.0				
50.25	42.99			40.43
50.5	42.99			41.50
51	42.99			41.50
52	42.99			41.50
66	42.97			41.50

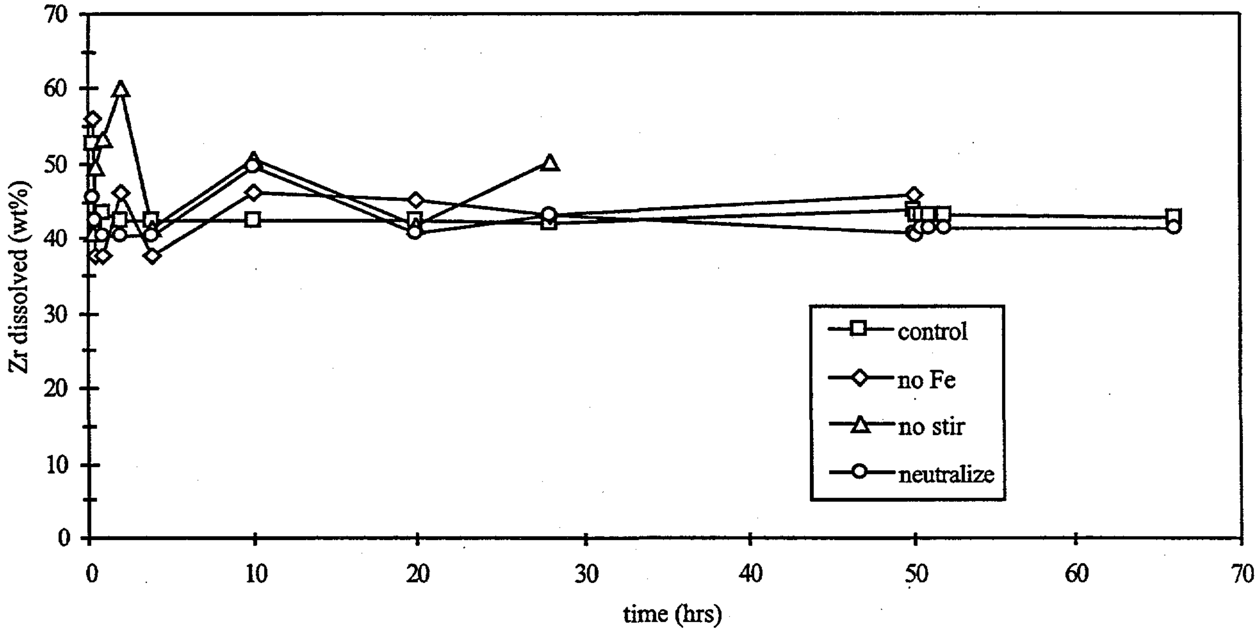

Figure B.14. Percent of Total System Zirconium in Solution

Table B.15. Comparison of Washed and Unwashed Sludge Simulants

	Slurry Simulant - ICP-AES - Unwashed				Slurry Simulant - ICP-MS - Washed			
element	µg/g-slurry							
Al		4135				4255		
Ca		1230				7225		
Cr		280				321		
Cs		na				<2		
Fe		23615				25200		
K		4480				2495		
Mg		210				190		
Mn		1755				2060		
Na		11410				4030		
Ni		1120				1230		
Si		9630*				1280*		
Sr		6530				8260		
Ti		50				46		
Zr		570				16		

*The unwashed slurry simulant was prepared for analysis by fusion, which digests most or all of the silica, whereas the washed slurry was acid digested, which does not dissolve most of the silica explaining the difference in the analytical values.

Graph based on analysis of washed simulant - 8/2/96
Analytical chemist noted that white ppt failed to go into solution

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