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Use of the TRUEX Process for the Pretreatment of Neutralized Cladding Removal Waste (NCRW) Sludge - Results of FY 1990 Studies

J. L. Swanson

September 1991

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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USE OF THE TRUEX PROCESS FOR THE PRETREATMENT OF
NEUTRALIZED CLADDING REMOVAL WASTE (NCRW) SLUDGE -
RESULTS OF FY 1990 STUDIES

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September 1991

Prepared for
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Pacific Northwest Laboratory
Richland, Washington 99352

MASTER

SUMMARY

Pacific Northwest Laboratory (PNL)^(a) is conducting a study for Westinghouse Hanford Company to develop suitable methods for the pretreatment of the neutralized cladding removal waste (NCRW) sludge that is currently stored at the U.S. Department of Energy's (DOE's) Hanford Site. The goal of the pretreatment process is to separate the transuranic elements from the bulk components so that the bulk components can be disposed of as low-level waste with only a small transuranic-containing fraction requiring geologic disposal. The portion of this study that was done in FY 1990 is summarized and discussed in this report.

The pretreatment process examined here is the one indicated to be most promising in the initial studies. It involves dissolving the unwashed sludge in nitric acid and then using the TRUEX solvent extraction process to remove the transuranic elements from the bulk components of the waste. Results obtained in FY 1990 indicated good progress in some areas, but also emphasized the need for additional study in some areas.

The areas identified in this work that need additional information are 1) gradual precipitate formation as dissolved sludge solutions age, and 2) formation of solid material (termed "interfacial crud") when the dissolved sludge solution is contacted with the solvent used in the TRUEX process. A third factor, corrosion of the piping and construction materials, was identified in a parallel study (Barker, Schwenk, and Divine 1990) as important in the use of the proposed process in an existing facility. Subsequent work is planned to address these three problem areas of the proposed process for NCRW sludge.

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1.0 INTRODUCTION

One of the unique types of radioactive waste currently being stored at Hanford is neutralized cladding removal waste (NCRW) sludge. This sludge contains large amounts of zirconium and sodium compounds, primarily hydroxides and fluorides, with smaller amounts of potassium, nitrite, and other materials. NCRW sludge also contains uranium, the transuranics (TRUs) plutonium and americium, and a mixture of fission products typical of the nonvolatiles present in irradiated reactor fuel.

This waste arose as a result of the method used to process the zirconium alloy-clad, metallic uranium fuel elements that were irradiated in N Reactor at Hanford. That method involved dissolution of the cladding in ammonium fluoride solution followed by a separate dissolution of the uranium in nitric acid. Because the ammonium fluoride solution also attacked the uranium, a portion (generally ~3%) of the uranium (and its contained TRUs and fission products) dissolved in the decladding step along with the zirconium alloy. Most of the reacted uranium and TRUs were recovered as fluoride precipitates, which were metathesized (with potassium hydroxide solution) to hydroxide precipitates before the acid dissolution step. The metathesis was done to lower the amount of fluoride in the dissolved uranium solution.

The spent decladding and metathesis solutions (plus the subsequent rinse solutions) were then adjusted for storage in underground, carbon steel-lined tanks. To protect these tanks against corrosion, this adjustment involved raising the pH with sodium hydroxide solution and adding nitrite ion (as the sodium salt). These additions led to the precipitation of zirconium hydroxide and sodium fluoride, which then formed a sludge layer in the underground tank. Supernate solution was periodically removed from above the settled sludge and then transferred to other tanks to make room for additional sludge. The NCRW sludge in its current form thus contains only portions of the soluble or partially soluble components that were added (e.g., sodium, fluoride, hydroxide, nitrite) along with all of the insoluble components (e.g., zirconium, plus a small fraction of the uranium and TRUs that were not recovered in the decladding and metathesis operations).

The concentration of TRU elements in this sludge gives an alpha activity of $\sim 10^3$ nCi/g sludge, which is too high to allow this waste to be disposed of as low-level waste (LLW). Disposal of this waste in a geologic repository would be more costly than disposal as LLW. Thus, an incentive exists to treat this waste to separate the TRUs from the bulk components so that the bulk components can be disposed of as LLW with only a small volume of TRU-containing waste requiring geologic disposal (e.g., in a vitrified form).

To study the feasibility of various methods to accomplish such a separation of the TRUs from the bulk components of NCRW sludge, Westinghouse Hanford Company has provided support to Pacific Northwest Laboratory (PNL) for an experimental program to determine the effectiveness of various methods. The early portion of this study (Swanson 1991) first examined approaches such as differences in settling rates and selective leaching of the TRUs away from the bulk solids; these approaches did not give the needed separations. The early study then centered on an approach involving nitric acid dissolution of the sludge followed by the use of the TRUEX (TRansUranium Extraction) solvent extraction process for separation of the TRUs from the inert components of the sludge; this approach has given very promising results and continues to be under development. This current report describes and discusses the results of such work obtained in FY 1990.

2.0 METHODS AND MATERIALS

The following descriptions of methods and materials used in the work presented in this report were previously described by Swanson (1991).

- The NCRW sludge samples were portions of those taken from Tanks 103-AW and 105-AW in 1986 and 1989; most experiments used composites containing portions of each sludge segment from one of these tanks.
- Sludge dissolutions were performed by adding water and nitric acid and stirring at room temperature.
- Dissolved sludge solutions were clarified by passage through a 0.2- μ m filter.
- The composition of TRUEX solvent was 0.2 M CMPO + 1.4 M TBP in normal paraffin hydrocarbon (NPH) diluent; CMPO is the acronym for octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide; TBP is the acronym for tributyl phosphate. The solvent had initially been washed with dilute sodium carbonate and nitric acid solutions, and was rewashed with dilute carbonate periodically during the course of this work.
- Solutions of HEDPA (1-hydroxyethane-1,1-diphosphonic acid) were used to strip extracted species from the TRUEX solvent.
- Solvent extraction contacts were performed by vigorous manual shaking for ~0.5 min. This was followed by centrifugation to effect phase clarification.
- Bulk metal ion concentrations were determined by inductively coupled plasma (ICP) analysis, fluoride concentrations were determined using a specific ion electrode, and acid concentrations were determined by titration to pH = 7 with standard base. The acid concentration determinations included corrections for the amount of base required to hydrolyze metal ions; corrections were based on 2 hydroxides/mole of zirconium and 3 hydroxides/mole of Al + Cr + Fe.

Some new procedures were employed this year for the analysis of nitrite in the sludge and for performing experiments on the suppression of NO_x evolution when the sludge was dissolved. The nitrite analysis modifications are discussed along with the results. The procedure used in these NO_x suppression tests was begun by adding (at room temperature) a solution of sodium carbonate plus sodium nitrite to a stirred nitric acid solution in a closed, slightly evacuated vessel, and then sweeping the evolved gases into a large reservoir that was then sampled (using Matheson-Kitagawa precision gas detector tubes)

to determine the NO_x concentration. The moles of NO_x formed were calculated from both this concentration and the volume of the reservoir by using the ideal gas law. Because most, if not all, of the nitrite present in NCRW sludge will be in the solution portion of the slurry that is fed to the dissolver, the results of these tests should be indicative of the results to be achieved with actual NCRW slurry.

The formation of hydrazoic acid, when using hydrazine to suppress NO_x evolution, was monitored during some of the experiments by using colorimetric measurements of the ferric azide complex, as described by Dukes and Wallace (1961).

In addition, some experiments were performed using solutions prepared by dissolving zirconyl nitrate salt. This approach was not extensively pursued because the zirconium in those solutions did not behave like the zirconium in the solutions prepared by dissolving NCRW sludge (these comparisons are discussed later).

3.0 RESULTS AND DISCUSSION

Results and discussion of various process steps are presented in the sequence in which the steps occur. Areas discussed are sludge retrieval, sludge dissolution, feed solution stability, and TRUEX processing. Finally, some results of general interest are discussed.

3.1 SLUDGE RETRIEVAL

In previous studies (Swanson 1991), it was assumed that retrieval of the sludge from the underground tanks would be preceded by the addition of water, followed by homogenization of the tank contents by mixing. Thus, sludge retrieved from a particular tank would be of a constant composition. Early in FY 1990, the proposed method of sludge retrieval was changed in two important ways: 1) the sludge was to be retrieved in layers rather than as a mixed composite; and 2) supernate solution (rather than water) was to be used to slurry the sludge for retrieval. Both of these changes would result in different dissolved sludge solution compositions than would have resulted from the previously considered procedure. On this basis, the studies described in this section were carried out. The results obtained, plus a decreased likelihood of future generation of more waste of this type, make it very unlikely that the use of supernate solution to slurry the sludge for retrieval will actually be performed.

In the FY 1990 proposed retrieval process, a layer of the well-settled sludge in the underground storage tank would be suspended in supernatant solution, and the resultant slurry would be transferred to a settling tank. After a settling period of a few days, the supernatant solution would be removed (for reuse in subsequent retrieval steps), and the settled slurry would be dissolved in nitric acid to provide feed for the TRUEX process. The composition of the resultant feed solution would thus depend on the following:

- the composition of the layer of well-settled sludge slurried and retrieved, including the interstitial liquid as well as the solids themselves
- the composition of the supernatant solution used for retrieval

- the relative volumes of the well-settled sludge in the underground storage tank and the few-days-settled sludge slurry in the settling tank
- the relative amounts of settled sludge, nitric acid, and water mixed in the dissolution step.

These parameters are discussed in the following sections.

3.1.1 Sludge Settling

As was discussed above, the relative volumes of the well-settled sludge in the underground storage tank and the few-days-settled sludge slurry in the settling tank are important in defining the composition of the solution resulting from dissolution of the slurry. The sludge settling rate is also important in defining the settling time required to reach a reasonable volume of settled sludge.

Sludge settling rates were measured with three different samples: 1) 103-AW (1989 composite), 2) 105-AW (1986 composite), and 3) one of the upper segments (segment 4B) taken from 105-AW in 1986. The latter two samples had dried during storage and were soaked in water before measurements were made; the more recent sample was still very moist. Each of the three samples was divided in two for side-by-side comparison of settling rates in solutions resulting from the addition of water or KF + NaOH solution as simulated supernate. These settling tests were done at room temperature ($\sim 23^{\circ}\text{C}$) in glass vials having cross-sectional areas of $\sim 1.8 \text{ cm}^2$.

The settling rate data obtained in the cases of water addition to the three sludge samples are shown in Figure 3.1. In each of these cases there was a well-defined boundary between the settling solids and the supernate solution, so that the measurements of the height of the sludge layer could be accurately taken. The supernate solutions were clear, indicating essentially complete separation of the solids; however, in each case there was a small amount of lighter solids floating on top of the clear supernate.

The initial settling rate values measured with these solids ranged from 0.2 to 1.6 cm/h. In one case (NCRW-44), there was a marked effect of solution composition on the settling rate, but in another case (NCRW-54), there was not. A much more detailed study would be needed to understand the

FIGURE 3.1. Sludge Settling Data

settling properties of these sludges; however, such an understanding is not required if the sludge is processed without recycling retrieval fluid. Based on the settled sludge volume data (to be discussed next) and on the increased uncertainty of additional NCRW supernate ever being generated, it now (early FY 1991) appears likely that the retrieval solution will not be recycled; thus, sludge settling rate data are not likely to be needed.

The sludge height data shown in Figure 3.1 as shaded symbols were measured after centrifugation for 10 min; these centrifuged sludge volumes were ~40% as large as the several-day-settled sludge volumes. In only one case (NCRW-52) was it possible to compare the volume of the as-sampled, well-settled sludge with that of the centrifuged sludge and of the few-day-settled sludge slurry. In this case, the volume of the centrifuged sludge was ~85% of the volume of the as-sampled sludge, and the volume of the few-day-settled sludge slurry was found to be nearly twice the volume of the as-sampled sludge. This second comparison indicates that unless a better solids/liquid separations method than gravity settling is used, a volume of retrieval solution approximately equal to the volume of well-settled sludge would accompany the sludge to the dissolution process. Because the NCRW tanks currently contain considerably more settled sludge than supernate solution, it appears that the supply of existing supernate would be far from sufficient for complete retrieval of the sludge. Thus, as was mentioned in the preceding paragraph, it now appears likely that recycling of retrieval solution will not be performed.

In the portions of these experiments that employed simulated supernate for the settling medium, both the settling rates and the solids volumes were comparable to those portions that used water. This was initially surprising, but much less so after it was determined that the solution compositions were not markedly different in the two cases. This appears to have been because the quantities of water used in the experiments gave sodium and fluoride concentrations in (water) solution that were at or near the solubility-controlled limits, with the result that addition of more of these components could not increase their concentrations substantially (solid NaF must have

formed instead). Data illustrating this fact are summarized in Table 3.1, along with data for some other components of interest.

In all three of the experiments summarized in Table 3.1, the concentrations of potassium and base found in the simulated supernate addition cases were within 20% of the concentrations expected from the concentrations of KF and NaOH that were added; this indicates that both potassium and base remained in solution. However, this was not the case with sodium and fluoride, which in two of the experiments were no higher in concentration in the simulated supernate addition cases than in the water addition cases, which indicates that the water addition cases were already at or near saturation with respect to NaF. In the other experiment (NCRW-44), increased levels of sodium and fluoride were found in the simulated supernate case, but the levels in the supernate were not as high as expected from the addition, which indicates that the water addition case was not saturated with respect to NaF, but that the simulated supernate was. The absence of saturation in the first water addition case of NCRW-44 was further indicated by the fact that the concentrations found in the second water addition case were approximately those expected from dilution considerations.

TABLE 3.1. Compositions Resulting from Solution Additions to Sludge Samples

Expt	Sludge	Solution, mL		Molarity ^(a)								Base to pH = 5
		Sludge, g	Added	Total	Na	K	Al	Cr	Si	U	F	
54	Segment 4 of 1986 105-AW Sampling	1.39	5.92 ^(b)	5.92	1.04	0.05	0.0012	--	0.19	--	0.89	0.18
		1.39	5.92 ^(c)	5.92	1.07	0.74	0.0030	0.0002	0.23	--	0.87	0.81
					(0.03)	(0.69)					(-0.02)	(0.63)
					[0.78]	[0.79]					[0.79]	[0.78]
44	Composite of 1986 105-AW Sampling	1.31	4.85 ^(b)	4.85	1.25	0.01	0.0018	0.0060	0.041	0.014	0.72	0.38
		1.31	4.85 ^(d)	4.85	1.37	0.66	0.0092	0.0060	0.050	--	0.98	0.86
					(0.12)	(0.65)					(0.26)	(0.48)
					[0.57]	[0.58]					[0.58]	[0.57]
52	Composite of 1989 103-AW Sampling	1.31	7.35 ^(b)	7.35	0.82	0.008	0.0012	0.0037	0.031	0.0084		0.22
		0.73 ^(e)	3.55 ^(b)	4.27 ^(e)	1.77	0.08	0.044	0.0018	0.030	--	0.56	0.53
		0.73 ^(e)	3.44 ^(c)	4.27 ^(e)	1.75	0.74	0.049	0.0019	0.026	--	0.56	1.22
					(-0.02)	[0.66]					(0.00)	(0.69)
					[0.65]	[0.66]					[0.66]	[0.66]

(a) Values in parentheses and brackets denote the increased concentration resulting from adding KF and NaOH; those in parentheses are the measured values and those in brackets are those expected in the absence of additional solids formation.

(b) Water addition.

(c) 0.79 M KF + 0.78 M NaOH addition.

(d) 0.58 M KF + 0.57 M NaOH addition.

(e) Assuming that the as-sampled sludge contained equal weights of dry sludge and water.

Other points of interest in the data of Table 3.1 include the following:

- The silicon concentration in NCRW-54, using an upper segment from Tank 105-AW, was much higher than in the other cases. The composite of Tank 105-AW segments (used in NCRW-44) was made from seven segments. These data indicate that much of the silicon in the composite could have come from the upper segment. There is no known reason why NCRW itself should show such a high variability in silicon content; perhaps other wastes, i.e., high-silica wastes, were disposed of in the same tank.
- The uranium concentration in the water addition cases of NCRW-44 is appreciable, even though no uranium was detected in any of the other cases. The reason for this is not known.
- Higher concentrations of aluminum were found in the simulated supernate cases than in the water cases; this is presumably due to an increased conversion of insoluble aluminum hydroxide to soluble aluminate species by the solutions having higher hydroxide concentrations.

3.1.2 Effect of Sludge Retrieval Procedure on Composition of Dissolved Sludge Solution

As was discussed in Section 3.1, the composition of the dissolved sludge solution depends not only on the relative amounts of settled sludge, nitric acid, and water that are mixed in the dissolution step, but also on the following:

- the composition of the layer of well-settled sludge slurried and retrieved, including the interstitial liquid as well as the solids themselves
- the composition of the supernatant solution used for retrieval
- the relative volumes of the well-settled sludge in the underground storage tank and the few-day-settled sludge slurry in the settling tank.

Data regarding the relative sludge volumes were presented in the preceding section. Data for the compositions of the supernatant solution as well as of the sludge layers are available for Tank 103-AW, but not for Tank 105-AW.

Table 3.2 lists some of the analytical data from an earlier study for the sample taken from Tank 103-AW in October 1986. Concentrations are summarized here for the predominant metal ions, the corrosion product metal ions,

and the corrosive anions that were present. These concentrations are given for the various sludge increments that were allowed by that core sampling. Assuming that these data are valid for the entire tank, average compositions of various sludge strata can be calculated. These average strata compositions can then be used in conjunction with the composition of the retrieval solution to calculate molar ratios of the components in the retrieved slurry (and in the dissolved sludge solution).

If the sludge is retrieved in such a way that each stratum retrieved corresponds to a sample segment listed in Table 3.2, then those data can be used in calculating the mole ratios present in various dissolved sludge strata. This retrieval pattern is thought to be unlikely. Table 3.3 presents weighted average compositions of strata selected to fit what is thought to be a more likely retrieval pattern, which is sequential removal of four strata of equal height. These strata compositions were weighted according to the height of the various analyzed segments (Table 3.2) in the various strata. Other retrieved strata compositions could be calculated in the same way, but those given in Table 3.3 should serve the present purpose.

If a solution other than water is used for sludge retrieval, the mole ratios that will exist in the dissolved sludge solution depend not only on the components of the sludge (Table 3.3), but also on the components introduced in the retrieval solution. The magnitude of this effect depends both on the concentrations of components in the added retrieval solution and on the volume of retrieval solutions that are not separated from the retrieved sludge.

In the experiments discussed in the preceding section it was found that the volume of the few-day-settled sludge would be approximately twice as large as that of the well-settled sludge in the storage tank. This indicates that unless a better solids/liquid separations method than gravity settling is used, an appreciable amount of retrieval solution will accompany the sludge to the dissolution process. This has two impacts on the proposed use of supernate for retrieval: 1) the supply of supernate may be exhausted before retrieval is completed, and 2) there may be an adverse effect (higher fluoride and sodium contents) on the composition of the dissolved sludge solution. This second impact is the one of concern here.

TABLE 3.2. Analytical Data for 103-AW Core Sample (1986 Sampling)

Distance Above Bottom, Inches	Segment Number	Serial Number	Molarity in Sludge									
			Na	K	Zr	Al	Fe	Cr	Ni	F	Cl	
0-4.5	Part of 9	7938	1.59	0.0559	0.00239	0.561	0.00196	0.0276	0.00080	0.123	0.176	
4.5-20	Parts of 8 and 9	7936	11.8	0.162	0.00348	1.90	0.0127	0.319	0.00643	0.002	0.115	
		7948	11.2	0.170	0.0182	2.35	0.0130	0.378	0.00772	0.002	0.115	
		Avg.	11.5	0.166	0.0108	2.12	0.0128	0.348	0.00708	0.002	0.115	
20-32	Part of 8	8022	7.27	0.572	1.55	0.0181	0.00583	0.00256	0.00126	5.69	0.021	
		7935	10.7	0.339	1.42	0.377	0.0132	0.00652	0.00210	4.86	0.070	
		Avg.	8.99	0.456	1.48	0.198	0.0095	0.00454	0.00168	5.28	0.046	
32-51	7	7932	9.59	0.474	1.55	0.0894	0.0184	0.00594	0.00376	5.65	0.032	
		7934	10.3	0.515	1.79	0.0861	0.0205	0.00650	0.00401	6.19	0.032	
		Avg.	9.94	0.494	1.67	0.0878	0.0194	0.00622	0.00389	5.92	0.032	
51-70	6	7930	6.70	0.537	1.49	0.0259	0.00577	0.00269	0.00119	5.30	0.010	
70-89	5	7929	5.40	0.529	1.29	0.0179	0.00865	0.00255	0.00153	4.36	0.007	
		7933	5.46	0.593	1.36	0.0179	0.0114	0.00265	0.00165	4.07	0.009	
		Avg.	5.43	0.561	1.32	0.0179	0.0100	0.00260	0.00159	4.22	0.008	
89-108	4	7928	3.34	0.524	1.02	0.0119	0.00733	0.00236	0.00109	4.04	0.007	
108-127	3	7927	3.29	0.499	0.749	0.0167	0.00459	0.00169	0.00042	2.57	0.007	
Supernate	2	7931	1.08	0.445	0.00132	0.00156	0.00002	0.00009	--	0.737	0.004	

TABLE 3.3. Weighted Average Composition of Selected Sludge Strata

Distance Above Bottom, Inches	Average Concentration in Stratum ^(a)								
	Na	K	Zr	Al	Fe	Cr	Ni	F	Cl
0-32 ^(b)	9.16	0.259	0.561	1.18	0.0100	0.174	0.00417	2.00	0.0977
32-64 ^(c)	8.62	0.512	1.60	0.0626	0.0139	0.00479	0.00279	5.67	0.0231
64-96 ^(d)	5.21	0.548	1.29	0.0181	0.00864	0.00256	0.00141	4.38	0.0082
96-127 ^(e)	3.31	0.509	0.854	0.0148	0.00565	0.00195	0.00068	3.14	0.0070
0-127	6.60	0.457	1.08	0.321	0.010			3.80	0.034

(a) Weighted according to height of segments (Table 3.2) in strata.

(b) $[4.5 (7938) + 15.5 (\text{average of } 7936 \text{ and } 7948) + 12 (\text{average of } 8022 \text{ and } 7935)] \div 32$.

(c) $[19 (\text{average of } 7932 \text{ and } 7934) + 13 (7930)] \div 32$.

(d) $[6 (7930) + 19 (\text{average of } 7929 \text{ and } 7933) + 7 (7928)] \div 32$.

(e) $[12 (7928) + 19 (7927)] \div 31$.

Table 3.4 gives the mole ratios of various components (relative to zirconium) in dissolved sludge solutions from different strata. Two sets of values are given for the components that are present in supernate: one set shows the ratios that would exist if water was used as the retrieval solution, and the other set shows the values that would result if supernate was used as the retrieval solution (using the experimentally indicated ratio of sludge volumes before and after retrieval). These ratios allow the appropriate concentrations of these components to be calculated for solutions containing varying concentrations of zirconium.

The data in Table 3.4 illustrate the wide variety of mole ratios that will be encountered in processing sludges that are retrieved from different strata within Tank 103-AW. Another important variation illustrated here is the increased fluoride-to-zirconium ratio that results from using (fluoride-containing) supernate as the retrieval solution; however, as was discussed earlier, the use of supernate as the retrieval solution may no longer be a practical consideration. The variability of these compositional data emphasizes the need for a greatly expanded program in the area of completeness of

TABLE 3.4. Mole Ratios (relative to zirconium) in Dissolved Sludge Strata with Water or Supernate as Retrieval Solution

Sludge Stratum, Inch	Mole/Mole Zr											
	Al			Fe			Cr			Ni		
	Water	(a)	Supernate	Water	(a)	Supernate	Water	(a)	Supernate	Water	(a)	Supernate
0-32	2.10	0.0178	0.310	0.0074	0.0017	0.0011	0.0023	0.0008	0.0008	0.0023	0.0008	0.0008
32-64	0.0391	0.0087	0.0030	0.0017	0.0011	0.0011	0.0023	0.0008	0.0008	0.0023	0.0008	0.0008
64-96	0.0140	0.0067	0.0020	0.0011	0.0011	0.0011	0.0023	0.0008	0.0008	0.0023	0.0008	0.0008
96-127	0.0174	0.0066	0.0023	0.0008	0.0008	0.0008	0.0023	0.0008	0.0008	0.0023	0.0008	0.0008
0-127	0.298	0.0089										

(a) Water used as retrieval solution.

(b) Supernate (composition in Table 3.2) used as retrieval solution, and a retrieved sludge settled volume (after a few days) being twice the in-tank settled sludge volume.

sludge dissolution and of dissolved sludge solution (and solvent extraction feed solution) stability with regard to precipitation.

3.2 SLUDGE DISSOLUTION

Additional data were obtained this year in three sludge dissolution areas. These are 1) suppression of NO_x release, 2) pH titration of sludge, and 3) completeness of dissolution and composition of the undissolved residue.

3.2.1 Suppression of NO_x Release

Nitrite is among the components of NCRW sludge, which can cause a problem when the sludge is dissolved for processing. This problem is the formation of NO and NO_2 (termed NO_x) by reactions such as

Regulations allow only limited release of these gases, and it is desired that their release be minimized. We have obtained additional data this year on both the quantity of nitrite present in the waste and on the suppression of NO_x formation in the dissolution process.

Suppression of NO_x Formation

Among the chemicals commonly used to react with nitrite in acid solution are sulfamic acid, hydrazine, hydroxylamine, and hydrogen peroxide. The latter chemical oxidizes nitrite to nitrate,

The others reduce nitrite to nitrogen and/or to nitrous oxide (N_2O).

The overall stoichiometry of these reduction reactions are, for sulfamic acid

for hydroxylamine (more properly, hydroxylamine nitrate or hydroxylammonium nitrate in nitric acid solution)

and, for hydrazine (more properly, hydrazinium nitrate in nitric acid solution)

The overall stoichiometry for the hydrazine reaction is the sum of two stepwise reactions: hydrazoic acid is the product of the first step,

which then reacts with additional nitrous acid

Under certain conditions (e.g., a large excess of hydrazine), a significant fraction of the nitrous acid reacts only as far as the hydrazoic acid intermediate. This fact must be considered in process evaluations because the azide ion (N_3^-) formed by disassociation of hydrazoic acid can form potentially explosive compounds with some heavy metals.

We first tested the use of these common chemicals in basic solution, as is NCRW supernate or washes of NCRW sludge, but found the reaction rates to be

slow (little or no decrease was observed in the nitrite absorption spectrum in several days at room temperature). We then studied these reactions in acid solutions.

The first set of experiments compared the effectiveness of the three reductant suppressor chemicals; these experiments involved the addition of 25 mL of a simulated supernate solution ($0.48 \text{ M NaNC}_2 + 0.38 \text{ M Na}_2\text{CO}_3$) to 50 mL of 2 M HNO_3 containing ~ 1.8 times the quantity of suppressor chemical required to react with the nitrite [according to Equations (3.5), (3.6), and (3.7)]. With sulfamic acid present at this ratio, $\geq 2.1\%$ of the nitrite was converted to NO_x ; this is roughly comparable to the value of $\sim 4\%$ observed previously (Swanson 1991) when sulfamic acid was present during an actual NCRW sludge dissolution experiment (NCRW-51). A markedly lower conversion of nitrite to NO_x was observed ($\sim 0.5\%$) when hydroxylamine was present, and another marked decrease (to $\sim 0.09\%$ conversion of nitrite to NO_x) was observed when hydrazine was used.

The fact that so much more NO_x was released in the presence of sulfamic acid than in the presence of hydroxylamine or hydrazine was not expected, based on published reaction kinetics data. The kinetics data of Biddle and Miles (1968) for sulfamic acid and hydrazine and of Barney (1971) for hydroxylamine indicate that, at the initial mixed solution composition ($\sim 0.6 \text{ M HNO}_3$ containing 0.29 M sulfamic acid or hydroxylamine or 0.145 M hydrazine), the half-times for the nitrite destruction reaction would have been $\sim 2 \times 10^{-4} \text{ min}$ with hydrazine, $\sim 3 \times 10^{-4} \text{ min}$ with sulfamic acid, and $\sim 7 \times 10^{-3} \text{ min}$ with hydroxylamine. Based on these kinetics data, sulfamic acid would be expected to suppress NO_x release nearly as well as hydrazine; however, this expectation was not met, for reasons not currently known.

Additional results obtained using hydrazine or hydroxylamine are summarized in Figure 3.2. The conditions used here were similar to those described earlier except for the quantities (and point of addition) of the suppressor chemicals. The lowest conversion of nitrite to NO_x occurred with hydrazine addition to the simulated supernate, with hydrazine addition to the acid being next lowest. There appeared to be little difference in NO_x release between the addition of hydroxylamine to the simulated supernate and to the acid.

The highest conversion of nitrite to NO_x (shown in Figure 3.2) is <1%. This is ~10-fold lower than the immediate NO_x release that has been observed in the absence of nitrite suppressor (Swanson 1991), but the potential benefit is even greater than that. This is because the suppressors destroy all of the nitrite so there is no possibility of later NO_x release, which would be expected to occur if nitrite suppressors were not used.

As was discussed earlier, a potential drawback to the use of hydrazine is the formation of hydrazoic acid. As seen in Figure 3.2, ~2% of the nitrite was converted to hydrazoic acid at a 10% excess of hydrazine, and ~15% conversion was observed at a 40% excess of hydrazine. Such an increase in hydrazoic acid yield with increasing hydrazine excess is expected from consideration of Equations (3.8) and (3.9).

Hydrazoic acid would be expected to extract into the TRUEX solvent and remain there until the solvent wash step, where it would be removed as sodium azide. This is similar to the behavior of hydrazoic acid in several cycles of the Hanford PUREX plant and in other reprocessing plants around the world.

The potential impacts of the presence of sodium azide in the solvent wash solution depend on the routing of that stream. If it is routed to grout feed along with the neutralized TRUEX raffinate, its fate will be the same as that formed in PUREX operation. If it is combined with the neutralized filter backflush (which contains the undissolved solids) and TRUEX strip steams, it would be fed to the glass melter instead; whether that would pose a problem is not known. The azide ion would be destroyed via Reaction (3.9) if the solvent wash solution were acidified in the presence of nitrite; if desired, this could be done in either the grout feed or the glass feed streams by adding the nitrite needed for corrosion passivation before the stream is neutralized for storage (in carbon steel tanks).

Thus, the hydrazoic acid formation that results from using hydrazine to suppress NO_x release is not judged to be a severe problem. However, it would be prudent to minimize the extent of its formation by using only a slight excess of hydrazine.

FIGURE 3.2. Results of NO_x Suppression Tests

One experiment was conducted with 88% of the stoichiometric amount of hydrazine plus 75% of the stoichiometric amount of hydroxylamine to see if low yields of both NO_x and hydrazoic acid could be realized. No hydrazoic acid was detected but the NO_x yield was 0.55% of the amount of nitrite destroyed. This NO_x yield is comparable to those obtained with hydroxylamine alone (Figure 3.2), so there appears to be no benefit in using such a mixture of hydrazine and hydroxylamine.

Results obtained during the preparation of this report (in early FY 1991) indicate that both sulfamic acid and hydrogen peroxide (used separately) give results intermediate between those obtained with hydrazine and hydroxylamine (used separately), when the suppressor chemical is added to the simulated supernate. Comparison of this sulfamate result with that obtained earlier with sulfamate added to the acid shows a large effect of sulfamate point of addition on NO_x release. More work with these suppressors is planned.

Nitrite Concentration in NCRW Sludge

Knowledge of the concentration of nitrite in the retrieved sludge is necessary for the efficient use of NO_x suppression chemicals, as was discussed in the preceding section. Data obtained this year in this area showed a high variability between different samples; this will make it more difficult to efficiently use NO_x suppression chemicals when NCRW sludge is dissolved.

Table 3.5 summarizes the results of experiments in which retrieval solutions that had contacted various sludge samples were analyzed to determine their nitrite contents. Results were obtained using both spectrophotometric and ion chromatographic techniques. The spectrophotometric technique involved measuring the absorbance at 373 nm, before and after adding a nitrite suppressor, and using the difference between these values as a measure of the nitrite concentration. Two different nitrite suppressors were tested in the spectrophotometric technique: hydroxylamine nitrate, as had been used in the previous work, and sulfamic acid. In some cases there was good agreement between the two suppressors, but in other cases hydroxylamine nitrate indicated higher nitrite concentrations than did sulfamic acid. It is likely that hydroxylamine nitrate reacted with another colored species (in addition to

TABLE 3.5. Nitrite in Sludge Samples - Based on Analysis of Retrieval Solutions

Expt	Dry	Solution, mL		Indicated Nitrite, g/g Dry Sludge		
	Sludge, g	Added	Total	Using HAN ^(a)	Using SA ^(b)	By IC ^(c)
<u>With Segment 4 of 1986 Sampling of Tank 105-AW</u>						
54	1.39	5.92	5.92	0.0049	0.0043	0.0052
<u>With Composite of 1986 Sampling of Tank 105-AW</u>						
43 ^(d)	1.45	14.4	14.4	0.0115	(e)	(e)
44	1.31	4.85	4.85	0.0198	0.0088	0.0104
<u>With Composite of 1986 Sampling of Tank 103-AW</u>						
48 ^(d)	1.57 ^(f)	13.6	15.2 ^(f)	0.0276	(e)	(e)
56	1.28	8.95	8.95	0.0830	(e)	0.0708
58	2.45	12.0	12.0	0.0444	0.0340	(e)
<u>With Composite of 1989 Sampling of Tank 103-AW</u>						
52	1.45 ^(f)	7.10	8.55 ^(f)	0.0450	0.0410	0.0453

- (a) Nitrite measured spectrophotometrically in acidified sample, based on peak heights before and after adding hydroxylamine to react with nitrous acid. HAN = hydroxylamine nitrate.
- (b) As (a) except using sulfamic acid (SA) to react with nitrous acid.
- (c) Ion chromatographic analysis.
- (d) Previously reported experiment.
- (e) Not analyzed by this technique.
- (f) Assuming that the as-sampled sludge contained equal weights of dry sludge and water.

nitrite) that absorbed light at the same wavelength as nitrite, thus giving an erroneously high indication of nitrite concentration. Agreement between the concentrations measured spectrophotometrically using sulfamic acid and those measured by ion chromatography was within ~20%; this agreement is felt to be quite good overall, but that large an uncertainty in input nitrite concentration would make it very difficult to achieve a guaranteed slight excess of reagent to suppress NO_x evolution during the acidification/dissolution step.

The data of Table 3.5 show a greater than tenfold variation in the nitrite content of the sludge samples that were analyzed. Such a variation

will also contribute to the difficulty of running an effective NO_x suppression process without using (periodically, at least) a substantial excess of suppressor chemical.

Many nitrite content values reported in earlier studies were based on analysis of (acidic) dissolved sludge solutions; these values were generally lower than those found in water leaches of sludge, such as those shown in Table 3.5. These discrepancies were thought to result from the decomposition of nitrous acid by reactions such as (3.2). To test this decomposition hypothesis, portions of the supernates from NCRW-44 and -52 were acidified and the nitrous acid concentrations were followed over time as the solutions sat in capped vials at room temperature. Results of these experiments are shown in Figure 3.3; nitrous acid decomposition is seen to occur relatively rapidly, reaction half-times being 0.3 h in NCRW-44 supernate acidified to $\sim 1.9 \text{ M}$ and 1.1 h in NCRW-52 supernate acidified to $\sim 0.8 \text{ M}$ HNO_3 . The zero-time values shown in Figure 3.3 (shaded symbols) were obtained from analysis of the basic solutions, plus the dilution factor involved in acidification.

3.2.2 pH Titration of Sludge

During the dissolution steps of two experiments (NCRW-56 and -58), pH measurements were made as a function of the quantity of nitric acid that had been added. In both experiments, the response of the (glass) pH electrode appeared to be altered by the exposure to the solution during the dissolution. This was evidenced by the fact that the readings obtained with standard solutions immediately after the dissolution did not agree with those obtained immediately before the dissolution; variations of up to 0.8 pH units were observed. Quantitative interpretation of these results was not attempted.

In spite of this uncertainty, there still appears to be at least a rough correlation between a) the amount of acid added beyond the point at which $\text{pH} = 1$ and b) the amount of free acid in the dissolved sludge solution. In NCRW-56, the amount of acid added beyond $\text{pH} = 1$ was sufficient to give 1.0 M , compared to 0.7 M found by analysis (making the usual corrections for the contribution of hydrolyzable metal ions). In NCRW-58, the respective values were 0.7 M and 0.6 M ; this degree of agreement is closer to that reported last year in experiments NCRW-42 and -48.

39105044.3

FIGURE 3.3. Rates of Nitrous Acid Decomposition in Acidified Supernate Solutions

3.2.3 Completeness of Sludge Dissolution and Composition of Undissolved Residue

The quantities and compositions of the undissolved residue from the dissolution step are important to estimating the quantity of glass that will be produced in the vitrification of this material (which is planned to be combined with the strip stream from the TRUEX process before vitrification). Data obtained this year relative to the metal ion components of such residues are summarized in Table 3.6; these data were all obtained with composites of sludge segments from Tank 103-AW.

TABLE 3.6. Recent Data on Metal Ion Components of Dissolution Residues with 103-AW Sludge Composites

	1986 Composite			1989 Composite
Experiment Number	49	56	58	50
Dissolution Time, h	3	3	2	2
Dissolved Sludge Solution Composite				
Na, <u>M</u>	1.9	2.2	2.0	2.1
Zr, <u>M</u>	0.27	0.25	0.27	0.17
Acid, <u>M</u>	0.9	0.7	0.6	0.8
Total Found, g/g sludge	(a)	(b)	(b)	(a)
Zr	0.0729	0.140	0.140	0.0747
Al	0.00652	0.0133	0.0131	0.00827
Cr	0.00193	0.00380	0.00391	0.00216
Fe	0.00041	0.00097	0.00083	0.00049
Si	0.0034	0.0050	0.0124	0.00090
Na	0.129	0.250	0.249	0.177
K	0.0136	0.0194	0.0204	0.0108
U	0.0055	0.0145	0.0153	0.0070
Found in Water Rinses, ^(c) % of total	(d)	(e)	(f)	(g)
Zr	3.1	13	4.3	24
Al	39	5.5	3.8	10
Cr	10	5.0	1.8	9.3
Fe	--	6.2	2.4	11
Si	8.0	7.0	3.7	11
Na	10	8.3	2.8	13
K	9.0	8.7	2.8	12
U	12	8.5	2.4	--
Found in Rinsed, Undissolved Residue, % of total				
Zr	7.0	14	4.8	10
Al	0.4	31	32	21
Cr	3.1	21	26	6.8
Fe	8.0	12	16	15
Si	72	39	7.7	17
Na	0.04	1.3	0.04	0.3
K	--	0.8	7.8	--
U	--	--	--	--

(a) Wet sludge.

(b) Air-dried sludge.

(c) Typically, solids were rinsed on the filter with 4 each, 3-mL portions of water.

(d) A 1-mL rinse with 0.3 M HNO₃ preceded the water rinses, which were done 2 months later.

(e) A 1-mL rinse with 0.3 M HNO₃ preceded the water rinses.

(f) A 2-mL rinse with 0.3 M HNO₃ preceded the water rinses.

(g) No rinse was performed before the water rinses.

These data contain many apparent inconsistencies that are not now understood, but several observations are worthy of note. Among these are the following:

- When the proportions of sludge and acid were such that a concentration of sodium in excess of 2 molar resulted, a portion of the "soluble" zirconium species was not in solution. This is indicated by the higher-than-usual zirconium contents of the water rinse solutions and of the undissolved residues in experiments NCRW-50 and -56, where the sodium concentration exceeded 2 M.
- The wet, flowing sludge typical of the condition when removed from the underground storage tank contains approximately equal weights of water and of air-dried (at ambient temperature) solids. This is indicated by the relative amounts of waste salt components found per gram of sludge used in the experiment.

Some data were also obtained this year regarding the quantities of some important (to glass-making specifications) nonmetal-ion components of the residues remaining after the sludge dissolution step. In NCRW-58, the washed residue was divided into two portions, one of which was dissolved in a mixture of nitric and oxalic acids for fluoride analysis, and the other was dissolved in a mixture of hydrochloric and hydrofluoric acids for sulfate and total organic carbon (TOC) analyses. Blank solutions containing identical amounts of reagents were also analyzed to ensure that the material in question truly originated in the undissolved residue.

The quantity of fluoride found in the NCRW-58 residue amounted to 0.9 mole fluoride/mole zirconium, which is much higher than the value of 0.04 observed last year (Swanson 1991) in NCRW-48 when a different portion of the same 103-AW composite was dissolved under conditions giving sludge component concentrations only about half as high as those in NCRW-58. However, this relatively high fluoride content is still below the upper level of that currently allowed in glass plant feed; a level of 5.8-g fluoride/100 g of residue oxides was found here, compared to the allowed upper level of 6.9. Because the glass plant feed will also contain oxides from sources other than the dissolution residue, the fluoride level in the feed will be even lower than the value shown here.

The quantity of sulfate found in the NCRW-58 residue was very low, only 0.0009 mole/mole of zirconium and 0.03-g sulfate/100 g of residue oxides (versus 2 g/100 g allowed in glass plant feed). The TOC level in this residue was also low, amounting to 0.1 mole/mole of zirconium and 0.45-g TOC/100 g of residue oxides (versus 11 g/100 g allowed).

Sulfate and carbon data were also obtained on the residue from NCRW-56 (the portion being dissolved for fluoride analysis was lost). The results were in general agreement with those obtained in NCRW-58; the sulfate level was 0.0012 mole/mole of zirconium, and the TOC level was 0.3 mole per mole of zirconium.

No work of this type was done this year with sludge from Tank 105-AW; an uncertain value was obtained last year for the sulfate content of the residue. Thus, a recheck with that sludge remains to be done.

3.3 PRECIPITATION FROM DISSOLVED SLUDGE SOLUTIONS

Results of recent experiments (primarily NCRW-58) have shown that solids can precipitate as dissolved sludge solutions age. This was not observed in the early work, but in those experiments the dissolved sludge solutions were generally used in other tests before they had aged very long. This year we did observe solids in several solutions that had been prepared last year; this was not of great concern because prompt processing of the solutions is assumed, but was still of interest. However, since precipitation occurred in the dissolved sludge solution of NCRW-58 within 2 days, considerable importance has been attached to this phenomenon.

3.3.1 Solution Stability Data

Table 3.7 summarizes data on the compositions of dissolved sludge solutions from which precipitation was observed, and on the approximate time frames in which precipitation occurred. Three different types of observation were used in attempting to determine whether precipitation had occurred: 1) visual observation within the vial, which was not very definitive because of the translucent nature of the white plastic vials used; 2) the feel and sound observed when a pipette tip was scraped over the bottom of the vial; and

TABLE 3.7. Observations of Precipitate Formation in Dissolved Sludge Solutions

Expt.	Solution Age, Days	Molarity										H ⁺ to pH 7	Free Acid(a)	F	Precipitate Observed?		
		Zr	Al	Cr	Fe	Na	Si	V(b)	S(c)	P(d)							
<u>105-AW (1986 Composite) Sludge</u>																	
41	0 32	0.126	0.0016	0.0053	0.012	0.82	0.020	0.97	0.6	0.61	No	No	No	No	No	No	Uncertain
42	0 10 441 10(e)	0.122	0.0113	0.0045	0.013	0.77	0.0105	1.56	1.2	0.58	No	No	No	No	No	No	Uncertain
<u>103-AW (1986 Composite) Sludge</u>																	
48	0 2 418	0.137	0.0338	0.0061	0.0013	0.95	0.0381	1.58	1.2	0.50	No	No	No	No	No	No	Yes
49	0 105	0.240 0.218	0.049 0.056	0.011 0.012	0.0023 0.0022	1.71 1.75	0.0081 0.0050	1.53 1.38	0.9 0.7	0.79	No	No	No	No	No	No	Yes
56	0 21 54 98	0.255 0.244 ^(f)	0.072 0.074 ^(f)	0.012 0.013 ^(f)	0.0032 0.0028 ^(f)	2.22 2.30 ^(f)	0.022 0.016 ^(f)	1.48 1.29	0.7	0.68	No	No	No	No	No	No	Yes
58	0 1 2 3	0.235	0.053	0.0092	0.0020	1.78	0.066	1.28	0.6	0.83	No	No	No	No	No	No	Yes
58SX(g)	1 2 3	0.10 ^(f)	0.023 ^(f)	0.0039 ^(f)	0.0009 ^(f)	0.76 ^(f)	0.028 ^(f)	1.68	1.4	0.35 ^(f)	No	No	No	No	No	No	Yes

TABLE 3.7. (contd)

Expt.	Solution Age, Days	Molarity							H ⁺ to pH 7	Freq Acid(a)	F	Precipitate Observed?		
		Zr	Al	Cr	Fe	Na	Si	V(b)				S(c)	P(d)	
103-AW (1989 Composite) Sludge														
50	0	0.174	0.067	0.011	0.0021	2.13	0.0074	1.34	0.8			No	No	No
	219	0.162	0.067	0.011	0.0021	2.12	0.0072	1.40	0.8	0.72		No	Yes	--
51	0	0.107 ^(h)	0.033 ^(h)	0.0055 ^(h)	0.0014 ^(h)	1.10 ^(h)	0.0035 ^(h)					No	No	No
	208	0.089	0.032	0.0055	0.0014	1.08	0.0024	0.92	0.6	0.39		No	--	Yes

(a) Assuming that the hydrolysis of zirconium contributes 2 moles of acid/mole zirconium and the hydrolysis of aluminum, chromium, and iron contribute 3 moles of acid/mole of metal ion.

(b) Observed visually; this is not a sensitive test for white solids in a translucent, white vial.

(c) Observed by feel and sound when scrape pipette tip over the bottom of the vial.

(d) Observed by pulling sample into glass pipette while scraping bottom of the vial.

(e) Portion of 10-day-aged solution heated at ~100°C for 3 h.

(f) Value calculated from dilution factor and the concentrations found in a preceding sample.

(g) Prepared from 1-day-aged dissolved sludge solution.

(h) Value calculated from the amounts found in the two phases after precipitation had occurred.

3) visual observation within a glass pipette when the solution was pulled into the pipette while scraping its tip across the bottom of the vial. The latter test is the most sensitive of the three.

These data were not obtained very systematically, primarily because precipitation was not considered to be a real problem until experiment NCRW-58 was performed and precipitate formation occurred within two days. It may be significant that the NCRW-58 solution had a higher silicon concentration than any of the others.

With the 0.235 M zirconium + 0.8 M acid dissolved sludge solution of experiment NCRW-58, precipitation from the 3-day-old solution had proceeded to the extent that the zirconium and silicon concentrations had decreased by concentrations of 0.031 and 0.052 M, respectively (these decreases amounted to 13% and 79% of the concentrations that were initially present). With the 0.10 M zirconium + 1.4 M acid solvent extraction feed solution that was prepared from that sludge solution after it had aged for only 1 day, the missing zirconium amounted to only ~5%, but the missing silicon amounted to ~73%. It is thought to be likely that this "missing" silicon had precipitated from the dissolved sludge solution during the 1-day period before the solvent extraction feed solution was prepared, because analysis of the solids that did precipitate from the feed solution showed little silicon to be present.

Only about 4% of the zirconium initially present in the (0.255 M zirconium + 0.7 M acid) dissolved sludge solution from NCRW-56 apparently precipitated in a 54-day time period. About 9% of the zirconium precipitated from the 0.24 M zirconium + 0.9 M acid solution from NCRW-49 in 105 days. Silicon decreases were also observed in both of these experiments.

In NCRW-42, precipitate formation occurred when the 10-day aged solution was heated at ~100°C for 3 h. Comparison of the concentrations found in solution before and after heating shows that only silicon underwent a significant decrease in concentration, which is a marked contrast to an earlier experiment (NCRW-46), where a large fraction of the zirconium precipitated when the dissolved sludge solution was digested at ~100°C (Swanson 1991). The earlier

solution was lower in acid (0.4 versus 1.2 M) and higher in zirconium (0.25 versus 0.12 M), so it is not surprising that a different result was obtained on heating.

Precipitation of zirconium, but not silicon, was observed in NCRW-50 after standing for 219 days at room temperature. In NCRW-51, the concentrations of both zirconium and silicon decreased when the solution aged for 208 days at room temperature.

3.3.2 Data on Separated Precipitates

Solids that separated out in NCRW-58 from both the dissolved sludge solution itself (0.235 M zirconium and 0.6 M free acid) and the solvent extraction feed solution (0.10 M zirconium and 1.4 M free acid) were collected for some limited characterization tests. After first washing with small portions of water, portions of the solids were mounted for scanning electron microscopy (SEM) examination. Additional water was then added, which gave complete dissolution of the solids that had separated from the feed solution, but not of the solids that had separated from the dissolved sludge solution. This non-water-soluble solid was also mounted for SEM examination.

Typical SEM photographs of these three solids are shown in Figure 3.4. The solids that separated from the dissolved sludge solution are seen to be comprised of two types of solids; not only are relatively large ($\sim 1 \times 3 \mu\text{m}$ to $\sim 3 \times 7 \mu\text{m}$), rectangular crystals present, but small (~ 0.2 to $\sim 0.5 \mu\text{m}$ diameter), round particles are also present. Microprobe analysis of the rectangular crystals showed zirconium to be the predominant metal present, with minor amounts of silicon, aluminum, and sodium also present. Microprobe analyses in areas occupied by the round particles also showed zirconium to be the predominant material, but the quantity of silicon was also appreciable in those areas (and minor amounts of aluminum and sodium were also evident).

In contrast, the solids that separated from the solvent extraction feed solution (which contained lower concentrations of the sludge components and a higher concentration of acid) were only of the large rectangular type. These

FIGURE 3.4. Scanning Electron Microscopy of Solids from NCRW-58 -
Solids from Dissolved Sludge Solution

FIGURE 3.4. (contd) - Solids from Solvent Extraction Feed Solution

FIGURE 3.4. (contd) - Non-Water-Soluble Solids from Dissolved Sludge Solution

solids contained little or no silicon; they were high in zirconium and contained traces of sodium and aluminum. As was mentioned in the preceding section, the absence of silicon in this precipitate may have resulted from a (unobserved) precipitation of a silicon compound from the dissolved sludge solution before that solution was used to prepare the solvent extraction feed solution.

The solids that separated from the dissolved sludge solution but did not dissolve in water were of the small round type. They contained both silicon and zirconium, in approximately equal amounts, with aluminum and chromium at trace levels.

Analysis of the solutions resulting from dissolution of the (water-washed) solids from NCRW-58 in a larger volume of water provided some interesting results. The water-soluble portion of the washed precipitate from the dissolved sludge solution was found to contain 1.1 mole sodium/mole zirconium and 3.9 mole fluoride/mole zirconium. The corresponding values for the washed precipitate from the solvent extraction feed solution were 1.0 and 4.2; this precipitate also contained ~0.02 mole silicon/mole zirconium. It thus appears that the large, rectangular crystals observed by SEM (Figure 3.4) were of a compound containing 1 sodium/zirconium and 4 fluorides/zirconium. Two possibilities for such a compound are $\text{NaZr}(\text{OH})\text{F}_4$ and $\text{NaZr}(\text{NO}_3)\text{F}_4$; additional work will be necessary to define the compound more closely.

The absence of significant amounts of silicon in these large, rectangular, zirconium-rich crystals indicates that this element was not a stoichiometric cause of their formation. However, the fact that the silicon concentration was so high in the initial NCRW-58 dissolved sludge solution (Table 3.7) makes one wonder if it didn't contribute to the rapid precipitation of these crystals by a "seeding" mechanism involving a silica-rich precipitate. If this mechanism is true, both the dissolved sludge solution and the solvent extraction feed solution prepared from it were super-saturated with respect to zirconium (in an equilibrium sense); if this is so, other "seeds" (e.g., specks of dirt) might also cause rapid zirconium precipitation.

In NCRW-51, the solids that formed on aging were white and crystalline and formed a "cake" on the bottom of the vial. These solids were dissolved

(in warm 0.3 M HNO_3) for ICP analysis after the solution had been removed; this dissolved solids solution had a sodium-to-zirconium mole ratio of 1.34 and a silicon-to-zirconium mole ratio of only 0.012. Assuming that the potassium found in this solution was a measure of the residual initial solution, and correcting the data accordingly, the mole ratios calculated to be present in the precipitate itself were 1.28 and 0.011, respectively. These results are fairly consistent with those of NCRW-58 in which the analytical data are more definitive.

3.3.3 Possible Flowsheet Modifications Due to Precipitation Problems

The recent observations of precipitate formation in dissolved sludge solutions (and in solvent extraction feed solution) suggest that feed clarification should be performed immediately prior to feeding the solution to the solvent extraction contactor to minimize the chance of solids accumulation in the contactor. If the solids removed by such a step were recycled to the dissolution step, the zirconium-rich solids should readily redissolve. The silicon-rich solids might not redissolve; they could then accompany the undissolved residue of NCRW solids to the vitrification feed stream.

Alternatively (or additionally), the contactor could periodically be flushed to remove any precipitates that had formed. Water flushing would readily dissolve zirconium-rich solids like those observed in NCRW-58, but other processes would be required for silicon-rich solids.

Still another approach that might be followed if silica-rich precipitates pose a severe problem would be to perform an initial sludge washing step, with its attendant complications, so that at least a portion of the silicon would be removed before acid is added to dissolve the sludge. If this were done, it would probably be necessary to add fluoride (or another complexant such as oxalate) to the dissolution step; this would result in additional fluoride (or other complexant) in the low-level waste stream.

No data are available on the exact extent of silicon removal that could be achieved by sludge washing. However, the quantities of silicon found in water leach solution per gram of sludge with one set of samples (Table 3.1) are comparable to the total amounts found in another set of samples

(Table 3.6). This suggests that sludge washing could be quite effective in removing silicon before dissolution, if desired.

3.4 TRUEX SOLVENT EXTRACTION

The TRUEX solvent extraction operations will include stages to accomplish extraction of the TRUs from the dissolved sludge solution, scrubbing of the organic extract to improve separation of the TRUs from other extracted species, stripping of the TRUs back into an aqueous phase, and washing of the solvent. Most of the data obtained this year in these areas addressed the problem of interfacial crud formation in the extraction operation. Comments are also made in the other three areas of solvent extraction.

3.4.1 Extraction

One of the major concerns in the TRUEX processing of dissolved NCRW sludge has been the observation that interfacial cruds have been formed in some cases during extraction operations. Such cruds could seriously hamper the effectiveness of continuous countercurrent extraction equipment, especially so if that equipment is a mixer-settler or a centrifugal contactor rather than a pulse column. While operational steps may be available to overcome such crud problems, avoiding them altogether would be preferable.

In the first experiment addressing this problem this year (NCRW-49), a portion of the 103-AW (1986 composite) sludge was dissolved in nitric acid and clarified by 0.2- μm filtration (as usual). An interfacial crud formed when a portion of this (freshly prepared) solution was contacted with 0.33 volume of TRUEX solvent (0.2 M CMPO-1.4 M TBP-NPH) that had been freshly washed with a carbonate solution. Extraction tests with three more portions of this solution were then run on the following day, at different feed dilution conditions. These tests were also performed with an organic-to-aqueous phase ratio of 0.33.

Interfacial crud formation was also observed with feed solutions obtained by diluting this dissolved sludge solution by 25% (giving 0.19 M zirconium) with either 1 M HNO_3 or 5 M HNO_3 ; the amount of crud was less in the case where 5 M HNO_3 was used as the dilution solution. However, no interfa-

cial crud was observed with feed solution obtained by a 75% dilution with 2.9 M HNO_3 , which gives 0.14 M zirconium in 1.7 M acid.

These results showed that interfacial crud could be avoided by adjustment of the composition of the feed solution to a certain range. Crud formation appeared to be less likely at higher concentrations of acid and at lower concentrations of the dissolved sludge components.

These results were evaluated along with those from earlier work, and a good correlation was obtained that indicated that interfacial crud would not form if the aqueous phase to be extracted contained less than 0.14 M zirconium at ~1.5 M total acid and less than 0.12 M zirconium at total acidities near zero. However, later results showed this correlation to not apply with all batches of sludge.

The next dissolved sludge solution (from NCRW-56) gave results in agreement with this correlation (no interfacial crud was observed when the solution was adjusted to 0.14 M zirconium + 1.6 M acid and contacted with 0.33 volume of TRUEX solvent). However, results in the next experiment (NCRW-58) did not agree with this correlation; with this dissolved sludge solution, crud was observed with a 0.12 M zirconium + 1.5 M acid feed but not with a 0.10 M zirconium + 1.5 M acid feed. Thus, it appears that the location of the line dividing crud-forming conditions from non-crud-forming conditions varies from sample to sample (even within a given composite). It is of interest to note that the same feed solution (from NCRW-58) that gave earlier precipitation problems (Section 3.3.1) also gave interfacial crud at a lower zirconium concentration; it is probable that these phenomena are related (perhaps affected by the higher-than-usual silicon level present in NCRW-58).

The data discussed in the preceding paragraphs are compared with earlier data in Tables 3.8 and 3.9. Table 3.8 summarizes the compositions of the dissolved sludge solutions used to prepare feeds for the extraction tests. Table 3.9 summarizes the observations regarding the formation of interfacial cruds (and other solids) in extraction contacts done with the different dissolved sludge solutions. This table includes the solution age at the time of

TABLE 3.8. Compositions of Dissolved Sludge Solutions Used in Study of Solids Formation in Extraction Contacts

	Molarity						H to pH 7	Free Acid ^(a)	F
Expt	Zr	Al	Cr	Fe	Na	Si			
<u>105-AW (1986 Composite) Sludge</u>									
41	0.126	0.0016	0.0053	0.012	0.82	0.020	0.97	0.6	0.61
42	0.122	0.011	0.0045	0.013	0.77	0.010	1.56	1.2	0.58
43	0.129	0.018	0.0050	0.014	0.81	0.035	1.88	1.5	0.52
<u>103-AW (1986 Composite) Sludge</u>									
34	0.127	0.029	0.0044	0.0012	0.88	0.0090	0.89	0.5	
37	0.225	0.054	0.011	0.0023	1.64	0.018	1.02	0.4	0.84
46 ^(b)	0.117	0.075	0.011	0.0022	1.52	0.017	0.89	0.4	0.58
47	0.153	0.036	0.0060	0.0013	1.06	0.017	1.01	0.6	0.55
48	0.137	0.034	0.0061	0.0013	0.95	0.038	1.52	1.1	0.50
49	0.240	0.049	0.011	0.0023	1.71	0.0081	1.53	0.9	0.79
56	0.255	0.072	0.012	0.0032	2.22	0.022	1.48	0.7	0.68
58	0.235	0.053	0.0092	0.0020	1.78	0.066	1.28	0.6	0.83

(a) Assuming that the hydrolysis of zirconium contributes 2 moles of acid/mole zirconium and the hydrolysis of aluminum, chromium, and iron contribute 3 moles of acid/mole metal ion.

(b) After digestion at 100°C for 4 h; 45% of zirconium precipitated.

the test and the volume used in the test; the first factor can affect whether solids formation occurs, and the latter factor affects the ease of observation of interfacial crud formation.

The primary conclusion that can be drawn from these data is that the likelihood of solids formation decreases with decreasing concentration of zirconium (and other dissolved sludge components). However, the level to which the concentration must be reduced (or other adjustment made) to ensure

TABLE 3.9. Observations of Solids Formation in Extraction Contacts

Contact ^(a)	Present in Feed, M			Solution Age, Days	Feed Volume, mL	O/A ^(d)	Solids Observed After Contact?
	Zr ^(b)	Acid	Oxalate ^(c)				
<u>105-AW (1986 Composite) Sludge</u>							
	41a	0.13	0.6	--	0	0.5	0.25No
	41c	0.13	0.6	--	31	3.0	0.5Yes
	41j	0.13	0.6	--	32	0.5	0.25No
	41j (cont)		0.13	0.6	--	32	0.8.5No
	42a	0.12	1.2	--	1	3.0	0.5No
	43a	0.13	1.5	--	0	3.0	0.5No
<u>103-AW (1986 Composite) Sludge</u>							
	34a	0.13	0.5	--	3	3.3	0.33Yes
	37a	0.22	0.4	--	7	3.9	0.33Yes
	37m	0.22	0.4	0.005	10	1.0	0.33Yes
	46a	0.12	0.4	--	1	0.5	0.5No
	46c	0.11	0.5	0.004	4	0.5	0.25No
	46e	0.12	0.4	0.002	13	3.0	0.5No
	47a	0.15	0.6	--	0	0.5	0.25No
	47c	0.15	0.6	--	28	3.0	0.5No
	48a	0.14	1.1	--	2	4.8	0.5Yes ^(e)
	49a	0.24	0.9	--	0	1.0	0.33Yes
	49b	0.19	0.9	--	1 ^(f)	1.2	0.33Yes
	49c	0.19	1.7	--	1 ^(f)	1.2	0.33Yes
	49d	0.14	1.7	--	1 ^(f)	1.8	0.33No
	49e	0.14	1.7	--	104 ^(f)	1.8	0.33Yes ^(e,g)
	56a	0.14	1.6	--	54 ^(f)	0.9	0.33No
	58a	0.12	1.5	0.010	1 ^(f)	1.8	0.33Yes
	58b	0.10	1.5	0.010	1 ^(f)	1.8	0.33No
	58c	0.10	1.5	0.010	2 ^(h)	18	0.33Yes ^(e,i)

- (a) The number portion of the contact identification refers to the number of the dissolved sludge solution (Table 3.8) used in the feed to the contact.
- (b) Ratios of other metal ions and fluoride are the same in these feeds as in the dissolved sludge solutions (Table 3.8).
- (c) Oxalate addition (if used) was just prior to the contact.
- (d) Organic-to-aqueous phase ratio.
- (e) Solids present, but not at the interface.
- (f) Diluted feed prepared just prior to the contact.
- (g) Indication of a small volume of a second organic phase.
- (h) Diluted feed prepared one day prior to the contact.
- (i) Possibility that solids were carried into the contacting vessel along with the feed solution.

the absence of solids formation with all possible sludge compositions remains to be determined. The currently available results are plotted in Figure 3.5. Two lines indicating the demarkation between solids-forming and non-solids-forming compositions are shown here; the one to the right is for the experiments other than the most recent one (NCRW-58), and the one to the left includes that one also. Other compositions need to be investigated, especially to reflect compositions that will result from layered retrieval of the sludge (Section 3.1) and from the addition of aluminum ion to reduce the corrosivity of the solutions.

In at least one case (NCRW-49), solution age was shown to be a factor in solids formation during the extraction step. In this case, conditions that gave no solids when the dissolved sludge solution was 1 day old did give solids when the solution was 104 days old. In addition, a small volume of a second organic phase was observed in the contact of the aged sludge solution. This observation appears to provide yet another example of changes in zirconium species over time; such changes should be kept in mind even though the plan is to process freshly prepared sludge solutions. The change in tendency to interfacial crud formation on aging was not accompanied by a substantial change in zirconium distribution coefficient; values of 0.22 and 0.26 were measured in the 1-day-aged and 104-day-aged cases, respectively.

Use of oxalate in scrub solutions will lead to its presence in the extraction stages unless the scrub section raffinate is routed elsewhere (e.g., to the extraction section raffinate). Some of the extraction contact tests contained oxalate; there appeared to be little if any effect of this material on the formation of solids during the contact (Table 3.9). However, as has been reported earlier (Swanson 1991), solids did form slowly in the oxalate-containing aqueous phases.

3.4.2 Scrubbing

As was mentioned, the use of oxalate-containing scrub solutions leads to the potential for the formation of oxalate precipitates in the contactor. Such precipitates might not lead to process problems because of their slow formation; however, it is desirable to minimize the formation of these solids.

FIGURE 3.5. Relationship Between Feed Composition and Solids Formation in Extraction Contact

One way of avoiding this problem, of course, is to avoid using oxalate in the scrub solution. Study of alternatives to oxalate was planned for this year, but was not completed.

An alternative way of minimizing the possibility of precipitates forming within the solvent extraction contactor system would be to route the scrub section raffinate directly to waste instead of having it pass through the extraction section (where the zirconium concentration is highest). Such a routing would increase the TRU content of the waste, but not necessarily to an

unacceptable level. For example, if the organic-to-aqueous-phase ratio is 0.33 in the extraction section and 3.0 in the scrub section, and if the distribution coefficient for TRU elements in the first scrub stage is 15 (Swanson 1991), then ~2% (as a first approximation) of the TRU elements would be present in the scrub raffinate. This quantity is low enough that the combined scrub section and extraction section raffinates would qualify as LLW. However, it would appear to be desirable to achieve the lower TRU levels possible by routing the scrub section raffinate through the extraction section, as is currently planned. Thus, further study of the scrub section is indicated.

3.4.3 Stripping

The optimum conditions for stripping the TRU elements from the TRUEX extract (after it has been scrubbed) remain to be determined; this area will be the subject of an in-depth study, for which preparations are in progress at year's end. The main problem is not in finding an effective stripping agent; HEDPA works very well in that regard. The problem is an uncertainty regarding the suitability of the stripped TRU stream as a feed to a vitrification process, because of the potential impacts of the carbon and the phosphorus in HEDPA on the vitrification process and/or product. The planned study will examine lower (than 0.2 M) concentrations of HEDPA (so that carbon and phosphate additions can be minimized), other stripping agents that allow easier destruction of their hydrocarbon content (so that the carbon can be removed before the stream is fed to vitrification), and means of separating (e.g., precipitation or ion exchange) the stripped TRUs from the stripping agent so that only the TRUs are sent to vitrification.

The behavior of uranium in the 0.2 M HEDPA stripping operation was not discussed in the earlier report (Swanson 1991), although pertinent data had been obtained in the ICP analyses that were done primarily to follow the path of zirconium. These data show that uranium is efficiently stripped into 0.2 M HEDPA. Most of these data were obtained at lower organic-to-aqueous phase ratios (O/A) than are of interest from a process standpoint, but good data were obtained under appropriate conditions in one experiment.

In this experiment (NCRW-37), a TRUEX extract (O/A = 0.333) of the dissolved sludge solution was scrubbed three times with 1.5 M HNO_3 + 0.05 M

$\text{H}_2\text{C}_2\text{O}_4$ at $\text{O/A} = 3.0$ and was then stripped twice with 0.2 M HEDPA; the first strip was done at $\text{O/A} = 2.0$, and the second strip was done at $\text{O/A} = 0.333$ (to ensure efficient stripping so that material balances could be established). The first strip step gave a uranium distribution coefficient of 0.14 and removed 78% of the uranium present in the scrubbed organic; two additional steps under the same conditions would give 99% removal of the uranium. Moreover, it is likely that uranium distribution coefficients would be lower in the second and third strips because the HNO_3 concentration would be lower as the extracted HNO_3 is also stripped out of the solvent. Thus, uranium will be stripped along with the TRUs in the current flowsheet rather than going on to the solvent wash step.

3.4.4 Solvent Washing

In many suggested applications of the TRUEX process, it is desirable to achieve high removals of plutonium and americium from the organic phase in the stripping operation so that the solvent wash solution (e.g., sodium carbonate) will meet LLW criteria and can thus be disposed of more economically. However, in the processing sequence currently planned for NCRW sludge, there appears to be little if any incentive for this and, in fact, there might be appreciable advantages to combining the solvent wash solution with the TRU waste stream.

In the currently planned NCRW sludge processing sequence, the two TRU-containing process streams (the undissolved residue that is filtered out prior to solvent extraction and the strip solution from TRUEX) are to be combined and stored until they are fed to a vitrification process. Because this storage is to take place in one of the existing carbon steel tanks, this stream must be adjusted to meet established criteria for feeds to such tanks. These criteria require certain concentrations of hydroxide and nitrite, which are now planned to be achieved by adding sodium hydroxide and sodium nitrite to the waste. The amount of hydroxide required to be added will depend on the acid content of the combined TRU streams as well as on the waste criterion. It is possible that the solvent wash solution could be added to the combined TRU streams without increasing the sodium content of the tank-stored waste by

using the contained sodium carbonate to neutralize part of the acid in the TRU streams. This appears to offer a "free disposal" route for the solvent wash solution.

In addition to the benefit of a "free disposal" route, there is the likelihood of an additional large benefit. This potential benefit is that the need for highly efficient removal of plutonium and americium in the stripping operation is greatly reduced if not eliminated. This could lead to the use of lower concentrations of complexants (or of alternative complexants) in the stripping operation, which, in turn, could lead to the TRU stream providing a more suitable feed to the vitrification process.

A side effect of adding the solvent wash solution to the vitrification feed stream is that such a step would give a lower (perhaps zero) concentration of fission product technetium-99 in the LLW stream. Even though technetium-99 is present at only a low concentration, it is highly mobile in the environment with the result that it can contribute the controlling dose in performance assessment evaluations of the proposed (grout) LLW form. Routing the solvent wash solution, which should contain a large fraction of the technetium that was present in the feed, to the vitrification process could thus provide a public perception benefit.

This concept should be investigated in future studies and considered in future flowsheet modifications.

3.5 OTHER RESULTS

This section discusses results obtained in a variety of areas. It includes discussion of the planning of a special experiment, of the solvent extraction behavior of fluoride through a series of contacts, and of some observations regarding zirconium species that adjust only slowly to changes in their solution environment.

3.5.1 Design Basis Experiment

One of the major activities of the year involved a "design basis experiment" (DBE), which was to involve a demonstration of integrated sludge dissolution and solvent extraction steps. The conditions to be tested in this

experiment largely reflected the status of our knowledge at the end of FY 1989. This was due to a significant delay in the funding of FY 1990 experimental activities and due to time-consuming documentation of the experimental planning and preparation efforts that was required because more stringent quality assurance requirements were placed on this experiment.

The processing steps to be tested in this DBE were to be representative, as best as could be done in simple batch contact experiments, of the conditions resulting from the flowsheet depicted in Figure 3.6. The steps included 1) sludge dissolution, 2) solution clarification (filtration), 3) feed adjustment, 4) extraction, 5) scrubbing (with three different streams), 6) stripping, and 7) solvent washing. The functions of the three different scrub streams were to 1) remove extracted zirconium (and fluoride) with oxalic acid, 2) remove extracted oxalic acid with nitric acid, and 3) remove extracted nitric acid with water.

The NCRW sludge used in this DBE was a composite of the segments taken from Tank 103-AW in 1986. It was dissolved by adding water and nitric acid and stirring for several hours at room temperature. The dissolved sludge solution was clarified by a filter having 0.2- μ m pore size.

The clarified feed solution was to be analyzed and then adjusted (in the initial plan) to a composition of $\sim 1.5 \text{ M HNO}_3 + \sim 0.15 \text{ M zirconium} + \sim 0.01 \text{ M H}_2\text{C}_2\text{O}_4$, which represents a blend of the feed and the three scrub streams shown in Figure 3.6. This adjusted solution was then to be contacted three times with previously washed TRUEX solvent (0.2 M CMPO + 1.4 M TBP in NPH) at an O/A of 0.33. Because of concerns regarding interfacial crud formation (Section 3.4.1), this plan was modified to 0.12 M zirconium and then, when crud was observed in a preliminary test at that concentration, the concentration was further reduced to 0.10 M zirconium.

The organic phase from the first contact was to be scrubbed twice with $1.5 \text{ M HNO}_3 + 0.05 \text{ M H}_2\text{C}_2\text{O}_4$ at O/A = 1.0; these conditions represent a blend of the three scrub streams shown in Figure 3.6. The organic was to then be scrubbed twice with 2.25 M HNO_3 at O/A = 1.5, representing a blend of the second and third scrub streams, and then with water at O/A = 3.0.

FIGURE 3.6. Flowsheet to Have Been Tested in Design Basis Experiment

The scrubbed organic stream was to then be stripped three times with 0.2 M HEDPA at O/A = 3.0 to remove the plutonium and americium. Finally, the stripped organic stream was to be contacted with sodium carbonate solution to remove hydrolytic degradation products.

In spite of all the documented planning and preparation that were involved in this effort, the experiment was not successfully completed because of a human failing--the experimenter spilled a portion of the organic phase during the solvent extraction steps, with the result that there was insufficient material to complete all of the planned steps. Adjustments to the planned steps were made in an effort to obtain adequate alternative data, but the judgement was eventually made that the objectives of a DBE could not be met from these data, and the experiment would have to be repeated in the future.

Because the objectives of the DBE could not be met from this experiment, most of the planned analytical work was not done. However, some valuable data were obtained, many of which were discussed earlier in this report (as NCRW-58). Data on the behavior of fluoride in the solvent extraction steps of this experiment are discussed in the following section.

3.5.2 Fluoride Extraction Behavior

The concentrations of total fluoride found in samples of both phases in each of the solvent extraction contacts of NCRW-58 are shown in Figure 3.7. Also shown in the plot are the total fluoride distribution coefficients; the condition of each contact and the total acid concentrations (including the contribution of hydrolyzable metal ions) are listed below the plot. The acid values could not be corrected for the contribution of hydrolyzable ions because metal ion analytical data were not obtained; however, the acid value listed for contact M is corrected for the contribution of the HEDPA. The shaded symbols represent data that were obtained by material balance rather than by direct analysis.

The distribution coefficient for total fluoride is seen to increase through the scrub and strip steps; values are eventually reached that lead to little removal of fluoride from the organic phase in additional contacts.

Contact	Initial Aqueous	Initial Organic	O/A	H to pH 7	
				Aqueous	Organic
A	0.1 M Zr + 1.4 M H	Fresh	0.33	1.51	0.70
B	From A	Fresh	0.33	1.36	0.61
C	From B	Fresh	0.33	1.15	0.54
D	1.5 M HNO ₃ + 0.05 M H ₂ C ₂ O ₄	From A	1.0	1.60	~0.6
E	1.5 M HNO ₃ + 0.05 M H ₂ C ₂ O ₄	From D	1.0	1.62	0.65
F	2.25 M HNO ₃	From E	1.2	1.79	0.85
G	2.25 M HNO ₃	From F	1.5	2.22	0.87
H	H ₂ O	From G	3.0	1.15	0.54
J	H ₂ O	From H	3.0	0.66	0.33
M	0.2 M HEDPA	From J	0.94	0.21	0.08
N	0.25 M Na ₂ CO ₃	From M	1.0	--	--

39105044.5

FIGURE 3.7. Fluoride Behavior in NCRW-58

However, the carbonate wash contact removed the residual fluoride from the organic phase apparently quantitatively. This fluoride behavior is interesting, but not understood; as was mentioned in an earlier report (Swanson 1991), it may well include effects of extractable zirconium fluoride species.

The amount of fluoride remaining in the organic phase through the scrubbing and stripping operations in NCRW-58 amounted to ~0.06% of that present in the dissolved sludge solution. This is much less than the ~1.3% of the fluoride that was present in the undissolved residue from the dissolution process (Section 3.2.3). Thus, routing of the solvent wash solution to the vitrification process, as suggested in Section 3.4.4, would not significantly increase the fluoride content of the vitrification feed.

3.5.3 Observations of Kinetically Inert Zirconium Species

After determining the ratios of dissolved sludge components that would result by dissolving different sludge strata, (Section 3.1.2) experiments were performed to determine whether stable solutions having these ratios could be prepared at appropriate zirconium concentrations. Such determinations were given a high priority to aid in establishing conditions to be used (by others) in corrosion tests, with the anticipation that they would also be useful in our flowsheet development activities in the areas of feed solution stability and solids formation in solvent extraction steps. This anticipation proved to be correct, but in a largely unexpected way--these experiments served to emphasize the potential problems resulting from kinetically inert (slowly equilibrating) zirconium species in solution.

These initial solution stability studies were done with simulated solutions prepared by mixing the appropriate quantities of stock solutions of nitric acid, hydrofluoric acid, potassium fluoride, sodium nitrate, and zirconyl nitrate. Stock solutions of one batch of zirconyl nitrate were prepared by dissolution in 1) hydrofluoric acid alone and 2) a mixture of nitric and hydrofluoric acids. It soon became apparent that different solution stability (precipitation) results were obtained with the two stock solutions. Mixtures of a given composition were much more likely to yield precipitate when they were made from a 0.4 M $\text{ZrO}(\text{NO}_3)_2$ + 0.8 M HF stock solution than when they were

made from a stock solution containing $0.4 \text{ M ZrO(NO}_3)_2 + 1.5 \text{ M HNO}_3 + 0.8 \text{ M HF}$. This indicated that different zirconium species existed in the two stock solutions, and that these species did not adjust rapidly to changes in their environment.

An even more striking comparison resulted from experiments where solvent extraction contacts were done with feed solutions prepared from the two stock solutions; the feed solution composition used here was $0.14 \text{ M ZrO(NO}_3)_2 + 0.049 \text{ M Al(NO}_3)_3 + 0.53 \text{ M NaNO}_3 + 1.0 \text{ M HNO}_3 + 0.43 \text{ M HF}$. When these (~5 min old) solutions were contacted with TRUEX solvent ($O/A = 0.3$), markedly different behavior was observed. A copious interfacial crud formed in one case (where the stock solution had contained nitrate as well as fluoride), but not in the other. Also, the zirconium distribution coefficients were markedly different in the two cases, 0.047 in the case where the stock solution had contained only hydrofluoric acid and 0.39 in the case where the stock solution contained both nitric and hydrofluoric acids. This latter distribution coefficient is only slightly higher than the values of 0.2 to 0.3 measured with solutions prepared by dissolving actual NCRW sludge.

A few tests were then done with a different batch of zirconyl nitrate (this one from GFS Chemicals), which had been obtained by others for use in the preparation of simulated dissolved sludge solutions for corrosion tests. This material did not dissolve in either 0.8 M HF alone or $0.8 \text{ M HF} + 1.5 \text{ M HNO}_3$ as completely as had the material from the first batch. These solutions were then used in some fluoride analysis tests, which gave yet another example of slowly equilibrating zirconium species.

In these experiments, portions of a $0.005 \text{ M ZrO(NO}_3)_2 + 0.01 \text{ M HF}$ solution (prepared by dilution of a 2-day-old $0.4 \text{ M ZrO(NO}_3)_2 + 0.8 \text{ M HF}$ solution) were spiked into the fluoride analysis medium for measurement of the apparent fluoride concentration after various treatments. (The fluoride analysis medium was TISAB III, a complexant-containing buffer mixture of the Orion Company). Measurements were made at two different spike levels after standing for different times and temperatures. These results are summarized in Table 3.10.

TABLE 3.10. Variation in Apparent Fluoride Concentration with Zirconium Concentration and with Aging of Analytical Dilution

Age of Stock Solution, Days ^(a)	Conditions in Interval Between Dilution and Measurement	Zr in Analytical Mixture, M	Indicated Fluoride, Percent of That Present
13	Brief stand at room temperature	4.6×10^{-4}	48
13		1.8×10^{-5}	66
14	Stand 1 day at room temperature	4.6×10^{-4}	55
14		1.8×10^{-5}	78
7	Stand 1 day at room temperature plus 1 day at -80°C	4.6×10^{-4}	60
7		1.8×10^{-5}	106

(a) Age of the $0.005 \text{ M ZrO}(\text{NO}_3)_2$ solution when portions were spiked into analytical medium.

It is seen that, for a given treatment of the analytical mixture, the indicated fluoride concentration in the stock solution increases with decreasing zirconium concentration in the analytical mixture. This is as would be expected if the complexant in the analytical mixture was not successful in displacing all of the fluoride from the zirconium. However, only in the dilute zirconium case where the analytical mixture had been heated to -80°C was all of the fluoride displaced from the zirconium so it could be detected by the fluoride electrode. This clearly demonstrates the existence of zirconium fluoride complexes (in zirconyl nitrate/hydrofluoric acid mixtures) that adjust only slowly to changes in the surrounding environment.

A similar result was obtained with the $0.4 \text{ M ZrO}(\text{NO}_3)_2 + 0.8 \text{ M HF}$ stock solution that also contained 1.5 M HNO_3 . Dilutions of this stock solution, when heated at -80°C for a day before analysis, indicated fluoride concentrations of 64% and 103% of that actually present at 5×10^{-4} and $2 \times 10^{-5} \text{ M}$ zirconium, respectively.

However, such behavior was not observed in similar tests with actual dissolved NCRW sludge solution (from NCRW-58). Duplicate measurements at both

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