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Pretreatment of Neutralized Cladding Removal Waste (NCRW) Sludge - Results of FY 1991 Studies

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Summary

Neutralized cladding removal waste (NCRW) sludge is a unique waste material that is currently stored in two underground double-shell tanks at the U.S. Department of Energy's Hanford Site. The origins and composition of this waste were described previously by Swanson (1991a, 1991b, 1991c). The NCRW sludge was formed by neutralization of the solution resulting from the chemical decladding of Zircaloy-clad metallic uranium fuel by the Zirflex process. The sludge consists primarily of zirconium and sodium hydroxides and fluorides, along with small amounts of potassium, nitrite, and other nonradioactive materials. The sludge also contains uranium, transuranic (TRU) elements (americium and plutonium), and mixed fission products typical of the nonvolatiles present in irradiated fuel (e.g., ^{137}Cs and ^{90}Sr).

Because of the amount of TRU material present (~ 1000 nCi/g), the NCRW sludge is considered a TRU waste, which must be vitrified for ultimate disposal in a geologic repository. However, the TRU portion of the waste may be separated from the larger amount of bulk waste material (Na and Zr compounds) so that only the smaller TRU portion would require vitrification and geologic disposal. Thus, separation would significantly reduce waste disposal costs. To facilitate the separation of TRU materials, work is underway to develop the transuranic extraction (TRUEX) process. This solvent extraction process, which follows dissolution of the sludge in nitric acid, has been demonstrated to separate a large percentage of the TRU elements from the bulk components of NCRW sludge (Swanson 1991a, 1991b, 1991c).

Earlier studies have identified several potential problems in the TRUEX processing of NCRW sludge, including: 1) potential corrosion of imbedded piping in the facility initially planned for the process, 2) instability of dissolved NCRW solutions towards precipitation, 3) formation of interfacial crud during the TRUEX solvent extraction step, and 4) the amount of phosphorus in the TRU product stream due to the use of a phosphorus-containing stripping agent. The corrosion problem relates to the initial plan of installing the TRUEX process in B Plant on the Hanford Site. But because B Plant is no longer an option, the problem of potential corrosion of the imbedded piping in that facility is no longer a concern. The second and third problems are associated with TRUEX processing of NCRW sludge, while the fourth problem is related to the vitrification of TRU material generated by TRUEX (excessive amounts of phosphorus in the feed to the vitrification plant would cause problems in the plant's operation). These four problems were studied in FY 1991 and the results, presented in this report, indicate that:

- a solution of 2 M HNO_3 at a F/(Zr+Al) ratio of ~2 adequately dissolves washed NCRW sludge; such solutions should not be corrosive towards stainless steel materials such as those found in the imbedded piping in B Plant

- dissolved NCRW sludge solutions obtained by dissolution of washed sludge at low F/(Zr+Al) ratios (~2) are much more stable with respect to precipitation

- interfacial crud in the TRUEX solvent extraction process can be prevented by adjusting the F/(Zr+Al) ratio in the feed solution to greater than 3.75

- the amount of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) needed to strip the TRUs can be greatly decreased, especially if mixed with sodium carbonate.

Because a new pretreatment facility will replace B Plant, the apparent conflict between dissolving the NCRW sludge at a low F/(Zr+Al) ratio and operating the TRUEX process at a high F/(Zr+Al) ratio can be resolved by choosing appropriate alloys for the equipment to be used at various stages of the process. The solutions generated by dissolution of washed NCRW sludge are stable for months, which should be adequate for processing conditions. By use of a combined HEDPA/Na_2CO_3 strip solution, the amount of phosphorus introduced into the vitrification feed by the stripping agent can be lowered to the point where phosphorus is no longer the limiting component in the number of glass canisters required to vitrify the TRU fraction of NCRW sludge.

In addition to addressing the four problem areas discussed above, a study of sludge settling behavior was performed. Settling behavior of the NCRW sludge during sludge washing is important in engineering considerations of how to achieve solid/liquid separations during waste processing. Settling rates were found to be a function of the Zr concentration in the sludge/wash liquid slurry. The settling rate decreased as the concentration of Zr increased.

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Contents

Summary iii

Acknowledgments v

1.0 Introduction 1.1

2.0 Methods and Materials 2.1

2.1 Analytical Methods 2.1

2.2 Sludge Washing 2.1

2.3 Sludge Dissolution 2.1

2.3.1 Unwashed Sludges 2.3

2.3.2 Washed Sludges 2.3

2.4 TRUEX Contacts 2.5

2.5 Sludge Settling 2.5

2.5.1 Settling Studies With Synthetic NCRW Sludge 2.5

2.5.2 Settling Studies of Actual NCRW Sludge 2.6

3.0 Results and Discussion 3.1

3.1 Sludge Washing 3.1

3.2 Sludge Dissolution 3.1

3.2.1 Adding Al Ion to Complex Fluoride 3.4

3.2.2 Removal of Fluoride by Washing 3.4

3.3 Sludge Solution Stability 3.7

3.4 TRUEX Solvent Extraction 3.9

3.4.1 Interfacial Crud Formation 3.9

3.4.2 Distribution of Transuranic Elements and Zr 3.13

3.4.3 Stripping 3.14

3.5 NCRW Pretreatment Flowsheet 3.23

3.6 Sludge Settling 3.25

3.6.1 Settling Studies Conducted With Synthetic NCRW Sludge 3.25

3.6.2 Settling Studies Conducted With Actual NCRW Sludge 3.33

3.7 Conclusion 3.36

4.0 References 4.1

Figures

3.1 Observations of Interfacial Crud Formation in the TRUEX Solvent Extraction Step 3.14

3.2 Distribution of Zr as a Function of F/(Zr+Al) 3.16

3.3 Distribution of Am(III) and Pu(IV) Between Aqueous HEDPA Solutions and the TRUEX Process Solvent 3.17

3.4 Distribution of Am(III) Between Aqueous HEDPA and the TRUEX Process Solvent 3.18

3.5 The Empirical Constant, k, as a Function of HEDPA Concentration 3.19

3.6 The Distribution of HNO_3 in the TRUEX Process 3.20

3.7 Removal of Am(III) from TRUEX Process Solvent With HEDPA as Calculated by Equation 3 . . . . . 3.21

3.8 Flowsheet for the Pretreatment of NCRW Sludge 3.24

3.9 Settling Comparison of Synthetic Sludge Contained in Small Vials and a Large Graduated Cylinder 3.26

3.10 Sludge Settling Data for Vessels Ranging in Diameter From 1.6 to 12.3 cm 3.27

3.11 Sludge Settling Data Fit to a First-Order Rate Equation 3.29

3.12 Zr Concentration in the Slurry as a Function of Settling Time 3.30

3.13 Settling of $Zr(OH)_4$ at Different Initial Concentrations 3.31

3.14 Settling Data at Different $Zr(OH)_4$ Ages 3.33

3.15 Sludge Settling Data for Three Portions of Actual NCRW Sludge 3.35

3.16 Sludge Settling Data for Actual NCRW Sludge With and Without Added Fe(II) 3.36

Tables

2.1 NCRW Sludge Samples and Settling Solutions 2.2

2.2 Origin and Weight of NCRW Sludge Samples 2.4

3.1 Summarized Results of Washed NCRW Sludge Dissolution 3.2

3.2 Variables Affecting NCRW Sludge Solution Stability 3.3

3.3 Summary of NCRW Sludge Dissolution in the Presence of Al 3.5

3.4 Summary of Dissolution Experiment 55, Portion 55A 3.6

3.5 Summary of Interfacial Crud Observations for TRUEX Solvent Extraction Contacts for Dissolved NCRW Solutions 3.10

3.6 Interfacial Crud Formation as a Function of Time 3.11

3.7 Summary of TRU and Zr Distribution Coefficients in TRUEX Solvent Extraction Contacts for Dissolved NCRW Solutions 3.15

3.8 Synthetic Sludge Settling Behavior Over a Period of Eight Days 3.34

1.0 Introduction

At the request of Westinghouse Hanford Company, Pacific Northwest Laboratory (PNL)[a] is investigating ways to pretreat Hanford's neutralized cladding removal waste (NCRW). Because of the amount of TRU material present in the NCRW (~ 1000 nCi/g), the sludge is considered a TRU waste, which must be vitrified for ultimate disposal in a geologic repository, unless the TRU materials are removed. Since vitrification and geologic disposal are very expensive, pretreating NCRW to partition the waste into a relatively large low-level waste (LLW) fraction (which can be disposed of inexpensively) and a small high-level waste (HLW) or TRU fraction can reduce costs substantially.

Previous studies indicated that the most promising method of pretreating NCRW involves dissolution of the sludge in nitric acid followed by TRU separation using the transuranic extraction (TRUEX) process (Swanson 1991a). Thus, efforts in FY 1991 focused on developing this pretreatment method. The pretreatment process as currently envisioned involves the following steps: sludge washing, sludge dissolution (in HNO_3/HF), TRUEX solvent extraction, scrubbing, stripping, and solvent washing. All aspects of the process, except solvent washing, were investigated in FY 1991. The results of these investigations are presented in this paper. Also presented are the results of a study of the settling behavior of the NCRW sludge. Settling is important regarding solid/liquid separations during the sludge washing step.

The following major problems were addressed in the FY 1991 studies:

- corrosion of imbedded piping in the initially proposed processing facility (B-plant) due to the nature of the NCRW process solutions
- precipitation from dissolved sludge solutions
- interfacial crud formation in the TRUEX solvent extraction step
- excessive amounts of phosphorus in the strip solution.

Major advances toward solving all four problems were achieved in FY 1991.

Following the Introduction, this report is organized in two major sections: Section 2, Methods and Materials; and Section 3, Results and Discussion. Both Section 2 and 3 are organized to discuss the investigations in the context of the waste pretreatment process.

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2.0 Methods and Materials

This section describes the analytical methods and materials that were used in these studies. Specific methods and materials used for sludge settling, sludge washing, and sludge dissolution are discussed in Sections 2.2, 2.3, and 2.4, respectively. Methods used for TRUEX contacts are discussed in Section 2.5.

2.1 Analytical Methods

Metal ion concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP); fluoride ion was determined potentiometrically using a fluoride-selective electrode; acidity was determined by potentiometric titration with standard NaOH. These analytical methods were described previously by Swanson (1991b).

Total alpha analyses were performed on 0.1-mL dried mounts of appropriate sample dilutions. Determination of the ^{137}Cs concentration in selected solutions was achieved by gamma-counting techniques using a well-type sodium iodide detector. The ^{137}Cs "standards" were prepared from a solution containing primarily ^{137}Cs that had recently been analyzed by gamma-energy analysis.[a] ^{241}Am and Pu tracers were used in some of the TRUEX stripping experiments; these were determined by liquid scintillation counting techniques using OPTI-FLUOR™ liquid scintillation cocktail.[b]

2.2 Sludge Washing

NCRW sludges from Experiments 55, 66, 67, 69, and 70 were washed with water at ambient temperature according to the scheme outlined in Table 2.1. Each wash cycle involved the following steps: 1) mixing sludge and water, 2) centrifuging, and 3) decanting the wash solution.

2.3 Sludge Dissolution

Sludge dissolution experiments were performed with unwashed and washed NCRW sludges. Procedures for dissolving unwashed NCRW sludge samples were similar to those reported earlier (Swanson 1991b) in which the sludge was slurried in water, and concentrated HNO_3 was added to obtain a final HNO_3 concentration of 1 to 2 M. The quantity of fluoride ion already present in the unwashed sludge is sufficient for adequate dissolution to occur. However, fluoride ion must be added to washed NCRW sludge to achieve good dissolution; thus, the washed sludge samples were dissolved in HNO_3/HF mixtures.

(a) This stock solution contained 0.582 μCi/mL ^{137}Cs and 0.00133 μCi/mL ^{60}Co. No other gamma emitters were detected.

(b) Manufactured by Packard Instrument Co., Downers Grove, Illinois.

Table 2.1. NCRW Sludge Samples and Settling Solutions

				Wash 1			Wash 2			Wash 3			Wash 4		
Experiment	Segment/ Tank	Core Date	Dry Sludge Weight, g	H_2O[a] In, mL	Solution[b] Out, mL	Contact[c] Time	H_2O In, mL	Solution Out, mL	Contact Time	H_2O In, mL	Solution Out, mL	Contact Time	H_2O In, mL	Solution Out, mL	Contact Time
55	4/105-AW	1986	3.10	16.3	8.7	6 days	10	14.6	10 min	10	11.5	10 min	10	11.7	10 min
66	3A/103-AW	1986	5.16	10	8	85 min	10	9.5	10 min	10	10.9	10 min	10	10.7	10 min
67	7A/103-AW	1986	6.43	10	8.1	95 min	10	10.5	15 min	10	10.6	15 min	10	10.1	15 min
69	3A/103-AW	1986	2.07	11	9.1	3 days	9.1	8.8	1 day	8.8	8.4	1 day			
70	3A/103-AW	1986	2.05	11	9.9	3 days	9.9[d]	9.7	1 day	9.7	9.6	1 day			

(a) Volume (in mL) of water added to wash the sludge.
(b) Volume (in mL) of wash solution decanted from vial.
(c) Total time wash solution contacted solids.
(d) 0.025 M Fe^{3+}.

2.3.1 Unwashed Sludges

Unwashed sludges were dissolved in Experiments 60 and 63. Tank supernatant solution was used in these experiments to simulate the case in which supernatant solution would be used in sludge retrieval operations. In Experiment 60, the sludge/supernate slurry was divided into three portions: 60A, 60B, and 60C. Portion 60A contained 2.22 g of centrifuged sludge and 4.30 g of tank supernate. Water (8 mL) was added, and the mixture was stirred. Concentrated HNO_3 was added slowly while the pH of the mixture was monitored. Bubbling was observed to occur at pH 4.5, which was presumably due to neutralization of carbonate. After 0.9 mL of concentrated HNO_3 had been added, the pH of the mixture was 0.8. At this point, an additional 1.15 mL of concentrated HNO_3 was added, and the mixture was stirred for 2 h at ambient temperature. The dissolved sludge solution was clarified by filtration using a 0.2-μm filter membrane. The remaining solids were washed with water, then dissolved in 1.1 M HCl/0.35 M HF at 100°C for analysis.

Portions 60B and 60C were combined and dissolved in a similar manner; these portions contained 4.23 g of sludge plus 8.18 g supernate. A 4-mL portion of water was added followed by 1.92 mL of concentrated HNO_3. As with 60A, the mixture was stirred for 2 h, then the dissolved sludge solution was clarified by filtration.

In Experiment 63, water (10 mL) was added to a mixture of 7.076 g of NCRW sludge plus 4.933 g of tank supernate. Concentrated HNO_3 (1.875 mL) was added slowly until pH reached 1. An additional 1.72 mL of concentrated HNO_3 was added, followed by water to bring the total volume to 27 mL. The sample was stirred for 2 h at ambient temperature, and the solution was filtered. The residual solids were washed with four 5-mL portions of water and were dissolved for ICP analysis in 1.1 M HCl/0.4 M HF that was heated to 100°C for ~3 h.

2.3.2 Washed Sludges

Washed sludges were dissolved in Experiments 55, 66, 67, and 69. The origins and weights (before washing) of each sludge samples used are listed in Table 2.2. In Experiment 55, the washed sludge was divided into three portions: 55A, 55B, and 55C. Portion 55A contained 33.7% of the washed sludge originally present and approximately 2 mL of water. To this portion of washed sludge, 1 mL of concentrated HNO_3 was added, then water was added to bring the volume to 8 mL ([HNO_3] $\approx$2 M). The sludge was stirred for 24 h, and a 0.5-mL sample of the slurry was removed for analysis. Then, 10 M HF was added in three successive increments of 0.158, 0.057, and 0.064 mL; between each addition of HF, the mixture was stirred overnight, and a 0.5-mL sample was removed for analysis. The solutions were analyzed by ICP. The final dissolved sludge solution was clarified by filtration. The undissolved residue was washed with three 5-mL portions of water and dissolved for ICP analysis in HCl and HF (1 mL 12 M and 0.2 mL 10 M, respectively), which was heated to 100°C for 25 min.

Table 2.2. Origin and Weight of NCRW Sludge Samples

Experiment	Tank	Core Date	Segment	Sludge Weight, g	Solution Added
55	105-AW	1986	4	3.10 (dry)	16 mL H_2O
60	105-AW	1990	3	10.18 (wet)	10.59 g tank supernate
63	105-AW	1990	3	7.08 (wet)	12.10 g tank supernate
69	103-AW	1986	3A	2.07 (dry)	9.1 mL H_2O
70	103-AW	1986	3A	2.05 (dry)	9.9 mL 0.025 M $Fe(NO_2)_3$

Portion 55B contained 33.2% of the washed sludge originally present and approximately 2 mL water. The dissolver mixture was stirred, then 0.64 mL of concentrated HNO_3 and 0.16 mL of 10 M HF were added. The volume was increased to 5 mL by adding water. After stirring for 1 h at ambient temperature, the solution was filtered. The remaining solids were washed with three 5-mL portions of water and dissolved for analysis in 15 mL of 0.4 M HCl/0.13 M HF, which was heated to 100°C for 1 h.

Portion 55C contained 33.1% of the washed sludge originally present and approximately 2 mL water. The dissolution process for this portion of sludge was identical to that for 55B, except that the dissolver mixture here was heated at 100°C for 1 h.

In Experiment 66, the washed sludge was stirred with 10 mL of water, then 3.4 mL of concentrated HNO_3 and 0.55 mL of 10 M HF were added. The mixture was stirred for 30 min and transferred to a larger vial. The mixture was then diluted to 27 mL with water, stirred another 30 min, and centrifuged. A large portion of the sludge had not dissolved. Another 0.55 mL of 10 M HF was added, and the mixture was stirred for 40 min. After centrifuging, the dissolved sludge solution was decanted. The undissolved residue was washed with three 5-mL portions of water and dissolved for analysis by heating to 100°C for 1.3 h in 20 mL of 2.9 M HNO_3/0.5 M HF.

In Experiment 67, the washed sludge was stirred with 35 mL of water, and 1 mL of 10 M HF and 6 mL of concentrated HNO_3 were added. Most of the sludge dissolved immediately. The solution was diluted to 45 mL with water, stirred for 2 h, then filtered. The undissolved residue was washed with three 5-mL portions of water and dissolved for analysis by heating at 100°C for 50 min in 13.6 mL 0.9 M HCl/0.15 M HF.

In Experiment 69, the washed sludge was diluted to 11 mL with water, then 1.4 mL concentrated HNO_3 and 0.22 mL of 10 M HF were added. This mixture was stirred for 2 h, then centrifuged. The solution was decanted, and the residue was washed with water and dissolved in 16.5 mL of 0.73 M HCl/0.24 M HF for analysis.

2.4 TRUEX Contacts

Batch TRUEX solvent extraction experiments were performed using small vials. Before the TRUEX solvent (0.2 M CMPO + 1.4 M TBP in NPH) was used, it was washed three times with 1/3 volume of 0.25 M Na_2CO_3. In some cases, the carbonate-washed TRUEX solvent was passed through a column of activated alumina (La Roche A-204-4 activated alumina with 4.6% Na_2O) to further remove acidic impurities (Mailen and Mattingly 1990). Contacts were effected by mixing an appropriate aqueous solution with an appropriate volume of TRUEX solvent for 30 to 60 s. The solutions were mixed either by shaking or with a vortex mixer. After mixing, the vials were centrifuged for 1 min to ensure complete phase separation. For those cases in which the phase disengagement time was of interest, the phases were allowed to separate by gravity before centrifugation.

2.5 Sludge Settling

The settling behavior of NCRW sludge during sludge washing operations is important in solid/liquid separations that must be performed during the sludge washing procedure. For this reason, a series of investigations was performed to determine the sludge settling rate under various conditions.

2.5.1 Settling Studies With Synthetic NCRW Sludge

Synthetic NCRW sludge was prepared in a manner simulating the formation of actual NCRW, by adding an ammonium fluorozirconate solution (prepared by dissolving Zircaloy-2 in an ammonium fluoride plus ammonium nitrate solution) to a sodium hydroxide solution. The resulting solids were washed repeatedly with water to remove (most of) the sodium, fluoride, and free hydroxide ions. During this washing process, the settling rates of these solids were investigated under a variety of conditions.

In a typical laboratory preparation, 130 g NaOH was first dissolved in 270 mL H_2O, and this mixture was cooled to ~30°C before addition of the fluorozirconate solution. The composition of the fluorozirconate solution was 0.48 M $(NH_4)_2ZrF_6$ + 0.9 M NH_4F + 0.07 M NH_4NO_3; 700 mL of this solution was gradually stirred into the primary mixture. The maximum observed temperature was ~40°C.

Based on the equations

$$(NH_4)_2ZrF_6 + 6\ NaOH = Zr(OH)_4 + 2\ NH_4OH + 6\ NaF \quad (1)$$

$$NH_4F + NaOH = NH_4OH + NaF \quad (2)$$

the resulting ~ 1 L of slurry contained 0.34 M $Zr(OH)_4$, 2.65 M NaF, 1.31 M NH_4OH, and 0.6 M NaOH. This mixture was stirred for ~2 h and then diluted with water to increase the volume to 2 L. The resulting mixture provided the initial slurry for these settling studies. Because of volatilization, the NH_4OH concentration in the slurry was undoubtedly lower than the concentration described above. Volatilization was probably substantial during the initial mixing step and probably continued gradually over the period covered by the settling tests.

Solution compositions during the slurry washing steps were estimated from the amounts of materials added and the volume measurements. For these estimations it was assumed 1) the solubility of NaF is 1 M (solid NaF would be expected only before the first wash step), and 2) the volume occupied by the solid particles themselves was negligible. The fluoride content of the final wash solution was in good agreement with the value estimated using Equations 1 and 2, thus verifying these assumptions.

The settling measurements were taken by stirring the sludge and wash solution until a homogeneous slurry was obtained. The stirring was then discontinued, and the sludge was allowed to settle. Depending upon the diameter of each vessel (ranging from 1.5 to 12.3 cm), either the sludge volume (when graduated cylinders or beakers were used) or the sludge height (when unmarked vials were used) was measured over time. In the cases where sludge volume was measured, the sludge height could be calculated from the known diameter of the vessels.

2.5.2 Settling Studies of Actual NCRW Sludge

Sludge settling studies with actual NCRW were performed by adding water or tank supernate to the sludge and stirring for at least 1 h with a magnetic stirrer. After stirring was stopped, the sludge was allowed to settle. The height of the sludge was periodically measured with a ruler. Each measurement was taken at the same location in each vial; the cross-sectional area of the vials was 800 mm^2.

The samples of actual NCRW sludge used in the settling experiments are listed in Table 2.2 along with the liquid phase added to slurry the sludge. In Experiments 69 and 70, the settling measurements were taken during the second and third wash cycles (see Table 2.1).

3.0 Results and Discussion

3.1 Sludge Washing

Sludge washing experiments were conducted using several different portions of NCRW sludge. The samples were washed with water as described in Table 2.1. For Experiments 55, 66, and 67, the sludge samples were washed four times, samples for Experiments 69 and 70 were washed three times.

The major sludge components identified in the sludge wash solutions are included in Table 3.1. According to these data, significant amounts of Cr, Na, and Si were removed from NCRW sludge when the samples were washed with water. In cases where P had been present in the sludge, all of the P was removed by water washing.[a] Most of the fluoride was also removed by water washing as evidenced by the fact that the fluoride content of the dissolved sludge solutions correlated well with the amount of HF added during the dissolution process (see Table 3.2). The behavior of Al varied from segment to segment. The Al present in upper layers of the sludge (from both Tanks 103-AW and 105-AW) appeared to be in a form that was predominantly insoluble in water (Experiments 55B, 55C, 66, and 69), whereas towards the bottom of Tank 103-AW the Al was more soluble (Experiment 67).

Radioanalytical data obtained on the wash solutions from Experiment 55 indicated that the wash solutions do not constitute a TRU waste. The TRU content of the first wash solution from this experiment was found to contain 0.02 nCi alpha/mL; TRU contents of subsequent washes were below detection limit.

Analysis of the wash, dissolved sludge solutions, and residual solids in Experiment 67 indicated that 98.2% of the ^{137}Cs in the sludge was removed to the wash solutions.

3.2 Sludge Dissolution

Because of concerns about the corrosivity of NCRW process solutions toward the imbedded piping in B-plant, two methods were investigated to reduce free fluoride concentrations in dissolved NCRW sludge solutions. In the first method, Experiment 61A, Al ion was added to complex fluoride, and in the second method, Experiment 55A, sludges were dissolved that had previously been washed to remove fluoride (see Section 3.1). Both methods were successful from a dissolution standpoint, but

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(a) This observation appears to contrast with what was observed previously in the acid dissolution of an unwashed composite NCRW sludge (103-AW, 1986), in which 43% of the phosphorus was found in the undissolved residue (Swanson 1991b). It is not known whether phosphorus could have been removed from that composite by water washing, or whether the composite contained phosphorus in a different form than was present in the individual segments used here. The concentration of phosphorus in the composite was ~2-fold greater than the maximum found here.

Table 3.1. Summarized Results of Washed NCRW Sludge Dissolution

Experiment No.	Segment	Source of Components	Sludge Components								
			Al	Cr	Fe	Na	P	Si	U	Zr	F/(Zr+Al)[1]
55B	4	% in water wash	5.7	43	0.3	90.1	100	68.5	0	0.1	
	105-AW	% in acid dissolution	94.4	57	89.8	9.9	0	27.8	100	92.9	1.3
	1986	% in residue	0	0	9.9	0	0	3.7	0	7	
		g/g in dry sludge	0.0021	0.0001	0.0005	0.135	0.0012	0.0311	0.0047	0.113	
55C	4	% in water wash	5.9	37.3	0.2	89.8	100	75.4	0	0.1	
	105-AW	% in acid dissolution	94.1	62.7	92.2	10.1	0	14.8	100.0	94.5	1.5
	1986	% in residue	0	0	7.7	0.1	0	9.8	0	5.4	
		g/g in dry sludge									
66	3A	% in water wash	21.5	57.7	3.7	91.5	–	59.2	0	0	
	103-AW	% in acid dissolution	64.1	42.3	83.2	8.4	–	25.7	80.3	91.9	2.3
	1986	% in residue	14.4	0	13.3	0.1	–	15.1	19.7	8.1	
		g/g in moist sludge	0.0004	0.0001	0.0003	0.101	0	0.0114	0.0098	0.093	
67	7A	% in water wash	42.7	53.2	0.7	81.4	–	60.3	0	0	
	1030-AW	% in acid dissolution	56.3	46.8	98.3	18.6	–	34.4	100	99.5	1.8
	1986	% in residue	1	0	1	0	–	5.3	0	0.5	
		g/g in moist sludge	0.0019	0.0003	0.0009	0.183	0	0.0078	0.0132	0.121	
69	3A	% in water wash	6.1	65.2	1.9	93.4	–	65.9	0	0.1	
	103-AW	% in acid dissolution	71	34.8	47	6.4	–	15	100	75.3	1.3
	1986	% in residue	22.9	0	51.1	0.2	–	19.1	0	24.6	
		g/g in moist sludge	0.0003	0.0001	0.0003	0.098	0	0.0137	0.0049	0.086	

(a) F/(Zr+Al) found in the dissolved sludge solution (see Table 3.4).

Table 3.2. Variables Affecting NCRW Sludge Solution Stability

Experiment	Tank/Segment (year)	Concentration, M/L								Days Stable[d]	
		[Al]	[Na]	[Si]	[Zr]	[F], found[a]	[F], expected[b]	F/(Zr+Al)	$[H^+]$[c]	Minimum	Maximum
55A	105-AW/4 (1986)	0.011	0.063	0.069	0.13	0.35	0.38	2.5	1.8	225	–
55B[e]	105-AW/4 (1986)	0.012	0.093	0.054	0.18	0.26	0.32	1.4	1.9	not available	
55B[f]		0.012	0.105	0.002	0.2	–	–		–	<1	
55C	105-AW/4 (1986)	0.011	0.092	0.024	0.17	0.24 (0.27)	0.32	1.5	1.7	<1	
60A	105-AW/3 (1990)	0.015	1.75	0.015	0.13	0.29 (0.30)	–	2.1	1.2	2	22
60B	105-AW/3 (1990)	0.020	1.08	0.020	0.12	0.31	–	2.2	0.1[g]	–	6
60B-3		0.017	0.91	0.017	0.1		0.32	2.7	1.2[h]	8	–
60B-4		0.017	0.91	0.017	0.1		0.36	3.1	1.1[h]	8	–
60B-5		0.017	0.91	0.017	0.1		0.4	3.4	1.1[h]	1	4
60B-6		0.017	0.91	0.017	0.1		0.44	3.8	1.1[h]	0	–
63B	105-AW/3 (1990)	0.017	0.95	0.017	0.17	0.36	–	1.9	0.9	2	–
63B-3		0.014	0.77	0.018	0.14		0.45	2.9	1.2	3	6
63B-4		0.014	0.77	0.018	0.14		0.51	3.3	1.2	6	250
63B-5		0.014	0.78	0.019	0.14		0.56	3.6	1.2	6[i]	250
63B-6		0.014	0.78	0.020	0.14		0.62	4.0	1.2	–	1
63B-7		0.015	0.81	0.025	0.15		0.67	4.1	1.0	–	1
63B-8[j]		0.014	0.79	0.019	0.14		0.45	2.9	1.0	1	2
63B-9[k]		0.007	0.36	0.008	0.064		0.2	2.8	0.6	250	–
66	103-AW/3A (1986)	0.002	0.065	0.018	0.16	0.26 (0.37)	0.4		2.3	1.7	534
67	103-AW/7A (1986)	0.006	0.204	0.013	0.18	0.27 (0.34)	0.22	1.8	1.7	172	–
69	103-AW/3A (1986)	0.001	0.046	0.011	0.12	0.13 (0.16)	0.17	1.3	1.5	151	–

(a) Values shown in parentheses were obtained after heating the fluoride analyte solution overnight at 80°C.
(b) Expected molar concentration of fluoride ion based on the amount of HF added during dissolution.
(c) Corrected for hydrolysis of the metal ions present in the solutions; $[H^+] = [H^+]total-2[Zr]-3\{[Al]+[Cr]+Fe]\}$; $[H^+]$ total was determined from the amount of NaOH needed to reach pH = 7.
(d) Solution stability was assessed by drawing the solution into a clear glass pipet and checking for precipitate.
(e) Before heating.
(f) After heating at 100°C for 20 min.
(g) The acid content of this solution was found to be much less than expected based on the dissolution 63A.
(h) Solution not titrated. $[H^+]$ was determined from the amount of solution 60B ($[H^+] = 0.1$ M) and concentrated HNO_3 used to prepare this solution.
(i) A transient precipitate was observed in the 2-day-old dissolved sludge solution.
(j) This solution also contained 0.14 M oxalic acid.
(k) This solution also contained 0.06 tetrahydrofuran tetracarboxylic acid.

both also led to formation of interfacial crud in the TRUEX solvent extraction step (see Section 3.4.1). The method involving dissolution of washed sludges appeared to be preferable, primarily because crud formation could more easily be avoided.

3.2.1 Adding Al Ion to Complex Fluoride

The effect of adding Al to control corrosion in the dissolution process was explored in Experiment 61A. The sludge used in this experiment was taken from a composite of segments from Tank 103-AW (1986), which had dried while standing. Half of a slurry containing 1.49 g of the dried composite sludge and 7.2 g of water was mixed for 4 h and divided in half. After the solids in the first half had settled overnight, the supernatant solution was sampled (0.2 mL) for nitrite and ICP analyses (the second half was set aside).

In the sludge dissolution step, the slurry was added dropwise to 4.07 mL of 4.5 M HNO_3 + 0.24 M aluminum nitrate nonahydrate (ANN). The operation proceeded smoothly in spite of some excessive splattering of solution when the slurry was added too rapidly. The mixture was stirred for 2 h and then clarified by filtration. The residue was rinsed with water and dissolved for ICP analysis.

The results from the ICP analyses of the leach and dissolution samples from Experiment 61A are summarized in Table 3.3. The percentages of the elements found in the undissolved residue from the HNO_3 + ANN dissolution step are essentially identical (except in the cases of B and Si) to those found when another portion of this composite sludge was dissolved in HNO_3 alone (Swanson 1991b).

The clarified dissolved sludge solution from Experiment 61A contained 0.14 M Zr + 0.16 M Al + 0.95 M Na. Titration to pH of 7 gave an "overall acidity" of 1.98 M; correction for the (assumed) hydrolysis of Zr and Al gave a "free acidity" of 1.2 M. No fluoride analyses were performed on this solution; however, a fluoride concentration of approximately 0.51 M was estimated assuming a F/Zr ratio of 3.65, as was found in other experiments with this composite sludge sample.

The results of Experiment 61A indicated that added Al does not affect the NCRW sludge dissolution process. However, because of the potential for interfacial crud formation in the TRUEX solvent extraction process (see Section 3.4.1), adding Al to the dissolved sludge solution is not suitable for controlling corrosion in the NCRW sludge dissolution step.

3.2.2 Removal of Fluoride by Washing

The second method of reducing the free fluoride concentration to decrease corrosion rates, removal of fluoride by sludge washing before dissolution, also gave good dissolution results. In Experiment 55A, a portion of washed NCRW sludge was treated with 1.8 M HNO_3 plus increasing amounts of HF. The results are summarized in Table 3.4. The amount of Zr in solution increased 44% upon the addition of one molar equivalent of HF. Subsequent addition of HF resulted in only modest increases in Zr dissolution.

Table 3.3. Summary of NCRW Sludge Dissolution in the Presence of Al

Steps	Elements, g/g of Sludge									
	Al	B	Ca	Cr	Fe	K	Na	P	U	Zr
A: Slurry Supernate[a]	3.5×10^{-5}	2.6×10^{-5}	9.5×10^{-5}	1.1×10^{-3}	7.3×10^{-5}	2.4×10^{-2}	1.8×10^{-1}	–	1.2×10^{-3}	6.3×10^{-5}
B: Dissolved Sludge	–[b]	7.8×10^{-5}	5.7×10^{-4}	3.5×10^{-3}	7.2×10^{-4}	3.9×10^{-2}	2.2×10^{-1}	7.6×10^{-4}	1.3×10^{-2}	1.3×10^{-1}
C: Wash	–[b]	7.4×10^{-6}	1.0×10^{-4}	2.9×10^{-4}	6.6×10^{-5}	3.6×10^{-3}	2.0×10^{-2}	8.4×10^{-5}	1.2×10^{-3}	1.2×10^{-2}
D: Washed Residue	3.8×10^{-3}	4.7×10^{-6}	2.0×10^{-5}	1.4×10^{-4}	5.2×10^{-5}	6.7×10^{-5}	2.5×10^{-4}	1.0×10^{-3}	–	5.3×10^{-3}
B+C+D: Total	–[b]	9.0×10^{-5}	6.9×10^{-4}	4.0×10^{-3}	8.4×10^{-4}	4.2×10^{-2}	2.4×10^{-1}	1.9×10^{-3}	1.4×10^{-2}	1.5×10^{-1}
% of Total										
in Supernate	0.2[c]	29	14	27	8.7	57	80	–	8.3	0.04
in Residue	24[c]	5.2	2.9	3.7	6.2	0.2	0.1	56	–	3.6

(a) 4.8 H_2O g dry sludge.
(b) Meaningless because Al was added to the dissolvent.
(c) Based on Al content found in another portion of this sludge composite (Swanson 1991b).

Table 3.4. Summary of Dissolution Experiment 55, Portion 55A

10 M HF Added, mL	Components, M								
	Al	Ca	Na	P	Si	U	Zr	F^-	H^+
0	1.03×10^{-2}	2.16×10^{-3}	6.06×10^{-2}	3.24×10^{-3}	8.57×10^{-2}	3.88×10^{-3}	8.57×10^{-2}		
0.158	1.05×10^{-2}	2.36×10^{-3}	6.23×10^{-2}	3.24×10^{-3}	6.50×10^{-2}	4.31×10^{-3}	1.24×10^{-1}	0	
0.215	1.05×10^{-2}	2.36×10^{-3}	6.15×10^{-2}	3.24×10^{-3}	6.00×10^{-2}	4.22×10^{-3}	1.27×10^{-1}	0.21[a]	
0.279	1.07×10^{-2}	2.66×10^{-3}	6.32×10^{-2}	3.89×10^{-3}	6.93×10^{-2}	4.22×10^{-3}	1.30×10^{-1}	0.35[b]	1.81[c]

(a) $[F^-]$ calculated from the amount of 10 M HF added.
(b) This is the value found experimentally; the $[F^-]$ calculated from the amount of 10 M HF added was 0.38.
(c) Free $[H^+]$ was calculated by assuming that the hydrolysis of Zr contributes two hydrogen ions per mole of Zr, and that the hydrolyses of Al, Cr, and Fe each contribute three hydrogen ions.

Several other experiments were conducted in which washed NCRW sludge was dissolved in HNO_3/HF. The results are summarized in Table 3.1. In each case, the washed sludge (see Table 2.1) was slurried with water, and concentrated HNO_3 was added to reach 2 M HNO_3; HF was then added to achieve the desired F/(Zr+Al) ratio. After it was stirred for several hours at ambient temperature, the dissolved sludge solution was clarified by filtration, and the remaining solids were dissolved in HCl/HF for analysis.

The F/(Zr+Al) ratios in these experiments were significantly less than previously encountered using composite sludge from the 1986 sampling of Tank 103-AW [F/(Zr+Al) ratio was 3.65 for such sludge samples], yet good dissolution of the sludge was achieved in each case. For Experiments 55B, 55C, and 67, greater than 90% of the Zr dissolved even though the F/(Zr+Al) ratio was less than 2. In Experiment 69, only 75.3% of the Zr dissolved when the F/(Zr+Al) ratio was 1.3; however, when a portion of NCRW sludge taken from the same segment was dissolved at F/(Zr+Al) = 2.3, 91.9% of the Zr dissolved (Experiment 66). Thus, the major portion of the Zr in these NCRW sludge samples can be dissolved at F/(Zr+Al) ≤ 2. Such solutions should be relatively noncorrosive to the imbedded piping in B Plant (Barker, Schwenk, and Divine 1990; Barker, Swanson, and Lumetta 1991).[a] The composition of the undissolved solids was observed to vary widely, indicating that the type of residue encountered in the process will depend on the strata of NCRW sludge being processed.

Brown fumes did not evolve during dissolution of washed NCRW sludges, indicating that NO_x did not form. Thus, the removal of nitrite ion before acid dissolution is a major advantage of sludge washing. Also, because most of the carbonate ion and hydroxide ion were removed from the sludge during washing, no splattering occurred during the acid dissolution of washed NCRW sludges.

It appears from these experiments that the desirable method of dissolving NCRW sludge for TRUEX processing is to first wash the sludge with water (or dilute NaOH), then dissolve the sludge in HNO_3/HF at a F/(Zr+Al) ratio of 2. This approach is preferable to that in which Al is added to control corrosion because 1) less fluoride must be added to the TRUEX feed to avoid interfacial crud formation, 2) there is less chance that solids will form upon storage of the dissolved sludge solution (see Section 3.3), and 3) NO_2^- is also removed (thus, eliminating NO_x release during dissolution).

3.3 Sludge Solution Stability

Previous investigations of NCRW sludge dissolution revealed a wide variation in the stability of dissolved sludge solutions towards precipitation. Therefore, a systematic study was undertaken to identify the variables that affect NCRW sludge solution stability. The results of this study are summarized in Table 3.2. The following general conclusions can be made:

(a) At the time of writing, corrosion to the imbedded piping in B-Plant was no longer considered an issue due to a decision not to use this plant for tank waste pretreatment.

- For a given waste sample, solution stability decreases with increasing fluoride concentration; however, if the F/(Zr+Al) ratio is too low, precipitation may also occur.

- Sludge washing before dissolution improves solution stability.

- Heating dissolved NCRW solutions promotes precipitation.

The first conclusion is illustrated best in Experiments 60 and 63. In Experiment 60, four identical solutions (Experiments 60B-3 to 60B-6) differing only in concentration of fluoride ion were prepared (fluoride was added as HF). When the F/(Zr+Al) ratio was ≤ 3.1, the solutions were stable for a minimum of 8 days. However, for solutions having a F/(Zr+Al) ratio of 3.4, precipitation occurred after 4 days. Furthermore, when the F/(Zr+Al) ratio was 3.8, precipitation occurred immediately. Similar results were obtained in Experiment 63, in which five solutions (Experiments 63B-3 to 63B-7) were prepared that differed only in the fluoride content. Solutions in which the F/(Zr+Al) ratio was 3.3 or 3.6 were stable for a minimum of 6 days, whereas those with F/(Zr+Al) ratios of 4 or 4.4 formed precipitates within 24 h. On the other hand, when F/(Zr+Al) ratios were only 2.9, precipitation occurred within 3 days. Thus, there appeared to be a range of F/(Zr+Al) ratios in which stable solutions were formed, but this range remains ill-defined.

When oxalic acid was present (oxalate/Zr = 1), large crystals precipitated within 24 h (Experiment 63B-8). Thus, use of oxalic acid as a Zr hold-back reagent to mitigate interfacial crud formation (see Section 3.4.1) did not appear promising. However, when tetrahydrofuran-2,3,4,5-tetracarboxylic acid (TCA)[a] was added to a dissolved NCRW solution (Experiment 63B-9), a very stable solution resulted. The lower Zr concentration in this solution, compared to other solutions investigated here, may have contributed to its stability. Nevertheless, TCA might be added to the TRUEX feed solution as Zr hold-back reagent without inducing precipitation.

Washing the NCRW sludge before acid dissolution dramatically increased the stability of dissolved sludge solution. Experiments 55, 66, 67, and 69 used water-washed sludge samples. Dissolved sludge solutions from Experiments 67 and 69 were stable for months; no precipitates were observed in these solutions after 172 and 151 days, respectively. In contrast, a precipitate formed after 34 days in the solution obtained in Experiment 66, which also employed unwashed sludge. The portion of NCRW sludge used in this experiment originated from the same sample used in Experiment 69; however, the F/(Zr+Al) ratio in Experiment 66 was 2.3 compared with 1.3 in Experiment 69. This discrepancy was consistent with the observation that sludge solution stability decreased with an increasing F/(Zr+Al) ratio. Dissolved sludge solution 55A was stable for months, but when solutions prepared from the same sludge sample (55B and 55C) were heated, precipitates formed, indicating that heating of dissolved NCRW solutions adversely affected sludge solution stability.

(a) The use of TCA as a Zr hold-back reagent was suggested by E. P. Horwitz of Argonne National Laboratory.

Thus, to obtain stable dissolved NCRW sludge solutions, the sludge should be washed with water (or dilute NaOH), then dissolved in HNO_3/HF at a low F/(Zr+Al) ratio (≤ 2) at ~25°C. It is possible that oxalic acid could be added to dissolved washed NCRW sludge solutions as a Zr hold-back reagent without precipitation occurring. This possibility will be tested in future experiments.

3.4 TRUEX Solvent Extraction

The TRUEX solvent extraction process is the primary component of the baseline pretreatment process for NCRW sludge. As of the end of FY 1990, the primary concerns associated with this process were 1) formation of interfacial crud, and 2) the addition of excessive amounts of P into the feed to the Hanford Waste Vitrification Plant that would be caused by the use of 0.2 M HEDPA to strip the TRUs from the solvent. Both issues were addressed in FY 1991. In addition, distribution data for the TRUs and Zr in the TRUEX process were obtained.

3.4.1 Interfacial Crud Formation

Earlier investigations of the TRUEX processing of NCRW sludge indicated the process may be hindered by the formation of interfacial crud (Swanson 1991a, 1991c). The factors affecting interfacial crud formation have now been examined in detail. The critical factor appears to be the F/(Zr+Al) ratio, which governs the distribution behavior of Zr ion; i.e., the higher the F/(Zr+Al) ratio, the less Zr is extracted. The effects of varying this ratio on the formation of interfacial crud were investigated. The ratio was adjusted by adding HF to the dissolved sludge solution or by dissolving the sludge in the presence of Al (see Section 3.2).

The data shown in Table 3.5 indicate that for a given concentration of Zr in the dissolved sludge solution, the tendency to form interfacial crud decreases with increasing F/(Zr+Al). For example, in the series of contacts 66-SX8 to -SX15 and 66-SX17 to -SX21, the Zr concentration was maintained at 0.082 M, while the F/(Zr+Al) ratio was varied between 2.2 and 4.6.[a] The amount of crud decreased visibly as the F/(Zr+Al) ratio was increased. When the F/(Zr+Al) ratio was ≥ 4.1, crud did not form. Similar observations were made in the series of contacts 602A-3 to -12, 602A-13A to -13F, 67-SX2 to -SX9, and 69-SX1 to -SX4.

Time was also an important variable in interfacial crud formation (Table 3.6). After adjusting the TRUEX feed solution with an appropriate Zr complexant (e.g., F^-), a certain period of time must be allowed before the solvent extraction contact is made, presumably due to slow equilibration of Zr-F species. For example, in contact 602A-8 interfacial crud was observed initially, but upon standing overnight the crud had disappeared. In solvent extraction Experiment 602A-12, the feed solution was

(a) A minimum of 0.7 h was allowed after adjusting the F/(Al+Zr) ratio before the contact with TRUEX solvent was made.

Table 3.5. Summary of Interfacial Crud Observations for TRUEX Solvent Extraction Contacts for Dissolved NCRW Solutions

Experiment	Organic Aqueous	Initial Aqueous Concentration, M/L							Crud Formation
		[Al]	[Na]	[Zr]	[F]	[H^+]	Time,h[a]	F/(Zr+Al)	
602A-3	0.33	0.11	0.7	0.12	0.28	1.1	–	1.2	Yes
602A-4	0.33	0.014	0.7	0.12	0.28	1.1	–	2.1	Yes
602A-5	0.33	0.11	0.7	0.12	0.28	1.1	–	1.2	Yes
602A-6	0.33	0.014	0.7	0.12	0.28	1.1	–	2.1	Yes
602A-8	0.33	0.014	0.71	0.12	0.53	1.1	0	4	Yes[b]
602A-9[c]	0.33	0.014	0.71	0.12	0.53	1.1	~24	4	No
602A-11	0.33	0.014	0.71	0.12	0.53	1.1	3	4	No
602A-12A	0.28	0.014	0.71	0.12	0.53	1.1	0	4	Yes
602A-12B	0.28	0.014	0.71	0.12	0.53	1.1	0.5	4	No
602A-13A	0.33	0.015	0.75	0.13	0.30	1.2	0.1	2.1	Yes
602A-13B	0.33	0.015	0.74	0.13	0.35	1.2	1	2.4	Yes
602A-13C	0.33	0.014	0.73	0.13	0.39	1.2	1	2.7	Yes
602A-13D	0.32	0.014	0.73	0.13	0.44	1.2	1	3	Yes
602A-13E	0.32	0.014	0.72	0.12	0.48	1.2	1	3.6	Yes
602A-13F	0.32	0.014	0.71	0.12	0.52	1.1	0.5	3.9	No
66-SX8	0.33	0.001	0.034	0.082	0.18	2.2	0.8	2.2	Yes
66-SX9	0.33	0.001	0.034	0.082	0.21	2.1	0.8	2.5	Yes
66-SX10	0.33	0.001	0.034	0.082	0.24	2.1	0.8	2.9	Yes
66-SX11	0.33	0.001	0.034	0.082	0.26	2.1	0.8	3.1	Yes
66-SX12	0.33	0.001	0.034	0.082	0.28	2	1.3	3.4	Yes
66-SX13	0.33	0.001	0.034	0.082	0.31	2	1.3	3.7	Yes
66-SX14	0.33	0.001	0.034	0.082	0.34	2	1.3	4.1	No
66-SX15	0.33	0.001	0.034	0.082	0.36	2	1.3	4.3	No
66-SX17	0.33	0.001	0.034	0.082	0.38	2	0.7	4.6	No
66-SX18	0.33	0.001	0.034	0.082	0.41	1.9	0.7	4.9	No
66-SX21	0.33	0.001	0.034	0.082	0.38	0.9	2.2	4.6	No
67-SX2	0.33	0.052	0.107	0.087	0.08	0.8	–	0.6	Yes
67-SX3	0.33	0.103	0.107	0.087	0.08	0.8	–	0.4	Yes
67-SX4	0.33	0.003	0.107	0.087	0.08	0.8	–	0.9	Yes
67-SX6	0.33	0.003	0.107	0.087	0.08	1.2	1.3	0.9	Yes
67-SX7	0.33	0.003	0.107	0.087	0.23	1.2	1.3	2.6	Yes
67-SX8	0.33	0.003	0.107	0.087	0.28	1.1	16.7	3.1	No
67-SX9	0.33	0.003	0.107	0.087	0.33	1.1	16.7	3.7	No
69-SX1	0.33	0.001	0.023	0.061	0.18	1.2	1.5	2.9	Yes
69-SX2	0.33	0.001	0.023	0.061	0.28	1.1	1.5	4.5	No
69-SX3	0.33	0.001	0.023	0.061	0.33	1	1.5	5.3	No
69-SX4	0.33	0.001	0.023	0.061	0.38	1	1.5	6.1	No

(a) Time lapse between adjustment of the feed with F^- and contact with the TRUEX solvent.
(b) Crud disappeared upon standing overnight.
(c) Aqueous solution was heated at 100°C for 40 min before contact. This induced a small amount of precipitation. The solution was clarified by centrifuging and decanting from the solid before doing the contact.

Table 3.6. Interfacial Crud Formation as a Function of Time

Experiment	Organic/ Aqueous	Initial Aqueous Concentrations, M/L [A]	[Na]	[Zr]	[F]	[H^+]	Time, h[a]	F/Al+Zr	Crud Formation
602A-8	0.33	0.014	0.71	0.12	0.53	1.1	0	4	Yes
							~24		No
602A-9[b]	0.33	0.014	0.71	0.12	0.53	1.1	~24	4	No
602A-11	0.33	0.014	0.71	0.12	0.53	1.1	3	4	No
602A-12	0.28	0.014	0.71	0.12	0.53	1.1	1 min	4	Yes
							2 min		Yes
							8 min		Yes
							30 min		No

(a) Time lapse between adjustment of the feed with KF and contact with the TRUEX solvent.
(b) Aqueous solution was heated at 100°C for 40 min before contact, which induced a small amount of precipitation. The solution was clarified by centrifuging and decanting from the solid before contact.

adjusted to a F/(Zr+Al) ratio of 4 and was contacted immediately with TRUEX solvent (organic-to-aqueous phase ratio = 0.28); interfacial crud formed. When the solution was stirred at ambient temperature for 30 min, the crud had dissolved. The time required to ensure that adequate Zr-F equilibration has occurred has not yet been rigorously defined.

Additional information about crud formation had been obtained earlier using the solution from Experiment 61A, in which NCRW sludge was dissolved in the presence of Al (see Section 3.2). Severe interfacial crud formation was observed with this dissolved sludge solution when a 0.85-mL portion of the 1-day-old sludge solution was diluted with water to 0.12 M Zr + 0.10 M Al + 1 M H^+ and then contacted with TRUEX solvent at an organic-to-aqueous phase ratio of 0.33 (contact 61A SXA). Because the crud tended to cling to the walls of the glass vial, it was possible to separate it from the organic and aqueous phases. The solid crud was washed twice with 0.1-mL portions of water, and a portion was mounted for scanning electron microscopy (SEM) examination. The remaining solids were then easily dissolved in 0.2 mL of 0.3 M HNO_3, which was diluted further and analyzed by ICP.

The following components (in moles per mole of Zr) were identified by ICP analysis of the dissolved interfacial crud. The components were 5 P, 4 Na, 0.9 Si, 0.5 Al, 0.2 Ca, 0.03 Cr, and

0.02 Fe. According to these results, Al is not a major component of the crud, even though the crud was much worse in this case, where added Al was present, than had been observed previously when Al was not added.

According to SEM analysis, a variety of solid species were present in this sample of interfacial crud. Interpretation of the SEM data is complicated by the overlap of the strongest x-ray emission line for P with that of the strongest line for Zr. Conclusions concerning the composition of individual crud species could not be drawn from these data.

Additional observations concerning the formation of interfacial crud were made with the dissolved sludge solution from Experiment 61A. Contact 61A-SXB initially involved a 2.35-fold dilution of the 2-day-old sludge solution with water (~0.06 M Zr + ~0.07 M Al + ~0.5 M H^+) at an organic-to-aqueous phase ratio of 0.165; much less crud was observed in this case compared with contact 61A-SXA, and the crud looked more like a slime than agglomerated chunks. HNO_3 was added to reach ~0.06 M Zr + ~0.07 M Al + ~1.3 M H^+ and organic-to-aqueous phase ratio of 0.158, and the phases were recontacted; more solids were present and they resembled the crud observed in contact 61A-SXA (rather than a slime). Additional recontacts were then performed with a series of increasing organic-to-aqueous phase ratios (0.32, 0.47, 0.63, 0.79, and 0.95). At an organic-to-aqueous phase ratio of ≥0.47, neither crud nor slime was evident, but droplets that did not coalesce (after 1 min of centrifugation) remained, indicating that a problem still existed. The number of such droplets present after 1 min of centrifugation steadily decreased as the organic-to-aqueous phase ratio increased, until very few remained at an organic-to-aqueous phase ratio of 0.95. However, when this mixture was recontacted (several hours later) and left to separate by gravity, an emulsion formed, which had not broken after 5 min. The phases had separated after standing for 4 days, and the phases broke rapidly in a recontact at that time.

Contact 61A-SXC, performed 2 days after dissolution, initially employed the same feed composition as contact 61A-SXA, but contact 61A-SXC had an organic-to-aqueous phase ratio of 1. Less crud was observed here than at an organic-to-aqueous phase ratio of 0.33 (in contact 61A-SXA), and even less crud was observed when the organic volume was increased to give an organic-to-aqueous phase ratio of 1.5. However, stable droplets (after centrifuging) were still a problem with this mixture. When water was added for organic-to-aqueous phase ratios of 1 and of 0.67, the number of stable droplets decreased (after centrifuging). Recontacting after adding water to give an organic-to-aqueous phase ratio of 0.5 gave an emulsion of droplets in the organic phase that remained stable over a 4-day settling period.

Contact 61A-SXD was made under the same conditions as contact 61A-SXA, except that 1) the solvent had been treated with basic alumina to remove any acidic degradation products remaining after carbonate washing, and 2) 28-day-aged solution was used. Copious quantities of interfacial crud were obtained in this contact as well, indicating that crud formation was not due to acidic impurities in the TRUEX solvent.

Another composite sample of NCRW sludge (Experiment 61B) was dissolved under conditions identical to Experiment 61A, except that no aluminum nitrate was added. Visual observations suggested that the dissolution process was similar to that observed in Experiment 61A. No analyses were

performed in this experiment, but the (bulk) concentrations should have been comparable (except for Al) to those in Experiment 61A. The Al concentration in Experiment 61B was estimated (from earlier results) to be 0.033 M.

No interfacial crud was observed when this 1-day-old dissolved sludge solution was diluted and contacted with TRUEX solvent that had been treated with carbonate and alumina. Thus, the crud that was observed in Experiment 61A must have been caused by the presence of added Al.

Contact 61A-SXE was aimed at assessing the possibility of minimizing interfacial crud formation by complexing Zr with sulfate. For this experiment, a portion of the 34-day-aged dissolved sludge solution from Experiment 61A was diluted with 1 M H_2SO_4 to give a solution containing 0.12 M Zr + .14 M Al + 0.43 M F + 0.15 M SO_4^{2-}. The solution was aged overnight, and solids were observed to have formed during this interval. Contact with 0.33 volumes of TRUEX solvent resulted in the formation of some interfacial crud, but not as much as had formed in the absence of sulfate. Recontacting after adjusting to 0.10 M Zr + 0.12 M Al + 0.38 M F + 0.25 M SO_4^{2-} resulted in a further decrease in interfacial crud. Recontacting a day later (without additional composition adjustment) led to still greater improvement. Thus, it appeared that interfacial crud formation could be minimized by adding sulfate ion as well as by adding fluoride ion. Whether the use of sulfate instead of fluoride is of any benefit remains to be seen.

These observations support the thesis that interfacial crud is formed when the organic phase becomes saturated in a certain Zr species. The concentration of this species in the organic phase can be kept below saturation (i.e., no interfacial crud) by either dilution or by lowering the distribution coefficient for Zr by complexing Zr in the aqueous phase. Fluoride ion complexes Zr and, thus, reduces extraction of Zr into the organic phase. Fluoride ion also complexes Al; therefore, when large amounts of Al are present (as in contact 61A-SXA), the amount of free fluoride available to complex Zr is low. This leads to increased extraction of Zr into the organic phase and formation of interfacial crud. Conversely, when the F/(Zr+Al) ratio is kept sufficiently high (see Figure 3.1), Zr is retained in the aqueous phase and interfacial crud does not form.

The data presented in Figure 3.1 suggest that, for feed solutions in which [Zr] <0.125 M, the ratio F/(Zr+Al) should be maintained at 3.75 or greater to avoid interfacial crud formation in the TRUEX solvent extraction step. Additional data need to be collected for solutions having higher Zr concentrations.

3.4.2 Distribution of Transuranic Elements and Zr

The distribution behavior of the transuranic elements (measured as total alpha activity) was determined in selected solvent extraction experiments. The distribution coefficients for the TRUs are summarized in Table 3.7. In all cases, the TRU distribution coefficients were high enough for the TRUEX process to adequately separate the TRUs from the bulk components of NCRW.

The distribution of Zr in these TRUEX contacts is summarized in Table 3.7 and Figure 3.2. In all cases, the distribution coefficient D_{Zr} is <1. The general trend is for D_{Zr} to decrease with increasing F/(Zr+Al). This supports the hypothesis that interfacial crud formation can be avoided by

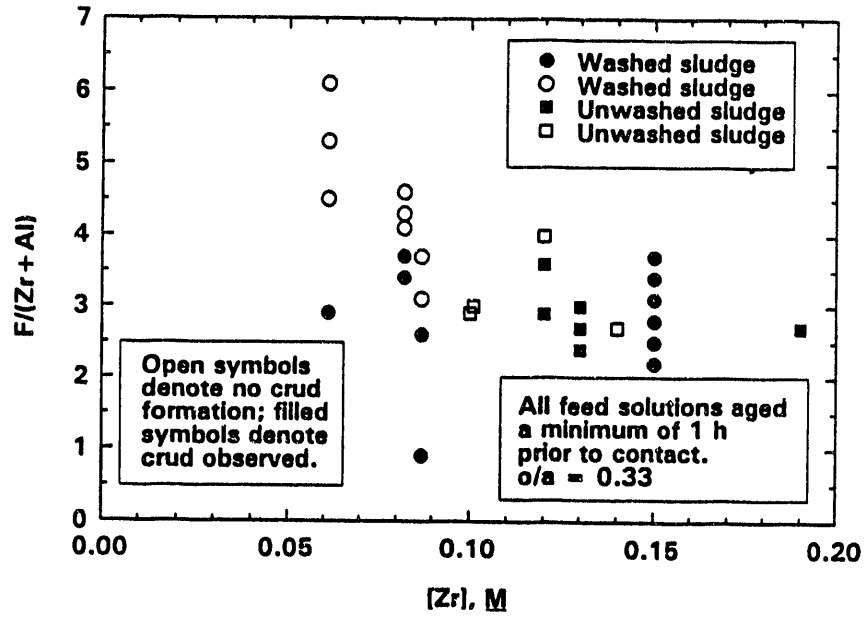


Figure 3.1. Observations of Interfacial Crud Formation in the TRUEX Solvent Extraction Step

suppressing the extraction of Zr. That is, by increasing F/(Zr+Al), D_{Zr} is decreased and the critical concentration of the crud-forming species is not exceeded in the organic phase.

3.4.3 Stripping

Initial flowsheets for the treatment of Hanford tank wastes specified the use of a 0.2 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) solution to strip the TRUs from the extract. The use of HEDPA as the stripping agent adds P to the HLW stream and, thus, into the feed to the vitrification plant. This addition has raised some concerns that the number of glass canisters needed to dispose of this waste would be driven by the amount of P present, in which case the economic incentive to use the TRUEX process would be reduced.

Methods of reducing the amount of P in the HLW stream were studied. Three approaches were investigated: 1) reducing the concentration of HEDPA in the strip solution; 2) using carbonate as stripping agent; and 3) using a strip solution containing both sodium carbonate and NaHEDPA (the sodium salt of HEDPA). The first approach was tried because even if the [HEDPA] was lowered by two orders of magnitude, there would still be a large excess of HEDPA compared to Am and Pu. (It was later found that the minimum HEDPA concentration needed is actually defined by the amount of U present in the waste; see discussion in Subsection 3.4.3.1.). The second approach, stripping with Na_2CO_3, was investigated because this would simplify the flowsheet by combining the stripping and solvent wash steps. However, precipitation of La was observed when the carbonate strip was tested

Table 3.7. Summary of TRU and Zr Distribution Coefficients in TRUEX Solvent Extraction Contacts for Dissolved NCRW Solutions

Experiment	Organic/ Aqueous	Initial Aqueous Concentrations, M/L								
		[Al]	[Na]	[Zr]	[F]	$[H^+]$	$[H_2C_2O_4]$	F/(Zr+Al)	D_{alpha} [a]	D_{Zr} [a]
63-SX1	0.33	0.003	0.412	0.074	0.29	1.6	0.01	3.8	33	0.045
66-SX14	0.33	0.001	0.034	0.082	0.34	2	0	4.1	72	0.38
66-SX15	0.33	0.001	0.034	0.082	0.36	2	0	4.3	62	0.30
66-SX17	0.33	0.001	0.034	0.082	0.38	2	0	4.6	70	0.25
66-SX18	0.33	0.001	0.034	0.082	0.41	1.9	0	4.9	95	0.31
66-SX21	0.33	0.001	0.034	0.082	0.38	0.9	0	4.6	17	
67-SX8	0.33	0.003	0.107	0.087	0.28	1.1	0	3.1	52	
67-SX9	0.33	0.003	0.107	0.087	0.33	1.1	0	3.7	51	
67-SX11	0.33	0.004	0.100	0.083	0.41	1.9	0	4.7	34	0.15

(a) Distribution coefficient = $C_o/C_a = V_a(C_{ai}-C_a)/V_oC_a$ (where C_{ai} = initial concentration in the aqueous phase; C_a, C_o = concentration in the aqueous and organic phase, respectively, at equilibrium; V_a and V_o = the volume of the aqueous and organic phase, respectively).

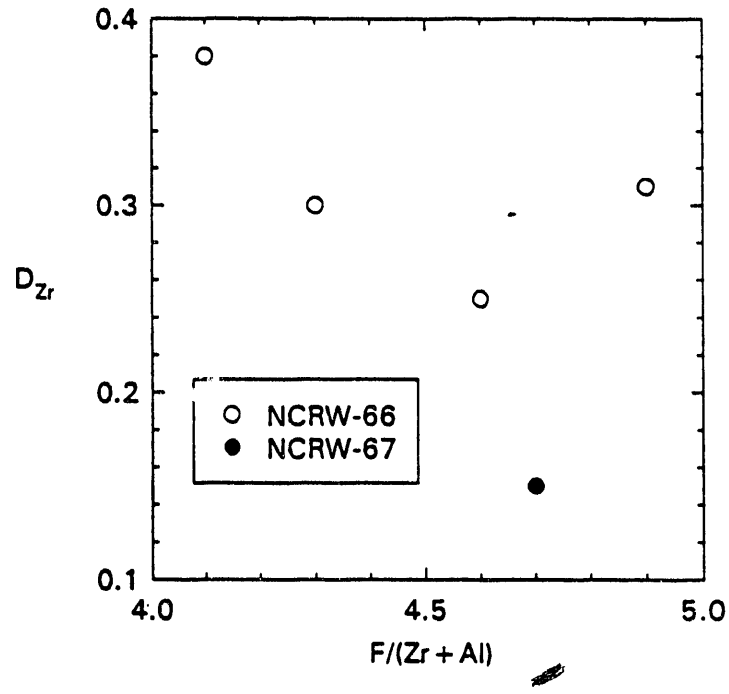


Figure 3.2. Distribution of Zr as a Function of F/(Zr + Al)

with an extract from actual dissolved NCRW sludge. Thus, the third method was tested in which a small amount of HEDPA was added to the Na_2CO_3 solution to complex La and prevent precipitation.

3.4.3.1 Stripping with HEDPA

Distribution coefficients (D) for the extraction of Am(III) and Pu(IV) from HEDPA solutions with TRUEX process solvent (0.2 M CMPO + 1.4 M TBP in NPH) have been determined as a function of HEDPA and HNO_3 concentration, using solutions spiked with Am or Pu tracers. Figure 3.3 shows the distribution coefficients for Am(III) and Pu(IV) as a function of HEDPA concentration at an aqueous acidity of 0.35 M HNO_3. The distribution coefficients for both of these ions decreased with increasing HEDPA concentration. The distribution coefficients for Am(III) were generally one order of magnitude greater than those for Pu(IV) under similar conditions. These observations were consistent with those reported by Horwitz et al. (1990). The lower distribution coefficients for Pu(IV) indicated that this ion can be stripped from the TRUEX process solvent with HEDPA more readily than can Am(III). Because Am(III) will be the limiting species in the efficiency of the HEDPA strip, subsequent efforts focused on stripping this ion from the TRUEX process solvent.

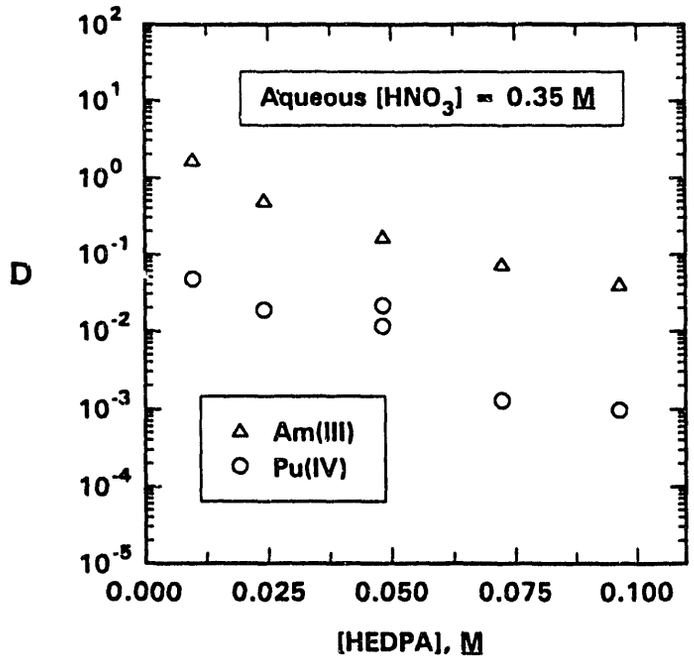


Figure 3.3. Distribution of Am(III) and Pu(IV) Between Aqueous HEDPA Solutions and the TRUEX Process Solvent

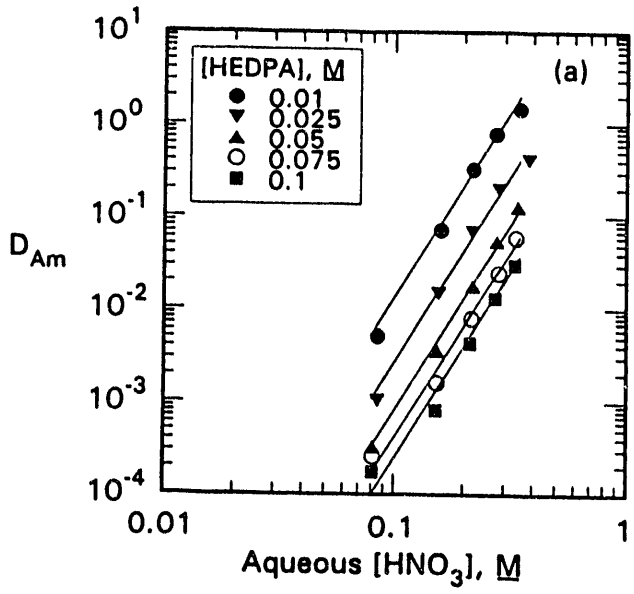
The distribution coefficients for Am(III) between the TRUEX process solvent and HEDPA solutions as a function of HEDPA and HNO_3 concentration are plotted in Figure 3.4. In this figure, the symbols represent the experimental results, and the lines are drawn based on the correlation discussed in the following paragraphs.

The plot of D_{Am} vs equilibrium $[HNO_3]$ in the aqueous phase (see Figure 3.4a) reveals a fourth-order dependence of D_{Am} on the aqueous HNO_3 concentration; whereas the plot of D_{Am} vs [HEDPA] (see Figure 3.4b) indicates that D_{Am} is inversely proportional to the square of the HEDPA concentration. Thus, an empirical model for the calculation of D_{Am} can be developed based on the following equation:

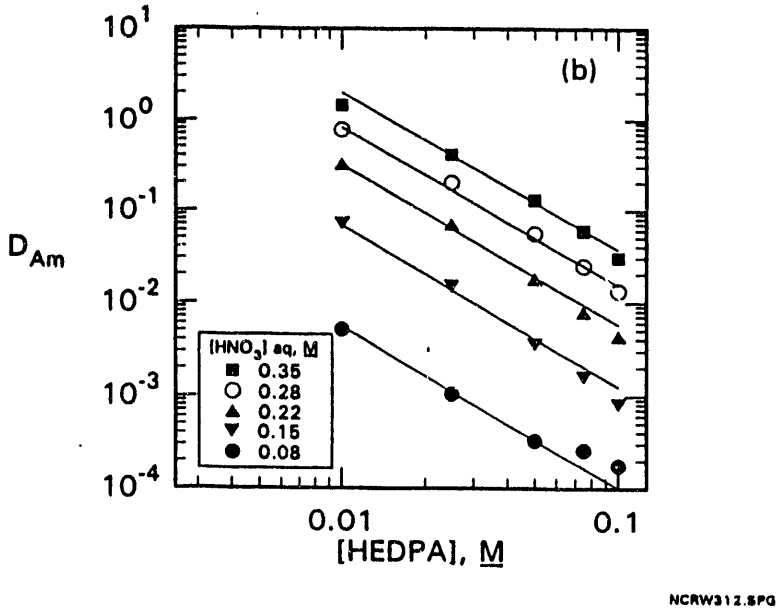
$$D_{Am} = k[HNO_3]^4[HEDPA]^{-2} \tag{3}$$

where k is an empirical constant.

The empirical constant k is truly constant only for a given concentration of HEDPA. The values of k for the five different concentrations of HEDPA used here were determined from the Am(III) distribution data plotted in Figure 3.4 ($k = D_{Am} \cdot [HEDPA]^2 \cdot [HNO_3]^{-4}$). The values of k are plotted as a



(a)



(b)

Figure 3.4. Distribution of Am(III) Between Aqueous HEDPA and the TRUEX Process Solvent. (a) is D_{Am} vs [HNO_3] in the aqueous phase, (b) is D_{Am} vs [HEDPA]. The solid lines represent distribution coefficients for Am(III) that were calculated using Equation 3.

function of [HEDPA] in Figure 3.5. A linear (logarithmic) relationship exists between k and [HEDPA]; thus, k can be determined for a given concentration of HEDPA that might be considered as a TRUEX stripping solution.

The distribution of HNO_3 between HEDPA solutions and the TRUEX solvent is summarized in Figure 3.6. The distribution of HNO_3 is independent of the HEDPA concentration; however, the distribution in the presence of HEDPA does appear to be higher than that observed in the absence of HEDPA (Figure 3.6, and Horwitz et al. 1985). For the purposes of the empirical model used to calculate D_{Am}, the solid line depicted in Figure 3.6 was used. This line was generated by linear regression on all the data points determined in the presence of HEDPA (regardless of [HEDPA]).

For any given set of input HEDPA and HNO_3 concentrations, and a given organic-to-aqueous phase ratio, the distribution coefficient for Am(III) can be calculated from Equation 3 and the equations given in Figures 3.5 and 3.6. Such calculations were carried out for the conditions under which the tracer experiments were conducted, and the results are displayed as the solid lines in Figure 3.4. As can be seen, the calculated values closely agree with the experimental values. The sum of the squares of the residuals is 0.29.

The empirical model described above can be used to predict the stripping efficiency of HEDPA solutions under a given set of conditions. The results of several such calculations are presented in Figure 3.7. For the purpose of these calculations, it was assumed that the strip step involved four successive batch contacts at an organic-to-aqueous phase ratio of 3. Three HEDPA concentrations were considered (0.025, 0.05, and 0.1 M), and the residual concentration of nitric acid in the extract coming

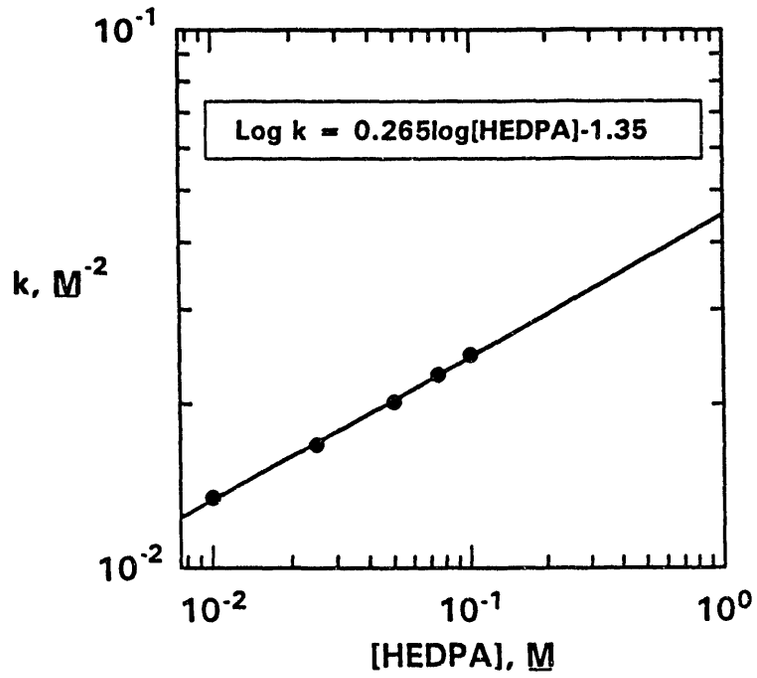


Figure 3.5. The Empirical Constant, k, as a Function of HEDPA Concentration

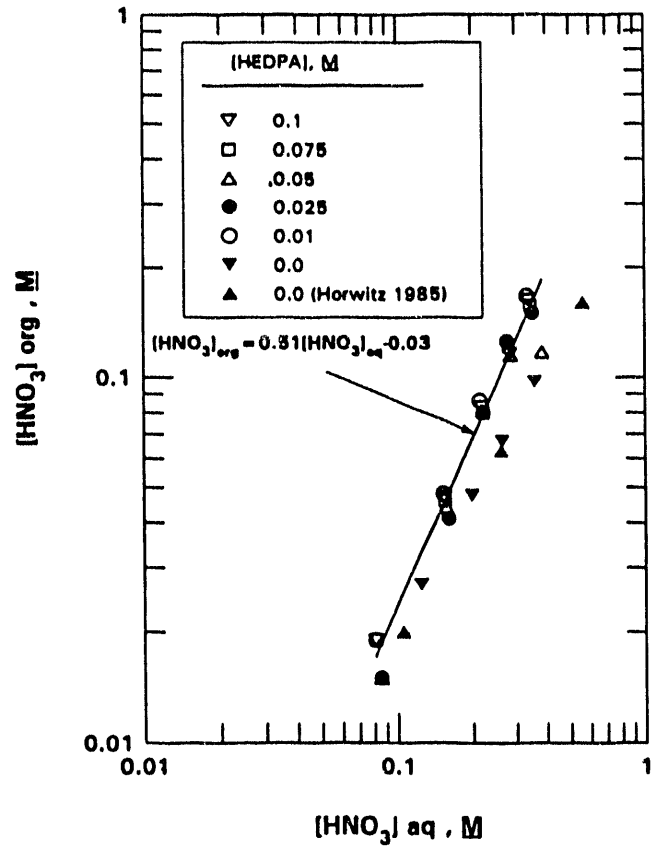


Figure 3.6. The Distribution of HNO_3 in the TRUEX Process

from the scrub step was assumed to be either 0.5 or 0.2 M. According to Figure 3.7, very efficient stripping of Am can be achieved at low HEDPA concentrations. For example, if the initial concentration of HNO_3 in the organic phase is 0.2 M, two contacts with 0.1 M HEDPA result in the removal of greater than 99.9% of the Am. However, by adding one more stage, this level of stripping can be exceeded with 0.025 M HEDPA. Figure 3.7 illustrates the importance of scrubbing HNO_3 from the extract before the strip step. For all HEDPA concentrations, markedly better stripping efficiencies are achieved when the initial organic nitric acid concentration is 0.2 M rather than 0.5 M. This is a result of the fourth-order dependence of D_{Am} on the nitric acid concentration (Figure 3.4, Equation 3).

An experiment was performed earlier to assess the effectiveness of the TRUEX process in treating actual NCRW. The experiment was designed to simulate the counter-current TRUEX solvent extraction processing of acid-dissolved NCRW waste. The results of this experiment are reported elsewhere (Swanson 1991b); however, the results of the stripping steps are relevant to this work and will be discussed here.

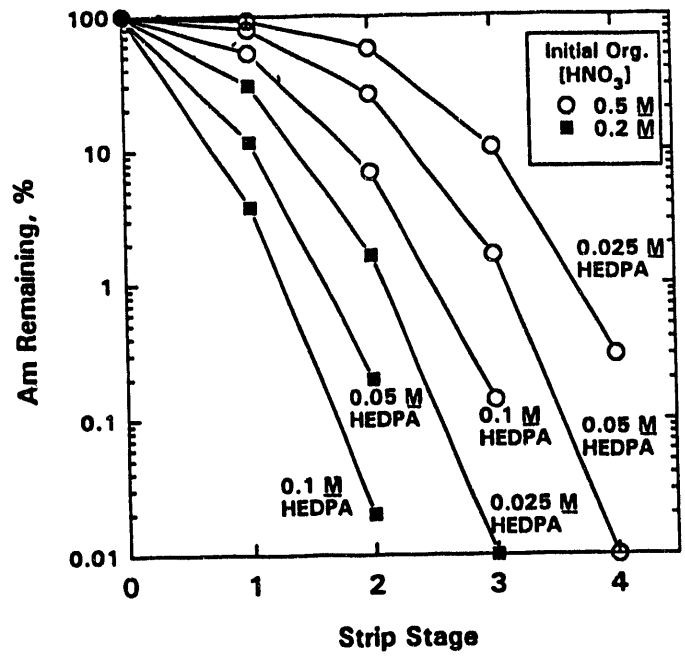


Figure 3.7. Removal of Am(III) from TRUEX Process Solvent With HEDPA as Calculated by Equation 3. The organic-to-aqueous phase ratio is assumed to be 3; each strip stage is assumed to be a simple batch contact.

The scrubbed NCRW extract was contacted with a 0.21 M solution of HEDPA at an organic-to-aqueous phase ratio of 3. Two subsequent strip steps using fresh 0.21 M HEDPA at the same organic-to-aqueous phase ratio ensured removal of the TRUs for mass-balance calculations. The aqueous-phase HNO_3 concentration in the first strip step was 0.36 M. Using Equation 3, a value of 0.011 was predicted for D_{Am} in this step. The value determined experimentally for D_{Am} was 0.02. Better agreement was obtained between the calculated and experimental values when the concentration of U in the waste sample was taken into account. The U concentration in the aqueous phase from the first strip step was 0.034 M. If each U binds two HEDPA ligands, the effective HEDPA concentration for the stripping of TRUs would be 0.14 M, and the predicted D_{Am} would be 0.023. The latter value is within experimental error of the measured value. Thus, the model developed from the tracer data accurately predicted the distribution behavior of Am in an actual waste.

In another series of experiments with actual waste, a scrubbed TRUEX extract (containing approximately 0.02 M HNO_3) from a dissolved NCRW solution was divided into several aliquots, each of which was contacted with a different strip solution (organic-to-aqueous phase ratio of 1). Four of these strip solutions contained only HEDPA at concentrations ranging from 0.2 to 0.01 M. The concentrations of alpha-emitting nuclides in 0.1, 0.05, and 0.01 M HEDPA strip solutions were respectively 104%, 104%, and 90% of the concentration found in the 0.2 M HEDPA strip solution. These

results provided additional, albeit less definitive, evidence that effective stripping of TRU elements from extracts of real Hanford wastes can be achieved at HEDPA concentrations much below 0.2 M.

The minimum concentration of HEDPA that must be used in the strip step will be dictated by the amount of U in the extract. Calculations indicated that to prevent P from becoming the limiting component in the glass waste form, the maximum concentration of HEDPA in the strip solution should be 0.002 M (Barker, Swanson, and Lumetta 1991). Because of the U content in NCRW sludge, such low concentrations of HEDPA cannot be achieved if HEDPA is the only constituent in the strip solution. However, these concentrations might be achieved if a combined HEDPA/sodium carbonate strip solution is used (see Subsection 3.4.3.3).

3.4.3.2 Stripping with Sodium Carbonate

Na_2CO_3 solutions were examined as an alternative to HEDPA for stripping the TRUs from the solvent. Stripping with Na_2CO_3 would have several advantages over using HEDPA. A Na_2CO_3 strip would eliminate the addition of P into the HLW waste stream. Because the Na_2CO_3 could be used to perform another needed function (neutralization of process acids before interim storage in carbon steel tanks), no extra sodium would be added to the HLW stream. Furthermore, the overall process would be simplified by combining the strip and solvent wash steps.

Tracer experiments were carried out in which 0.25 M Na_2CO_3 solutions were contacted with an equal volume of TRUEX solvent that had been spiked with Pu(IV) or Am(III). D_{Am} was found to be 0.001, and D_{Pu} was 0.009. This result suggested that Na_2CO_3 would be an effective stripping agent. However, an experiment with an actual NCRW extract was less encouraging. When a TRUEX extract of actual NCRW ([HNO_3] in the extract = 0.15 M) was contacted with a 0.5 M Na_2CO_3 solution (organic-to-aqueous phase ratio of 3), a precipitate formed in the aqueous phase. This precipitate was found to be rich in La. The distribution coefficient for the total alpha activity was 0.2. Thus, with NCRW extract, the performance of Na_2CO_3 as a stripping agent was not as efficient as expected from tracer experiments. Furthermore, the quantity of La present in this type of waste would cause precipitation problems in the contactor if carbonate was used to strip the TRUs.

3.4.3.3 Combined Sodium Carbonate/NaHEDPA Stripping

A third approach to stripping the transuranic elements from the TRUEX process solvent is under consideration. This approach involves using a strip solution that contains both NaHEDPA (the sodium salt of 1-hydroxyethane-1,1-diphosphonic acid) and Na_2CO_3. The effectiveness of such solutions for stripping TRUs from the solvent has been compared with that of HEDPA solutions alone. Aliquots of the scrubbed extract (containing approximately 0.02 M HNO_3) discussed in Section 3.4.3.1 were contacted with NaHEDPA and Na_2CO_3 mixtures to compare their stripping effectiveness with those of the various HEDPA solutions. The concentration of alpha-emitting nuclides in a 0.01 M NaHEDPA + 0.25 M Na_2CO_3 strip solution was 104% of that found in the 0.01 M HEDPA strip solution, while the concentration in a 0.002 M NaHEDPA + 0.25 M Na_2CO_3 strip was 107% of that in the 0.01 M

HEDPA strip solution. The 0.002 M NaHEDPA strip solution represented a 100-fold decrease in the amount of P in the strip solution (as compared with the 0.2 M HEDPA currently specified in Hanford TRUEX process flowsheets); at this HEDPA concentration, P is no longer the component that determines the number of glass canisters needed to vitrify the TRU product (Barker, Swanson, and Lumetta 1991). No precipitation was observed in these NaHEDPA/Na_2CO_3 strips, but the concentration of La present in the feed solution was much less than that present in the experiment in which precipitation was observed with the carbonate only strip (1.4×10^{-5} M compared with 6.5×10^{-4} M). Thus, it could not be determined from this experiment whether NaHEDPA will prevent La from precipitating in the presence of carbonate. However, these results are encouraging, and further study is warranted.

3.5 NCRW Pretreatment Flowsheet

Figure 3.8 depicts an overview of the NCRW pretreatment flowsheet as envisioned at the end of FY 1991. The pretreatment process involves the following steps:

- sludge washing
- sludge dissolution
- TRUEX process
  - extraction
  - scrub with $H_2C_2O_4/HNO_3$
  - scrub with water
  - strip.

The NCRW sludge will be washed with a 0.1 M NaOH solution to remove the bulk of the sodium and fluoride along with any other soluble non-TRU sludge components. The wash solution will contain greater than 95% of the ^{137}Cs. Depending on the required specifications for grout, the wash solution will be made into grout directly, or after the ^{137}Cs is removed by cation exchange.

The washed NCRW sludge will be dissolved in HNO_3 plus HF to give final concentrations of 1.5 to 2 M and ~0.3 M, respectively. The dissolved sludge solution is expected to contain ~98% of the Zr and to have a Zr concentration of about 0.15 M. If deemed necessary, a secondary dissolver may be added to dissolve the remaining solids. The secondary dissolver could use higher HNO_3 and HF concentrations and a higher temperature. If a secondary dissolver is used, the solution from this dissolver would be combined with the solution from the primary dissolver for TRUEX processing. If a secondary dissolver is not used, the solid residue would be stored for vitrification.

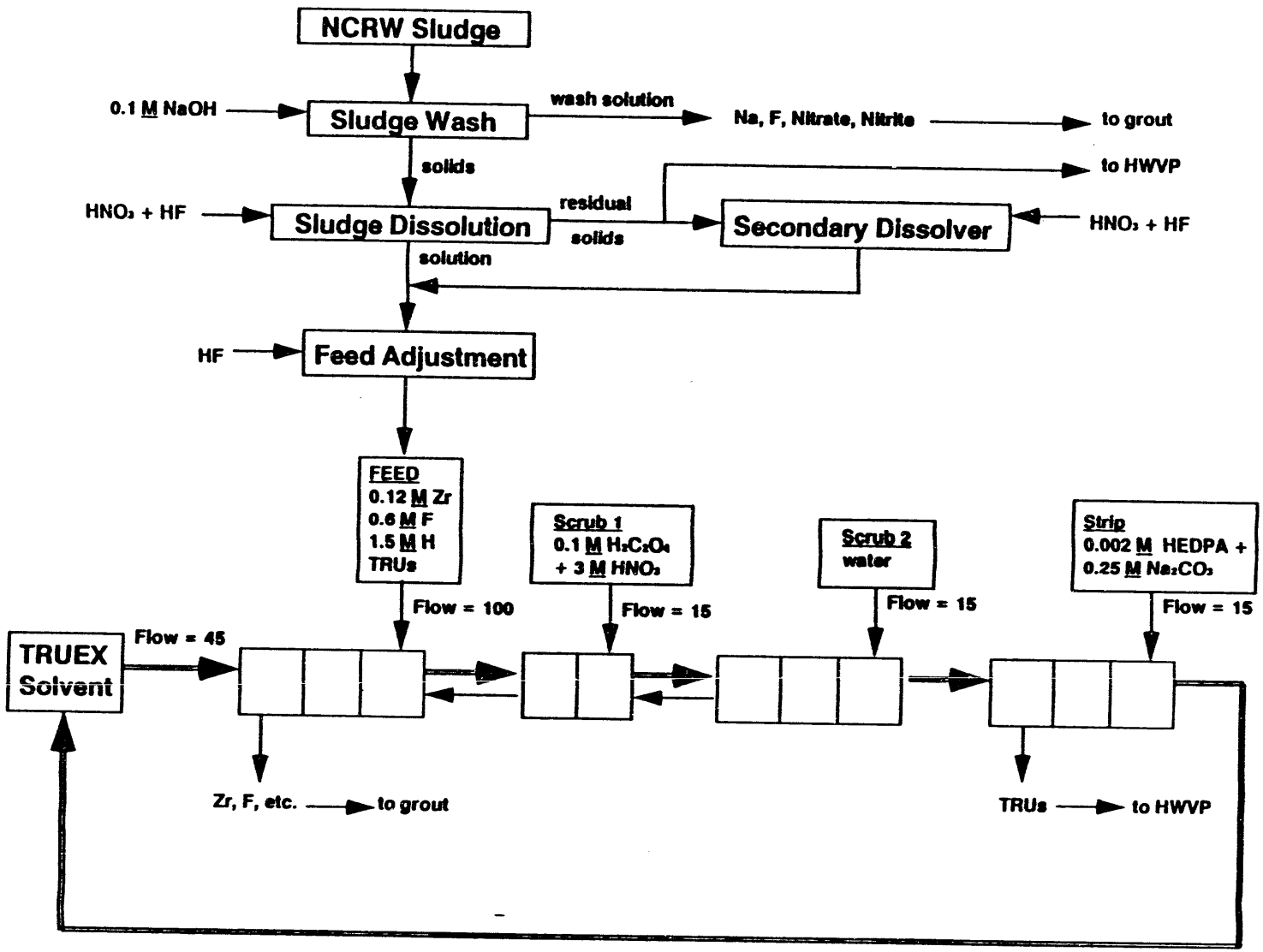


Figure 3.8. Flowsheet for the Pretreatment of NCRW Sludge

Shortly before the dissolved sludge solution is fed to the TRUEX process, HF is added until the F/(Zr+Al) ratio is 5. This feed adjustment step ensures that interfacial crud will not form in the extraction contactors. Three extraction stages are expected to be adequate, but additional stages could be easily included if necessary. The raffinate from the final extraction stage will be LLW, which can be disposed of as grout.

The extract is scrubbed first with 0.05 M $H_2C_2O_4$ + 1.5 M HNO_3 to remove Zr and F. This step is followed by a water scrub to lower the residual acid content in the extract. The TRUs are then stripped from the solvent with a solution consisting of 0.002 M HEDPA + 0.25 M Na_2CO_3. The strip solution containing the TRU material will be vitrified.

Finally, the TRUEX solvent can be recycled to the extraction contactors. Because the strip solution contains Na_2CO_3, it acts as the solvent wash step as well as the stripping agent. Thus, a separate wash step should not be necessary.

It is likely that the flowsheet depicted in Figure 3.8 will be further modified. For example, the number of stages required for various steps in the process might be altered, and the various flow rates might be changed as well. The choice of stripping agent is not yet considered to be final. The use of HEDPA may be eliminated entirely to avoid adding P into the vitrification feed (other than that present in undissolved solids). Also, the presence of large amounts of Na in the vitrification feed might be undesirable, in which case the use of Na_2CO_3 in the strip solution might be precluded.

3.6 Sludge Settling

Sludge settling behavior is an important parameter regarding the NCRW sludge processing rate. The purpose of this investigation was to determine whether the rate of settling during sludge washing was too slow, which would limit the processing rate. Slow settling may indicate that more sophisticated solid/liquid separation methods (e.g., centrifugation or filtration) are required

3.6.1 Settling Studies Conducted With Synthetic NCRW Sludge

One of the major points of interest in this study was a comparison of the settling rates measured in small vials with those measured in larger vessels (diameters ranged from 1.5 to 7.8 cm). Figure 3.9 contains such comparative data obtained using synthetic NCRW sludge. These data were collected on the same day using the same slurry to eliminate uncertainties about the nature of solids and solution composition. After an initial induction period, the settling rate observed for the slurry in the 7.8-cm-diameter graduated cylinder was approximately five times greater than in the 2.4-cm-diameter vial and ~9-fold greater than in the 1.5-cm-diameter vial. Results presented in the following discussion indicated that these differences were primarily due to slurry height rather than container diameter and that better agreement might have been obtained in a comparison involving slurries containing lower concentrations of zirconium hydroxide.

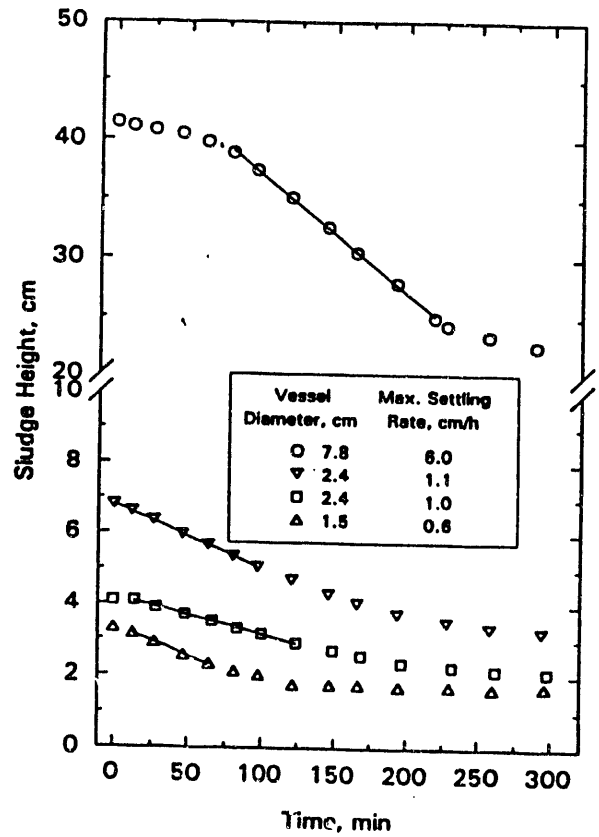
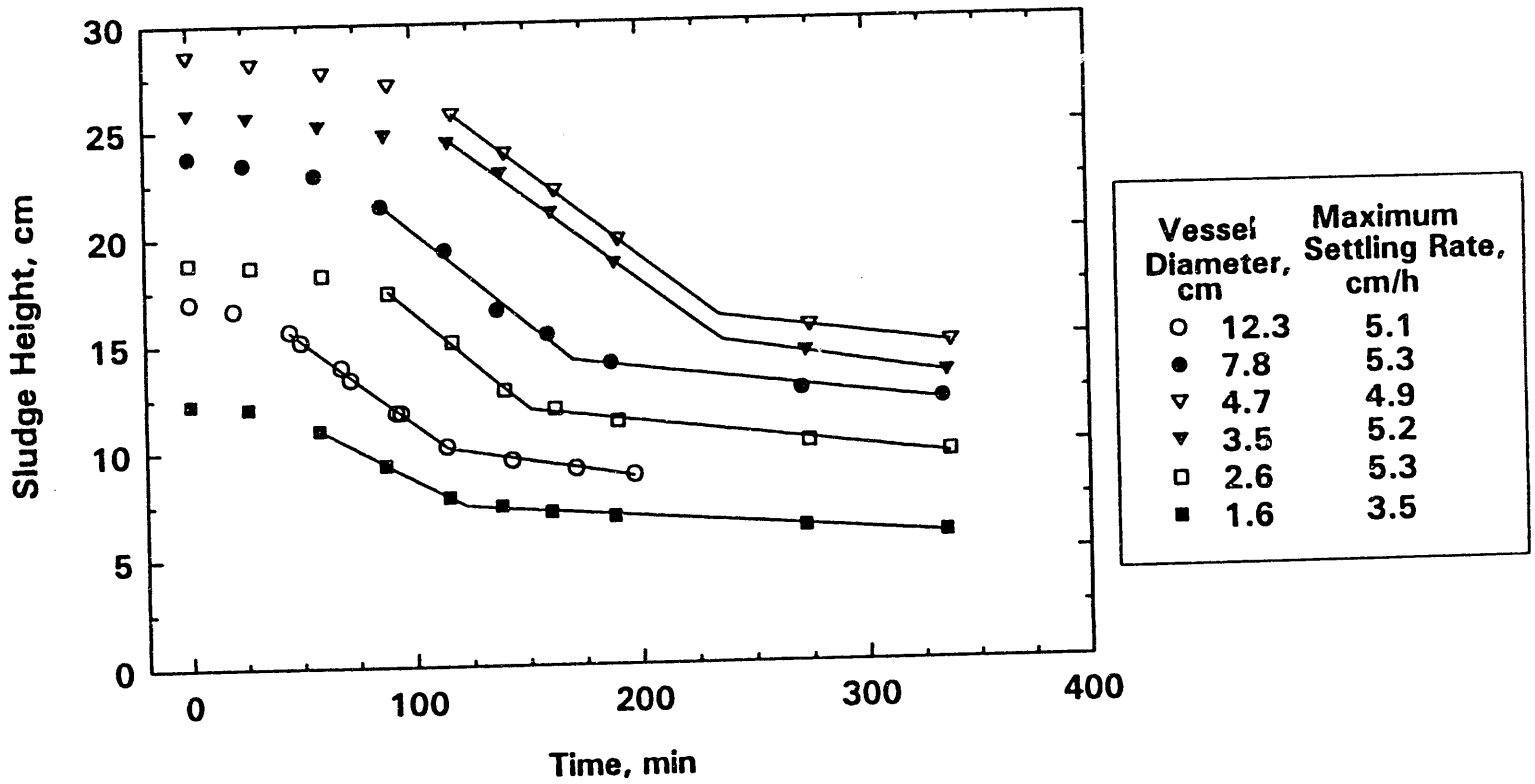


Figure 3.9. Settling Comparison of Synthetic Sludge Contained in Small Vials and a Large Graduated Cylinder. The initial slurries were 0.17 M $Zr(OH)_4$ in 0.3 M NaF + 0.04 M NaOH (aged 7 days).

Comparative settling data for the same slurry (except for longer aging) in a large number of different containers (diameter ranged from 1.6 to 12.3 cm) are shown in Figure 3.10. The diameters of some of these containers were comparable to those of the small vials used in the experiments summarized in Figure 3.9. However, the containers used for Figure 3.10 data were taller and, therefore, afforded a longer path through which the particles fell. Three distinct regions were defined in the settling curves: an initial period of slow settling, then a period of rapid settling, followed by a period in which settling slowed dramatically. The initial period of slow settling was presumed to be due to a surface effect; after the solids reached a certain level below the surface, this effect became negligible and the solids settled rapidly. Eventually, a concentration of particles was reached in which settling was hindered, and the settling rate decreased.

The settling rates during the rapid settling periods (Figure 3.10) were relatively constant in the vessels with diameters ranging from 1.6 to 12 cm, with initial slurry heights of at least 13 cm. Thus, it did not appear that vessel diameter caused the markedly lower settling rates measured in small vials



91NCRW32.SPG

Figure 3.10. Sludge Settling Data for Vessels Ranging in Diameter from 1.6 to 12.3 cm. Initial slurries were 0.17 M $Zr(OH)_4$ in 0.3 M NaF + 0.04 M NaOH (aged 18 to 19 days).

(Figure 3.9). Instead, the data suggested that the short slurry height dictated by the size of the small vials was responsible for the measurement of abnormally low settling rates in those vials; i.e., the slurry could not fall to a depth where surface effects were negligible. Therefore, to obtain meaningful sludge settling data when using small vials, an initially low solids concentration is required to permit enough distance between the liquid surface and the top of the solids so that maximum settling rates may be measured.

Figure 3.11 shows an alternative treatment of the data presented in Figure 3.10. In this treatment, the settling curve is divided into two regions: an initial period of slow settling followed by a region where the settling obeys a first-order rate law, which is described by the following equation:

$$h = (h_0 - h_\infty)e^{-Kt} + h_\infty \tag{4}$$

where h = the sludge height at time t

h_o = the sludge height at the time in which the sludge settling begins to follow the first-order rate law (i.e., when the surface effect becomes negligible)

h_∞ = the sludge height at an infinite time and

K = the first-order rate constant.

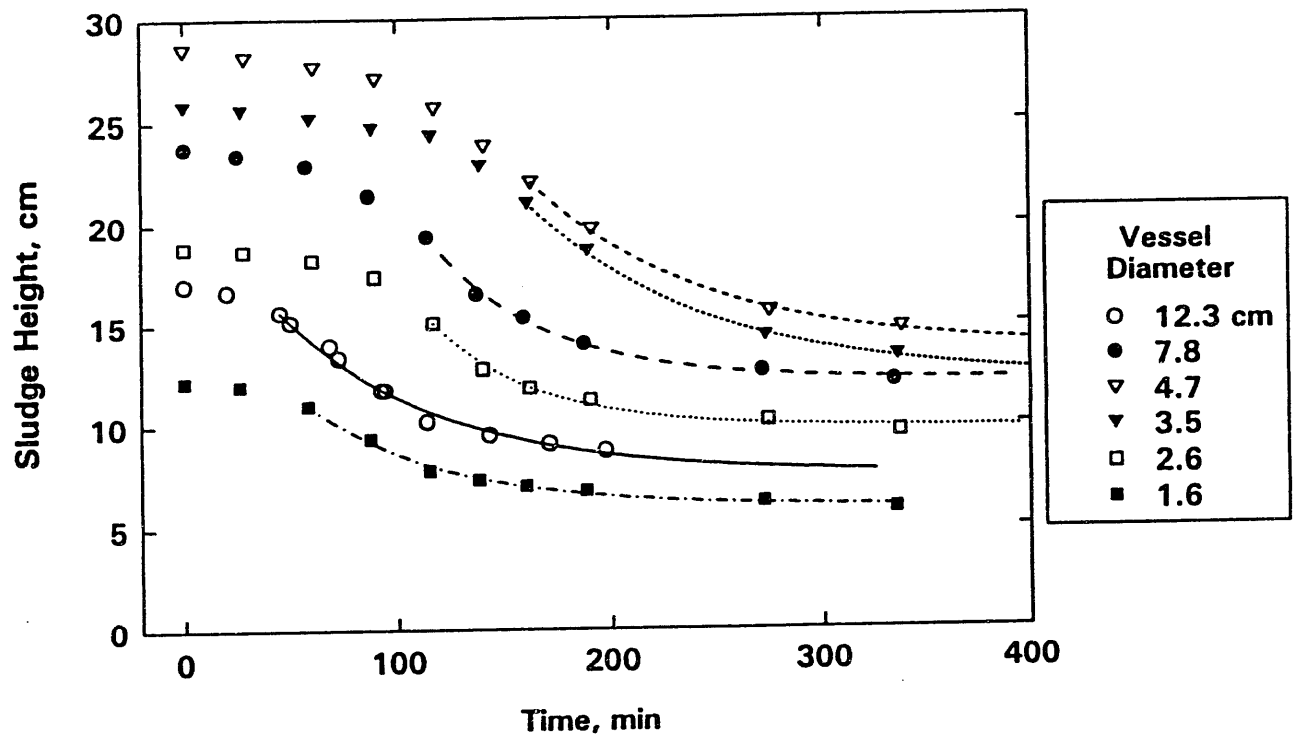
The fact that settling behavior follows first-order kinetics indicates that settling rate depends on the concentration of particles in the slurry. That is, an increase in particle concentration hinders settling.

The data presented in Figure 3.11 are presented somewhat differently in Figure 3.12. In this case, the concentration of particles in the slurry (represented as the concentration of Zr in the sludge) is plotted against time. The first-order rate law in this case takes the following form:

$$[Zr] = ([Zr]_0 - [Zr]_\infty)e^{-Kt} + [Zr]_\infty \tag{5}$$

where [Zr] is the concentration of Zr in the slurry at time t, and $[Zr]_\infty$ is the concentration of Zr in the slurry at an infinite time. The final Zr concentration in the slurry is approximately the same regardless of the container in which the settling is performed.

Other experiments with this slurry showed that solids content markedly affected the solids settling rate; data in Figure 3.13 illustrate this point. These data were obtained by mixing different proportions of settled solids and supernatant solution, so the solids and solution had the same properties (except for minor differences in the amount of time the solids had aged) in all cases. The magnitude of the effect of solids concentration was initially surprising; however, this effect is now presumed to be

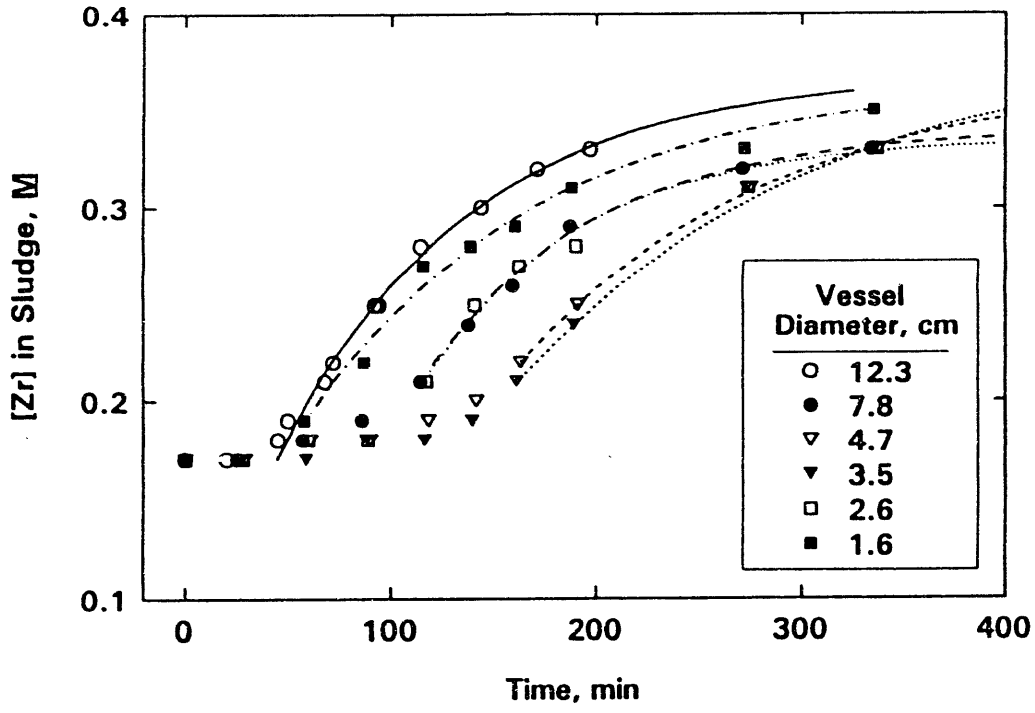


Vessel Diameter, cm	K, s^{-1}	h_{∞}, cm	Norm[1]
12.3	0.0136	7.53	0.81
7.8	0.0190	12.2	0.38
4.7	0.0124	13.6	0.25
3.5	0.0118	12.1	0.18
2.6	0.0203	9.78	0.48
1.6	0.0153	5.94	0.39

1. Norm = sum of the square of the residuals.

91NCRW33.SPG

Figure 3.11. Sludge Settling Data Fit to a First-Order Rate Equation

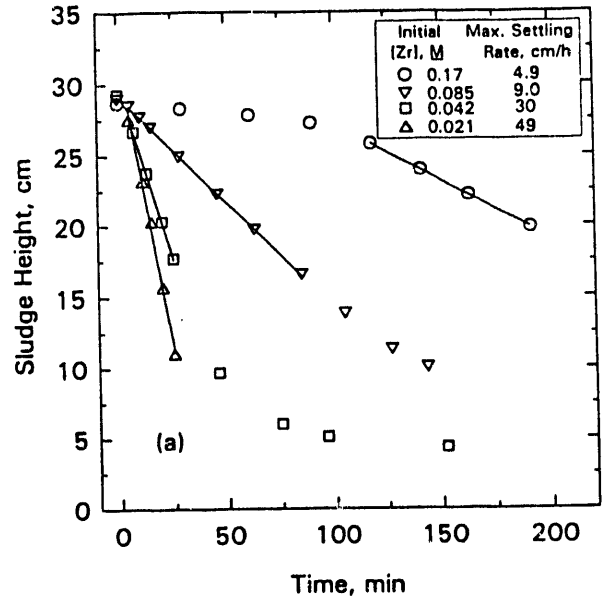


Vessel Diameter, cm	K, s^{-1}	$[Zr]_{\infty}$, M	Norm[1]
12.3	0.0109	0.37	0.015
7.8	0.0122	0.34	0.005
4.7	0.0080	0.37	0.006
3.5	0.0068	0.38	0.005
2.6	0.0131	0.34	0.012
1.6	0.0090	0.36	0.013

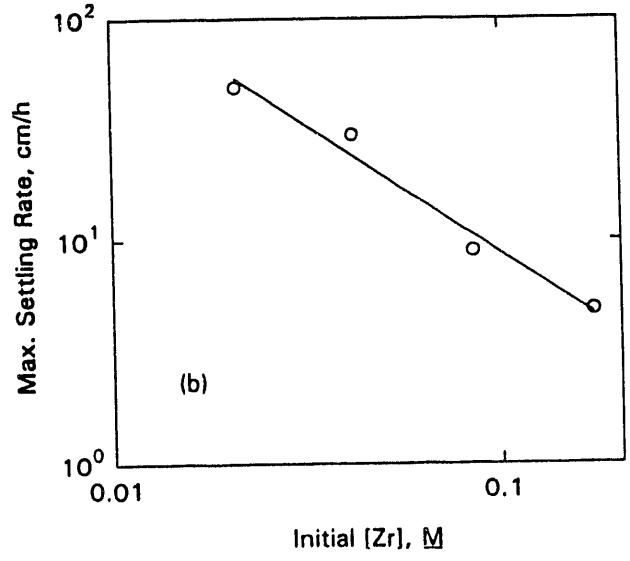
1. Norm = sum of the square of the residuals.

91NCRW34 SPG

Figure 3.12. Zr Concentration in the Slurry as a Function of Settling Time



(a)



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(b)

Figure 3.13. Settling of $Zr(OH)_4$ at Different Initial Concentrations. The solution was 0.3 M NaF + 0.04 M NaOH, the solids were aged 19 to 25 days, and the vessel diameter was 4.7 cm.

due to differences (caused by nearby particles) in the viscosity and the density of the fluid through which the particles fell (Figure 3.13a). This is the same phenomenon that caused the settling rate to decrease as settling proceeded. The data shown in Figure 3.13a (initial Zr concentration of 0.042 M) were fit to Equation 4, giving $K = 0.043\ s^{-1}$. This value for the first-order rate constant is much greater than those observed when the initial Zr concentration was 0.17 M (Figures 3.11 and 3.12). Thus, K is a function of the initial Zr concentration; the reason for this is not understood at present.

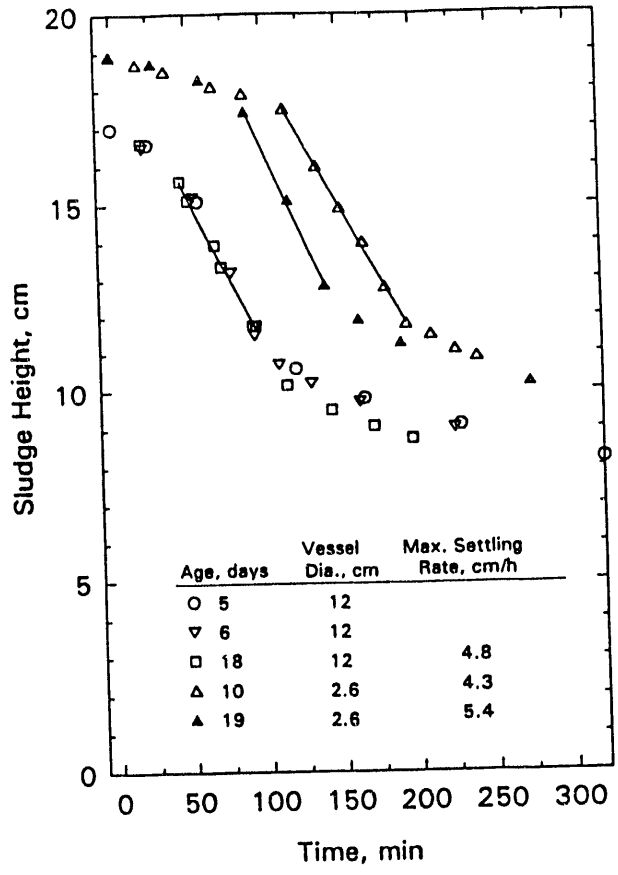
The data shown in Figures 3.9, 3.10, 3.11, 3.12, and 3.13 were obtained during one intermediate point in the washing procedure; the solution composition at this point was estimated to be 0.3 M NaF + 0.04 M NaOH. The settling data comparisons were made during the same day (or as close together as was possible) to minimize the effects of solids aging on the results. However, regarding the maximum settling rate,[a] concern over the possible effects of aging was unnecessary. Figure 3.14 contains data obtained over time for this slurry; no trend in maximum settling rate is apparent.

After the settling study at composition 0.3 M NaF + 0.04 M NaOH was completed, two additional wash steps were performed. The first of these wash steps resulted in an estimated composition of 0.1 M NaF + 0.01 M NaOH, and the second led to 0.04 M NaF + 0.005 M NaOH. In the 0.1 M NaF + 0.01 M NaOH case, the settling behavior of the bulk solids was comparable to that in the 0.3 M NaF + 0.04 M NaOH case, but the supernatant solution was noticeably cloudier. In the 0.04 M NaF + 0.005 M NaOH case, the solution remained so cloudy that the settling rate of the bulk solids could not be measured. This observation appears to be another illustration of the effect of decreased solution ionic strength on particle agglomeration and settling properties.

In addition to the data collected over the first several hours of settling, the heights of the settled sludges after settling periods of ≥ 1 day were also often measured; these data are summarized in Table 3.8. This table provides the Zr concentrations (calculated from its concentration in the initial slurry and the initial and final slurry heights) found in the settled sludges; these values all fell within the range of 0.4 to 0.5 M Zr after settling times of 1 to 8 days. These values are in good agreement with previous observations on actual NCRW sludge, where it was found that the volume of few-day settled sludges was approximately twice as great as the volume of long-settled tank sludges, which contained ~ 1 M Zr (Swanson 1991c). These "final" Zr concentrations are somewhat greater than predicted by Equation 4 (see Figure 3.12); the accuracy of the fit is limited by the number of data points used.

These data show only slight increases in the concentration of Zr in the settled sludges as the settling time increases from 1 to 8 days. It also appears that the precipitate that was aged for 32 days settled to give a Zr concentration ~ 10% greater than did precipitate that was aged for 3 days. The data obtained with 19- to 24-day aged precipitate show no correlation of the settled sludge concentration with sludge height; these data covered the sludge heights from 3 to 11 cm.

(a) In this discussion, the term settling rate refers to the linear velocity at which the top of the sludge layer is falling at a given point in time.



91NCRW36.SPG

Figure 3.14. Settling Data at Different $Zr(OH)_4$ Ages. The initial $Zr(OH)_4$ concentration was 0.17 M, and the supernatant solution was 0.3 M NaF + 0.04 M NaOH.

3.6.2 Settling Studies Conducted with Actual NCRW Sludge

In addition to work with synthetic sludge, sludge settling data were collected from actual NCRW sludge samples in small vials. In these experiments, the initial slow settling period was not observed; rather the settling displayed first-order behavior from t = 0. Figure 3.15 shows the settling data for three portions of NCRW sludge. Sludge taken from segment 4 of the 1986 sampling of Tank 105-AW was used in Experiment 55, whereas sludge from segment 3 of the 1990 sampling of Tank 105-AW was used in Experiments 60 and 63. The data were fit to Equation 4 using the curve-fit program supplied with SigmaPlot 4.1. The lines drawn represent the values calculated using the best-fit parameters, which are also shown in the figure. Differences in sludge settling rates are likely due to differences in the Zr concentration in the slurries and/or differences in the composition of the supernatant solutions.

Table 3.8. Synthetic Sludge Settling Behavior Over a Period of Eight Days

Precipitate Age, Days(a)	Vessel Diameter, cm	Settled Sludge Height, cm[a]	Concentration in Initial Slurry, M/L			$Zr(OH)_4$ Concentration in Settled Slurry, M/L, After:					
			$Zr(OH)_4$	NaF	NaOH	1 Day	2 Day	3 Day	4 Day	5 Day	8 Day
3	12.3	6.3	0.17	1.3[b]	0.3			0.45			
4	12.3	6.4	0.17	0.8	0.1	0.44					
5	12.3	6.5	0.17	0.3	0.04	0.44					
6	12.3	6.2	0.17	0.3	0.04	0.46					
7	12.3	6.2	0.17	0.3	0.04	0.46					
10	7.8	14.2	0.17	0.3	0.04			0.49			
11	7.8	15.2	0.17	0.3	0.04	0.41			0.48		0.5
11	2.6	7.4	0.17	0.3	0.04	0.43			0.45		0.46
19	12.3	5.9	0.17	0.3	0.04	0.49					
20	7.8	8.8	0.17	0.3	0.04	0.46					
20	4.7	10.8	0.17	0.3	0.04	0.45					
20	3.5	9.7	0.17	0.3	0.04	0.44	0.47			0.47	
20	2.6	7.2	0.17	0.3	0.04	0.45	0.45				
20	1.6	5.2	0.17	0.3	0.04	0.42	0.43			0.43	
21	4.7	5.5	0.085	0.3	0.04	0.45					
24	4.7	3.1	0.042	0.3	0.04			0.41			
25	12.3	5.9	0.17	0.3	0.04	0.49					
28	12.3	5.9	0.17	0.1	0.014	0.49					
32	12.3	5.7	0.17	0.04	0.005				0.5		

(a) At time of first measurement.

(b) Presumably divided (by solubility constraints) ~ M/L dissolved and ~ M/L as solid.

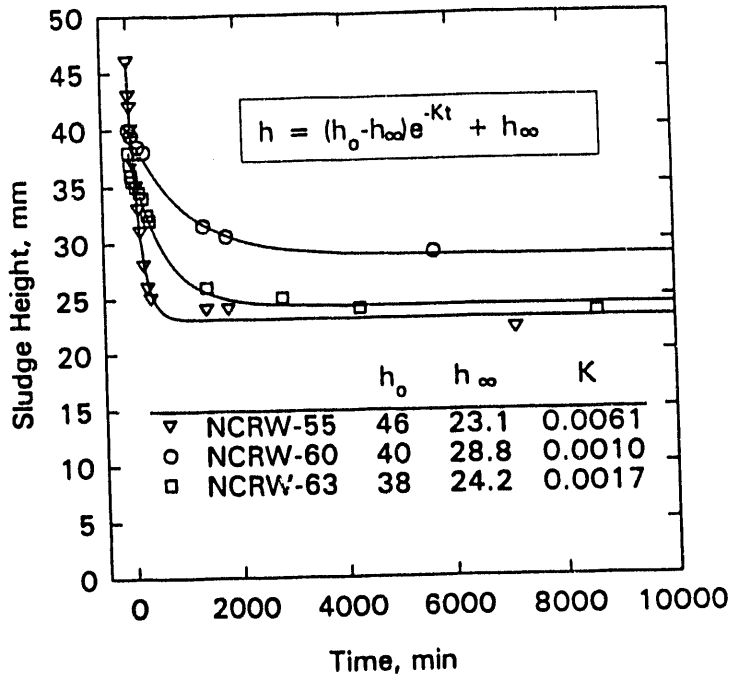


Figure 3.15. Sludge Settling Data for Three Portions of Actual NCRW Sludge

The effects of added Fe^{3+} on the settling behavior of NCRW sludge were assessed. For each of Experiments 69 and 70, a portion of NCRW sludge (both portions were taken from segment 3A of the 1986 sampling of Tank 103-AW) was washed once with 11 mL of water. After centrifuging the sludge, the wash solution (9.1 mL from 69 and 9.9 mL from 70) was decanted and replaced with an equal volume of water. Iron(III) nitrate was added to Experiment 70 so that the concentration of Fe^{3+} (before precipitation) was 0.025 M. The sludge/water slurries were then mixed thoroughly, and the sludges were allowed to settle. After measuring the settling rate over a period of 1 day, each mixture was centrifuged, and the supernatant solution was decanted. The volume of supernatant solution removed (8.8 mL for 69 and 9.7 mL for 70) was replaced by an equal volume of water. The sludge was again slurried and allowed to settle.

The addition of Fe^{3+} did not significantly increase the settling rate of the sludge (see Figure 3.16), but it did have some beneficial effects in reducing the amount of fine solids observed. After the third wash, fine solids in Experiment 69 (after centrifugation) had a tendency to puff up into the supernatant liquid when the vial was disturbed. No similar phenomenon was observed for Experiment 70. The solids in both Experiments 69 and 70 flowed freely; those in Experiment 70 seemed to be slightly more fluid than those in Experiment 69. Filtration of these solids would not be expected to present problems.

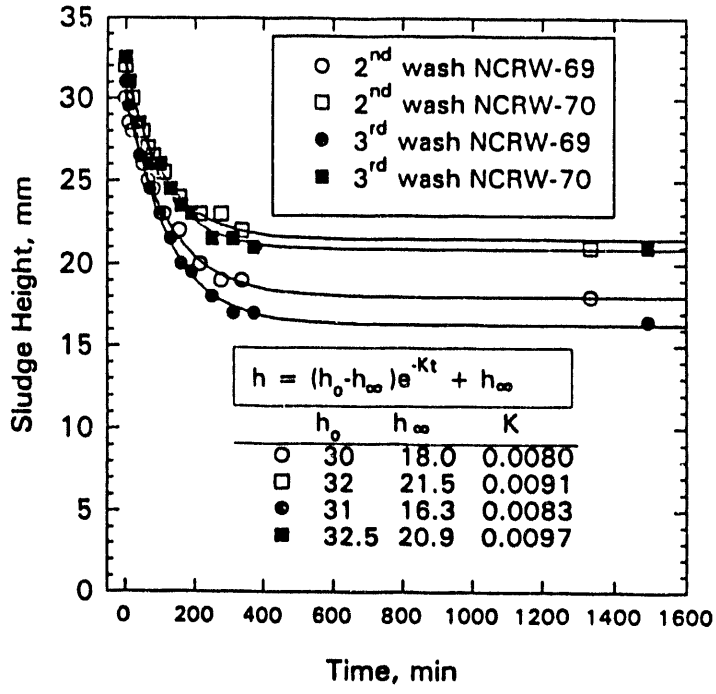


Figure 3.16. Sludge Settling Data for Actual NCRW Sludge With and Without Added Fe(II)

3.7 Conclusion

The results of this study indicate the TRUEX process is a very promising method for reducing the volume of HLW glass produced in the disposal of Hanford NCRW sludge.

The washed NCRW sludge can be dissolved in media [~2 M HNO_3 plus HF at F/(Zr+Al) ~2] that is noncorrosive to many types of stainless steel. Solutions prepared under these conditions are generally stable for months.

Interfacial crud formation in the TRUEX solvent extraction process can be prevented by adjusting the F/(Zr+Al) to greater than 3.75 (for [Zr] ~0.1 M). Further work will be needed to better define the operating range for the TRUEX solvent extraction process.

A solution consisting of 0.25 M Na_2CO_3 plus 0.002 M NaHEDPA appears to be a promising reagent for stripping the TRUs from the TRUEX process solvent. However, at the time of writing, there is some concern that this solution would introduce too much Na into the HLW stream. Thus, future work will include study of alternative stripping schemes.

Sludge settling is dependent on the Zr concentration in the slurry. The greater the Zr concentration, the slower the settling rate. Also, the settling rate is initially hindered by an apparent interaction of the solids with the solution/air interface.

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