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The Chemistry of Sludge Washing and Caustic Leaching Processes for Selected Hanford Tank Wastes

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March 1996

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

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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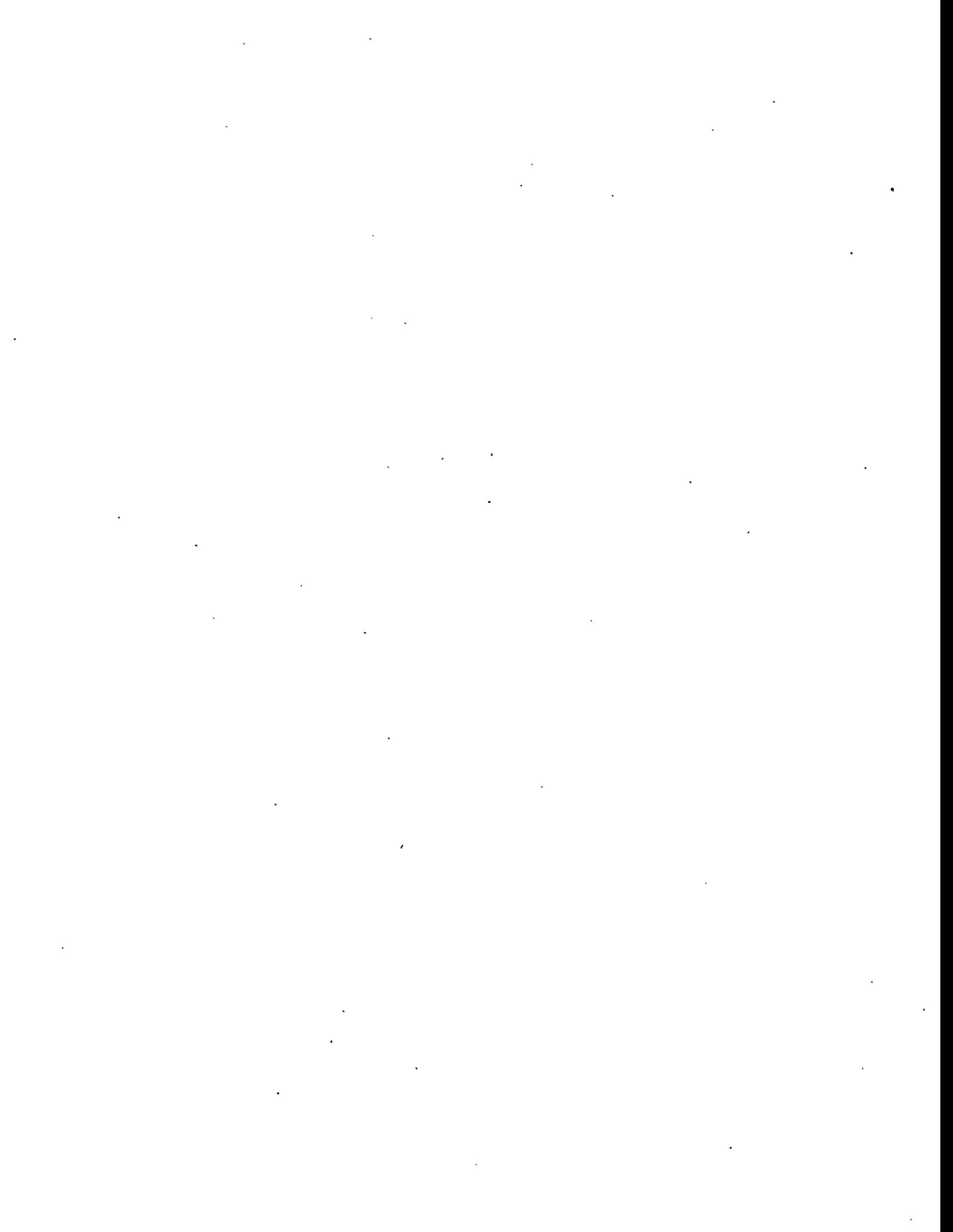
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Summary

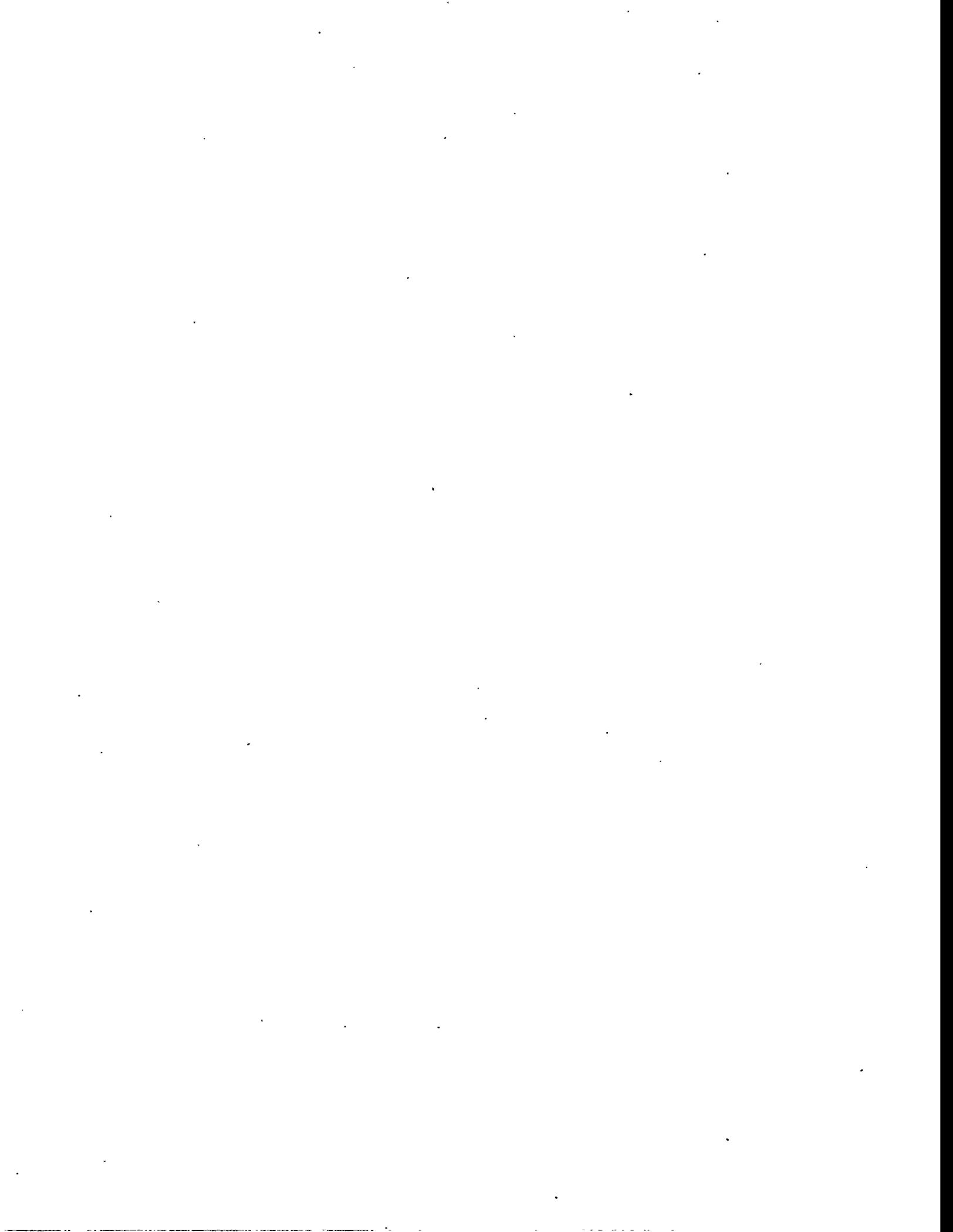
A broad-based study on washing and caustic leaching of Hanford tank sludges was performed in FY 1995 to gain a better understanding of the basic chemical processes that underlie this process. This approach involved testing of the baseline sludge washing and caustic leaching method on several Hanford tank sludges, and characterization of the solids both before and after testing by electron microscopy, X-ray diffraction, and X-ray absorption spectroscopy. A thermodynamically based model was employed to help understand the factors involved in individual specie distribution in the various stages of the sludge washing and caustic leaching treatment. The behavior of the important chemical and radiochemical components throughout the testing is summarized and reviewed in this report. Several interim conclusions have been made concerning this behavior:

- Experimental results and thermodynamic calculations suggest that significant amounts of aluminum, when present in its simple oxide, hydroxide, and phosphate phases, can be removed from the sludges by contact with caustic at the concentrations found under the currently contemplated processing conditions, provided adequate solution-to-solid volumes are used.
- At present there are no data to suggest that, under the proposed processing conditions, appreciable aluminum will dissolve from the aluminosilicate phases in the sludges. However, no experiments exploring the kinetics of aluminosilicate dissolution were performed as part of these tests, and the current status of the thermodynamically based modeling does not allow evaluation of the solubility of these phases under typical sludge washing and caustic leaching experimental conditions.
- Most of the phosphorus can be metathesized and dissolved away from the sludges. However, adequate volumes of the final, low sodium wash are required because of the limited solubility of sodium phosphate at the high sodium concentrations resulting from the caustic leach steps. At present there are no data to suggest that, under the proposed processing conditions, appreciable metathesis of the alkaline earth phosphates will occur.
- Chromium in the sludges has been shown to exist in both the +3 and +6 oxidation states. The relative concentrations of Cr(III) to Cr(VI) can vary greatly. X-ray spectroscopy revealed, unsurprisingly, that the Cr(VI) was readily removed. Conclusions based on thermodynamic modeling suggest that caustic leaching under the current processing conditions may remove some of the Cr(III) present as the $[\text{Cr}(\text{OH})_4]^-$ ion, but the thermodynamically based model currently is valid only at 25°C, and not at the higher temperatures (100°C) used during the first wash and caustic leach steps. Consequently, with these limitations, the modeling results suggest that chromium removal is constrained by the solubility limits of $[\text{Cr}(\text{OH})_4]^-$ under the conditions of caustic leaching. Currently, there are no data on the chromium oxidation state in solution during the caustic leaching steps. At the very least, current indications are that markedly greater (and probably prohibitive) leachate-to-solids ratios may be required to remove the majority of chromium present as Cr(III) from systems with very high concentrations of chromium in the +3 oxidation state, such as Tank SY103 sludge.

- How components in the interstitial fluid of the settled/centrifuged solids are carried over into subsequent stages of the sludge washing and caustic leaching was evaluated to determine at what stage additional components dissolve during each of the individual processing steps. The analysis suggests that most components removed during sludge washing, caustic leaching, and final sludge washing cycle are removed during the retrieval wash and the first caustic leach step. The most significant function of additional caustic leach stages appears to be the removal of additional aluminum in selected sludges. The primary function of the final washes is to remove the sodium introduced during the caustic leach and, in selected instances, to remove metathesized phosphate. This analysis illustrates how sludge compaction following each wash step can influence the volume of wash solution required to effectively separate the water-soluble components from the sludge.
- The combination of experimental testing, sludge characterization, and modeling gave a more complete understanding of the chemistry associated with sludge washing and caustic leaching than would have been obtained from experimental testing alone. However, several factors limited the interpretation of the chemistry of the sludge washing and caustic leaching. The most important limiting factors include 1) an inability to quantify the phase information supplied by electron microscopy, 2) uncertainties regarding the representative nature of the samples, and 3) limitations in the experimental design.
 - Electron microscopy revealed the major phases present before and after sludge washing and caustic leaching. However, the description remained qualitative. X-ray absorption measurements can complement this qualitative information and, in these cases, specifically allowed quantification of the Cr(III) versus Cr(VI) distributions present in the tank sludges. In conjunction with the sludge washing and caustic leaching test data, these measurements gave an indication of the efficacy of removing each oxidation state during the course of the measurement.
 - These studies also point out important additional areas that must be addressed to better understand sludge washing and caustic leaching of Hanford tank sludges. A key limitation in the previous experimental design was the inability to fully examine factors such as the rate of component dissolution (kinetics). The lack of such information prevented resolution of alternative explanations of the observed component dissolution. In addition, the lack of information regarding the kinetics of dissolution limited the applicability of the thermodynamically based modeling and, ultimately, the applicability of these small-scale experimental results. The lack of control over the actual free hydroxide concentration in solution from test to test complicated comparisons of the response of different sludges. Changes in the design of further testing will take these points into account.

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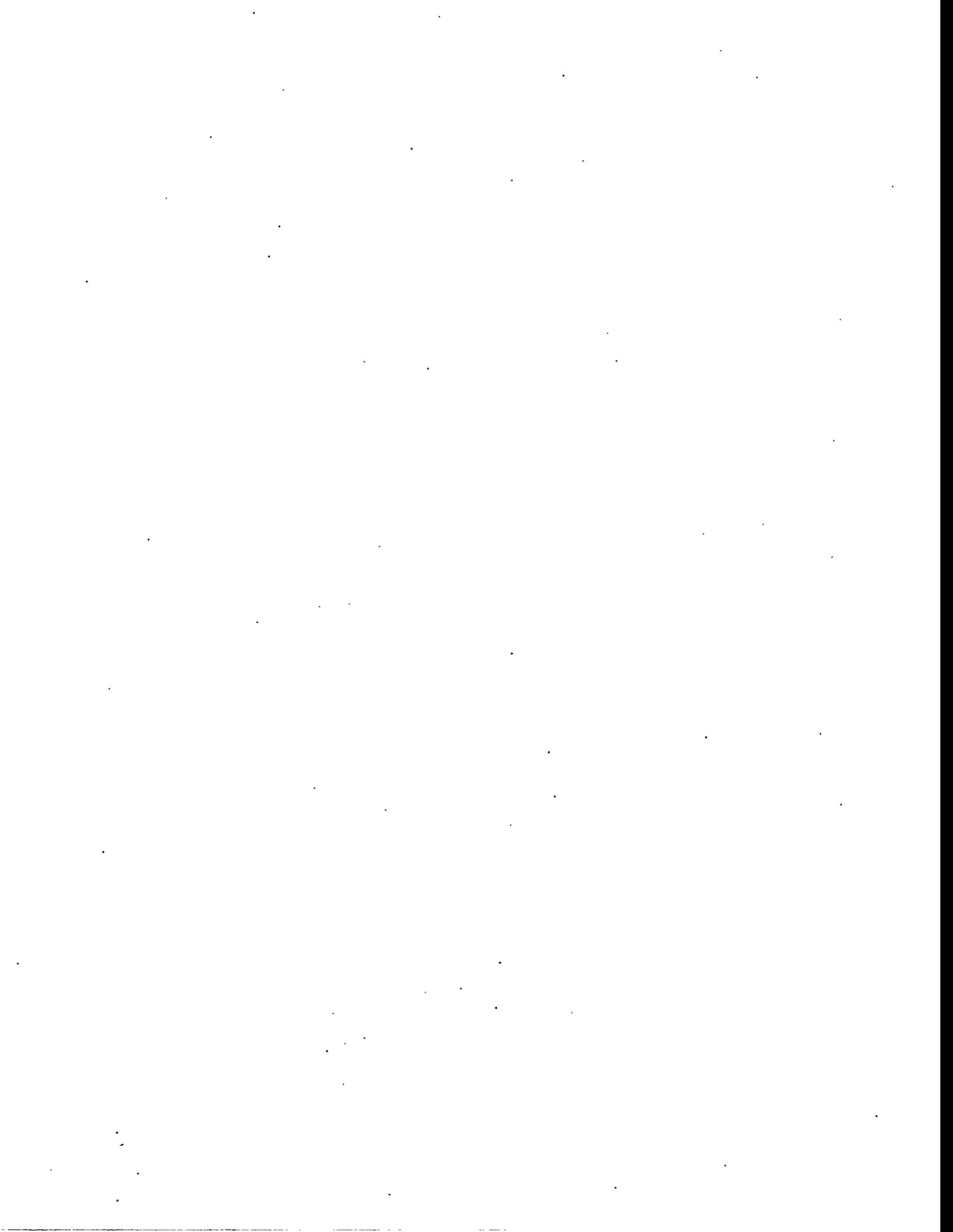
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1.0 Introduction

Until 1990, the primary mission of the U.S. Department of Energy's (DOE) Hanford Site was to produce plutonium for defense purposes. The methods used for isolating plutonium from the dissolved nuclear reactor fuel included a precipitation approach (the bismuth phosphate process) and two solvent extraction methods (the REDOX and PUREX processes) (Ballinger and Hall 1991). The resulting radioactive wastes from these production efforts have been stored in 177 underground tanks that range in size from 210 to 3800 kL (55 to 1000 kgal). Over the years, portions of these wastes were subjected to several radionuclide fixation and recovery processes, along with mixing and evaporation campaigns, in order to reduce stored waste volumes. As a result of this complex and varied processing history, the Hanford waste storage tanks contain a complicated mixture of poorly soluble metal compounds (sludge), crystallized salts (saltcake), and liquids (both supernatant and interstitial). Although some attempts have been made to sort the 177 Hanford storage tanks into certain characteristic groups (Hill et al. 1995), the composition is unique in each tank. Indeed, significant compositional variations have been observed even between different points in the same tank. These variations in composition provide challenges in understanding and implementing a single waste processing scheme.

After the primary mission at the Hanford Site changed from plutonium production to environmental restoration (1990), the Tank Waste Remediation System (TWRS) was established to safely manage and dispose of the radioactive wastes stored in the underground tanks. A key element of the disposal activities under TWRS involves pretreating the wastes prior to disposal. Pretreatment strategies include utilizing processes and equipment to separate and/or destroy waste components to minimize treated waste volumes and produce waste fractions that are compatible with final high-level waste (HLW) and low-level waste (LLW) forms (glass) and their disposal criteria.

The currently envisioned pretreatment scenario is focused on a strategy for 1) removing radionuclides from the aqueous waste fractions to produce streams suitable for vitrification as LLW and 2) using washing and selective caustic leaching of sludges to reduce the volume of immobilized HLW. Such volume reductions are attainable because this strategy should remove three important sludge components (aluminum, chromium, and phosphorus). Removal of aluminum, a bulk component in some sludges, will reduce HLW glass volumes by reducing the mass of feed to the HLW vitrification. Phosphorus and chromium tend to interfere with HLW glass integrity and melter performance; therefore, removal of these components from the HLW sludges will allow higher waste loadings in the glass, and produce a more homogeneous HLW glass as well.

The work described in this report centers on developing an understanding of the chemistry of the tank waste sludges so that their behavior during processing by caustic leaching can be predicted. Several issues need to be addressed to achieve this goal. First, what are the specific materials (compounds) present in the tanks? A correlation between the chemical species present and the processing history of the tanks would be useful for obtaining a predictive capability. Second, is the observed distribution/reactivity consistent with the individual, identified phases in the sludge? This issue is important since it is difficult to identify all phases in sludges, and the question of whether existing methods for phase

identification yield sufficient information to rationalize the observed sludge behavior during pretreatment is key: such structure/reactivity correlations are a basic tenet behind any scientifically based understanding of tank processing. For example, unexplained deviations in component removal could signal the presence of unidentified phases. Phase identification is especially problematic with the radionuclides, which are present in a relatively low (molar) concentration and provide a rationale for developing new methods of species identification applicable to tank sludges. Finally, can the observed partitioning be accounted for in terms of a thermodynamically based explanation or are kinetic phenomena important in the distribution of important components? If kinetic phenomena are identified, can this behavior be correlated to the presence of specific phases?

Accordingly, a broad-based process science activity was initiated at Pacific Northwest National Laboratory^(a) to provide further technical support and develop the scientific understanding required to evaluate the sludge washing and caustic leaching process for pretreating Hanford sludges. This activity, which was part of the Pretreatment Technology Development Project, integrated research efforts that focused on describing the physical and chemical nature of tank sludges; the distribution of important waste components as these sludges proceed through a baseline sludge washing and caustic leaching flowsheet, involving multiple contacts of tank sludges with water and caustic solutions at elevated temperature and separation of the resulting supernatants from the residual solids; the physical and chemical changes that occur in these sludges as a result of sludge washing and caustic leaching; and a thermochemical justification of the observed component distribution.

This report presents an overview of that work and illustrates how the collective results serve to support current engineering flowsheet assumptions or, in some cases, provide the bases for new assumptions. An overview of the level of technical and scientific understanding is given, along with results and discussions of the specific studies conducted.

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2.0 Experimental Studies and Analyses

The experimental work was divided among the project team and encompassed three individual areas: sludge washing and caustic leaching testing, characterization analysis, and chemical equilibrium modeling. This section describes the activities carried out in these three areas.

2.1 Sludge Washing and Caustic Leaching Tests

Studies on seven sludges were completed in FY 1995. The seven tanks are listed in Table 2.1, along with the primary and secondary waste types stored in those tanks. The test procedure used to mimic the baseline sludge washing and caustic leaching flowsheet on a laboratory scale is outlined in Figure 2.1. The test procedure has been described in more detail elsewhere (Rapko et al. 1995). Before the tests began, a small portion of the untreated sludge sample was extensively washed with 0.01 M NaOH/0.01 M NaNO₂, "inhibited water," then dried and weighed to obtain the amount of "insoluble" solids present in the sludge. This value was used to determine the volume of inhibited water needed to obtain a slurry containing 2.3 wt% solids.

Table 2.1. Sludges Examined During FY 1995

Tank	Core #	Primary Waste	Secondary Waste
B111	29 & 30	2C	5-6
BX107	41	1C	TBP
C103	63	SRS	SR-WASH
S104	43	R	(a)
SY103	62	CC	(a)
T104	46	1C	(a)
T111	33	2C	224

Note: The waste types are defined as follows (Hill et al. 1995):

- C Complexant concentrate.
- R Reduction oxidation (REDOX) process HLW.
- SRS Sludge feed for the strontium extraction process at B Plant.
- SR-WASH Particulates from strontium wash of plutonium/uranium extraction (PUREX) wastes in AR Vault.
- TBP Waste from the tributyl phosphate uranium extraction process at U Plant.
- 1C First-cycle decontamination waste from the bismuth phosphate process.
- 2C Second-cycle decontamination waste from the bismuth phosphate process.
- 224 Lanthanum fluoride decontamination waste from the bismuth phosphate process.
- 5-6 HLW from Tank 5-6 at B Plant.
- (a) No major secondary waste type.

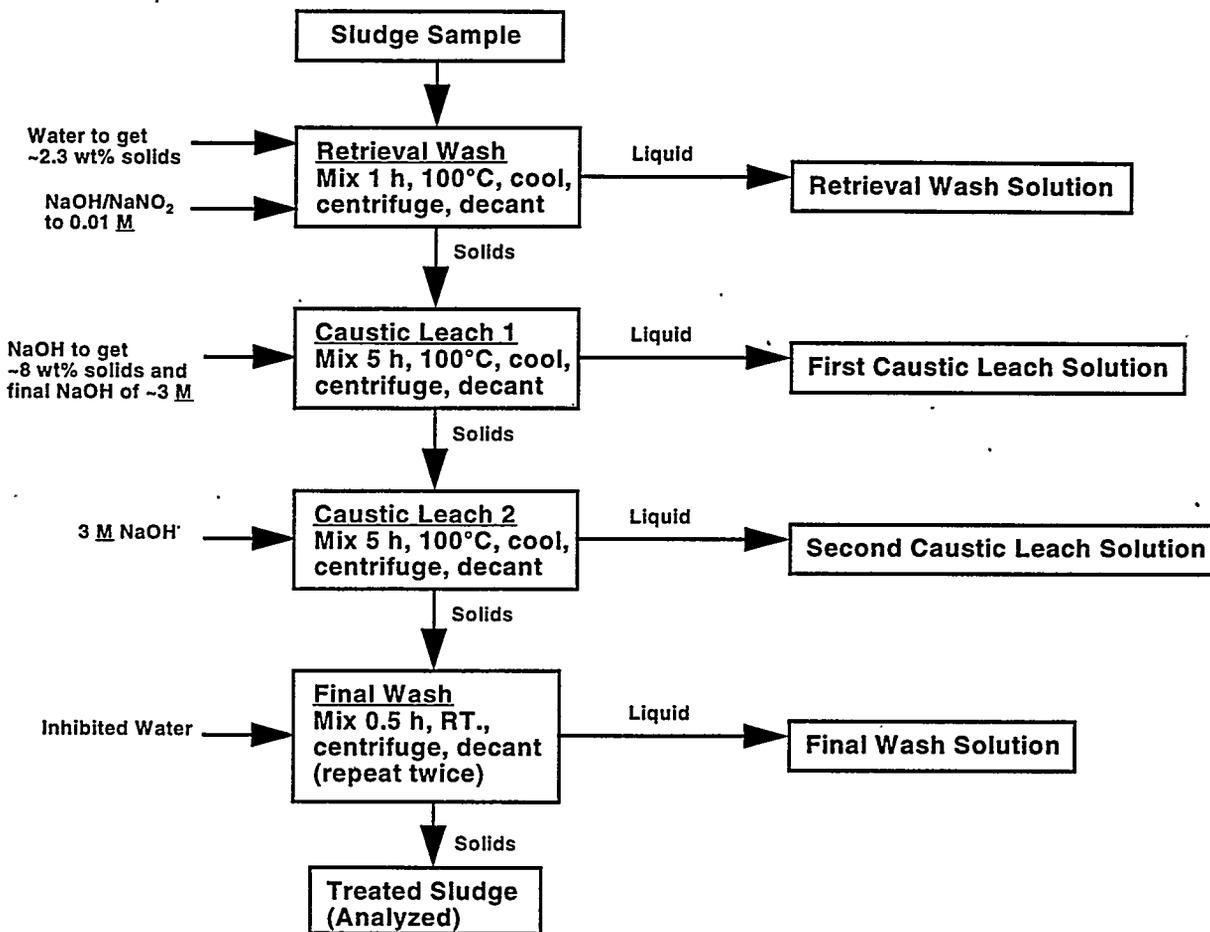


Figure 2.1. Simplified Schematic of Standard Sludge Washing and Caustic Leaching Procedure

When this work began, the baseline processing flowsheet indicated that the average solids concentration in the retrieval wash solution would be 2.3 wt%, and the average solids concentration in the caustic leaching and subsequent washing steps would be 8 wt% (Orme 1994). For the volume of caustic leach and final wash solutions, it was assumed that 30% of the water-insoluble solids would dissolve during the first caustic leaching step.

For the “retrieval wash,” the sludge was contacted with inhibited water at a targeted concentration of 2.3 wt% solids for 1 hr at 100°C. The washed solids then were leached with two contacts of approximately 3 M NaOH solution (targeted solids concentration of 8 wt%) for 5 hr at 100°C. Residual solids were contacted three times with inhibited water, with each contact again at a targeted solids concentration of 8 wt%; however, this step was performed at room temperature. In each instance, the solid was separated from the liquid by decanting the supernatant liquid following centrifugation of the suspension. Sludge solids were sampled for analysis before and after treatment. Solid samples were solubilized for analysis by a potassium hydroxide fusion method. The wash and leach solutions were analyzed as well. Leach solutions were cooled to room temperature (~25°C) and acidified with HNO₃ prior to analysis. The major

metallic elements (Al, Bi, Cr, Fe, Mn, Na, P, Si, etc.) were determined by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). Alpha spectroscopy was used to establish the transuranic (TRU) elements present, and gamma spectroscopy was used to measure the gamma-emitting radionuclides such as ^{137}Cs . Uranium concentrations were obtained by laser fluorimetry. A proportional beta counter was used to determine ^{90}Sr and ^{99}Tc after chemical separation of these isotopes from the other radionuclides. Free hydroxide concentrations in the caustic leach solutions were obtained by titration with standard HCl. The titrations were performed potentiometrically using a Mettler DL21 automatic titrator equipped with a ROSS[®] combination pH electrode (Orion Research, Inc., Boston, Massachusetts).

2.2 Characterization Analyses

The following analytical techniques were used to better understand sample characteristics: X-ray diffraction, transmission electron microscopy, and X-ray absorption spectroscopy. The procedures are described below.

2.2.1 X-ray Diffraction (XRD)

Samples were prepared by slurring a dried sludge sample (derived from a small aliquot, typically 1/500th of the original sample used in the sludge washing and caustic leaching test) with an amyl acetate based, low X-ray background glue, placing the slurry on a glass slide, and drying the prepared sample prior to analysis. XRD measurements were performed with a Sintag PAD V X-Ray Powder Diffractometer, using Cu radiation and a solid-state detector. Typical measurement parameters included operation at 2 kW power, with 0.2 degrees/step, and an overnight run time.

2.2.2 Transmission Electron Microscopy (TEM)

Samples were derived from the same aliquot supplied for the XRD examination described above. Samples were prepared by dispersing a small amount of solid sample (approximately 1 mg) in methanol solution (<5 mL), a drop of which was placed on TEM copper grids covered with carbon films. Sample analysis was performed using a JEOL 1200 analytical TEM at 120 kV. The examination then proceeded as follows: 1) the morphology, distribution, and sizes of particles were evaluated by electron imaging; 2) the elemental compositions of the particles were identified by electron dispersion spectroscopy (EDS); 3) the crystal structures of the particles were studied by electron diffraction; and 4) the diffraction patterns were compared with the JCPDS-EDD Data Base published by the International Center for Diffraction Data.

2.2.3 X-ray Absorption Spectroscopy (XAS)

XAS spectra were collected for both untreated and treated sludge samples. Treated samples were prepared using a washing and leaching procedure similar to that described above, except that all steps were carried out at ~2.5 wt% solids loading. XAS measurements were performed at the Cr and Mn K edges. XAS spectra also were collected for various reference compounds. All XAS measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL), California. An XAS spectrum may be divided into two regions for analysis. The first region comprises the spectrum roughly 50 eV below to

100 eV above the absorption edge. This is called the near-edge region, and is used for X-ray absorption near-edge spectroscopy (XANES). The second region comprises the data at energies greater than roughly 50 eV above the absorption edge, and is used for extended X-ray absorption spectroscopy (EXAFS).

XANES of the Cr K edge from the tank samples was used to determine the Cr(III)/Cr(VI) ratio. The spectra were analyzed following the standard procedure of pre-edge background subtraction and normalization to the absorption step height (Sayers and Bunker 1988). XANES of the Mn K edge from the tank samples was used to determine the oxidation state of manganese in these samples. Like many transition metals, the manganese absorption edge has been shown to shift to higher X-ray energy as the oxidation state increases (Belli et al. 1980). The spectra were analyzed following standard procedures (Sayers and Bunker 1988).

EXAFS measurements were performed at SSRL under dedicated operating conditions (3.0 GeV, 40 to 90 mA current) and at ambient temperature. Theta, the angle between the two crystals of the monochromator, was maintained at 0 (fully tuned) with harmonic rejection accomplished by critical angle reflection off a rhodium-coated mirror. All measurements on the waste samples were performed in the fluorescence mode using a 13-element Ge detector. Intrinsic radiation emitted by the samples had only minimal effects on these data. The number of scans varied with the concentration, preferred data range, and beam quality. Reference compounds for chromium (Cr_2O_3 , $\text{K}_2\text{Cr}_2\text{O}_7$) and manganese (MnO , Mn_2O_3 , MnO_2) were ground to a fine powder with mortar and pestle and pressed onto tape for transmission data collection at ambient temperature. Transmission data for chromium (manganese) foils were collected simultaneously with the chromium (manganese) reference compounds. Transmission data for the foils were collected after fluorescence mode data collection on each waste sample.

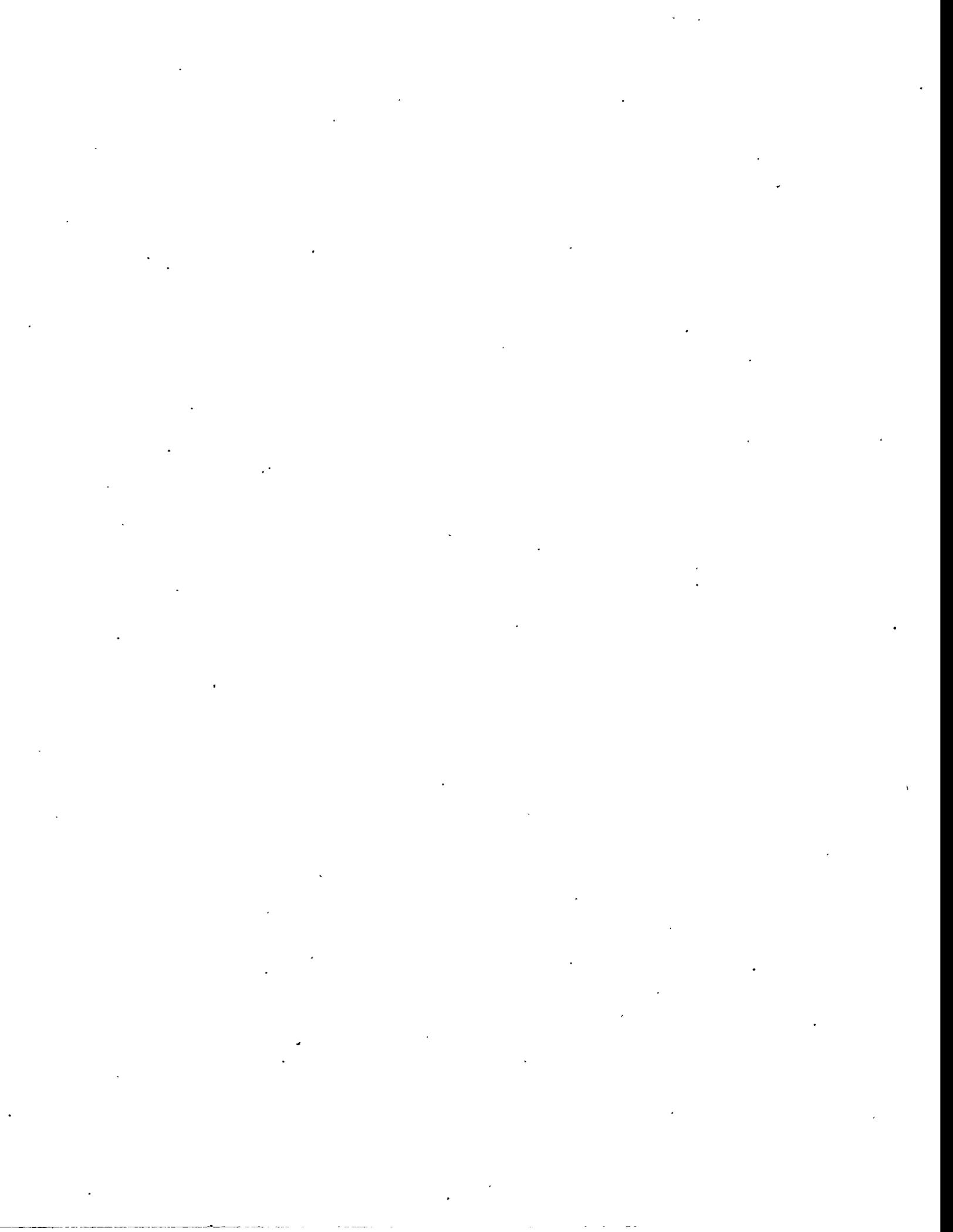
2.3 Chemical Equilibrium Modeling

The aqueous chemical equilibrium model is based on the ion-interaction approach (Pitzer 1991; Felmy and Weare 1995). The model presents a detailed description of the specific ion-interactions in the chemical system and is valid to high ionic strengths. Parameters for this model have been determined for the chemical components of interest here over the temperature range of 25°C to 100°C.

In the experimental sludge washing and caustic leaching tests, samples were heated to 100°C during the extraction process and then cooled to room temperature (~25°C) prior to analysis (*vide supra*). These temperature changes can dramatically affect the solubilities for several solid phases, especially aluminum compounds, such as gibbsite and boehmite. The solubility of these phases can change by an order of magnitude across this temperature range. As a result of these potential temperature changes, concentrations were predicted for the temperature range of 25°C to 100°C, when possible. The actual measured chemical component concentrations in each individual wash or caustic leach solution were used in all calculations.

In the case of chromium, amorphous chromium hydroxide, $\text{Cr}(\text{OH})_3(\text{am})$ was chosen for the modeling calculations because this phase is the most likely to form under strongly basic conditions. Modeling calculations on the solubility of $\text{Cr}(\text{OH})_3(\text{am})$ were conducted solely at 25°C since accurate thermodynamic data are not available at other temperatures for this phase.

In the case of phosphorus, the solubilities of three sodium phosphate compounds, $\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$, and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, were included in the modeling. The thermodynamic data for these phases, as well as osmotic data for Na_3PO_4 solutions were used to parameterize the activity coefficient expressions.



3.0 Results and Discussion

In the following discussion, the results from the characterization of tank sludges, both before and after washing and caustic leaching, are described together with the experimental measurements of how bulk chemical and radiochemical components partition during the testing. The thermodynamic calculations describing the expected concentrations of selected chemical components at equilibrium are also given. Simulating the sludge washing and caustic leaching baseline processing in the laboratory can validate or challenge the engineering assumptions used in baseline flowsheet development. However, by merging the baseline testing results with sludge characterization and thermodynamic predictions of sludge component behavior under these processing conditions, a more detailed understanding of process chemistry should result with concomitant confidence that the results from these limited tests may be appropriately generalized to other processing conditions.

This section provides a summary and overview of the experimental results. Other published reports are available that supply additional detail (LaFemina et al. 1995a,b,c; Rapko et al. 1995).

3.1 Experimental Variability

As explained in Section 2.1, the study started with the assumption that 30% of the water-insoluble solids would dissolve during the first caustic leaching step, with no additional component dissolution during the remaining steps. This assumption would then be used to determine the volume of leach solution needed to achieve the targeted 8% by weight insoluble solids. However, the actual amount of solids dissolved during the caustic leaching portion of the sludge washing and caustic leaching treatment varied significantly from sludge to sludge (Table 3.1). In two cases (Tanks BX107 and S104), the assumption of 30% dissolution was reasonable. In the other cases, the actual amount of dissolved material was either overestimated (Tanks B111, T104, and T111) or markedly underestimated (Tank SY103). Consequently, the actual solid-to-liquid ratios examined from test to test varied significantly.

Table 3.1. Estimated Sludge Mass Loss Through Caustic Leaching

Tank	Estimated Mass Loss, %
B111	0
BX107	36
C103	NA
S104	33
SY103	56
T104	1
T111	10

NA = data not available.

The amount of hydroxide consumed during the leaching step was similarly unknown before each test was performed. Thus, for each first leaching step, an initial NaOH concentration of 3.2 M was targeted,^(a) based on the assumption that sufficient hydroxide would react to give a final free hydroxide concentration of 3.0 M. Table 3.2 indicates that in most cases the free hydroxide concentration was less than 3.0 M after the first leach step. For the second leach step, 3.0 M NaOH was added; it is unclear why the free hydroxide concentration in the second B111 and BX107 leach step was above 3 M free NaOH.

The variabilities in the solid-to-liquid ratios and in the actual hydroxide concentrations need to be considered when comparing the results from different tests. In instances where dissolution of a component is limited by either its solubility product or by its rate of dissolution, direct comparisons from test to test will be misleading. Such complicating factors emphasize the need to more precisely control important experimental parameters if such direct comparisons are to be made. The differing free hydroxide concentration, especially the relatively low concentrations found with Tanks T104 and C103, might have significant impact on the results. The consequences of these varying free hydroxide concentrations should be considered when comparing component dissolution for these sludges.

Table 3.2. Free Hydroxide Ion Concentrations Found in the Sludge Washing and Caustic Leaching Tests

Tank	Free [OH ⁻], <u>M</u>	
	First Leach	Second Leach
B111	2.3	4.3
BX107	2.0	3.6
C103	0.6	1.0
S104	3.8	3.0
SY103	2.2	2.8
T104	0.3	2.2
T111	3.5	3.4

3.2 Chemical Behavior of Nonradionuclide Components

The distribution of important nonradioactive components during the sludge washing and caustic leaching procedure is summarized in Table 3.3. The behavior of these components tends to fall into three classes. The first class of behavior is characterized by good removal (often >90%) of the constituent by sludge washing and caustic leaching; sodium generally falls into this category. The second class of

(a) The initial 3.2 M NaOH concentration was achieved by adding an appropriate amount of 10 M NaOH to give a 3.2 M solution when the leaching mixture was adjusted to the desired volume with water.

Table 3.3. Summary of Nonradionuclide Removal by the Baseline Caustic Leaching Method

Components	Tanks						
	B111	BX107	C103	S104	SY103	T104	T111
Mass Dry Sludge Solids, kg ^(a)	4.05E+05	6.77E+05	1.22E+05	1.08E+06	3.25E+05	5.65E+05	4.52E+05
Al, wt %	0.30	3.5	14	15	4.7	4.7	0.49
Al Removed, %	2	68	48	38	90	62	13
Bi, wt %	5.2	4.8	<0.07	<0.02	0.02	5.2	6.3
Bi Removed, %	0	0	NA	NA	0	0	0
Cr, wt %	0.31	0.22	0.16	0.47	1.3	0.31	0.45
Cr Removed, %	40	29	11	97	12	27	63
Fe, wt %	4.6	2.8	20	0.34	0.41	2.8	6
Fe Removed, %	0	0	0	1	25 ^(b)	0	0
Mn, wt %	0.04	0.04	0.58	0.22	0.14	0.04	5.3
Mn Removed, %	0	11	0	0	0	0	0
Na, wt %	24	21	4.6	20	28	19	37
Na Removed, % ^(c)	91	91	24	92	99	40	85
P, wt %	4.1	5.6	0.5	<0.02	0.78	6.9	2.6
P Removed, %	91	93	66	NA	98	55	72

(a) Estimated total for the tank.

(b) This value is suspect due to possible external iron contamination.

(c) Because so much of the total sodium present in the tanks was added in the form of NaOH during the leaching process, the amount of sodium initially present in the sludge that was removed could not be determined per se. The value reported here is the amount of sodium found in the dried, leached residue relative to the amount in the untreated sludge, expressed as a percentage.

behavior is characterized by no dissolution of the component during sludge washing and caustic leaching. Typical components in this category are iron, bismuth, and manganese. An exception is found for Tank SY103, where some iron appears to dissolve. However, experimental records suggest that external iron contamination of the sampled leach solution was possible in this specific test: this possibility has yet to be validated. The third class of behavior is characterized by widely varying removal efficiencies. Understanding the variations in observed partitioning behaviors is critical to understanding the overall impact of sludge washing and caustic leaching methods on HLW glass production since several key components show significant variability in the effectiveness of their removal by the baseline sludge washing and caustic leaching process (Table 3.3). Sludge samples were analyzed by various methods in an attempt to achieve this understanding for the work performed, and the crystalline species and major phases in the sludge were identified both before and after washing and caustic leaching. The composition of the amorphous solids also was examined. The results are summarized in Table 3.4. This information can be correlated with specific types of waste. For example, the primary waste in Tanks B111 and T111 is from the second decontamination cycle of the bismuth phosphate process (Table 2.1). Both of these sludges contain

Table 3.4. Significant Phases Identified in Untreated and Treated Hanford Tank Solids

Tank	Identified Phases	Present After Treatment?
B111	<u>Major Phases</u>	
	Na ₃ PO ₄	Y
	Amorphous Fe(OH) ₃ ^(a)	Y
	Iron bismuth silicate hydroxide	Y
	<u>Minor Phases</u>	
	Crystalline aluminosilicates	Y
	Bi ₂ O ₃	Y
Bi ₃₈ CrO ₆₀	Y	
BX107	<u>Major Phases</u>	
	Na ₃ PO ₄	Y
	Amorphous Fe(OH) ₃ ^(a)	Y
	Iron bismuth silicate hydroxide	Y
	AlPO ₄	N
	Crystalline and amorphous ^(a) aluminosilicates	Y
	Amorphous aluminum hydroxide ^(a)	N
	<u>Minor Phases</u>	
Bi ₂ O ₃	Y	
Bismuth iron phosphate	Y	
S104	Boehmite [Al(O)OH]	Y
SY103	<u>Major Phases</u>	
	Amorphous ^(a) and weakly crystalline Al(OH) ₃	N
	Amorphous ^(a) Cr(OH) ₃	Y
	<u>Minor Phases</u>	
	Crystalline aluminum oxide hydrate	N
(Fe, Mn) oxide	Y	
T104	<u>Major Phases</u>	
	Na ₃ PO ₄	Y
	Amorphous Fe(OH) ₃ ^(a)	Y
	Iron bismuth silicate hydroxide	Y

Table 3.4. (contd)

<u>Tank</u>	<u>Identified Phases</u>	<u>Present After Treatment?</u>
	AlPO ₄	N
	Crystalline and amorphous ^(a) aluminosilicates	Y
	Amorphous aluminum hydroxide ^(a)	N
	<u>Minor Phases</u>	
	Bi ₂ O ₃	Y
T111	<u>Major Phases</u>	
	Na ₃ PO ₄	N
	Amorphous Fe(OH) ₃ ^(a)	Y
	Iron bismuth silicate hydroxide	Y
	<u>Minor Phases</u>	
	Ca ₅ (OH)(PO ₄) ₃	Y
	La ₄ (P ₂ O ₇) ₃	Y
	Bismuth iron phosphate	Y
	Mn ₂ MnO ₄	Y
	Fe ₂ MnO ₄	Y
	Goethite [Fe(O)OH]	Y

(a) Identified by EDS together with an observed characteristic morphology for the material.

Na₃PO₄, Fe(OH)₃(am), and an iron bismuth silicate hydroxide phase as major phases. Tank T111 sludge also contains hydroxyapatite, [Ca₅(OH)(PO₄)₃], and La₄(P₂O₇)₃ as major phases. The presence of a lanthanum-containing species is expected for T111 since this tank also contains waste generated during the final plutonium purification steps associated with the bismuth phosphate process, which employed a LaF₃ precipitation. Similar correlations of the observed species can be made for Tanks BX107 and T104, which contain waste from the first decontamination cycle of the bismuth phosphate process.

In the following discussion, the chemical behavior of individual sludge components is rationalized in terms of the chemical species identified in the sludges and the thermodynamic modeling results. This discussion focuses on aluminum, phosphorus, and chromium because removal of these three elements is critical to the success of the baseline sludge pretreatment method.

3.2.1 Aluminum

Aluminum is present in large quantities in the Hanford tank wastes, primarily as a result of decladding of aluminum-clad irradiated fuel and the use of aluminum nitrate as a salting-out agent in a solvent extraction process. Aluminum exists in a variety of different chemical species in the Hanford tank sludges. For example, in BX107 and T104 sludges, the same aluminum-containing phases, aluminum phosphate, amorphous aluminum hydroxide, and aluminosilicates, were identified (Table 3.4), which would be

expected since the two tanks contain the same primary waste type. However, in S104 sludge, boehmite, Al(O)(OH) , was the only aluminum-containing phase observed.

Two general types of aluminum behavior were seen during sludge washing and caustic leaching. In the first type, the aluminum present in the sludge is reactive under the leaching and washing conditions, and the concentration in solution either approaches or achieves the solubility limits predicted for gibbsite or boehmite in the 25°C to 100°C temperature range. Sludges from Tanks C103, SY103, T104, and S104 fall under this category (Figure 3.1a-d). In the second type, typified by Tanks B111 and T111, the aluminum appears less easily dissolved and remains substantially below the gibbsite or boehmite solubility limit. One possible explanation for this behavior would be that the aluminum is tied up in aluminosilicate phases that are insoluble under the conditions of the caustic leaching experiment (Figure 3.2a,b). However, while aluminosilicates were observed in B111 sludge, no such phases were observed in T111 sludge (Table 3.4), even though the aluminum concentration in T111 is comparable to that seen in B111. Still, Tanks B111 and T111 contain the same primary waste type, so similar behavior would be expected.

The behavior of aluminum dissolution for Tank BX107 (Figure 3.3) appears to fall between the two categories described above. Furthermore, in the retrieval wash step, the measured aluminum concentration is greater than that expected based on the calculated aluminum concentrations for gibbsite or boehmite. The lack of quantitative information regarding the various aluminum-containing species prevents a detailed explanation. Still, it should be noted that Table 3.4 indicates aluminum in BX107 is present in several different forms, including both species that should readily react with NaOH (AlPO_4 and amorphous Al_2O_3) and species not expected to be reactive with NaOH under these conditions (aluminosilicates). Therefore, the complex behavior of aluminum in BX107 is not surprising, although these characteristics also apply to Tank T104, whose behavior is fairly well described by the gibbsite modeling results.

With Tank S104 sludge, only 38% of the aluminum was removed by the washing and leaching process. Modeling results (Figure 3.1c) indicate that the aluminum concentrations during the S104 test were near the gibbsite or boehmite solubility limit at 25°C. This suggests that during the system cooling before sampling was performed, gibbsite or amorphous Al(OH)_3 should have precipitated. However, the microscopy studies argue against this explanation. Microscopic examination of the treated S104 residue provide no evidence for either gibbsite or amorphous Al(OH)_3 , suggesting that such boehmite dissolution/gibbsite precipitation did not occur. Indeed, the only aluminum-containing phases identified in any of the treated sludges examined, except S104, were aluminosilicates. Differences between the actual and predicted aluminum dissolution behavior might be due to the test system not achieving equilibrium. Further study on the kinetics of aluminum dissolution upon heating and precipitation upon cooling in sludges would be valuable in understanding the details behind the aluminum dissolution observed in the present study.

3.2.2 Phosphorus

Most of the phosphorus found in these dried tank sludges before sludge washing and caustic leaching appeared to be present as sodium phosphate. The original source of the phosphate, whether present as part of the solids or deposited from the sludge's interstitial liquid during the drying prior to analysis, was not addressed here. This salt was identified in sludges from four of the six tanks examined: B111, BX107,

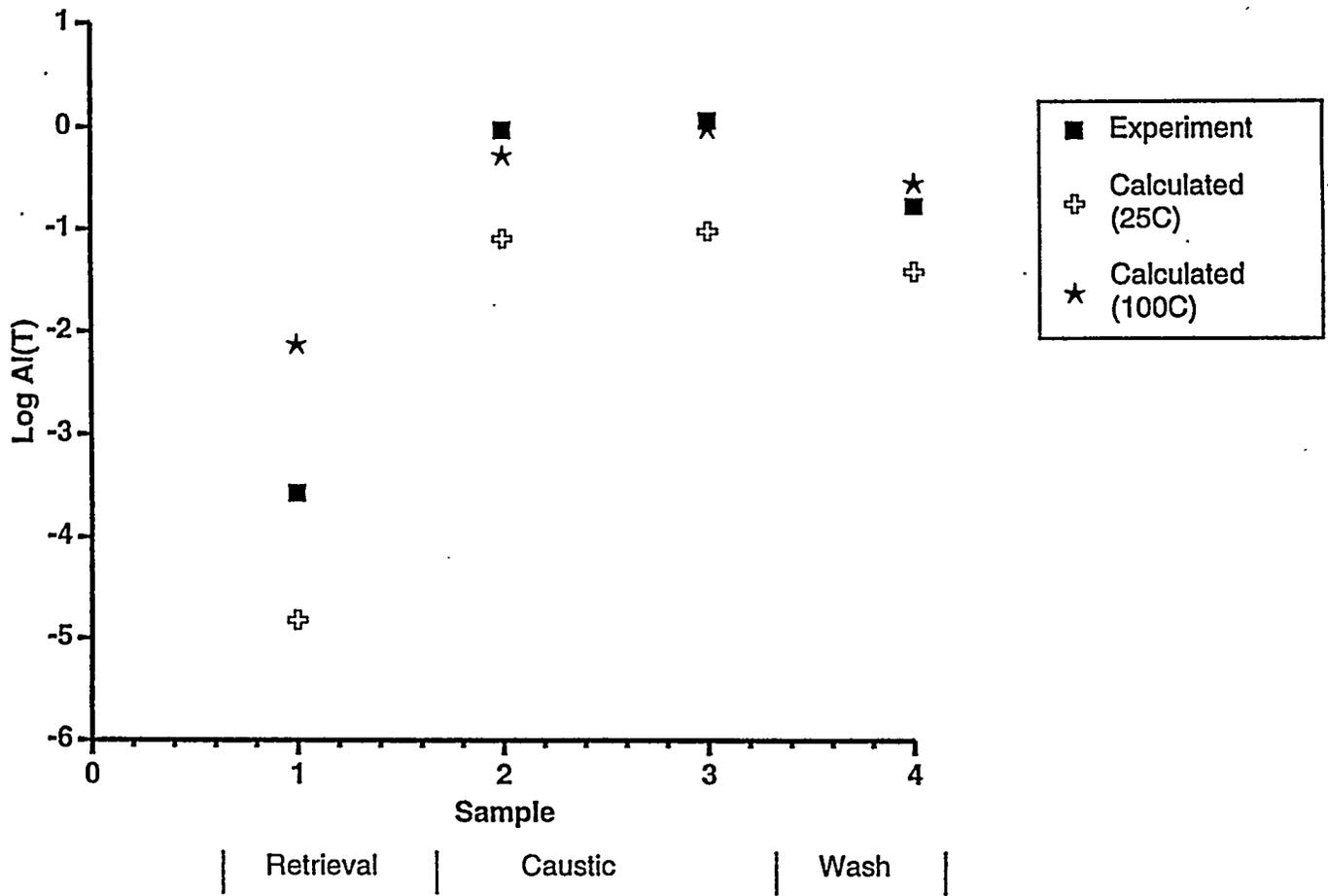


Figure 3.1a. Experimental and Calculated Aluminum Solubilities for Tank C103. Calculated solubilities assume equilibrium with gibbsite.

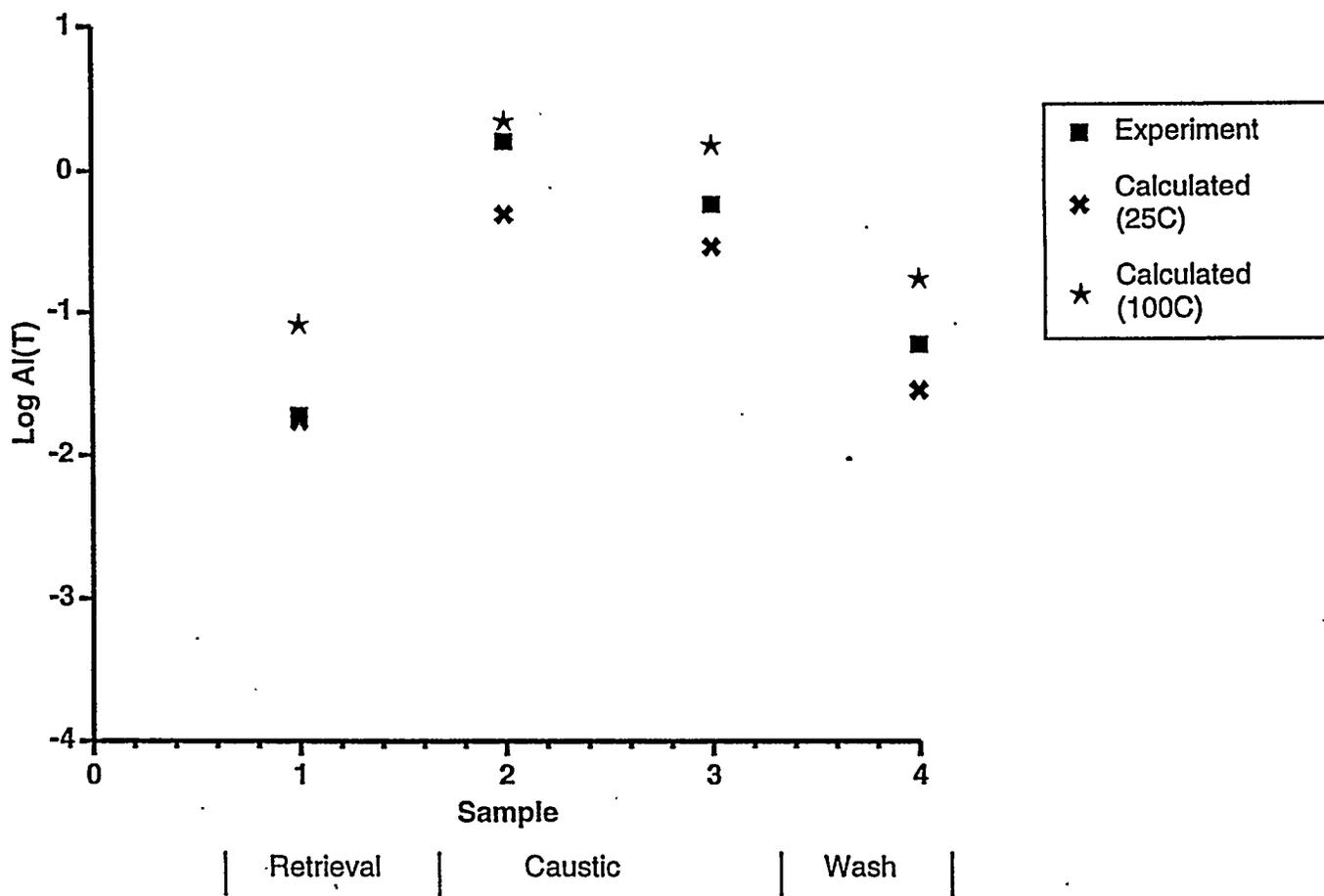


Figure 3.1b. Experimental and Calculated Aluminum Solubilities for SY103.
 Calculated solubilities assume equilibrium with gibbsite.

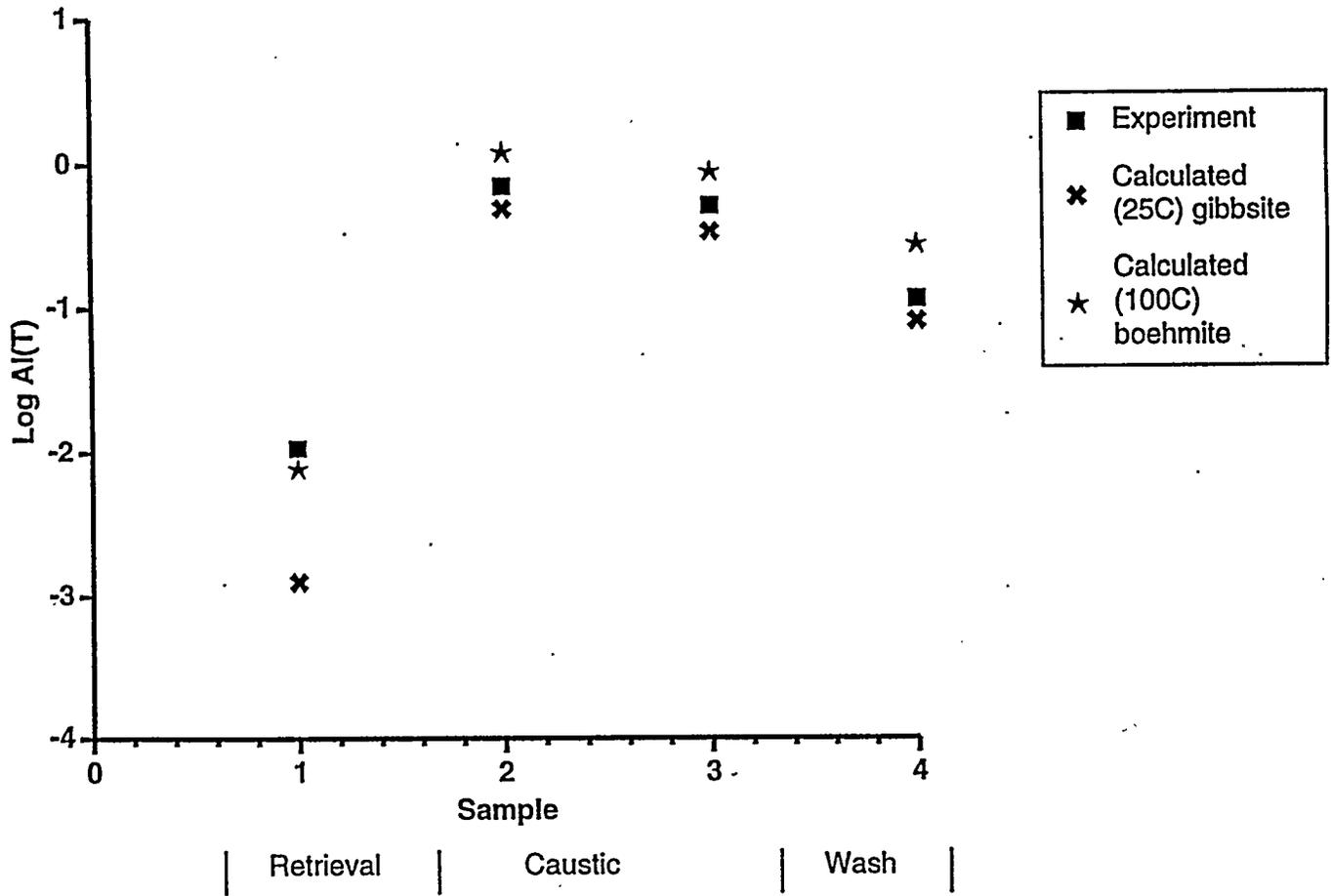


Figure 3.1c. Experimental and Calculated Aluminum Solubilities for Tank S104 (Gibbsite and Boehmite). Calculated solubilities assume equilibrium with gibbsite and boehmite.

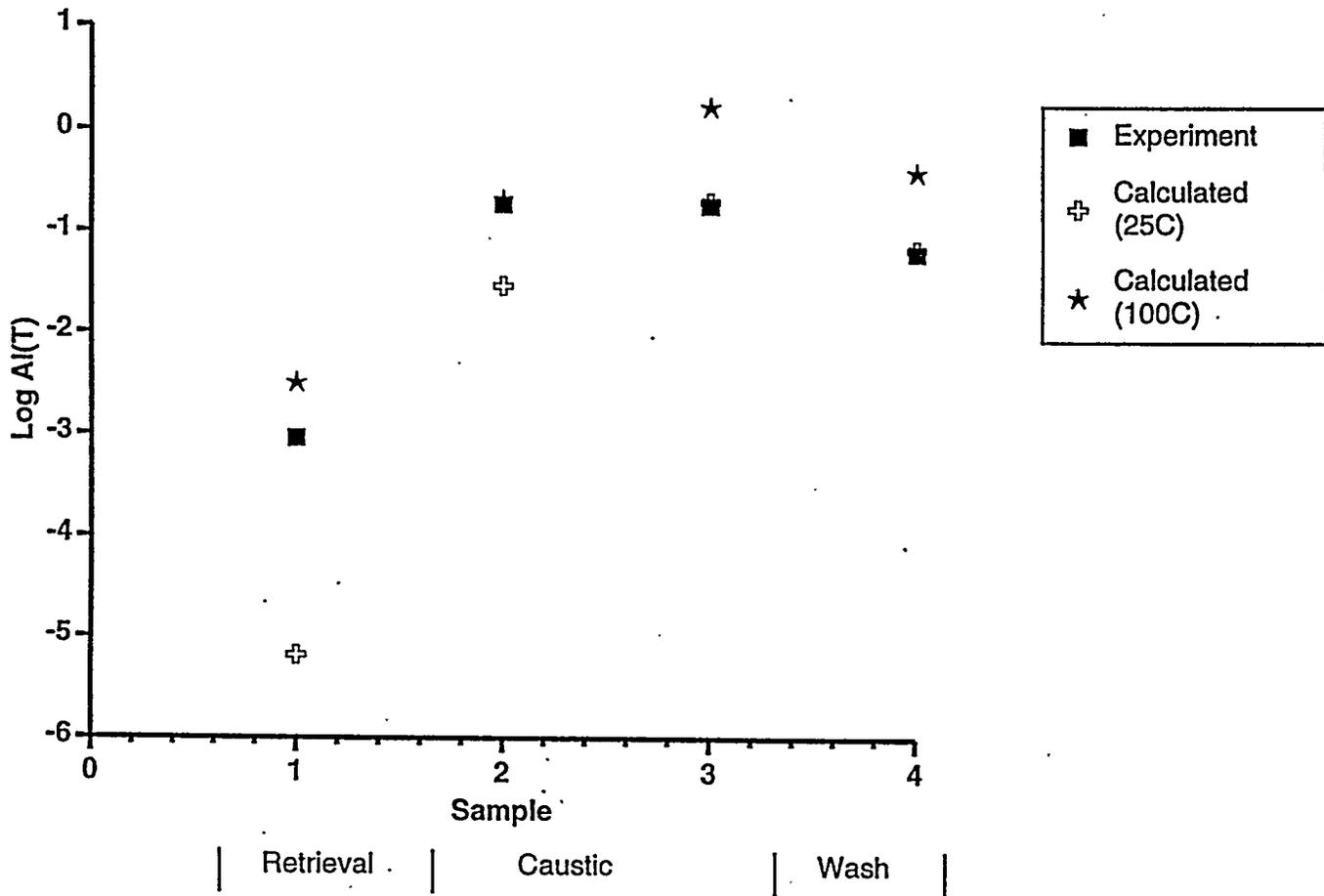


Figure 3.1d. Experimental and Calculated Aluminum Solubilities for Tank T104.
 Calculated solubilities assume equilibrium with gibbsite and boehmite.

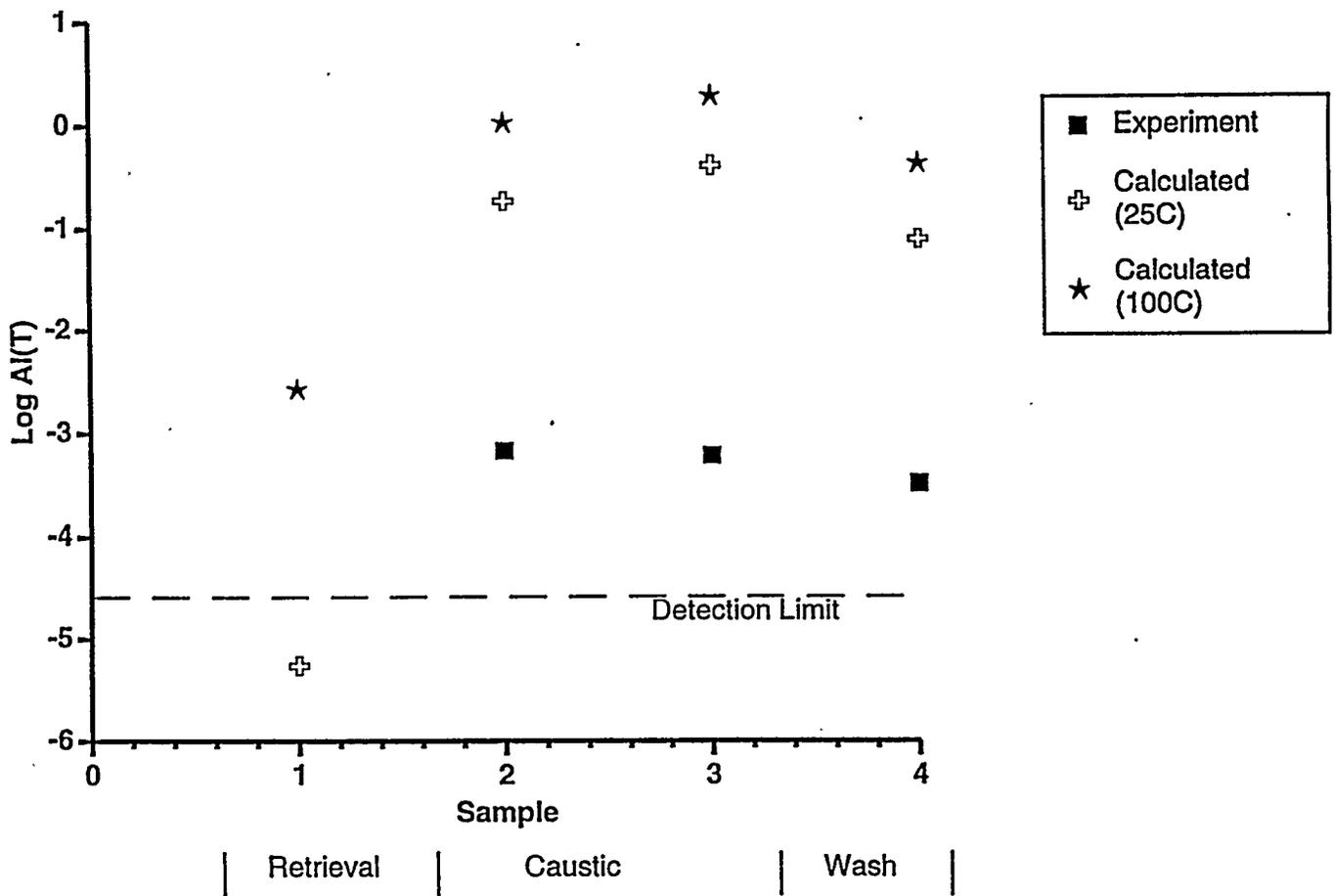


Figure 3.2a. Experimental and Calculated Aluminum Solubilities for Tank B111.
 Calculated solubilities assume equilibrium with gibbsite.

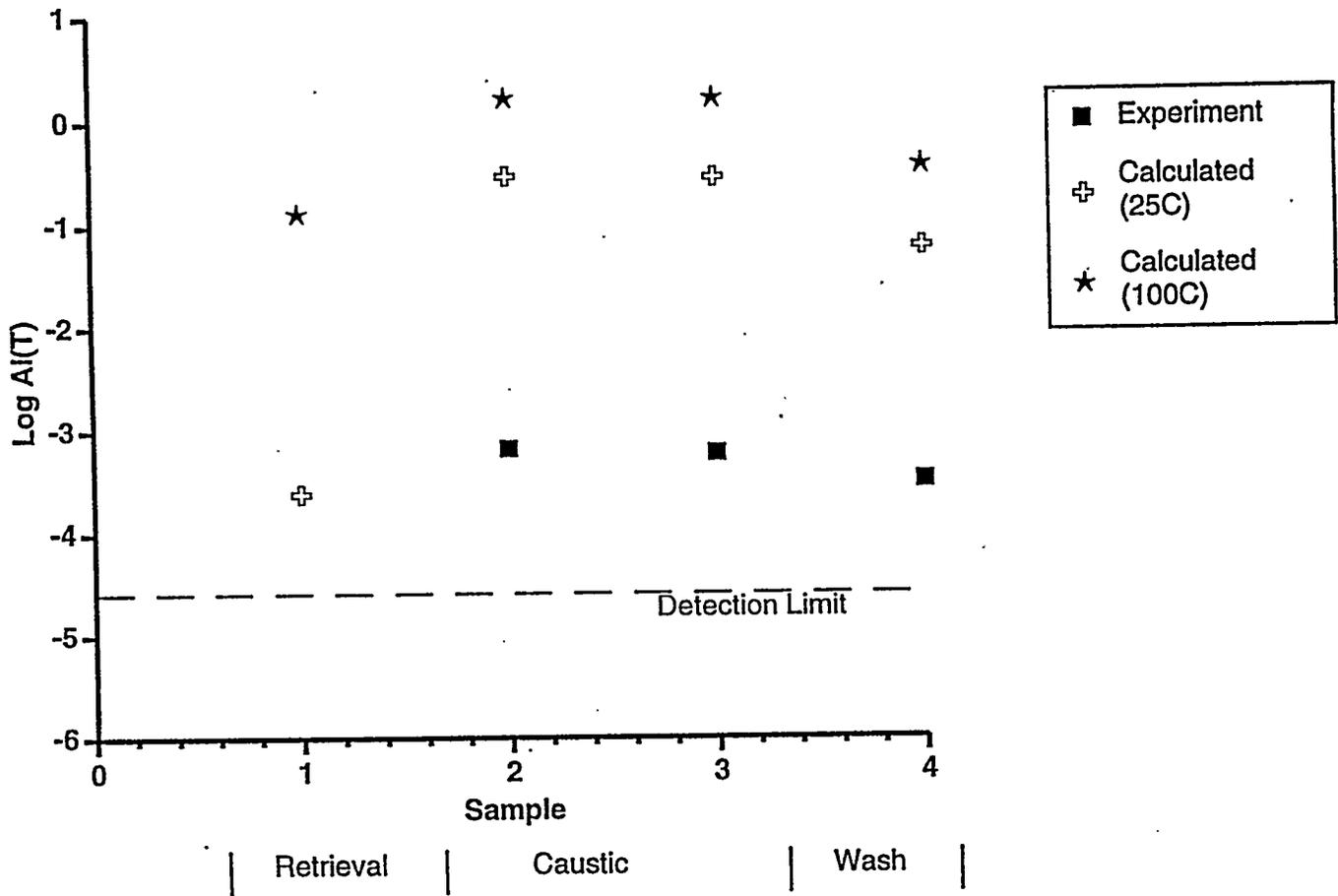


Figure 3.2b. Experimental and Calculated Aluminum Solubilities for Tank T111. Calculated solubilities assume equilibrium with gibbsite.

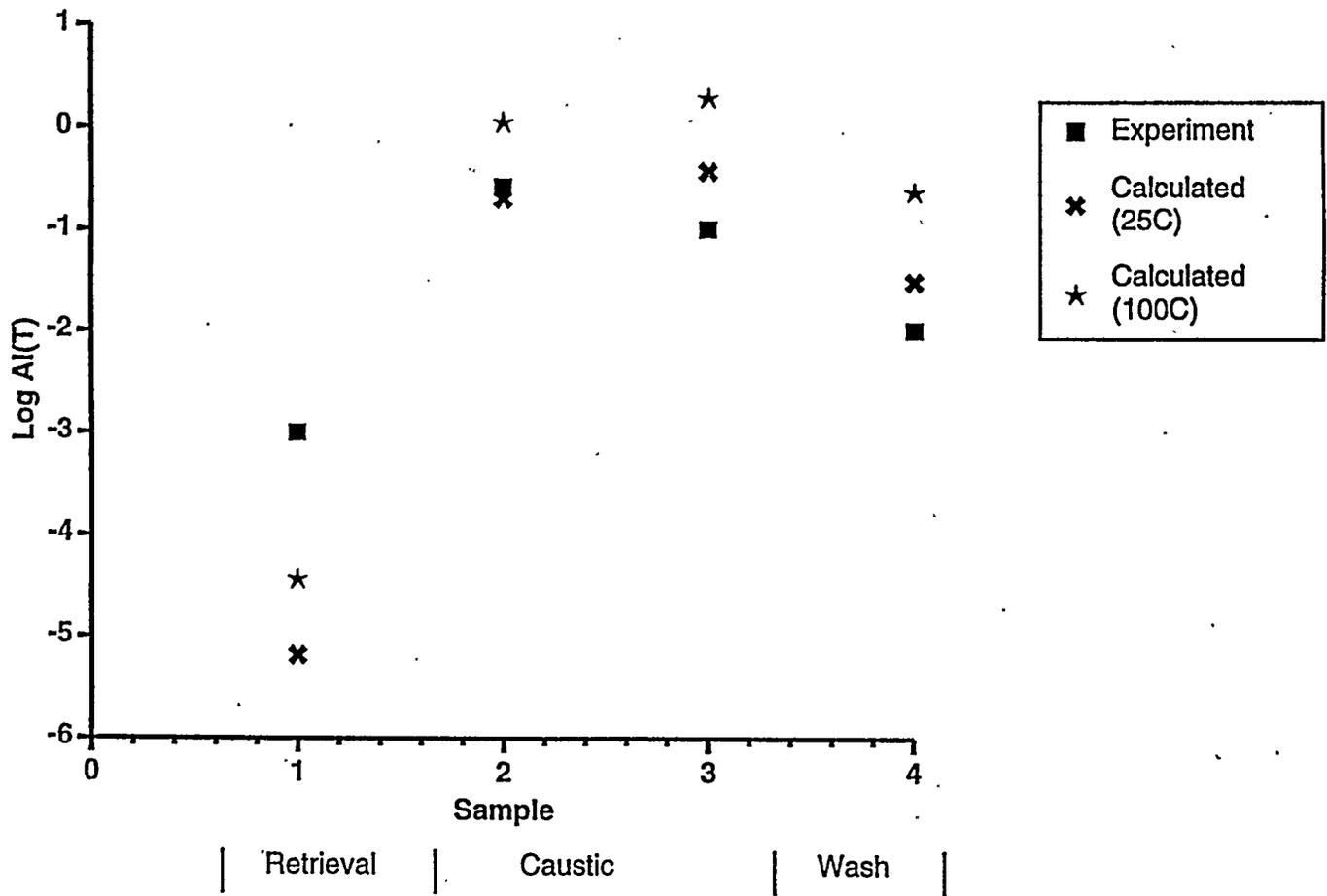
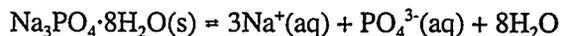


Figure 3.3. Experimental and Calculated Aluminum Solubilities for Tank BX107. Calculated solubilities assume equilibrium with gibbsite.

T104, and T111. In these cases, except T111, some sodium phosphate was also identified in the dried sludge samples even after sludge washing and caustic leaching. Sludge from Tank BX107 also possessed a mixed bismuth iron phosphate phase. This phase was also identified following sludge washing and caustic leaching. Two additional phosphorus-containing phases were identified in sludge from T111: lanthanum pyrophosphate, $\text{La}_4(\text{P}_2\text{O}_7)_3$, and hydroxyapatite, $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$. These phases were also identified following sludge washing and caustic leaching. Aluminum phosphate was identified in Tanks BX107 and T104 before, but not after, sludge washing and caustic leaching. Other metal phosphates are presumed present in the sludges but were not specifically identified.

Thermodynamic modeling suggests that the retrieval solutions for all of these tanks were undersaturated with respect to the three sodium phosphate phases considered, indicating that the amount of sodium phosphate present in the tank sludges can be readily solubilized at the 2.3 wt% solids loading. Importantly, in the cases of Tanks B111, BX107, and T104, the amount of phosphorus removed in the final wash was greater than in the caustic leaching steps. The following hypothesis has been formulated to explain this behavior. During the caustic leaching steps, phosphate salts insoluble in the retrieval wash are metathesized to sodium phosphate and the corresponding metal hydroxides. But at the high sodium concentration present in the caustic leaching step, sodium phosphate is poorly soluble. That is, the high sodium concentration during the caustic leaching steps forces the following equilibrium to the left, whereas during subsequent final washing of the sludge the sodium concentration is low, shifting the equilibrium to the right.



The thermodynamic model suggests that the observed amounts of phosphorus in the caustic leach solutions are well predicted by the solubility of $\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$ at 100°C, as illustrated for Tank B111 in Figure 3.4. The addition of water in the final wash solutions then dissolves the precipitated sodium phosphate, causing the rise in dissolved phosphorus concentration in the final wash solution observed with these three sludges (B111, BX107, and T104). Aluminum phosphate appears as the most likely identified source of metathesizable metal phosphate, identified in BX107 and T104. However, no plausible source of metathesizable metal phosphate was identified from the TEM/SEM/XRD analysis of B111.

In processing the Hanford tank sludges by caustic leaching it will be important to ensure that adequate wash water volumes are used to solubilize the $\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$. The required volumes will be decreased by minimizing the volume of liquid entrained in the solids from one step to the next.

Results of tests with Tank T104 sludge illustrate the importance of using adequate wash volumes. Three tests with this material have been performed to date; the results are summarized in Table 3.5. As can be seen, the relative volumes of wash solution used in the second and third tests were much greater than the volume used in the first test. Thus, it is probable that the low phosphorus removal in the first test was due to inadequate washing of the sludge. As mentioned previously, Na_3PO_4 was identified in treated B111, BX107, and T104 sludges. Additional washing would have undoubtedly removed the remaining Na_3PO_4 , leaving the final, limiting amount of phosphate present in the treated solids determined by the presence of such materials as lanthanum pyrophosphate and calcium phosphate.

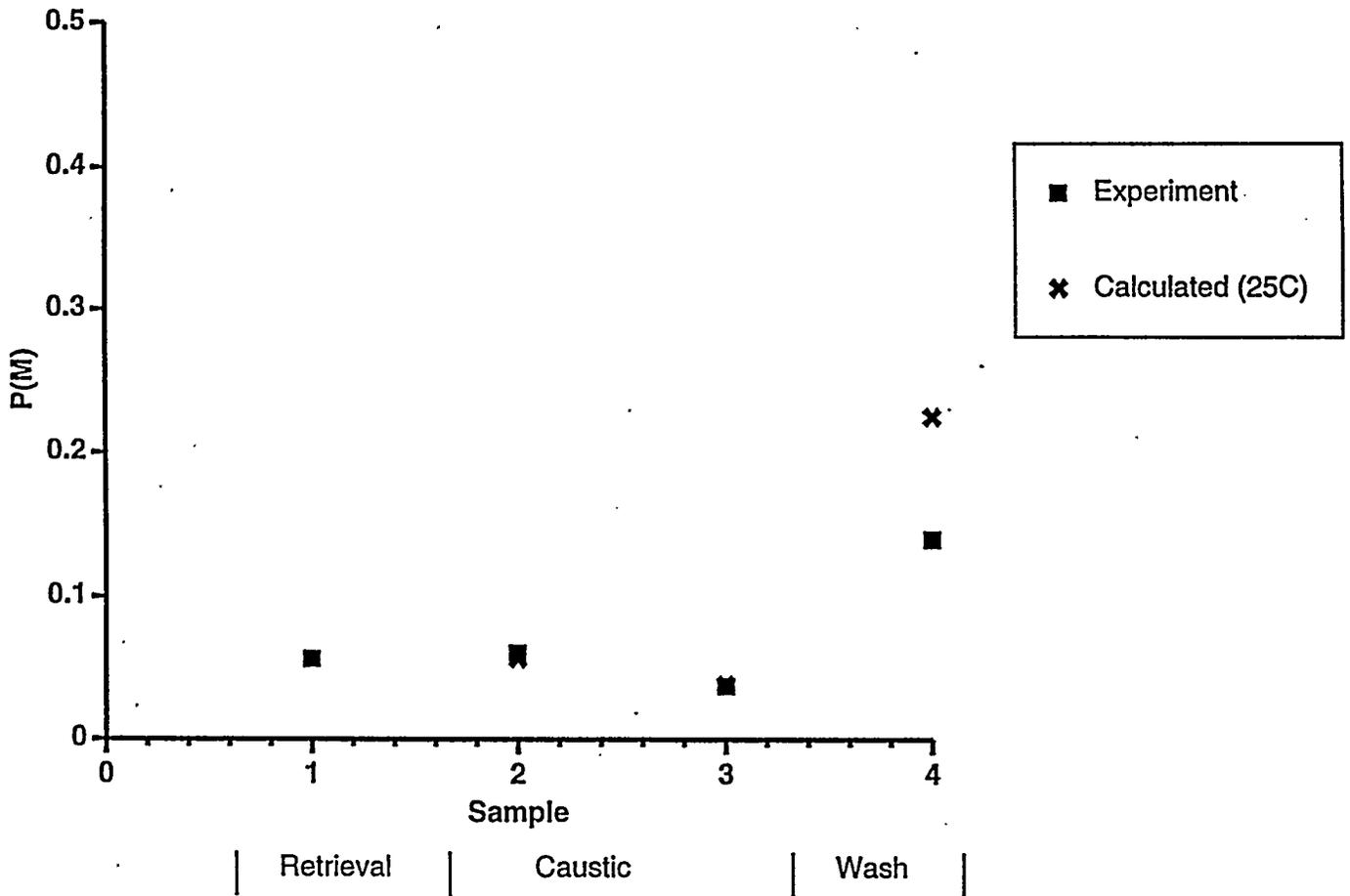


Figure 3.4. Experimental and Calculated Phosphorus Solubilities for Tank B111.
 Calculated solubilities assume equilibrium with $\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$ at 100°C .

Table 3.5. Comparison of the Phosphorus Behavior in the T104 Leaching Tests

Test	Amount of Phosphorus in Solution, %				Wash Solution Vol., mL/g of Fe in solids
	Retrieval Wash	First Caustic Leach	Second Caustic Leach	Final Wash	
1 ^(a)	26	9	3	17	33
2 ^(b)	27	4	1	66	135
3	30	1	1	66	240

(a) Test 1 shows the results described above (Rapko et al. 1995).

(b) Test 2 was performed at Los Alamos National Laboratory (Temer and Villareal 1995).

A previous report (Rapko et al. 1995) attempted to evaluate the relative ratios of phosphorus with alkaline earth elements in the treated residues to evaluate whether or not the ultimate removal of phosphorus is indeed dictated by the amount of phosphorus present in such insoluble phases as calcium phosphate. Most of the concentration of alkaline earth elements is dominated by the amount of calcium and strontium present. If the amount of residual phosphate were dominated by the formation of this species, then the mole ratio of $P/(Ca + Sr)$ should be about 0.67. Table 3.6 summarizes the observed mole ratios as previously reported (Rapko et al. 1995).

In the previous report, the varying mole ratios observed were taken as evidence that a variety of insoluble phosphate species might be involved in limiting the amount of phosphorus removed during sludge washing and caustic leaching. However, a reevaluation of the data suggests an alternative explanation. Tank T111 is only slightly over the 0.67 mole ratio expected if alkaline earth phosphates were the primary limiting factor in phosphate removal. In this case, lanthanum pyrophosphate was also identified as a phosphorus-containing phase after sludge washing and caustic leaching. Its contribution would explain the slightly greater $P/(Ca + Sr)$ mole ratio. The other treated sludges with a higher-than-expected $P/(Ca + Sr)$

Table 3.6. Phosphorus, Calcium, and Strontium Mole Ratios in Leached Sludges

Tank	$P/(Ca + Sr)$ in Leached Sludge
B111	2.7
BX107	11
C103	0.44
S104	0
SY103	0.18
T104	38
T111	0.74

mole ratio, namely B111, BX107, and T104, all also show residual sodium phosphate in the treated solids. The possibility then exists, contrary to the previous conclusion, that the alkaline earth phosphates are indeed the major limit in the amount of phosphate removed by sludge washing and caustic leaching.

3.2.3 Chromium and Manganese

As chromium is poorly tolerated in the production of HLW borosilicate glass, the efficacy of its removal by sludge washing and caustic leaching is important. Among the sludges examined in this study, in only one case was a pure crystalline, chromium-containing phase identified in the microscopy studies. This was a minor phase in sludge from Tank B111 and was identified as $\text{Bi}_{38}\text{CrO}_{60}$, which suggests that chromium is present here in the +6 oxidation state. In Tank SY103, EDS revealed that the observed chromium was associated mainly with aluminum hydroxide. EDS indicates that in Tanks T111, BX107, and T104, the chromium appears to be associated with amorphous iron hydroxide. Chromium substitution for either iron or aluminum suggests that it is present in the +3 oxidation state when associated with these phases.

X-ray absorption spectroscopy was used to investigate chromium speciation in selected treated and untreated sludges. As with phosphorus, the original source of the chromium, whether present as part of the solids or deposited from the sludge's interstitial liquid during the drying prior to analysis, was not addressed. The oxidation state of manganese was also investigated to establish the role (if any) that manganese plays in determining the ratio of Cr(VI) to Cr(III), and in the dissolution of chromium during sludge washing and caustic leaching.

The X-ray absorption spectra for the untreated and treated Tank T104 sludge solids are shown in Figure 3.5. The fit for the Cr(III)/Cr(VI) pre-edge peak is good, and indicates that 16% of the chromium in this sample is Cr(VI). Similar fits were obtained for the other tank sludges investigated. The Cr(III)/Cr(VI) results from the pre-edge peak fits for both the treated and untreated tank samples are reported in Table 3.7. Untreated sludges from all the tanks that contain primarily bismuth phosphate process wastes (B111, BX107, T104, and T111) contain both Cr(III) and Cr(VI). On the other hand, sludges derived from the REDOX process (S104) or complexant concentrate waste (SY103) contain chromium in only a single oxidation state, at least within the detection limits of the experiment. However, these oxidation states are different for each tank; chromium is present only as Cr(VI) in S104 and Cr(III) in SY103. In addition, Table 3.7 combines the information concerning observed chromium removal (Table 3.2) and the oxidation state information to illustrate the relative removal of each of the oxidation states of chromium. Two features are apparent from the results in Table 3.7. First, except for Tank BX107, an excellent correlation is observed between percent of chromium present in the +6 oxidation state and the amount of chromium removed in the retrieval wash. This result is expected: the much greater solubility of CrO_4^{2-} versus $\text{Cr}(\text{OH})_4^-$ indicates that Cr(III) participation in the amount of chromium dissolved in the retrieval wash is unimportant. Second, in all cases, after the sludge wash and caustic leach treatment, the chromium remaining is, as expected, Cr(III). This result is inconsistent with the TEM analysis of treated B111 sludge, which suggests that Cr(VI) is present after treatment as $\text{Bi}_{38}\text{CrO}_{60}$. However, in the absence of quantitative information concerning the prevalence of this phase, the TEM and X-ray absorption analyses might still be compatible.

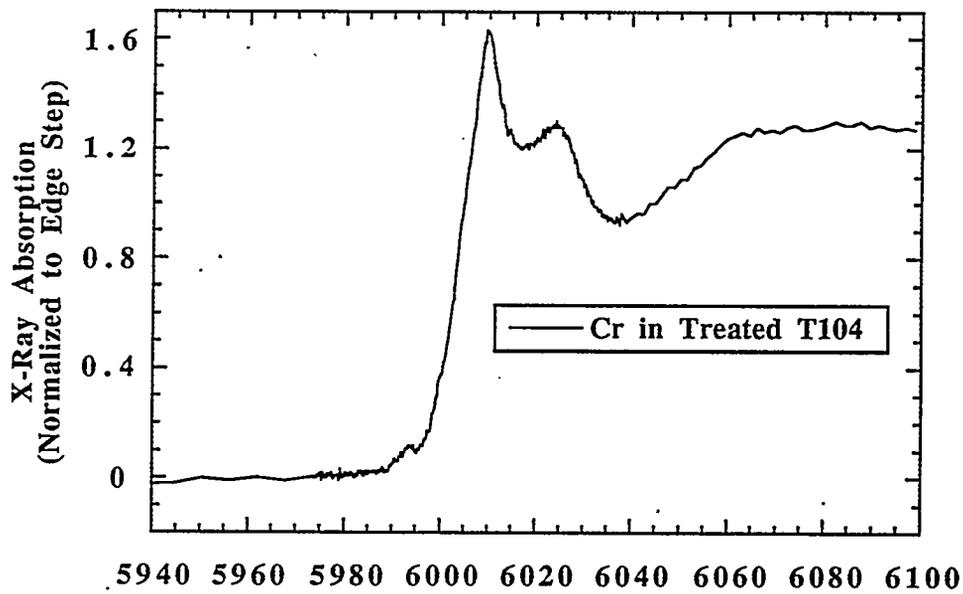
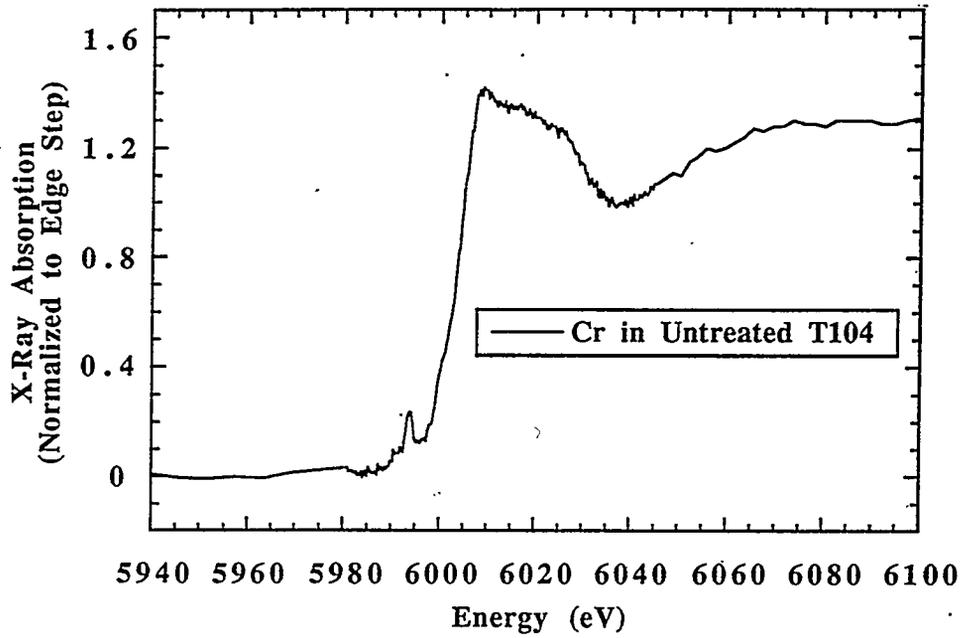


Figure 3.5. X-ray Absorption K Edge of Chromium for the Untreated and Treated Samples of Tank T104 Waste. The presence of the pre-edge peak and the shape of the spectrum above the absorption edge jump reveal the presence of Cr(VI) in the untreated sample. In contrast, the treated sample appears to have little or no Cr(VI).

Table 3.7. Chromium Oxidation States in Sludges as Determined by X-ray Spectroscopy

Tank	Untreated		% Rem. ^(a) 1st Wash	Treated ^(b)		% Removed		
	% Cr(III)	% Cr(VI)		% Cr(III)	% Cr(VI)	Total Cr	Cr(III)	Cr(VI)
B111	73	27	27	> 95	< 5	41	18	> 95
BX107	91	9	21	> 95	< 5	29	22	> 95
S104	< 5	> 95	90	(c)	(c)	96	(c)	> 95
SY103	> 95	< 5	5	> 95	< 5	13	13	> 95
T104	84	16	17	> 95	< 5	27	13	> 95
T111	78	22	24	> 95	< 5	64	54	> 95

(a) Percentage of total chromium removed by the first wash.

(b) A wash (0.01M NaOH/0.01M NaNO₂), two leaches (3M NaOH at 100°C) and three washes (same as first wash, at room temperature). All washes and leaches were performed at 2.5 wt% solids loadings. Error in Cr(III) and Cr(VI) percentages is +/-5 percentage points.

(c) Calculations of the percentage of Cr(III) and Cr(VI) in the treated S104 samples, and the percent removal of Cr(III) from the S104 samples, were not possible due to the low concentration of chromium in the treated material and the low concentration of Cr(III) in the untreated material.

The Mn XANES for three of the tank samples is shown in Figure 3.6. The alignment of the absorbance edge clearly indicates that, although the manganese in the different samples may be present in different species, the manganese oxidation state is the same and, in the case of Tank S104 at least, remains unchanged as a result of sludge washing and caustic leaching. The Mn XANES in the Tank T111 sample is also compared at the bottom of Figure 3.6 with the Mn XANES of a series of manganese reference samples in various oxidation states. The coincidence of the T111 Mn K edge with that of the manganese dioxide (MnO₂) Mn K edge makes it clear that the manganese in the tank samples is in the +4 oxidation state as opposed to the +2 or +3 oxidation states. The differences in the shape of the edge suggests that the Mn(IV) species may not be simply MnO₂. The focus of this examination was to determine the oxidation state of manganese in the sludges because of possible oxidation/reduction reactions of manganese with other metals possessing varying accessible oxidation states, specifically chromium. For this reason, the specific details of manganese speciation were deemed of lesser importance, and the Mn EXAFS of these samples was not analyzed. The observance of only Mn(IV) suggests that a substantial amount of the manganese likely did not undergo oxidation/reduction reactions with the Cr(III) in the sludge during leaching.

The calculated and experimental chromium concentrations in the leach solutions (Figure 3.7) suggest that solubility constraints can affect the total amount of chromium leached. The wash solutions appear exceptionally high in chromium, based on the amorphous Cr(III) hydroxide solubilities at 25°C, which is consistent with the chromium being present in its more readily soluble Cr(VI) oxidation state during the retrieval wash step. The data in Figure 3.7a,b for Tanks B111 and BX107 do show a rough parallel between the calculated experimental chromium concentrations and the predicted values at 25°C. These results suggest that Cr(OH)₃(am) may be an effective solubility control in these leaching solutions. The predictions for Tanks C103 (Figure 3.7c) and SY103, T104, and T111 (Figure 3.7d-f), however, show even higher observed leachable chromium concentrations in the caustic leach solutions than predicted from equilibrium with Cr(OH)₃(am). Furthermore, the magnitude of the agreement can vary significantly from step to step within the same sludge washing and caustic leaching test. Such oversaturation with respect to

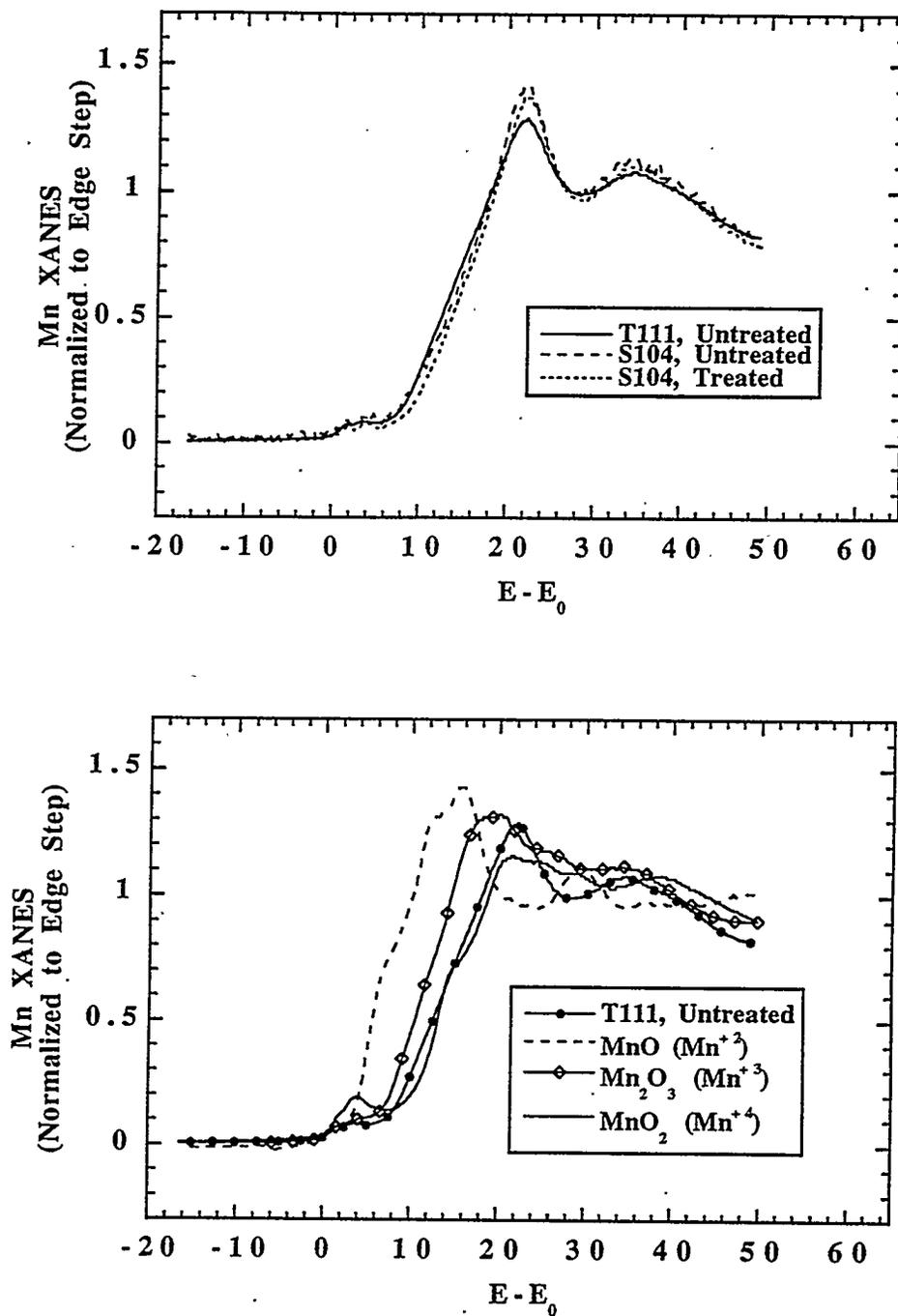


Figure 3.6. X-ray Absorption K Edge of Manganese for Several of the Tank Samples (Top). Alignment of the edges indicates that all manganese in the samples is in the same oxidation state. Comparison with manganese reference compounds (bottom) indicates that the manganese oxidation state in the waste samples is +IV. The energy scale, $E - E_0$, is relative to the Mn K edge of a manganese foil.

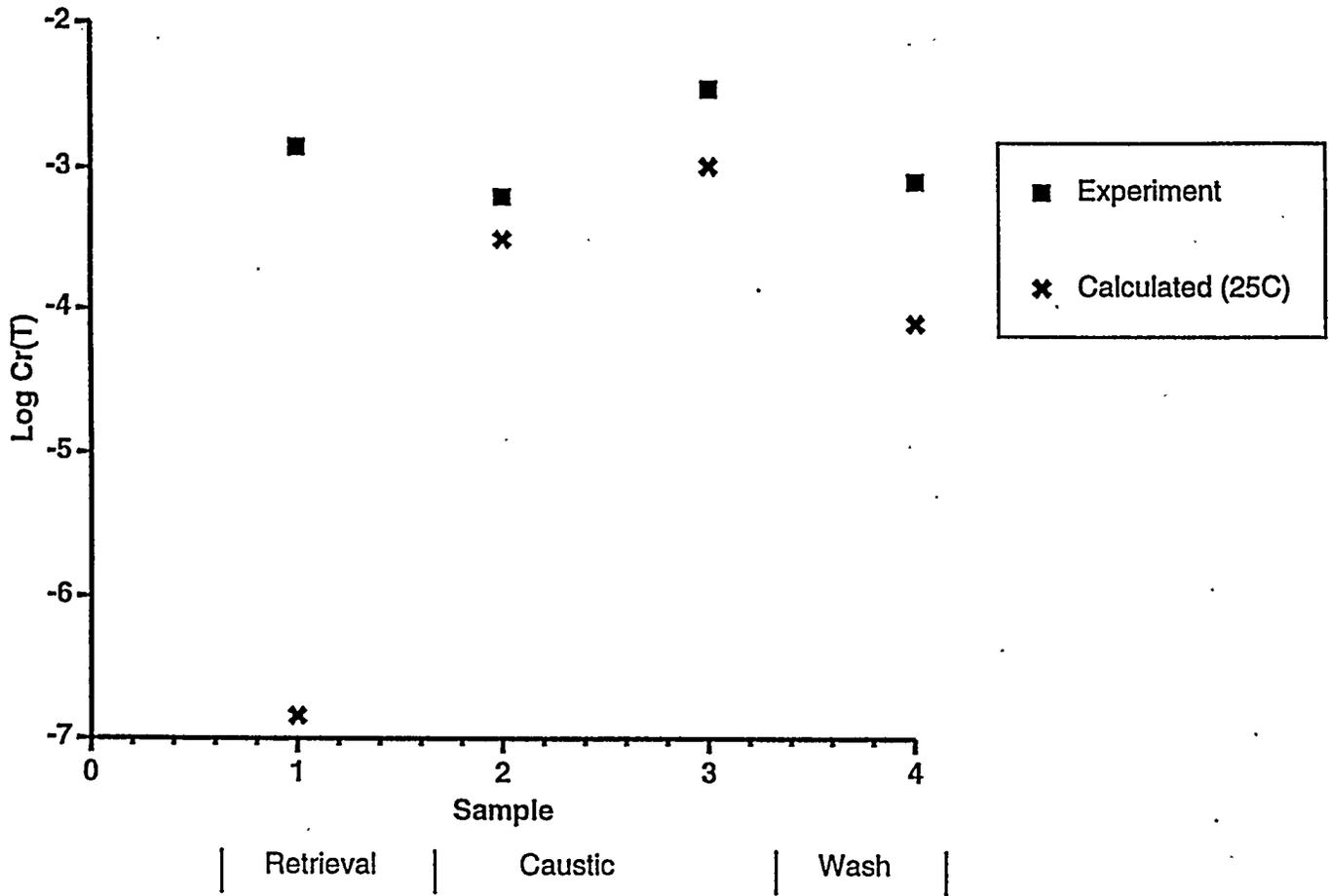


Figure 3.7a. Experimental and Calculated Chromium Solubilities for Tank B111. Calculated solubilities assume equilibrium with amorphous chromium hydroxide at 25°C.

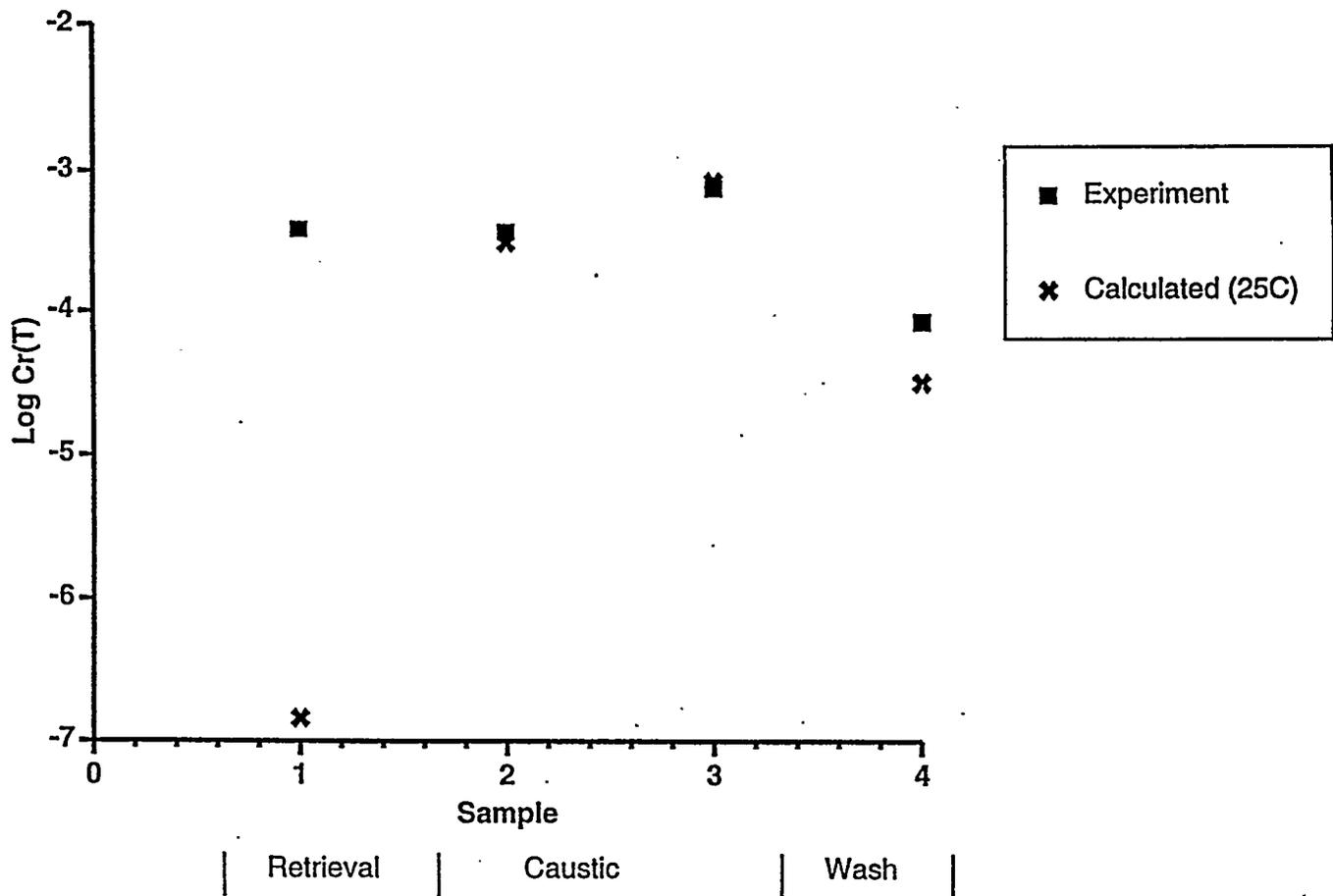


Figure 3.7b. Experimental and Calculated Chromium Solubilities for Tank BX107. Calculated solubilities assume equilibrium with amorphous chromium hydroxide at 25°C.

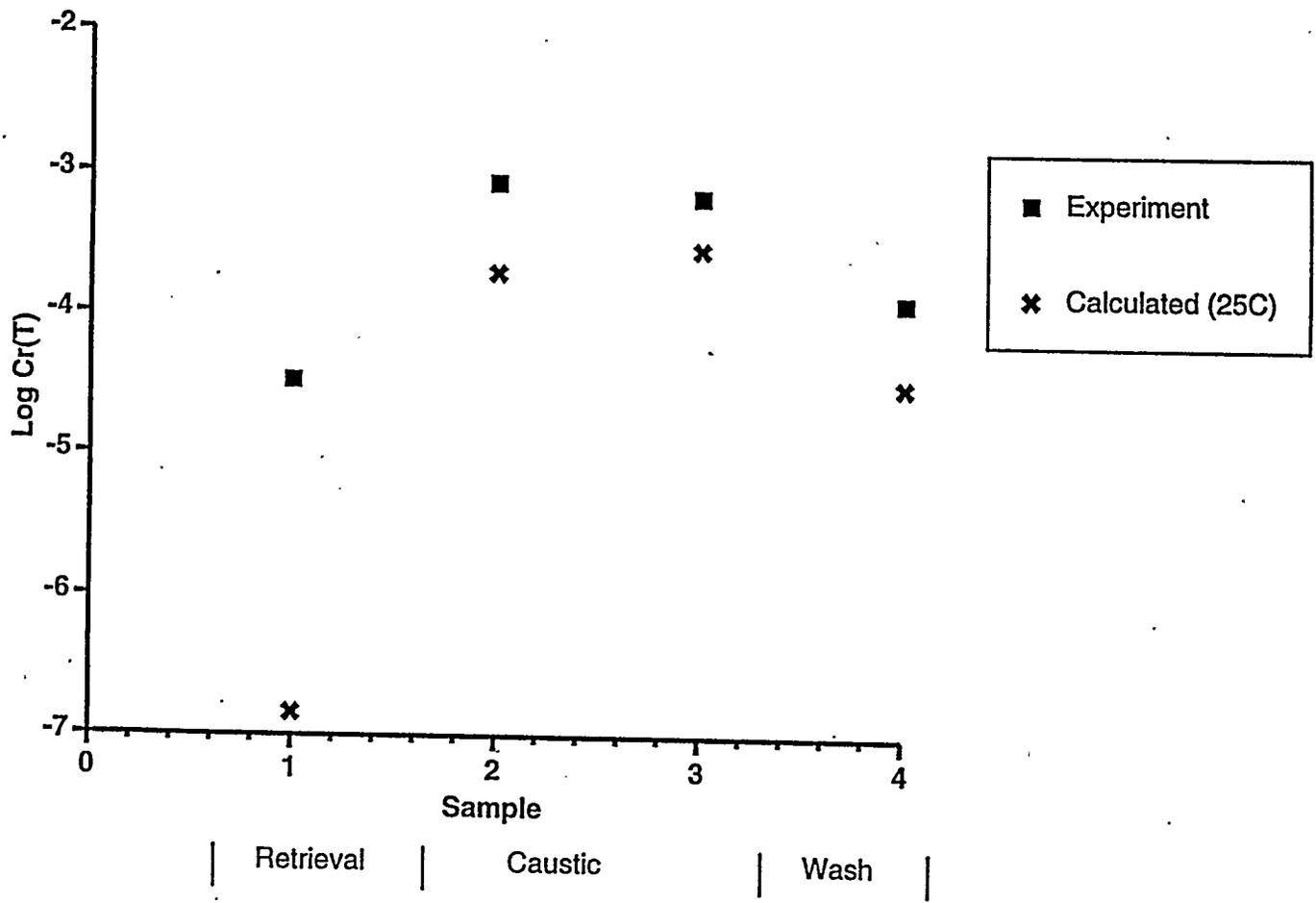


Figure 3.7c. Experimental and Calculated Chromium Solubilities for Tank C103. Calculated solubilities assume equilibrium with amorphous chromium hydroxide at 25°C.

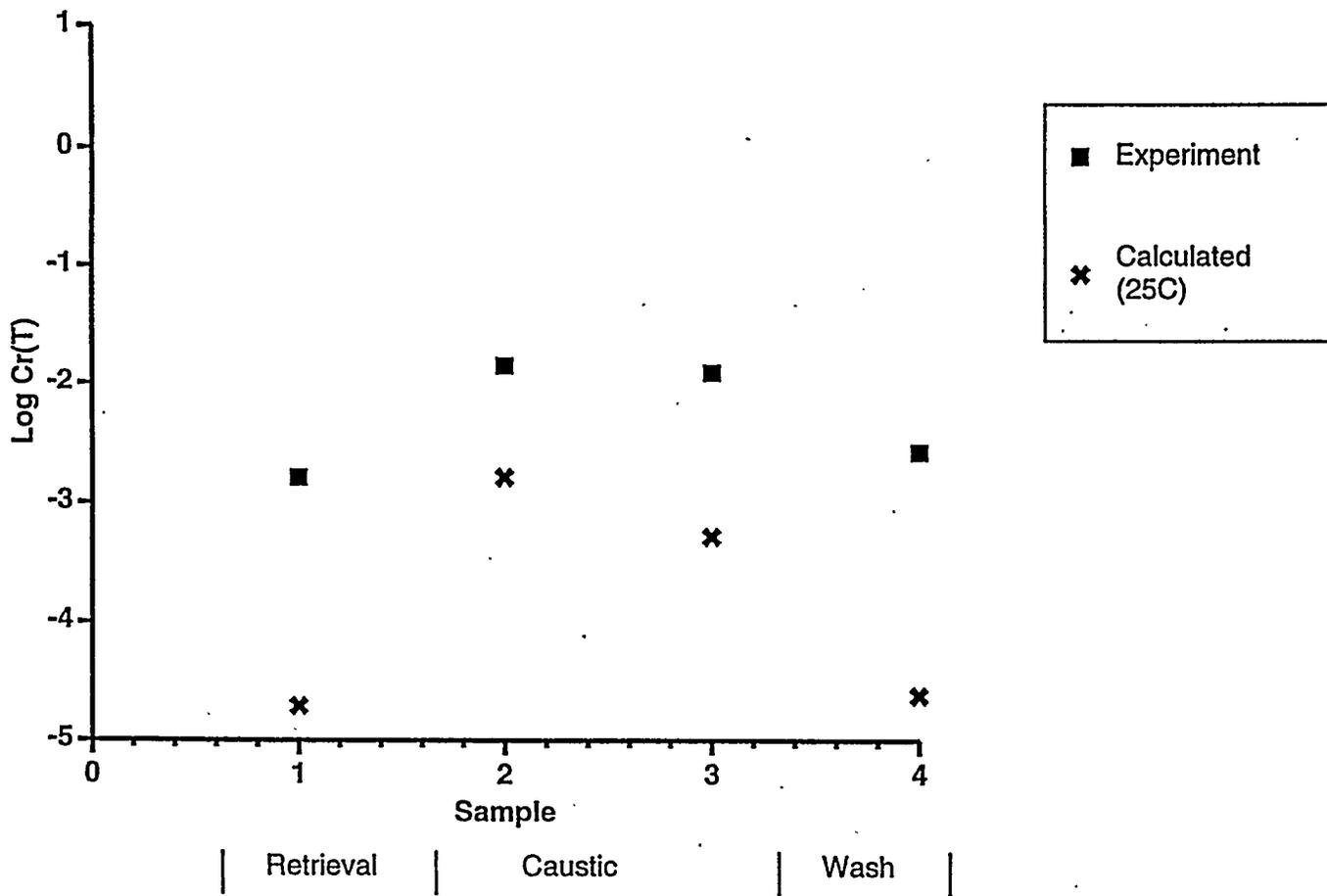


Figure 3.7d. Experimental and Calculated Chromium Solubilities for Tank SY103. Calculated solubilities assume equilibrium with amorphous chromium hydroxide at 25°C.

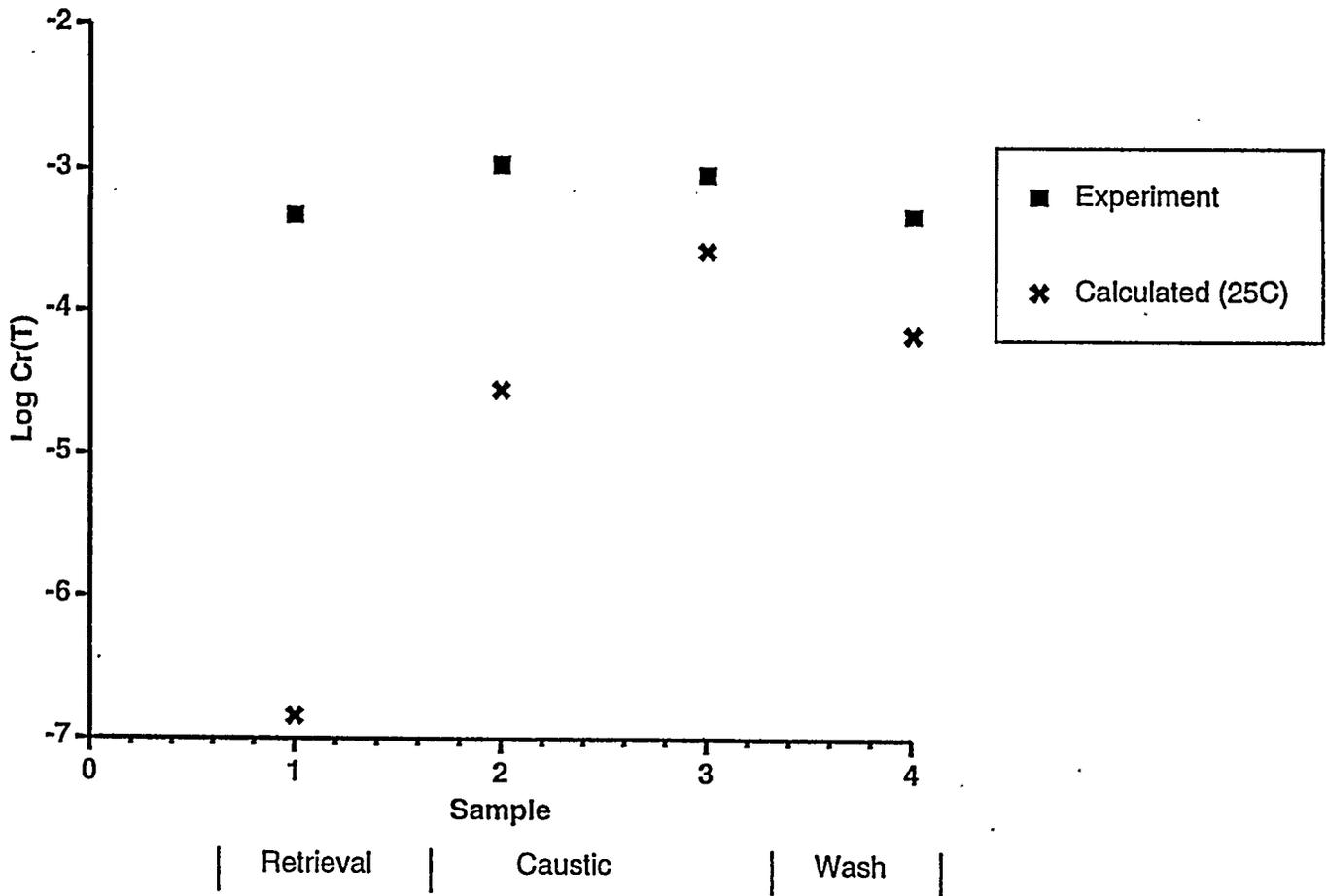


Figure 3.7e. Experimental and Calculated Chromium Solubilities for Tank T104. Calculated solubilities assume equilibrium with amorphous chromium hydroxide at 25°C.

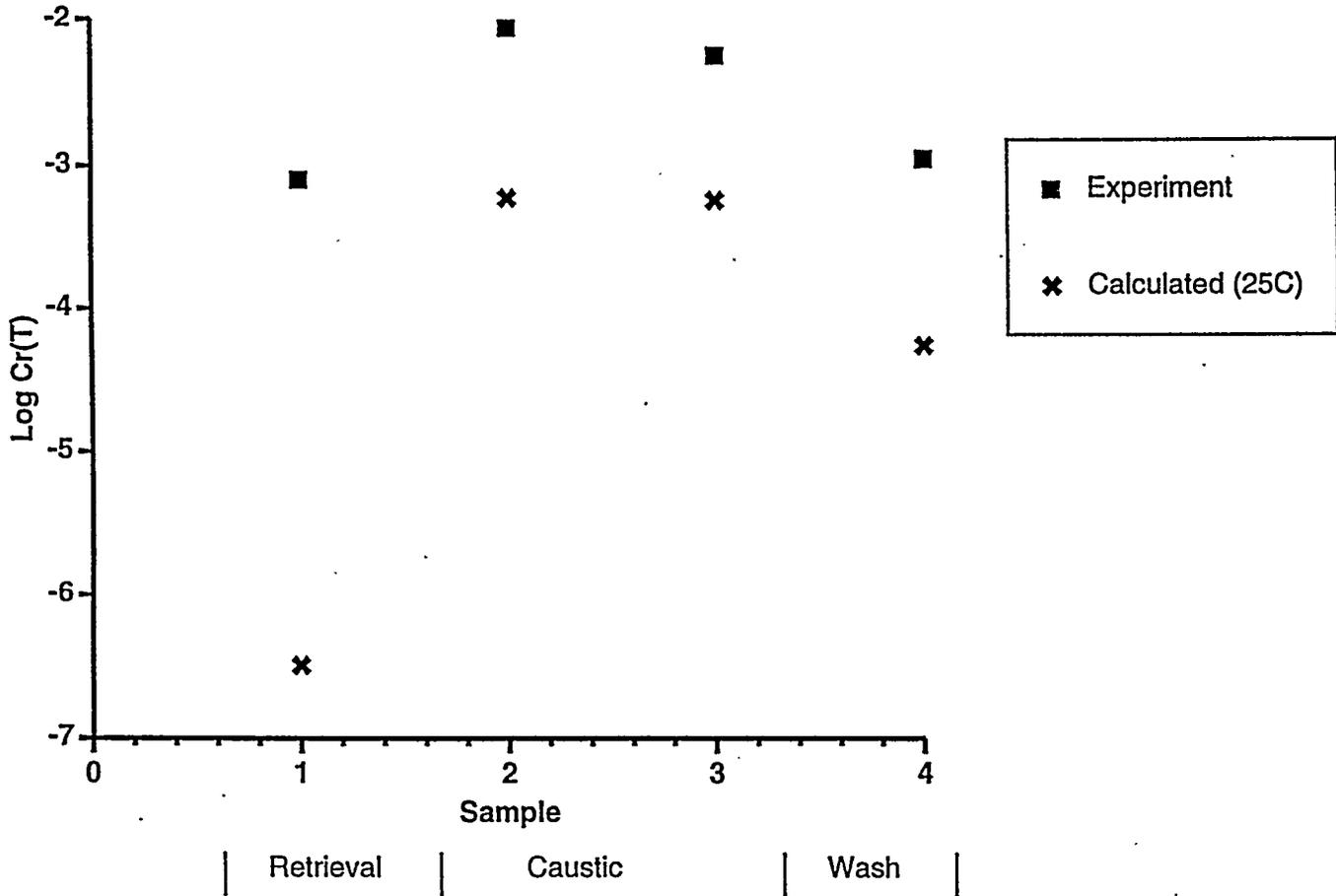


Figure 3.7f. Experimental and Calculated Chromium Solubilities for Tank T111. Calculated solubilities assume equilibrium with amorphous chromium hydroxide at 25°C.

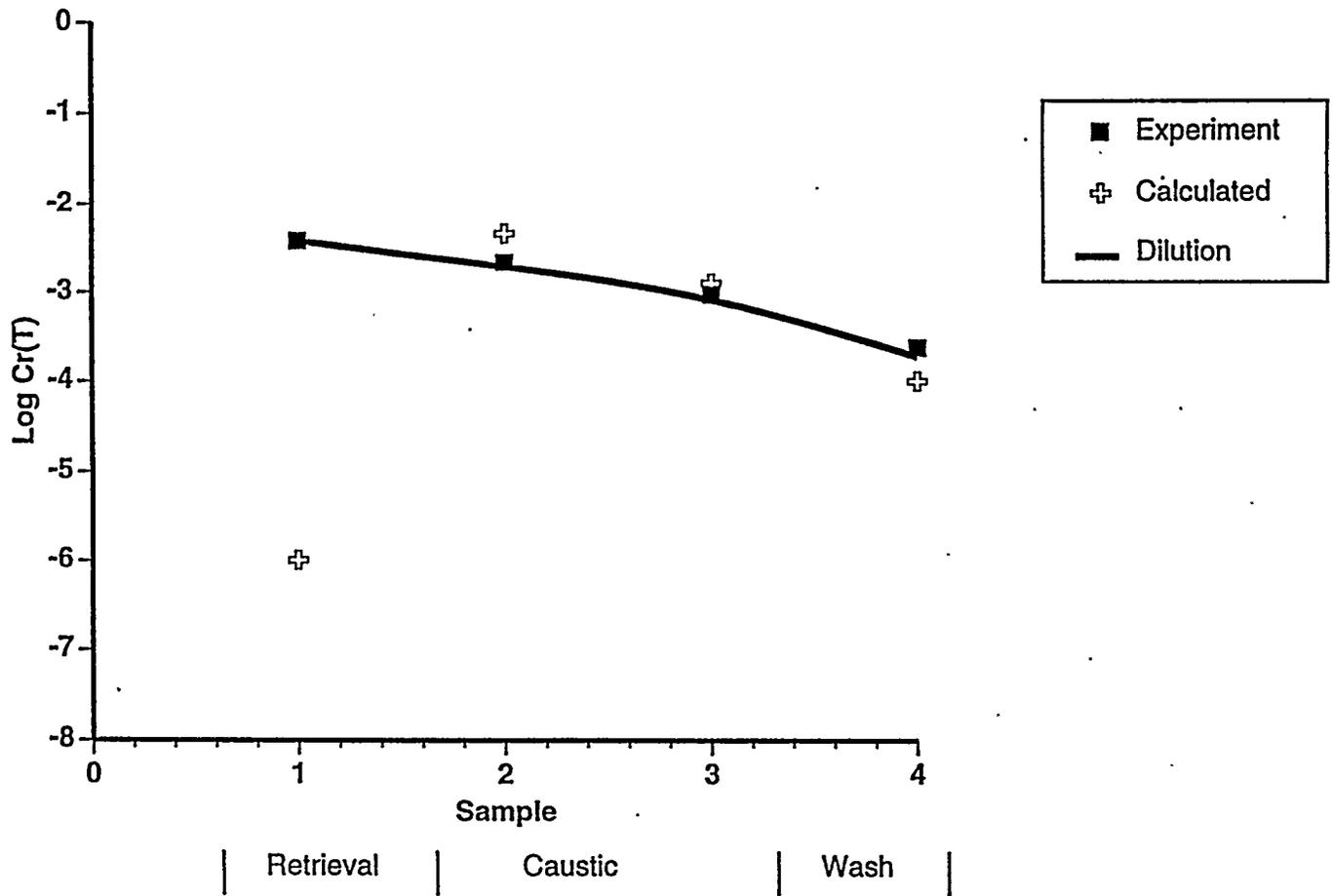


Figure 3.7g. Experimental and Calculated Chromium Solubilities for Tank S104. Calculated solubilities assume equilibrium with amorphous chromium hydroxide at 25°C.

Cr(OH)₃(am) at 25°C is not unusual and has been attributed to slow crystallization or restructuring of the precipitates with time (Rai et al. 1987). Since the caustic leach contacts were at higher temperature, the observed concentrations might represent a situation far from the 25°C equilibrium values calculated here. It has also been observed that higher temperatures can crystallize the amorphous precipitates (Rai et al. 1987). More accurate thermodynamic data on Cr(OH)₃(am) and aqueous Cr(III) species are clearly needed at higher temperatures in order to utilize the thermodynamic models with confidence. Although the Cr(VI) that dissolved during the retrieval wash and remained in the interstitial fluid will impact the observed chromium concentration in the subsequent steps, the chromium concentration in the retrieval wash was not greater than the predicted equilibrium concentration for Cr(III) during the subsequent leach steps under the experimental conditions, except perhaps with Tank B111, and thus cannot account for the significantly greater chromium solubility observed. In any event, the observed chromium leaching behavior for the tanks, except Tank S104, does appear to be affected by the relative solubility limitations of Cr(III) versus Cr(VI), as expected.

In the case of Tank S104 (Figure 3.7g), the predicted solubilities for the caustic leach solutions, assuming equilibrium with Cr(OH)₃(am), are in good agreement with the experimental values; indeed the agreement for S104 is the closest of all the sludges examined, but this fact is simply fortuitous. The chromium in S104 is all present as a chromium species (presumably chromate) that is highly soluble in the dilute base retrieval wash. This soluble chromium can account for the observed chromium concentrations in the subsequent caustic leach and wash solutions through simple dilution of this initial chromium concentration by the base or water added in the subsequent stages. The solid line in Figure 3.7g illustrates this dilution curve calculation.

3.3 Radionuclide Partitioning Behavior

The behavior of major radionuclides is summarized in Table 3.8. Two types of behavior are observed. The first is exemplified by strontium and the TRUs. These radionuclides show no inclination to dissolve

Table 3.8. Percent Radionuclide Removal by Sludge Washing and Caustic Leaching

Sludge	TRUs ^(a)	¹³⁷ Cs	⁹⁰ Sr	⁹⁹ Tc
B111	0	95	0	100
BX107	0	94	0	99
C103	0	44	0	88
S104	0	98	0	100
SY103	1	100	4	85
T104	0	69	2	(b)
T111	0	56	0	12

(a) Primarily americium and plutonium.

(b) Radionuclide activity below detection limits in this sludge.

during sludge washing and caustic leaching. SY103 sludge shows a small amount of strontium and TRU dissolution; this finding is consistent with the presence of organic complexants that are expected to exist in this waste. The second behavior is exhibited by ^{137}Cs and ^{99}Tc and is characterized by very good removal of these radionuclides, with certain exceptions, by the sludge wash and caustic leach treatment. In the case of the radionuclides, it is preferable for the radionuclides to remain in the sludge solids as they are to be treated as HLW. As the liquids are destined for the LLW stream, understanding the factors behind the varying observed dissolution behavior is of significance. However, studies of radionuclide speciation in the sludges is limited, since in this instance, unlike the bulk sludge components, the radioactive elements (with the possible exception of strontium) are present in such dilute concentrations that direct investigation is not possible.

3.4 Implications of the Interstitial Liquids Present During Sludge Washing and Caustic Leaching

The sludge washing and caustic leaching tests were designed to evaluate the retrieval wash, caustic leach, and final wash stages of the sludge washing and caustic leaching flowsheet. The retrieval washing mimics conditions that will be used to slurry and transfer the sludge from the tank to the processing area. The retrieval wash should dissolve, and so separate, the most highly soluble salts (mostly sodium hydroxide, nitrate, and nitrite) from the remainder of the tank sludge. The caustic leach contacts should serve a twofold purpose: first to dissolve aluminum and chromium, and second, to metathesize insoluble phosphate salts to the corresponding metal hydroxide and water-soluble sodium phosphate. Finally, three contacts with inhibited water should remove NaOH; dissolved components from the interstitial liquid in the residual solids; and sodium phosphate, which has limited solubility in the caustic leach solutions.

The reported values (Rapko et al. 1995; Temer and Villareal 1995) of the relative amount of a component in the sample after each respective process may not accurately describe the efficiency of that process since the concentration of the component in the interstitial liquid entrained in the solids is not considered. A significant portion of the component may actually be removed from the solids and still be measured in the sample because it is entrained in the centrifuged solids as interstitial liquid and "carried over" to subsequent processing steps.

Comparing the weight of the interstitial liquid to the weight of isolated supernatant indicates what fraction of the wash or leach solution is transferred to the subsequent stage. The weight of the solids in the retrieval step was obtained from the direct measurement of water-insoluble solids in a sludge aliquot. For the caustic leach and final wash steps it was assumed that all of the solids dissolved during the first caustic leach step, which allowed the directly measured weight of the residual solids following completion of sludge washing and caustic leaching to be used for the weight of solids present for all steps after the retrieval wash. In Table 3.9, the magnitude of this carryover from step to step is estimated for one set of sludge washing and caustic leaching tests (Rapko et al. 1995). Clearly, significant amounts of dissolved components will contribute to the total dissolved components found in solution during later processing stages. It is of interest to separate out this effect to evaluate how much "new" component is dissolved during the later stages of the sludge wash and caustic leach treatment.

Table 3.9. Estimate of Carryover Volumes in Sludge Wash and Caustic Leach Testing of Hanford Tank Sludges

Tank	RW ^(a) to 1st CL, %	1st CL to 2nd CL, %	2nd CL to FW, %	FW to Residue, %
B111	8.84	48.74	58.21	22.90
BX107	7.18	35.38	46.21	6.44
C103	10.55	56.12	50.11	27.93
S104	5.95	61.35	51.56	11.96
SY103	2.87	38.18	21.41	9.00
T104	6.30	37.13	30.93	21.66
T111	7.68	53.71	42.22	14.10

(a) RW = Retrieval Wash Step. 1st CL = 1st Caustic Leach Step. 2nd CL = 2nd Caustic Leach Step. FW = Final Wash Step.

Tables 3.10 through 3.16 attempt to reevaluate component dissolution after factoring out carryover contributions. These tables reveal a different picture about the relative impact of the individual steps of the sludge wash and caustic leach process on component removal. Using Tank BX107 as an example, the apparent dissolution of aluminum and ¹³⁷Cs in the second leach and final wash steps is shown instead to be the result of materials that dissolved during the first caustic leach step and were carried over into these subsequent stages. In general, it appears that once carryover effects are accounted for, most of the component removal occurs during the retrieval wash and first caustic leach steps. The major exceptions are found to be for aluminum removal in the second caustic leach step in Tanks BX107, C103, S104, and T104 and for phosphorus removal in the final wash with Tanks B111, BX107, and T104. The reasons for continued dissolution of these components in these stages have been discussed earlier in this report.

Table 3.10. Component Dissolution in Sludge Wash and Caustic Leach Testing of B111. Comparison of results uncorrected and corrected for solution carryover from preceding steps.

Component	Retrieval Solution, % ^(a)	1st Caustic Leach, % ^(a)	2nd Caustic Leach, % ^(a)	Final Wash, % ^(a)	Undissolved Residue, % ^(a)
Al	0/0	1/1	0/0	1/0	98/98
Cr	26/29	2/1	6/14	6/-1	60/58
P	43/48	6/7	3/1	39/48	9/-3
U	57/62	1/-3	2/3	1/-1	39/39
¹³⁷ Cs	51/56	25/44	10/0	9/-3	5/2
⁹⁹ Tc	93/102	4/-1	1/0	1/0	0/0

(a) Uncorrected for carryover effects/corrected for carryover effects.

Table 3.11. Component Dissolution in Sludge Wash and Caustic Leach Testing of BX107. Comparison of results uncorrected and corrected for solution carryover from preceding steps.

Component	Retrieval Solution, % ^(a)	1st Caustic Leach, % ^(a)	2nd Caustic Leach, % ^(a)	Final Wash, % ^(a)	Undissolved Residue, % ^(a)
Al	1/1	49/75	11/-5	7/-2	32/31
Cr	21/22	3/3	3/5	2/0	71/71
P	20/22	2/2	1/0	70/74	7/2
U	16/18	2/1	1/1	1/0	80/80
¹³⁷ Cs	17/19	52/80	14/-2	10/-2	6/5
⁹⁹ Tc	92/99	5/1	1/-1	1/0	1/1

(a) Uncorrected for carryover effects/corrected for carryover effects.

Table 3.12. Component Dissolution in Sludge Wash and Caustic Leach Testing of C103. Comparison of results uncorrected and corrected for solution carryover from preceding steps.

Component	Retrieval Solution, % ^(a)	1st Caustic Leach, % ^(a)	2nd Caustic Leach, % ^(a)	Final Wash, % ^(a)	Undissolved Residue, % ^(a)
Al	0/0	16/48	23/29	9/-3	52/26
Cr	2/4	4/18	4/4	2/0	89/73
P	27/36	21/55	12/-7	7/1	34/15
U	73/95	1/-6	1/4	0/0	24/11
¹³⁷ Cs	20/32	10/31	9/4	5/2	56/31
⁹⁹ Tc	83/99	3/-3	2/-1	1/0	12/5

(a) Uncorrected for carryover effects/corrected for carryover effects.

Table 3.13. Component Dissolution in Sludge Wash and Caustic Leach Testing of S104. Comparison of results uncorrected and corrected for solution carryover from preceding steps.

Component	Retrieval Solution, % ^(a)	1st Caustic Leach, % ^(a)	2nd Caustic Leach, % ^(a)	Final Wash, % ^(a)	Undissolved Residue, % ^(a)
Al	3/3	10/25	12/10	13/2	62/59
Cr	90/96	2/1	2/0	2/1	3/3
P	None detected	None detected	None detected	None detected	None detected
U	0/0	0/0	0/0	0/0	100/100
¹³⁷ Cs	90/96	3/2	2/0	3/0	2/2
⁹⁹ Tc	95/100	2/0	2/0	2/0	0/0

(a) Uncorrected for carryover effects/corrected for carryover effects.

Table 3.14. Component Dissolution in Sludge Wash and Caustic Leach Testing of SY103. Comparison of results uncorrected and corrected for solution carryover from preceding steps.

Component	Retrieval Solution, % ^(a)	1st Caustic Leach, % ^(a)	2nd Caustic Leach, % ^(a)	Final Wash, % ^(a)	Undissolved Residue, % ^(a)
Al	9/9	48/78	25/2	7/1	10/10
Cr	5/5	3/4	3/3	2/1	88/87
P	74/76	15/22	7/-1	2/1	2/2
U	2/2	0/1	1/1	0/0	96/96
¹³⁷ Cs	97/100	2/0	1/0	0/0	0/0
⁹⁹ Tc	80/82	2/1	2/2	1/1	15/15

(a) Uncorrected for carryover effects/corrected for carryover effects.

Table 3.15. Component Dissolution in Sludge Wash and Caustic Leach Testing of T104. Comparison of results uncorrected and corrected for solution carryover from preceding steps.

Component	Retrieval Solution, % ^(a)	1st Caustic Leach, % ^(a)	2nd Caustic Leach, % ^(a)	Final Wash, % ^(a)	Undissolved Residue, % ^(a)
Al	1/1	24/37	26/24	11/2	38/35
Cr	17/19	4/4	4/3	2/1	73/73
P	26/28	9/12	3/-1	17/21	45/40
U	1/1	1/1	5/7	2/0	91/90
¹³⁷ Cs	0/0	25/38	30/30	14/5	31/27
⁹⁹ Tc	0/0	0/0	0/0	0/0	100

(a) Uncorrected for carryover effects/corrected for carryover effects.

Table 3.16. Component Dissolution in Sludge Wash and Caustic Leach Testing of T111. Comparison of results uncorrected and corrected for solution carryover from preceding steps.

Component	Retrieval Solution, % ^(a)	1st Caustic Leach, % ^(a)	2nd Caustic Leach, % ^(a)	Final Wash, % ^(a)	Undissolved Residue, % ^(a)
Al	0/0	4/8	5/5	4/1	87/86
Cr	24/26	15/30	14/7	11/2	37/35
P	50/54	9/14	8/4	6/1	28/27
U	0/0	1/1	1/1	0/0	98/98
¹³⁷ Cs	25/27	12/24	11/5	8/1	44/43
⁹⁹ Tc	12/14	0/-1	0/0	0/0	88/88

(a) Uncorrected for carryover effects/corrected for carryover effects.

4.0 Conclusions and Recommendations

Because of the complex and varied chemical processing history at Hanford, the sludge wastes stored in underground tanks are complicated mixtures of many crystalline and amorphous phases. Several conclusions have emerged from an integrated research effort that included sludge characterization, sludge washing and caustic leaching, process testing, and thermodynamic modeling of test results.

Experimental results and thermodynamic calculations suggest that most of the aluminum, when present in its simple oxide, hydroxide, and phosphate phases, can be removed from the sludges by metathesis and leaching with caustic at the concentrations found under the currently contemplated processing conditions, provided adequate solution volumes are used. At present there are no data to suggest that, under these proposed processing conditions, appreciable removal of aluminum will occur from aluminosilicate phases. The current status of the thermodynamically based model does not allow evaluation of the solubility of these latter phases under typical sludge washing and caustic leaching experimental conditions.

Likewise, most phosphate can be leached from the sludges, but adequate final wash volumes are required due to the limited solubility of $\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$ at the high sodium concentrations found in the caustic leach steps. Available data suggest that, under these proposed processing conditions, no appreciable removal of phosphorus will occur from phosphorus present as alkaline earth phosphates.

Chromium in sludge samples has been shown to exist in both the +3 and +6 oxidation states. The relative concentrations of Cr(III) to Cr(VI) vary greatly from sludge to sludge. Not surprisingly, the Cr(VI) is readily removed. Conclusions based on modeling suggest that caustic leaching under the current processing conditions may remove some of the Cr(III) present as the $[\text{Cr}(\text{OH})_4]^-$ ion; current indications are that markedly greater (and probably prohibitive) leachate-to-solids ratios may be required to remove the majority of chromium present as Cr(III) from systems with very high concentrations of chromium present in the +3 oxidation state.

Carryover of dissolved components that remain with the settled/centrifuged solids was considered in evaluating how components dissolve during each of the individual processing steps. This analysis suggests that most components removed during the sludge washing and caustic leaching cycle are removed during the retrieval wash and the first caustic leach step. The most significant function of additional caustic leach stages appears to be to allow the removal of additional aluminum in selected sludges. The primary function of the final washes is to remove the sodium introduced during the caustic leach and, in selected instances, to remove metathesized phosphate.

This review also illustrates the limitations of even a broad-based approach on understanding the quantitative details behind the chemistry taking place during sludge washing and caustic leaching of Hanford tank sludges. The purpose of this work, as stated in the Introduction, was to develop an understanding of the chemistry of the tank sludges and how the sludges are altered as a consequence of sludge washing and caustic leaching. The results of the work reviewed in this report suggest that while an

increased understanding of the chemistry of the tank sludges can be achieved as a result of such a broad-based approach, the utility of this gained understanding is limited by several factors. The most important limiting factors are 1) the lack of quantitation in the phase information, 2) uncertainties as to the representative nature of the test samples, and 3) limitations in the experimental design.

The first factor is the inability to quantitatively describe how the phases in the sludge solids change during the sludge washing and caustic leaching treatment. In general, specific phase information has been obtained through electron microscopy/XRD measurements. Our current understanding from these measurements remains qualitative: phases are observed in the untreated solids, and their presence or absence in the solids after treatment is noted. The assumption is then made that the absence of a phase following sludge washing and caustic leaching can be correlated with the amount of the element that dissolved as revealed by analysis. This assumption might be misleading. For example, in several sludges examined in FY 1995, aluminum was observed in several phases, either as gibbsite and/or aluminum phosphate, as well as in a variety of either amorphous or crystalline aluminosilicates. Gibbsite and aluminum phosphate disappeared, and the aluminosilicates were still observed after sludge washing and caustic leaching. However, it is not possible at this point to conclude that the observed aluminum dissolution can be explained merely by the dissolution of gibbsite and aluminum phosphate and, furthermore, that the potential amount of aluminum dissolution is limited by the amount of aluminum present in these phases. Since information about the quantity of each of these phases is unavailable, it is unclear if the amount of aluminum dissolved can be accounted for by the gibbsite and aluminum phosphate only or whether some dissolution of aluminosilicates actually occurred under the experimental conditions. This lack of quantitation constitutes an important obstacle to achieving an understanding of how the specific chemical species present in tank sludges change as a result of sludge washing and caustic leaching.

Other tools can be used to address this obstacle, but, in general, they also have their limitations. For example, modeling of aluminum dissolution can be employed to indicate whether or not the observed aluminum concentration is thermodynamically limited under the experimental conditions. If the observed concentrations are well represented by the model, it supports (but by no means proves) the hypothesis that the modeled phases are the major feature in explaining the observed changes. Deviations from model predictions are more problematic and are discussed later in this section.

Another tool used in this study to overcome the lack of phase quantitation is X-ray absorption spectroscopy. In conjunction with elemental concentration information about the treated and untreated sludges, XAS, unlike electron microscopy, can provide quantitative information about how each specific elemental environment is altered by sludge washing and caustic leaching. This tool was illustrated with respect to the $\text{Cr}^{3+}/\text{Cr}^{6+}$ dissolution behavior in tank sludges. In addition, the greater size of the sample required for the measurements lends more confidence that a representative portion of the material used in the sludge washing and caustic leaching test is present. The major drawback to X-ray spectroscopy is its inability to readily examine important light elements such as phosphorus and aluminum.

The second factor concerns the representative nature of the samples used in testing and characterization. For example, TEM measurements on untreated Tank B111 sludge did not reveal a metathesizable metal phosphate. However, when applying this information, it must be noted that the sample used for the

phase determination is only a fraction of the sample supplied from the composite used in the sludge washing and caustic leach testing. The total amount supplied for the electron microscopy/XRD study was only about 1/500 of the sample used in the sludge wash and caustic leach test. An alternative explanation, then, of the lack of an identified source of metathesizable metal phosphate is simply that the examined sample was not wholly representative of the sample contents. However, such arguments then qualify any conclusions based on apparent changes in the phases present before and after sludge washing and caustic leaching. These difficulties serve to emphasize the hazards of extrapolating the results of any one measurement or test to general statements about tank sludge chemistry.

The third factor concerns how limitations in the experimental design constrain the use of other tools, in particular thermodynamically based modeling, and affect the ability to interpret sludge washing and caustic leaching behavior. In the standard method used for all of the sludge washing and caustic leaching tests, the small size of the system prevented accurate sampling at the actual inhibited-water wash and caustic leach temperatures. The problem with cooling followed by sampling brings up the question of the rate at which the system comes to equilibrium. This has a direct impact on the reliability of the modeling results. In general, the modeling of aluminum dissolution yielded concentrations close to those expected, but generally still slightly above the calculated room temperature concentrations. In several cases, however, the values varied significantly between the calculated concentrations at the leaching temperature and those expected at room temperature. Such circumstances add to the difficulty in comparing modeling predictions with the actual experimental results.

Another problem with the single, set, experimental design deals with the inability to address the contribution of kinetics to the observed component concentrations found in the wash and leach solutions. Without addressing kinetic contributions, conflicts in the experimental data may not be resolved. Two examples dealing with aluminum dissolution in Tank S104 and B111 sludges serve to illustrate this point. As noted above, the second leach step in the S104 test showed a large amount of aluminum being dissolved. Modeling suggested that larger amounts of aluminum dissolved during the leach steps but reprecipitated during cooling. However, electron microscopy measurements of the treated solids showed no evidence of precipitated alumina. Does the explanation lie in the microscopy results not being representative (Factor 1) or rather that the amount of dissolution is limited by the rate of aluminum dissolution, i.e., an unaddressed kinetics contribution? Further examination of the aluminum concentration in the leachate as a function of time and solid-to-liquid ratio would serve to address the kinetics question, but was not possible in the experimental task as designed. The inability to address these questions as they come up inevitably leaves gaps in interpretation.

The second example deals again with the amount of aluminum dissolution in the tank sludges. In B111 and BX107, the aluminum concentration in the second leaching step was appreciably lower than calculated for gibbsite even at room temperature. One interpretation would be to suggest that all of the aluminum dissolvable by caustic leaching was removed in these sludges. However, aluminum-containing phases (aluminosilicates) were in fact found in the treated solids. Is the further lack of aluminum removal constrained by the solubility of the aluminosilicate phases under the experimental conditions, or are these materials slower to react? Currently, thermodynamically based modeling is

incapable of addressing this question, and again kinetics questions cannot be addressed within the experimental task as designed.

The points noted here need to be incorporated in future work if the optimum amount of information is to be gleaned from these studies. The broad-based approach, despite the problems noted above, is quite useful: each piece contributed significantly to the overall level of understanding. Modifications in the approach should provide additional help. First, it should be emphasized that a base test procedure for sludge washing and caustic leaching remains the linchpin for understanding sludge behavior. Maintaining a standard set of testing conditions is important for the most facile comparison of results from test to test. However, greater attention to experimental conditions, particularly to the free hydroxide concentration in each individual leaching step, appears warranted to facilitate comparisons between tests.

Additional attention to details like the chromium oxidation state in the test solutions should be given to assist interpretation of modeling results. Variations in the test procedure to examine kinetic effects are critical in resolving solubility questions as described above. Reexamination of caustic leaching in sludges such as S104 as a function of time and solid-to-liquid ratio should be performed as soon as is practical. Experiments directed towards understanding aluminosilicate and Cr(III) dissolution over a 25°C to 100°C temperature range are needed to expand the modeling efforts to help address remaining unknown questions in aluminum and chromium dissolution. With these improvements, and as experimental conditions and procedures are refined based on the results of these initial tests, understanding of the basic chemistry accompanying sludge washing and caustic leaching of Hanford tank sludges should expand. As more and more systems are examined, the consistency of the data provides confidence that limitations accompanying any single set of measurements are not being overlooked.

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R. K. Quinn
B. M. Rapko (5)
D. R. Rector
B. A. Reynolds
R. D. Scheele
L. J. Sealock, Jr.
G. J. Sevigny
P. A. Smith
L. Song
D. L. Styris
L. E. Thomas
J. M. Tingey
A. J. Villegas
M. J. Wagner
Y. Wang
Information Release (7)