

**Contaminant Release from Residual Waste in Single Shell Tanks at the Hanford Site, Washington, USA - 9276**

K.J. Cantrell, K.M. Krupka, W.J. Deutsch, and M.J. Lindberg  
Pacific Northwest National Laboratory  
P.O. Box 999, Richland, Washington 99352

**ABSTRACT**

Determinations of elemental and solid-phase compositions, as well as contaminant release studies have been performed in support of an ongoing study of residual tank wastes (i.e., waste remaining after final retrieval operations) from five of 149 underground single-shell storage tanks (241-C-103, 241-C-106, 241-C-202, 241-C-203, and 241-S-112) at the U.S. Department of Energy's Hanford Site in Washington State. This work is being conducted to support performance assessments that are required to evaluate long-term health and safety risks associated with tank farm closure. The results of studies completed to date show significant variability in the compositions, solid phase properties, and contaminant release characteristics from these residual tank wastes. This variability is the result of differences in the chemistry/composition of wastes produced from several different spent fuel reprocessing schemes, subsequent waste reprocessing to remove certain target constituents, tank farm operations that concentrated wastes and mixed wastes between tanks, and differences in tank retrieval processes used to remove the wastes from the tanks.

Release models were developed based upon results of chemical characterization of the bulk residual waste, solid-phase characterization (see companion paper 9277 by Krupka et al.), leaching and extraction experiments, and geochemical modeling. In most cases empirical release models were required to describe contaminant release from these wastes. Release of contaminants from residual waste was frequently found to be controlled by the solubility of phases that could not be identified or for which thermodynamic data or dissolution rates have not been measured. For example, significant fractions of Tc-99, I-129, and Cr appear to be coprecipitated in metal oxide phases that could not be identified unambiguously. In the case of U release from tank 241-C-103 residual waste, geochemical calculations indicated that leachate concentrations of U were likely controlled by the solubility of schoepite ( $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ); therefore, a reactive transport model based upon the solubility of schoepite and the expected composition and infiltration rates of pore water could be used to simulate future release of U from this residual tank waste.

In addition to the development of release models, the residual tank waste studies completed so far have provided a number of new insights that have changed our understanding of residual tank waste. For example, the release of contaminants from different tanks, although governed by the same general chemical principles, can be very different. It has also been found that significant fractions of Tc-99 and other typically highly mobile contaminants are frequently not readily released from tank residuals and occur in recalcitrant phases that are resistant to aqueous dissolution. As these studies progress, such key cross-cutting geochemical processes and solid phase characteristics important to contaminant release from residual tank waste are becoming apparent. This may allow the grouping of tanks into general categories with certain common chemical features and contaminant release characteristics – an important goal because complete characterization of residual wastes from all 149 single-shell storage tanks is not practical.

## INTRODUCTION AND BACKGROUND

The Hanford Site, located in southeastern Washington State, produced plutonium for the DOE weapons program from 1943 to 1989. Plutonium production involved the fission of uranium fuels using nine nuclear reactors along the Columbia River, followed by the extraction and concentration of trace product plutonium through chemically intensive processing regimes performed in the central portion of the site. Three primary reprocessing schemes were used during the lifetime of plutonium operations at the Hanford Site:

- Bismuth Phosphate (1944-1956)
- REDOX (1952-1967)
- PUREX (1956-1972, 1983-1989).

Overviews of these processes are provided in Gephart [1].

Large volumes of radioactive waste were generated during the extraction of plutonium from the spent fuel, and the waste chemistry and composition varied significantly between the three processing schemes. The most concentrated and radioactive of these wastes, termed high-level waste (HLW), were sent to 177 underground waste storage tanks. The first of these were so-called single-shell tanks (SSTs) with single-shell steel wall construction encapsulated in a protective concrete dome. The 149 large, single-shell, underground storage tanks ranged in volume from 209,000 L (55,000 gal) to over 3.8 million L (1.0 million gal) with a total storage volume of 357 million L (94 million gal). The wastes were stored to allow for decay of highly radioactive, short-lived isotopes and the secondary extraction of uranium from Bismuth Phosphate wastes and other desired constituents. Tank storage was originally intended to be interim storage. DOE's original intent was to seek means for the permanent disposal of HLW within 20 years, but this has not yet been accomplished.

Each plutonium reprocessing scheme (Bismuth Phosphate, REDOX, and PUREX) and the uranium recovery process, generated a series of three or more waste streams that differed in composition. These in turn differed between reprocessing schemes [2,3]. Waste streams included cladding dissolution wastes, the primary reprocessing waste stream with maximum fission products, and start-up and rinse cycle wastes of different sorts. At least 50 different HLW waste streams are recognized and have been categorized into 23 or more distinct waste types [4]. All Hanford Site HLWs were initially acidic ( $\text{HNO}_3$ ), but were overneutralized with NaOH to high pH to minimize tank corrosion. HLW waste compositions changed significantly after initial routing to the tank farms as: 1) in the case of some tanks, the waste solutions boiled and self-concentrated; 2) wastes were mixed and intentionally condensed through evaporation to maximize storage space that became limited with time; 3) atmospheric  $\text{CO}_2$  was absorbed by high pH supernate; 4) Bismuth Phosphate wastes were subjected to uranium recovery at U Plant; and 5) REDOX and PUREX HLWs were reprocessed at B Plant to remove heat generating isotopes Cs-137 and Sr-90. Because of these operational and chemical complexities, it is difficult to estimate average compositions for different HLW waste types.

Because some of the SSTs have leaked in the past, the wastes in the SSTs are being retrieved for interim storage in newer double shell tanks (DSTs) prior to final treatment by vitrification to minimize the potential for further waste release. At this time, all free liquid waste has been pumped from the SSTs into

DSTs. Retrieval of the remaining wastes has been completed on seven tanks [5]. Because complete removal of the wastes is not feasible, small amounts of residual wastes will remain in the storage tanks. The residual waste remaining on the bottom of tanks is expected to be less than one inch thick (less than 1% of the initial volume).

Migration of released tank waste constituents through the vadose zone to underlying groundwater is a primary environmental health and safety risk associated with tank farm closure. Release of contaminants from residual tank wastes that remain after final retrieval is an important component of the total inventory of contaminants that could potentially migrate from the tanks through the vadose zone to underlying groundwater and must be well understood for future performance assessments associated with site closure [6, 7]. To support closure of the retrieved tanks, Pacific Northwest National Laboratory (PNNL) has completed characterization and contaminant release studies of residual waste from five retrieved Hanford SSTs: 241-C-103 (C-103), 241-C-106 (C-106), 241-C-202 (C-202), 241-C-203 (C-203), and 241-S-112 (S-112), as part of its Residual Tank Waste Contaminant Release Project funded by CH2M HILL Hanford Group, Inc.

PNNL is using a multi-tiered approach to study these residual wastes. Tier 1 tests focus on general characterization of the residual wastes (e.g., concentration measurements of contaminants and major components in the bulk residual waste) and identification of water-leachable constituents. Additional Tier 2 analyses augment this characterization work and endeavor to determine the controlling mechanisms for release of contaminants. Tier 2 tests include selective extractions to quantify the release of contaminants from particular solid phases; solubility studies; and analyses by x-ray diffraction (XRD), scanning electron microscopy/energy dispersive spectrometry (SEM/EDS), and other techniques, such as synchrotron-based x-ray adsorption analysis, to identify phases in the as-received samples of residual wastes and solids remaining after water leach and selective extraction studies.

A major component of this project is the development of contaminant release models for residual waste that can be used in performance assessments to evaluate the long-term risks to human health, safety and the environment associated with closure of Hanford's underground storage tanks. Release of contaminants from residual waste has been quantified by leaching with aqueous solutions, selective extractions, and thermodynamic modeling. Leachants used in these studies include deionized water, a  $\text{Ca}(\text{OH})_2$  saturated solution, and a calcite ( $\text{CaCO}_3$ ) saturated solution. The  $\text{Ca}(\text{OH})_2$  leachant is used to simulate conditions associated with the tanks being filled with cement, and represents the composition of a pore fluid that has contacted fresh cement prior to contacting the residual waste. The calcite-saturated leachant is used to simulate a future scenario in which rain infiltrates through the vadose zone into the interior of the SSTs and then reacts with aged concrete that has undergone carbonation and become coated with calcite. The aqueous leaching experiments were conducted using both single contact experiments and sequential contact experiments. The single contact experiments typically included 1 day and 2 month contact periods. The sequential contact experiments typically included six stages in which the leachate solution was replaced with fresh leachant after each contact period. The contact periods were typically one day for the first five stages and 30 days for the sixth stage.

Detailed results of the residual waste testing in terms of contaminant occurrence (concentration and solid phase associations) and leachate concentrations (contaminant release) are documented in the following reports:

- C-103: PNNL-16738 [6]
- C-106: PNNL-15187 Rev. 1 [9]; PNNL-15544 [10]
- C-202: PNNL-16229 [11]
- C-203: PNNL-16229 [11] (published with C-202 data)
- S-112: PNNL-17593 [12]

Another report is also available that summarizes characterization and release model results obtained for residual waste from tanks C-103, C-106, C202, and C-203 [5]. All of these technical reports are available online to the public in pdf format at <http://www.pnl.gov/main/publications/>.

## COMPOSITION OF RESIDUAL TANK WASTE

The elemental and contaminant concentrations of the wastes were measured by dissolution of the bulk residual waste solids using fusion-dissolution procedures and acid digestion methods. These methods are described in detail in Deutsch et al. [11]. The elemental and contaminant compositions of the bulk residual waste solids are then determined from the dissolved concentrations in these solutions using a combination of methods including inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES). Because these two solid digestion methods require the addition of acids to fully solubilize the waste solids, they are not appropriate techniques for determining the anion concentrations of the bulk residual waste. Anion concentrations were estimated separately by summing results from sequential deionized water extracts of the bulk residual wastes [5]. The anion concentrations in these extracts are measured using ion chromatography (IC). This approach may underestimate the total quantities of anions in the sample, particularly for anions that can form insoluble precipitates.

Residual waste composition results for the five tanks studied to date are shown in Table I. The values shown for major cations and important contaminants in Table 1 were determined from the average of one to three samples run in duplicate by acid digestion or fusion (whichever extraction produced the highest concentration). For tanks C-103 and S-112, only acid digestion analyses were conducted. In the C-103 waste the predominant metals in terms of weight percent (dry basis) were aluminum (13.6 wt%), iron (1.2 wt%), sodium (0.8 wt%), silicon (0.9 wt%), and uranium (0.4 wt%). Water extractable anion concentrations were below the quantification limit. For tank C-106 the predominant metals in the waste were aluminum (13.1 wt%), manganese (11.8 wt%), sodium (6.0 wt%), and iron (4.4 wt%). The predominant water extractable anions were oxalate (6.4 wt%) and carbonate (4.0 wt%). Note that the high oxalate concentrations determined in residual waste from tank C-106 did not derive from the waste itself but from the retrieval process [13], in which a 0.9 M oxalic acid solution was used to promote the dissolution of the tank waste. For the C-202 waste the predominant metals were uranium (23.6 wt%), iron (12.2 wt%), sodium (5.9 wt%), manganese (2.6 wt%), calcium (1.5 wt%), aluminum (1.4 wt%), and chromium (1.3 wt%). The predominant water extractable anions were oxalate (3.2 wt%), phosphate (1.7 wt%), carbonate (1.2 wt%), fluoride (0.6 wt%), and nitrate (0.4 wt%). For tank C-203 the predominant metal concentrations were uranium (58.6 wt%), sodium (9.6 wt%), iron (1.6 wt%), and chromium (0.6 wt%). The predominant anion concentrations in dry weight percent were carbonate (5.0 wt%), phosphate (4.3 wt%), nitrate (0.5 wt%), and fluoride (0.3 wt%). For tank S-112 the predominant metal

Table I. Average Concentrations of Major Components and Important Contaminants in Residual Waste Samples from Five SSTs as Determined by Acid Digestion (Major Cations and Contaminants) and Water Leaching (Anions) [8, 9, 10, 11, 12].

Analyte	C-103	C-106	C-202	C-203	S-112
	Acid Digestion/Fusion ( $\mu\text{g/g dry wt.}$ )				
Al	136,000	131,000	13,600	<710	291,200 <sup>a</sup>
Ba	181	1,030	208	<142	12.6
Ca	616	46,500	14,500	3,140	56.9
Cr	193	(896) <sup>b</sup>	13,200	5,910	1,730
Fe	12,000	43,800	122,000	16,300	2,280
K	BDL <sup>c</sup>	8,526	<15,800	<355,000	68.9
Mg	(42)	3,162	2,560	(729)	4.82
Mn	470	118,000	25,700	1,210	14.4
Na	7,840	60,400	58,800	95,800	49,100
Ni	420	5,373	9,070	2,440	9.01
Pb	892	4,814	7,980	5,630	7.11
Si	9,070	(19,100)	25,000	3,490	1,220
Sr	90.7	(493)	1,510	409	4.02
U-283	3,730	310	236,000	586,000	23.8
Pu-293	8.02	29.8	435	18.2	NA <sup>d</sup>
Np-237	1.30	9.27	2.16	(0.0519)	NA
Am-241	0.053	2.05	0.449	0.0140	NA
Tc-99	0.231	1.16	0.149	(0.0947)	0.474
I-129	( $1.11 \times 10^{-5}$ )	0.673	NA	NA	NA
Analyte	Water Leach ( $\mu\text{g/g dry wt.}$ )				
F <sup>-</sup>	(31)	33	6,030	2,760	NA
Cl <sup>-</sup>	(5.4)	87	161	201	NA
NO <sub>2</sub> <sup>-</sup>	(59)	<73	485	610	NA
NO <sub>3</sub> <sup>-</sup>	(250)	<70	3,540	4,840	NA
CO <sub>3</sub> <sup>2-</sup>	BDL	39,500	12,200	49,900	NA
SO <sub>4</sub> <sup>2-</sup>	BDL	<66	334	288	NA
PO <sub>4</sub> <sup>3-</sup>	(66)	<91	17,700	43,300	NA
Oxalate	(31)	63,900	32,400	1,500	NA

<sup>a</sup> The Al concentration listed above is that reported by analyses completed by Hanford's 222-S Laboratory. It was assumed that the 222-S Laboratory result for Al is correct, because it is consistent with the XRD results which indicates the solid is essentially all gibbsite [Al(OH)<sub>3</sub>]. The average Al concentration determined by Cantrell et al. [12] was 77,200  $\mu\text{g/g dry wt.}$  and was much lower than expected. The reason for this discrepancy is being evaluated.

<sup>b</sup> Values in parentheses were less than the estimated quantification limit (EQL).

<sup>c</sup> BDL = Below detection limit.

<sup>d</sup> NA = Not analyzed .

concentrations in dry weight percent were aluminum (29.1 wt%), sodium (4.9 wt%), iron (0.2 wt%), and chromium (0.2 wt%). Anions were not analyzed for the samples from this tank.

Using the results shown in Table I and the results of the solid phase characterization [14] generalizations can be made regarding the major phase or compositional features of these residual wastes. The generalized phase or compositional features of the five residual tank waste samples are shown in Table II. C-103 is composed primarily of gibbsite [Al(OH)<sub>3</sub>] with minor amounts of hematite (Fe<sub>2</sub>O<sub>3</sub>), and a uranium oxide tentatively identified as schoepite (UO<sub>3</sub>·2H<sub>2</sub>O). In addition to hematite, another iron oxide phase appeared to be present in the C-103 residual waste. The iron oxides often contained minor amounts of other metals such as Cr, Ni, Pb, and Mn.

Table II. Major Phase or Compositional Features of Residual Wastes Studied to Date [8, 9, 10, 11, 12].

Tank	Major Phases or Phase Compositions Identified in SSTs Studied to date	Important Secondary Phases
C-103	gibbsite [Al(OH) <sub>3</sub> ]	hematite, possibly additional iron oxide(s), uranium oxide (possibly schoepite [UO <sub>3</sub> ·2H <sub>2</sub> O])
C-106	gibbsite, böhmite (AlOOH), dawsonite [NaAlCO <sub>3</sub> (OH) <sub>2</sub> ], hematite, rhodochrosite (MnCO <sub>3</sub> ), lindbergite (MnC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O), whewillite (CaC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O)	
C-202	poorly crystalline U-Na-C-O-P±H (possibly more than one phase)	iron oxide
C-203	poorly crystalline U-Na-C-O-P±H (possibly more than one phase)	iron oxide
S-112	gibbsite	Al-Na-O(±H±C) [possibly dawsonite]

A variety of phases were identified in residual waste from tank C-106, including gibbsite, böhmite (AlOOH), dawsonite [NaAlCO<sub>3</sub>(OH)<sub>2</sub>], hematite, rhodochrosite (MnCO<sub>3</sub>), lindbergite (MnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O), and whewillite (CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O). The oxalate phases in the residual waste from this tank formed as a result of the retrieval process in which oxalic acid was used. The oxalate retrieval process was only used in tank C-106 [13, 15, 16].

The dominant phase (or phases) in the residual waste samples from tanks C-202 and C-203 was a poorly crystalline or amorphous uranium phase with a general composition of U-Na-C-O-P±H. It was not clear if one or more uranium phases were present. An iron oxide phase was also present in the C-202 and C-203 residual wastes, often containing minor amounts of other metals such as Mn, Cr, and Pb.

The residual waste from S-112 was dominated by gibbsite which often appeared to be coated with a thin layer of a phase that had a composition similar to dawsonite.

## **CONTAMINANT RELEASE FROM RESIDUAL WASTE**

The primary geochemical processes that affect the release of contaminants from the residual waste and the migration of these contaminants are dissolution/precipitation of minerals containing the contaminants and adsorption/desorption of contaminants to the surfaces of solids. Secondary reactions that can influence solid-phase solubility and contaminant adsorption include hydrolysis, aqueous complexation, oxidation/reduction, and ionic strength effects. The results of testing of residual waste from the SSTs C-103, C-106, C-202, C-203, and S-112 suggest that the dominant control on the release of contaminants from the residual tank wastes is the solubility of the solid containing each contaminant of interest (COI). Furthermore, retrieving the waste from the tanks with water or an oxalic acid solution (as was done for tank C-106) removes the readily soluble solids, leaving behind relatively insoluble solid phases.

The characterization studies conducted for developing release models were designed with the aim of developing mechanistic contaminant release models. Mechanistic release models rely on an understanding of the fundamental geochemical processes governing the release of contaminants of interest from the residual waste. For example, if a particular phase is controlling the release of a contaminant, it is necessary to know what that phase is, its concentration in the waste, its thermodynamic solubility constant and other relevant thermodynamic data, and its dissolution rate for the chemical conditions under consideration. It is also necessary to know if the solid phase comes to equilibrium with water quickly, relative to the rate of vadose water infiltration. If equilibrium between the water and solid phase is not attained during this time frame, determination of dissolution rate constants is required. Other mechanistic data that are potentially necessary include rates of redox reactions, equilibrium surface adsorption/desorption constants, and diffusion coefficients. Mechanistic release models are preferred over empirical release models because mechanistic models are more scientifically defensible, can be used with greater confidence than empirical models when extrapolating to different disposal/waste release environments, and do not have to be as conservative as empirical models, which are generally associated with greater uncertainty especially when used for conditions not explicitly studied.

For most of the contaminants present in the residual wastes studied to date, it was not possible to establish mechanistic release models as it was generally not possible to identify the solubility controlling phases for the primary contaminants of interest in the residual waste. For a number of contaminants, their concentrations in the bulk solid waste were too low to be detected by routine solid-phase characterization techniques such as SEM/EDS or synchrotron-based x-ray methods. This problem is further complicated if any of the contaminant solubility controlling phases are amorphous. Although the compositions of such amorphous solids can be determined by methods such as energy-dispersive x-ray spectroscopy (EDS) or electron microprobe (EMP), the compositions of such phases are often variable. Moreover, the identity of amorphous solids cannot be determined by XRD, and thermodynamic and/or dissolution rate data rarely exist for such phases. In addition, the residual waste solids can be aggregates of numerous phases, further complicating phase identification. For the residual waste samples from the five SSTs studied to date, it has not been possible to develop mechanistic release models for many of the contaminants of interest; therefore, the models described below had to be based on empirical water leach measurements.

Two different closure scenarios have been considered in the development of the release models. In Scenario 1, the tank is filled with a relatively inert material such as Hanford sand or gravel that does not significantly affect the chemistry of infiltrating water that will contact the residual waste. For this scenario, it is assumed that the water contacting the waste is similar to a typical Hanford groundwater. Site groundwater is generally in equilibrium with calcite, has a pH near 8.2, and a low ionic strength ( $I < 0.01 \text{ M}$ ) [17].

In Scenario 2, the tank is filled with a cementitious grout. Cements have a complex pore fluid chemistry that evolves over time [18, 19]. Pore fluids in fresh cement have a high pH as a result of the presence of portlandite [ $\text{Ca}(\text{OH})_2$ ] and reactive silicates in the cement and high ionic strength from dissolved salts that remain in the pores of the cement after it cures. As infiltrating vadose zone pore water contacts the cement, salts in the pore fluids will be diluted and  $\text{CO}_2$  dissolved in infiltrating water will react with the basic components to form  $\text{CaCO}_3$ . As this process comes to completion, the pore fluids in the weathered cement will become buffered by  $\text{CaCO}_3$  and come to resemble that of Hanford pore water. As a result of these processes, Scenario 2 has been divided into two stages. Stage 1 of Scenario 2 is the fresh cement scenario, which was simulated in the laboratory by leaching the residual waste with a  $\text{Ca}(\text{OH})_2$ -saturated solution. Stage 2 of Scenario 2 is the aged cement scenario, which was simulated by leaching the waste with a  $\text{Ca}(\text{CO}_3)$ -saturated solution. Stage 2 of Scenario 2 is considered to be identical to Scenario 1.

Results determined for the empirical release models are shown in Table III. The total concentration of key contaminants in the residual waste and the maximum release concentrations as determined by the water leach tests are included for the two scenarios: 1) vadose zone pore water and aged cement and 2) fresh cement. The key contaminant I-129 was not detected above its minimum analytical detection limit in any of the extraction tests. The maximum release concentrations for the remaining contaminants of interest were derived from the highest measured dissolved contaminant concentrations determined in the laboratory leaching experiments using  $\text{CaCO}_3$ -saturated water (Scenario 1) and  $\text{Ca}(\text{OH})_2$ -saturated water (Scenario 2). There are noteworthy differences in the total concentrations and release concentrations of the contaminants for the five tanks listed in Table III. In general, the leachability of the various contaminants of interest is highly variable among the various residual tank wastes. For example, uranium release concentrations range from 510,000  $\mu\text{g/L}$  for Scenario 1 in tank C-203 to 1.4  $\mu\text{g/L}$  for Scenario 1 in tank S-112. For each of the residual tank wastes, uranium is more leachable for Scenario 1 than for Scenario 2. This is likely due to the lower solubility of uranium minerals under the higher pH conditions of Scenario 2 Stage 1. The higher release concentrations for uranium appear to be correlated to higher uranium concentrations in the residual waste. Chromium release concentrations also exhibit considerable variability, ranging from 13,000  $\mu\text{g/L}$  for tank C-203 to 19  $\mu\text{g/L}$  for tank C-103. Unlike uranium, chromium shows similar leachability for both release scenarios. As with uranium, higher release concentrations of chromium appear to be correlated with higher concentrations in the residual waste. Of the three major contaminants of interest, the release concentrations for Tc-99 have the least variability, ranging from 1.2  $\mu\text{g/L}$  for tank C-106 to 0.041  $\mu\text{g/L}$  for tank C-202. Similar to chromium, Tc-99 release is similar for both release scenarios.

The contaminant release model concentrations shown in Table III are based upon the highest measured results determined from all the leaching experiments and are expected to be very conservative from an environmental impact perspective. To illustrate this, the water leaching experiments for residual waste from tank C-106 will be discussed in more detail. Table IV shows results from the single contact and sequential leaching experiments for Tc-99 and uranium, along with the average total percent leachable

Table III. Empirical Contaminant Release Models for SST Residual Waste [8, 9, 10, 11, 12].

Tank	Release Scenario	Component	Concentration (µg/g dry wt.)	Maximum Release Concentration (µg/L solution)
C-103	1 (Calcite-saturated system)	U	$4.2 \times 10^3$	$4.1 \times 10^3$
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			2.0
	1 (Calcite-saturated system)	Cr	230	18
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			19
	1 (Calcite-saturated system)	Tc-99	0.28	0.16
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			0.19
C-106	1 (Calcite-saturated system)	U	310	49
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			36
	1 (Calcite-saturated system)	Cr	897	<283
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			<470
	1 (Calcite-saturated system)	Tc-99	1.2	0.39
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			1.2
C-202	1 (Calcite-saturated system)	U	$2.4 \times 10^5$	$6.1 \times 10^4$
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			$1.7 \times 10^3$
	1 (Calcite-saturated system)	Cr	$1.0 \times 10^4$	$2.0 \times 10^3$
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			$7.1 \times 10^3$
	1 (Calcite-saturated system)	Tc-99	0.23	0.041
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			0.054
C-203	1 (Calcite-saturated system)	U	$5.9 \times 10^5$	$5.1 \times 10^5$
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			$3.0 \times 10^5$
	1 (Calcite-saturated system)	Cr	$4.3 \times 10^3$	$1.3 \times 10^4$

	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			$1.1 \times 10^4$
	1 (Calcite-saturated system)	Tc-99	0.11	0.16
	2 (Fresh cement [Ca(OH) <sub>2</sub> -saturated])			0.38
<b>S-112</b>	1 (Calcite-saturated system)	U	36	1.4
	1 (Calcite-saturated system)	Cr	1,800	$1.8 \times 10^3$
	1 (Calcite-saturated system)	Tc-99	0.48	0.85

Tc-99 and uranium determined for residual waste from tank C-106. The results for Tc-99 indicate that only a small fraction of the total is leachable and the majority of what is leachable, dissolved during the first stage contact with the leachant.

Table IV. Percentages of Tc-99 and Uranium Released During Leaching Tests from Tank C-106 Residual Waste Relative to Fusion Results [9]

Leachate	Tc-99	Uranium
	(% Leachable)	
<b>1-Month Single-Contact</b>		
C-106 Water Leach	2.4 to 3.2	1.3 to 1.4
C-106 Ca(OH) <sub>2</sub>	8.6 to 11.8	1.8 to 2.9
C-106 CaCO <sub>3</sub>	< 6.0	2.2 to 3.4
<b>Stage 1 (1 day contact)</b>		
C-106 Water Leach	1.3 to 2.0	2.8 to 3.4
C-106 Ca(OH) <sub>2</sub>	5.2 to 6.3	0.3
C-106 CaCO <sub>3</sub>	ND <sup>a</sup>	0.02 to 0.04
<b>Stage 2 (1 day contact)</b>		
C-106 Water Leach	<0.58	0.5 to 0.7
C-106 Ca(OH) <sub>2</sub>	<6.4	0.02 to 0.1
C-106 CaCO <sub>3</sub>	ND	0.03 to 0.04
<b>Stage 3 (1 day contact)</b>		
C-106 Water Leach	<0.58	0.2 to 0.3
C-106 Ca(OH) <sub>2</sub>	<6.4	0.06 to 0.09
C-106 CaCO <sub>3</sub>	ND	0.02 to 0.05
<b>Stage 4 (4 day contact)</b>		
C-106 Water Leach	<0.58	0.08 to 0.11
C-106 Ca(OH) <sub>2</sub>	<6.4	0.05 to 0.09
C-106 CaCO <sub>3</sub>	ND	0.04 to 0.05
<b>Stage 5 (1 day contact)</b>		
C-106 Water Leach	<0.58	0.03 to 0.04
C-106 Ca(OH) <sub>2</sub>	<6.4	0.02 to 0.08
C-106 CaCO <sub>3</sub>	ND	0.02 to 0.05
<b>Stage 6 (43 day contact)</b>		
C-106 Water Leach	<0.58	0.09 to 0.10
C-106 Ca(OH) <sub>2</sub>	<6.4	0.02 to 0.04
C-106 CaCO <sub>3</sub>	ND	0.04 to 0.05
<b>Average Total of Six Single Contact Stages</b>		
C-106 Water Leach	1.7	4.2
C-106 Ca(OH) <sub>2</sub>	5.8	0.6
C-106 CaCO <sub>3</sub>	ND	0.2

<sup>a</sup> ND = Detection limit is higher than the measured value.

These results indicate that for Tc-99, the release concentrations indicated in Table III will only occur during initial stages of contact with water. After this period of initial contact with water, the leachable concentrations of Tc-99 would be expected to fall off rapidly to near zero. In addition, it appears that only a small fraction of the total Tc-99 in the residual waste will ever be mobile, with the bulk of the inventory being highly recalcitrant.

The situation for uranium is somewhat different. The highest concentrations of leachable uranium occur in the first stage contacts with concentrations in subsequent stages decreasing significantly. Leachable uranium concentrations stabilize at a low and relatively constant level at approximately stage 3. These results suggest that uranium concentrations in water contacting C-106 residual waste may be controlled initially by the solubility of a relatively soluble phase that occurs at low concentrations in the residual waste or by desorption of uranium adsorbed to the surfaces of residual waste particles. After this source of uranium has dissolved, further release of uranium is likely controlled by the dissolution of a uranium phase with a lower solubility.

## **SUMMARY AND CONCLUSIONS**

Determinations of elemental and solid-phase compositions, as well as contaminant release studies have been performed in support of an ongoing study of residual tank wastes (i.e., waste remaining after final retrieval operations) from five of 149 underground single-shell storage tanks (241-C-103, 241-C-106, 241-C-202, 241-C-203, and 241-S-112) at the U.S. Department of Energy's Hanford Site in Washington State. This work is being conducted to support performance assessments that are required to evaluate long-term health and safety risks associated with tank farm closure. The results of studies completed to date show significant variability in the compositions, solid phase properties, and contaminant release characteristics from these residual tank wastes. This variability is the result of differences in the chemistry/composition of wastes produced from several different spent fuel reprocessing schemes, subsequent waste reprocessing to remove certain target constituents, tank farm operations that concentrated wastes and mixed wastes between tanks, and differences in tank retrieval processes used to remove the wastes from the tanks.

Release models were developed based upon results of chemical characterization of the bulk residual waste, solid-phase characterization [14], leaching and extraction experiments, and geochemical modeling. In most cases empirical release models were required to describe contaminant release from these wastes. Release of contaminants from residual waste was frequently found to be controlled by the solubility of phases that could not be identified or for which thermodynamic data or dissolution rates have not been measured. For example, significant fractions of Tc-99, I-129, and Cr appear to be coprecipitated in metal oxide phases that could not be identified unambiguously. In the case of U release from tank 241-C-103 residual waste, geochemical calculations indicated that leachate concentrations of U were likely controlled by the solubility of schoepite ( $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ); therefore, a reactive transport model based upon the solubility of schoepite and the expected composition and infiltration rates of pore water could be used to simulate future release of U from this residual tank waste.

In addition to the development of release models, the residual tank waste studies completed so far have provided a number of new insights that have changed our understanding of residual tank waste. For example, the release of contaminants from different tanks, although governed by the same general chemical principles, can be very different. It has also been found that significant fractions of Tc-99 and other typically highly mobile contaminants are frequently not readily released from tank residuals and occur in recalcitrant phases that are resistant to aqueous dissolution. As these studies progress, such key cross-cutting geochemical processes and solid phase characteristics important to contaminant release from residual tank waste are becoming apparent. This may allow the grouping of tanks into general categories with certain common chemical features and contaminant release characteristics – an important goal because complete characterization of residual wastes from all 149 single-shell storage tanks is not practical.

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