

## **Waste Form Development for Solidification of Liquid Secondary Wastes to Support Hanford Direct Feed Low Activity Waste Vitrification – 17484**

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### **ABSTRACT**

The US Department of Energy/Office of River Protection DOE/ORP has funded a program led by Washington River Protection Solutions (WRPS) to develop and test cementitious waste forms for immobilization of liquid secondary waste (LSW) at the Hanford site in Southeastern Washington State. The LSW comprises a concentrated brine from processing liquid effluents at Hanford's Effluent Treatment Facility. The liquid effluents include condensates from the 242-A tank waste evaporator and future offgas condensates from the Low Activity Waste (LAW) Vitrification Facility. To facilitate waste form formulation development and testing, WRPS developed LSW simulants and engaged subject matter experts at the Savannah River National Laboratory (SRNL) and Pacific Northwest National Laboratory (PNNL). This paper describes results of recent work done to develop and test a grout formulation tailored to address the elevated sulfate levels in Hanford LSW.

### **INTRODUCTION**

Radioactive byproduct wastes from nuclear weapons production are stored in underground tanks at the Hanford Site, located in the state of Washington. The waste tanks contain a complex and diverse mix of radioactive and chemical waste in the form of sludge, salts, and liquids, necessitating a variety of unique waste retrieval, treatment, and disposition methods. In general, the tank waste can be characterized as the following:

1. Sludge – Insoluble materials largely consisting of metal hydroxides and oxides that precipitated when acidic wastes from spent nuclear fuel processing and other activities were neutralized and converted to high pH for storage in carbon steel tanks. The sludge fraction of the waste makes up the bulk of the material that will be processed via high-level waste (HLW) Vitrification into a stable glass form.
2. Supernatant – Liquid waste with high sodium content and high pH.
3. Saltcake – a mixture of salts that precipitated from supernatant as the concentration was increased by evaporation to reduce tank storage space requirements. Saltcake must be re-dissolved and processed as supernatant waste. The supernatant and saltcake contain the majority of highly radioactive cesium which must be separated and processed with the sludge

stream into HLW glass. The decontaminated supernatant will then be processed via low-activity waste (LAW) vitrification into a stable glass form.

4. Potential contact-handled transuranic waste (CH-TRU): There are approximately 1.4 million gallons of waste in 11 specific single-shell tanks (SSTs). The material in these tanks is being reviewed to determine the potential for transfer to the Waste Isolation Pilot Plant (WIPP) versus being processed on-site into HLW and LAW glass fractions.

In order to begin immobilization of tank waste as soon as practicable, a Direct Feed LAW (DFLAW) flowsheet has been initiated. In the DFLAW configuration, LAW feed will be provided to the LAW Pretreatment System (LAWPS). The LAWPS will separate the HLW and LAW fractions and provide qualified feed to the Waste Treatment and Immobilization Plant (WTP) LAW Vitrification Facility. Liquid effluents from the WTP-LAW Facility will be managed in the DFLAW configuration by the WTP Effluent Management Facility (EMF). The EMF will generate a secondary liquid waste stream to be treated at the Hanford Effluent Treatment Facility (ETF) and a concentrate stream for recycle to LAW vitrification or alternatively for immobilization and disposal as low-level waste (LLW).

This paper discusses the need for data on non-glass waste forms to evaluate their ability to immobilize radioactive and non-radioactive contaminants of concern (COCs). Such data are needed as input to a performance assessment (PA) of Hanford's Integrated Disposal Facility (IDF) to allow the immobilized liquid secondary wastes from DFLAW operations to be disposed there. Alternatively, if off-site disposal is to be considered, data are needed to show compliance with the receiving facility's waste acceptance criteria (WAC).

## **BACKGROUND**

The Hanford LAW Vitrification facility is planned to immobilize waste feed for on-site, near-surface disposal at the IDF. During this process, liquid and solid secondary wastes will be generated which are also slated for disposal in the IDF, a RCRA-permitted mixed low-level waste (MLLW) disposal facility. In order to receive authorization to dispose of the waste, a PA must be completed in accordance with DOE Order 435.1, Radioactive Waste Management, and its accompanying Manual. The PA must include calculations of potential releases of radioactive contaminants and resultant doses to a member of the public for a 1,000-year period after closure to provide a reasonable expectation that performance objectives will not be exceeded and that the waste will be managed in a manner that is protective of worker and public health and safety, and the environment.

The IDF will be used to dispose of both primary waste (vitrified LAW) and immobilized liquid and solid secondary wastes from waste treatment operations. Because the LAW glass is a highly durable waste form, release of contaminants is extremely slow and the impact to groundwater is expected to be orders-of-magnitude below the performance objective. The immobilized secondary wastes are expected to represent a greater risk to human health and the environment depending on the rate of release of contaminants from the final waste forms. To support development and maintenance of a PA for the IDF, data on waste form

performance are needed to model the long-term release of contaminants over the compliance period (1,000 years) and beyond (10,000 years or longer) to verify that impacts to groundwater will be within performance objectives, e.g. Environmental Protection Agency (EPA) drinking water standards at a well 100 meters down-gradient from the facility boundary.

### **Previous Performance Assessments**

The study of solidification and stabilization of Hanford waste using cementitious waste forms began in the 1980s, led by the Hanford Grout Development Program. The laboratory testing and field demonstration supported a PA that was produced in 1995 (Kincaid et al. 1995). However, the program was discontinued in the mid-1990s when vitrification was selected as the preferred alternative for treatment of Hanford LAW. Subsequent PAs (Mann et al., 1996, 2001, 2003a) evaluated glass as the LAW waste form initially to be disposed of in existing concrete vaults, then later in a lined burial trench, which evolved to become the IDF.

In 2003, a risk assessment (RA) for supplemental LAW waste forms was prepared (Mann et al. 2003b). The purpose of the RA was to evaluate the long-term performance of ILAW glass and supplemental waste forms that were under consideration at that time (bulk vitrification, Cast Stone, and fluidized bed steam reforming) and the impacts of the release of contaminants to groundwater below the IDF. Because of budget, schedule, and technical limitations, Mann et al. (2003b) acknowledged that the RA was less rigorous and less detailed than a PA, but had sufficient technical credibility to support decision-making.

The Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland, Washington (TC&WM EIS; DOE/EIS-0391, 2012) evaluated a number of alternatives, including waste treatment options wherein liquid secondary waste, solid secondary waste, and supplemental LAW would be immobilized in cementitious grout waste forms. A diffusion-limited release model was used in the TC&WM EIS impact analyses to estimate the release of contaminants from grouted waste forms. The diffusion-limited release model used contaminant-specific diffusivities and retardation factors along with waste form properties such as bulk density ( $\rho$ ), tortuosity ( $\tau$ ), and effective porosity ( $\epsilon$ ) to calculate contaminant releases over a 10,000-year time period.

Although several analyses have been conducted over the last decade, a formally reviewed PA has not been issued since the 2001 ILAW PA. Since that PA was completed the mission for the IDF has been expanded from accepting only LAW glass to include other waste forms from WTP operations and other non-WTP waste forms. Also, construction of the IDF was completed in 2006 so data on the actual IDF location, design, and geology are available. The new IDF PA, being prepared in 2017, will utilize currently available data and will provide the basis for IDF Waste Acceptance Criteria (WAC) and disposal authorization needed to support DFLAW operations.

## METHODS

Washington River Protection Solutions is conducting waste form development and testing programs to produce the data required for assessing the long-term performance of cementitious waste forms for the IDF PA. This program is a combined effort involving National Laboratories with expertise in waste form development. The work involves developing and testing waste forms tailored to the waste characteristics with additives selected to more tightly bind environmentally mobile constituents such as technetium-99 and iodine-129. Initial results from this work were incorporated in a waste form performance data package for the IDF PA in 2016 (Cantrell, et. al., 2016). Results from ongoing development work will be included in annual update for PA Maintenance as required by DOE 435.1.

Waste to be disposed of in the IDF will include solidified wastes from treatment of liquid secondary wastes at Hanford's Effluent Treatment Facility (ETF). The ETF currently treats liquid effluents from various waste cleanup activities on the Hanford Site. In the current ETF flowsheet, contaminants in aqueous wastes are removed and/or destroyed through a series of filtration, ultraviolet oxidation, reverse osmosis, and ion exchange processes. The treated liquids are disposed in a state-approved land disposal site. Residual solids are dried in a thin-film dryer and packaged in 55-gallon drums for disposal.

Aqueous wastes to be treated in ETF are collected in one of three surface impoundments (Basin 42, Basin 43, and Basin 44) that comprise the Liquid Effluent Retention Facility (LERF) in the northeast corner of the 200 East Area. Liquid wastes in the individual basins are processed through the ETF on a campaign basis. During DFLAW operations, the wastes to be processed through the ETF will include WTP liquid secondary wastes, 242-A evaporator condensates, liquid wastes from the LAW pretreatment system, leachates from the IDF and mixed waste burial trenches, and other miscellaneous wastes (May, et. al., 2009).

In the mid-2000s, Cooke and Lockrem (Cooke and Lockrem, 2005; Cooke, et. al., 2006), conducted screening studies of hydraulic binder formulations for solidification of the concentrated brine resulting from processing 242-A evaporator condensates in the ETF. Because the ETF brine has elevated sulfate content, Cooke, et. al. (2006) tested a number of mixes with ordinary portland cement (OPC), blast furnace slag (BFS), fly ash (FA), and hydrated lime as an alternate source of calcium to facilitate rapid ettringite formation. Early ettringite formation would consume sulfate and preclude or minimize late ettringite formation. The latter could result in desiccation and cracking of the waste form. Their final recommended formulation was a dry blend mix of 36 wt% OPC, 36 wt% BFS, and 28 wt% hydrated lime.

In FY15 and FY16, a team lead by WRPS, PNNL, and SRNL tested a matrix of lime-based grout formulations following the recommendations of Cooke, et. al. (2006). Tests were conducted on simulated ETF brine that would be generated from processing the following feeds; DFLAW Vitrification off-gas condensate, 242-A evaporator condensate, and LLW disposal trench leachate. The matrix included

cementitious waste forms using blends of hydrated lime, OPC, and BFS. A standard Cast Stone dry blend mix was included as a control. Cast Stone was developed at Hanford in early 2000s and consists of 45 wt% FA, 47 wt% BFS and 8 wt% OPC. Waste form characteristics included properties such as hydraulic conductivity, porosity, density, and water retention curves (i.e. matric potential) for use in contaminant release modeling as well as effective diffusivity measurements via EPA Method 1315, Tc solubility, and Tc desorption  $K_{ds}$  that may also be used for modeling near-field contaminant releases from the waste forms for PA analyses.

A rigorous framework for modeling the long-term performance of a waste form utilizes a mechanism in which matrix hydrolysis and contaminant release are controlled by the rate that chemical bonds are broken. Such a mechanistic approach has been successfully employed for vitrified waste forms (McGrail et al. 2000). While similar arguments can be made regarding the importance of modeling chemical reactions and transport in cement pore waters (Bacon et al. 2002), with cementitious waste forms, a physical model of contaminant diffusion has been almost universally adopted (Cook et al. 2005; Serne and Westsik 2011).

Diffusional release of species from cementitious waste forms is best treated as a combination of physical transport and chemical interactions. The fundamental basis for the diffusion model is Fick's Second Law wherein mass transport into or out of a porous media is expressed in terms of component-specific diffusion coefficients. For each species, the apparent diffusion coefficient for a porous media ( $D_a$ ) is a measure of the physical contribution to diffusion, and depends on the molecular diffusion coefficient ( $D_o$ ) of a particular solute in dilute solution, and the tortuosity ( $\tau$ ), constrictivity ( $\delta$ ), and porosity ( $\epsilon$ ) of the porous medium:

$$D_a = D_o \frac{\epsilon \delta}{\tau^2} \quad (1)$$

Chemical interactions can be quite varied (adsorption, ion exchange, precipitation, specific and irreversible adsorption), and each process may have fast or slow kinetics. The simplest process that is mathematically tractable is reversible adsorption with fast kinetics and a linear isotherm at equilibrium. This simple chemical process can be described using the equilibrium distribution coefficient  $K_d$ :

$$K_d = \frac{C_s}{C} \quad (2)$$

where  $C_s$  is the concentration of the solute of interest in the solid and  $C$  is the concentration in solution. For this relationship to be accurate, the chemical reaction processes it is intended to describe must be fast and reversible and the sorption process must satisfy the linear isotherm constraint at equilibrium. Chemical reactions for contaminants do not always meet these requirements. Regardless, this simple construct is often applied in quantifying the release of contaminants from cementitious waste forms because it allows one to separate the physical and chemical processes that control transport of contaminants. The impact of the chemical interactions of the solute with the porous media on the effective diffusion coefficient is described by the following equation:

$$D_e = \frac{D_a}{R} \quad (3)$$

where  $D_a$  is the apparent diffusion coefficient and  $R$  is the retardation factor. The retardation factor is related to the  $K_d$  by the following equation:

$$R = 1 + \frac{\rho_b K_d}{\varepsilon} \quad (4)$$

where  $\rho_b$  is the bulk density of the porous solid waste form and  $\varepsilon$  is its porosity. There are several experimental methods that one can use to measure the  $K_d$  and then compute  $R$  after measuring the porosity and bulk density of the waste form. Conversely, one can determine the apparent diffusion coefficient by using a non-reactive species ( $K_d = 0$ ) and measuring the penetration profile of that species into the solid porous medium or diffusion out of the porous medium using a standard leach test.

Empirical diffusion coefficients measured in short-term laboratory experiments have been widely used in modeling long-term performance of cementitious waste forms (Albenesius 2001). These procedures have changed little since the International Atomic Energy Agency (IAEA) method was proposed by Hespe (1971) over 40 years ago. Effective or observed diffusion coefficients for each contaminant have been used for diffusion-controlled transport analysis of both intact cementitious monolith waste forms emplaced in subsurface porous environments and fractured cementitious waste forms where contaminant release is dominated by diffusive-advective processes.

The cementitious waste form modeling approach for the IDF PA utilizes a simple shrinking core diffusion model as has been used for previous analyses. Thus, it can use effective diffusivities as measured in standard leach tests and may be adjusted to account for solid phase affinities ( $K_d$ s) and solubilities of COCs for which those data are available. It should be noted that other mechanisms of cementitious waste form degradation and contaminant release are being considered and incorporated in the Savannah River Site saltstone PA; for example, solubility controlled release of technetium under reducing conditions, desorption  $K_d$  for technetium release under oxidizing conditions, sulfate attack, carbonation, and redox capacity change due to oxygen influx (SRR CWDA 2014).

## RESULTS AND DISCUSSION

Previous analyses have shown the primary constituents of potential concern (COPCs) in solid and liquid secondary wastes to be disposed of in the IDF include Tc-99, I-129, U, Cr,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$ . The primary purpose of the PA analyses is to model the fate and transport of the radionuclides in order to estimate future radiation doses to members of the public. However, the same models may be used to predict chemical exposures and concentrations relative to health-based limits for RCRA permitting purposes.

Much of the data needed for PA modeling will be derived from selected tests from

the Leaching Environmental Assessment Framework (LEAF) which is a collection of four leaching tests that can be used to develop a characteristic leaching profile of the subject material under equilibrium- and mass transfer-controlled release conditions (Kosson et al., 2002). Testing for the Hanford Liquid Secondary Waste Treatment program has focused primarily on EPA Methods 1313 and 1315 supplemented with Tc adsorption/desorption  $K_d$  and Tc empirical solubility measurements on the LSW lime-based grout waste form.

EPA Method 1315 is a tank-type monolith immersion leach test similar to predecessor methods ANSI/ANS 16.1 and ASTM C1308 and is most useful for measuring observed (effective) diffusivities of COPCs such as Tc-99, I-129, and Cr. Previous work by the Pacific Northwest National Laboratory (PNNL) (Mattigod, et al. 2011) using cementitious and hybrid geo-polymer waste forms made from simulated liquid secondary wastes demonstrated that each of these three standard leach test methods yielded essentially equivalent observed (effective) diffusivity results allowing cross-comparison of results from current testing programs to results from prior work extending back years or even decades that employed one of these leach test protocols.

Based on the 2016 data package for cementitious waste forms, values of effective diffusion coefficients for solidified liquid secondary wastes suitable for use in the IDF PA analyses are presented in Table 1. Recent data taken from ongoing tests are included. Data from tests of Cast Stone formulations for immobilization of LAW are included for comparison purposes. Notable differences between the waste forms are seen regarding the Tc-99 diffusivity which is more than an order-of-magnitude lower in the lime-based grout vs. a standard Cast stone formulation (Um et al., 2016). Sodium and nitrate diffusivities are lower for the LSW grout formulations than for LAW Cast Stone indicating the pore structure for the LSW grout formulations may be tighter thereby restricting release of these non-sorbing species.

Further testing by Um, et. al. conducted after the 2016 Data Package was published included additional lime-based LSW grout formulations as well as samples that contained additives to increase retention of technetium and iodide. A Tin(II) Apatite (Sn-A) additive was tested that acts by a redox mechanism to hold Tc in a less soluble Tc(IV) oxidation state and a silver-loaded zeolite (Ag-Z) was selected to improve iodide retention. The results showed no benefit from the Tc additive Sn-A in fact showing slightly higher effective Tc diffusivity than with no additive. The Ag-Z additive was effective in reducing the I diffusivity to less than  $10^{-12}$  cm<sup>2</sup>/s but with a corresponding increase in Tc diffusivity, potentially due to consuming reducing capacity of sulfides present in the BFS.

A further refinement in modeling of contaminant transport from cementitious waste forms involves modeling the retardation of contaminant release due to adsorption/desorption between the contaminant and the waste form solids. This requires knowledge of contaminant distribution coefficients ( $K_d$ s) in contact with the waste form material. Actual  $K_d$  data for key contaminants specific to Hanford's immobilized liquid secondary waste were not available and thus data from SRR

**Table 1. Observed (Effective) Diffusion Coefficients for Cementitious Waste Forms**

Effective Diffusion Coefficient (cm <sup>2</sup> /s)									
Contaminant	Secondary Waste Lime-Based Grout (Based on Um et al. 2016)			Secondary Waste Fly-Ash-Based Cast Stone (Based on Um et al. 2016)			LAW Waste Cast Stone (Based on Westsik et al. 2013)		
	Tests	Range	Geometric Average	Tests	Range	Geometric Average	Tests	Range	Geometric Average
Technetium	15	$4.0 \times 10^{-15} - 3.0 \times 10^{-12}$	$1.8 \times 10^{-13}$	3	$5.0 \times 10^{-14} - 2.0 \times 10^{-11}$	$1.3 \times 10^{-12}$	24	$5.0 \times 10^{-12} - 2.0 \times 10^{-10}$	$5.3 \times 10^{-11}$
Iodine	-	$3.0 \times 10^{-10} - 5.0 \times 10^{-9}$ (a)	-	-	$8.0 \times 10^{-10} - 2.0 \times 10^{-9}$	-	24	$2.0 \times 10^{-9} - 2.0 \times 10^{-8}$	$5.7 \times 10^{-9}$
Sodium	15	$3.0 \times 10^{-10} - 5.0 \times 10^{-9}$	$1.6 \times 10^{-9}$	3	$8.0 \times 10^{-10} - 2.0 \times 10^{-9}$	$1.3 \times 10^{-9}$	24	$2.0 \times 10^{-9} - 2.0 \times 10^{-8}$	$5.8 \times 10^{-9}$
Nitrate	12	$3.0 \times 10^{-11} - 8.0 \times 10^{-10}$	$12.5 \times 10^{-10}$	2	$2.0 \times 10^{-10} - 9.0 \times 10^{-10}$	$4.8 \times 10^{-10}$	24	$2.0 \times 10^{-9} - 2.0 \times 10^{-8}$	$6.1 \times 10^{-9}$
Nitrite	-	$3.0 \times 10^{-11} - 8.0 \times 10^{-10}$ (a)	-	-	$2.0 \times 10^{-10} - 9.0 \times 10^{-10}$	-	24	$2.0 \times 10^{-9} - 2.0 \times 10^{-8}$	$6.1 \times 10^{-9}$
Chromium <sup>(b)</sup>	-	-	-	-	-	-	24	$7.0 \times 10^{-13} - 1.0 \times 10^{-12}$	$1.1 \times 10^{-13}$
Uranium <sup>(c)</sup>	-	-	-	-	-	-	24	$<6.0 \times 10^{-16}$	-

(a) Recommended values for effective diffusion coefficients for iodine from the lime-based secondary waste grouts are based on the effective diffusion coefficient measured for sodium and the assumption that nitrite and nitrate diffuse at the same rate.

(b) The effective diffusion coefficient range for Cr likely represents a combination of solubility-controlled release of a Cr(III) solid and re-oxidation of the Cr(III) to Cr(VI). The EPA-1315 test have not been run long enough to show any significant deviation in the rate of “net” Cr diffusion release that would suggest that the Cr(III) solid has been totally dissolved or re-oxidized, which would imply that all the internal reductive capacity in the waste form has been exhausted.

(c) The effective diffusion coefficient range for U may represents a combination of solubility-controlled release of a U(IV) solid and re-oxidation of the U(IV) to U(VI). The EPA-1315 tests have not been run long enough to show any significant deviation in the rate of “net” U diffusion release that would suggest that the U(IV) solid has been totally dissolved or re-oxidized, which would imply that all the internal reductive capacity in the waste form has been exhausted. Further, there are insoluble U(VI) solids such as uranyl-oxyhydroxide phases that, over time, transform to uranyl-silicate phases and then ultimately to uranyl-phosphate phases as long as adequate phosphate is present.

CWDA 2014 were provided as interim values (see Table 2). Since then measurements of Tc-99 distribution coefficients from lime-based LSW grout formulations have been performed and the results are shown in Table 3.

Table 2. Recommended Desorption  $K_d$  (ml/g) values for Cementitious Materials (from SRR CWDA 2014, Table 4.1-4)

Component	Reduced Region II	Oxidized Region II	Oxidized Region III	Reference
Tc	Solubility Control	0 to 0.5	0 to 0.5	a
I	0 to 9	0 to 15	0 to 4	a
NO <sub>3</sub>	0 to 1 <sup>(*)</sup>	0 to 1 <sup>(*)</sup>	0 to 1	b
NO <sub>2</sub>	0 to 1 <sup>(*)</sup>	0 to 1 <sup>(*)</sup>	0 to 1	b
Cr	1000	10	0 to 1	a
U	2500	1000	3 to 100	c

(a) Kaplan (2010) and Hanford geochemist's expert opinion based on observed diffusivities in EPA 1315 tests.

(b) Krupka et al. (2004) and current Hanford geochemist's expert opinion

(c) Seaman and Kaplan (2010) and current Hanford geochemist's expert opinion

(\*) Kaplan (2010) shows desorption  $K_d$  values of 10 for nitrate and nitrite for both reducing and oxidizing conditions in Region II. However, the recommended values were based on measurements for chloride and there are no actual measurements for nitrate or nitrite. Discussions with Kaplan indicate that 0 to 1 are better desorption  $K_d$  values to use. The DOE Technical Guidance Document (DOE 2005) gives a value of 0 for nitrate.

Table 3. Tc-99 Desorption Distribution Coefficients ( $K_d$ s) and Solubility Values (from Um, et. al., 2016)

Test ID	Simulant	Water / Dry Blend		Dry Blend Components	$K_d$ , Oxidizing* (mL/g)	$K_d$ , Reducing (mL/g)	Solubility, Reducing (M)
		Ratio	Dry Blend Mix (wt%)				
3	WTP	0.5	20%, 35%, 45%	lime, OPC, BFS	17.8	267	$3.4 \times 10^{-9}$
6	WTP	0.6	20%, 35%, 45%	lime, OPC, BFS	28.0	275	$4.3 \times 10^{-9}$
11	WTP	0.6	20%, 35%, 45%	OPC, FA, BFS	26.2	266	$5.1 \times 10^{-9}$
Average		-	-	-	24.0	269	$4.3 \times 10^{-9}$

\* Tc  $K_d$  in oxidizing conditions was determined using a fresh grout where BFS still provided some reducing condition. Therefore these values are representative of transition condition between reduced region II and oxidized region II in Table 3.2.

Although diffusion is the primary mechanism used to describe contaminant release from cementitious waste forms, it is likely that under certain circumstances, solubility constraints will control release of specific contaminants, such as Tc, Cr, and U which are redox sensitive contaminants. This would be particularly true under low-flow conditions and low redox environments. In order to discretely model this effect, the solubility of the contaminant in the waste form must be measured. Recently, it has been demonstrated that under reducing conditions, Tc release from

Saltstone is controlled by  $TcO_2 \cdot xH_2O$  solubility (Cantrell and Williams 2013). Measured Tc-99 solubilities in lime-based LSW grout are also shown in Table 3.

Finally, in order to model flow and transport of contaminants from grouted waste forms, fundamental physical properties are needed that largely govern the rate at which the vadose zone pore water percolating through the disposal facility can flow into and through the waste form. Example values appear in Table 4 below. The first five in the list are parameters determined or used in previous PAs for saltstone and the Hanford Grout Development Program. The last two in the list are candidate waste forms for disposal in the IDF and data will be updated when available.

**Table 4.** Physical Properties of Cementitious Waste Materials

Waste Type	Porosity (%)	Dry Bulk Density (g/cm <sup>3</sup> )	Particle Density (g/cm <sup>3</sup> )	Hydraulic Conductivity K <sub>sat</sub> (cm/s)	Source
DDA (deliquification, dissolution and adjustment)	0.55	1.06	2.37	$9.6 \times 10^{-11}$	a
ARP/MCU (Actinide Removal Process/Modular Caustic Side Solvent Extraction Unit)	0.59	0.97	2.38	$8.5 \times 10^{-10}$	a
SWPF (Salt Waste Processing Facility)	0.58	1.01	2.42	$6.0 \times 10^{-09}$	a
All wastes in saltstone PA	0.58	1.01	2.40	$6.4 \times 10^{-09}$	b
Hanford DSSF (double-shell slurry feed)	-	1.10	2.61	$2.3 \times 10^{-08}$	c
Immobilized liquid secondary waste (lime-based grout)	0.53-0.56	1.2-1.3	2.7	$3 \times 10^{-09}$	d
Encapsulation barrier grout	TBD	TBD	TBD	TBD	

<sup>a</sup>Serne and Westsik (2011), <sup>b</sup>SRR CWDA (2014), <sup>c</sup>Rockhold et al. (1993), <sup>d</sup> – Cozzi et al. (2015)

The values in Table 4 are for freshly cured laboratory samples. The PA analyses will need to consider how these properties may change over long periods of time, e.g. hundreds to thousands of years. Methods to address the evolution in grout properties at long weathering times range from a simplistic assumption that the waste form degrades to rubble instantly after 500 years to mechanistic modeling of changes in waste form properties over time due to oxidation, carbonation, sulfate attack, etc.

## CONCLUSIONS

The Hanford LAW Vitrification facility is planned to immobilize waste feed for on-site, near-surface disposal at Hanford's IDF. During this process, liquid secondary wastes will be generated, which are also slated for disposal in the IDF. Liquid secondary wastes are planned to be immobilized within cementitious waste forms similar to those used elsewhere in the United States and around the world for permanent disposal of LLW. Data packages and supporting documents have been

developed to provide the technical underpinning for the analyses of contaminant releases to the environment from these waste forms for the IDF PA. Traditionally, releases from cementitious waste forms have utilized a diffusion limited release model using contaminant-specific effective diffusivities measured in standard leach tests as inputs. More mechanistic modeling techniques are under development to increase the rigor of the PA analyses.

Results of ongoing testing of Hanford cementitious waste forms indicate improvement (as indicated by the diffusion coefficients listed in Table 1) by using improved dry blend formulations and additives to bind contaminants. Work on the lime-based LSW grout formulation is continuing in particular to better understand the mechanism for improved Tc-99 retention. As more mechanistic modeling techniques are pursued, more data may be needed on different waste form characteristics and behaviors. Hence the cementitious waste form testing program is expected to continue for the foreseeable future to accommodate such data needs.

## REFERENCES

- Albenesius EL. 2001. *Computer Modeling of Saltstone Landfills by Intera Environmental Consultants*. DPST-83-529, Savannah River Site, Aiken, South Carolina.
- Bacon DH, BP McGrail, VL Freedman, G Ventura, P Risoluti, and KM Krupka. 2002. *Performance Assessment of Low-Level Waste Disposal Facilities Using Coupled Unsaturated Flow and Reactive Transport Simulators*. Mat. Res. Soc. Symp. Proc. 713:267-274.
- Cantrell KJ, JH Westsik, Jr., RJ Serne, W Um, and AD Cozzi. 2016. *Secondary Waste Cementitious Waste Form Data Package for the Integrated Disposal Facility Performance Assessment*, PNNL-25194, Pacific Northwest National Laboratory, Richland, WA.
- Cook JR, EL Wilhite, RA Hiergesell, and GA Flach. 2005. *Special Analysis: Revision of the Saltstone Vault 4 Disposal Limits (U)*. WSRC-TR-2005-00074, Westinghouse Savannah River Company Aiken, South Carolina.
- Cooke GA, and LL Lockrem. 2005. *Effluent Treatment Facility Waste Stream Stabilization Testing*, RPP-RPT-26851, CH2M Hill Hanford Group, Inc. Richland, WA.
- Cooke GA, LL Lockrem, M Avila, and RA Westberg. 2006. *Effluent Treatment Facility Waste Stream Monolith Testing Phase II*, RPP-RPT-31077, CH2M Hill Hanford Group, Richland, WA.

Cozzi AD, KL Dixon, KA Hill, WD King, and RL Nichols. 2015. *Liquid Secondary Waste: Waste Form Formulation and Qualification*, SRNL-STI-2015-00685, Savannah River National Laboratory, Aiken, SC.

Kosson DS, F Sanchez, CH Mattus, and MI Morris. 2002. "Use of a New Leaching Test Framework for Evaluating Alternative Treatment Processes for Mercury-Contaminated Soils", *Environmental Engineering Science*, 19(4), pp. 251-269.

DOE M 435.1, Chg 1, *Radioactive Waste Management*, US Department of Energy, Washington DC, 2001.

DOE O 435.1, *Radioactive Waste Management*, US Department of Energy, Washington DC, 1999.

Hespe ED. 1971. *Leach Testing of Immobilized Radioactive Waste Solids: A Proposal for a Standard Method*. In *Atomic Energy Review*, Vol. 9, pp. 195-207, International Atomic Energy Agency, Vienna, Austria.

Kaplan DI. 2010. *Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site*, SRNL-STI-2009-00473, Rev. 0, Savannah River National Laboratory, Aiken, SC.

Kincaid CT, JW Shade, GA Whyatt, MG Piepho, K Rhoads, JA Voogd, JH Westsik Jr., KA Blanchard, and BG Lauzon. 1995. *Performance Assessment of Grouted Double-Shell Tank Waste Disposal at Hanford*. WHC-SD-WM-EE-004, Rev. 1, Westinghouse Hanford Company, Richland, WA.

Mann FM, KC Burgard, RJ Puigh, SK Finfrock, DH Bacon, EJ Freeman, and PE Lamont. 2001. *Hanford Low-Activity Waste Performance Assessment: 2001 Version*, DOE/ORP-2000-24, Department of Energy, Office of River Protection, Richland WA.

Mann FM, CR Eiholzer, AH Lu, PD Rittmann, NW Kline, Y Chen, and BP McGrail. 1996. *Hanford Low-Level Tank Waste Interim Performance Assessment*. WHC-EP-0884, Rev. 0, Richland, WA.

Mann FM, RJ Puigh, SH Finfrock, R Khaleel, and MI Wood. 2003a. *Integrated Disposal Facility Risk Assessment*. RPP-15834, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, WA.

Mann FM, RJ Puigh, R Khaleel, S Finfrock, BP McGrail, DH Bacon, and RJ Serne. 2003b. *Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies*. RPP-17675, Revision 0, CH2M Hill Hanford Group Inc., Richland, WA.

Mattigod SV, JH Westsik, Jr., CW Chung, MJ Lindberg, and KE Parker. 2011. *Waste Acceptance Testing of Secondary Waste Forms: Cast Stone, Ceramicrete, and DuraLith*. PNNL-20632, Pacific Northwest National Laboratory, Richland, WA.

May TH, PD Gehner, G Stegen, J Hyman, A Pajunen, R Sexton, and A Ramsey. 2009. *Secondary Waste – ETF Pre-Conceptual Engineering Study*, RPP-RPT-43588, Washington River Protection Solutions, Richland, WA.

McGrail BP, DH Bacon, WL Ebert, and KP Saripalli. 2000. *A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford*. PNNL-11834, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Seaman JC, and DI Kaplan. 2010. *Chloride, Chromate, Silver, Thallium, and Uranium Sorption to SRS Soils, Sediments, and Cementitious Materials*. SRNL-STI-2010-00493, Rev. 0, Savannah River Site, Aiken, South Carolina.

Serne RJ, and JH Westsik, Jr. 2011. *Data Package for Secondary Waste Form Down-Selection—Cast Stone*. PNNL-20706, Pacific Northwest National Laboratory, Richland, WA.

SRR Closure & Waste Disposal Authority (SRR CWDA). 2014. *FY2014 Special Analysis for the Saltstone Disposal Facility at the Savannah River Site*. SRR-CWDA-2014-00006, Revision 2, Savannah River Remediation, Aiken, South Carolina.

TRW. 2000. *Total System Performance Assessment for the Site Recommendation*, TDR-WIS-PA-000001 REV 00 ICN 01, TRW Corporation, Las Vegas, NV.

Um W, BD William, MMV Snyder, and G Wang. 2016. *Liquid Secondary Waste Grout Formulation and Preliminary Waste Form Qualification*. PNNL-25129, Rev.0. Pacific Northwest National Laboratory, Richland, WA.

Van der Sloot, HA, 2000. "Comparison of the characteristic leaching behavior of cements using standard (EN 196-1) cement mortar and an assessment of their long-term environmental behavior in construction products during service life and recycling", Cement and Concrete Research, 30:7, pp. 1079-1096.