

**Technetium Oxidation in Slag-Based Sodium Salt Waste Forms
Exposed to Water and Moist Hanford Soil - 15514**

C. A. Langton

Savannah River National Laboratory, Savannah River Nuclear Solutions,
Savannah River Site, Aiken, SC 29808

ABSTRACT

Several U.S. DOE sites use or plan to use waste forms and/or concrete containment structures for radioactive waste disposal that are designed to have a chemically reducing environment to immobilize selected contaminants such as Tc(VII)O_4^- and Cr(VI)O_4^{2-} . These waste forms and containment structures are typically deployed in near surface unsaturated oxidizing environments. Consequently, the effect of exposure to air (oxygen) and water containing dissolved oxygen during production, during the period of institutional control, and over the long term period of performance is important for predicting the speciation and mobility of the redox sensitive radioactive and stable contaminants.

Both the SRS and Hanford waste streams contain soluble technetium which may require stabilization to meet disposal requirements. Technetium stabilization is a difficult problem because: 1) Tc is soluble and very mobile in the oxidized form typical of near surface environments, and 2) Tc-99 is a long-lived isotope with a half-life of $2.1\text{E}+05$ years which places demanding requirements on the engineered barriers and environment to meet current regulatory disposal requirements.

A depth-discrete sampling and leaching method approach for measuring contaminant oxidation rate (effective contaminant specific oxidation rate) was used in this study. The method was modified by coating all sides of a cylindrical sample with an impermeable epoxy and cutting a fresh surface 2 to 2.5 cm from the original top surface eliminates sample inhomogeneity as the result of settling as a reason from observed results and provides 1-D soluble ion transport and gas transport information.

Soluble Tc was leached from all of the depth-discrete subsamples from both Tc2-9 and Tc2-10 which strongly suggests that oxygen was present in the entire length of both samples. About 24 mass percent of the Tc in the original sample, was leached (soluble) from subsamples between 0.8 and 46 mm below the exposed surface of Tc2-9 (exposed to Hanford sediment). The same percent (24%) was leached from the subsamples between 0.8 and 11 mm below the exposed surface of Tc2-10 (exposed to DI water). This suggests that the rate of oxygen migration into the sample exposed to soil was faster than the rate of migration into the sample exposed to water which is consistent with the more rapid transport of ions through a gas phase as compared to a liquid phase. It is assumed that moisture in the Hanford sediment was not sufficient to completely block the surface pores with respect to gas transport across the soil-waste form boundary. Based on nitrate leaching results for the depth-discrete subsamples, regions depleted in nitrates were identified from the top surfaces to 9.5 and 3 mm into samples Tc2-9 (exposed to moist Hanford sediment) and Tc2-10 (DI water). Low mass fractions of nitrate were leached from these depth-discrete samples compared to samples further from the exposed surface presumably because a significant portion of the nitrate had already migrated into the soil or water, respectively. Depth-discrete subsample leaching results for Na can be interpreted in the same way over the same regions in the two samples tested.

In conclusion, leaching monolithic porous cementitious waste forms in water appears to be conservative for non-redox sensitive contaminants. However, leaching data obtained under saturated exposure conditions do not appear to be conservative for redox sensitive contaminants which are easily oxidized. Leaching crushed samples in water still seems to be a conservative approach to estimating the concentrations of soluble contaminants in a waste form.

INTRODUCTION

Several U.S. DOE sites use or plan to use waste forms and/or concrete containment structures for radioactive waste disposal that are designed to have a chemically reducing environment to immobilize selected contaminants such as Tc(VII)O_4^- and Cr(VI)O_4^{2-} . These waste forms and containment structures are typically deployed in near surface unsaturated oxidizing environments. Consequently, the effect of exposure to air (oxygen) and water containing dissolved oxygen during production, during the period of institutional control, and over the long term period of performance is important for predicting the speciation and mobility of the redox sensitive radioactive and stable contaminants.

The rate of oxidation is important to the long-term performance of reducing salt waste forms because the solubility of some contaminants, e.g., technetium, is a function of oxidation state. TcO_4^- in the salt solution is reduced to Tc(IV) and has been shown to react with ingredients in the waste form to precipitate low solubility sulfide and/or oxide phases [1, 2, and 3]. Upon exposure to oxygen, the compounds containing Tc(IV) oxidize to the pertechnetate ion, Tc(VII)O_4^- , which is highly soluble in water and aqueous solutions. Consequently the rate of technetium oxidation front advancement into a monolith and the technetium leaching profile as a function of depth from an exposed surface are important to waste form performance and ground water concentration predictions. The rate of oxidation front advancement into a monolith and the effect of oxygen ingress on redox sensitive contaminants are needed to:

- 1) Develop the conceptual model for performance predictions,
- 2) Provide data to parameterize fate and transport models, and
- 3) Validate computational codes.

Objective

The objectives of this study were to: utilize depth-discrete sampling and zero head space leaching to explore the effect of exposing cured waste forms to moist soil and DI water in a 1-D experimental configuration. More specifically, the effect of these exposure conditions on Tc leachability as a function of distance from the exposed surface was determined.

Background

Low temperature waste forms are currently being used and considered for solidification of low-level radioactive wastes across the DOE complex. Examples include saltstone, a cementitious waste form used at the Savannah River Site (SRS) to immobilize low-activity sodium salt waste, and Cast Stone which was recently selected for solidification of secondary waste from the Hanford Tank Waste Treatment and Immobilization Plant (WTP). Cast Stone is also being considered to provide supplemental Low Activity Waste (LAW) immobilization capacity for the Hanford site.

Both the SRS and Hanford waste streams contain soluble technetium which may require stabilization to meet disposal requirements. Technetium stabilization is a difficult problem because: 1) Tc is soluble and very mobile in the oxidized form typical of near surface environments, and 2) Tc-99 is a long-lived isotope with a half-life of 2.1×10^5 years which poses a great challenge to prediction performance and places demanding requirements on the engineered barriers and environment to meet current regulatory disposal requirements.

Cast Stone and saltstone contain portland cement and fly ash in addition to ground granulated blast furnace slag (GGBFS). These hydraulic and pozzolanic ingredients react with water and other constituents in the waste stream to form the waste form matrix. The GGBFS stabilizes (reduces mobility) redox sensitive contaminants, such as, Tc and Cr. In a high pH environment, GGBFS chemically reduces

perchnetate, $Tc(VII)O_4^-$, to the less soluble $Tc(IV)$ oxidation state.¹ Over time, oxygen in the air, soil pore gas, and oxygen dissolved in the vadose zone pore water can oxidize the waste form and re-oxidize the $Tc(IV)$ to the highly soluble $Tc(VII)$ form.

An understanding of factors that affect the oxidation state of redox sensitive contaminants stabilized in cementitious waste forms is required to improve waste forms and engineered barriers for shallow land disposal. In addition, the parameters and relationships for the 1) rate of bulk matrix oxidation and 2) potential for and efficiency of re-reduction of soluble Tc in cured un-oxidized portions of waste forms are required for predicting long-term performance.

EXPERIMENTAL METHOD

A method for measuring contaminant oxidation fronts for redox sensitive contaminants in cementitious waste forms containing GGBFS was recently developed at the Savannah River National Laboratory (SRNL) [4, 5, and 6]. This method is based upon leaching depth-discrete subsamples obtained as a function of distance from an exposed surface. Leaching is performed in a zero head space container using deionized, de-aerated water to minimize oxidation during the leaching process. Leaching time was 48 ± 4 hours.

Waste Form Sample Preparation

Simulant. The Hanford Tank Waste Operations System (HTWOS) “Average” 5 M Na simulant was used rather than the CBP reference waste form [7] because the materials are very similar and the Tc -spiked cast stone samples were already prepared. The composition was derived from an overall average of the 1046 weeks of modeled LAW feed to a supplemental immobilization facility over a 20 year mission and is referred to as the HTWOS “Average” 5 M Na simulant [8, 9, 10]. The overall average concentrations in this simulant are listed in Table 1. The ingredients and proportions in the 5M Na simulated are provided in Table 2. Compounds were added to the liquid in the order they are listed in Table 2. $Tc-99$ was added to the 5 M Na simulant prior to addition of the premixed reagents as NH_4TcO_4 as indicated in Table 3.

Table 1. LAW 5 M Simulant based on Hanford Tank Waste Operations Simulator [9].

Waste Constituent	Overall Average Concentration		
	(moles / L)	(g / L)	(mg / g)*
Na	5.000	115.00	93.50
K	0.03	1.28	1.04
Al	0.31	8.28	6.73
Cl	0.04	1.5	1.22
F	0.030	0.6	0.49
S	0.090	2.74	2.23
P	0.050	1.52	1.24
NO2	0.57	26	21.14
NO3	1.63	101	82.11
CO3	0.27	16.5	13.41
OH	1.56	26.5	21.54

* 1 ml 5 M Na simulant = 1.230g 5M simulant. 1 gram of Cast Stone made with 5 M Na simulate and a water to cementitious solids ratio = 0.60 contains 0.451g 5 M Na simulant.

¹ The fraction of pertechnetate chemically reduced to the less soluble $Tc(VI)$ oxidation state depends on several factors including the: initial concentration, initial chemical form (inorganic or organic), and chemistry of the waste form and waste form pore solution.

Table 2. Ingredients and proportions of the 5 M Na simulant used to prepare the waste form.

Compound	Amount (g / L)
Water	819.50
Al(NO ₃) ₃ ·9 H ₂ O	115.165
50% by Weight NaOH	223.04
Na ₂ SO ₄	12.215
Na ₃ PO ₄ ·12 H ₂ O	18.5
NaCH ₃ COO·3 H ₂ O	5.25
Na ₂ CO ₃	29.05
NaNO ₃	56.79
NaNO ₂	38.975
NaCl	2.48
NaF	1.35
KNO ₃	3.33
Density	1.230
Wt.% Solids	27.06

Table 3. Tc-99 spike added to the HTWOS Average 5 M Na simulant [9].

Cast Stone w/cm	Average 5 M Na Simulant Tc-99 Concentration* (μCi / L)	Waste form Batch Size (g)	5M Na Average Simulant (g)	5M Na Average Simulant (ml)	NH ₄ TcO ₄ 0.5 mCi/ml Stock Solution (ml)	8:47:45 Cement : slag : fly ash Blend (g)	5M Waste form Tc-99 Concentration μCi / g
0.60	189	1800	812.5	660.57	0.25 (250 μL)	987.5	0.0694

* The HTWOS estimated maximum concentration for Tc-99 is 4.13 E-05 Ci / moles of Na. For 5 M Na simulant, the maximum Tc-99 value is 20.58 E-05 Ci per liter of simulant (205.8 uCi / L).

Cementitious reagents. The cement, blast furnace slag, and fly ash used in this study were obtained from a supplier in the Hanford area via PNNL and were shipped to SRNL. The three cementitious materials were pre mixed in the following proportions: portland cement : slag : fly ash ratios of 8:47:45 by mass manually shaking the bags. The cementitious materials were supplied by Hanford personnel.

Waste form. An 1800 g batch of the waste form was prepared with a water to cementitious reagent ratio (w/cm) = 0.60. See Table 4. The ingredients and proportions are shown in Table 3. The waste form slurry was mixed for 3 minutes before being transferred to 90 x 35 mm cylindrical containers. Ingredients in a 1000 g batch of cementitious waste form are shown in Table 3. The containers were filled to the top to the extent possible and capped. They were placed in an overpack container with moist towels for and cured for 103 days at ambient temperature (about 22 °C) and 65% to 75% relative humidity.

Table 4. Ingredients in Tc Spiked waste forms.

Batch Size (g)	Cement (g)	Slag (g)	Fly ash (g)	Simulant (g)
1800	79	464.1	444.4	812.5

Waste Form Exposure Conditions

Two samples, Tc2-9 and Tc2-10, were removed from the curing containers and exposed to moist Hanford sediment and DI water, respectively. Both samples were coated with 3 layers of epoxy on all sides. After the epoxy hardened which took about 3 hr., the top 2.5 cm and 2.2 cm were removed from samples Tc2-9 and Tc2-10, respectively, so that a “fresh” surface would be in contact with either DI water or as received Hanford soil. Sample Tc2-9 was placed in a container containing sieved Hanford sediment and then covered with about 3 cm of additional sediment. Sample Tc2-10 was placed in a container with DI water. Both containers had air space above the exposure media. Lids were placed on the containers and they were returned to secondary containment trays in a rad hood. See Figure 1. A summary of the curing and exposure times is provided in Table 5.



Figure 1. Epoxy coated sample with uncoated top surface, soil leaching media before sample was covered with about 3 cm of additional sediment, and container during exposure.

Table 5. Summary of curing and exposure times.

Sample	Prepared	Cured in Sealed Container (days)	Exposure Condition	Exposure Time (days)	Total Age (days)
Tc2-9	6-3-13	113	Hanford soil: 9-24-13 to 2-25-14	154	267
Tc2-10	6-3-13	113	DI water: 9-24-13 to 2-25-14	154	267

The Hanford sediment was collected in 2010 from an elevation consistent with the elevation of the sediment exposed in the Integrated Disposal Facility (IDF) [11]. The sediment was sent to SRNL by D. Wellman, PNNL, in the spring of 2013. Material from three 5-gallon buckets, Buckets 17, 18, and 19 was sieved through a No. 18 (1 mm) sieve and homogenized.² The as-received moisture content of the sieved material was determined by drying at 110 °C and found to be 4.9 wt. %. (The saturated moisture content for the composite sieved sample was determined to be 9.5 wt. % based on moisture-density relationship for a maximum dry density of 2.15 g/cc (134.4 lbs/cu.ft.)) See Attachment 1. The material was stored in a plastic 5 gallon bucket with a lid. The sieved sediment is shown in Figure 2 (left). The coarse fraction retained on the sieve is shown in Figure 2 (right). The coarse fraction was not used in the exposure test.

² Information accompanying Buckets 17, 18, and 19 provided detailed location information C7536 I020-B24P34, C7536 I-021 B24P35, C7536 I-026 B24P40, respectively. All of the material was collected from Well: 299-E13-114: C7536: 200E.



Figure 2. Hanford sediment passing No. 18 sieve (left) and retained on No. 18 sieve (right).

Waste Form Depth Discrete Leaching

The details of the sampling and leaching methods are described elsewhere [5, 6, and 7]. In summary, layers of the waste form from 2 to over 20 mm were removed from the cylindrical monoliths starting at the top exposed surface. The wafers were size reduced in air (crushed to a powder) with a mortar and pestle. A short term leach test based on EPA 1311 was used [12]. All or a portion of the crushed wafer was weighed and placed in a leaching container. The time required for crushing, weighing and covering each sub- sample with leachate was less than 10 minutes. Deionized, de-aerated ASTM Type I/II water was used as the leachate. Zero head space leaching containers were used to minimize exposure to oxygen and sample oxidation during leaching. The filled leach vessels were loaded into a large mouth plastic bottle which was tumbled end-over-end at 30 rpm for 48 ± 2 hours.

After tumbling, leachates were filtered using 0.45 micron filters attached to 20 mL syringes. Ca, K, Al, and Na concentrations were measured using an Inductively Coupled Plasma- Optical Emission Spectrometer (ICP-OES), Varian 730-ES. NO_3^- , NO_2^- , and SO_4^{2-} were analyzed using Ion Chromatography (IC), Dionex ICS-5000 EG. Tc-99 was analyzed by liquid scintillation. Sample preparation and the appearance of the leachates before tumbling and after filtering are illustrated in earlier reports [5 and 6]. Leaching results for all analytes are tabulated in Attachment 2.

Fraction Leached. The fraction of selected anions and cations leached or percent leached (fraction leached X 100) from each crushed subsample was selected as the parameter for indicating 1) the effect of exposure to air (i.e., oxidation) on the redox sensitive contaminants such as TcO_4^- and CrO_4^{2-} , Na and NO_3^- and 2) the depth of penetration of oxygen into the waste form (i.e., rate of oxidation front advancement). The percent leached was calculated using Equation 1.

$$\text{Equation 1. } \% \text{ Leached} = 100 * \left(\frac{m_{i\text{-leachate}}}{m_{i\text{-total in solid}}} \right)$$

Where:

$m_{i\text{-leached}}$ = mass of species i leached (mg). The leachate was filtered prior to analysis using a 0.45 μm filter.

$M_{i\text{-total}}$ = mass of species i in the subsample leached (mg). The total amount in the waste form was approximated and only reflects the contribution to the waste form from the spiked mixing solution.

RESULTS

Two samples, Tc2-9 and Tc2-10 with identical curing histories were coated with epoxy and the top 25 to 22 mm were removed from the samples to achieve a “fresh” cut surfaces. See Figure 3. Sample Tc2-9 was exposed to Hanford sediment with 4.5 % moisture (as received condition). Sample Tc2-10 was exposed to DI water. After exposure for 154 days, the depth-discrete subsamples were cut, crushed and leached in deaerated, DI water in zero head space container.

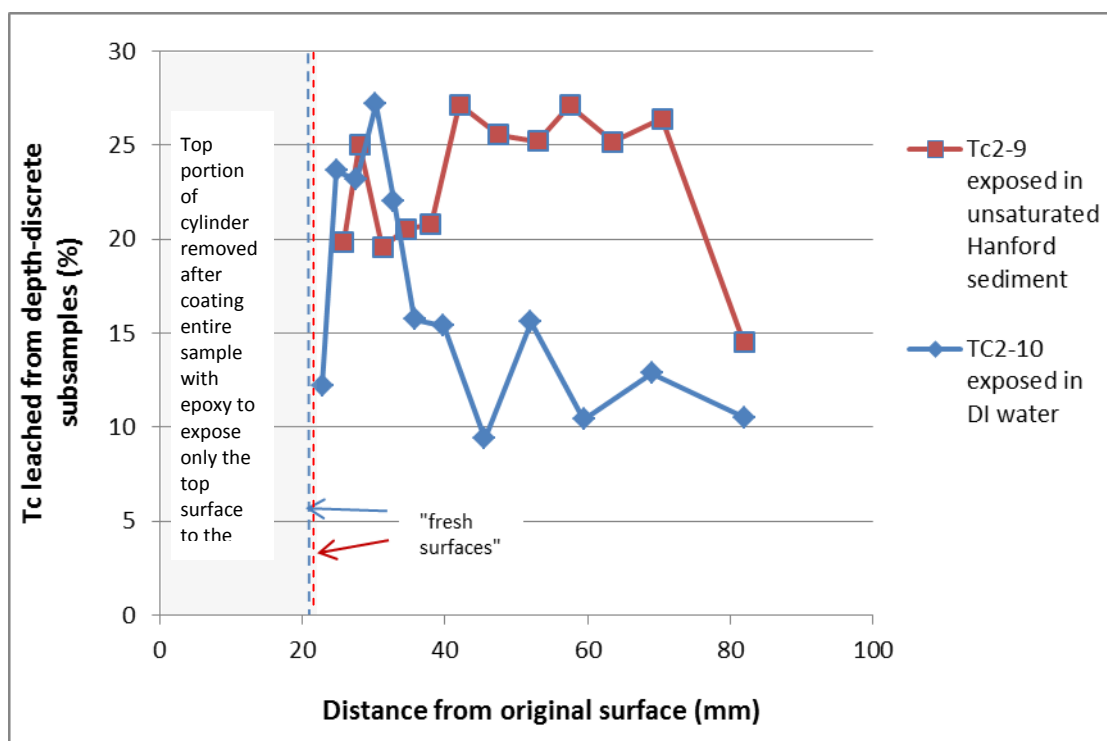


Figure 3. Percent Tc-99 leached from depth-discrete subsamples as a function of distance from the as cast sample illustrating that the top portion was removed in order to expose a “fresh” surface to unsaturated Hanford sediment and DI water.

Tc-99 Leaching

Tc-99 leachate results are provided in Tables 6 and 7, respectively. Results are re-plotted in Figure 4 as a function of the “fresh surface” sample. Subsample leaching results from the top 10 to 15 mm of the “fresh” cut surfaces of both samples showed an initial depletion and then a spike in the mass fraction Tc-99. The spike was more apparent for the sample exposed to DI water.

The Tc fraction leached from depth-discrete subsamples of Tc2-9 (exposed to Hanford sediment) dropped back to the value measured for the surface subsample between about 3 and 12 mm before increasing to 0.25 to 0.27. The mass fraction Tc-99 leached from bottom subsample (16mm thick) dropped to the lowest value measured, 0.145, and may indicate the oxidation front resulting from exposure in soil.

The Tc-99 mass fraction leached from depth-discrete subsamples of Tc2-10 (exposed to DI water) dropped to 0.09 to 0.16 between 12 and 65 mm below the exposed surface. The leveling off of the

leachable Tc below 12 mm may indicate the location of the oxidation front resulting from oxygen supplied to the fresh cut surface by the DI water.

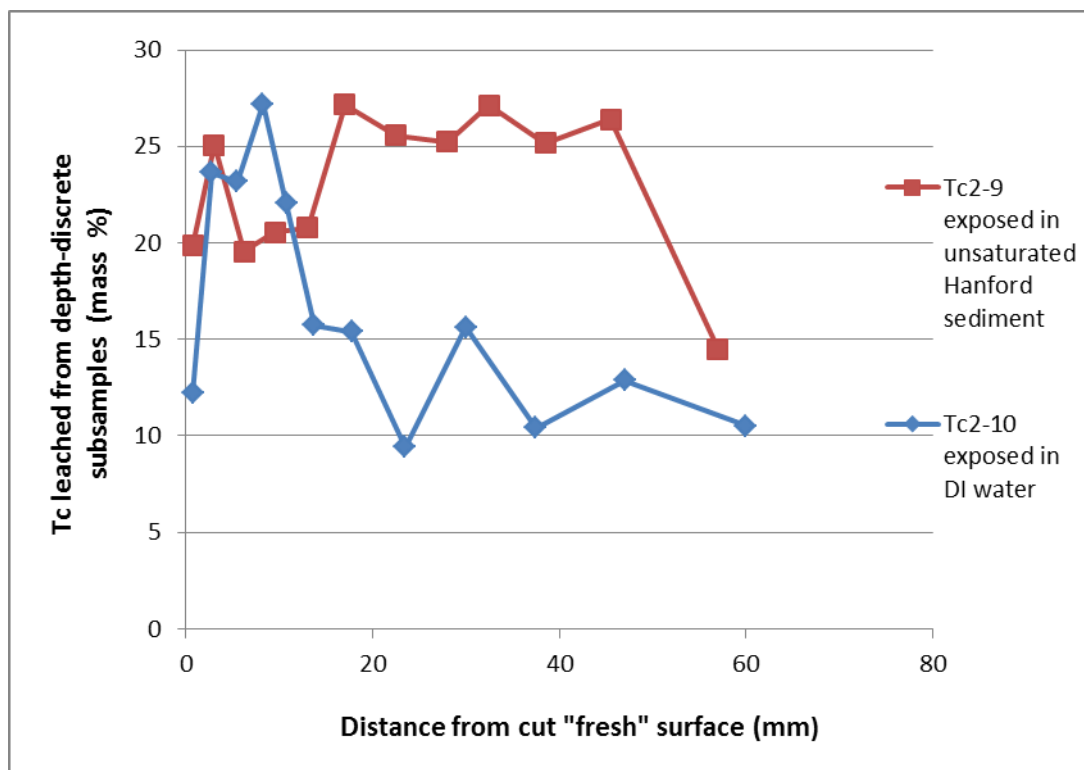


Figure 4. Percent Tc-99 leached from depth-discrete subsamples as a function of distance from fresh surfaces exposed to unsaturated Hanford sediment and DI water.

The lowest Tc-99 mass fractions leached from Tc2-9 and Tc2-10 subsamples were 0.155 and 0.094, respectively. Soluble Tc-99 throughout the entire length of these samples may be due to one or several of the following:

- Oxidation during exposure to Hanford unsaturated soil (Tc2-9) and DI water (Tc2-10).
- Oxidation during the subsampling, grinding, weighing, and leaching process. (Previous results indicate that $\leq 5\%$ of the Tc oxidized during sample handling and leaching [6]).
- Incomplete reduction of the Tc(IV) by the waste form.
- Movement of re-oxidized Tc throughout the sample during curing and exposure.
- Incomplete isolation of all surfaces of the cylindrical samples with respect to oxygen. Only the top surface was intended to be exposed to the environmental media.

Table 6. Tc-99 leachate results for depth-discrete subsample cut from Sample Tc2-9 cured in a humid environment after which a ‘freshly cut’ surface was exposed to and leached in unsaturated Hanford sediment with 5 wt.% moisture.

Tc 2-9 waste form sub-sample No.	Sample length, distance from top surface (mm)	Ave. sub-sample thickness (mm)	Sub-sample ave. distance from top surface (mm)	Sub sample mass (g)	Leachate mass (g)	Tc leached from Tc 2-9 (dpm/ml)	Tc leached from Tc2-9 (uCi/ml)	uCi Tc/ 1g waste form	Tc leached (uCi)	Tc in sample before leached (uCi)	% Tc leached
--	65	0	--	--	--	--	--	--	--	--	--
1	63.5	1.5	0.8	2.14	41.6762	1.57E+03	7.07E-04	6.94E-02	2.95E-02	1.49E-01	19.85
2	60.5	3	3.0	2.9398	41.881	2.71E+03	1.22E-03	6.94E-02	5.11E-02	2.04E-01	25.06
3	57	3.5	6.3	3.2305	40.7152	2.39E+03	1.08E-03	6.94E-02	4.38E-02	2.24E-01	19.55
4	54	3	9.5	4.5142	39.9093	3.58E+03	1.61E-03	6.94E-02	6.44E-02	3.13E-01	20.54
5	50	4	13.0	2.6674	41.0332	2.08E+03	9.37E-04	6.94E-02	3.84E-02	1.85E-01	20.77
6	46	4	17.0	3.2903	40.5942	3.39E+03	1.53E-03	6.94E-02	6.20E-02	2.28E-01	27.15
7	39	7	22.5	3.5838	40.7836	3.46E+03	1.56E-03	6.94E-02	6.36E-02	2.49E-01	25.56
8	35	4	28.0	2.9481	41.5034	2.76E+03	1.24E-03	6.94E-02	5.16E-02	2.05E-01	25.22
9	30	5	32.5	2.5505	39.7714	2.68E+03	1.21E-03	6.94E-02	4.80E-02	1.77E-01	27.12
10	23	7	38.5	3.6458	40.6267	3.48E+03	1.57E-03	6.94E-02	6.37E-02	2.53E-01	25.17
11	16	7	45.5	3.5538	40.7068	3.55E+03	1.60E-03	6.94E-02	6.51E-02	2.47E-01	26.39
12	0	16	57.0	3.9778	40.7542	2.18E+03	9.82E-04	6.94E-02	4.00E-02	2.76E-01	14.50

Table 7. Tc-99 leachate results for depth-discrete subsample cut from Sample Tc2-10 cured in a humid environment after which a ‘freshly cut’ surface was exposed to and leached in DI water.

Tc 2-10 waste form subsample No.	Sample length, distance from top surface (mm)	Ave. sub sample thickness (mm)	Sub-sample ave. distance from top surface (mm)	Sub-sample mass (g)	Leachate mass (g)	Tc leached from Tc 2-9 (dpm/ml)	Tc leached from Tc2-9 (uCi/ml)	uCi Tc/ 1g waste form	Tc leached (uCi)	Tc in sample before leached (uCi)	% Tc leached
--	68	0	0	--	--	--	--	--	--	--	--
1	66.5	1.5	0.8	2.1023	41.2665	9.59E+02	4.32E-04	6.94E-02	1.78E-02	1.46E-01	12.22
2	64	2.5	2.8	2.6947	41.066	2.39E+03	1.08E-03	6.94E-02	4.42E-02	1.87E-01	23.64
3	61	3	5.5	3.5261	40.8766	3.08E+03	1.39E-03	6.94E-02	5.67E-02	2.45E-01	23.17
4	58.5	2.5	8.3	3.2316	40.7629	3.32E+03	1.50E-03	6.94E-02	6.10E-02	2.24E-01	27.18
5	56	2.5	10.8	3.1107	41.0904	2.57E+03	1.16E-03	6.94E-02	4.76E-02	2.16E-01	22.03
6	52.5	3.5	13.8	4.8403	39.87	2.94E+03	1.32E-03	6.94E-02	5.28E-02	3.36E-01	15.72
7	48	4.5	17.8	6.424	39.2801	3.88E+03	1.75E-03	6.94E-02	6.87E-02	4.46E-01	15.40
8	41	7	23.5	9.9767	37.3432	3.87E+03	1.74E-03	6.94E-02	6.51E-02	6.92E-01	9.40
9	35	6	30.0	6.2243	39.6078	3.78E+03	1.70E-03	6.94E-02	6.74E-02	4.32E-01	15.61
10	26	9	37.5	7.4323	38.5899	3.09E+03	1.39E-03	6.94E-02	5.37E-02	5.16E-01	10.41
11	16	10	47.0	5.7655	39.8804	2.87E+03	1.29E-03	6.94E-02	5.16E-02	4.00E-01	12.89
12	0	16	60.0	7.632	38.6221	3.20E+03	1.44E-03	6.94E-02	5.57E-02	5.30E-01	10.51

Nitrate and Sodium Leaching

Nitrate and sodium are not redox sensitive species under the curing and exposure conditions of this test. Depth-discrete subsamples leachate results for sodium and nitrate are provided in Tables 8 to 11 and are plotted in Figure 4 for comparison with technetium, a redox sensitive radionuclide. Nitrate is not bound in any low solubility solid phases. However, a portion of the sodium is thought to be bound in calcium silicate hydrate phases and calcium aluminate hydrate phases [Langton, 2014] and is therefore not completely soluble.

An initial depletion in leachable nitrate and sodium is more obvious for these species than for Tc. The NO_3^- and Na mass fractions leached from depth-discrete subsamples below about 10 to 15 mm showed a slight downward trend from about 15 mm to the final bottom subsample.

Slightly higher mass fractions of Na and NO_3^- were leached from depth-discrete subsamples of samples Tc2-9 (exposed to Hanford sediment) below about 15mm than from corresponding depth-discrete samples of Tc2-10 (cured in Hanford sediment). Somewhat higher fractions of Na were leached from the Tc2-9 (exposed to sediment) subsamples than from Tc2-10 which was exposed to DI water. The reverse was found for NO_3^- . Higher fractions of NO_3^- were leached from subsamples of Tc2-10 (exposed to DI water) when compared to subsamples of Tc2-9 (exposed to moist Hanford sediment).

The low Na and NO_3^- mass fractions leached from the near surface subsamples of Tc2-9 and Tc2-10 strongly suggests that the top portions of these samples were depleted in Na, and NO_3^- prior to the depth-discrete sampling due to migration of these soluble ions into the exposure media. Consequently the actual mass of these ions in the uppermost depth-discrete subsamples after exposure was less than the mass calculated for the original material.

Based on the mass fraction of nitrate leached (assumed to be 100 % soluble throughout the curing and exposure), the depth of depletion in Tc2-9 (exposed to Hanford sediment) was about 9.5 mm and in Tc2-10 exposed to DI water it was about 3 mm. Inhomogeneity due to settling or surface effects resulting from sample preparation is unlikely in these samples because the top 2.2 to 2.5 cm of the as cast sample was removed within a few minutes prior to exposure.

In addition, about 24 percent of the Tc-99 in the subsamples of Tc2-9 (exposed to Hanford sediment) between 0.8 and 46 mm was extracted in the depth-discrete leaching test. About 24 percent of the Tc-99 in the subsamples of Tc2-10 (exposed to DI water) was extracted between 0.8 and 11 mm. This is about 2X as much as was leached from the lower portions of both samples. These data suggest that oxidation of the reduced Tc species extended further into the sample exposed to unsaturated Hanford sediment compared to the samples exposed to DI water. A summary of the fractions Na, NO_3^- and Tc leached as a function of distance from the exposed surfaces of Tc2-9 and Tc2-10 is provided in Table 12.

Table 8. Na leachate results for depth discrete-subsample cut from Sample Tc2-9 cured in a humid environment after which a ‘freshly cut’ surface was exposed to and leached in unsaturated Hanford sediment with 5 wt.% moisture.

Tc 2-9 waste form sub-sample no.	Ave. distance from top surface (mm)	Sub-sample mass (g)	Leachate mass (g or ml)	Na leached from Tc 2-9 (mg/L)	Na in 1g waste form (mg)	Na Leached (mg)	Na in sample before leached (mg)	% Na leached
1	0.8	2.14	41.6762	898	42.07	37.43	90.03	41.57
2	3	2.9398	41.881	1750	42.07	73.29	123.68	59.26
3	6.3	3.2305	40.7152	2630	42.07	107.08	135.91	78.79
4	9.5	4.5142	39.9093	2600	42.07	103.76	189.91	54.64
5	13	2.6674	41.0332	2550	42.07	104.63	112.22	93.24
6	17	3.2903	40.5942	3160	42.07	128.28	138.42	92.67
7	22.5	3.5838	40.7836	3380	42.07	137.85	150.77	91.43
8	28	2.9481	41.5034	2830	42.07	117.45	124.03	94.70
9	32.5	2.5505	39.7714	2380	42.07	94.66	107.30	88.22
10	38.5	3.6458	40.6267	3170	42.07	128.79	153.38	83.97
11	45.5	3.5538	40.7068	3270	42.07	133.11	149.51	89.03
12	57	3.9778	40.7542	3110	42.07	126.75	167.35	75.74

Table 9. NO₃⁻ leachate results for depth discrete-subsample cut from Sample Tc2-9 cured in a humid environment after which a ‘freshly cut’ surface was exposed to and leached in DI water.

Tc 2-9 waste form sub-sample no.	Ave. distance from top surface (mm)	Sub-sample mass (g)	Leachate mass (g or ml)	NO ₃ ⁻ leached from Tc 2-9 (mg/L)	NO ₃ ⁻ in 1g waste form (mg)	NO ₃ ⁻ Leached (mg)	NO ₃ ⁻ in sample before leached (mg)	% NO ₃ ⁻ Leached
1	0.8	2.14	41.6762	583	36.3	24.30	77.66	31.29
2	3	2.9398	41.881	1567	36.3	65.63	106.69	61.52
3	6.3	3.2305	40.7152	2597	36.3	105.74	117.23	90.19
4	9.5	4.5142	39.9093	2243	36.3	89.52	163.82	54.64
5	13	2.6674	41.0332	2420	36.3	99.30	96.80	102.58
6	17	3.2903	40.5942	3005	36.3	121.99	119.40	102.16
7	22.5	3.5838	40.7836	3165	36.3	129.08	130.06	99.25
8	28	2.9481	41.5034	2668	36.3	110.73	106.99	103.50
9	32.5	2.5505	39.7714	2239	36.3	89.05	92.56	96.21
10	38.5	3.6458	40.6267	3014	36.3	122.45	132.31	92.55
11	45.5	3.5538	40.7068	3048	36.3	124.07	128.97	96.21
12	57	3.9778	40.7542	3042	36.3	123.97	144.35	85.88

Table 10. Na leachate results for depth-discrete subsample cut from Sample Tc2-10 cured in a humid environment after which a ‘freshly cut’ surface was exposed to and leached in unsaturated Hanford sediment with 5 wt.% moisture.

Tc 2-10 wasteform sub-sample no.	Ave. distance from top surface (mm)	Sub-sample mass (g)	Leachate mass (g or ml)	Na leached from Tc 2-10 (mg/L)	Na in 1g waste form (mg)	Na leached (mg)	Na in sample before leached (mg)	% Na leached
1	0.8	2.1023	41.2665	515	42.07	21.25	88.44	24.03
2	2.8	2.6947	41.066	1450	42.07	59.55	113.37	52.53
3	5.5	3.5261	40.8766	2820	42.07	115.27	148.34	77.71
4	8.3	3.2316	40.7629	2750	42.07	112.10	135.95	82.45
5	10.8	3.1107	41.0904	2930	42.07	120.39	130.87	92.00
6	13.8	4.8403	39.87	4380	42.07	174.63	203.63	85.76
7	17.8	6.424	39.2801	5720	42.07	224.68	270.26	83.14
8	23.5	9.9767	37.3432	8070	42.07	301.36	419.72	71.80
9	30.0	6.2243	39.6078	5540	42.07	219.43	261.86	83.80
10	37.5	7.4323	38.5899	6270	42.07	241.96	312.68	77.38
11	47.0	5.7655	39.8804	4880	42.07	194.62	242.55	80.24
12	60.0	7.632	38.6221	5840	42.07	225.55	321.08	70.25

Table 11. NO₃⁻ leachate results for depth-discrete subsample cut from Sample Tc2-10 cured in a humid environment after which a ‘freshly cut’ surface was exposed to and leached in unsaturated Hanford sediment with 5 wt.% moisture.

Tc 2-10 wasteform sub-sample no.	Ave. distance from top surface (mm)	Sub-sample mass (g)	Leachate mass (g or ml)	NO₃⁻ Leached from Tc 2-10 (mg/L)	NO₃⁻ in 1g waste form (mg)	NO₃⁻ Leached (mg)	NO₃⁻ in sample before leached (mg)	% NO₃⁻ Leached
1	0.8	2.1023	41.2665	153	36.3	6.31	76.29	8.28
2	2.8	2.6947	41.066	1120	36.3	45.99	97.79	47.03
3	5.5	3.5261	40.8766	2780	36.3	113.64	127.96	88.81
4	8.3	3.2316	40.7629	2710	36.3	110.47	117.27	94.20
5	10.8	3.1107	41.0904	2950	36.3	121.22	112.89	107.38
6	13.8	4.8403	39.87	4360	36.3	173.83	175.65	98.96
7	17.8	6.424	39.2801	6060	36.3	238.04	233.13	102.11
8	23.5	9.9767	37.3432	9320	36.3	348.04	362.05	96.13
9	30.0	6.2243	39.6078	5740	36.3	227.35	225.88	100.65
10	37.5	7.4323	38.5899	6900	36.3	266.27	269.72	98.72
11	47.0	5.7655	39.8804	5170	36.3	206.18	209.23	98.54
12	60.0	7.632	38.6221	6530	36.3	252.20	276.97	91.06

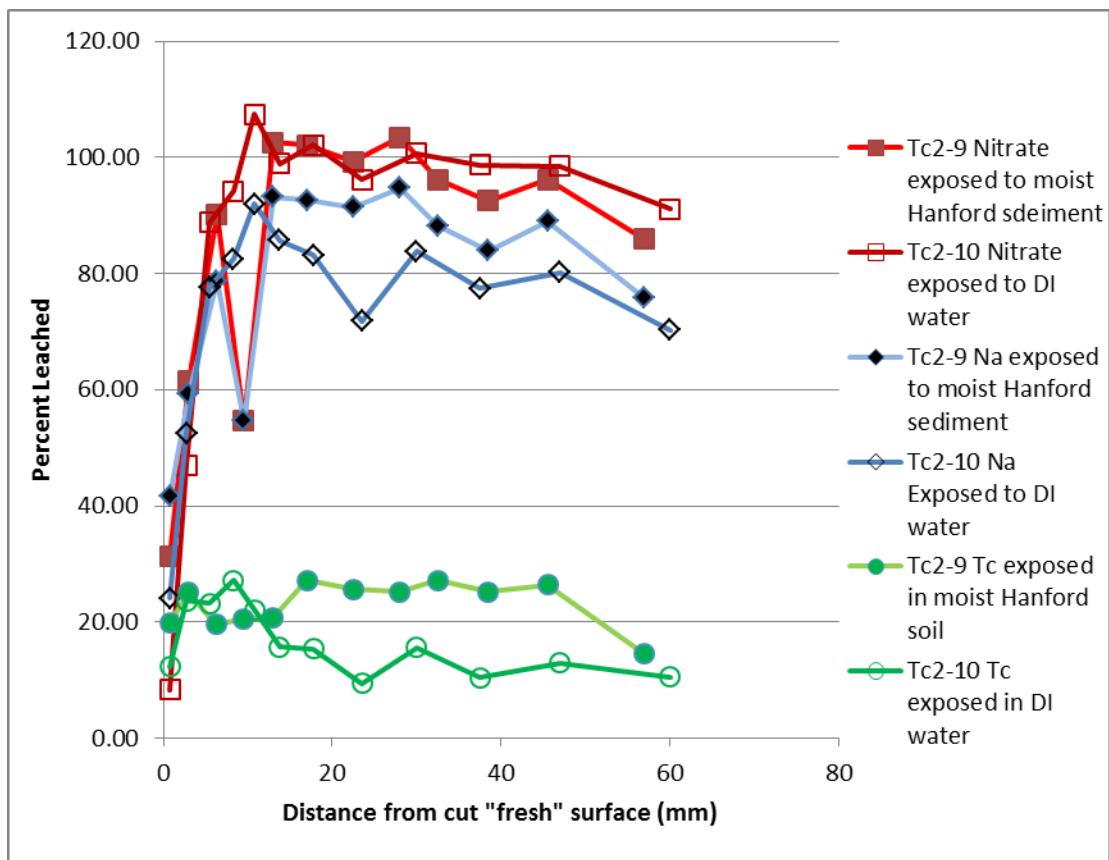


Figure 5. Na, NO₃⁻, and Tc-99 percents leached from depth-discrete subsamples as a function of distance from fresh surfaces exposed to unsaturated Hanford sediment and DI water.

Table 12. Summary of NO₃⁻, Na, and Tc leached as a function of distance from top surface of TC2-9 (exposed to Hanford sediment) and Tc2-10 (exposed to DI water).

Tc2-9 Exposed to Hanford sediment				Tc2-10 Exposed to DI water			
Distance from exposed surface (mm)	NO ₃ ⁻	Na	Tc	Distance from exposed surface (mm)	NO ₃ ⁻	Na	Tc
	% Leached				% Leached		
0 to 0.8	31	42	20	0 to 0.8	8	24	12
0.8 to 9.5	69	64	24	0.8 to 3	47	53	24
9.5 to 46*	99	91		3 to 60	97	80	--
46 to 57	86	76	13	3 to 11*	--	--	24
--	--	--	--	11 to 60	--	--	13

* Approximate depth of oxygen ingress during exposure.

Equation 2.
$$\frac{\text{Mass extracted from depth-discrete subsample}}{(\text{Initial concentration} - \text{Mass transferred to soil / water})}$$

CONCLUSIONS

The mineralogy of the reaction products for materials and blends of materials hydrated with caustic 4.4 M Na salt solution depended on the mineralogy and proportions of the cementitious ingredients and the bulk oxide compositions of the mixtures. Poorly ordered /amorphous C-S-H was detected in mixtures of cement and slag, cement and fly ash, slag and fly ash and the waste form blend containing cement, slag, and fly ash when hydrated with caustic 4.4 M Na salt solution. Only the neat slag and cement + slag mixture hydrated with caustic 4.4

M Na salt solution contained fairly well crystallized C-S-H I and Al substituted 11 Å tobermorite.

Hydrotalcite and hydrocalumite-like phases and mixtures of these LDH phases were present in the all of the blended samples. However the proportions of these phases and probably their compositions varied. Not surprisingly, the phase assemblage in the 10:45:45 blend of cement : slag : fly ash resembled that of the slag : fly ash blend.

The mineralogy of the hydrated materials evaluated did not change significantly between 2 months and 14 months curing in sealed containers. Characterization of samples cured for much longer times is recommended. Both drying conditions and curing in the presence of excess water are may (are expected to) result in changes in the mineralogy.

Cement hydrated for up to 14 months in water and up to 14 months in salt solution contained, poorly ordered C-S-H, portlandite ($\text{Ca}(\text{OH})_2$), and an AFm phase. The AFm phase identified in the salt solution hydrated sample was a sodium aluminate sulfate. Ettringite ($\text{Ca}_6(\text{Al,Fe})_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) was identified in the water hydrated cement sample but not in the salt solution hydrated sample. Unreacted larnite (Ca_2SiO_4) from the cement and NaNO_3 from the salt solution were detected in the salt solution hydrated sample.

Class F fly ash showed no significant reaction with water in the samples hydrated for 2 and 14 months. Hydration of the fly ash in salt solution resulted in dissolution of some of the glassy material as indicated by residual mullite “baskets”. The only crystalline phases detected in the x-ray diffraction patterns were the refractory phases, mullite and quartz, present in the anhydrous fly ash.

GGBFS did not hydrate or hydration was very limited after 2 months in water based on x-ray diffraction results. However, after 14 months, a small amount of LDH phase (hydrotalcite and / or hydrocalumite (AFm) or a mixture) was detected in the x-ray pattern. In contrast, activation of the slag in the 4.4 M Na salt solution resulted in formation of fairly well crystallized C-S-H I and Al substituted 11 Å tobermorite ($\text{Ca}_5\text{Si}_3\text{Al}(\text{OH})\text{O}_{17} \cdot 5\text{H}_2\text{O}$). These two ordered calcium silicate hydrates were detected in slag and mixtures of slag and cement hydrated with 4.4 M Na salt solution.

The mineralogy of the cured cementitious material influences the physical properties (strength, stiffness, etc.) of the cured material due to the degree of polymerization (chain length) and tetrahedron arrangement. Information about the mineralogy of hydrated cementitious materials and blends of these ingredients is needed to design waste form matrices, select ingredients and make adjustments in material proportions. Information presented in this report is an initial step in developing phases diagrams for the hydrated systems in which caustic sodium salt solutions are used as the hydration fluid for waste forms.

REFERENCES

1. ASTM C150-12. "Standard Specification for Portland Cement," 2012, ASTM International, West Conshohochen, PA, 19428.
2. ASTM C989-14. "Standard Specification for Slag Cement for Use in Concrete and Mortars," 2014, ASTM International, West Conshohochen, PA, 19428.
3. ASTM D1193-11. "Standard Specification for Reagent Water," 2011, ASTM International, West Conshohochen, PA, 19428.
4. Bumrongjaroen, W., I. S. Muller, and I. L. Pegg, 2007. "Characterization of Glassy Phase in Fly Ash from Iowa State University", VSL-07R520X-1, Vitreous State laboratory, Washington DC, 2007.
5. Chen, W, H. J. H. Brouwers, 2007. "The hydration of slag, Part 1: Reaction models for alkali-activated slag," J. Mater. Sci. 42:428-443.
6. Chen, W, H. J. H. Brouwers, and Z. H. Shui, 2007. "Three-dimensional computer modeling of slag cement hydration," J. Mater. Sci., 42:9595-9610.
7. Katsioti, M, P.E. Tsakiridis, P. Giannatos, Z.Tsibouki, and J. Marinos, 2009. "Characterization of various cement grinding aids and their impact on grindability and cement performance," Construction and Building Mat., 23(5):1954-1959.
8. Keppeler, J.G. and W.T.Frady, 2009. "Carbon Burn-Out, commercialization and experience update," <http://www.pmiash.com/cbo/aaa01paper.html>.
9. Kirkpatrick, R. J., P. Yu, X Hou, and Y. Kim, 1999. "Interlayer structure, anion dynamics, and phase transitions in mixed-metal layered hydroxides: Variable temperature ^{35}Cl NMR spectroscopy of hydrotalcite and Ca-Aluminate hydrate (hydrocalumite)," Am. Min. 4:1186-1190.
10. Langton, C.A. and D. M. Missimer, 2014. "X-ray Diffraction of Slag-Based Sodium salt Waste forms," Cementitious Barriers Partnership, CBP-TR-2014-0005, Savannah River National Laboratory, Savannah River Site, Aiken, South Carolina 29808.
11. Langton, C.A. and H.H. Burns, 2012. "Characterization of phases in Savannah River Site saltstone using neutron diffraction at the ORNL Spallation Neutron Source, Task Technical and Quality Assurance Plan (TT/QAP)", SRNL-RP-2012-00448, Savannah River National Laboratory, Aiken, SC 29801.
12. Langton, C.A., D.S. Kosson, A.C. Garrabrants, and K.G. Brown, 2009. "Reference cases for us in the Cementitious Barriers Partnership Project," SRNL-STI-2009-00005, WM Symp, 2009.
13. Li, Chao, H. Sun, and L.Li, 2011. "Glass phase structure of blast furnace slag," *Advanced Materials Research*, 168-170:3-7.
14. Matschei, T., B. Lothenbach, F.P. Glasser, 2007. The AFm phase in portland cement," Cem. And Concrete Res. 37:118-130

15. McCarthy G. J., 1988. "X-ray powder diffraction for studying the mineralogy of fly ash." Fly ash and coal conversion by-products: characterization, utilization and disposal, Mat. Res. Soc. Proc., 113:75-86.
16. Myers, R. J., S. A. Bernal, R.S.Nicolas, and J. L. Provis, 2013. "Generalized structural description of calcium-sodium aluminosilicate hydrate gels: The cross-linked substituted tobermorite model," Langmuir, 29:5294-45406.
17. Palmer, S.J., T. Nguyen, and R. L. Frost, 2009. "Hydrotalcites and their role in coordination of anions in Bayer liquors: Anion binding in layered double hydroxides," Coordination Chemistry Reviews 253(1-2):250-267.
18. Richardson, I.G. and G. W. Groves, 1992. "Microstructure and microanalysis of hardened cement pastes involving ground granulated blast-furnace slag," J. Mater. Sci. 27:6204-6212.
19. Stutzman, P., 2014. Personal communication.
20. Taylor, H. F. W, 1997. Cement Chemistry, 2nd ed., Thomas Telford, NY, NY.
21. Zhang, M and E. J. Reardon, 2003. "Removal of B, Cr, Mo, and Se from wastewater by incorporation into hydrocalumite and ettringite," Environ. Sci. Technol., 37(13):2947-295.

ACKNOWLEDGEMENTS

This paper was prepared in conjunction with work accomplished at the Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, in support of the Savannah River Nuclear Solutions Cooperative research Agreement (CRADA) CR-08-001, Cementitious Barriers Partnership, under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.