

## Comparison of Depth Discrete Oxidation Front Results and Reduction Capacity Measurements for Cementitious Waste Forms - 14330

C. A. Langton, P. M. Almond, D. B. Stefanko, D. H. Miller, D. P. Healy, and R. L. Minichan  
Savannah River National Laboratory, Savannah River Nuclear Solutions,  
Savannah River Site, Aiken, SC 29808

### ABSTRACT

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.  $\text{TcO}_4^-$  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. Upon exposure to oxygen, the compounds containing Tc(IV) oxidize to the pertechnetate ion,  $\text{Tc(VII)O}_4^-$ , which is very soluble. 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.

An approach for measuring contaminant oxidation rate (effective contaminant specific oxidation rate) based on leaching of select contaminants of concern is described in this report. In addition, the relationship between reduction capacity and contaminant oxidation is addressed. Chromate, Cr(VI), was used as a non-radioactive surrogate for pertechnetate, Tc(VII), in Cast Stone samples prepared with 5 M Simulant. Cast Stone spiked with pertechnetate was also prepared and tested. Depth discrete subsamples spiked with Cr were cut from Cast Stone exposed to Savannah River Site (SRS) outdoor ambient temperature fluctuations and moist air. Depth discrete subsamples spiked with Tc-99 were cut from Cast Stone exposed to laboratory ambient temperature fluctuations and moist air. Similar conditions are expected to be encountered in the Cast Stone curing container.

The Cr oxidation front (depth to which soluble Cr was detected) for the Cast Stone sample exposed for 68 days to ambient outdoor temperatures and humid air (total age of sample was 131 days) was determined to be about 35 mm below the top sample surface exposed. The Tc-99 results indicate that the oxidation front is at least 38 mm below the exposed surface for a sample exposed to ambient laboratory conditions and humid air for 50 days. The total age of the sample was 98 days.

Technetium appears to be more easily oxidized than Cr in the Cast Stone matrix, and Tc(VII) reduction to Tc(IV) appears to occur relatively fast. Results demonstrated that about 95 percent of the Tc(VII) was reduced to Tc(IV) during the setting and very early stage setting for a Cast Stone sample cured 10 days. Additional testing at longer curing times is required to determine whether additional time is required to reduce 100 % of the Tc(VII) in Cast Stone or whether the Tc loading exceeded the ability of the waste form to reduce 100 % of the Tc(VII). Depth discrete sampling and leaching appears to be useful for evaluating chemical durability of cementitious waste forms containing reduction / sequestration reagents to control redox sensitive contaminant chemistry and leachability.

Reduction capacity measurements (per the Angus-Glasser method) performed on depth discrete samples could not be correlated with the amount of chromium or technetium leached from the subsamples or with the oxidation front inferred from mass fraction of soluble chromium and technetium. Residual reduction capacity in the oxidized region of the test samples indicates that the remaining reduction capacity is not effective in re-reducing Cr(VI) or Tc(VII) in the presence of oxygen. Based on these results, reduction capacity measured by the Angus-Glasser Ce(IV) method is not an appropriate or meaningful parameter for determining or predicting Tc and Cr oxidation / retentions, speciation, or solubilities in cementitious materials such as Cast Stone.

## INTRODUCTION

### Objective

The objectives of this study were to:

- Utilize depth-discrete sampling and zero head space leaching to determine the contaminant specific oxidation rates / fronts for redox sensitive contaminants, such as Tc, in Cast Stone, a cementitious waste form prepared with the Hanford Tank Waste Operations System (HTWOS) “Average” 5 M Na simulant.
- Determine the relationship between the Cast Stone reduction capacity measured by the Angus-Glasser Method and leachability of Tc from depth-discrete samples.
- Determine the kinetics of Tc(VII) reduction to Tc(IV) in Cast Stone.

### 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 Hanford and SRS waste streams contain soluble technetium and chromium which may require stabilization to meet disposal requirements. Technetium stabilization is a difficult problem because: 1) Tc(VII) 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  $2.1 \times 10^5$  years which places demanding performance requirements on the engineered barriers and environment. Cast Stone and saltstone both contain ground granulated blast furnace slag (GGBFS) which provides chemical reduction of certain redox sensitive contaminants such as Tc and Cr. In a high pH environment, GGBFS chemically reduces pertechnetate,  $\text{Tc(VII)O}_4^-$  to the less soluble Tc(IV) oxidation state [1]. Over time, oxygen in the air and dissolved in water moving through the vadose zone 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 form designs and engineered barriers for shallow land disposal. In addition, the relationship between the matrix reduction capacity and contaminant specific reduction and re-oxidation rates are parameters 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) [2, 3, and 4]. This method is based upon leaching depth discrete sub-samples collected from a waste form exposed to air. Leaching is performed in a zero head space container using deionized, de-aerated water to minimize oxidation during the leaching process.

### Cast Stone Sample Preparation

**Simulant.** The Hanford LAW tank waste simulant was used in this study. 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 [5, 6].

The ingredients and proportions in the 5M Na simulated salt solution used to prepare the waste form are provided in TABLE I. The compounds were added to the liquid in the order they are listed in TABLE I.

**TABLE I. Ingredients in the HTWOS average 5 M Na simulant prepared for this study [5].**

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

**Cast Stone Premix Reagents.** The cement, blast furnace slag, and fly ash used in this study were obtained from a supplier in the Hanford area and were shipped to SRNL. The three cementitious materials were pre mixed in the following proportions: cement : slag : fly ash ratios of 8:47:45 by mass manually shaking the bags.

**Cast Stone Spiked with Chromium.** Cr(VI) was used as a non-radioactive redox surrogate for Tc(VII) in the initial testing. Cast Stone was prepared in 1 kg batches using a water to cement + slag + fly ash ratio (w/cm) of 0.60. Ingredients and proportions of the Cr spiked Cast Stone mixes are listed in TABLE II. The process was as follows:

1. The amount of average 5 M Na simulant was calculated for a 1 kg batch of Cast Stone based on the w/cm ratio and the weight percent water in the simulant.
2. Na<sub>2</sub>CrO<sub>4</sub> was added to the 5 M Na simulant. For Cast Stone targeting a Cr concentration of 500 mg/kg, 1.5575 g of Na<sub>2</sub>CrO<sub>4</sub> was added to 451.33 g of 5 M Na simulant. The sodium chromate was completely dissolved prior to mixing the solution with the premix reagents.
3. 548.67 g of premix was added to the spiked salt solution and mixed with an overhead stirrer for three minutes after all of the ingredients were incorporated into the liquid.

**TABLE II. Ingredients in chromium spiked cast stone, w/cm = 0.60.**

Cr Concentration in Cast stone (mg / kg)	Cast Stone Batch Size (g)	5M Na Ave. Simulant (g)	Na <sub>2</sub> CrO <sub>4</sub> (g)	8:47:45 Blend (g)	Blend Proportions (g)
500	1000	451.33	1.5575	548.67	Cement = 43.89 Slag = 257.87 Fly Ash = 246.90

After mixing, the grout slurry was poured into 90 x 35 mm cylindrical molds and capped and cured at ambient temperature (about 22 °C) and 65% to 70% relative humidity for 63 days before being uncapped and relocated to a storage cooler which was located outdoors in Z-Area at the SRS. See Fig. 1. The samples were subjected to “natural” temperature fluctuations, and the top surfaces of the samples were exposed to moist air. The “field” location provided exposure conditions intended to simulate the environment in a partially or completely filled disposal unit. To date, one exposure time has been

analyzed for a sample containing 500 mg/kg Cr. This sample was exposed for 68 days after being cured for 63 days. (Total age was 131 days.)



**Fig. 1. Laboratory Curing Container (left); Cast Stone Sample After Curing for 30 Days Prior to Exposure Testing (center), Outdoor Exposure Container (right).**

**Cast Stone Spiked with Technetium.** The general method for preparing Cast Stone samples spiked with Tc-99 was the same as that described for preparing Cr spiked samples. Rather than adding the spike to achieve a pre-determined concentration in the Cast Stone, Tc-99 was added to the 5 M Na simulant to achieve a concentration of 7.66 MBq / L (207  $\mu$ Ci / L) which is the current flow sheet 5 M Na design case. The Tc-99 was added as Tc(VII) by spiking with a stock solution of  $\text{NH}_4\text{TcO}_4$  in water. The Tc-99 concentration of the stock solution was 18.5 MBq / ml (0.5 mCi / ml). The batch size for the Tc spiked samples was 1800 g. One batch was prepared with a water to cementitious materials ratio (w /cm) of 0.60 and another with a w/cm of 0.5. Ingredients and Tc concentrations are listed in TABLE III.

**TABLE III. Ingredients in cast stone prepared with average 5 M Na simulant spiked with Tc-99.**

Cast Stone w/cm	Average 5 M Na Simulant Tc-99 Concentration (MBq / L) ( $\mu$ Ci / L)	Cast Stone Batch Size (g)	5M Na Average Simulant (g)	5M Na Average Simulant (ml)	$\text{NH}_4\text{TcO}_4$ 18.5 MBq / ml (0.5 mCi / ml) Stock Solution (ml)	8:47:45 Cement:Slag: Fly Ash Blend (g)	5M Cast Stone Tc-99 Concentration (kBq / g) ( $\mu$ Ci / g)
0.60	6.99 189	1800	812.5	660.57	0.25 (250 $\mu$ L)	987.5	2.57 (0.0694)

\* HTWOS estimated maximum value for Tc-99 = 1.53 MBq (4.13 E-05 Ci) / mole of Na. For 5 M Na simulant, the maximum Tc-99 value is 7.64 MBq (20.65 E-05 Ci) per liter of simulant (7.61 MBq L or 205.8  $\mu$ Ci / L).

After mixing, the grout slurry was poured into 90 x 35 mm cylindrical molds and capped. The capped cylinders were placed in 2-liter plastic containers containing wet towels to assure a moist environment around the sealed samples. The containers were stored in the rad laboratory. Sample Tc2 was cured for 48 days at ambient temperature ( $\sim 22^\circ \text{C}$ ) after which the cap was removed and the sample was relocated to another container in the rad lab where it was exposed to moist air at ambient temperature for 50 days. At the time the depth discrete subsamples were collected, the total age of the sample was 98 days.

**10-Day Old Cast Stone Spiked with Technetium-99.** In order to determine the kinetics of Tc-99 reduction in Cast Stone, a set of samples (Tc 4-1 to Tc 4-10) was prepared with the intent of leaching depth discrete subsamples at several ages without exposing the top surface to moist air. Samples were prepared with 5 M Na HTWOS Average Simulant and spiked with Tc-99 stock solution. Concentrations and proportions are listed in TABLE IV.

The 90 x 35 mm containers were filled to the top to the extent possible. The samples were stored at ambient laboratory conditions in the closed containers which were placed in an over pack container with moist towels. Depth discrete subsamples were collected from the first sample, Tc 4-1, after 10 days.

**TABLE IV. Tc-99 concentrations in spiked 5 M Na HTWOS average simulant and cast stone.**

Tc-99 Concentration in Stock Solution (mCi / mL)	5 M Na HTWOS Average Simulant (g)	Volume Tc-99 Stock Solution (µL)	Measured Tc-99 concentration in 5 M Na HTWOS Average Simulant			Mass Fraction 5 M Na HTWOS Average Simulant in Cast Stone w / pm = 0.60	Tc-99 Concentration in 1 g of Cast Stone w / pm = 0.60 (uCi Tc-99 / 1 g)
			Sample No. 300307438 (dpm / ml)	(dpm Tc-99 / g simulant)	(uCi Tc-99 / g simulant)		
0.5	1495.8	500	4.71E+05	3.83E+05	1.72E-01	0.4514	7.79E-02

### Cast Stone Depth Discrete Sub-Sampling and Leaching

The sampling and leaching methods are described elsewhere [2, 3, and 4]. Each layer removed from the Cr and Tc spiked monoliths was size reduced in air (crushed to a powder) with a mortar and pestle. See Fig. 2(a) and (b). A short-term leach test based on US EPA 1311 was used [7]. The size reduced samples were divided; one portion was leached. Reduction capacity was measured on the other portion. The time required for cutting, crushing, weighing, and covering the sample with leachate was about 5 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 for samples Cr 500-1 and Tc2 were loaded into a large mouth plastic bottle which was tumbled end-over-end at 30 rpm for approximately  $48 \pm 2$  hours; sample Tc4-1 was tumbled for 56 hours.

Only the top of the cylindrical sample was directly exposed to air. The sides of the sample may also have been exposed to air if a gap was present between the container and sample and / or if oxygen diffused through the thin walled polypropylene vial. However, discolored / oxidized material was not observed on the sides of the samples when they were de-molded. Consequently, the extent of oxidation on the unexposed surfaces was assumed to be minimal.

After tumbling, leachates were filtered using 0.45 micron filters attached to 20 mL syringes. Ca, K, Al, Cr, and Na concentrations were measured using an Inductively Coupled Plasma- Optical Emission Spectrometer (ICP-OES), Varian 730-ES.  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{SO}_4^{2-}$  were analyzed using Ion Chromatography (IC), Dionex ICS-5000 EG. Data for the full set of analytes and leachate pHs are reported elsewhere [8]. Tc-99 was analyzed by liquid scintillation. Sample preparation and the appearance of the leachates before tumbling and after filtering are illustrated in Figure 2(c) and (d). The yellow color of the leachates is related to reducing chemistry. The leachates become clear within a few hours after filtering.

### Fraction Leached

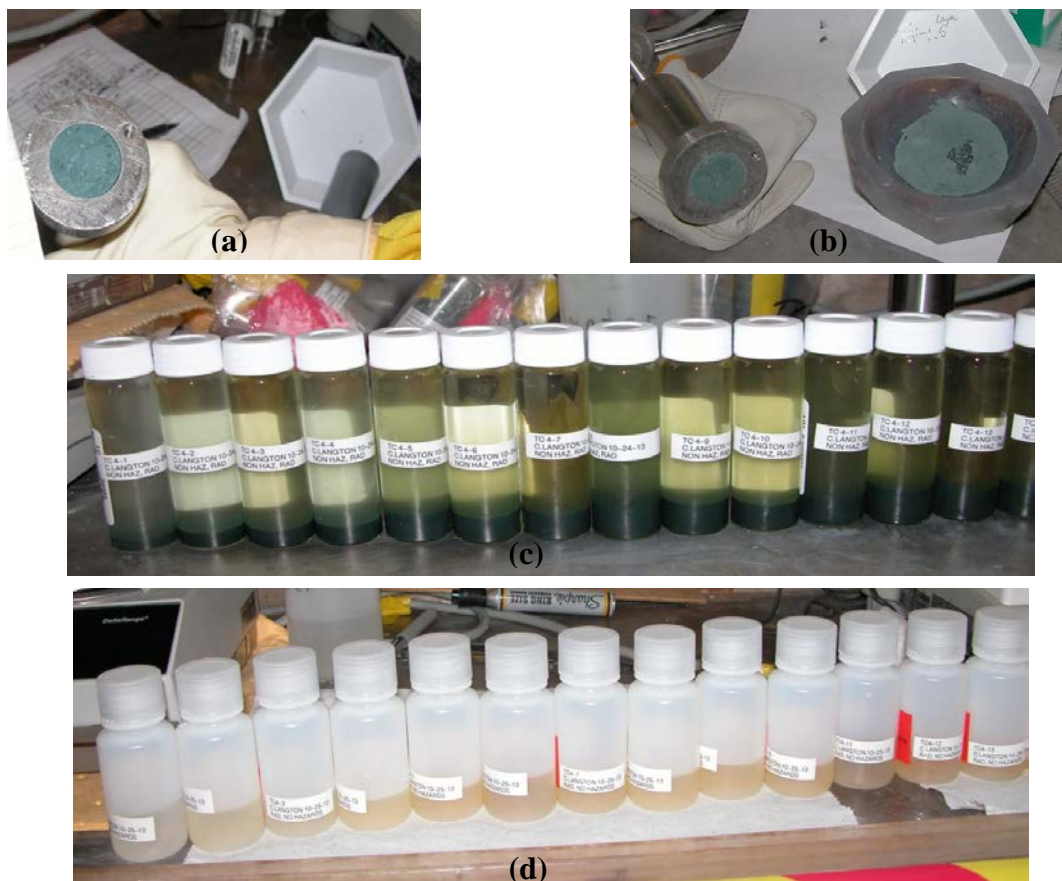
The fraction of selected anions and cations leached or percent leached (fraction leached X 100) from each crushed subsample was selected as the parameter for indicating: 1) the effect of exposure to air (i.e., oxidation) on the redox sensitive contaminants, Na and  $\text{NO}_3^-$  and 2) the depth of penetration of oxygen into the waste form (i.e., rate of oxidation front advancement). The percent leached was calculated using Equation 1.

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

Where:

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



**Fig. 2. Depth discrete Cast Stone sample preparation. (a) Monolithic cylinder in sample holder prior to sectioning. (b) Ground depth discrete sample prior to leaching. (c) Leaching samples prior to tumbling. (d) Leached samples after tumbling.**

### Reduction Capacity Measurements

Reduction capacity measurements were carried out following a redox titration method based on the Ce(IV)-Fe(II) chemical system [9]. Ground cementitious material was dissolved in a 0.0608 M Ce(IV) acidic solution for one hour after which the resulting solution was titrated with ferrous ammonium sulfate (FAS) in the presence of the indicator 1-10 phenanthroline (ferroin). The reduction capacity of the cementitious material was calculated based on the amount of FAS needed to reach the endpoint.

The Hanford fly ash and consequently Cast Stone contained magnetic particles which did not dissolve in the dissolution. The particles were assumed to be magnetite and if they had dissolved, would have added to the reduction capacity value. Given that they did not dissolve, they were treated as inert for the purpose of reducing redox sensitive contaminants in the simulant solution.

**RESULTS**

**Leaching Result for Cast Stone Spiked with Chromium**

Sample Cr 500-1 leaching results for Cr, a redox sensitive species,  $\text{NO}_3^-$  and Na, are presented in TABLES V and VI and plotted in Fig. 3. Results for the top 12 mm of the 90 mm sample are not representative of the bulk material. The near surface portion of the sample may have been altered by: 1) repeated wetting and drying during exposure, 2) inhomogeneity in the original sample due to slurry stratification prior to setting, or 3) a combination of phenomena. Additional testing is required to characterize the near surface portion of the sample.

Most of the  $\text{NO}_3^-$  (75 to 97 % of the amount supplied by the 5 M Na simulant) and essentially all of the Na (90 to 112 weight % of the amount supplied by the 5 M Na simulant) leached out of the depth discrete subsamples in deionized water. Na results greater than 100 % suggest that the cementitious reagents contain some soluble sodium which was also extracted during the leaching process. In contrast, less than 0.7 wt. % of the Cr (added to the simulant as soluble chromate) leached from the top 35 mm of the sample. Below about 35 mm, the amount of leachable Cr decreased to < 0.01 wt. %, i.e. below the Cr detection limit of 0.01 mg/L of the amount in the as-prepared sample. Based on these results, the chromium-specific oxidation front in Cast Stone sample Cr 500-1 was estimated to be at  $35 \pm 3$  mm below the exposed surface for a 131 day old sample exposed to moist air and variable outdoor temperature in a closed cooler for 68 days.

**TABLE V. Cr leaching results for cast stone mix Cr 500-1 depth-discrete subsamples.**

Sub-sample No.	Cylinder Length (mm)	Mean Location		Sub-sample Mass (g)	Leachate Volume (g or ml)	Cr in Leachate duplicate analyses			Cr in 1 g of Cast Stone (mg / g)	Total Cr leached (mg)	Cr in Sub-sample before leach (mg)	% Cr leached
		Bottom (mm)	From Exposed Surface (mm)			A (mg / L)	B (mg / L)	Ave. (mg / L)				
0	88.3											
1	86.8	87.55	0.75	0.731	42.8531	0.119	0.119	0.12	1.00	0.0051	0.73	0.70
2	85.3	86.05	2.25	1.413	42.419	0.242	0.242	0.24	1.00	0.0103	1.41	0.73
3	83.8	84.55	3.75	1.420	42.236	0.100	0.099	0.10	1.00	0.0042	1.42	0.30
4	82.3	83.05	5.25	1.213	42.907	0.052	0.055	0.05	1.00	0.0023	1.21	0.19
5	80.8	81.55	6.75	1.313	42.874	0.066	0.067	0.07	1.00	0.0029	1.31	0.22
6	79.3	80.05	8.25	1.276	42.850	0.096	0.096	0.10	1.00	0.0041	1.28	0.32
7	77.8	78.55	9.75	1.559	42.540	0.085	0.084	0.08	1.00	0.0036	1.56	0.23
8	76.3	77.05	11.25	1.362	42.714	0.080	0.086	0.08	1.00	0.0035	1.36	0.26
9	74.8	75.55	12.75	1.550	42.476	0.211	0.215	0.21	1.00	0.0090	1.55	0.58
10	73.3	74.05	14.25	1.482	42.780	0.189	0.186	0.19	1.00	0.0080	1.48	0.54
11	71.8	72.55	15.75	1.357	42.899	0.195	0.199	0.20	1.00	0.0085	1.36	0.62
12	70.3	71.05	17.25	1.607	42.364	0.198	0.203	0.20	1.00	0.0085	1.61	0.53
13	68.8	69.55	18.75	1.431	42.723	0.218	0.217	0.22	1.00	0.0093	1.43	0.65
14	67.3	68.05	20.25	1.561	42.691	0.204	0.205	0.20	1.00	0.0087	1.56	0.56
15	65.8	66.55	21.75	1.311	43.800	0.164	0.162	0.16	1.00	0.0071	1.31	0.54
16	64.3	65.05	23.25	1.529	42.392	0.258	0.252	0.26	1.00	0.0108	1.53	0.71
17	62.8	63.55	24.75	1.376	42.250	0.188	0.191	0.19	1.00	0.0080	1.38	0.58
18	61.3	62.05	26.25	1.465	42.441	0.174	0.173	0.17	1.00	0.0074	1.47	0.50
19	59.8	60.55	27.75	1.480	42.744	0.184	0.178	0.18	1.00	0.0077	1.48	0.52
20/21	53 to 50	51.5	36.8	3.718	41.377	<0.010	<0.010	<0.01	1.00	0.0004	3.72	<0.01
22/23	45 to 42	43.5	44.8	3.536	41.655	<0.010	<0.010	<0.01	1.00	0.0004	3.54	<0.01
24/25	37 to 34	35.5	52.8	3.622	41.345	<0.010	<0.010	<0.01	1.00	0.0004	3.62	<0.01

TABLE VI. NO<sub>3</sub><sup>-</sup> and Na leaching results for cast stone mix Cr 500-1 depth-discrete subsamples.

Sub-sample No.	Cylinder Length (mm)	Mean Location		Sub-sample Mass (g)	Leachate Volume (g or ml)	NO <sub>3</sub> <sup>-</sup> in Leachate duplicate analyses			NO <sub>3</sub> <sup>-</sup> in 1 g of Cast Stone (mg/g)	NO <sub>3</sub> <sup>-</sup> Total Leached (mg)	NO <sub>3</sub> <sup>-</sup> in Sub-sample before leach (mg)	% NO <sub>3</sub> <sup>-</sup> Leached	Na in Leachate duplicate analyses			Na in 1 g of Cast Stone (mg/g)	Na Total Leached (mg)	Na in Sub-sample before leach (mg)	% Na Leached
		Bottom (mm)	From Exposed Surface (mm)			A (mg/L)	B (mg/L)	Ave. (mg/L)					A (mg/L)	B (mg/L)	Ave. (mg/L)				
0	88.3	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
1	86.8	87.55	0.75	0.731	42.853	536	535	536	42.17	22.95	30.82	74.46	569	576	573	37.03	24.53	--	90.7
2	85.3	86.05	2.25	1.413	42.419	1080	1080	808	42.17	34.25	59.58	57.49	1140	1150	1145	37.03	48.57	27.06	92.8
3	83.8	84.55	3.75	1.420	42.236	1210	1210	1145	42.17	48.36	59.86	80.78	1270	1280	1275	37.03	53.85	52.32	102.4
4	82.3	83.05	5.25	1.213	42.907	1020	1020	1115	42.17	47.84	51.13	93.57	1110	1100	1105	37.03	47.41	52.57	105.6
5	80.8	81.55	6.75	1.313	42.874	1080	1080	1050	42.17	45.02	55.35	81.34	1200	1210	1205	37.03	51.66	44.90	106.3
6	79.3	80.05	8.25	1.276	42.850	1050	1050	1065	42.17	45.63	53.83	84.77	1200	1200	1200	37.03	51.42	48.60	108.8
7	77.8	78.55	9.75	1.200	42.540	1250	1250	1150	42.17	48.92	50.60	96.67	1070	1070	1070	37.03	45.52	47.27	78.85
8	76.3	77.05	11.25	1.362	42.714	1100	1100	1175	42.17	50.19	57.44	87.38	1300	1290	1295	37.03	55.31	57.73	109.7
9	74.8	75.55	12.75	1.550	42.476	1330	1330	1215	42.17	51.61	65.37	78.95	1470	1470	1470	37.03	62.44	50.44	108.8
10	73.3	74.05	14.25	1.482	42.780	1250	1250	1290	42.17	55.19	62.50	88.29	1370	1390	1380	37.03	59.04	57.40	107.6
11	71.8	72.55	15.75	1.357	42.899	1180	1180	1215	42.17	52.12	57.23	91.08	1320	1310	1315	37.03	56.41	54.89	112.3
12	70.3	71.05	17.25	1.607	42.364	1400	1400	1290	42.17	54.65	67.78	80.63	1550	1560	1555	37.03	65.88	50.25	110.7
13	68.8	69.55	18.75	1.431	42.723	1250	1250	1325	42.17	56.61	60.35	93.79	1390	1390	1390	37.03	59.38	59.52	112.5
14	67.3	68.05	20.25	1.561	42.691	1340	1340	1295	42.17	55.28	65.82	83.99	1510	1520	1515	37.03	64.68	53.00	111.9
15	65.8	66.55	21.75	1.311	43.800	1130	1130	1235	42.17	54.09	55.28	97.86	1240	1240	1240	37.03	54.31	57.80	111.9
16	64.3	65.05	23.25	1.529	42.392	1310	1130	1220	42.17	51.72	64.48	80.21	1470	1500	1485	37.03	62.95	48.54	111.2
17	62.8	63.55	24.75	1.376	42.250	1170	1170	1150	42.17	48.59	58.02	83.75	1320	1300	1310	37.03	55.35	56.62	108.6
18	61.3	62.05	26.25	1.465	42.441	1270	1270	1220	42.17	51.78	61.78	83.81	1380	1410	1395	37.03	59.20	50.95	109.1
19	59.8	60.55	27.75	1.480	42.744	1300	1300	1285	42.17	54.93	114.6	88.02	1440	1450	1445	37.03	61.77	54.25	112.7
20/21	53 to 50	51.5	36.8	3.718	41.377	3180	3190	2240	42.17	92.68		80.88	3220	3200	3210	37.03	132.82	54.80	96.48
22/23	45 to 42	43.5	44.8	3.536	41.655	3040	3040	3115	42.17	129.65	149.1	86.95	3030	2980	3005	37.03	125.17	137.6	95.60
24/25	37 to 34	35.5	52.8	3.622	41.345	3240	3240	3140	42.17	129.82	152.7	84.99	3240	3220	3230	37.03	133.54	130.9	99.56



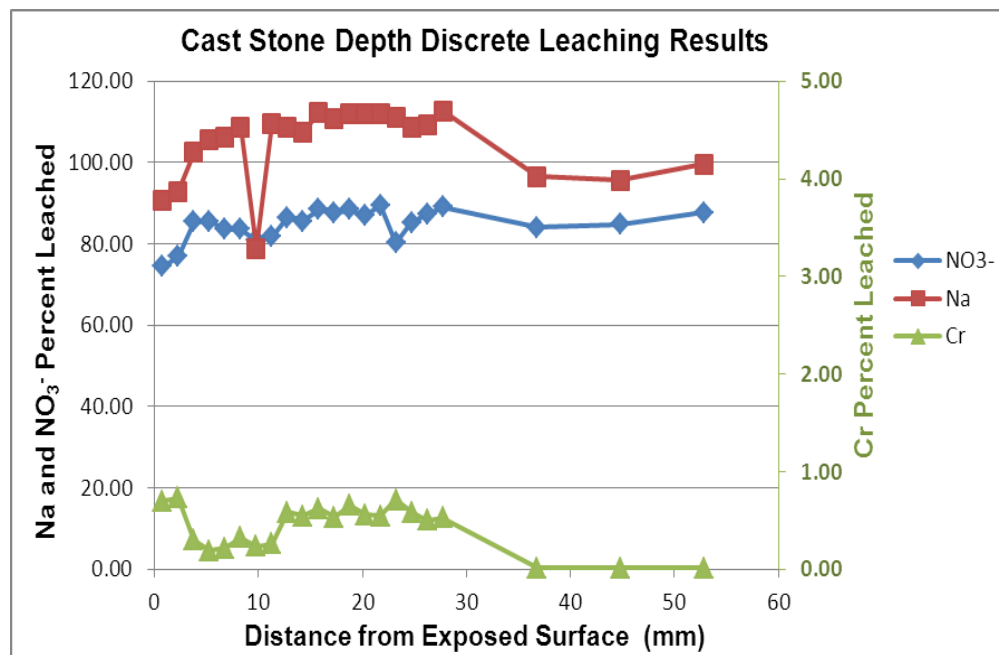


Fig. 3. Cast Stone Cr 500-1 Leachate Results for NO<sub>3</sub><sup>-</sup>, Na, and Cr as a Function of Distance from the Top Exposed Surface.

#### Leaching Result for Cast Stone Spiked with Technetium

Leachate results for sample Tc2 are provided in Tables VII and VIII and are plotted as a function of depth from the exposed surface in Fig. 4. Na and NO<sub>3</sub><sup>-</sup> show the same patterns as the non-radioactive Cr-spiked sample. The top 10 mm of the sample is not representative of the bulk.

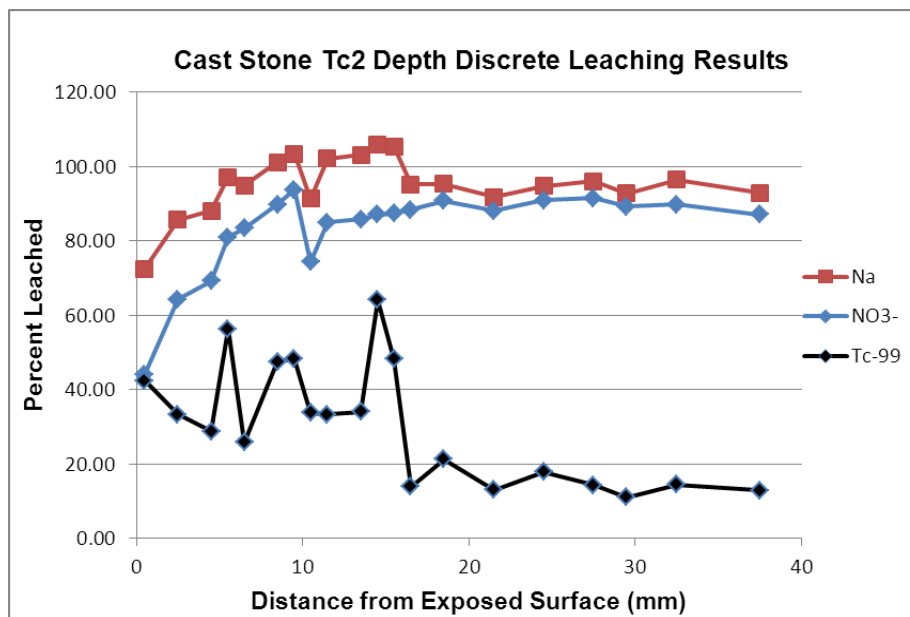
The mass fraction of Tc-99 leached from samples 10 to 16 mm below the exposed surface ranged from 0.33 to 0.64 (33 to 64 wt. %), and the mass fraction of Tc-99 that leached from sub-samples between 16 to 38 mm below the exposed surface ranged from 0.11 to 0.21 (11 to 21 wt. % of the amount spiked into the Cast Stone). The average Tc-99 wt. % leached from this depth interval was 15 compared to 94 and 89 wt. % for Na and NO<sub>3</sub><sup>-</sup> respectively. The differences in Na, NO<sub>3</sub><sup>-</sup> and Tc-99 fractions leached indicates that Tc is chemically stabilized in the waste form relative to Na and NO<sub>3</sub><sup>-</sup>.

TABLE VII. Tc-99 leaching results for cast stone mix Tc-2 depth-discrete subsamples.

Sub-sample No.	Length of cylinder (mm)	Mean Distance from Surface (mm)	Sub sample mass (g)	Leachate Volume (ml)	Tc-99 Leachate Concentration		Cast Stone Tc-99 Concentration $\mu\text{Ci Tc} / \text{1g}$	Tc-99 Leached (uCi)	Tc-99 in Cast Stone Subsamples Before Leaching (uCi)	% Tc-99 Leached
					(dpm/ml)	(uCi/ml)				
0	90	0	--	--	--	--	--	--	--	--
1	89	0.5	1.557	42.549	2.39E+03	1.08E-03	6.94E-02	4.58E-02	1.08E-01	42.39
2	87	2.5	1.425	42.570	1.72E+03	7.75E-04	6.94E-02	3.30E-02	9.89E-02	33.35
3	85	4.5	1.330	42.585	1.39E+03	6.26E-04	6.94E-02	2.67E-02	9.23E-02	28.89
4	84	5.5	1.068	42.121	2.20E+03	9.91E-04	6.94E-02	4.17E-02	7.41E-02	56.32
5	83	6.5	1.557	41.850	1.48E+03	6.67E-04	6.94E-02	2.79E-02	1.08E-01	25.82
6	81	8.5	1.134	41.736	1.99E+03	8.96E-04	6.94E-02	3.74E-02	7.87E-02	47.54
7	80	9.5	0.807	41.663	1.44E+03	6.49E-04	6.94E-02	2.70E-02	5.60E-02	48.25
8	79	10.5	1.097	43.043	1.33E+03	5.99E-04	6.94E-02	2.58E-02	7.61E-02	33.87
9	78	11.5	1.184	42.884	1.42E+03	6.40E-04	6.94E-02	2.74E-02	8.22E-02	33.38
10	76	13.5	1.196	42.991	1.46E+03	6.58E-04	6.94E-02	2.83E-02	8.30E-02	34.06
11	75	14.5	1.037	42.859	2.39E+03	1.08E-03	6.94E-02	4.61E-02	7.20E-02	64.11
12	74	15.5	0.990	42.766	1.72E+03	7.75E-04	6.94E-02	3.31E-02	6.87E-02	48.23
13	73	16.5	2.730	42.156	1.39E+03	6.26E-04	6.94E-02	2.64E-02	1.89E-01	13.93
14	71	18.5	2.807	41.812	2.20E+03	9.91E-04	6.94E-02	4.14E-02	1.95E-01	21.27
15	68	21.5	2.966	40.602	1.48E+03	6.67E-04	6.94E-02	2.71E-02	2.06E-01	13.15
16	65	24.5	3.018	41.722	1.99E+03	8.96E-04	6.94E-02	3.74E-02	2.09E-01	17.86
17	62	27.5	2.727	42.030	1.44E+03	6.49E-04	6.94E-02	2.73E-02	1.89E-01	14.41
18	60	29.5	3.240	41.701	1.33E+03	5.99E-04	6.94E-02	2.50E-02	2.25E-01	11.11
19	57	32.5	2.674	42.016	1.42E+03	6.40E-04	6.94E-02	2.69E-02	1.86E-01	14.48
20	52	37.5	3.064	41.842	1.46E+03	6.58E-04	6.94E-02	2.75E-02	2.13E-01	12.94

TABLE VIII. NO<sub>3</sub><sup>-</sup> and Na leaching results for cast stone mix Tc-2 depth-discrete subsamples.

Sub-Sample No.	Cylinder Length (mm)	Mean Distance From Surface (mm)	Sub-sample Mass (g)	Leachate Volume (ml)	NO <sub>3</sub> <sup>-</sup> Leachate Concentration (mg/ L)	NO <sub>3</sub> <sup>-</sup> in 1 g Cast Stone (mg/ g)	Total NO <sub>3</sub> <sup>-</sup> Leached from Sub-sample (mg)	NO <sub>3</sub> <sup>-</sup> in Cast Stone Subsample Before Leaching (mg)	% NO <sub>3</sub> <sup>-</sup> Leached	Na Leachate Concentration (mg/ L)	Na in 1 g Cast Stone (mg)	Na in 1 g of Cast Stone (mg/ g)	Na in Subsample before Leaching (mg)	% Na Leached
0	90	0	--	--	--	--	29.02	--	--	--	--	--	--	--
1	89	0.5	1.557	42.549	682	42.17	38.65	65.66	44.20	1120	42.17	47.65	65.66	72.58
2	87	2.5	1.425	42.570	908	42.17	38.84	60.09	64.33	1210	42.17	51.51	60.09	85.72
3	85	4.5	1.330	42.585	912	42.17	36.52	56.08	69.25	1160	42.17	49.40	56.08	88.08
4	84	5.5	1.068	42.121	867	42.17	54.82	45.04	81.09	1040	42.17	43.81	45.04	97.27
5	83	6.5	1.557	41.850	1310	42.17	42.99	65.66	83.50	1490	42.17	62.36	65.66	94.97
6	81	8.5	1.134	41.736	1030	42.17	31.91	47.82	89.90	1160	42.17	48.41	47.82	101.24
7	80	9.5	0.807	41.663	766	42.17	34.39	34.03	93.78	845	42.17	35.21	34.03	103.45
8	79	10.5	1.097	43.043	799	42.17	42.46	46.26	74.35	982	42.17	42.27	46.26	91.37
9	78	11.5	1.184	42.884	990	42.17	43.29	49.93	85.03	1190	42.17	51.03	49.93	102.21
10	76	13.5	1.196	42.991	1007	42.17	38.10	50.43	85.84	1210	42.17	52.02	50.43	103.14
11	75	14.5	1.037	42.859	889	42.17	36.52	43.73	87.13	1080	42.17	46.29	43.73	105.85
12	74	15.5	0.990	42.766	854	42.17	101.76	41.75	87.48	1030	42.17	44.05	41.75	105.51
13	73	16.5	2.730	42.156	2414	42.17	107.50	115.12	88.40	2600	42.17	109.60	115.12	95.21
14	71	18.5	2.807	41.812	2571	42.17	110.23	118.37	90.82	2700	42.17	112.89	118.37	95.37
15	68	21.5	2.966	40.602	2715	42.17	115.86	125.07	88.14	2830	42.17	114.90	125.07	91.87
16	65	24.5	3.018	41.722	2777	42.17	105.20	127.26	91.04	2890	42.17	120.58	127.26	94.74
17	62	27.5	2.727	42.030	2503	42.17	122.02	114.99	91.48	2630	42.17	110.54	114.99	96.13
18	60	29.5	3.240	41.701	2926	42.17	101.34	136.63	89.31	3040	42.17	126.77	136.63	92.79
19	57	32.5	2.674	42.016	2412	42.17	112.60	112.76	89.88	2590	42.17	108.82	112.76	96.51
20	52	37.5	3.064	41.842	2691	42.17	29.02	129.20	87.15	2870	42.17	120.09	129.20	92.94



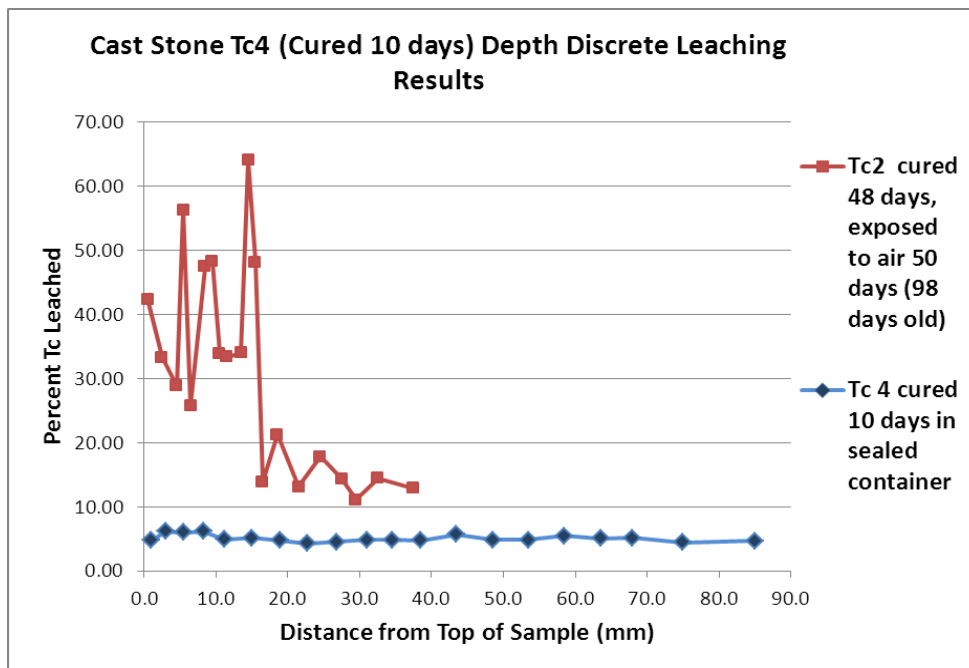
**Fig. 4. Cast Stone Tc2 Leachate Results for Na and Tc-99 as a Function of Distance from the Top Exposed Surface.**

#### Leaching Results for 10 Day Old Cast Stone Spiked With Technetium

Depth discrete subsamples were collected from a Cast Stone sample cured only 10 days in a sealed container, Tc 4-1. This sample was leached in de-aerated deionized water for 56 hours. The amount of Tc-99 leached from the 10 day-old depth discrete samples ranged from 4.3 to 6.2 percent of the amount in each sub sample. Results are provided in Table IX and are plotted in Fig. 5. The average amount of Tc-99 leached over the entire sample length was about 5.0 %, which is about 8X less that the average amount of Tc leached from the top 16 mm and about 3X less that the average amount of Tc leached over the depth interval 16 to 38 mm of Cast Stone sample Tc2.

**TABLE IX. Tc-99 leaching results for depth discrete subsamples from cast stone mix Tc 4-1 cured for 10 days in closed container.**

Sub Sample No.	Length of Cylinder (mm)	Mean Distance from Top Surface (mm)	Sub sample mass (g)	DI Water Leachate Volume (ml)	Tc-99 Leachate Concentrations		Cast Stone Tc-99 Concentration (uCi Tc / 1g)	Tc-99 Leached (uCi)	Tc-99 in Cast Stone Sub Sample Before leaching (uCi)	Percent Tc-99 Leached (%)
					(dpm/ml)	(uCi/ml)				
0	90	0								
1	88	1	2.1609	42.1633	4.25E+02	1.91E-04	7.79E-02	8.07E-03	1.68E-01	4.80
2	86	3	2.9084	41.5735	7.50E+02	3.38E-04	7.79E-02	1.40E-02	2.27E-01	6.20
3	83	5.5	2.909	41.1037	7.37E+02	3.32E-04	7.79E-02	1.36E-02	2.27E-01	6.02
4	80.5	8.25	3.4912	40.2783	9.23E+02	4.16E-04	7.79E-02	1.67E-02	2.72E-01	6.16
5	77	11.25	4.96	39.9538	1.06E+03	4.77E-04	7.79E-02	1.91E-02	3.86E-01	4.94
6	73	15	5.3442	39.6903	1.21E+03	5.45E-04	7.79E-02	2.16E-02	4.16E-01	5.20
7	69	19	5.423	39.726	1.12E+03	5.05E-04	7.79E-02	2.00E-02	4.22E-01	4.74
8	65.5	22.75	5.3715	40.1881	9.91E+02	4.46E-04	7.79E-02	1.79E-02	4.18E-01	4.29
9	61	26.75	4.9629	39.7714	9.85E+02	4.44E-04	7.79E-02	1.76E-02	3.87E-01	4.56
10	57	31	5.1564	40.0101	1.08E+03	4.86E-04	7.79E-02	1.95E-02	4.02E-01	4.85
11	54	34.5	4.872	40.1005	1.02E+03	4.59E-04	7.79E-02	1.84E-02	3.80E-01	4.85
12	49	38.5	6.9912	38.6415	1.50E+03	6.76E-04	7.79E-02	2.61E-02	5.45E-01	4.79
13	44	43.5	6.1877	39.1299	1.56E+03	7.03E-04	7.79E-02	2.75E-02	4.82E-01	5.70
14	39	48.5	6.5364	39.217	1.41E+03	6.35E-04	7.79E-02	2.49E-02	5.09E-01	4.89
15	34	53.5	6.8626	38.8619	1.49E+03	6.71E-04	7.79E-02	2.61E-02	5.35E-01	4.88
16	29	58.5	6.541	38.597	1.61E+03	7.25E-04	7.79E-02	2.80E-02	5.10E-01	5.49
17	24	63.5	6.9296	39.3212	1.56E+03	7.03E-04	7.79E-02	2.76E-02	5.40E-01	5.12
18	20	68	5.7246	39.1323	1.30E+03	5.86E-04	7.79E-02	2.29E-02	4.46E-01	5.14
19	10	75	8.1058	38.2424	1.65E+03	7.43E-04	7.79E-02	2.84E-02	6.31E-01	4.50
20	0	85	6.3431	39.4348	1.31E+03	5.90E-04	7.79E-02	2.33E-02	4.94E-01	4.71



**Fig. 5. Tc-99 Leachate Results for 10 day and 98 day old Cast Stone Samples.**

### Reduction Capacity of Starting Materials and Fresh Cast Stone

The reduction capacities of freshly ground Hanford slag, cement, and fly ash, and the 5 M Na HTWOS average simulant spiked with Tc-99 were measured by the Ce(IV)–Fe(II). The reduction capacity for Hanford Cast Stone prepared with these ingredients was also measured and a reduction capacity value was calculated from the sum of fractions of the reduction capacities of the individual components. Results are tabulated in TABLE X.

**TABLE X. Reduction capacities of cement slag, fly ash, and 5 M Na HTWOS simulant.**

Material*	Mass (g)	FAS Volume Titrated (mL)	Fe (mole e-)	(mole e-)	(mole e- / g)	Measured Red. Capacity (µeq / g)	Calculated Red. Capacity (µeq / g)
no solids calibration	0.0001	31.65	0.001520	0.000000	0.000000	0	--
5M Na HTWOS Average Simulant Spiked with 1.72E-01 (µCi Tc-99 / g simulant)	0.5026	21.66**	0.001070	0.000450	0.000895	895	--
Hanford Fly Ash	0.5000	29.79	0.001431	0.000089	0.000179	179	--
Hanford Slag (lightly ground)	0.5002	22.44	0.001078	0.000442	0.000884	884	--
Hanford Cement	0.4992	28.85	0.001386	0.000134	0.000269	269	--
Hanford Cast Stone prepared at SRNL from PNNL supplied material and cured for 35 days in a closed container (ground)	0.4996	23.76	0.001141	0.000379	0.000758	758	687 Sum of Fractions of Ingredients

\* The freshly re-ground value for SRS slag is in agreement with and benchmarked to the value of 820 µeq e<sup>-</sup>/g previously measured by Roberts and Kaplan, 2008.<sup>10</sup>

\*\* The no solids calibration of the FAS solution was 30.76 ml of the FAS solution.

The reduction capacity measured by the Angus-Glasser Ce(IV)-Fe(II) method for the 5 M Na waste simulant is higher than any of the solid ingredients. Nitrite, NO<sub>2</sub><sup>-</sup>, dissolved in the 5 M Na HTWOS Average simulant is the most likely species contributing to the high reduction capacity measured by this method. Cr and Tc in the 5 M Na simulant are present as the oxidized species, pertechnetate, Tc(VII), and chromate, Cr(VI). Consequently, the reduction capacity measurements made on salt solutions containing nitrite by the Ce(IV)-Fe(II) method do not correlate with and are not an indication of the speciation of the redox sensitive contaminants.

### Reduction Capacity of Depth Discrete Cast Stone Samples

Reduction capacity measurements were made on each depth discrete subsample from Cast Stone Cr 500-1 and Tc2. Results are tabulated in Tables XI and XII, respectively, and are plotted as a function of distance from the exposed surface in Fig. 6. The surface and near surface subsample of both of these Cast Stone specimens had the lowest reduction capacity values for their individual data sets. The averaged values of the Cr 500-1 and Tc2 subsamples were 595 µeq / g and 567 µeq / g, respectively, which are lower than 758 µeq / g, the value measured for Cast Stone cured for 35 days in a closed container and the calculated value, 687 µeq / g.

Bulk reduction capacity measurements performed according to the Angus-Glasser method (ability to chemically reduce Ce(IV) in solution) did not correlate with the fraction of redox sensitive contaminants (Cr and Tc) leached in de-aerated deionized leachate.

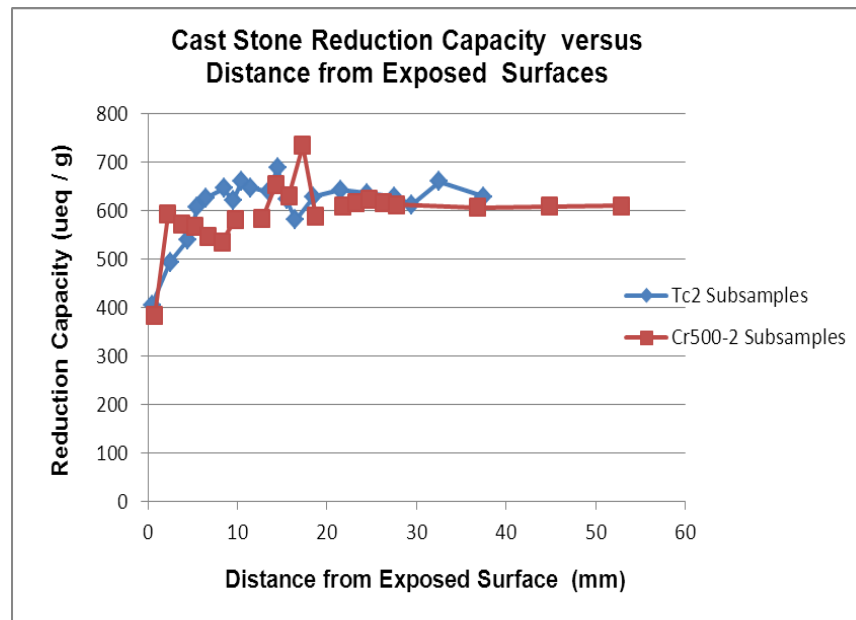
Based on results obtained in this study and results reported by W. Um, et.al [10] reduction capacity measured by this method is not an appropriate or meaningful parameter for determining or predicting Tc and Cr oxidation states, speciation, and / or solubilities in cementitious materials containing GGBFS such as Cast Stone. Furthermore, the use of reduction capacity as a general parameter in calculating long-term performance of a porous cementitious solid is not appropriate.

**TABLE XI. Reduction capacity results for cast stone Cr 500-1 depth discrete subsamples.**

Sub Sample No.	Distance From Exposed Surface (Top) (mm)	Cast Stone Cr500-1 (g)	Volume Titrated FAS (mL)	Fe (mole e-)	Cast Stone (mole e-)	Cast Stone (mole e-/g)	Reduction Capacity (meq/g)	Reduction Capacity (µeq/g)	Comment
1	0.75	0.5062	27.67	0.001325	0.000195	0.000385	0.385043	385	air bubbler in line
2	2.25	0.5097	25.42	0.001217	0.000303	0.000594	0.593799	594	
3	3.75	0.5102	25.63	0.001227	0.000293	0.000574	0.573505	574	
4	5.25	0.4929	25.88	0.001239	0.000281	0.000569	0.569345	569	
5	6.75	0.5036	25.98	0.001244	0.000276	0.000548	0.547739	548	
6	8.25	0.5010	26.13	0.001251	0.000269	0.000536	0.536243	536	
7	9.75	0.5082	25.57	0.001225	0.000295	0.000581	0.581416	581	
8	11.25	0.5013	26.10	0.001250	0.000270	0.000539	0.538788	539	
9	12.75	0.5102	25.52	0.001222	0.000298	0.000584	0.583830	584	
10	14.25	0.4976	24.95	0.001195	0.000325	0.000653	0.653471	653	
11	15.75	0.4983	25.18	0.001206	0.000314	0.000630	0.630449	630	
12	17.25	0.4937	24.16	0.001157	0.000363	0.000735	0.735263	735	auto titrator not zeroed
13	18.75	0.5052	25.53	0.001223	0.000297	0.000589	0.588661	589	
14	20.25	0.4995	34.24	0.001640	-0.000120	-0.000240	-0.239685	-240	no indicator
15	21.75	0.5041	25.32	0.001213	0.000307	0.000610	0.609895	610	
16	23.25	0.4988	25.32	0.001213	0.000307	0.000616	0.616375	616	
17	24.75	0.4933	25.32	0.001213	0.000307	0.000623	0.623248	623	
18	26.25	0.4986	25.32	0.001213	0.000307	0.000617	0.616623	617	
19	27.75	0.5010	25.32	0.001213	0.000307	0.000614	0.613669	614	
20-21	36.8	0.5058	25.32	0.001213	0.000307	0.000608	0.607845	608	
22-23	44.8	0.5047	25.32	0.001213	0.000307	0.000609	0.609170	609	
24-25	52.8	0.5034	25.32	0.001213	0.000307	0.000611	0.610743	611	
Average of Subsamples 2 to 11 plus 13 plus 15 to 25								595	

**TABLE XII. Reduction capacity results for cast stone Tc2 depth discrete subsamples.**

Sub Sample No.	Distance From Exposed Surface (Top) (mm)	Cast Stone Tc2 (g)	Volume Titrated FAS (mL)	Fe (mole e-)	Cast Stone (mole e-)	Cast Stone (mole e-/g)	Reduction Capacity (meq/g)	Reduction Capacity (µeq/g)	Comment
1	0.5	0.5167	24.56	0.001283	0.000237	0.000458	0.458099	458	air bubble in line
2	2.5	0.5038	24.28	0.001269	0.000251	0.000499	0.498869	499	
3	4.5	0.5056	23.61	0.001234	0.000286	0.000566	0.566335	566	
4	5.5	0.4983	23.20	0.001212	0.000308	0.000618	0.617624	618	
5	6.5	0.5045	23.09	0.001206	0.000314	0.000621	0.621427	621	
6	8.5	0.5083	23.67	0.001237	0.000283	0.000557	0.557159	557	
7	9.5	0.5006	23.20	0.001212	0.000308	0.000615	0.614786	615	
8	10.5	0.5100	23.11	0.001208	0.000312	0.000613	0.612676	613	
9	11.5	0.5022	22.81	0.001192	0.000328	0.000653	0.653406	653	
10	13.5	0.5138	23.48	0.001227	0.000293	0.000571	0.570517	571	
11	14.5	0.5092	23.58	0.001232	0.000288	0.000565	0.565409	565	
12	15.5	0.5032	23.66	0.001236	0.000284	0.000564	0.563844	564	
13	16.5	0.5019	22.79	0.001191	0.000329	0.000656	0.655878	656	refilled titrator
14	18.5	0.5025	23.90	0.001249	0.000271	0.000540	0.539674	540	
15	21.5	0.5079	24.10	0.001259	0.000261	0.000513	0.513360	513	
16	24.5	0.5026	23.69	0.001238	0.000282	0.000561	0.561398	561	
17	27.5	0.5006	23.60	0.001233	0.000287	0.000573	0.573035	573	
18	29.5	0.5181	24.05	0.001257	0.000263	0.000508	0.508296	508	
19	32.5	0.4852	23.99	0.001254	0.000266	0.000549	0.549224	549	
20	37.5	0.4736	24.44	0.001277	0.000243	0.000513	0.513028	513	
Average of Subsamples 2 to 12 plus 14 to 20								567	



**Fig. 6. Reduction Capacity Results for Cr500-1 and Tc2 Depth Discrete Subsamples.**



## CONCLUSIONS AND RECOMMENDATIONS

Leaching crushed depth discrete subsamples appears to be a suitable method for evaluating the effects of exposure to moist air and other environmental conditions expected in disposal environments on solubility/leachability of redox sensitive contaminants in cementitious waste forms. The method is useful in identifying the contaminant specific oxidation fronts in cured chemically reducing cementitious waste forms and provides the mass fraction of soluble redox sensitive contaminants and other soluble contaminants as a function of distance from a surface exposed to moist air. The soluble fraction of a chemical species is that portion available to diffusion through the waste form pore solution. The effective diffusion coefficients for the soluble fractions of redox sensitive contaminants will be approximately the same as that for nitrate.

The top 10 mm of the samples tested appears to be slightly different than the bulk material based on visual appearance and leachability of soluble species. This suggests that the fresh samples may have experienced a minor amount of settling prior to setting and / or that exposure to moist air results in redistribution of the soluble species in the near-surface regions of the samples, or both.

Based on the preliminary depth discrete subsample leaching results, Tc(IV) appears to be more easily oxidized than Cr(III). Cr(III) can also substitute for Fe(III) in calcium alumino-ferrite monosulfate hydrate structures (AFm phases) or other hydrated crystalline and non-crystalline phases in the matrix. Tc(IV) and Tc(VII) have been reported to be present in cementitious waste forms as a sulfide (reduced environment) or oxide or hydrated oxide phases (oxidized or partially oxidized environments).<sup>12, 13</sup> However, due to the Tc (IV) and Tc(VII) ions size and charge, it is less likely that either will substitute for ions in calcium silicate or calcium aluminate cementitious phases.

The oxidation front and leachability of redox sensitive contaminants appears to be contaminant specific. The Cr(III)/Cr(VI) oxidation front in Cast Stone was identified at about 35mm below the top surface for a 111 day old sample which was exposed to moist air for 68 days. The oxidation front for Tc in Cast Stone appears to be more than 38 mm below the surface of a 98 day old sample exposed to moist air for 50 days. Other possible interpretations of the data include: 1) the possibility that about 5 wt. % of the Tc in the Cast Stone sample may have oxidized very quickly as a result of the subsampling process and / or 2) some of the Tc(VII) in the sample may never have been reduced. Additional testing is needed.

The reduction capacity measured for the 5 M Na waste simulant by the Angus-Glasser Ce(IV)-Fe(II) method was higher than any of the solid ingredients or resulting Cast Stone waste forms. Nitrite, NO<sub>2</sub><sup>-</sup>, dissolved in the 5 M Na HTWOS Average simulant is the most likely reductant contributing to the high reduction capacity measured by the Ce(IV)-Fe(II) method. Reduction capacity measurements performed according to the Angus-Glasser method did not correlate with the fraction of redox sensitive contaminants (Cr and Tc) leached in de-aerated deionized leachate. Consequently, reduction capacity measured by this method is not predictive of the reducing effect on contaminants. Furthermore, it is not an appropriate or meaningful parameter for determining or predicting Tc and Cr oxidation states, speciation, and solubilities in cementitious materials such as Cast Stone.

Finally, the kinetics of Tc reduction in Cast Stone appears to be relatively fast. Ninety five percent of the soluble / leachable Tc in Cast Stone with Tc-99 concentration of 2.88 kBq / g (7.79E-02μCi / g) was insoluble (assumed to be as the result of chemical reduction and precipitation of a low solubility solid phase) after the sample was cured for 10 days at ambient laboratory conditions.

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