

**CEMENTITIOUS BARRIERS PARTNERSHIP**

**EFFECT OF OXIDATION ON CHROMIUM LEACHING  
AND REDOX CAPACITY OF SLAG-CONTAINING  
WASTE FORMS**

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## **SUMMARY**

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 [Shuh, et al., 1994, Shuh, et al., 2000, Shuh, et al., 2003]. 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 was used as a non-radioactive surrogate for pertechnetate in simulated waste form samples. Depth discrete subsamples were cut from material exposed to Savannah River Site (SRS) "field cured" conditions. The subsamples were prepared and analyzed for both reduction capacity and chromium leachability.

Results from field-cured samples indicate that the depth at which leachable chromium was detected advanced further into the sample exposed for 302 days compared to the sample exposed to air for 118 days (at least 50 mm compared to at least 20 mm). Data for only two exposure time intervals is currently available. Data for additional exposure times are required to develop an equation for the oxidation front progression.

Reduction capacity measurements (per the Angus-Glasser method, which is a measurement of the ability of a material to chemically reduce Ce(IV) to Ce(III) in solution) performed on depth discrete samples could not be correlated with the amount of chromium leached from the depth discrete subsamples or with the oxidation front inferred from soluble chromium (i.e., effective Cr oxidation front).

Exposure to oxygen (air or oxygen dissolved in water) results in the release of chromium through oxidation of Cr(III) to highly soluble chromate, Cr(VI). 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) in the presence of oxygen.

Consequently, this method for determining reduction capacity may not be a good indicator of the effective contaminant oxidation rate in a relatively porous solid (40 to 60 volume percent porosity). The chromium extracted in depth discrete samples ranged from a maximum of about 5.8 % at about 5 mm (118 day exposure) to about 4 % at about 10 mm (302 day exposure). The use of reduction capacity as an indicator of long-term performance requires further investigation.

The carbonation front was also estimated to have advanced to at least 28 mm in 302 days based on visual observation of gas evolution during acid addition during the reduction capacity measurements.

Depth discrete sampling of materials exposed to realistic conditions in combination with short term leaching of crushed samples has potential for advancing the understanding of factors influencing performance and will support conceptual model development.

## **INTRODUCTION**

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.

Several U.S. DOE sites use waste forms and concrete containment structures for radioactive waste disposal that are designed to have a chemically reducing environment to immobilize selected contaminants such as  $\text{Tc(VII)O}_4^-$  and  $\text{Cr(VI)O}_4^{2-}$ . 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.

In this study, small monoliths of a sodium salt waste form were spiked with sodium chromate,  $\text{Na}_2\text{Cr(VI)O}_4$ . The waste forms contained blast furnace slag and were formulated to be chemically reducing. After curing and exposure to air for up to 300 days, the samples were sectioned perpendicular to the exposed surface (depth-discrete samples), crushed and leached in de-aerated, deionized water for  $18 \pm 2$  hours and also for 28 days. Leachates were analyzed for Na,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and Cr.

## **OBJECTIVE**

The objective of this study was to provide information for developing a conceptual model for redox-controlled contaminant release from cementitious waste forms. Specific lines of investigation include:

- 1) Evaluate leaching of depth discrete subsamples of a reducing salt waste form exposed to field conditions (i.e., top surface of the sample exposed to air in a closed container at the SRS Z-Area versus bulk sample 4 to 5 cm from the surface of a sample exposed to the same conditions).
- 2) Determine the relationship between the Angus and Glasser Reduction Capacity Measurement (i.e., ability of a slag containing waste form to reduce cerium), and leachability of depth discrete subsamples for:
  - a. A redox sensitive contaminant, Cr(VI) / Cr(III), for a waste form cured under SRS “field conditions”, and
  - b. Non-redox sensitive contaminants, Na, and  $\text{NO}_3^-$ .
- 3) Evaluate the effect of exposure time to air on leachability of Cr in depth discrete subsamples.
- 4) Evaluate the effect of leaching time interval (18 hours versus 28 days) for crushed depth discrete subsamples.

## **BACKGROUND**

Disposal of long-lived radionuclides and non-radioactive stable redox sensitive contaminants in the near surface environment requires prediction of performance over long times, up to and greater than 1000 years. To develop understanding and conceptual models, characterization of the following properties is necessary:

- 1) Rate of oxidation of redox sensitive contaminants stabilized in a reducing porous cementitious waste forms (up to 60 volume percent pores) and reducing concrete containment structures (about 10 % pores) and
- 2) Boundary conditions for the transport of moisture and gas across material interfaces.

Recent work has addressed the reduction capacity of cementitious materials and to use this information to determine rate of oxidation assuming thermodynamic equilibrium applied to a shrinking core model [Smith and Walton, 1993 and Flach et al., 2009]. Recent experimental studies regarding the persistence of reducing conditions and their impact on contaminant behavior have been conducted to reduce uncertainty in the Performance Assessments (PA) [SRR-CWDA-2009-00017; Kaplan et al. 2005; Kaplan et al. 2008; Pabalan 2009; Painter and Pabalan 2009; Pabalan et al. 2012, Almond et al. 2012]. In addition the effect of oxidation front advancement from surfaces exposed to air has recently been determined for a redox sensitive contaminant, Cr, in the SRS saltstone waste form using Extended X-ray Absorption Fine Structure (EXAFS) and depth discrete samples that were crushed and leached in de-aerated water [Langton et al. 2012a-b; Almond et al. 2012].

Chemically reducing containment structures and waste forms typically contain ground granulated blast furnace slag (GGBFS). This slag has been demonstrated to chemically reduce and stabilize Tc(VII) [Shuh, et al., 1994, Shuh, et al., 2000; Shuh, et al., 2003; Lukens et al. 2005; Icenhower et al. 2010; MMES, 1992, Cantrell and Williams, 2012] and Cr (VI) [Langton and Oji, 1994] and precipitate these species as solid phases with low solubility. A titration technique was also developed to quantify the total reduction capacity of GGBFS and other cementitious solids [Angus and Glasser 1985]. The total reduction capacity has been applied to DOE Performance Assessments (PAs) using a shrinking core model which assumes progression of a completely oxidized front (100 % oxidized) as a function of disposal time (time the waste form is exposed to oxygen in air or oxygen dissolved in water [Lukens et al. 2005; Roberts and Kaplan 2009; Flach, et al., 2009; Savannah River Remediation, LLC, 2009].

## EXPERIMENTAL METHOD

An experimental plan was developed to determine an effective Cr oxidation front and the total reducing capacity of depth discrete samples cut from a cementitious sodium salt waste form, similar to the CBP reference salt waste form [CBP, 2010]. The samples were prepared and allowed to set in a laboratory curing chamber at ambient temperature for 21 days. The lids on the sample containers were opened and the samples were moved to a storage chest located in the SRS Z-Area where they were exposed to “field conditions” for an additional 97 or 281 days. The total ages of the samples were 118 and 302 days at the time subsamples were prepared and characterized. The waste form was spiked with 1000 mg/kg Cr(VI) added as sodium chromate.

**Spiked salt solution:** The ingredients and proportions in the simulated salt solution used to prepare the waste form are provided in Table 1. The compounds were added to the liquid in the following order: Al(NO<sub>3</sub>)<sub>3</sub>·9 H<sub>2</sub>O, NaOH, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaNO<sub>3</sub>, NaNO<sub>2</sub>, and Na<sub>2</sub>CrO<sub>4</sub>.

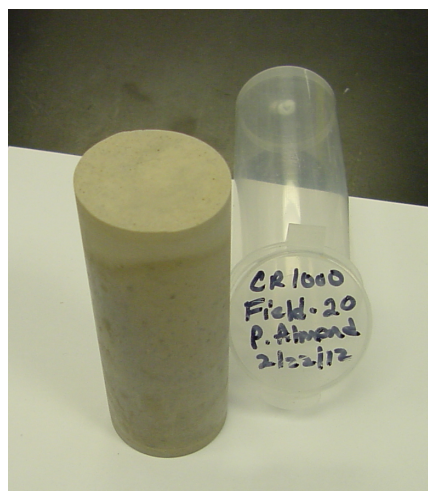
**Table 1. Simulated Salt Solution Composition.**

Compound	Molarity (moles / liter)	Molecular Wt. (grams / mole)	Amount (g / L)
Water	0	18.015	819.50
Al(NO <sub>3</sub> ) <sub>3</sub> ·9 H <sub>2</sub> O	0.110	375.129	41.26
50% by Weight NaOH	1.551	39.998	124.07
Na <sub>2</sub> SO <sub>4</sub>	0.059	142.042	8.32
Na <sub>2</sub> CO <sub>3</sub>	0.148	105.990	15.64
NaNO <sub>3</sub>	2.116	84.995	179.86
NaNO <sub>2</sub>	0.336	68.996	23.20
Total Salt mass	--	--	312.47
Total Na Molarity	4.42	--	--
Density		1.2084	
Wt.% Solids		25.6	

**Waste form Preparation:** The dry ingredients were pre-blended to make a premix containing 10 wt. % Lafarge Type I/II Portland cement, 45 wt. % Holcim Grade 100 blast furnace slag, and 45 wt. % SEFA Class F fly ash. The premixed blend was added to the salt solution and mixed for three minutes after all of the powder was added to the mixing container. The water to premix ratio (w/pm) was 0.60. The ingredients in the simulated waste form are listed in Table 2. The simulated salt solution was spiked with sodium chromate that completely dissolved prior to mixing the solution with the premix reagents. After mixing, the grout slurry was poured into cylindrical molds approximately 1 inch in diameter by 4 inches high and capped. See Figure 1.

**Table 2. Ingredients and Proportions in Samples Prepared for the Leach Method Development.**

Sample Description	Batch Number	Premix (g)	Cr(VI) Spiked Salt Solution		w/pm
			Na <sub>2</sub> CrO <sub>4</sub> (g)	Salt Solution (g)	
Slag Waste Form , 1000 mg / kg Cr	11	830.4	4.6726	669.6	0.60

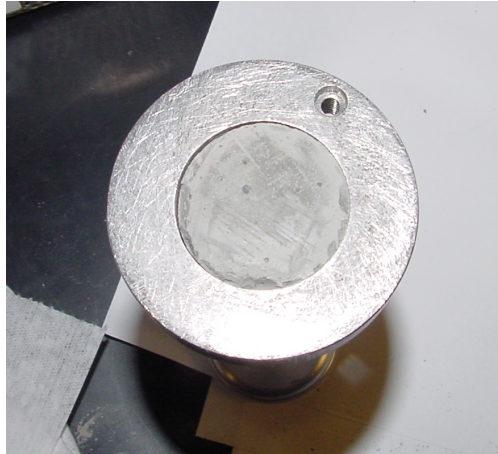


**Figure 1. Slag-based waste form cured in container SRS Z-Area after demolding.**

**Curing Environment:** The capped cylinders were cured at ambient temperature (~ 22° C) and 65% to 70% relative humidity for 21 days before being relocated to a field site [Almond et al. 2012]. Prior to placing the samples in the storage chest, the lids were opened to expose the top surface to air and humidity. The field site was located under the Saltstone Production Facility (SPF) premix silos in Z-area at the Savannah River Site. Field conditions consisted of storage in a closed chest containing water. Temperature and humidity in the chest were recorded. The location provided exposure to outdoor ambient temperature fluctuations while providing some shelter from rain and direct sunlight, in an attempt to simulate the environment in a partially or completely filled disposal unit.

**Leach Sample Preparation:** The objective of the leaching was to evaluate the depth to which chromium solubility was impacted by the air-exposed surface during the time the samples were cured. A sample was retrieved from Z-Area after exposure to air for 302 days and taken to the laboratory. Depth discrete subsamples were collected from the cured slag-based waste form cylinders. Twenty one subsamples were taken from a 302 day cured monolith and subdivided for leaching and reduction capacity measurements.

Each layer removed from the original sample was size reduced (crushed to a powder) with a mortar and pestle to produce a sample for a short term leach test (Modified EPA 1311). (Particle size of the damp powder was not measured.) The size reduced sample was divided; one portion was leached, the other portion was used for the reduction capacity measurements. The sample holder fabricated for the sectioning the cylindrical sample is shown in Figure 2.



**Figure 2. Sample holder utilized to excise depth-discrete samples of a cementitious monolith.**

**Leach Method:** A modified TCLP method (modified EPA Method 1311) was used for leaching the depth discrete samples. Deionized, de-aerated ASTM Type I/II water was used as the leachate. Zero head space leaching containers were used to leach the samples in an oxygen free environment, thereby preventing additional oxidation caused by the leaching method. Filled leach vessels were loaded into a large mouth plastic bottle which was tumbled end-over-end at 30 rpm for approximately  $18 \pm 2$  hours for the standard leaching experiments. A second set of samples was leached in this configuration for 28 days.

**Leachate Analysis:** After tumbling, leachates were filtered using a 0.45 micron membrane 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 (See Attachments 1 and 2). The pH of the leachates was also determined using an IQ Scientific pH meter. Leachate analyses were run in duplicate. Values were averaged and used to calculate the fraction leached (percent leached).

**Fraction Leached Calculation:** 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 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.

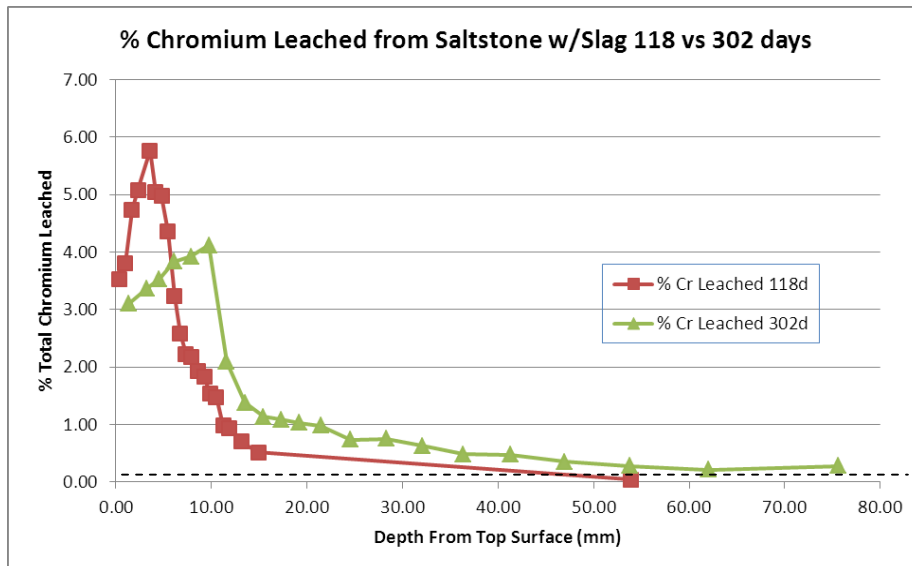
$$\text{Equation 1. } \% \text{ Leached} = 100 * \left( \frac{m_{i\text{-leachate}}}{m_{i\text{-total in solid}}} \right)$$

Where:  $m_{i\text{-leachate}}$  = mass of species i leachate (mg)  
 $m_{i\text{-total in solid}}$  = mass of species i in the waste form (mg).

**Reduction Capacity Measurements:** Reduction capacity measurements were carried out following a redox titration method based on the Ce(IV)-Fe(II) chemical system [Angus and Glasser, 1985, and Roberts and Kaplan, 2009]. The cementitious material in ceric ammonium sulfate 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 reduction capacity of freshly (immediately re-ground before titration) ground blast furnace slag was measured, 831  $\mu\text{eq e}^-/\text{g}$ . The reduction capacity of as received GGBFS was 691  $\mu\text{eq e}^-/\text{g}$ . The freshly re-ground value is in agreement with and benchmarked to the value of 820  $\mu\text{eq e}^-/\text{g}$  previously recommended by Roberts and Kaplan, 2009.

## RESULTS AND DISCUSSION

**Chromium Leaching from Field Samples:** Depth discrete leaching results for two samples, one exposed to air for 118 days [Stefanko, 2012], the other exposed to air for 302 days (this study) are plotted in Figure 3. The results are presented as percent leached from each subsample because the mass of each subsample and the amount of leachate required for filling the leach container varied slightly. The level of detection for Cr in the leachate was 0.01 mg/L which results in a range of detection levels for the subsamples between 0.05 and 0.09 % (depending on the sample size when results are plotted as percent leached). Leachate analyses are provided in Attachments 1 and 2 for 18 hour and 28 day leach intervals.



**Figure 3. Comparison of leachable chromium versus sample depth for 118 and 302 day aged samples. (Dashed line is the Cr detection level.)**

The leading edge of the oxidation front advanced to a depth estimated to be at least 20 mm for the 118 day sample and to a depth of at least 50 mm in the 302 day sample. As previously observed, a spike in the leachability profile near the surface was observed. The spike in percent leached just below the exposed surface was also observed for Na and  $\text{NO}_3^-$  exposed to air for 118 days [Stefanko, et.al, 2012] and 302 days. The observed peaks in percent leached were more pronounced in the samples exposed for 118 days compared to the peaks observed in the samples exposed for 302 days, as shown in Figures 4 and 5, respectively.

The initial spikes in the fractions of these contaminants extracted from the near surface layer were interpreted as being a surface phenomenon, such as, initial settling of the waste form slurry and / or



drying, repeated wetting and drying, and/or carbonation of the cured waste form since the contaminants that are not redox sensitive, e.g., Na and  $\text{NO}_3^-$ , are expected to have about the same fraction leached regardless of location of the sample relative to the top surface [Langton and Stefanko, 2012b].

The nitrate and sodium fractions leached from the bulk material after  $18 \pm 2$  hours were about 15 weight percent of the totals in the sample exposed for 118 days which is about two orders of magnitude higher than the amount of Cr leached from the reduced portion of the bulk samples. The fraction of nitrate leached from the bulk sample exposed for 302 days also averaged about 15 weight percent. However, the amount of sodium leached from the samples cured for 302 days decreased to about 10 weight percent. Aging may result in an increase in the amount of sodium incorporated in one or more low solubility hydrated phases or formation of more or new sodium salt phases.

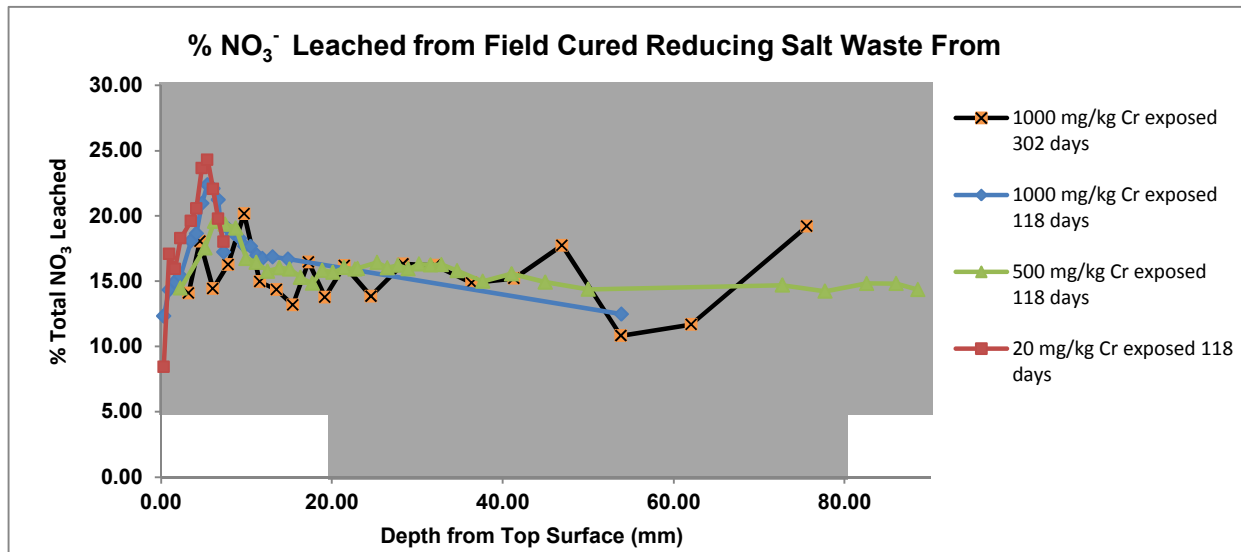


Figure 4. Percent nitrate leached from depth discrete samples exposed to air for 118 and 302 days for samples spiked with various amounts of Cr.

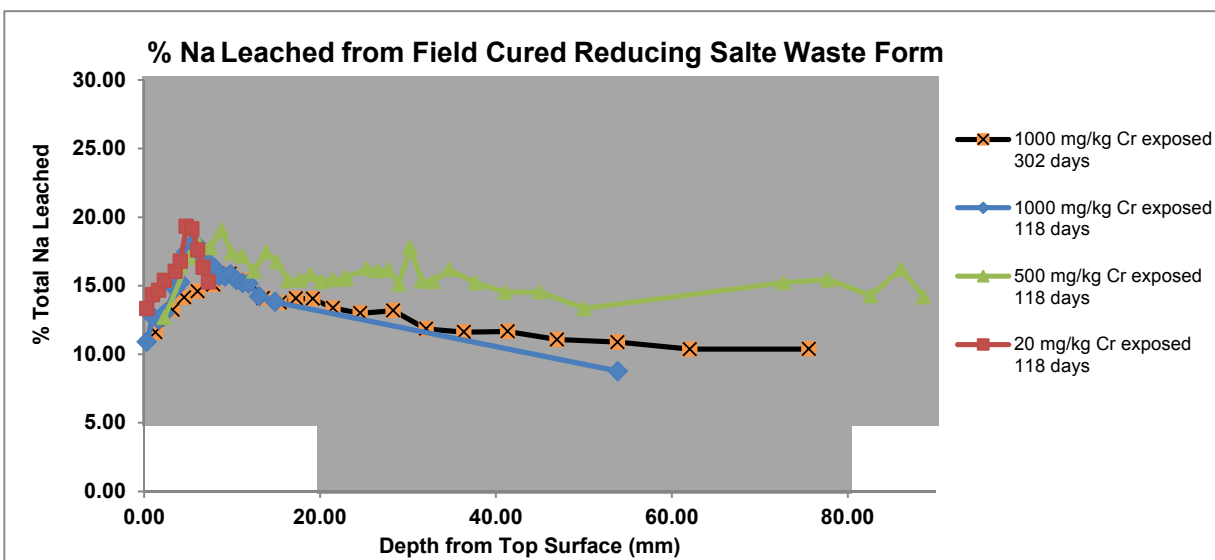


Figure 5. Percent sodium leached from depth discrete samples exposed to air for 118 and 302 days for samples spiked with various amounts of Cr.

**Reduction Capacity:** Reduction capacity to chemically reduce Ce(IV) in solution is a bulk material property and therefore, is only loosely correlated to the ability to reduce specific contaminants or to keep reduced contaminants from oxidizing. Ce(IV) reduction capacities of the individual premix components as well as simulated saltstone samples have previously been measured and are summarized below (Roberts and Kaplan 2009):

- Measured Values [Roberts and Kaplan, 2009]:
  - Ground granulated blast furnace slag from Holcim Inc., Birmingham, AL = 819  $\mu\text{eq e}^-/\text{g}$
  - Class F carbon burnout fly ash from SEFA, Inc., = 299  $\mu\text{eq e}^-/\text{g}$
  - Type I/II Portland cement from LaFarge Inc., Holly Hill, SC = 198  $\mu\text{eq e}^-/\text{g}$
  - Cured simulated saltstone containing 45% Grade 100 slag, 45% Class F fly ash, and 10% Portland cement = 607 to 849  $\mu\text{eq e}^-/\text{g}$  of cured saltstone.<sup>1</sup>
- Calculated values based on results from Roberts and Kaplan, 2009:
  - Premix containing 45% Grade 100 slag (819  $\mu\text{eq e}^-/\text{g}$ ), 45% Class F fly ash (299  $\mu\text{eq e}^-/\text{g}$ ), and 10% Portland cement (198  $\mu\text{eq e}^-/\text{g}$ ) = 523  $\mu\text{eq e}^-/\text{g}$  of premix.
  - Cured simulated saltstone containing 45% Grade 100 slag, 45% Class F fly ash, and 10% Portland cement with a water to premix ratio of 0.600 (saltstone prepared from ingredients above and salt solution containing 74.4 wt. % water) = 290  $\mu\text{eq e}^-/\text{g}$  cured saltstone.

In this study, reduction capacities of the depth discrete slag-based waste form (similar to saltstone tested by Roberts and Kaplan, 2009) sub-samples were measured in the range of 450 to 644  $\mu\text{eq e}^-/\text{g}$ . This range is consistent with previously measured values but is higher than the calculated value for saltstone (290  $\mu\text{eq e}^-/\text{g}$ ) using results reported by Roberts and Kaplan, 2009.<sup>2</sup> Additional work is required to better understand the differences in the Ce(IV) reduction capacity measurements and calculated results for cured cement- and slag-based waste forms and premix blends.

The depth discrete Ce(IV) reduction capacity results from this study indicated a peak near the surface which coincides with the peak in the percent Cr leached from the subsamples. See Figure 6. The maximum percent of Cr (4% of the total) was extracted from the subsample about 10 mm from the exposed surface which indicates that the majority of the chromium was still reduced even near the air/waste form surface. The maximum reduction capacity was also measured from the subsample taken about 10 mm from the exposed surface.<sup>3</sup> Reduction capacity data are provided in Attachment 3.

Between 10 and about 35 to 40 mm, both reduction capacity and percent Cr extracted decrease as illustrated in Figure 6. (It should be noted that the reduction capacity in the first surface layer is similar to that in the bulk sample.) The remaining reduction capacity present in the surface layer and partially oxidized layers may not be accessible or not capable of re-reducing chromate in the presence of oxygen. The detection level for Cr in the leachates is indicated by the dashed line.

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<sup>1</sup> Roberts and Kaplan, 2009, reported reduction capacity as a function of the percent slag in saltstone premix rather than per gram of saltstone sample. They recommended a reduction capacity value for saltstone of 819  $\mu\text{eq e}^-/\text{g}$ .

<sup>2</sup> The calculated premix reduction capacity for a 10:45:45 blend of is 523  $\mu\text{eq e}^-/\text{g}$  based sum of fractions of the individual premix components using reduction capacity values measured by Roberts and Kaplan, 2009. The calculated reduction capacity for the saltstone prepared for this study is 290  $\mu\text{eq e}^-/\text{g}$  based a water to premix = 0.600 and mass fraction of 0.744 water in the salt solution.

<sup>3</sup> Partial drying of the subsamples near the surface would have altered (increased) the mass fraction of reacted premix ingredients in the subsamples. Surface carbonation may also have contributed to the near surface Cr leachability profiles.

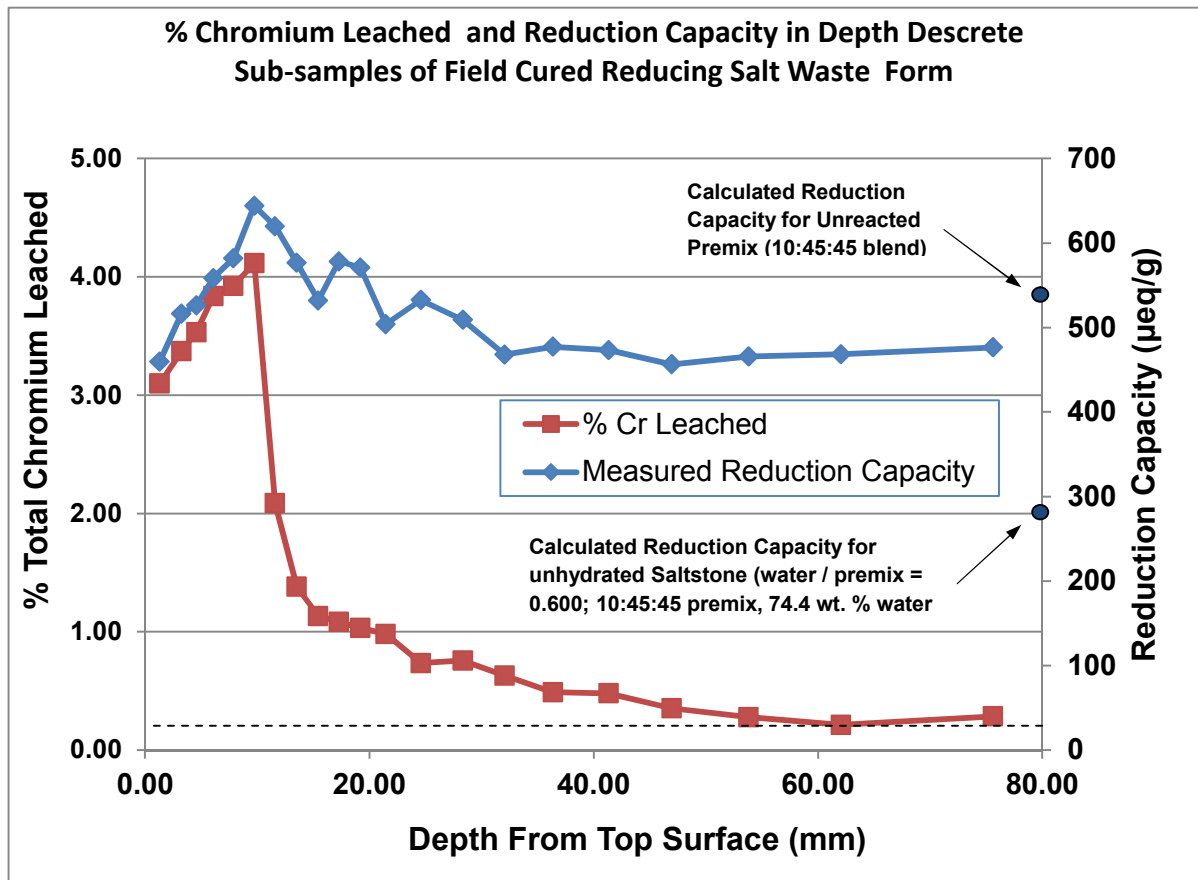
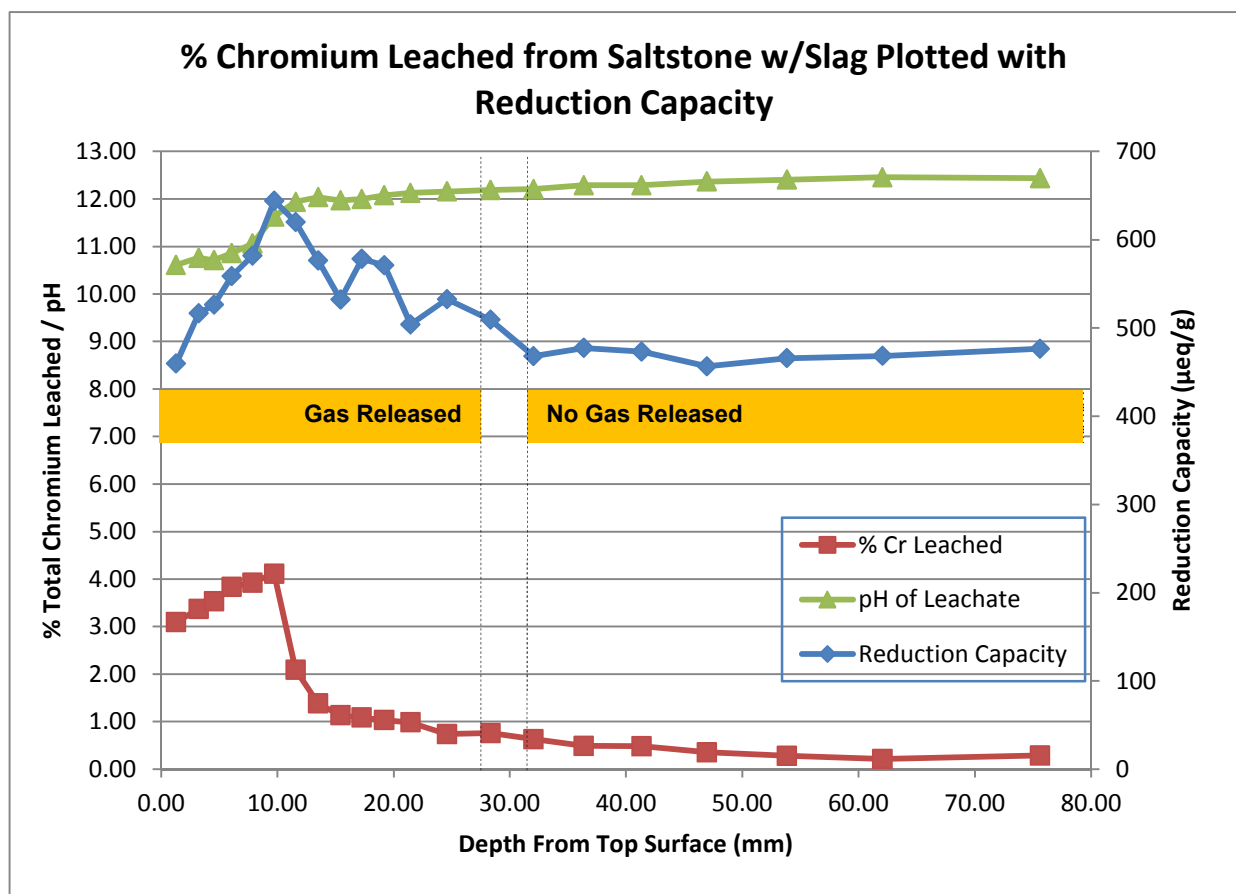


Figure 6. Comparison of leachable chromium, Cr(VI), and reduction capacity for the 302 day field cured sample. (Dashed line represents the detection level).

**Carbonation Front:** Alkalinity, pH, of the depth discrete subsamples was also measured. Results are plotted in Figure 7. The pH of the depth discrete samples increased from about 10.5 in the surface subsample to about 11.8 at 10 mm below the surface and then gradually increased to about 12.4 at about 45 mm. The decrease in pH in the near surface samples was assumed to be the result of ingress of and reaction of the matrix phases with CO<sub>2</sub> in the air. In addition, samples to a depth of 28 mm released gas (i.e., “fizzed” when contacted with sulfuric acid as part of the reduction capacity measurements). The gas was assumed to be CO<sub>2</sub> release as the result of dissolving carbonated phases. Below 32 mm, no gas release (fizz) was detected.



**Figure 7. Comparison of leachable chromium, reduction capacity, and pH in depth discrete subsamples of the waste form cued for 302 days.**

**Effect of Leaching Duration (18 Hours Versus 28 Days):** To determine if the 18 hours leach test extracted only some of the oxidized, leachable chromium, ( $\text{Cr}^{+6}$ ), a portion of each depth discrete subsample was leached for 28 days rather than 18 hours in the zero head containers with deionized, deaerated water according to the modified EPA 1311 test.

**Chromium:** Depth discrete subsamples collected between 10 and 75 mm and leached for 18 hour or 28 days had similar profiles for the percent Cr extracted as a function of distance from the surface as shown in Figure 8. For both leaching durations, oxidation of the Cr was detected to a depth of at least 50 mm.

Subsamples collected between 0 and 10 mm had different Cr profiles. The subsamples leached for 28 days varied and did not show an increase in fraction Cr extracted from the surface to 10 mm. The values suggest a linear trend in the first 10 mm rather than an positive increase seen in the 18 hour leach tests.

The fractions of Cr leached from the surface subsamples (between 0 and 10 mm) leached for 28 days were about 4.2 to 5 weight percents of the total spike concentration. The fractions of Cr leached from the subsamples leached for 18 hours were between about 3 and 4 weight percents of the spike concentration. Possible explanations of the leachate concentration spikes in the 0 to 10 mm profiles include: 1) a portion of the oxidized Cr was somehow protected / isolated from contact with the leaching solution as the result of a surface coating of a carbonate phase and/or other reaction products, or 2) isolation of soluble Cr in very small pores or pore openings, or 3) incorporation of  $\text{Cr}^{+3}$  in moderately soluble phases.

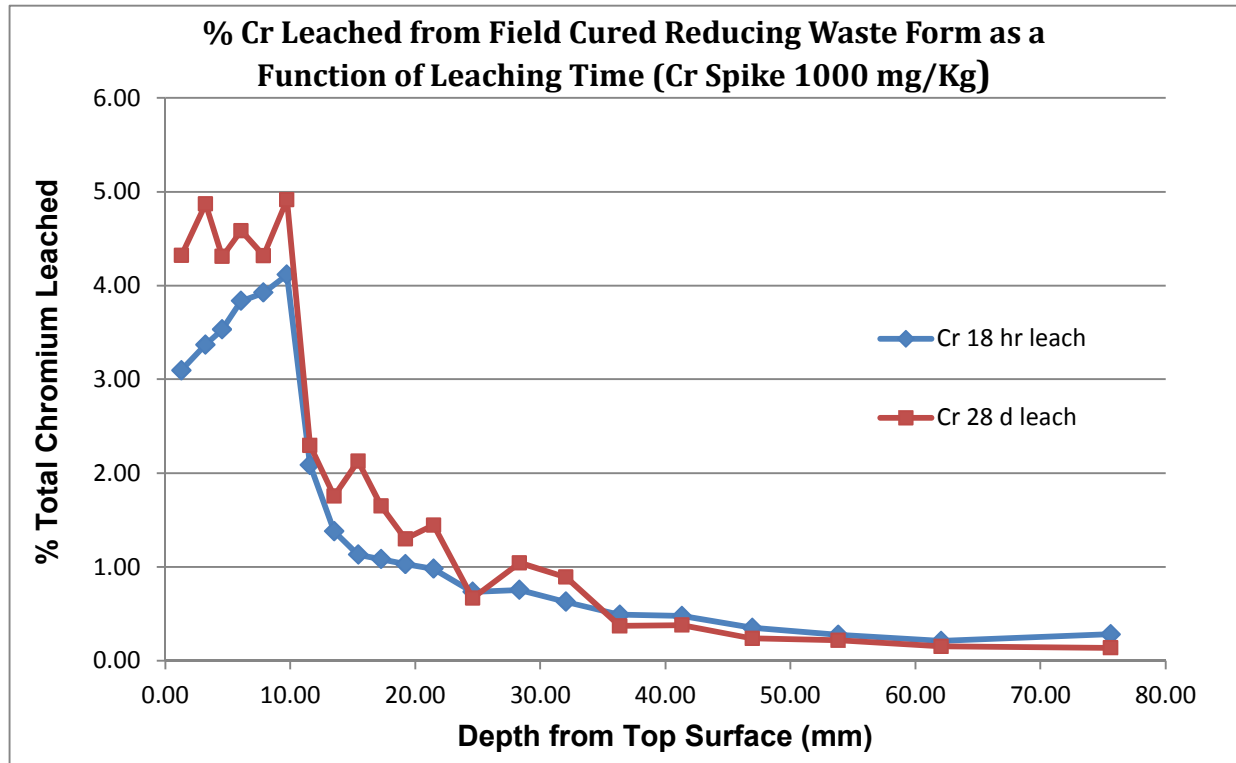


Figure 8. Comparison of chromium leached from 18 hour and 28 day leach experiments.

**Nitrate:** The fractions of nitrate leached from the depth discrete subsamples varied between about 12 and 20 percent of the total in the waste form. The nitrate fractions leached from depth discrete samples leached for 28 days were similar to those measured for samples leached for 18 hours. The 28 day leaching results did not indicate a spike in extracted nitrate between 0 and 10 mm which again suggests that a portion of the soluble species are somewhat isolated in the near surface material. Prolonged exposure of the near surface subsamples to water seems to result in eliminating the near surface spike in nitrate concentrations. Results are plotted in Figure 9.

An interesting observation is that about 12 to 18 weight percents of the nitrate is extracted from each subsample regardless of location in the sample and regardless of the leaching time. The assumption that all of the nitrate is present in the waste form as  $\text{NaNO}_3$  may be incorrect because the sodium nitrate is 100 weight percent soluble in deionized water. A significant portion of the nitrate may be somewhat less soluble / leachable (i.e., present in AFm phases<sup>4</sup> or isolated in small pores).

<sup>4</sup> AFm cement phases contain calcium hydroxide and can be described as  $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$  (1) single charge anion or ( $\frac{1}{2}$ ) double charged anion. They have a layer structures based on portlandite in which 1 of 3  $\text{Ca}^{2+}$  ions are replaced by  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ . The charge is balanced by interlayers containing the anions and water.

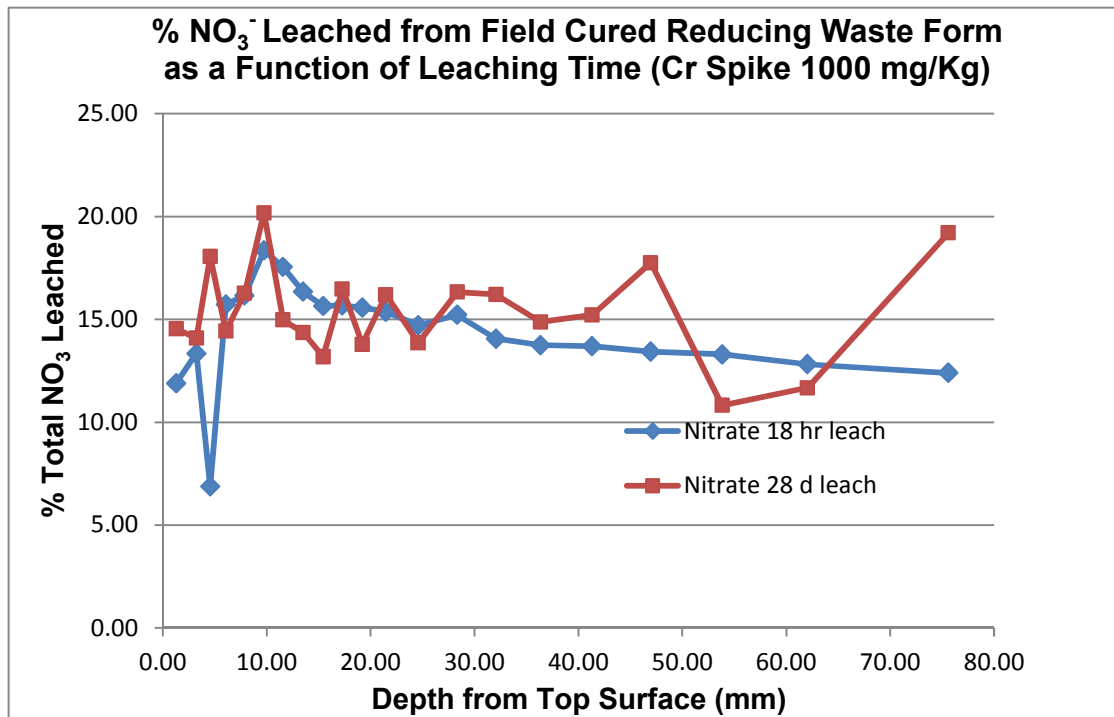


Figure 9. Comparison of nitrate leached from 18 hour and 28 day leach experiments.

**Sodium:** The extractable sodium appears to have increased from about 12-14 % for the 18 hours leach period to about 16 to 18 % of the total present for the 28 day leach period. Results are plotted in Figure 10. The higher fractions leached for the longer leach interval suggest that some of the sodium is present as soluble salt and some (possibly the majority) is present as less soluble precipitates and/or isolated in pores with limited access.

The near surface increase in the fraction leached between 0 and 10 mm for subsamples leached for 18 hours was not apparent for subsamples leached for 28 days. The subsamples leached for 28 days showed more variability than those leached for 18 hours.

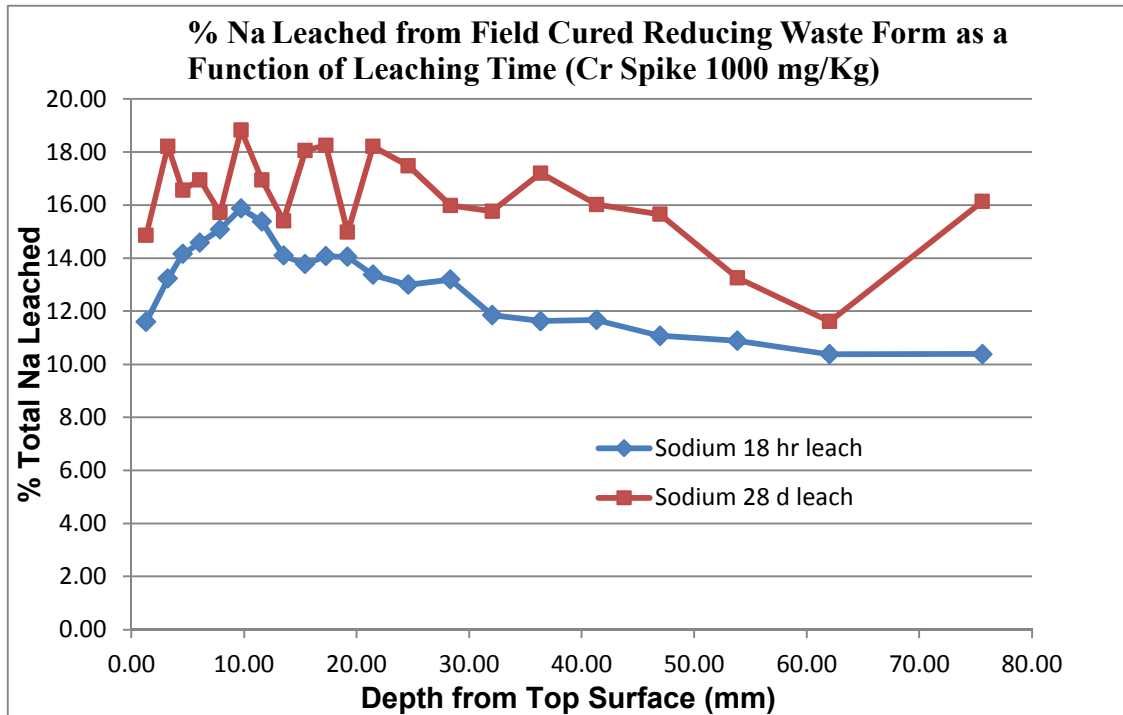


Figure 10. Comparison of sodium leached from 18 hour and 28 day leach experiments.

## CONCLUSIONS

**Depth discrete sampling:** Leaching crushed depth discrete subsamples appears to be a suitable method for evaluating the effects of curing and exposure on contaminant chemistry as the result of exposure to environmental conditions. Moisture content, carbonate extracted by dilute acid and mineralogy are additional parameters that can be quantified from the depth discrete subsamples to support conceptual model for oxidation and carbonation rates and consequences.

**Leaching time:** The longer leach time extracted more Cr from the top 10 mm of the sample which suggests restricted access of leachate to these species which is overcome by longer contact time with water. Below 10 mm, leaching time made little difference for Cr extraction from crushed samples.

The longer leach time did not have much of an effect on the nitrate fraction leached from subsamples collected below about 10 mm from the surface. Values ranged from 12 to 18 percent of the total. Subsamples between 0 and 10 mm and leached for 18 hours showed a spike that peaked at about 10 mm. This profile was not observed for the samples leached for 28 days.

The longer leach time resulted in a higher fraction of Na extracted for samples collected at all distances from the surface below 10 mm.

More data are required to confirm and interpret the observations above. However, increasing the leaching time by ~ 37 times did not result in large changes in the fractions of Na,  $\text{NO}_3^-$  and Cr leached as a function of distance from the exposed surface.

**Reduction capacity:** Bulk reduction capacity measurements on all subsamples did not correlate with the fraction of redox sensitive contaminant leached in de-aerated deionized leachate. The use of reduction capacity as an indicator of long-term performance requires further investigation because the system may not respond to environmental conditions in an equilibrium manner.

Exposure to oxygen (air or oxygen dissolved in water) results in the release of chromium through oxidation of Cr(III) to highly soluble chromate, Cr(VI). Residual reduction capacity in the oxidized region of the test samples indicates that the remaining reduction capacity does not appear to be effective in re-reducing Cr(VI) in the presence of oxygen.

**Exposure time:** Increasing the exposure time from 118 to 302 days had an effect on the fractions of Cr and Na leached from depth discrete subsamples as a function of distance from the exposed surface. The Cr profile below about 10 mm appears roughly exponential whereas the profile for  $\text{NO}_3^-$  and Na are roughly linear with a slight negative slope. Additional exposure times are required to identify and quantify rates of oxygen and carbonate ingress.

**Surface and Near Surface Leaching Profiles:** The top ~ 10 mm of the samples responded to leaching differently than subsamples collected from 20 to 80 mm below the surface. Further investigation is required to determine whether this profile is due to sample inhomogeneity related to sample preparation (settling and bleed) and / or to exposure to air (drying, carbonation).

**Fractions Leached:** Nitrate is generally assumed to be completely soluble and sodium is assumed to be highly soluble in reducing cementitious waste forms. Sodium is known to form soluble salts and substitute for other cations in low solubility solid phases in cementitious systems. Results from the depth discrete samples indicate that less than 20 weight percent of the nitrate and sodium was extracted from crushed samples during 28 days of leaching. Additional work is required to identify the speciation, mineralogy and leachability of these contaminants in salt waste forms.

**Oxidation Front:** The oxidation front appears to have advanced to a depth of at least 50 mm in 302 days from the surface as indicated by oxidation of Cr(III) to soluble Cr(VI) which was detected in depth discrete subsamples.

**Carbonation Front:** Although the objective of this effort did not include measurement of a carbonation front, based on visible gas evolution during the redox potential measurements, the carbonation front appears to have advanced at least to a depth of 28 mm in 302 days.

**Measurement error:** Measurement error was not evaluated in this study which was intended to be a scoping study for method development and further work on oxidation and carbonation fronts in cementitious waste forms and barrier materials.

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Cementitious Barriers Partnership  
Effect of Oxidation on Chromium Leaching and Redox Capacity of Slag-Containing Waste Forms

**ATTACHMENT 1. Analytical results for leachate compositions for 18 hour leach.**

Sample ID	Lab ID	Avg Depth (mm)	As	Ce	Cr	Na	Se	V
SF 100A (A)	13-0001	1.29	0.159	0.024	0.569	525	0.252	0.309
SF 100A (B)	13-0001		0.119	0.019	0.568	524	0.119	0.279
SF 101A (A)	13-0002	3.24	0.078	<0.010	0.409	400	<0.100	0.192
SF 101A (B)	13-0002		0.071	<0.010	0.410	392	<0.100	0.190
SF 102A (A)	13-0003	4.56	0.067	<0.010	0.374	369	<0.100	0.166
SF 102A (B)	13-0003		0.060	<0.010	0.378	374	<0.100	0.166
SF 103A (A)	13-0004	6.08	0.106	0.021	0.761	716	0.118	0.298
SF 103A (B)	13-0004		0.100	0.021	0.757	706	0.103	0.296
SF 104A (A)	13-0005	7.87	0.115	0.031	0.912	859	0.122	0.366
SF 104A (B)	13-0005		0.116	0.032	0.908	866	0.127	0.365
SF 105A (A)	13-0006	9.74	0.142	0.037	0.919	871	0.210	0.391
SF 105A (B)	13-0006		0.117	0.032	0.914	872	0.151	0.372
SF 106A (A)	13-0007	11.58	0.053	0.014	0.462	839	0.124	0.251
SF 106A (B)	13-0007		0.043	0.014	0.462	840	0.114	0.249
SF 107A (A)	13-0008	13.52	0.046	0.016	0.356	910	0.115	0.264
SF 107A (B)	13-0008		0.045	0.017	0.360	892	0.113	0.265
SF 108A (A)	13-0009	15.44	0.037	<0.010	0.247	748	<0.100	0.215
SF 108A (B)	13-0009		0.034	<0.010	0.252	748	<0.100	0.218
SF 109A (A)	13-0010	17.28	0.025	<0.010	0.223	703	<0.100	0.225
SF 109A (B)	13-0010		0.024	<0.010	0.217	704	<0.100	0.220
SF 110A (A)	13-0011	19.21	0.034	0.012	0.253	842	<0.100	0.241
SF 110A (B)	13-0011		0.034	0.011	0.247	837	<0.100	0.236
SF 111A (A)	13-0012	21.47	0.043	0.016	0.286	972	0.100	0.272
SF 111A (B)	13-0012		0.043	0.015	0.294	974	0.099	0.277
SF 112A (A)	13-0013	24.59	0.050	0.032	0.350	1520	0.142	0.385
SF 112A (B)	13-0013		0.052	0.034	0.348	1520	0.137	0.389
SF 113A (A)	13-0014	28.34	0.047	0.025	0.309	1310	0.113	0.340
SF 113A (B)	13-0014		0.048	0.026	0.305	1330	0.113	0.335
SF 114A (A)	13-0015	32.06	0.042	0.017	0.271	1280	<0.100	0.273
SF 114A (B)	13-0015		0.038	0.017	0.277	1260	<0.100	0.277
SF 115A (A)	13-0016	36.37	0.057	0.029	0.299	1730	0.106	0.354
SF 115A (B)	13-0016		0.058	0.028	0.295	1730	0.109	0.354
SF 116A (A)	13-0017	41.33	0.062	0.030	0.309	1760	0.112	0.371
SF 116A (B)	13-0017		0.058	0.030	0.297	1880	0.106	0.366
SF 117A (A)	13-0018	46.96	0.117	0.048	0.299	2360	0.212	0.479
SF 117A (B)	13-0018		0.089	0.048	0.310	2350	0.177	0.473
SF 118A (A)	13-0019	53.83	0.096	0.052	0.288	2800	0.196	0.509
SF 118A (B)	13-0019		0.096	0.054	0.296	2840	0.195	0.520
SF 119A (A)	13-0020	62.05	0.119	0.067	0.296	3580	0.250	0.614
SF 119A (B)	13-0020		0.118	0.064	0.297	3590	0.247	0.607
SF 120A (A)	13-0021	75.61	0.098	0.055	0.361	3190	0.217	0.546
SF 120A (B)	13-0021		0.100	0.056	0.355	3270	0.210	0.541
SF 130A (A)	13-0022		<0.010	<0.010	<0.010	<0.100	<0.010	<0.010
SF 130A (B)	13-0022		<0.010	<0.010	<0.010	<0.100	<0.010	<0.010

Cementitious Barriers Partnership  
Effect of Oxidation on Chromium Leaching and Redox Capacity of Slag-Containing Waste Forms




Process Science Analytical Laboratory  
Customer: David Stefanko and Chris Langton  
Date: 1/10/13  
Sample ID: SF 100A - SF 120A, SF 130A  
Lab ID: 13-0001-0024  
Units: mg/L

Sample ID	Lab ID	NO2	NO3	SO4	pH
SF 100A (A)	13-0001	87.0	803	65.0	10.61
SF 100A (B)	13-0001	86.9	804	64.7	
SF 101A (A)	13-0002	64.5	596	47.8	10.76
SF 101A (B)	13-0002	64.4	597	47.2	
SF 102A (A)	13-0003	61.8	269	45.4	10.71
SF 102A (B)	13-0003	61.7	269	44.7	
SF 103A (A)	13-0004	124	1140	95.1	10.86
SF 103A (B)	13-0004	124	1150	94.7	
SF 104A (A)	13-0005	147	1380	117	11.06
SF 104A (B)	13-0005	148	1380	117	
SF 105A (A)	13-0006	160	1510	126	11.63
SF 105A (B)	13-0006	160	1500	125	
SF 106A (A)	13-0007	151	1430	106	11.94
SF 106A (B)	13-0007	151	1430	106	
SF 107A (A)	13-0008	159	1560	113	12.04
SF 107A (B)	13-0008	159	1560	113	
SF 108A (A)	13-0009	130	1270	89.9	11.97
SF 108A (B)	13-0009	130	1270	89.2	
SF 109A (A)	13-0010	120	1170	82.7	12.00
SF 109A (B)	13-0010	119	1170	82.4	
SF 110A (A)	13-0011	140	1390	98.1	12.08
SF 110A (B)	13-0011	140	1390	97.5	
SF 111A (A)	13-0012	165	1670	117	12.13
SF 111A (B)	13-0012	166	1670	117	
SF 112A (A)	13-0013	246	2570	182	12.16
SF 112A (B)	13-0013	247	2570	182	
SF 113A (A)	13-0014	221	2270	159	12.19
SF 113A (B)	13-0014	221	2280	159	
SF 114A (A)	13-0015	220	2250	146	12.21
SF 114A (B)	13-0015	220	2250	145	
SF 115A (A)	13-0016	291	3050	196	12.29
SF 115A (B)	13-0016	292	3060	196	
SF 116A (A)	13-0017	303	3190	205	12.29
SF 116A (B)	13-0017	303	3190	205	
SF 117A (A)	13-0018	394	4260	272	12.37
SF 117A (B)	13-0018	394	4270	272	
SF 118A (A)	13-0019	466	5140	325	12.41
SF 118A (B)	13-0019	467	5150	325	
SF 119A (A)	13-0020	564	6610	410	12.46
SF 119A (B)	13-0020	585	6620	410	
SF 120A (A)	13-0021	516	5760	358	12.44
SF 120A (B)	13-0021	517	5760	358	
SF 130A (A)	13-0022	<10.0	<10.0	<10.0	10.03
SF 130A (B)	13-0022	<10.0	<10.0	<10.0	

Cementitious Barriers Partnership  
Effect of Oxidation on Chromium Leaching and Redox Capacity of Slag-Containing Waste Forms

**ATTACHMENT 2. Analytical results for leachate compositions for 28 day leach.**

								
Process Science Analytical Laboratory								
Customer: Philip Almond and Chris Langton								
Date: 2/5/13								
Sample ID: SF 100B - SF 120B, SF 125B								
Lab ID: 13-0215-0236								
Units: mg/L								
Sample ID	Lab ID	Avg Depth (mm)	Al	As	Ba	Ca	Ce	Cr
SF 100B (A)	13-0215	1.29	0.601	0.115	<0.010	7.40	0.037	0.795
SF 100B (B)	13-0215		0.603	0.108	<0.010	7.54	0.041	0.790
SF 101B (A)	13-0216	3.24	0.228	0.051	<0.010	16.2	0.024	0.596
SF 101B (B)	13-0216		0.231	0.056	<0.010	16.2	0.023	0.588
SF 102B (A)	13-0217	4.56	0.168	0.030	<0.010	19.8	0.012	0.459
SF 102B (B)	13-0217		0.170	0.034	<0.010	20.1	0.012	0.459
SF 103B (A)	13-0218	6.08	0.160	0.085	<0.010	15.6	0.035	0.903
SF 103B (B)	13-0218		0.263	0.083	<0.010	16.5	0.034	0.910
SF 104B (A)	13-0219	7.87	0.202	0.094	<0.010	17.2	0.043	1.019
SF 104B (B)	13-0219		0.208	0.086	<0.010	17.9	0.044	0.985
SF 105B (A)	13-0220	9.74	0.686	0.066	<0.010	20.6	0.043	1.093
SF 105B (B)	13-0220		0.777	0.076	<0.010	21.0	0.047	1.096
SF 106B (A)	13-0221	11.58	2.86	<0.010	<0.010	24.2	0.023	0.502
SF 106B (B)	13-0221		2.88	<0.010	<0.010	24.3	0.022	0.515
SF 107B (A)	13-0222	13.52	3.74	<0.010	<0.010	24.4	0.022	0.433
SF 107B (B)	13-0222		3.52	<0.010	<0.010	23.7	0.018	0.479
SF 108B (A)	13-0223	15.44	3.64	<0.010	<0.010	24.4	0.016	0.481
SF 108B (B)	13-0223		4.46	<0.010	<0.010	23.9	0.024	0.458
SF 109B (A)	13-0224	17.28	3.99	<0.010	<0.010	24.0	0.017	0.337
SF 109B (B)	13-0224		3.97	<0.010	<0.010	23.9	0.016	0.333
SF 110B (A)	13-0225	19.21	4.05	<0.010	<0.010	24.5	0.016	0.306
SF 110B (B)	13-0225		4.43	<0.010	<0.010	24.7	0.018	0.325
SF 111B (A)	13-0226	21.47	6.03	<0.010	<0.010	22.1	0.035	0.427
SF 111B (B)	13-0226		6.25	<0.010	<0.010	21.7	0.034	0.428
SF 112B (A)	13-0227	24.59	8.08	0.016	<0.010	20.1	0.055	0.313
SF 112B (B)	13-0227		8.08	0.015	<0.010	20.3	0.056	0.321
SF 113B (A)	13-0228	28.34	7.07	0.014	<0.010	19.4	0.045	0.422
SF 113B (B)	13-0228		7.06	0.010	<0.010	19.4	0.045	0.427
SF 114B (A)	13-0229	32.06	8.08	<0.010	<0.010	16.2	0.039	0.396
SF 114B (B)	13-0229		8.07	<0.010	<0.010	16.3	0.039	0.381
SF 115B (A)	13-0230	36.37	10.8	0.042	<0.010	14.5	0.071	0.219
SF 115B (B)	13-0230		11.1	0.043	<0.010	14.9	0.075	0.231
SF 116B (A)	13-0231	41.33	10.4	0.044	<0.010	15.0	0.070	0.241
SF 116B (B)	13-0231		10.7	0.042	<0.010	15.1	0.065	0.241
SF 117B (A)	13-0232	46.96	13.5	0.079	<0.010	15.0	0.092	0.196
SF 117B (B)	13-0232		12.6	0.086	<0.010	14.7	0.072	0.217
SF 118B (A)	13-0233	53.83	11.9	0.100	<0.010	14.6	0.065	0.221
SF 118B (B)	13-0233		11.0	0.114	<0.010	14.8	0.057	0.237
SF 119B (A)	13-0234	62.05	16.7	0.115	<0.010	14.7	0.106	0.214
SF 119B (B)	13-0234		16.8	0.116	<0.010	14.7	0.103	0.216
SF 120B (A)	13-0235	75.61	18.2	0.137	<0.010	14.6	0.107	0.160
SF 120B (B)	13-0235		16.9	0.162	<0.010	14.7	0.092	0.188
SF 125B (A)	13-0236		<0.100	<0.100	<0.010	<0.100	<0.010	<0.010
SF 125B (B)	13-0236		<0.100	<0.100	<0.010	<0.100	<0.010	<0.010

Cementitious Barriers Partnership  
Effect of Oxidation on Chromium Leaching and Redox Capacity of Slag-Containing Waste Forms



Process Science Analytical Laboratory  
Customer: Philip Almond and Chris Langton

Date: 2/5/13

Sample ID: SF 100B - SF 120B, SF 125B

Lab ID: 13-0215-0236

Units: mg/L

Sample ID	Lab ID	Cu	Fe	Ga	K	Mg	Mn
SF 100B (A)	13-0215	<0.100	<0.010	<0.010	24.1	<0.010	<0.010
SF 100B (B)	13-0215	<0.100	<0.010	<0.010	23.9	<0.010	<0.010
SF 101B (A)	13-0216	<0.100	<0.010	<0.010	22.0	<0.010	<0.010
SF 101B (B)	13-0216	<0.100	<0.010	<0.010	21.8	<0.010	<0.010
SF 102B (A)	13-0217	<0.100	<0.010	<0.010	18.1	<0.010	<0.010
SF 102B (B)	13-0217	<0.100	<0.010	<0.010	18.3	<0.010	<0.010
SF 103B (A)	13-0218	<0.100	<0.010	<0.010	31.0	<0.010	<0.010
SF 103B (B)	13-0218	<0.100	<0.010	<0.010	32.8	<0.010	<0.010
SF 104B (A)	13-0219	<0.100	<0.010	<0.010	34.4	<0.010	<0.010
SF 104B (B)	13-0219	<0.100	<0.010	<0.010	35.8	<0.010	<0.010
SF 105B (A)	13-0220	<0.100	<0.010	<0.010	47.7	<0.010	<0.010
SF 105B (B)	13-0220	<0.100	<0.010	<0.010	47.9	<0.010	<0.010
SF 106B (A)	13-0221	<0.100	<0.010	0.011	57.2	<0.010	<0.010
SF 106B (B)	13-0221	<0.100	<0.010	0.012	57.5	<0.010	<0.010
SF 107B (A)	13-0222	<0.100	<0.010	0.014	67.2	<0.010	<0.010
SF 107B (B)	13-0222	<0.100	<0.010	0.014	65.1	<0.010	<0.010
SF 108B (A)	13-0223	<0.100	<0.010	0.016	70.3	<0.010	<0.010
SF 108B (B)	13-0223	<0.100	<0.010	0.025	68.8	<0.010	<0.010
SF 109B (A)	13-0224	<0.100	<0.010	0.016	65.1	<0.010	<0.010
SF 109B (B)	13-0224	<0.100	<0.010	0.016	65.2	<0.010	<0.010
SF 110B (A)	13-0225	<0.100	<0.010	0.015	65.6	<0.010	<0.010
SF 110B (B)	13-0225	<0.100	<0.010	0.017	66.4	<0.010	<0.010
SF 111B (A)	13-0226	<0.100	<0.010	0.026	97.3	<0.010	<0.010
SF 111B (B)	13-0226	<0.100	<0.010	0.029	95.8	<0.010	<0.010
SF 112B (A)	13-0227	<0.100	<0.010	0.041	146	<0.010	<0.010
SF 112B (B)	13-0227	<0.100	<0.010	0.042	150	<0.010	<0.010
SF 113B (A)	13-0228	<0.100	<0.010	0.034	130	<0.010	<0.010
SF 113B (B)	13-0228	<0.100	<0.010	0.035	127	<0.010	<0.010
SF 114B (A)	13-0229	<0.100	<0.010	0.034	131	<0.010	<0.010
SF 114B (B)	13-0229	<0.100	<0.010	0.032	127	<0.010	<0.010
SF 115B (A)	13-0230	<0.100	<0.010	0.052	203	<0.010	<0.010
SF 115B (B)	13-0230	<0.100	<0.010	0.054	206	<0.010	<0.010
SF 116B (A)	13-0231	<0.100	<0.010	0.051	199	<0.010	<0.010
SF 116B (B)	13-0231	<0.100	<0.010	0.051	195	<0.010	<0.010
SF 117B (A)	13-0232	<0.100	<0.010	0.073	259	<0.010	<0.010
SF 117B (B)	13-0232	<0.100	<0.010	0.070	256	<0.010	<0.010
SF 118B (A)	13-0233	<0.100	<0.010	0.071	273	<0.010	<0.010
SF 118B (B)	13-0233	<0.100	<0.010	0.066	263	<0.010	<0.010
SF 119B (A)	13-0234	<0.100	<0.010	0.096	310	<0.010	<0.010
SF 119B (B)	13-0234	<0.100	<0.010	0.093	310	<0.010	<0.010
SF 120B (A)	13-0235	<0.100	<0.010	0.107	375	<0.010	<0.010
SF 120B (B)	13-0235	<0.100	<0.010	0.107	402	<0.010	<0.010
SF 125B (A)	13-0236	<0.100	<0.010	<0.010	0.184	<0.010	<0.010
SF 125B (B)	13-0236	<0.100	<0.010	<0.010	0.180	<0.010	<0.010

Cementitious Barriers Partnership  
Effect of Oxidation on Chromium Leaching and Redox Capacity of Slag-Containing Waste Forms



Process Science Analytical Laboratory  
Customer: Philip Almond and Chris Langton

Date: 2/5/13

Sample ID: SF 100B - SF 120B, SF 125B

Lab ID: 13-0215-0236

Units: mg/L

Sample ID	Lab ID	Mo	Na	Rb	S	Se	Si
SF 100B (A)	13-0215	0.091	674	0.336	50.1	<0.010	106
SF 100B (B)	13-0215	0.079	670	0.339	50.2	<0.010	105
SF 101B (A)	13-0216	0.062	551	0.320	39.9	<0.010	101
SF 101B (B)	13-0216	0.062	540	0.320	39.8	<0.010	101
SF 102B (A)	13-0217	0.051	435	0.298	32.2	<0.010	85.0
SF 102B (B)	13-0217	0.050	434	0.299	32.2	<0.010	85.8
SF 103B (A)	13-0218	0.093	821	0.400	63.5	0.014	124
SF 103B (B)	13-0218	0.093	832	0.402	64.3	0.013	127
SF 104B (A)	13-0219	0.103	897	0.439	74.3	0.026	127
SF 104B (B)	13-0219	0.101	900	0.457	72.9	0.025	129
SF 105B (A)	13-0220	0.117	1027	0.577	90.5	0.039	91.9
SF 105B (B)	13-0220	0.118	1042	0.581	90.9	0.041	91.9
SF 106B (A)	13-0221	0.090	927	0.783	70.0	0.019	40.8
SF 106B (B)	13-0221	0.092	924	0.780	71.9	0.020	41.0
SF 107B (A)	13-0222	0.096	977	0.915	74.8	0.019	36.1
SF 107B (B)	13-0222	0.102	993	0.853	79.7	0.029	35.4
SF 108B (A)	13-0223	0.108	985	0.849	85.0	0.042	35.1
SF 108B (B)	13-0223	0.130	977	1.02	87.0	0.058	34.8
SF 109B (A)	13-0224	0.096	905	0.890	69.3	0.025	33.4
SF 109B (B)	13-0224	0.093	920	0.890	68.4	0.016	33.3
SF 110B (A)	13-0225	0.089	891	0.897	65.4	0.012	33.0
SF 110B (B)	13-0225	0.092	899	0.946	68.9	0.019	33.1
SF 111B (A)	13-0226	0.130	1300	1.41	96	0.064	35.8
SF 111B (B)	13-0226	0.135	1350	1.47	95	0.062	35.3
SF 112B (A)	13-0227	0.183	2050	2.16	137	0.130	39.0
SF 112B (B)	13-0227	0.184	2040	2.15	136	0.135	39.4
SF 113B (A)	13-0228	0.157	1600	1.79	117	0.097	39.0
SF 113B (B)	13-0228	0.156	1600	1.80	118	0.100	39.4
SF 114B (A)	13-0229	0.164	1690	1.93	114	0.075	41.0
SF 114B (B)	13-0229	0.159	1690	1.95	113	0.073	41.2
SF 115B (A)	13-0230	0.239	2590	3.08	180	0.154	44.2
SF 115B (B)	13-0230	0.250	2530	3.14	177	0.171	44.7
SF 116B (A)	13-0231	0.233	2490	2.85	172	0.152	44.2
SF 116B (B)	13-0231	0.238	2510	2.93	174	0.160	44.5
SF 117B (A)	13-0232	0.338	3300	4.15	228	0.259	43.5
SF 117B (B)	13-0232	0.361	3360	3.77	228	0.279	43.2
SF 118B (A)	13-0233	0.412	3450	3.58	242	0.306	42.5
SF 118B (B)	13-0233	0.433	3420	3.24	241	0.322	42.7
SF 119B (A)	13-0234	0.422	3990	6.02	286	0.359	42.3
SF 119B (B)	13-0234	0.423	4030	5.77	285	0.341	42.3
SF 120B (A)	13-0235	0.520	4990	7.04	358	0.367	38.8
SF 120B (B)	13-0235	0.592	5050	6.30	350	0.416	39.2
SF 125B (A)	13-0236	<0.010	0.913	0.185	<0.100	<0.010	2.34
SF 125B (B)	13-0236	<0.010	0.938	0.186	<0.100	<0.010	2.40

Cementitious Barriers Partnership  
Effect of Oxidation on Chromium Leaching and Redox Capacity of Slag-Containing Waste Forms



Process Science Analytical Laboratory  
Customer: Philip Almond and Chris Langton

Date: 2/5/13

Sample ID: SF 100B - SF 120B, SF 125B

Lab ID: 13-0215-0236

Units: mg/L

<u>Sample ID</u>	<u>Lab ID</u>	<u>Sn</u>	<u>Sr</u>	<u>V</u>	<u>W</u>	<u>Zn</u>
SF 100B (A)	13-0215	0.274	0.118	0.437	0.216	<0.010
SF 100B (B)	13-0215	0.272	0.119	0.432	0.123	<0.010
SF 101B (A)	13-0216	0.200	0.135	0.311	0.112	<0.010
SF 101B (B)	13-0216	0.197	0.135	0.309	0.110	<0.010
SF 102B (A)	13-0217	0.157	0.144	0.227	0.101	<0.010
SF 102B (B)	13-0217	0.153	0.144	0.226	0.103	<0.010
SF 103B (A)	13-0218	0.307	0.157	0.403	0.111	<0.010
SF 103B (B)	13-0218	0.313	0.157	0.408	0.113	<0.010
SF 104B (A)	13-0219	0.350	0.172	0.447	0.115	<0.010
SF 104B (B)	13-0219	0.329	0.177	0.437	0.116	<0.010
SF 105B (A)	13-0220	0.379	0.242	0.456	0.120	<0.010
SF 105B (B)	13-0220	0.380	0.242	0.456	0.117	<0.010
SF 106B (A)	13-0221	0.176	0.404	0.299	0.114	<0.010
SF 106B (B)	13-0221	0.184	0.406	0.305	0.114	<0.010
SF 107B (A)	13-0222	0.157	0.449	0.310	0.113	<0.010
SF 107B (B)	13-0222	0.182	0.420	0.325	0.119	<0.010
SF 108B (A)	13-0223	0.187	0.417	0.337	0.120	<0.010
SF 108B (B)	13-0223	0.161	0.513	0.350	0.237	<0.010
SF 109B (A)	13-0224	0.116	0.472	0.285	0.133	<0.010
SF 109B (B)	13-0224	0.114	0.469	0.283	0.122	<0.010
SF 110B (A)	13-0225	0.105	0.476	0.270	0.120	<0.010
SF 110B (B)	13-0225	0.110	0.497	0.282	0.120	<0.010
SF 111B (A)	13-0226	0.141	0.509	0.388	0.128	<0.010
SF 111B (B)	13-0226	0.140	0.531	0.394	0.130	<0.010
SF 112B (A)	13-0227	0.103	0.554	0.556	0.139	<0.010
SF 112B (B)	13-0227	0.105	0.556	0.559	0.143	<0.010
SF 113B (A)	13-0228	0.139	0.515	0.473	0.132	<0.010
SF 113B (B)	13-0228	0.137	0.518	0.478	0.133	<0.010
SF 114B (A)	13-0229	0.127	0.498	0.425	0.132	<0.010
SF 114B (B)	13-0229	0.128	0.500	0.416	0.136	<0.010
SF 115B (A)	13-0230	0.072	0.553	0.623	0.154	<0.010
SF 115B (B)	13-0230	0.071	0.559	0.640	0.158	<0.010
SF 116B (A)	13-0231	0.077	0.539	0.618	0.151	<0.010
SF 116B (B)	13-0231	0.077	0.552	0.629	0.152	<0.010
SF 117B (A)	13-0232	0.063	0.636	0.830	0.178	<0.010
SF 117B (B)	13-0232	0.073	0.589	0.852	0.185	<0.010
SF 118B (A)	13-0233	0.081	0.558	0.933	0.201	<0.010
SF 118B (B)	13-0233	0.089	0.519	0.950	0.203	<0.010
SF 119B (A)	13-0234	0.066	0.787	0.963	0.198	<0.010
SF 119B (B)	13-0234	0.066	0.766	0.961	0.200	<0.010
SF 120B (A)	13-0235	0.049	0.831	1.058	0.224	<0.010
SF 120B (B)	13-0235	0.061	0.759	1.144	0.243	<0.010
SF 125B (A)	13-0236	<0.010	<0.100	<0.010	<0.100	<0.010
SF 125B (B)	13-0236	<0.010	<0.100	<0.010	<0.100	<0.010



Cementitious Barriers Partnership  
Effect of Oxidation on Chromium Leaching and Redox Capacity of Slag-Containing Waste Forms



Process Science Analytical Laboratory  
Customer: Philip Almond and Chris Langton

Date: 2/5/13

Sample ID: SF 100B - SF 120B, SF 125B

Lab ID: 13-0215-0236

Units: mg/L

Sample ID	Lab ID	NO <sub>2</sub>	NO <sub>3</sub>	SO <sub>4</sub>	pH
SF 100B (A)	13-0215	96.6	983	74.0	10.0
SF 100B (B)	13-0215	96.4	983	66.2	
SF 101B (A)	13-0216	61.0	630	39.3	10.7
SF 101B (B)	13-0216	59.5	631	34.4	
SF 102B (A)	13-0217	68.2	707	45.1	10.8
SF 102B (B)	13-0217	68.3	709	40.4	
SF 103B (A)	13-0218	106	1050	76.1	10.8
SF 103B (B)	13-0218	105	1050	74.9	
SF 104B (A)	13-0219	142	1390	107	10.8
SF 104B (B)	13-0219	142	1390	103	
SF 105B (A)	13-0220	171	1660	131	11.4
SF 105B (B)	13-0220	170	1650	126	
SF 106B (A)	13-0221	122	1220	80.7	11.6
SF 106B (B)	13-0221	122	1220	76.8	
SF 107B (A)	13-0222	135	1370	95.2	11.6
SF 107B (B)	13-0222	135	1370	91.2	
SF 108B (A)	13-0223	102	1070	78.4	11.7
SF 108B (B)	13-0223	101	1070	72.0	
SF 109B (A)	13-0224	117	1230	85.7	11.5
SF 109B (B)	13-0224	117	1230	80.4	
SF 110B (A)	13-0225	118	1230	84.9	11.7
SF 110B (B)	13-0225	118	1230	80.0	
SF 111B (A)	13-0226	173	1760	124	11.8
SF 111B (B)	13-0226	173	1760	119	
SF 112B (A)	13-0227	235	2420	181	11.9
SF 112B (B)	13-0227	234	2420	176	
SF 113B (A)	13-0228	238	2440	177	11.8
SF 113B (B)	13-0228	238	2440	172	
SF 114B (A)	13-0229	253	2590	173	11.7
SF 114B (B)	13-0229	254	2600	169	
SF 115B (A)	13-0230	323	3300	225	11.9
SF 115B (B)	13-0230	322	3310	221	
SF 116B (A)	13-0231	346	3540	243	11.9
SF 116B (B)	13-0231	347	3550	239	
SF 117B (A)	13-0232	549	5640	391	11.9
SF 117B (B)	13-0232	547	5640	386	
SF 118B (A)	13-0233	407	4190	279	12.0
SF 118B (B)	13-0233	408	4190	274	
SF 119B (A)	13-0234	584	6020	410	12.0
SF 119B (B)	13-0234	584	6030	405	
SF 120B (A)	13-0235	859	8910	606	12.0
SF 120B (B)	13-0235	860	8940	603	
SF 125B (A)	13-0236	<50	<50	<50	8.88
SF 125B (B)	13-0236	<50	<50	<50	

**ATTACHMENT 3. Reduction Capacity Measurements for samples leached 18 hr.**

12/20/2012	FAS Molarity (calc)	0.049143
	Ce Molarity	0.0608
	Ce total (mole e-)	0.00152

Titration Sample No. No solids	Slag- Based Waste Form (g)	Volume Titrated FAS (mL)	Fe (mole e-)	Slag- Based Waste Form (mole e-)	Slag- Based Waste Form (mole e-/g)	Reduction Capacity (meq e <sup>-</sup> /g)	Reduction Capacity (μeq e <sup>-</sup> /g)
	0.0000	30.93	0.001520	0.000000	0.000000	0.000000	0
<b>GGBFS as received</b>	0.5025	23.86	0.001173	0.000347	0.000691	0.691428	691
<b>GGBFS ground</b>	0.4984	22.5	0.001106	0.000414	0.000831	0.831215	831
<b>100</b>	0.5037	26.22	0.001289	0.000231	0.000460	0.459529	460
<b>101</b>	0.5225	25.44	0.001250	0.000270	0.000516	0.516357	516
<b>102</b>	0.5053	25.52	0.001254	0.000266	0.000526	0.526152	526
<b>103</b>	0.5156	25.07	0.001232	0.000288	0.000559	0.558532	559
<b>104</b>	0.5127	24.86	0.001222	0.000298	0.000582	0.581821	582
<b>105</b>	0.4968	24.42	0.001200	0.000320	0.000644	0.643966	644
<b>106</b>	0.5058	24.55	0.001206	0.000314	0.000620	0.619877	620
<b>107</b>	0.4969	25.10	0.001233	0.000287	0.000577	0.576585	577
<b>108</b>	0.5016	25.50	0.001253	0.000267	0.000532	0.531993	532
<b>109</b>	0.4930	25.13	0.001235	0.000285	0.000578	0.578156	578
<b>110</b>	0.4976	25.15	0.001236	0.000284	0.000571	0.570836	571
<b>111</b>	0.5072	25.73	0.001264	0.000256	0.000504	0.503834	504
<b>112</b>	0.5066	25.44	0.001250	0.000270	0.000533	0.532563	533
<b>113</b>	0.5193	25.55	0.001256	0.000264	0.000509	0.509129	509
<b>114</b>	0.5220	25.96	0.001276	0.000244	0.000468	0.467896	468
<b>115</b>	0.5129	25.95	0.001275	0.000245	0.000477	0.477156	477
<b>116</b>	0.5183	25.94	0.001275	0.000245	0.000473	0.473133	473
<b>117</b>	0.5094	26.20	0.001288	0.000232	0.000456	0.456316	456
<b>118</b>	0.5182	26.02	0.001279	0.000241	0.000466	0.465637	466
<b>119</b>	0.5080	26.09	0.001282	0.000238	0.000468	0.468215	468
<b>120</b>	0.5148	25.94	0.001275	0.000245	0.000476	0.476349	476