Chemical Stabilization of Chromate in Blast Furnace Slag Mixed Cementitious Materials

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Abstract

Cement waste form (CWF) technology is among the leading approaches to disposing of metals and liquid low-level nuclear waste in the United States. One such material, saltstone, includes slag, fly ash and Portland cement to enhance the immobilization of contaminants (e.g.,

Cr, ^{99}Tc) in alkaline liquid wastes. To evaluate the stability of such redox sensitive contaminants in saltstone, the effects of slag as a source of reductant on Cr immobilization was evaluated in aged (<300d) saltstone monoliths. Specifically, we investigated the effects of artificial cement porewaters on the Cr release and the spatially resolved Cr chemical state analysis using synchrotron based microfocused X-ray microprobe analysis. The microprobe analysis indicated the heterogeneous distribution of insoluble Cr(III)- species in saltstone. Although at most of 20% Cr_{total} was leached at the top few (2-3) millimeter depth, the release of Cr(VI) was small (< 5%) at 5-30 mm with slight changes, indirectly suggesting that Cr is likely present as insoluble Cr(III) species throughout the depths. The study suggests that this saltstone formulation can effectively retain/immobilize Cr under the oxic field condition after ≤ 300 d of aging time.

Introduction

In 2009, 136 million liters of liquid nuclear waste from nuclear plutonium production from the Cold War is still stored at the Savannah River Site (SRS) in Aiken, SC (Savannah River Remediation LLC. 2012). Approximately 10% of liquid nuclear waste is classified as the low-

level nuclear waste (LLW) that contains technetium (^{99}Tc) as well as toxic heavy metals like Cr (Icenhower, et al., 2010; EPA, 2002).

Technetium and Cr exist as soluble oxyanions (Tc(VII)O_4^- and Cr(VI)O_4^{2-}) in oxidized LLW. To immobilize these contaminants, one of solidification/stabilization methods, CWF immobilization method, is appealing to U.S. Department of Energy due to low cost, strict production regulations, permanence, and low temperature levels during manufacture (Atkins and Glasser. 1992). Cement technology has been widely used to stabilize hazardous heavy metals in solid phases (Bhatty et al., 1999; Cullinane et al., 1986; Li et al., 2001; Paria and Yuet. 2006). Chemical stabilization of metal contaminants is generally accomplished by reducing their solubility within the cement matrix. An effective CWF in use at SRS is called ‘saltstone’. It has a standard composition of 6% wt, type 2 portland cement, 25% wt, fly ash, 25% wt, blast furnace slag (BFS), and 45 wt. % salt solution (Savannah River Remediation, 2013). Blast furnace slag is included in the CWF formulation to increase strength, decrease porosity, and create a chemically reducing environment (Langton, 1987). Complete saltstone mixtures are dispositioned to the Saltstone Disposal Facility (SDF), a facility on the SRS that contains two rectangular near-surface vaults, as well as more recently constructed cylindrical units (Cook, 2005).

Both iron (Fe(II)) and sulfur (S(0) , S^{2-}) species within slag have been considered as important electron donors to reduce Tc(VII) and Cr(VI) , resulting in the formation of Tc(IV) -sulfur and or Cr(III) hydrous oxide species (Allen et al., 1997; Angus, M., F. Glasser. 1985). While CrO_4^{2-} and TcO_4^- are highly soluble, these solid compounds have much lower solubilities and are therefore less mobile within the cement matrix. The successful immobilization of Cr and Tc in saltstone CWF remediation depends on the stabilization of Cr and Tc via reduction to

prevent diffusion resulting from pore water contact, and the long-term resiliency and weathering of the saltstone (Savannah River Remediation, 2013). Consequently, the reducing environment within saltstone is imperative for effective containment, as oxygen diffusion into the cement matrix could result in rapid oxidation of Tc(IV)/Cr(III) species to soluble Cr(VI)O_4^{2-} and Tc(VII)O_4 . If this occurs, soluble oxyanions are likely to diffuse through pore fluid and microcracks, leading to a significantly greater leaching rate (Mattigod et al., 2009; Kaplan et al., 2011). Therefore, understanding the reducing capacity of saltstone is important for predicting the long-term behavior of CWFs.

Thus far, most studies have used indirect approaches (e.g., leaching tests) to investigate the reduction capacity of CWF using Tc and Cr (Langton, 1987; Langton et al., 2013; Almond et al., 201; Hang and Kaplan, 2007; Smith and Walton, 1992). Chromium is often used as a testing compound since its redox potential is more sensitive than Tc and it is non-radioactive. Under alkaline pH conditions of LLW, the standard reduction potential for Tc(IV/VII) is -360 mV, which is lower than that of Cr(III/VI) (-110 mV) (Bard et al., 1985; Magee and Cardwell, 1974). These values have an indication that Tc is more difficult to get reduced than Cr; therefore subsequent Cr oxidation would be a useful indicator in predicting the Tc solubility in CWFs.

A bench mark leaching test conducted at the SRS showed that 0.035 cumulative fraction of Tc was leached over ~ 3.5 mo from saltstone (Langton, 1987). In other saltstone studies, they observed the development of oxidizing zone up to 7 mm depth after ~ 1 mo (2×10^{-4} – 0.17 fraction Cr leached) under oxic condition (Langton and Sefanko, 2012), 20 mm after ~ 4 mo (up to 0.06 fraction Cr leached) (Langton et al., 2013) and 50 mm after ~10 mo (up to 0.04 fraction Cr leached) (Almond et al. 2013).

Furthermore, a two-dimensional reactive transport model was used to predict the Tc

retention capacity in a saltstone block (Hang and Kaplan. 2007). The results showed that ~15.8% of the reduction capacity would be exhausted after 213,000 yrs. Hang and Kaplan (2007) later discussed that their estimate is in agreement with the results of empirical diffusion modeling based on measurements using X-ray absorption spectroscopy (Lukens, 2005).

There are some inconsistencies in describing the reducing capacity of saltstone between the results of leaching tests and modeling. The fraction of Cr(III) and the reduction capacity of saltstone samples have been measured concomitantly and there was no correlation (Almond et al., 2013). In order to evaluate these research outcomes to establish geochemical models to predict the long-term performance of saltstone, it would be useful to support the macroscopic leaching data with the direct chemical speciation data.

The objective of this study was to evaluate: 1) the solid state Cr speciation in the surface layer (up to 3cm) of field aged (135-290 days) saltstone monoliths, and 2) the extent of Cr release in artificial cement porewaters (deoxygenated Ca(OH)_2 and oxygenated CaCO_3 solutions to simulate the porewaters in young and old cement, respectively) as a function of depth. The surface layer was chosen because it is most sensitive to O_2 diffusion. The general experimental approach was to couple the conventional leaching tests and synchrotron based X-ray microprobe analysis. The integrated results of Cr redox chemistry study in CWF should provide an important information about the reducing capacity of saltstone to immobilize Cr in LLW.

Materials and Methods

Materials

All reagents were prepared in degassed distilled deionized (DI) MilliQ water (18.2 M Ω) using ACS grade chemicals unless otherwise mentioned. Chromate, as Na_2CrO_4 , amended

([Cr]_{Total}: 500 mg/kg and 1000 mg/kg) saltstone monolith (height: 10cm, O.D.: 25cm) were prepared using the method described by Almond and co-workers (2012). They are listed in Table-1. Sample preparation is described in detail and the radionuclide-free simulant mixture used for the saltstone samples is shown in Table-2. The simulant was combined with a premix of 45 wt-% BFS, 45 wt-% Class F fly ash, and 10 wt-% ordinary portland cement at a nominal 0.6 water to premix ratio. Elemental composition and mineralogy of these materials are summarized in Tables-3 and -4. Samples were cured in polypropylene cylinders in a humid chamber for one to three weeks. The samples were transferred to the Z-area at SRS for field aging in a closed chest with an open container of water inside.

Segmentation and Leaching Tests

Aged (250-280 days old) saltstone samples were handled inside of a N₂ filled anaerobic glove chamber using a 5% H₂ and 95% N₂ gas mixture. Each monolith was drilled in approximate millimeter increments using a Dremel 200 Drill equipped with a tungsten carbide drill bit. Since the oxidation is expected to progress from the surface, we were interested in the top 2-3 cm of monolith for this experiments. It was vertically mounted on a Dremel factory stand (Dremel 220-01 Rotary Tool Work Station) to ensure the accuracy of drilling depth. Depth was measured by inserting a ruler into the hole and measuring from the top of the sample. A 1.5 cm wide hole was drilled in the center of the samples to a depth of 3 cm. Ground powder was collected at each increment and further ground in a Diamonite mortar and pestle. Then ~ 0.5 g powder samples were transferred into two Nalgene Oak Ridge High-Speed Centrifuge tubes. The tubes contained 15 mL of two different leachate solutions (i.e., 0.001 M CaCO₃ prepared in oxygenated MilliQ water, and 0.017 M Ca(OH)₂ prepared in boiled/degassed DI water). These

solutions were selected to simulate a simplified porewater in contact with a fresh cement (0.017 M $\text{Ca}(\text{OH})_2$ at pH 11.3 ± 0.12) where the systems chemistry was controlled predominantly by portlandite, and an aged (thousands of years) cement (0.001 M CaCO_3 at pH 8.25 ± 0.02), where the systems chemistry is controlled predominately by calcite (Criscenti et al., 1996; Krupka et al., 2012). Tubes were shaken on an end-over-end shaker at 26 rpm for 24 hrs. The samples were then removed from the glove chamber and centrifuged at 10,500 rpm for eight min. The centrifugation method was sufficient to remove from suspension cement particles with a hydrodynamic radius greater than 100 nm to be removed from the supernatant. Approximately 10 mL of leachate was collected and filtered through a 0.2 μm polyvinylidene fluoride (PVDF) filters. Filtrates were analyzed for total Cr(VI) using the following methods. The s-diphenyl carbazide UV-Vis spectrophotometric method (Bartlett and James, 1979; Fendorf, 2003) was used to analyze the filtrate for total hexavalent Cr. The data were normalized with respect to $[\text{Cr}]_{\text{total}}$ added during the saltstone preparation.

Synchrotron Based X-ray Microbe Analysis

The microfocused (μ) synchrotron X-ray fluorescence (SXRF) measurements of a 135 days old saltstone monolith were performed at beam line 2-3 equipped with a double crystal Si(111) monochromator at Stanford Synchrotron Radiation laboratory, Menlo Park, CA. The monolith contains Cr_{total} of 1000 mg/kg. A saltstone chip (W: 2cm x H 3 cm x D: 0.5cm) was separated from the top 2cm of a monolith using a utility knife and a cement saw in an anaerobic chamber. The selection of cross sectional area was to detect the development of oxidizing zone at the near surface. A chip was mounted in a custom made flow cell that was sealed with 8 μm Kapton tape. The outlet and inlet tubing of gas flow cells were clamped with alligator clips to

trap N₂ gas. Each cell was individually sealed in a Mylar bag with oxygen scrubbers. Chromium and valence state map measurements were conducted using a 7-element Ge solid-state detector. The energy calibration was performed at 5989 eV using a Cr foil and at 10,534 eV. Beam size and dwell time were 3(H) x 5(V) μ m and 200 ms/pixel, respectively. Selected absorption edge energies are 5993eV for Cr(VI), 6003eV for Cr(III), 6010eV for total Cr. We selected 6003 eV where the intensity ratio of Cr(III) and Cr(VI) reference spectra is maximized. We selected the energy of 5993 eV that provides the maximum pre-edge peak height of Cr(VI), and the maximum white line peak for Cr(III) was chosen at 6010eV.

Chromium K-edge μ X-ray absorption near edge structure spectroscopy (XANES) measurements were performed at regions selected from valence state maps. Three to four XANES spectra were collected in fluorescence mode using a Canberra 9-element Ge Array detector. Step sizes of 10 eV, 0.35 eV, and 0.8eV were taken in the energy regions of 5880-5970 eV, 5970-6019 eV, and 6034-6080 eV, respectively. An integration time was 4 sec at each step. To facilitate the analysis of μ -XANES spectra, XANES spectra of reference compounds (ACS grade sodium chromate, Cr(III) oxide) were also collected in transmission mode at ID-12 equipped with a double crystal Si(111) monochromator at Advanced Photon Sources, Argonne, IL. All salts were freshly ground and trapped in Kapton tape. Chemical composition maps and XANES spectra were processed using Smak and Sixpack software (Webb, 2005; Webb, 2006). The XAS data reduction and normalization was carried out as described by Arai et al.(2005). Valence state maps were generated according to the method described by Sutton et al. (2002).

Results and Discussion

Chromate Leachability as a Function of Depth

If one assumes the oxidation of Cr in saltstone is preceded by oxygen diffusion at shallow depth, two half-reactions (eq. 1 and 2) can be suggested in alkaline cement pore waters.

Accordingly, the overall reaction can be written as follows (eq. 3):

Using the average redox potential (+36 mV) at the surface of saltstone reported in a similar saltstone study (Kaplan and Coates, 2007), the ΔG of the reaction is estimated to be -156 kcal/mol, indicating that this reaction is thermodynamically favorable. Based on the thermodynamic calculation, one should expect to see Cr released if oxygen diffused into saltstone.

The Cr leaching data (Figs 1A and 1B) are shown as a function of leached Cr (%) vs. increasing drill depth up to nearly three centimeters. The amount of Cr release was less than 20% of the total Cr at all depths and for both the 500 and 1000 mg/kg samples. The degree of chromate leaching was drastically decreased with increasing depths in both saltstone systems. There were spikes in the data that might suggest the heterogeneity of the sample matrices, where Cr may have concentrated in certain segments of the saltstone. When the CaCO_3 solutions were used as a leachate solution, the difference was more pronounced than the $\text{Ca}(\text{OH})_2$ solution. The % Cr leached decreased from 20% to 10% with increasing depth from 0 to 5 mm in the Cr 500 mg/kg sample (Fig. 1A), while % Cr leached decreased from ~4 to 2% with increasing the depth

from 0 to 10 mm in the Cr 1000 mg/kg sample (Fig. 1B). It is important to note that the contribution of background Cr to total Cr leached in control monoliths (i.e., no Cr spikes) was less than 3.6 % of total Cr leached. For this reason, observed trend is attributed to the speciation changes in the spiked Cr. While the amount of total chromate leached slightly decreased with increasing depth (Figs 1A and 1B), the decrease in total chromate leached (from 20% to 7% in the 500 mg/kg Cr sample and 4.5% to 1% in the 1000mg/kg Cr sample) was not enough to warrant the fully oxidizing condition in either sample.

Effects of leaching solutions on Cr(VI) Release

The range of chromate leaching in both 500 and 1000 mg/kg samples was generally greater in the oxygenated CaCO_3 solutions as compared to the deoxygenated Ca(OH)_2 solutions. For example, in the 500 mg/kg Cr sample, the chromate concentrations ranged from 2.70-20.18% in the CaCO_3 leachate and only 0.48-6.13% Cr(VI) leached in the Ca(OH)_2 leachate (Fig. 1A). Similarly, in the 1000 mg/kg Cr sample, the Cr(VI) concentrations ranged from 0.77-4.40% Cr(VI) leached in the CaCO_3 leachate and only 0.02-1.58% Cr(VI) leached in the Ca(OH)_2 leachate (Fig. 1B). For the Cr(VI) leaching from the Cr 500 mg/kg sample, the average leached at all depths was 3.51 % less for the Ca(OH)_2 compared to the CaCO_3 leachate. In the Cr 1000 mg/kg sample, the difference in chromate leaching between leachate solutions was less pronounced at 1.58%.

The retention of Cr in saltstone is expected through reductive precipitation reactions. It is well documented that the reduction of Cr(VI) would lead to the formation of stable Cr(III) oxyhydroxide phases (e.g., Cr(OH)_3 , $(\text{Cr}_x, \text{Fe}_{1-x})(\text{OH})_{3(s)}$) at pH range ~6-12 (Davis and Olsen, 1995; Papassiopi, 2012). Our synchrotron based microprobe data also show the presence of Cr(III) phases in the saltstone (see the section below). If one assumes the presence of Cr(OH)_3 in

saltstone, the following leaching mechanisms can be proposed to support the experimental evidence above. They are 1) oxidative dissolution of Cr(III) precipitates in the oxygenated CaCO_3 solutions, 2) Ca enhanced co-sorption of Cr(VI) in the degassed Ca(OH)_2 solutions and 3) carbonate enhanced desorption of Cr(VI).

The oxidative dissolution of Cr(OH)_3 is likely facilitating the release of Cr(VI) in the oxygenated 0.001M CaCO_3 system. Chromium(III) might have been already oxidized during aging, and or slowly oxidized during the desorption experiments. Under oxidizing conditions, it has been reported the accelerated dissolution of Cr(OH)_3 occurs via oxidation of Cr(III) to Cr(VI) (Lee and Hering, 2005).

pH-dependent dissolution of Cr(OH)_3 was also considered. Rai and co-workers (1987) previously discussed the amphoteric dissolution property of Cr(OH)_3 in 0.1 M perchlorate medium. The solubility decreased from pH 4 to ~6 and increased again around pH 10 due to the formation of soluble $\text{Cr(OH)}_x^{-(x-3)}_{(\text{aq})}$ hydrolysis product. Due to the lower leaching of Cr in Ca(OH)_2 (pH 11.3 ± 0.12) compared to CaCO_3 (pH 8.25 ± 0.12), it is unlikely that pH dependent solubility of Cr(OH)_3 is controlling [Cr].

Additionally, dissolved Ca may facilitate the retention of Cr(VI) in alkaline soils (Avudainayagam et al., 2001). The activity of Ca^{2+} in the Ca(OH)_2 solution herein was estimated at $8.34 \cdot 10^{-3}$, which is greater than that in the CaCO_3 leaching solution ($7.55 \cdot 10^{-4}$). This difference in Ca^{2+} activity indirectly suggests the enhanced Cr(VI) sorption might have been occurring in saltstone mineral components (e.g., gypsum, hydrotalcite tri- and di-calcium silicate, tricalcium aluminate and calcium silicate hydrate) (Cozzi and Duncan, 2011), resulting in less Cr(VI) release in the degassed Ca(OH)_2 solution.

Under the experimental condition, high bicarbonate concentration could have enhanced the desorption of Cr(VI) anions via ligand exchange mechanisms. It is known that carbonate is strongly complex on the mineral surfaces (Villalobos et al., 2001).

Synchrotron Based X-ray Microprobe Analysis

Results of synchrotron based microprobe analysis are shown in Figs 2A-2D. In the sodium chromate reference spectrum (Fig. 2C), there is a large pre-edge peak (a vertical dotted line at 5993 eV). The pre-edge resonances of Cr K-edge XANES spectra are characteristic for the local symmetry of tetrahedral coordination of Cr(VI)O₄ molecules. Since the tetrahedral structure symmetry causing considerable overlap of empty d-orbitals with the p-states that the photoelectron must fill (Newville, 2004). Since the tetrahedral structure lacks an inversion center, it exhibits a single intense pre-edge peak which is indicative of a dipole transition of 1s electron to an unoccupied anti bonding t₂* tetrahedral orbital. On the contrary, the XANES spectrum of Cr(III)₂O₃ shows lack of feature at the pre-edge region, allowing for a distinction between the two valences using the pre-edge feature of XANES spectra.

Chromium Valence State in Saltstone

A saltstone chip from a Cr 1000 mg/kg sample (Fig. 2A) aged for ~134 days was analyzed for the distribution of Cr. To account for the sample heterogeneity, a large Cr XRF map (0.8mm x 18.8mm) was taken (Fig 2A), showing a distinct distribution pattern of Cr in cement matrices at top ~ 2 cm depth. Although the surface of cement is rough, Cr is distributed throughout the depth. The higher intensity in a color contour bar corresponds to higher Cr content, while the top section (1.01 x 0.99 mm) was used for a Cr(VI) valence state map (Fig. 2B). The increasing intensity in the valence state map corresponds to Cr(VI) valence state in the heterogeneous

media. In the valence state map, dark blue corresponds to void spaces in the saltstone matrix, such as the one shown in Fig. 2D. Correlation plots of Cr constructed from microprobe analysis (Figure 2B) are shown in Fig. 3. The scatter plot of Cr(VI) vs. Cr(III) (Fig. 3) shows that most of the Cr is present as Cr(III) (probably as insoluble $\text{Cr}(\text{OH})_3$) while some high fluorescence counts for Cr(VI) are shown where the fluorescence counts of Cr(III) are low. As it can be seen in a comparison of Cr(III) and Cr(VI) reference spectra (Fig 2C), the fluorescence intensity at 6003 eV is overlapped in a mixed oxidation sample (i.e., a large Cr(III) contribution with a small background from Cr(VI)). Therefore, it is important to assure the interpretation of scatter plots. For this reason, selected fluorescence counts (a hollow circle on Fig. 2B.) were back transformed into a X-ray fluorescence (XRF) map. There are few isolated Cr(VI) high-intensity hotspots visible in this map, which were chosen for XANES analysis (Fig. 2C). Furthermore, the corresponding XANES spectra show that the Cr speciation in the hot-spots is predominately Cr(III). We conducted linear combination of reference compound fit at 5920-6020eV using the Cr(III) and Cr(VI) reference compounds shown in Fig 2. The Cr(III) fraction was 96.4 %(± 0.2) at spot 1, 97.0%(± 0.2) at spot 2, 99.1 %(± 0.2) at spot 3, 97.0 %(± 0.3) at spot 4, and 96.5 %(± 0.3) at spot 5, suggesting the Cr valence state is predominantly Cr(III).

This is evident because of the lack of a Cr(VI) pre-edge feature (i.e., predominantly Cr(III)), which can be seen in the Cr(VI) standard, in the XANES from the saltstone segment. This is in agreement with only 20% of chromate released in the Cr leaching tests.

The reduction of Cr(VI) has been studied in cement mixtures using XAS technique. In a similar study, 1000 mg/kg CrO_4^{2-} spiked cement mixtures (47% BFS, 47% FA, 6% PC) aged 28 days were analyzed by XANES and found to contain between 2-3% of Cr(VI) content. Using the same cement mixture, Lee and co-workers (1995) spiked samples with 2500 mg/kg Na_2CrO_4

and cured for 9 days (Lee et al., 1995). Chromium was estimated to be 75% Cr(III) and 25% Cr(VI) by XANES and EXAFS analysis, which is similar to the amount of Cr(VI) released in our leaching tests ($\leq 20\%$). The speciation of Cr(III) was suggested as $\text{Cr}(\text{OH})_3$ in the cement and CrOOH in a BFS only mix (Lee et al., 1995). Their results agree with our findings that little Cr(VI) is visible in our valence state maps and XANES data due to successful reduction of Cr(III) in saltstone and lower loading of Cr in our samples.

Conclusions

The results of Cr leaching analysis in degassed $\text{Ca}(\text{OH})_2$ solution showed no apparent oxidization was occurring in saltstone samples with a total aging time of < 300 days. Instead, there was some residual Cr(VI) release at the top few millimeters of monoliths (maximum of 20% and 4% for Cr 500 and 1000 mg/kg, respectively). Depth dependent Cr(VI) release was not clearly observed at the 5-30mm depth. X-ray microprobe analysis showed the majority of Cr was stabilized as Cr(III). The presence of Cr(III) oxidation in these samples suggests that the reducing compounds present in saltstone have not prevented or reversed Cr oxidation. However, when the samples were exposed to oxygenated CaCO_3 solution (i.e., simulated aged cement pore waters), the Cr(VI) leaching slightly increased, indirectly suggesting that subtle increases in O_2 content via diffusion could potentially oxidize Cr(III) to Cr(VI).

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References

Allen, P.G., Siemering, G.S., Shuh, D.K., Bucher, J.J., Edelsteign, N.M., Langton, C.A., Clark, S.B., Reich, T., Denecke, M.A., 1997. Technetium speciation in cement waste forms determined by x-ray absorption fine structure spectroscopy, *Radiochim. Acta.* 76,77-86.

Almond, P., Kaplan, D., Langton, C., Stefanko, D., Spencer, W., Hatfield, A., Arai, Y., 2012. Method evaluation and field sample measurements for the rate of movement of the oxidation front in saltstone. Savannah River National Laboratory SRNL-STI-2012-00468.

Almond, P., Stefanko, D., Langton, C., 2013. S.R. Site, Cementitious barriers partnership effect of oxidation on chromium leaching and redox capacity of slag-containing waste forms.

Cementitious Barriers Partnership CBP-TR-2013-02.

Angus, M., Glasser, F., 1985. The chemical environment in cement matrices. MRS Proceedings. Cambridge Univ. Press. 50 .

Arai, Y., Sparks D.L., Davis, J.A., 2005. Arsenate adsorption mechanisms at the allophane-water interface: Environ. Sci. Technol. 39,2537-2544.

Atkins, M., Glasser, F., 1992. Application of Portland cement-based materials to radioactive waste immobilization, Waste Manage. 12,105-131.

Avudainayagam, S., Naidu, R., Kookana, R.S., Alston, A.M., McClure, S., Smith, L.H., 2001. Effects of electrolyte composition on chromium desorption in soils contaminated by tannery waste, Aust. J. Soil. Res. 39,1077-1089.

Bard, A.J., Parsons, R., Jordan, J., 1985. Standard Potentials in Aqueous Solution, Marcel Dekker, Inc, New York, New York.

Bartlett, R., James, B, 1979. Behavior of chromium in soils: III. Oxidation. J. Environ. Qual. 8, 31-35.

Bhatty, J.I., Miller, F., West, P.B., Ost, B., 1999. Stabilization of heavy metals in portland cement, silica fume/portland cement and masonry cement matrices, Portland Cement Association. PCA RP348. Skokie, IL.

Cook, J.R., Wilhite, E.L., Hiergesell, R.A., Flach, G.P., 2005. Special analysis: Revision of saltstone vault 4 disposal limits. Westinghouse Savannah River Company WSRC-TR-2005-00074. Aiken SC.

Criscenti, L., Serne, R., Krupka, K., Wood, M., 1996. Predictive calculations to assess the long-term effect of cementitious materials on the pH and solubility of uranium(VI) in a shallow land disposal environment. Pacific Northwest National Laboratory PNNL-11182. Richland, WA.

Cozzi, A., Duncan, A., 2011. Characterization of core sample collected from the Saltstone Disposal Facility. In: Sundaram, S.K., Ohji, T., Fox, K., Hoffman, E., (Eds.), Advances in Materials Science for Environmental and Nuclear Technology II, John Wiley & Sons, New Jersey. p.135.

Cullinane, M.J., Jones, L.W., Malone, P.G., 1986. Handbook for stabilization/solidification of hazardous waste, Hazardous Waste Engineering Research Laboratory, Office of Research and Development, US Environmental Protection Agency, 1986. Cincinnati, OH.

Davis, A., Olsen, R.L., 1995. The geochemistry of chromium migration and remediation in the subsurface, Ground Water. 33,759-768.

EPA facts about technetium-99. 2002.

<http://www.epa.gov/superfund/health/contaminants/radiation/pdfs/technetium.pdf>

Fendorf, S., 2003. Kinetics and structural constraints of chromate reduction by green rusts, Environ. Sci. Technol. 37,2750-2757.

Hang, T., Kaplan, D.I., 2007. Modeling of the sub-surface reducing environment of the Z-Area Saltstone disposal facility at the Savannah River Site. Westinghouse Savannah River Company WSRC-STI-2005-00367. Aiken, SC.

Icenhower, J.P., Qafoku, N.P., Zachara, J.M., Martin, W.J., 2010. The biogeochemistry of technetium: a review of the behavior of an artificial element in the natural environment, *Am. J. Sci.* 310,721-752.

Kaplan, D., Lilley, M., Almond, P., Powell, B., 2011. Long-term technetium interactions with reducing cementitious materials, Savannah River National Laboratory SRNL-STI-2010-00668.

Krupka, K.M., Cantrell, K.J., Schaef, H.T., Arey, B.W., Heald, S.M., Deutsch, W.J., Lindberg, M.J., 2012. Characterization of solids in residual wastes from single-shell tanks at the Hanford Site, Washington, USA.

Kaplan, D.I., Coates, J.T., 2007. Partitioning of dissolved radionuclides to concrete under scenarios appropriate for tank closure performance assessments. Westinghouse Savannah River Company WSRC-STI-2007-00640.

Langton, C., 1987. Slag-based saltstone formulations. *MRS Proceedings*. Cambridge Univ. Press. 112 .

Langton, C., Stefanko, D., 2012. Oxidation study: Chromium and Rhenium leaching front results. Savannah River National Laboratory SRNL-L3100-2012-00033. Aiken, SC.

Langton, C., Stefanko, D., Burns, H., 2013. Saltstone oxidation study: leaching method. Savannah River National Laboratory SRNL-STI-2012-00728.

Lee, G., Hering, J.G., 2005. Oxidative dissolution of chromium (III) hydroxide at pH 9, 3, and 2 with product inhibition at pH 2, Environ. Sci. Technol. 39,4921-4928.

Lee, J., Bajt, S., Clark, S., Lamble, G., Langton, C., Oji, L., 1995. Chromium speciation in hazardous, cement-based waste forms, J. Phys. Cond. Matter. 208 & 209,577-578.

Li, X., Poon, C., Sun, H., Lo, I., Kirk, D., 2001. Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials, J. Hazard. Mater. 82,215-230.

Lukens, W.W., Bucher, J.J., Shuh, D.K., Edelstein, N.M., 2005. Evolution of technetium speciation in reducing grout, Environ. Sci. Technol. 39, 8064-8070.

Magee, R.J., Cardwell, T.J., 1974. Rhenium and technetium, in: Encyclopedia of Electrochemistry of the Elements, Marcel Dekker, New York. p. 126.

Mattigod, S.V., Bovaird, C.C., Wellman, D.M. Skinner, D.C.J., Cordova, E.A., Wood, M.I., 2009. Effect of concrete waste form properties on radionuclide migration. Pacific Northwest National Laboratory PNNL-18745. Richland, WA.

Newville, M. 2004. Fundamentals of X-ray absorption fine structure. Consotium for Advanced Radiation Sources, University of Chicago. <http://xafs.org>

Papassiopi, N., 2012. Stabilization of chromium in the form of mixed Fe(III)-Cr(III) hydroxides, Fresenius Environmental Bulletin. 21,2399-2405.

Paria, S., Yuet, P.K., 2006. Solidification-stabilization of organic and inorganic contaminants using Portland Cement: a Literature Review, *Env. Rev.*14:217-255.

Rai, D., Sass, B.M., Moore, D.A., 1987. Chromium (III) hydrolysis constants and solubility of chromium (III) hydroxide, *Inorg. Chem.* 26,345-349.

Savanna River Remediation Saltstone disposal units. 2013. www.srremediation.com/saltstone.pdf

Smith, R.W., Walton, J.C., 1992. The role of oxygen diffusion in the release of technetium from reducing cementitious waste forms. *MRS Proceedings*. Cambridge Univ. Press. 294.

Sutton S.R., Bertsch P.M., Newville M., Rivers M.L., Lanzirotti A., Eng P.J.. 2002. Microfluorescence and microtomography analyses of heterogeneous earth and environmental materials In: Applications of synchrotron radiation at low-temperature geochemistry and environmental sciences, *Review in Mineralogy and Geochemistry* Vol. 49 (ed. Fenter, P.A., Rivers, M.L., Sturchio, N.C., Sutton S.R.) Chantilly, VA: Mineralogical Society of America. pp. 429–483.

Um, W., Valenta, M.M., Chung, C.W., Yang, J., Engelhard, M.H., Serne, R.J., Parker, K.E., Wang, G., Cantrell, K.J., Westsik, J.H., 2011. Radionuclide retention mechanisms in secondary waste-form testing: phase II. Pacific Northwest National Laboratory PNNL-20753.

Villalobos, M., Trotz, M A., Leckie, J. O.2001. Surface complexation modeling of carbonate effects on the adsorption of Cr(VI), Pb(II), and U(VI) on goethite. *Environ. Sci. Technol.*35, 3849-3856.

Webb, S.M., 2005. SIXpack: a graphical user interface for XAS analysis using IFEFFIT. Phys. Scr. 1011.

Webb S.M., 2006. SMAK: Sam's Microprobe Analysis kit, V0.46. Stanford Synchrotron Radiation Laboratory, Menlo Park, CA.

Table-1. Description of Cr(VI) amended saltstone samples and the chemical composition of leaching solutions. The Ca(OH)₂ and CaCO₃ based leaching solutions were prepared in boiled and oxygenated MilliQ water, respectively.

Chemical amendments in saltstone (mg/kg)	Aging time in field (days)	Chemical composition of leaching solutions
Na ₂ CrO ₄ 500	253	0.001M CaCO ₃
Na ₂ CrO ₄ 500	272	0.017M Ca(OH) ₂
Na ₂ CrO ₄ 1000	289	0.017M Ca(OH) ₂
Na ₂ CrO ₄ 1000	279	0.001M CaCO ₃

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e-2. Chemical composition of artificial Tank 50 simulant used in saltstone preparation (Almond et al., 2012)

Compound	Concentrations (M/L)
Al(NO ₃) ₃ ·9H ₂ O	0.11
NaOH	1.55
Na ₂ SO ₄	0.05
Na ₂ CO ₃	0.14
NaNO ₃	2.11
NaNO ₂	0.33

(wt%)	Al ₂ O ₃	CaO	BaO	CeO ₂	CoO	Cr ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	MnO ₂
Slag	8.41	37.9	0.041	0.01	0	0.022	0.352	0.295	12.9	0.572
Fly Ash	28.5	0.678	0.114	0.028	0.015	0.051	6.11	2.58	0.911	0.035
Cement	5.44	64.7	0.022	0.009	0	0.019	3.65	0.479	1.21	0.027
(wt%)	Na ₂ O	NiO	P ₂ O ₅	SO ₄	SiO ₂	SrO	TiO ₂	V ₂ O ₅	ZnO	ZrO ₂

Slag	0.247	0.005	0	0.906	38.1	0.033	0.381	0	0	0.026
Fly Ash	0.25	0.02	0.094	0.102	54.4	0.063	1.58	0.052	0	0.041
Cement	0.12	0.011	0.245	3.21	20.5	0.086	0.331	0.032	0.048	0

Table-3: Elemental composition of slag, fly ash, and cement used in this study.

Component	Mineralogy
Fly Ash	Quartz, mullite, hematite, magnetite, maghemite, calcite, and portlandite
Blast furnace slag	Akermanite, quartz, calcite, monoticelite
Portland cement	Alite, belite, tricalcium aluminate, gypsum and calcium aluminoferrite

Table-4: Bulk Mineralogy determined using X-ray diffraction measurements of saltstone components.

Figure captions

Fig. 1. Results of metal leaching data in CaCO_3 and Ca(OH)_2 leaching solutions are shown in black squares and open triangles, respectively. A) Cr(VI) leaching data from the Cr 500 mg/kg sample. B) Cr(VI) leaching data from the Cr 1000 mg/kg sample. To clearly show the data points in the Cr data, error bars for Cr(VI) (% error range: 2.1- 4.3) are not shown.

Fig. 2. Results of synchrotron based microprobe analysis of 134 d aged Cr 1000 mg/kg saltstone sample. A) Total Cr XRF map (0.8mm x 18.8mm) at the depth of 0-18.8 mm. B) Cr(VI) valence state map (0.8mm x 1.01 mm) at the depth of 0-1.01 mm. C) Normalized bulk Cr K-edge XANES spectra of reference compounds and Cr(VI) hotspots in B. D) A section of total Cr XRF map from Fig. 2A showing a large void (in dark blue) in saltstone matrix.

Fig. 3. Correlation plots constructed from synchrotron based microprobe results of Cr 1000 mg/kg saltstone (XRF map shown in Fig. 2B). Intensity of the Cr(VI) pre-edge peak plotted against the ratio of Cr(III) (6003/5993 eV).

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