Chemical stabilization of chromate in blast furnace slag mixed cementitious materials

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HIGHLIGHTS

- Cement waste form saltstone technology was evaluated for chromate immobilization.
- Blast furnace slag was effective in reducing Cr(VI) to Cr(III) in saltstone.
- Microprobe analysis showed heterogeneous distribution of Cr(III) in saltstone.
- Chromium was effectively immobilized after <300 days of aging time.

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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 (<300 d) saltstone monoliths. Specifically, we investigated the effects of artificial cement pore waters 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 $\leqslant$300 d of aging time.

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1. 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

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facility on the SRS that contains two rectangular near-surface vaults, as well as more recently constructed cylindrical units (Cook et al., 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 and 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 to $Cr(VI)O_4^{2-}$ 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., 2012; 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 Stefanko, 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 y. 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 et al., 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 3 cm) of field aged (135–290 days) saltstone monoliths, and (2) the extent of Cr release in artificial cement pore waters (deoxygenated Ca(OH)$_2$ and oxygenated CaCO$_3$ solutions to simulate the pore waters 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.

2. Materials and methods

2.1. Materials

All reagents were prepared in degassed distilled deionized (DI) MilliQ water (18.2 MΩ) using ACS grade chemicals unless otherwise mentioned. Chromate, as Na$_2$CrO$_4$, amended ([Cr]$_{total}$: 500 mg/kg and 1000 mg/kg) saltstone monolith (height: 10 cm and O.D.: 25 cm) were prepared using the method described by Almond et al. (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.

2.2. Segmentation and Leaching Tests

Aged (250–280 days old) saltstone samples were handled inside of a N$_2$ filled anaerobic glove chamber using a 5% H$_2$ and 95% N$_2$ 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 CaCO$_3$ 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 pore water in contact with a fresh cement (0.017 M Ca(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., 2010). Tubes were shaken on an end-over-end shaker at 26 rpm for 24 h. The samples were then removed from the glove chamber and centrifuged at 10,500 rpm for eight min. The

Table 1

Description of Cr(VI) amended saltstone samples and the chemical composition of leaching solutions. The Ca(OH)$_2$ and CaCO$_3$ 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	0.001 M CaCO$_3$
Na$_2$CrO$_4$ 500	272	0.017 M Ca(OH)$_2$
Na$_2$CrO$_4$ 1000	289	0.017 M Ca(OH)$_2$
Na$_2$CrO$_4$ 1000	279	0.001 M CaCO$_3$