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5 **Sulfur Speciation in Untreated and Alkali Treated Ground-**

6 **Granulated Blast Furnace Slag**

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Abstract

Reduced sulfur species in ground-granulated blast furnace slag (GGBFS) play an important role in immobilizing radionuclide contaminants in caustic cement-GGBFS mixtures via reductive precipitation reaction. However, sulfur (S) speciation and its stability in GGBFS have not been clearly understood. In this study, S speciation of GGBSF in alkaline radionuclide liquid waste simulant solutions was investigated using S K-edge X-ray absorption near edge structure spectroscopy (XANES) and powder X-ray diffraction (XRD) measurements. Although S mineralogy was not detectable by XRD due to the amorphous nature in GGBFS, XANES analysis revealed that GGBSF contained high concentration of sulfoxide (~57%), followed by S(0) (~37%), sulfate (~3.81%), and sulfonate (~2.33%). When GGBFS was reacted with anoxic or oxygenated alkali solutions, it retained most of sulfoxide with some changes in the fraction of elemental S, sulfonate and sulfate, indicating the involvement of reduced S species in the reductive precipitation of radionuclides. This study shows the presence of intermediate S valence species in GGBFS.

1. Introduction

Cement stabilization technology (CST) for low-level nuclear waste (LLNW) has been evaluated at the United State Department of Energy (DOE) sites (e.g., Savannah River Site (SRS) in Aiken, SC (Defense waste processing facility, 2012) and Hanford site, Richland, WA) (Mattigod et al., 2010; Shi and Spence, 2004). Such remediation method is appealing due to low cost, strict production regulations, permanence, and low-temperature levels during manufacture (U.S. DOE, 2010). Among radionuclides like I-129 and U-238 in LLNW, Tc-99, in particular, mandates an

elevated level of concern for long-term non-hazardous storage due to its conservative behavior in water, high inventory, high mobility in soils, and long half-life of 2.11×10^5 y (Reigel et al., 2011; U.S. DOE, 2010). While toxicological data on Tc-99 are insufficient, certain levels of exposure to ionizing radiation can lead to cancer, leukemia, and genetic and teratogenic effects (EPA, 2005). In caustic ($\text{pH} > 12$) LLNW, Tc-99 is present as pertechnetate anion (Tc(VII)O_4^- (aq)) that is highly soluble. The aim of CST is to make Tc(VII) less soluble and encapsulate it in dense cement mixtures. The current cement waste form (CWF) formulation to immobilize Tc-99 at the Savannah River Site consists of approximately 25wt-% ground granulated blast-furnace slag (GGBSF), 6wt-% type 2 Portland cement, 25wt-% fly ash and 45wt-% radioactive waste salt solution (SRR, 2013). Ground-granulated blast furnace slag is incorporated due to its ability to increase strength in a calcium–silicate–hydrate (C–S–H) type phase, decrease porosity and create a reducing environment (Atkins and Glasser, 1992, Langton, 1987, Bernal et al., 2014). Ground granulated blast-furnace slag (GGBFS) is a coproduct of the steel industry by adding limestone to ore for the purpose of removing non-ferrous contaminants, and it consists of four major chemical components: CaO , SiO_2 , Al_2O_3 and MgO (Snellings et al., 2012). These components are highly reactive with alkaline solutions to form alkali-activated GGBS. Reduced S and Fe species in GGBFS have been considered as important electron donors to reduce Tc(VII) to Tc(IV), resulting in the formation of Tc(IV) species (Langton, 1987, Allen et al., 1997, Angus, 1985). The formation of less soluble TcO_2 (Um et al., 2011), TcS_2 (Allen et al., 1997) and Tc_2S_7 (Luken et al., 2005) have been documented in the CWF mixed with GGBFS. Consequently, the success of cement stabilization technology for LLNW is dependent on the reducing capacity of GGBFS in the CWF. Therefore, understanding the presence of these electron donors such as S

species in GGBSF is of great interest to the U.S. DOE and other environmental remediation agencies in the world.

Previously, Roy (2009) investigated sulfur speciation in granulated BFS using X-ray absorption spectroscopy (XAS). Based on the peak position comparison and linear combination fit, the dominant S species in GBFS were sulfides with a small quantity of sulfate. After reacting with alkali solutions (saturated $\text{Ca}(\text{OH})_2$ and 5N NaOH), it was reported that there was an increase in sulfate species, and the sulfide fraction was decreased. Interestingly, there was a reduction in the amplitude of a broad peak at ~2,470-2,480 eV after reacting with alkali solutions. However, the interpretation of this broad peak was inconclusive. It is too broad to be assigned for only sulfides. If the broad peak corresponds to other reduced S species in addition to sulfides, this could add insight in evaluating the reduction capacity of GGBFS for Tc(VII)-99 cement immobilization technology.

The objective of this study is to investigate the distribution of exact chemical state of S in GGBFS and changes in S speciation when reacted with alkaline LLNW simulant solution and artificial alkaline cement pore waters. Sulfur K-edge X-ray absorption near edge structure spectroscopy (XANES) was used to assess the solid state S speciation in addition to the bulk X-ray diffraction (XRD) analysis. The synchrotron-based technique is a unique spectroscopic technique for studying the local structure around selected elements (e.g., S) that are contained within a solid/liquid material. Spectral features are sensitive to the oxidation state therefore it is useful in understanding S speciation in GGBFS.

2. Materials and Methods

2.1. Blast furnace slag

Ground-granulated blast furnace slag was obtained from Holcim Inc. (Dundee, MI, USA). X-ray fluorescence (XRF) spectrometry was used for total elemental analysis. The results of elemental analysis are reported in our previous work (Meena et al., 2015). Briefly, the major elements in wt. % are CaO (37.9 %), SiO₂ (38.1 %), MgO (12.9%), Al₂O₃ (8.41%) and SO₄ (0.91%). The loss on ignition (LOI) method (ASTM D7348, 2011) was used to estimate total C in GGBFS. Dried GGFS placed in platinum crucibles were heated at 110 ± 3 °C in an oven for overnight. Then, it was heated in a furnace in a stepped schedule for 2 hr to reach 950 °C. The samples were cooled down to room temperature in a desiccator, and then the weight loss by ignition was calculated. The LOI was approximately 3.13 wt%, suggesting the presence of C in GGBFS.

Applied to GGBFS were oxygenated CaCO₃, anoxic Ca(OH)₂ and LLNW simulant solutions. This experiment was conducted in duplicate. In assessing the stability of S species in fresh and aged CST, two Ca-bearing solutions were selected to simulate a simplified porewater in contact with a fresh cement (0.017 M Ca(OH)₂ at pH 11.3 ± 0.12) where the cement chemistry was controlled predominantly by portlandite, and an aged (thousands of years) cement (0.001 M CaCO₃ at pH 8.25 ± 0.02), where the systems chemistry is controlled predominately by calcite (Criscenti et al., 1996, Krupka et al., 2012). The chemical composition of this non-radioactive LLNW simulant solution is listed in Table-1 and was designed to represent the non-radioactive waste generated at the Savannah River Site (Almond et al., 2012; Reigel, 2011). Approximately 4 g of dry GGBFS was reacted with 40mL of alkali solutions, 0.001 M CaCO₃ prepared in oxygenated ultrapure water, and of 0.017 M Ca(OH)₂ that was prepared in boiled/degassed ultrapure water. In preparing the degassed Ca(OH)₂ solution, boiled water was cooled and was

mixed with $\text{Ca}(\text{OH})_2$ salts in a N_2 filled glove bag. The mixtures were shaken on an end-over shaker for 30hr, and wet paste was recovered by centrifugation and then immediately analyzed for S speciation using XANES analysis (See Section 2.3). The samples for XANES analysis were prepared at the beam line. Subsamples were immediately dried for the XRD measurements (See section 2.2). To maintain the dispersed state, it was vacuum filtered and then freeze using liquid nitrogen, and then freeze-dry for a week.

2.2 Bulk X-ray diffraction analyses

Powder XRD data were collected from 10 to 90° 2 θ using a Siemens-Bruker D5000 diffractometer (Siemens Corp., Washington, D.C.) (graphite monochromatized Cu K radiation, 0.02° 2 θ step size, scanning speed of 1°/min). All samples were analyzed as random mounts using the back-packed procedure (Moore and Reynolds, Jr., 1997). The detection limit for crystalline phases by bulk XRD analyses is approximately 2% by wt. Mineral identifications were conducted using the JCPDS reference files.

2.3. Sulfur K-edge X-ray absorption near edge structure (XANES) analysis

Sulfur K-edge XANES measurements were conducted at beamline 4-3 Stanford Synchrotron Radiation Laboratory (Menlo Park, CA). A monochromator consisting of a double-crystal Si (111) at $\Phi=0^\circ$ with an entrance slit width of 0.5 mm and minimum energy resolution of 10^{-4} at the S K-edge (2472eV) was used. Saltstone samples were ground and homogenized using a mortar and pestle and packed into a 1.2 mm layer on 28 X 32 mm polycarbonate sample holders with a 0.2 mm XRF film (SPEX sample prep Inc. Metuchen, NJ) and S-free mylar tape. The measurements were performed with continuous He purging at room temperature. Spectra were

collected in fluorescence mode using a one-element passivated implanted planar silicon (PIPS) detector. Spectra were recorded from 2440 to 2575 eV with five regions: 2 eV steps from 2,440 to 2,460 eV with 1sec. dwell, 0.08 eV steps over the pre-edge from 2,460 to 2,478 eV at 1sec. dwell, 0.2eV steps from 2478 to 2490 eV with 1sec., 0.5 eV steps from 2,490 to 2,525 eV with 1sec. and 5ev steps from 2525 to 2575 eV with 1sec. Beam size was 10mm in width x 1mm in height. An incident of X-ray energy was calibrated using a thiosulfate powder every 24hr. The first whteline peak of thiosulfate powder was set at 2,472.02 eV for every scan. Minimum of three spectra were recorded for each sample. Acquiring multiple spectra across time allows us to quantitative evaluation of reproducibility including beam induced reduction. The background was subtracted, and the step-edge height was normalized up to ~2,500 eV to unity for all samples prior to data processing. In order to elucidate changes in S speciation, the decomposition of XANES spectra with a series of Gaussian functions was conducted at 2,420 to 2,488 eV using SIXpack (Webb, 2012). The peak positions of reference S species are listed in Table-2. It was assumed that each grouping of sulfur oxidation state produces a single peak that corresponds to s→p photoelectron transition. In this analysis, the first spectra were corrected for self-absorption using the function in SIXpack, and then two arctangent step functions representing the transition of the photoelectron to the continuum were used at low energy for all reduced S species, and another at higher energy for oxidized S species (Huffman et al., 1991; Prietzel et al., 2011; Vairavamurthy, 1998). The parameters (energy, amplitude, and FWHW) were not fixed during the fit. Various S species were identified based on the respective maximum energies for the reference compounds. The respective proportions of the S species were estimated by comparing the area under each peak with the sum of all areas. And then the correction factors for each oxidation state were applied to identified oxidation state according to Prietzel et al.

(2011). This is because the fraction of different S functionalities are not directly proportional to the relative area of each Gaussian peak because the probability of the $s \rightarrow p$ transition (i.e., absorption cross section) increases with increasing oxidation state (Waldo et al., 1991).

3. Results and Discussion

3.1. Mineralogy of GGBFS

Figure-1 shows X-ray diffractograms of GGBFS. Our analysis showed the amorphous nature of untreated GGBFS. No peaks corresponding to specific S minerals were identified. The elemental composition analysis supports the results of XRD. Elemental composition of sulfate is only ~0.9 wt %, and GGBFS contain a large quantity of SiO_2 (38.1%), CaO (37.9%), MgO (13.1%), and Al_2O_3 (8.41%). When GGBFS was treated with CaCO_3 and $\text{Ca}(\text{OH})_2$ solutions, aragonite and calcite were identified. Several researchers reported the fast formation of aragonite in cement mixed with GGBFS (Stark et al., 2001; Ludwig, 1996; Wowra et al., 2000). When the LLNW simulant solution was reacted with GGBFS, evaporates like NaNO_3 and $\text{Na}_3(\text{NO}_2)\text{O}$ were identified instead of Ca-carbonate and -oxide phases. Overall, XRD analysis did not provide useful information about S mineralogy in GGBFS due to amorphous nature of minerals. The observation is consistent with the previous investigation by Roy (2009).

3.2. Sulfur speciation in untreated dry GGBFS

Figure-2 shows the result of XANES spectra analysis. In the S XANES analysis, most of the important information for S oxidation state is hidden at 2467-2490 eV. Each Gaussian function corresponds to a specific S oxidation state in the GGBFS (Prietz et al., 2011; Roy 2009). The

distribution of S oxidation states is shown in the XANES spectrum of each GGBFS sample in Fig 2 and Table-3. The energy of Gaussian peak position increases with the increasing S oxidation state. Among our reference compounds, we observed elemental sulfur (S^0) at the lowest energy at $\sim 2472.6 \pm 0.2$ eV, sulfoxide at ~ 2476 eV, sulfonate at ~ 2481 eV and sulfate (S^{6+}) at ~ 2482 eV.

In dry untreated GGBFS, most of the S oxidation state is dominated by sulfoxide (S^{2+} ; $\sim 56.7\%$) followed by elemental sulfur (S^0 , $\sim 37.2\%$), sulfate (S^{6+} , 3.8%) and sulfonate (S^{5+} $\sim 2.3\%$). Carbon sulfoxide is known to form during the metal slag smelting process with C-H-O-gas systems with other S byproducts such as hydrogen sulfide and elemental sulfur (Stewart Jr. et al., 2000). The weight loss determined by LOI may support the presence of carbon sulfoxide-like compounds. Sulfide can be associated with CaS. It is known to form during the coal gasification process (Hebden, and Stroud, 1981). These reduced S species like sulfoxide were not clearly identified in the previous investigation by Roy (2009). This might be attributed to lack of reference spectra in the linear combination of reference compound fit analysis and or self-absorbed spectra.

3.3. Sulfur speciation in alkali reacted GGBFS

It is of our interest to quantify reduced S species (i.e., important electron donors to immobilize radionuclide contaminants) after reacting with alkali solutions. Even after GGBSF was reacted with LLNW simulant solutions, sulfoxide ($\sim 51.5\%$) was the dominant S species and followed by elemental sulfur ($\sim 40.9\%$), sulfate ($\sim 6\%$) and sulfonate ($\sim 2\%$). Although the LLNW simulant solution is oxygenated, reduced S species are still present that can contribute as electron donors to reduce radionuclides like $^{99}\text{Tc(VII)}$. Since the redox potential of sulfoxide-sulfate couple at alkaline pH is not available in the literature, a redox couple of elemental sulfur-thiosulfate (eq.1) was used to estimate the thermodynamic preference of the Tc(VII) reduction to Tc(IV)O₂ (eq. 2)

by S^0 . In this thermodynamic calculation, a kinetic limitation was not considered. The overall reaction in eq.3 shows that $Tc(VII)O_4^-$ is preferably reduced to $Tc(IV)O_2(s)$ at basic pH.

$$\Delta G = -472.40 \text{ kJ}$$

When GGBFS was reacted with an oxygenated $CaCO_3$ solution, there are same four S oxidation states (elemental, sulfoxide, sulfonate and sulfate) (Fig. 2 and Table-3). Sulfoxide (~29%) and elemental sulfur (~58.6%) are two dominant species. Sulfonate and sulfate are less than 10% of total S in this sample. It is difficult to compare the % fraction of respective S species in the untreated sample. Because desorption and dissolution reactions of different S species are occurring during the treatment. This makes total S in each sample different. It is, however, possible that the release of oxidized sulfonate and sulfoxide might have occurred, resulting in the % fraction of elemental sulfur large.

The treatment with anoxic $Ca(OH)_2$ solution resulted in the same S oxidation states (S^0 , sulfoxide, sulfonate, sulfate) (Fig. 2 and Table-3). As observed in previous two treatments, most of the S is dominated by sulfoxide (~69.3 %) followed by elemental sulfur (25.4%), sulfate (~3.5%), and sulfonate (~1.77%).

Because of the anoxic nature of this alkali solution, some of intermediate S species was reduced by potential electron donor like Fe(II), resulting in a decrease in the fraction of sulfoxide. Ferrous ion is known to be present in untreated slag (Arai and Powell, 2015). Overall, alkali reacted GGBFS still contains reduced S species that could have an important role as electron donors to reduce radionuclides.

4. Conclusions

Because of low S concentration (< 1% by wt) and X-ray amorphous phases, the exact S compounds could not be identified using conventional XRD analysis. Sulfur K-edge XANES technique in conjunction with Gaussian peak fit analysis were used effectively to elucidate the solid state S speciation (e.g., sulfur oxidation state). It was found that reduced S forms in dry GGBFS were sulfoxides and sulfide/elemental sulfur. Surprisingly, sulfoxide was a dominant species. When it was reacted with various caustic alkali solutions, including a LLNW simulant solution, these reduced S species were relatively stable. Sulfur speciation in the two simulated cement pore water solutions, the Ca(OH)₂ and CaCO₃ solutions, were similar. Our investigation showed for the first time the presence of reduced and intermediate S oxidation state (sulfoxide) in GGBFS, and they are relatively stable in anoxic and oxygenated alkali solutions, suggesting the important electron donor source for ⁹⁹Tc(VII). This information may be especially important for identifying an appropriate geochemical model in risk assessment models for describing the long-term fate of ⁹⁹Tc under long-term disposal conditions.

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Tables

Table-1. Chemical composition of artificial LLNW simulant used in saltstone preparation at the U.S. DOE Savannah River Site (Almond et al., 2012; Reigel, 2011). The solution was passed through a 0.2 μm PVDF filter prior to the use.

Compound	Concentrations (mol/L)
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.11
NaOH	1.55
Na_2SO_4	0.05
Na_2CO_3	0.14
NaNO_3	2.11
NaNO_2	0.33

Table-2. Whiteline peak positions of S K-edge XANES spectra of reference compounds used in the peak fit analysis. *Prietz et al., 2011.

Species	Whiteline peak maxima (eV)	Sulfur oxidation state and S environment	Correction factor for the peak area*
Elemental sulfur (S^8)	2472.6 $\pm$ 0.2	0	1
Dimethyl sulfoxide ($\text{C}_2\text{H}_6\text{SO}$)	2476 $\pm$ 0.4	2+ (sulfoxide: R-S=O)	0.61
Taurine ($\text{C}_2\text{H}_7\text{NO}_3\text{S}$, Sulfonate)	2481.5 $\pm$ 0.3	5+ (sulfonate: SO_3^-)	0.39
Sodium sulfate (Na_2SO_4), gypsum (CaSO_4), alunogen ($\text{Al}_2(\text{Si}_4)_3\text{SO}_4 \cdot 17\text{H}_2\text{O}$), ettringite ($\text{Ca}_6[\text{Al}(\text{OH})_6](\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$)	2481.9-2483.5	6+ (sulfate)	0.34

Table-3. Results of Gaussian peak fit analysis of S K-edge XANES spectra of GGBFS that are (un)treated with different alkali solutions (Fig 2). LLNW: Low level nuclear waste. Each fraction is shown in mole %. % peak area is corrected with correction factors for each oxidation state are according to Prietzel et al., 2011 and Roy 2009.

Treatment	S(0)	Sulfoxide	Sulfonate	Sulfate	R factor
0.017M Ca(OH) ₂	25.41±0.94	69.30±0.09	1.77±0.02	3.54±0.07	0.0002
0.001M CaCO ₃	58.61±1.54	28.94±4.35	3.16±0.27	9.34±0.2	0.0043
LLNW simulant (Table-1)	40.93±4.99	51.5±6.76	1.84±0.37	5.82±0.02	0.0003
Untreated	37.16±1.61	56.7±2.3	2.33±0.15	3.81±0.8	0.0018

Figure-1: X-ray diffraction patterns of ground-granulated blast Furnace slag (GGBFS) treated with/without alkali solutions. From the bottom to top, air-dried untreated GGBF, CaCO₃ solution treated GGBFS, Ca(OH)₂ solution treated GGBFS, and low level waste simulate solution treated GGBFS. Peaks corresponding to calcite, aragonite, sodium nitrate and sodium oxide nitrite are denoted as C, A, SN and SON, respectively.

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421 Figure-2: Sulfur K-edge XANES spectra of ground-granulated blast Furnace slag (GGBFS) with/without
422 treatment of alkali solutions. From the bottom to top, dry untreated GGBF, low level waste simulate
423 solution treated GGBFS, CaCO_3 solution treated GGBFS, and Ca(OH)_2 solution treated GGBFS. The
424 results of Gaussian peak fit analysis with two arctangent lines are shown under each unknown XANES
425 spectrum. The XANES spectra and fit are shown in solid black lines and dashed black lines, respectively.
426 Each Gaussian peak (from lower to higher energy) is corresponding to S^0 (red), sulfoxide (blue), sulfonate
427 (green) and sulfate (magenta).