



## Short Communication

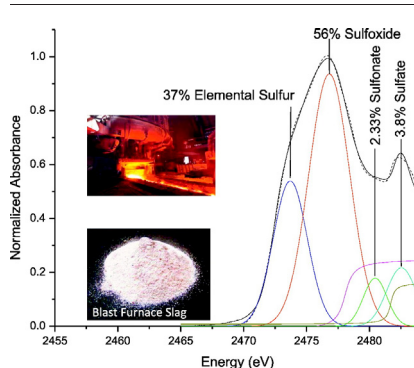
## Sulfur speciation in untreated and alkali treated ground-granulated blast furnace slag

Yuji Arail<sup>a,\*</sup>, Brian A. Powell<sup>b</sup>, Daniel I. Kaplan<sup>c</sup><sup>a</sup> Department of Natural Resources and Environmental Sciences, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States<sup>b</sup> Department of Environmental Engineering and Earth Sciences, L.G. Rich Environmental Laboratory, 342 Computer Court, Anderson, SC 29625, United States<sup>c</sup> Savannah River National Laboratory, Aiken, SC 29808, United States

## HIGHLIGHTS

- Reduced sulfur speciation in blast furnace slag was investigated using S K-edge XANES analysis.
- Blast furnace slag contains high concentration of sulfoxide (~57%).
- The sulfoxide fraction in slag was stable when treated with anoxic or oxygenated alkali solutions.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 4 January 2017

Received in revised form 18 February 2017

Accepted 19 February 2017

Available online xxxx

Editor: J Jay Gan

## Keywords:

Blast furnace slag

Slag

Sulfur speciation

XANES

Sulfoxide

## 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 GGBFS 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 GGBFS 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.

© 2017 Elsevier B.V. All rights reserved.

## 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)

\* Corresponding author.

E-mail address: [yarai@illinois.edu](mailto:yarai@illinois.edu) (Y. Arail).

(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  $2.11 \times 10^5$  y (Reigel, 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, 2008). In caustic (pH > 12) LLNW, Tc-99 is present as pertechnetate anion ( $\text{Tc(VII)O}_4^-$  (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 25 wt% ground granulated blast-furnace slag (GGBFS), 6 wt% type 2 Portland cement, 25 wt% fly ash and 45 wt% 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<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> 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 and Glasser, 1985). The formation of less soluble TcO<sub>2</sub> (Um et al., 2011), TcS<sub>2</sub> (Allen et al., 1997) and Tc<sub>2</sub>S<sub>7</sub> (Lukens 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 GGBFS 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 Ca(OH)<sub>2</sub> and 5 N 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 ~2470–2480 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%), SiO<sub>2</sub> (38.1%), MgO (12.9%) Al<sub>2</sub>O<sub>3</sub> (8.41%) and SO<sub>4</sub> (0.91%). The loss on ignition (LOI) method (ASTM D7348, 2011) was used to estimate total C in GGBFS. Dried GGBFS placed in platinum crucibles were heated at  $110 \pm 3$  °C in an oven for overnight. Then, it was heated in a furnace in a stepped schedule for 2 h 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 CaCO<sub>3</sub>, anoxic Ca(OH)<sub>2</sub> 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)<sub>2</sub> at pH  $11.3 \pm 0.12$ ) where the cement chemistry was controlled predominantly by portlandite, and an aged (thousands of years) cement (0.001 M CaCO<sub>3</sub> at pH  $8.25 \pm 0.02$ ), where the systems chemistry is controlled predominantly 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 40 mL of alkali solutions, 0.001 M CaCO<sub>3</sub> prepared in oxygenated ultrapure water, and of 0.017 M Ca(OH)<sub>2</sub> that was prepared in boiled/degassed ultrapure water. In preparing the degassed Ca(OH)<sub>2</sub> solution, boiled water was cooled and was mixed with Ca(OH)<sub>2</sub> salts in a N<sub>2</sub> filled glove bag. The mixtures were shaken on an end-over shaker for 30 h, 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° 2θ using a Siemens-Bruker D5000 diffractometer (Siemens Corp., Washington, D.C.) (graphite monochromatized Cu K radiation, 0.02° 2θ step size, scanning speed of 1°/min). All samples were analyzed as random mounts using the back-packed procedure (Moore and Reynolds, 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 (2472 eV) was used. Saltstone samples were ground and

**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)
Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	0.11
NaOH	1.55
Na <sub>2</sub> SO <sub>4</sub>	0.05
Na <sub>2</sub> CO <sub>3</sub>	0.14
NaNO <sub>3</sub>	2.11
NaNO <sub>2</sub>	0.33

Download English Version:

<https://daneshyari.com/en/article/5751535>

Download Persian Version:

<https://daneshyari.com/article/5751535>

[Daneshyari.com](https://daneshyari.com)