



Sulfur speciation in granulated blast furnace slag: An X-ray absorption spectroscopic investigation

Amitava Roy *

J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices, Louisiana State University, Baton rouge, Louisiana 70806, USA

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ABSTRACT

Sulfur speciation in a granulated blast furnace slag (GGBFS) was analyzed by X-ray absorption near edge structure spectroscopy (XANES) before and after activation by saturated calcium hydroxide and five normal sodium hydroxide solutions. The solution to GGBFS ratio was 0.4.

XANES showed that sulfur in GGBFS existed mostly as sulfides (frozen in calcium polyhedra) with a minor amount as sulfate. A slowly-cooled blast furnace slag, in contrast, had most of the sulfide transformed to sulfate. After activation of GGBFS, more sulfate formed and crystalline sulfide phases became more apparent. More slag reacted at lower pH than at higher pH.

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1. Introduction

Sulfur species, particularly in the sulfate form, exert an inordinately strong influence on the stability of cementitious materials even though they constitute a very small portion of the mass or volume. For example, the sulfate containing phase ettringite is implicated in sulfate attack in concrete and cement-stabilized soil, even though the amount of ettringite is low and the exact mechanism is not fully understood [1]. Radwan [2] noted that there was an optimum sulfide content for Egyptian GGBFS for Portland cement clinker, GGBFS, and gypsum mixtures for strength and other physical properties. These values decreased on both sides of the maximum. He suggested that these components be mixed in only those proportions which will keep the overall sulfide content down.

It is not easy to monitor the sulfur species in cementitious materials as it can be distributed among different phases and it can also be in the pore solution. Apart from the ettringite, the calcium silicate hydrate and monosulfate can contain some of the sulfate. In addition, some of the original sulfates phases such as gypsum and anhydrite may remain. If a sulfite sludge from a coal-fired power plant is used in some form of stabilization, the speciation of sulfur will be different [3]. Granulated blast furnace slag also has a different speciation for sulfur. Radwan [2] quoted Russian studies from the 1960s which showed that sulfide and sulfate are the main species of sulfur in GGBFS. Scott et al. [4] reported that a small amount of oldhamite (CaS) is a common occurrence in a

group of 11 GGBFS from Britain and France. Oldhamite occurred both as independent dendritic crystals and inclusions in melilite. Van Dam et al. recently suggested that coarse slag aggregate (slowly-cooled blast furnace slag) can potentially supply sulfate for sulfate attack by oxidation of the calcium sulfide in it [5].

It is common knowledge that the interior of activated GGBFS (usually very light brown in color) assumes a green color when activated. The color is pale green within the first few hours and becomes darker over time. Scott et al. [4] reported metallic iron inclusions within melilite crystals and also as globules of immiscible iron, tens of micrometer in diameter. GGBFS is often used in waste stabilization with cementitious materials as it provides a reducing environment for the waste. Bajt et al. [6] showed by X-ray absorption spectroscopy that this environment reduced toxic hexavalent chromium to the more benign trivalent form. The iron content of GGBFS typically ranges from 0.2 to 1.6% (<http://www.tfhrc.gov/hnr20/recycle/waste/GGBFS1.htm>). The amount of iron as Fe_2O_3 in the GGBFS used in this study is 1.3%.

X-ray absorption spectroscopy is an element-specific analytical technique which can be used to study directly the speciation and oxidation state without any extensive wet chemical procedures. For example, the sulfide, sulfite and sulfate species in a sulfur-containing material can be easily identified and quantified by X-ray absorption near edge structure (XANES) spectroscopy [7] from the same specimen all at once. XANES focuses on the total sulfur, independent of exact speciation, or whether it is in crystalline, amorphous or aqueous form. In contrast, wet chemical methods would identify the species extracted in solution, not necessarily the species actually present in the solid sample. The objective of this study is to investigate speciation of sulfur in GGBFS and its changes after activation. The fate of sulfur speciation during slow cooling of slag was also studied.

* Tel.: +1 225 578 6706; fax: +1 225 578 6954.

E-mail address: reroy@lsu.edu.

2. Experimental procedure

2.1. Sample preparation

The slag used in the study was obtained from Buzzi Unicem. It was a 120 Grade slag. The slowly-cooled slag also came from the same source. The chemical composition of the slag is listed in Table 1. The sulfur content, however, was not provided. The typical sulfur (S) content of GGBFS is 1.4%, and ranges between 1.0 and 1.9%, as found by the National Slag Association from 18 analyses (<http://www.tfhrc.gov/hnr20/recycle/waste/GGBFS1.htm>).

The specimens for this study were prepared by weighing approximately 40 gm of slag in a Tri-pour™ polyethylene beaker and adding a solution so that a 0.4 solution to slag ratio was obtained. The solutions used were 5 N NaOH (pH 14.69), and saturated solutions of calcium hydroxide (pH ca. 12.6) [8,9]. (These conditions also simulate the pH in cementitious systems, including supersaturated pore water.) The slag and solution were thoroughly mixed with a stirrer, the beaker was covered with parafilm, and cured for required lengths of time. The mixes usually set within minutes to hours with the green color in the interior developing within hours of activation. The specimens were stored in air. After five months, the interior of most specimens was dark green while only a 1 to 2 mm thick light brown exterior shell remained. The data presented in this report came from specimens which were analyzed five months after preparation. The younger specimens showed very similar trends. The specimens were crushed to a fine powder with an agate mortar and pestle just before XANES measurements.

2.2. X-ray absorption spectroscopy

The sulfur K edge measurements were performed at the Double Crystal Monochromator beamline of the J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices (CAMD), Louisiana State University, Baton Rouge, Louisiana. The beamline operates in “windowless” mode, a 13-μm-thick Kapton™ window separating the experimental setup from the ring. The CAMD synchrotron ring operates at 1.3 GeV, with a typical ring current between 230 and 100 mA.

A thin layer of the finely-powdered sample was uniformly spread on a sulfur-free Kapton™ tape and placed in the chamber at 45° for fluorescence measurements and normal to the beam for transmission measurements.

The S K edge measurements were made with InSb 111 crystals. The resolution of the monochromator at this energy range is ca. 1 eV. The monochromator was detuned by 60% to remove the harmonics. The step sizes for measurements (with respect to the sulfur K edge, 2472.0 eV) were from −70 eV to −10 eV (1.5 eV steps), −10 eV to 30 eV (0.1 eV steps), and from 30 eV to 125 (1.5 eV steps); integration period was 2 s through all regions. The fluorescence X-rays were measured with a Canberra™ single-element germanium detector. S K edge measurements were made at the partial pressure of nitrogen 180 mTorr. The sulfur K edge was calibrated with the zinc sulfate hydrate (ZnSO₄·2H₂O) peak set at 2881.44 eV. The fluorescence spectra were collected repeatedly until good counting statistics were achieved. Data reduction was performed with Athena [10] and WinXAS [11].

The XANES standards used in the study were either reagent grade chemicals obtained from Alfa Aesar or Sigma Aldrich or naturally occurring minerals. These phases are typical sulfur-containing phases expected in construction materials. The source of each standard, their

Table 2

XANES peaks of some selected sulfur compounds.

Phase/mineral	Peak position (eV)	Sulfur oxidation state	Source
Reagent grade gypsum (CaSO ₄ ·2H ₂ O)	2481.94	S ⁺⁶	Sigma-Aldrich
Reagent grade anhydrite (CaSO ₄)	2481.9	S ⁺⁶	Alfa Aesar
Ettringite (Ca ₆ [Al(OH) ₆](SO ₄) ₃ ·26H ₂ O)	2481.89	S ⁺⁶	Prepared in the laboratory by CTL, Skokie, Ill.
Hannebachite (CaSO ₃)	2471.13, 2477.45, 2481.59	S ⁺⁴	A mineral specimen of hannebachite from Hannebach, Eifel, Germany, was obtained through Roger's Minerals, Ontario, Canada.
Reagent grade calcium sulfide (oldhamite) (CaS)	2473.98, 2477.51	S ^{−2}	Alfa Aesar
Sulfur	2472.71	S ⁰	Ward's Natural Science
Zinc sulfide (Sphalerite) (ZnS)	2473.32	S ^{−2}	Ward's Natural Science

chemical formula, oxidation state of sulfur in them, and peak locations are given in Table 2.

3. Results and discussion

3.1. Sulfur in granulated blast furnace slag

In XANES spectroscopy the strongest peak is known as the white line (Fig. 1, A). This peak is due to the resonance of the excited electron between 1s and np states. The subsequent peaks at higher energy are usually due to multiple scattering of the excited electron between different shells (for example, peaks B and C in Fig. 1). The absorption edge of sulfur shows a wide distribution depending on the oxidation state, −2 to +6, with the edge moving to higher energy with increasing oxidation state, spanning as much as 13 eV [12].

Fig. 1 shows the XANES spectra of sulfur and some sulfide phases. The absorption edge of sulfur (the first derivative) is at 2472.0 eV. Oldhamite (CaS), with sulfur oxidation state of −2, has the strongest peak (white line labeled A) at 2473.98 eV. The other minor peaks B, C and D occur at higher energies. Another sulfide phase, copper sulfide, is also included in the figure showing that when the sulfur is in the same oxidation state the peaks occur in the very similar energy range. The differences in peak intensities are due to the type of cation [13]. Fig. 2 shows the XANES spectra of gypsum, anhydrite, ettringite and

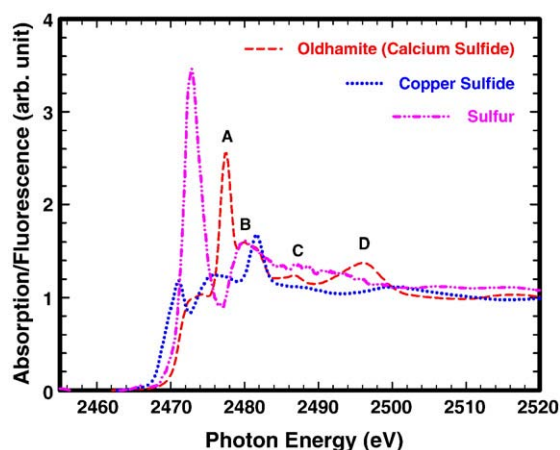


Fig. 1. Sulfur K edge XANES of sulfur and some sulfide minerals.

Table 1
Chemical composition of GGBFS.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
34.5	9.5	1.3	39.6	10.9	1.3	0.5

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