

STUDY OF THE BLUE/GREEN COLOUR OF BLAST FURNACE SLAG BASED MATERIALS

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Introduction

Slag-rich mortars and concretes, including slag/Portland blended and geopolymer-based cements, manifest a blue/green colour. The presence of this specific colour is usually observed after setting. When the concrete is exposed to air, the specific colour of the exterior surface turns to “grey” (cement concrete) or “white” (slag concrete). However, if the concrete is left to set for long time in formwork or cured under water (case of precast), it can maintain the blue/green colour for a long period. This specific colour is of particular concern in concrete applications where visual aesthetics are important but its origin is not well understood. In the literature, the origin of this colouration is often assumed, without any detailed investigation, to be due to the presence of sulphur in slags. Undoubtedly, in-depth understanding of the colouration mechanism is the key point if an effective decolourising treatment is to be found.

In the present study, it is assumed that the origin of colouration is indeed the sulphur species. X-ray absorption near edge structure (XANES) spectroscopy is an element-specific analytical tool that is well-suited to our requirements. S K-edge XANES has already been used to investigate S speciation in slag-based binders but no correlation with colouration has yet been made. Two methods of slag activation were considered: Portland cement and sodium silicate.

Experimental procedure

The GGBS used in this study was from ECOCEM (France). It was a fine white powder with a D50 of 10.7 μm and a Blaine fineness of 4380 cm^2/g . It contained less than 1% (in mass) of total sulphur. The consolidated pastes were prepared following the two most commonly used methods in the literature for GGBS activation: a) alkali-activation with different amounts of sodium silicate powder (SILMACO NV, $\text{SiO}_2/\text{Na}_2\text{O}$ modulus

=1) (referred to as NaSi); b) activation with ordinary Portland cement with different GGBS/CEMI ratios: 30%, 50% and 70% by weight. The curing of the pastes was performed at 20°C.

All the pastes were prepared at the same water/binder ratio of 0.47. They were casted in a plastic tube covered with a lid to avoid contact with the air and a subsequent eventual oxidation of the sulphur species. Several days after casting, the samples were demoulded and split in half for colour research.

The sulphur K edge XANES measurements were performed at the beamline ID21 of the ESRF Synchrotron radiation facility (Grenoble, France)¹. The XANES spectra present the average collections from different points.

Results and Discussions

Sulphur speciation in OPC and in sodium silicate (NaSi) activated GGBS

The XANES spectra of the OPC-activated GGBS and of alkali-activated GGBS samples are shown in Figure 1. The identifications of peaks are reported in Table 1.

The sulphate peak (B) is significantly enhanced in the presence of OPC and upon hydration, whereas the low oxidation features are mitigated (peaks C). This effect increases with OPC content. The increase of OPC content may impact the sulphur chemistry in at least two ways: increase of sulphate-bearing species content (ettringite, monosulfoaluminate and possibly anhydrite), and increase of the reaction degree of the GGBS.

The S K-edge XANES spectra of alkali-activated GGBS samples are more complex than in the case of OPC activation. Formation of several S bearing species is suspected. The increase in NaSi content leads to an increase of the amount of sulphates (peak B) and probably thiosulphate $S_2O_3^{2-}$ (peak B') according to the ESRF reference database². Increasing the concentration of NaSi (4%) leads to a significant rise of these two peaks. In addition, the broad peak at low energy (peak C) splits into several distinctive peaks and the appearance of a shoulder can be observed at the very low energy of 2469.6 eV (lower than that corresponding to the lowest sulphur oxidation state). A zoom on this zone was studied.

Several studies on the origin of the deep blue colour of the stone lapis lazuli or the ultramarine pigment (derived from the mineral lazurite) have been reported in the literature³. This colour has been generally attributed to the presence of the trisulphur radical, which is trapped in a zeolitic type cage^{4,5}. A zoom on the low energy area of the XANES spectra also shown in Figure 1. As in case of OPC, the energy position of the shoulder is about 2469.6 eV, which is slightly higher than that reported in the literature³. The exact position of the shoulder may depend on the chemical environment of the radical and also on the calibration of the experimental setup. The

distinctive aspect of this feature is that it is located below the peak of the most reduced sulphur, and this was the case here. As in case of NaSi, except for 1% NaSi (white samples), the XANES spectra presented were obtained within the blue/green zones. The XANES signals do indeed display a shoulder at low energy in the case of the blue coloured samples with 4% and 10% NaSi, which is a signature of the presence of the trisulphur radical anion³. Moreover, the shoulder is absent in the case of 1% NaSi (white sample).

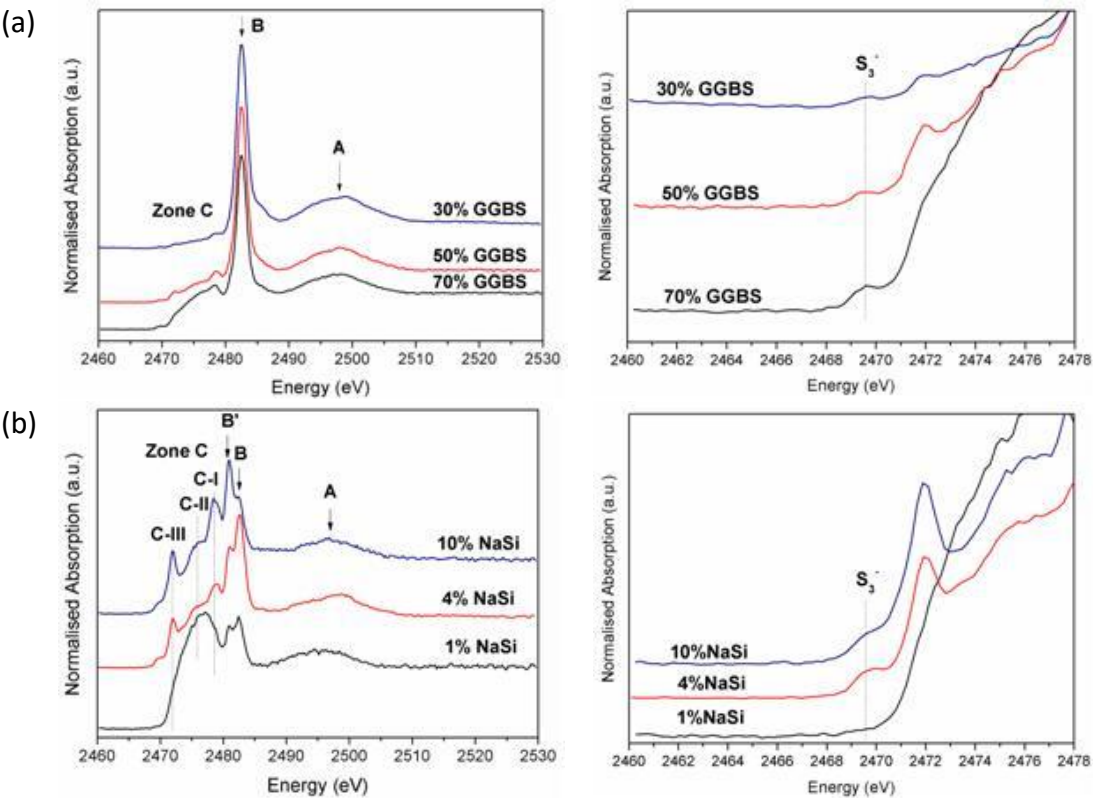


Figure 1: Sulphur K-edge XANES spectra and zoom on low energy area. (a) OPC activated GGBS, (b) NaSi activated GGBS

Table 1: S K-edge XANES peak positions of the different sulphur species considered in this study

Feature	Energy position (eV)	Identification and oxidation state
A	2498.8	First EXAFS feature: crystalline sulphate (gypsum)
B	2482.5	SO ₄ ²⁻ : sulphate (+6)
B'	2481.0	S ₂ O ₃ ²⁻ : Thiosulphate (-2, +6)
	2471.7	Second peak for S ₂ O ₃ ²⁻
C	2477.2	S ²⁻ : sulfide (-2)
	2472.8	S ⁰ : native sulphur (0)
	2470.2	Second peak for S ²⁻
	2469.6	S ₃ ⁻ : trisulphur radical

Possible origin of the trisulphur radical anion in hydrated GGBS

The GGBS framework is suspected to contain a variety of possible sulphur species with different chemical environments. The sulphur in an anhydrous GGBS is mainly present in reduced form, which is likely to consist principally of S^{2-} and S^0 . When the GGBS is activated, the S_3^- radical starts to form by reaction of sulfide (S^{2-}) and elemental sulphur (S^0) under the alkaline environment. At the same time, along with the hydration of GGBS, an aluminosilicate framework forms, which is likely to be similar in structure to sodalite (Na, Ca) $(Al_6Si_6O_{24})$. The formed aluminosilicate, having a zeolite-like structure, acts as a “cage”, which can trap the trisulphur (S_3^-) formed to give *alapis lazuli* – like material (Na, Ca) $(Al_6Si_6O_{24})(S_3)$. However, the formed compound is not stable as in the case of *lapis lazuli*. Under atmospheric conditions it can be oxidised to (Na, Ca) $(Al_6Si_6O_{24})(SO_4 \text{ or } S_2O_3)_x$ phase leading to the loss of the blue colour.

Conclusions

In this study, it was proved that the blue/green colouration of the hydrated samples was correlated to the presence of a pre-peak: the trisulphur radical anion, which has already been reported at the origin of the blue colouration of the medium considered. It was assumed that this radical might be formed in slag binders under hydration as *alapis lazuli* – like material (Na, Ca) $(Al_6Si_6O_{24})(S_3)$, contributing to the blue colouration of the sample. Other possible origins of the colouration of slag-based materials cannot be excluded, in particular those related to the presence of transition metals. The latter may associate with ligands present in the alkaline solution and form various chromophore complexes.

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