



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



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Introduction - « blue/green » color

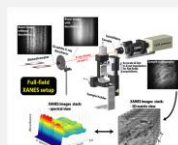
- Slag-rich mortars and concretes, including slag/Portland blended and geopolymer-based cements, manifest a blue/green color;
- This specific color is usually observed after setting;
- When the concrete is left to set for long time in formwork or cured under water (case of precast), the blue/green color is maintained for a long period;
- The origin of coloration is assumed to be related to sulfur species.



- Example: 100% GGBS activated by sodium silicate, kept 2 weeks in polystyrene mould

XANES spectroscopy

- X-ray absorption near edge structure (XANES) spectroscopy is an element-specific analytical tool, for example used for S speciation.



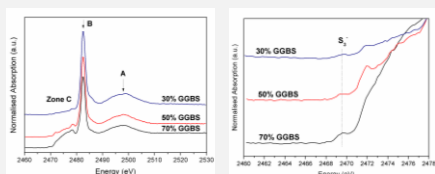
The sulfur K edge XANES measurements were performed at the beamline ID21 of the ESRF(Grenoble, France)

Experimental procedure

- GGBS (ECOCHEM) : fine white powder with D_{50} of 10.7 μm , Blaine fineness of 4380 cm^2/g . It contains < 1% (in mass) of total sulfur.
- The consolidated pastes cured at 20°C were prepared following the two most commonly activation systems:
 - activation with Ordinary Portland cement with different GGBS/CEM I ratios: 30%, 50% and 70% by weight.
 - alkali-activation with different amounts of sodium silicate powder (marked as NaSi).

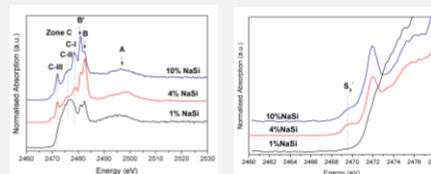
Results : GGBS/CEM I mix

- Peak (B), identified as sulfate, is significantly enhanced in the presence of OPC and upon hydration, whereas the low oxidation features are mitigated (peaks C).
- The position of shoulder at 2469.6 eV is attributed to a trisulfur radical anion (S_3^-).



Results : Sodium silicate activated GGBS

- The broad peak at low energy (peak C) splits into several peaks.
- The appearance of a shoulder at 2469.6 eV (S_3^-) can be observed for 4% and 10% NaSi (blue colored samples), not for 1% NaSi sample (white sample).



Discussion

- Identification of XANES peaks
- The sulfur in anhydrous GGBS is mainly present as S^{2-} and S^0 .
- When GGBS is activated, S_3^- radical anion starts to form by reaction of sulfide (S^{2-}) and elemental sulfur (S^0) under alkaline environment.
- S_3^- radical anion can be trapped by hydrated product $(\text{Na,Ca}) (\text{Al}_6\text{Si}_6\text{O}_{24})$ to form stable material $(\text{Na,Ca}) (\text{Al}_6\text{Si}_6\text{O}_{24})(\text{S}_3^-)$ – lapis lazuli - like material.



| Feature | Energy position (eV) | Identification and oxidation state |
|---------|----------------------|---|
| A | 2498.8 | First EXAFS feature: crystalline sulfate (gypsum) |
| B | 2482.5 | SO_4^{2-} : sulfate (+6) |
| B' | 2481.0 | $\text{S}_2\text{O}_3^{2-}$: trisulfate (-2, +6) |
| | 2471.7 | Second peak for $\text{S}_2\text{O}_3^{2-}$ |
| | 2477.2 | S^{2-} : sulfide (-2) |
| | 2472.8 | S^0 : native sulfur (0) |
| | 2470.2 | Second peak for S^0 |
| | 2469.6 | S_3^- : trisulfur radical |

Conclusion

- A pre-peak around 2469.6 eV was detected by XANES, attributed to trisulfur radical anion.
- It was assumed that this radical anion might be formed in slag binders under hydration as a lapis lazuli - like material $(\text{Na,Ca}) (\text{Al}_6\text{Si}_6\text{O}_{24})(\text{S}_3^-)$, contributing to blue color.
- Other possible origins of the coloration cannot be excluded, especially with the presence of transition metals.

ECOCHEM Materials

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