

ENGINEERING OF $\text{CaO-Al}_2\text{O}_3\text{-FeO}_x\text{-SiO}_2$ SLAGS FOR HYBRID CEMENTS

Jorn VAN DE SANDE^{1,2,3}, Roberto MURILLO ALARCÓN^{2,3}, Yiannis PONTIKES², Hubert RAHIER¹

¹ Vrije Universiteit Brussel, Department of Materials and Chemistry, 1050 Brussels, Belgium

² KU Leuven, Department of Materials Engineering, 3001 Leuven, Belgium

³ SIM vzw, Technologiepark 935, 9052 Zwijnaarde, Belgium

jorn.van.de.sande@vub.be, robertoeduardo.murilloalarcon@kuleuven.be

yiannis.pontikes@kuleuven.be, hubert.rahier@vub.be

Introduction

Ordinary Portland cement (OPC) is a large contributor to the global anthropogenic CO_2 production, about 8-9% of the total.¹ Inorganic polymers (IP) are in this case promising,² however, they have yet to realise their full market potential. Alternatives are being sought to overcome the need for expensive (due to their high molarity) sodium silicates. Hybrid cements could be a possible solution. They consist of 5-30% OPC mixed with a source that is used for inorganic polymer synthesis, such as fly ash or slags, and an alkali activator with a lower alkalinity compared to activators used for IP synthesis, such as sodium carbonates or sulfates.³ This could be a practical step forward to reduce emissions related to the cement industry and using by-products from the non-ferrous metal industries. Structure-property relationships for IP-based on Fe-rich slags have been investigated to some extent. The effect of slag chemistries on the properties of inorganic polymers derived from iron-rich slags has been studied more systematically for the ternary $\text{CaO-FeO}_x\text{-SiO}_2$ system.⁴

In this work, the effect of the slag chemistry of synthetic $\text{CaO-Al}_2\text{O}_3\text{-FeO}_x\text{-SiO}_2$ slags for the synthesis of hybrid cements, containing 80 wt% iron-rich slag and 20 wt% OPC using Na_2SO_4 as activator, was investigated. The influence of the chemistry on the reaction was studied using isothermal calorimetry. Secondly, the influence of the chemistry on the compressive strength at 2, 7 and 28 days was investigated.

Experimental

Eight synthetic $\text{CaO-Al}_2\text{O}_3\text{-FeO}_x\text{-SiO}_2$ slags with different chemistries, *i.e.* different $(\text{FeO}+\text{CaO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$, FeO/CaO and $\text{Al}_2\text{O}_3/\text{SiO}_2$ molar ratios, representing industrial non-ferrous metallurgy slags. These were produced using the procedure outlined elsewhere⁴, except that all slags were quenched in water by tilting the furnace, as this was shown⁵ to be more effective in delivering higher amorphous content. The chemical composition of the slags was assessed using a Philips PW2400

X-Ray (XRF) spectrometer. The crystallinity of the slags was determined by XRD (Bruker D2 PHASER). The addition of 10 wt% of ZnO enabled a quantification by Rietveld refinement using Topas Academic⁵. For isothermal calorimetry, samples were prepared by mixing 0.19 g Na₂SO₄, 0.80 g Portland cement (Heidelberg CEM I 52.5N) and 3.20 g of synthetic slag with 1.67 g of distilled water (W/B = 0.4), using a Heidolph RZR 2041 mixer at approx. 2500 rpm for 90 seconds. The heat flow was recorded for 7 days using a TAM-air isothermal calorimeter at 20°C. For compressive strength, cubic paste samples (2x2x2 cm³) were prepared using the same percentages in the formulation above, using 274.9 g of total solid and an IKA RW20 (Labortechnik) mixer at approx. 1600 rpm for 2 min. After one day, the samples were demoulded and were cured at 20°C and a relative humidity of > 95%. Compressive strength measurements were carried out at 2, 7 and 28 days using a 5567 Instron testing device equipped with a 30 kN load cell using a crosshead speed of 1 mm/min. The software JMP Pro 14 was used for the statistical analysis.

Results and discussion

The chemical compositions and the amorphous fractions of the slags are presented in Table 1. They are denoted by S followed by a value (L=low, H=high, M=middle) for the molar ratios in the following order (FeO+CaO)/(SiO₂+Al₂O₃), FeO/CaO, Al₂O₃/SiO₂. In Figure 1a, two distinct exothermic features can be seen in the heat flow curve. First the cement hydration occurs around 6 h, time-independent for the different slag chemistries. The second exotherm only appears if slag is added to the cement. The slag chemistry has a profound effect on the kinetics and the quantity of heat produced. Therefore, the second peak is attributed to the reaction of the slag. The amorphous content (*e.g.* the lower amorphous fraction of S-H-H-L) has less effect on the kinetics than the slag chemistry in hybrid cements. This differs from IPs, in which case the lower amorphous content slows down the reaction and lowers the compressive strength.⁴ Therefore, semi-vitreous slags can be valorised in hybrid cements, even when they are not sufficiently amorphous for IPs.

In Figure 2, the compressive strength at 2, 7 and 28 days is shown. The 28 d strength of OPC reference paste (W/B = 0.4) was 99 MPa. The 2 d strength is significantly influenced by all three molar ratios and can be modelled as follows:

$$2 \text{ d (MPa)} = 2.174 \frac{\text{FeO}+\text{CaO}}{\text{SiO}_2+\text{Al}_2\text{O}_3} + 0.245 \frac{\text{FeO}}{\text{CaO}} + 29.130 \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} - 3.180, R^2 = 0.97. \quad (1)$$

Therefore the 2 d strength is strongly influenced by the Al₂O₃/SiO₂ ratio, where a higher ratio results in a higher early age strength. For the same (FeO+CaO)/(SiO₂ + Al₂O₃), higher CaO contents (*i.e.* lower FeO/CaO molar ratio) in the slag lowers the 2 d strength, which has also been observed for inorganic polymers.⁴ The highest 2 d

strength was observed for S-L-H-H and S-H-H-H and was 10.1 and 9.8 MPa, respectively. Interestingly, the cumulative heat of the hybrid cements was correlated to their 2 days compressive strength, *i.e.* the strongest and weakest have the highest and lowest cumulative heat, respectively.

Table 1: Chemical composition of the studied slags in wt%, the (FeO+CaO)/(SiO₂+Al₂O₃), FeO/CaO and Al₂O₃/SiO₂ molar ratios and the amorphous content in wt%

| Slag | Chemical composition | | | | Molar ratios | | | Amorphous fraction |
|---------|----------------------|------------------|------|--------------------------------|---|---------|--|--------------------|
| | FeO | SiO ₂ | CaO | Al ₂ O ₃ | (FeO+CaO)/(SiO ₂ +Al ₂ O ₃) | FeO/CaO | Al ₂ O ₃ /SiO ₂ | |
| S-L-L-L | 41.2 | 35.5 | 16.6 | 6.0 | 1.34 | 1.93 | 0.10 | > 98 |
| S-L-L-H | 39.8 | 31.6 | 16.5 | 11.5 | 1.33 | 1.88 | 0.21 | > 98 |
| S-L-H-L | 55.9 | 33.6 | 3.7 | 6.4 | 1.36 | 11.94 | 0.11 | 92 |
| S-L-H-H | 57.4 | 28.1 | 3.6 | 10.5 | 1.51 | 12.62 | 0.22 | > 98 |
| S-M-M-L | 56.1 | 27.7 | 10.4 | 5.2 | 1.89 | 4.20 | 0.11 | 97 |
| S-H-L-L | 49.9 | 25.4 | 19.3 | 4.8 | 2.21 | 2.01 | 0.11 | 94 |
| S-H-H-L | 66.7 | 23.6 | 4.4 | 4.7 | 2.29 | 11.76 | 0.12 | 67 |
| S-H-H-H | 64.4 | 22.4 | 4.5 | 8.2 | 2.16 | 11.22 | 0.21 | 88 |

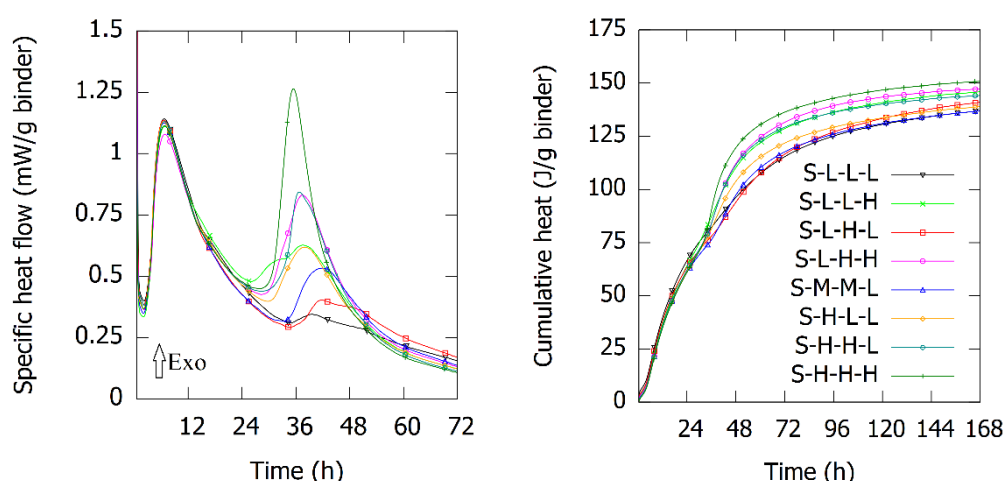


Figure 1: Isothermal calorimetry at 20°C a) heat flow b) cumulative heat

For 7 and 28 d, no statistically significant relationship was found between strength and slag chemistry. The largest strength increase was observed for the slags with higher CaO content, which has also been observed for inorganic polymers.⁴ Similarly, the highest 28 d strength is observed for the slags with the lowest FeO/CaO ratio (highest CaO content), *i.e.* S-L-L-H and S-H-L-L, and is 23 and 24 MPa, respectively. These observations with respect to the influence of CaO suggest Ca affects/participates in a strength giving phase at late age.

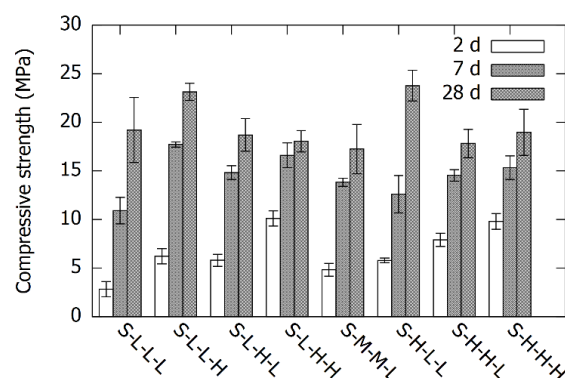


Figure 2: Compressive strength at 2, 7 and 28 days of hybrid cements synthesised from the different slags; The error bars represent the standard deviation

Conclusion

In the studied range of $\text{CaO-Al}_2\text{O}_3\text{-FeO}_x\text{-SiO}_2$ slags, a relationship between 2 d strength and the slag chemistry was found. The molar ratios, $(\text{FeO}+\text{CaO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$, FeO/CaO , $\text{SiO}_2/\text{Al}_2\text{O}_3$ all influence the strength. The highest early strength was observed for slags with low calcia and high alumina content in the studied range. For 28 d strength, the FeO/CaO ratio of the slag was proven to be the most important; the highest strength gain with respect to 2 d and the highest strength were observed for the slags with high CaO content, *i.e.* low FeO/CaO . These results allow to propose well-defined slag chemistries for different products and performance requirements (low and early strength requirements).

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