

HIGH-VOLUME OPC REPLACEMENT BY IRON-RICH NON-FERROUS METALLURGY SLAG

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Introduction

Supplementary cementitious materials (SCMs) are commonly blended with ordinary Portland cement (OPC) in order to adjust the properties and reduce CO₂ emissions in the concrete industry. These SCMs typically show pozzolanic or (latent) hydraulic behaviour thereby often contributing to (late) compressive strength. In contrast to the classical SCMs, which are typically calcium-aluminosilicates, such as ground granulated blast furnace slag or fly ash, slags originating from non-ferrous metallurgy (NFM) are often richer in (ferrous) iron.¹

The use of NFM slags as OPC replacement in literature is often limited to low volume replacement (< 30 wt%) as high volume replacements often lead to low strengths, even at late ages.² However, for 60:40 lead/zinc slag:OPC blends, 90 d compressive strengths of up to 85% of an OPC reference have been reported by Benkendorff³, indicating that in some cases high-volume OPC replacement is possible. Moreover, previous work on a blended cement composed of 70 wt% OPC and 30 wt% of a comparable NFM slag to the one of Benkendorff,³ revealed that the compressive strength after 90 d is higher than that of the reference.⁴

Therefore, in this work, high-volume replacement, up to 70 wt%, of OPC by NFM slag is investigated and mechanical properties are reported. Additionally, the phase assemblage of hydrated NFM slag-OPC blends are investigated, as the higher iron contents in these systems with respect to classical OPC systems might have an impact on the hydration products.

Materials & Methods

A water-quenched NFM slag from a pilot installation was used. The chemical composition and phase assemblage are shown in Table 1, as analysed by X-ray fluorescence (XRF; Bruker S8 TIGER) and quantitative X-ray powder diffraction (QXRD; D2 Phaser, Bruker) respectively. Quantification of X-ray diffractograms was conducted using Rietveld analysis in TOPAS Academic V5 software. The slag was

milled to a specific surface area of $4500 \pm 200 \text{ cm}^2/\text{g}$, as determined by the Blaine permeability method and blended with CEM I 52.5N cement in 30:70, 50:50 and 70:30 slag:OPC mass ratios. In all experiments a liquid/solid mass ratio of 0.4 was used. After 28 d, hydration of pastes was stopped by solvent exchange with isopropanol and diethylether followed by drying at low vacuum at room temperature. The phase assemblage was then investigated using XRD and thermogravimetric analysis (TGA), the latter under N_2 flow of 100 ml/min with a heating rate of $10^\circ\text{C}/\text{min}$. The $\text{Ca}(\text{OH})_2$ content was determined from TGA data in the region between 400 and 500°C by the tangential method and is reported relative to the dry mass, which is considered as the mass at 550°C . Finally, bound water of the pastes was estimated by subtracting the dry mass at 550°C from the initial mass of the TGA measurement, thereby assuming that all unbound water is removed due to the solvent exchange with isopropanol and diethylether. Finally, compressive strength was measured on mortars in accordance with EN 196-1⁵ but with a liquid/binder mass ratio of 0.4.

Table 1: Chemical composition and phase assemblage of the slag

Elements	Composition (wt%)	Phases	Chemical formula	Phase content (wt%)
FeO	35-45	Wüstite	FeO	8
SiO_2	25-30	Spinel	$(\text{Mg, Fe})(\text{Al, Fe})_2\text{O}_4$	11
CaO	15-20	Quartz	SiO_2	< 1
Al_2O_3	3-6	Undetected/ Amorphous	/	80
MgO	1-2			
Other	7-12			

Results & discussion

The phase assemblage after 28 d, as determined by XRD (Figure 1a), indicated calcium-silicate-hydrate (C-S-H), ettringite (AFt), monosulfoaluminate (Ms), portlandite (CH) and siliceous hydrogarnet (Hdg) as the main hydration products. Furthermore, the addition of the slag did not appear to yield new (X-ray crystalline) phases or phases that can be clearly determined from TGA results (Figure 1b). As the amount of slag increased, there was less formation of both AFt and Ms, since the $\text{SO}_3^{2-}/\text{OPC}$ ratio is constant, and therefore the total amount of SO_3^{2-} available for the formation of these phases also decreased. A main thermodynamically stable iron-containing phase in classical OPC hydration, Hdg, was detected in most of the blends. Even though an increase in the amount of Hdg could be expected due to the higher Fe-availability with increasing slag content, this was not observed. In fact, for very high replacement (70 wt%), clear peaks for this phase in either XRD or TGA can hardly be distinguished. This could be attributed to a lower overall degree of reaction of the

slag, considering the lower amount of OPC as activator, therefore still leading to a lower amount of iron that is available. On the other hand, increased incorporation of iron in other phases, *e.g.* C-S-H, or formation of other X-ray amorphous phases cannot be excluded.

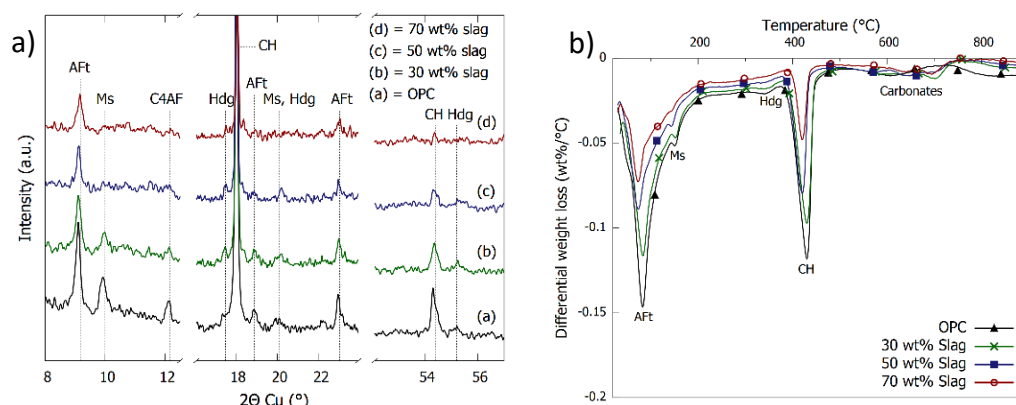


Figure 1: Phase assemblage of the blended cements after 28 days as determined by XRD (a) and TGA (b); Phases named as indicated in the main text; Phase positions in TGA from Scrivener *et al.*⁶

The TGA results indicated a decreasing amount of CH with increasing slag content. This was expected due to lower OPC content, and thus lower CH production, as well as due to the pozzolanic reactions. However, when normalised to the amount of OPC (Figure 2a), the wt% CH per wt% OPC does not decrease, as it can be expected for a pozzolanic material, but rather seems to increase or stay similar for lower replacement values. This might be explained by a combination of factors. First, the filler effect typically leads to increased alite and belite dissolution and therefore higher CH production at earlier ages⁷. Additionally, as the slag contains a considerable amount of CaO, Ca^{2+} will also be released in the solution during the slag reaction, which was also observed in previous work on a similar slag⁴. The increased CH production due to the filler effect, combined with the reduced CH consumption due to CaO in the slag may lead to these slightly increased CH contents with respect to OPC. Considering the Ca^{2+} release from the slag, it is likely more correct to look at the amount of bound water in the blended cement pastes (Figure 2a). When normalised to the amount of OPC, there is a clear increase with increasing slag content, indicating a contribution of the slag to hydration products. Compressive strengths (Figure 2b) confirm this result and correlate well with the amount of bound water ($R^2 = 0.94$). While early strengths of the blended cements are low, as the slag does not seem to contribute significantly to strength even after 7 d, after 28 d compressive strengths of about 58, 47 and 23 MPa are reached for 30, 50 and 70 wt% slag, respectively. This leads to strength activity indexes (SAI), *i.e.* $\text{strength}_{\text{blended cement}}/\text{strength}_{\text{OPC}}$, that are higher than the replacement percentage after 28 d, showing a clear, albeit slow, slag contribution to strength at later ages.

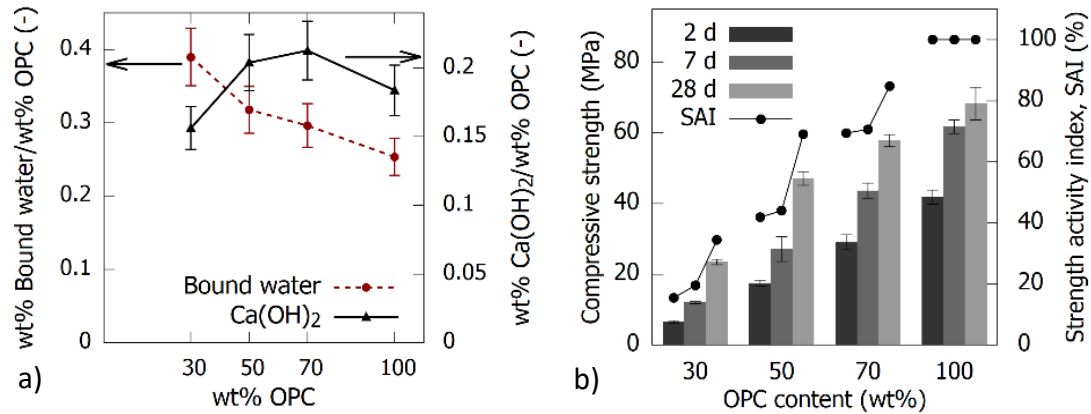


Figure 2: Amount of bound water and Ca(OH)_2 after 28 d, as determined by TGA and normalised to wt% of OPC (a), compressive strength and SAI (b) of the blended cements; Error bars indicate a relative error of 10% (a) or standard deviation (b)

Conclusion

Blending OPC with 30, 50 and 70 wt% slag did not yield any clear new phases with respect to pure OPC at 28 d. However, formation of X-ray amorphous phases could not be excluded and increased iron incorporation with increasing slag content in such or other phases remains a plausible scenario. The slag contributed to compressive strength at late ages, with 28 d strength still reaching 47 MPa (SAI = 70%) with 50 wt% OPC replacement. As early strengths were low, slag-OPC blended cements may be a suitable alternative for OPC for applications where low early strength is acceptable, assuming durability aspects are not affected.

References

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