INFLUENCE OF COMPOSITION AND COOLING RATE ON THE REACTIVITY AND PERFORMANCE OF NOVEL STEEL SLAGS AS CEMENT REPLACEMENTS

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Introduction

Blast furnace slag (BFS) is an industrial by-product of steelmaking that is widely used to partially replace cement,[1] resulting in cheaper, greener concrete with lower CO_2 emissions. However, as the steel industry transitions itself towards greener process technologies, the composition and cooling methods of resulting slag materials may significantly change in the future. As such, verifying the impact of such changes on performance of slag-containing cement blends is of utmost importance. This is needed to ensure that the reduction in CO_2 emissions achieved by steelmaking is not offset by an associated increase in emissions from the cement industry due to more limited slag utilisation. To this end, two EAF pilot slags from the fossil-free HYBRIT process were evaluated in comparison to traditional BFS for their reactivity and performance as supplementary cementing materials (SCMs). Four synthetic slags produced to span a compositional range centred around the two pilot slags were also evaluated.[2]

Materials and methods

All slags were used as-provided, with compositions shown in Table 1 below.

Table 1: Chemical compositions of the slags used in this study (wt%). Mineralogical composition of the synthetic slag materials is provided in Tyybäkinoja, S. *et al*[2]

	Fe_2O_3	Al_2O_3	MgO	CaO	SiO_2	CaO/SiO_2
Synthetic Slag B1[2]	27.8	7.0	9.0	28.1	28.1	1.0
Synthetic Slag B2[2]	27.8	7.0	9.0	33.7	22.5	1.5
Synthetic Slag B3[2]	27.8	7.0	9.0	37.5	18.7	2.0
Synthetic Slag B4[2]	27.8	7.0	9.0	40.1	16.1	2.5
Pilot Slag 1	26.7	9.4	7.8	22.3	21.0	1.1
Pilot Slag 2	34.3	7.1	8.3	23.7	13.3	1.8
Blast Furnace Slag	-	9.0	11.0	39.0	38.0	1.0

Synthetic slags are identical to those produced in reference [2] (SSA ≈ 500 m^2/kg), while the pilot slags and the blast furnace slag were provided by SSAB and Finnsementti, respectively (SSA ≈ 1950 m^2/kg). Cement paste, mortar, and concrete blends produced in this study were made using SR Sementti (Finnsementti, SSA ≈ 350 m^2/kg), a CEM I conforming to EN 197-1 (42.5 MPa). Cement blends containing up to 30% (wt%) of slag and/or limestone were made to be equivalent to relevant CEM II compositions outlined in that standard. Reactivity testing of cement pastes (w/c = 0.5) was carried out along the lines of standard EN 196-11 (calorimetry). Mechanical strength testing was carried out along the lines of the standard EN 196-1. Concrete specimens were produced according to EN 12390-1, for use in frost-salt and chloride migration durability tests as outlined in standards EN 12390-9 and EN 12390-18, respectively.

Results and discussion

Blends equivalent to CEM II with 30% replacement of clinker by SCMs were produced, using blast furnace slag and limestone to represent theoretical upper and lower bounds, respectively, in terms of potential SCM reactivity. The reactivity of the two pilot slags can be seen to be broadly similar (Figure 1a), while the synthetic slags more clearly show the role of high basicity increasing apparent cementitious reactivity (Figure 1b). Though reactivity of similar aluminosilicate SCMs like fly ash is reported to depend strongly on the amount and composition of their amorphous components,[3] there is similar reactivity among the slags B2, B3, and B4, despite quite different amorphous content (87%, 35%, and 24%, respectively). This indicates that for these slags, the detail of which crystalline phases form (and thus the cooling rate) would be an important consideration in their performance, and should be investigated in more detail in follow-up studies.

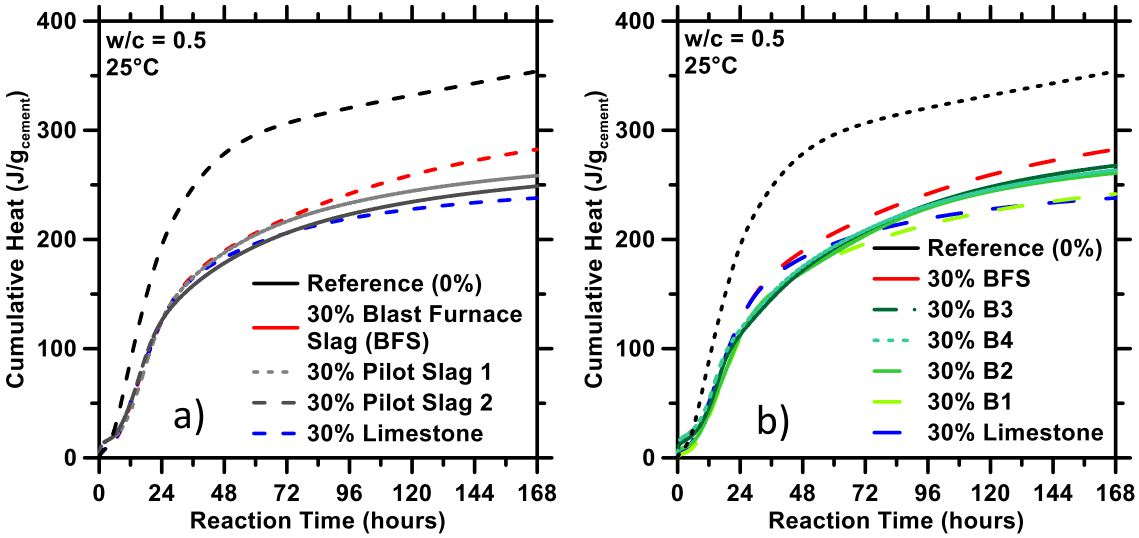

Figure 1: Cumulative heat release from CEM II blends shown for **a)** the two pilot slags and **b)** the four synthetic slags. The black line represents a reference CEM I (SR Sementti) and the red and blue lines represent blast furnace slag and limestone blends, respectively

Similar to the decrease in reactivity relative to blast furnace slag, the two EAF pilot slags also exhibit small decreases in compressive strength when added to cement mortars at equivalent replacement levels of 30% (Figure 2a). While this may be offset by altering the slag processing (e.g., cooling rate, granulation, grinding), use of lower w/c has also been employed for utilisation of steel slag,[4] to which these new EAF slags bear some similarity.[5] Such a test for these slags demonstrates that the strength loss can also be offset by such simple changes to mixture proportions (Figure 2a). However, when substituted alongside limestone (15% slag + 15% limestone), a composition that is closest to the current most widely used commercial cements in Finland, performance is more closely comparable to that of blast furnace slag (not shown, 30 ± 1 MPa). Nonetheless, the low cementitious reactivity of the two pilot slags, similar to steel slag,[5] is expected to limit its application when pushing towards even higher replacement levels (above 15-30%), as will soon be desirable for improved long-term binder sustainability.

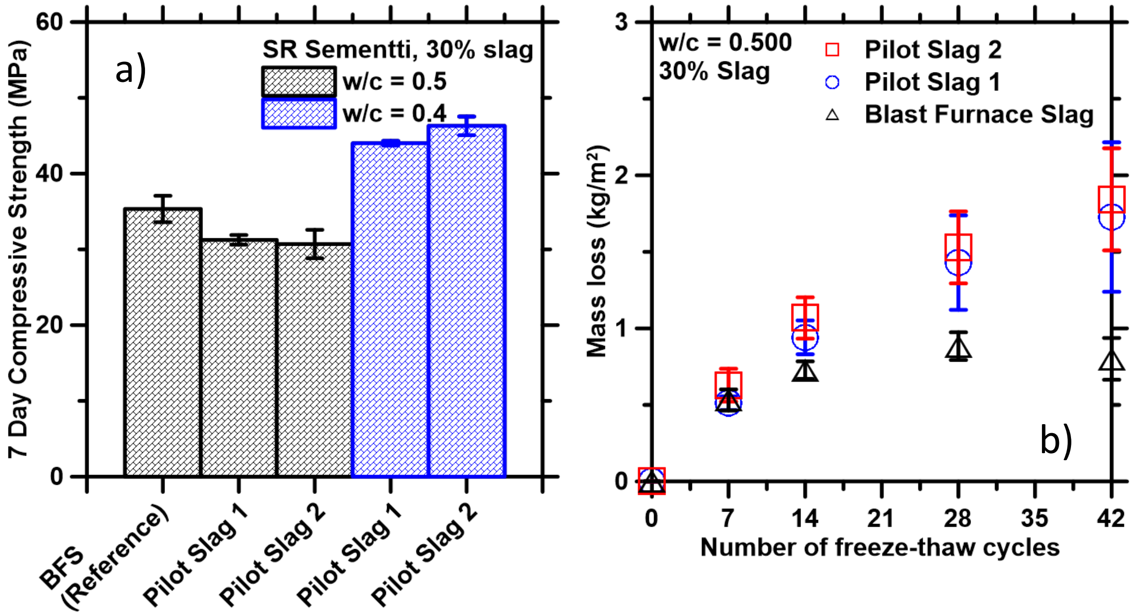

Figure 2: Mechanical and durability performance of slag-cement blends, showing **a)** the compressive strength (EN 196-1) compared with blast furnace slag and between two different w/c ratios, and **b)** the mass loss during a cyclic frost-salt scaling test (EN 12390-9)

Though strength loss can be easily mitigated, both pilot slags are shown to increase mass loss during frost-salt scaling tests substantially. While these levels of scaling are still on the order of what can be reasonably expected from Portland-slag and Portland-limestone CEM II cements,[6] they still represent a reduction in durability relative to the currently employed blast furnace slag. Likewise, chloride migration coefficients also exhibit a two-to-threefold increase for the concretes containing Pilot Slag 1 and Pilot Slag 2, relative to the blast furnace slag concrete (40.1×10^{-12} m^2/s, 45.8×10^{-12} m^2/s, and 13.5×10^{-12} m^2/s, respectively), confirming reduced durability performance.

Summary and Conclusions

The two EAF pilot slags from the fossil-free HYBRIT process were confirmed to be less reactive than currently used blast furnace slag, when utilised as cement replacements up to 30% by mass. Although broad trends hold regarding the role played by slag basicity in dictating reactivity, more detailed investigation is required with regard to the role played by amorphous content vs reactive crystalline phases, specifically to what extent the slag performance may be more sensitive to cooling rate and processing conditions. The performance of the slags, similar to their composition, was shown to bear similarity to that of steel slags (rather than blast furnace slags), with the modest strength loss able to be easily mitigated by reducing w/c. However, several key durability metrics such as frost-salt scaling and chloride penetration were demonstrated to be negatively influenced by the use of these slags rather than blast furnace slag. In summary, these results suggest that use of the novel slag in its current form would impose limitations on both (1) the ability to continue pushing toward higher cement replacement levels in meeting binder sustainability goals, and (2) the range of practical applications (e.g., pavements exposed to frost-salt scaling) for which concretes containing the new slags would be deemed suitable without first making other design considerations. Both of these areas would benefit from improved understanding of the role played by chemical structure of the EAF pilot slags, as it relates to reactivity and subsequent performance.

References

1. Juenger, M. C. G., Winnefeld, F., Provis, J. L. & Ideker, J. H. Advances in alternative cementitious binders. *Cement and concrete research* **41**, 1232–1243 (2011).
2. Tyybäkinoja, S. *et al.* Influence of slag basicity and cooling rate on the structure of EAF steelmaking slags. in *Proceedings of the 8th International Slag Valorisation Symposium* (2023).
3. Oey, T. *et al.* An improved basis for characterizing the suitability of fly ash as a cement replacement agent. *Journal of the American Ceramic Society* **100**, 4785–4800 (2017).
4. Wang, Q., Yan, P., Yang, J. & Zhang, B. Influence of steel slag on mechanical properties and durability of concrete. *Construction and Building Materials* **47**, 1414–1420 (2013).
5. Yi, H. *et al.* An overview of utilization of steel slag. *Procedia Environmental Sciences* **16**, 791–801 (2012).
6. Skripkiūnas, G., Nagrockienė, D., Girskas, G., Vaičienė, M. & Baranauskaitė, E. The Cement Type Effect on Freeze – Thaw and Deicing Salt Resistance of Concrete. *Procedia Engineering* **57**, 1045–1051 (2013).