

# ASSESSING THE REACTIVITY OF INDUSTRIAL BY-PRODUCTS IN CALCIUM ALUMINATE CEMENT-BASED FORMULATIONS

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## Introduction

The use of supplementary cementitious materials (SCM) has been under extensive research in the past decade as a critical pathway in reducing the substantial carbon dioxide emission associated with cement production. In this study, three types of industrial by-products (iron residue slags, fumed fayalite slag and bottom ash) were incorporated in a calcium aluminate cement (CAC)-based formulation to assess their potential as novel SCM. CAC is a collective term adopted for high-alumina cement, having calcium aluminates as the principal constituents, used in special applications such as self-levelling underlayment, refractory, and in aggressive environment.<sup>1</sup> The reactivity of the industrial by-products will be evaluated in this study in a ternary binder system with CAC and calcium sulphate hemihydrate (HH). The latter is added as a sulphate source to facilitate the formation of strength-forming hydrates, such as ettringite, and to prevent the conversion phenomenon in pure CAC systems.<sup>2</sup>

## Materials and Methods

A summary of the raw materials' properties is presented in Table 1. The metal-depleted industrial by-products evaluated as SCM consist of: slowly-cooled iron residue slag (FS), granulated iron residue slag, fumed fayalite slag, and a municipal waste incinerator bottom ash. The iron residue slags were produced from a test work using high temperature processing of iron residue from zinc industry. The CAC used is a commercial cement, Secar 51, based on monocalcium aluminate ( $\text{CaAl}_2\text{O}_4$ ). Inert quartz filler is used to take the physical contribution of the SCM addition into account.

**Table 1:** Properties of the raw materials used in the study

|  | CAC  | quartz filler | slowly-cooled FS | granulated FS | fumed fayalite slag | bottom ash | HH   |
|--|------|---------------|------------------|---------------|---------------------|------------|------|
| Specific surface area, m <sup>2</sup> /g | 1.02 | 1.12          | 1.35             | 0.84          | 1.03                | 3.87       | 3.52 |
| Density, g/cm <sup>3</sup>               | 3.02 | 2.66          | 3.47             | 3.67          | 3.50                | 2.70       | 2.64 |
| PSD 80% passing, $\mu$ m                 | 35   | 29            | 30               | 31            | 34                  | 33         | 16   |
| Amorphous content, wt%                   | –    | –             | 49               | 92            | 99                  | 15         | –    |
| Chemical composition, wt%                |      |               |                  |               |                     |            |      |
| CaO                                      | 37.7 | –             | 17.6             | 12.5          | 4.2                 | 18.3       | 41.7 |
| Al <sub>2</sub> O <sub>3</sub>           | 52.3 | –             | 6.0              | 4.8           | 10.3                | 11.4       | 0.1  |
| SiO <sub>2</sub>                         | 4.9  | 99.8          | 31.1             | 25.9          | 30.6                | 42.9       | 0.8  |
| Fe <sub>2</sub> O <sub>3</sub>           | 1.8  | –             | 33.4             | 46.0          | 42.4                | 9.9        | 0.1  |
| MgO                                      | 0.4  | –             | 3.0              | 2.2           | 1.3                 | 2.3        | 0.1  |
| SO <sub>3</sub>                          | 0.2  | –             | 0.7              | 0.7           | 0.8                 | 2.9        | 56.5 |
| K <sub>2</sub> O                         | –    | –             | 0.5              | 0.6           | 0.2                 | 1.3        | –    |
| P <sub>2</sub> O <sub>5</sub>            | 0.1  | –             | 0.2              | 0.2           | 1.6                 | 1.5        | –    |
| Na <sub>2</sub> O                        | –    | –             | 4.8              | 4.0           | 2.1                 | 5.6        | –    |
| Cr <sub>2</sub> O <sub>3</sub>           | 0.1  |               | 0.1              | 0.1           | 1.6                 | 0.1        | –    |
| CuO                                      | –    | –             | 0.3              | 0.4           | 0.5                 | 0.4        | –    |
| ZnO                                      | –    | –             | 0.6              | –             | 2.3                 | 0.5        | –    |
| Others                                   | 2.5  | 0.2           | 1.6              | 2.6           | 2.1                 | 3.0        | 0.7  |

Mortars were prepared with a constant CAC to HH mass ratio of 4.5 at water to binder (w/b) ratio of 0.5. SCM were incorporated following the formulation shown in Table 2, while keeping the volume substitution consistent with those of the mortars incorporating 30 wt% granulated FS.

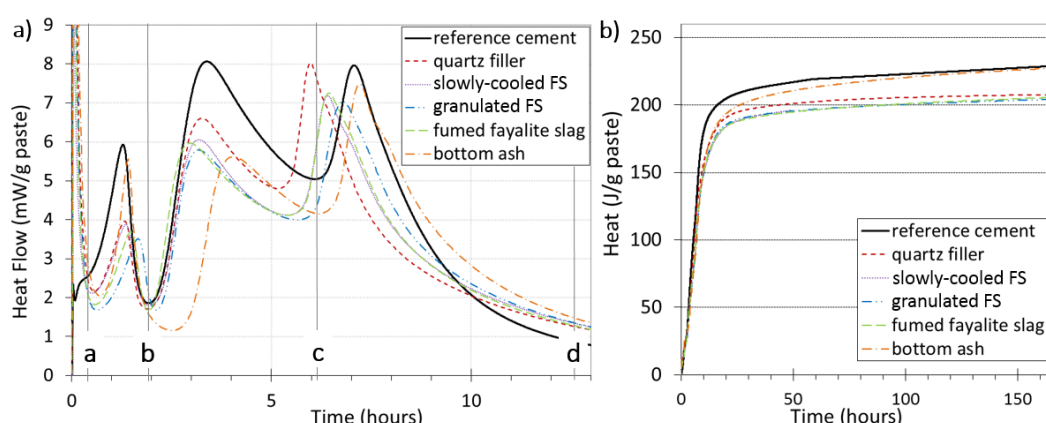
**Table 2:** Mortar composition (in g)

|        |     | reference cement |     | quartz filler |     | slowly-cooled FS |     | granulated FS |     | fumed fayalite slag |     | bottom ash |     |
|--------|-----|------------------|-----|---------------|-----|------------------|-----|---------------|-----|---------------------|-----|------------|-----|
| binder | CAC | 368              | 450 | 258           | 413 | 258              | 443 | 258           | 450 | 258                 | 444 | 258        | 414 |
|        | HH  | 82               |     | 57            |     | 57               |     | 57            |     | 57                  |     | 57         |     |
|        | SCM | 0                |     | 98            |     | 128              |     | 135           |     | 129                 |     | 99         |     |
| Water  |     | 225              |     |               |     |                  |     |               |     |                     |     |            |     |
| Sand   |     | 1350             |     |               |     |                  |     |               |     |                     |     |            |     |

Mechanical strength was determined based on the EN 191-1 standard under air curing conditions at 20°C. The reactivity index was calculated by dividing the compressive strength of the blends incorporating SCM with that of the reference cement blend. Additionally, early hydration was followed using paste samples through ex-situ isothermal calorimetry at 20°C with a w/b ratio of 0.65.

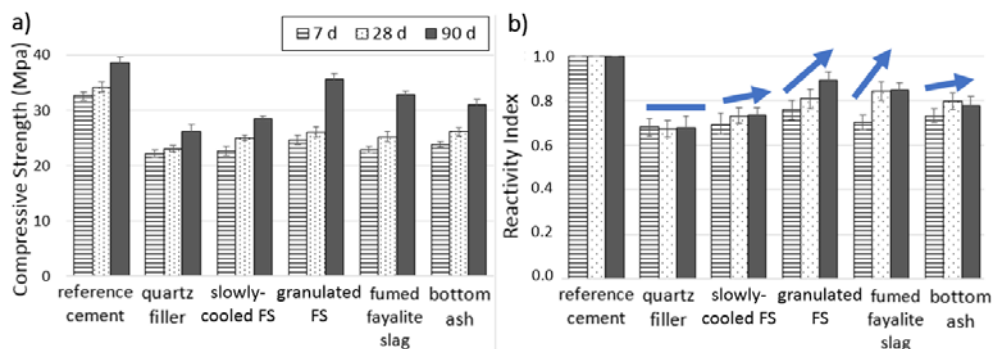
## Results and Discussion

The results of the isothermal calorimetry test presented in Figure 1a suggest that the addition of SCM only affected the kinetics and extent of hydration but did not seem to alter the hydration mechanism at least in the early stage. This is evident with the presence of the three main heat flow peaks for all the blend types. These peaks are each assumed to correspond to the same phenomenon although displaying variations in intensity and position. As already studied by XRD and TGA,<sup>2</sup> the three main peaks in this low sulphate CAC system correspond to: the fast dissolution of hemihydrate simultaneously leading to rapid gypsum precipitation (a-b); monocalcium aluminate and gypsum dissolution leading to massive ettringite precipitation (b-c); and monosulphate formation, as gypsum is depleted (c-d). Meanwhile, the cumulative heat release graph presented in Figure 2b shows that the addition of the SCM lowered the heat release in the paste samples. Only the total heat release of the paste incorporating the bottom ash has reached a comparable level to that of the reference cement paste. This could be an indication of the early reactivity of the bottom ash, especially considering its relatively high specific surface area (Table 1), providing more sites for reaction.



**Figure 1:** a) Heat flow and b) cumulative heat release curve derived from the isothermal calorimetry test at 20°C for 10 g of paste (binder + water) samples for each blend type

From the results presented in Figure 2, it can be seen that the substitution with the SCM significantly decreased the compressive strength after 7 and 28 days, to the same extent for all blend types. It was not until 90 days that the strength significantly increased for granulated FS yielding the highest strength among the ternary blends. Nonetheless, it is interesting that the mortars incorporating the bottom ash obtained a relatively high early strength after 7 days which is assumed to be related to the high heat release observed from the isothermal calorimetry test. On the other hand, mortars with the fumed fayalite slag had a faster strength development between 7 and 28 days while those with slowly-cooled FS and the bottom ash did not generally display a substantial strength increase throughout the curing period.



**Figure 2:** a) Compressive strength of the reference cement and the standard mortars incorporating SCM; b) reactivity index calculated from the compressive strengths

The incorporation of the industrial by-products especially the highly amorphous slags (granulated FS and fumed fayalite slag) appear to have a contribution on the chemical reactivity as they significantly surpassed the strength of the mortars incorporating the inert quartz filler. Nevertheless, despite this strength development pattern, the biggest challenge for these types of blended cement remains to be the critical requirement on high early strength (< 24 h) for CAC-based applications (e.g. fast repairs). This would require an extensive understanding of the hydration mechanism of the blends in order to come up with ways, such as modification of physical and chemical properties, to further improve their performance.

## Conclusions

Among the industrial by-products investigated, the highly amorphous slags appear to have the highest reactivity in the cement blends developed. Although slow strength development in the first 28 days could be an issue in CAC-based applications, the industrial by-products could have potential as novel SCM with further modification and activation. Characterisation techniques including XRD, TGA and thermodynamic modelling will be performed in the succeeding studies to further explore the hydration mechanism of these formulations incorporating industrial by-products.

## Acknowledgement

This research has received funding from the European Union Framework Program for Research and Innovation Horizon 2020 under Grant Agreement No.721385 (EU MSCA-ETN SOCRATES; project website: <http://etn-socrates.eu>)

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