

VALORISING AN INDUSTRIAL RESIDUE TOWARDS A CALCIUM SULFOALUMINATE CEMENT

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Introduction

Calcium sulfoaluminate (CSA) cements and the formation of the ye'elimite (C_4A_3S) phase was first synthesised and studied by Ragozina¹ in 1957, and its composition was identified as $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ by Fukuda² in 1961. CSA cements can be a feasible alternative binder with major benefits such as quick setting, fast strength development, and less shrinkage, while achieving lower CO_2 emissions during production.³ CSA cements consists predominantly of C_4A_3S , which react with H_2O in the presence of anhydrite ($CaSO_4$) to form a binder phase of monosulfate (AFm), ettringite (AFt) and aluminium hydroxide ($Al(OH)_3$).⁴ The sulphate-bearing phase C_4A_3S can be synthesised in the temperature range between 1200 and 1450°C depending upon the initial chemical composition used.⁵ However, Khessaimi *et al.*⁶ stated that optimal solid state synthesis condition for C_4A_3S was at 1300°C for 3 h. In general, any oxide source of Al, Ca and S and industrial by-products, such as fly ash, lime kiln dust and scrubber sludge might be a potential candidate for the synthesis of CSA cements. Sahu *et al.*⁷ showed that fly ash can be used to produce belite – CSA–based cements. Investigations were carried out by firing different kinds of fly ash (class C and F) along with limestone and gypsum at 1200°C. In this paper a rather unexplored industrial residue generated as a slurry during the acid leaching of Zn metal (Jarosite) is studied. Due to the presence of the high sulphur content, this residue might be a suitable candidate in making CSA cements. The primary objective is to produce therefore a CSA clinker from these industrial residues, by following the necessary thermal treatment in order to transform the unreactive industrial residue into a CSA cement. The reactivity of the clinker was assessed by thermogravimetric analysis (TGA) and heat flow calorimetry. The compressive strength of the 100% CSA mortar was also evaluated.

Experimental Methods

An industrial residue was used as the starting material. It was dried in a Binder oven (Series ED 56) at 105°C for 24 h. Laboratory-grade CaO and Al_2O_3 were used as additives for the heat treatment. The characterisation of the chemical composition

of the starting materials and their mineralogy was carried out by X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis, respectively. Modified Bogue equations were used to find an optimal mix design; eventually a mix consisting of (in wt%) 25 Al₂O₃, 25 CaO and 50 industrial residue was used. The sample was mixed using a Turbula Mixer (WAB, Switzerland) for 24 h and afterwards pelletised using water. The pellets were fired in an alumina crucible at 1250°C for 1 h. During thermal processing, an inert atmosphere was maintained. The thermally processed pellets were slowly cooled (10°C/min). The pellets were milled in a disk mill (Fritsch pulverisette 13) and followed by milling in an attritor mill (Wiener 1S) for 8 h. The milled material is stated as a “CSA cement”. Isothermal calorimetry (TAM Air, TA instruments) in combination with an admix ampoule was used to investigate the reaction kinetics during setting and hardening of the paste at a constant temperature of 20°C. Due to the presence of C₄A₃\$, a higher amount of water compared to conventional cement paste was used (water to cement = 0.8). TGA was used to identify the presence of hydration product such as AFm, AFt and AH₃. The equipment used was a SDT Q600 of TA instruments with a balance sensitivity of 0.1 µg. The heating rate was 10°C/min and the crucible used was made of alumina. Mortars with 100% CSA cement along with reference mortars (100 wt% OPC) were prepared as per norm EN 196-1 and cured at 23 ± 1°C and 100% relative humidity for 24 h to evaluate their compressive strength.

Results and Discussion

Characterisation of the raw material and CSA cement

The industrial residue is mainly composed of SO₃ and Fe₂O₃ with minor oxide contents of Ca, Si, Na and Al (Table 1). Table 2 provides the quantified XRD results of the industrial residue with sulphur, natrojarosite and gypsum being the major phases, with quartz being a minor component. Table 3 and 4 provide the chemical composition and quantified XRD results of the synthesised CSA cement from the industrial residue, showing more than 80 wt% of the hydraulic C₄A₃\$.

Table 1: Chemical composition (industrial residue)

| Component | SO ₃ | Fe ₂ O ₃ | CaO | SiO ₂ | Others |
|-----------|-----------------|--------------------------------|-----|------------------|--------|
| wt% | 64.6 | 16.7 | 7.1 | 4.8 | 6.8 |

Table 2: Mineralogy of the industrial residue

| Phase | Sulphur | Natrojarosite | Gypsum | Quartz | Others |
|-------|---------|---------------|--------|--------|--------|
| wt% | 39 | 26 | 25 | 6 | 4 |

Table 3: Chemical composition of the synthesised CSA cement

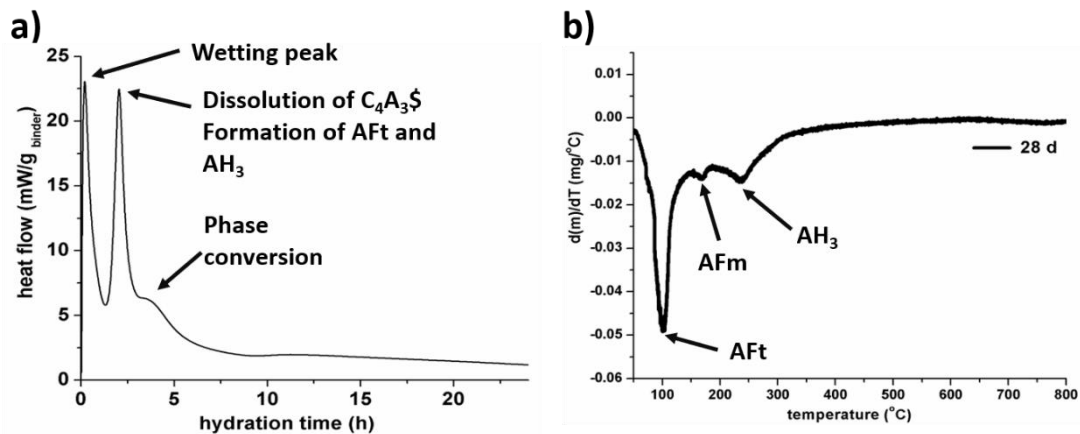
| Component | CaO | Al ₂ O ₃ | Fe ₂ O ₃ | SO ₃ | Others |
|-----------|------|--------------------------------|--------------------------------|-----------------|--------|
| wt% | 35.0 | 30.0 | 15.0 | 13.5 | 6.5 |

Table 4: Mineralogy of the synthesised CSA cement

| Phase | Ye'elimite | Gehlenite | Magnetite | Others |
|-------|------------|-----------|-----------|--------|
| wt% | 83.7 | 8.1 | 3.9 | 4.3 |

Isothermal calorimetry and thermogravimetrical analysis of the hydrated paste

Results of heat flow calorimetry of the system showed a maximum heat flow up to 22.5 mW/g_{binder} within the first 30 min proving its reactive and strong exothermic behaviour. The heat flow can be divided into three regions as shown in Figure 1a), mainly 1) wetting peak, 2) dissolution of C_4A_3S to form strength developing phases, such as AFt or AFm and AH_3 , and 3) minimum heat flow observed in the hydration time between 3 to 4 h, possibly due to the phase conversion (AFt to AFm). The nature of reaction products forming can be investigated *via* the derivatives of mass loss (Figure 1b). The first region, between 110 and 130°C shows the decomposition of AFt.⁹ The second region, between 180 and 200°C, and third region, between 230 and 250°C, reveal the decomposition of hydrates from AFm and AH_3 respectively.⁸

**Figure 1:** a) Calorimetry curve of hydrated paste b) Mass loss derivative of hydrated paste

Mechanical properties

The 2 d compressive strength of the CSA cement was higher compared to the OPC reference (Table 5). A strength of 40 MPa was observed in the mortar made from CSA whereas the OPC system showed 35 MPa. This high early day strength of the CSA mortar is due to the presence of C_4A_3S which reacts with H_2O to form a strength providing crystalline binders such as AFt, AFm and AH_3 . The exact chemistry of these reactions products is currently investigated by energy dispersive X-ray spectroscopy

mapping. At later ages, the strength gain of the OPC mortar is substantial, surpassing that of CSA mortar already at 7 d. The end values at 28 days are approximately 59 MPa for the OPC mortar and 48 MPa for the CSA.

Table 5: Mechanical properties of the synthesised mortars

| Mortar | 2 d strength (MPa) | 7 d strength (MPa) | 28 d strength (MPa) |
|---------------|--------------------|--------------------|---------------------|
| OPC reference | 35.4 ± 0.8 | 51.6 ± 2.3 | 59.3 ± 0.3 |
| CSA | 40.4 ± 0.3 | 42.5 ± 1.5 | 47.5 ± 2.7 |

Conclusion

In this study, an industrial residue rich in sulphur was blended with (in wt%) 25 Al₂O₃ and 25 CaO, and was thermally processed at 1250°C, leading to a ye'elimite-rich, highly reactive CSA cement. TGA analysis of the hydration products of the CSA cement showed the presence of AFm, AFt and AH₃ phases, and possibly proving that the C₄A₃S phase reacts with H₂O to form these binder phases which provides good mechanical properties, exceeding 40 MPa.

References

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