

SYNTHESIS AND CHARACTERISATION OF CALCIUM SULFO-FERROALUMINATE CEMENT CLINKER PREPARED WITH BAUXITE RESIDUE AS RAW MATERIAL

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Introduction

In view of the relatively high embodied CO₂ in OPC, there is intense research on alternative cements. The available work in the area is immense and there are different strategies and cementitious systems suggested. Bauxite residue (BR) is a candidate material in a number of these novel binders. Especially in the production of calcium sulfoaluminate (CSA) and calcium sulfo-ferroaluminate (CSFA) based cements, a solution that appears realistic, use of BR has been already a research topic.^a

CSA cements contain calcium sulfoaluminate, aka ye'elimite or "Klein's compound" (C₄A₃Ŝ) as a major constituent (30–70 wt%), whereas CSFA cements contain C₄A₃Ŝ and ferrite (C₆A₃F_x; 1 ≤ x ≤ 2). Both types of cements accommodate also a substantial amount of C₂S phase¹. The production process requires few modifications in the raw meal and firing conditions compared to OPC. Significant benefits can be derived from the lower energy consumption during production (clinkering temperature between 1250 and 1350°C) and the reduced CO₂ emissions per mass of clinker produced. In addition, due to their low porosity and ability of ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·32H₂O) and AFm^b phases to bind heavy metals, CS(F)A cements and their blends with Portland cement are of interest in the field of hazardous waste encapsulation.

Material and Methods

The BR used in this study was provided by Aluminium of Greece. The received filter pressed cake was dried at 150°C for 48 h and then crushed into a fine powder using a mortar and pestle. The chemical composition of BR was determined by XRF (PW 2400, Philips). The mineralogy was determined by quantitative X-ray powder diffraction analysis (QXRPD, D2 Phaser, Bruker AXS). For the QXRPD preparation, 10 wt% of

^a Cement notation is followed, *i.e.* C = CaO; A = Al₂O₃; F = Fe₂O₃; S = SiO₂; Ŝ = SO₃

^b AFm stands for "alumina, ferric oxide, mono" phase

analytical grade crystalline ZnO was added and the BR-standard mixture was milled (McCrone Micronizing mill) in hexane for 7.5 min. Diffraction patterns were measured in 2 θ range of 10–70° using CuK α radiation of 30 kV and 10 mA, with a 0.02° step size and step time of 0.3 s. Qualitative analysis was performed using EVA V.3.1 (Bruker AXS). Quantitative results were obtained adopting the normalised Rietveld method^{2,3} using the “Topas® Academic” software⁴. Clinker samples were prepared by mixing BR and calcium sulphate, with calcium carbonate and aluminium oxide to obtain mostly ye’elimite and ferrite phases. The proportioned raw materials (Table 1) were dispersed in ethanol (1.0/1.2 volume ratio) and homogenised for 16 hours in a Turbula mixer followed by drying.

Table 1: Mix design composition

| Component | BR | CaSO ₄ · 2H ₂ O | CaCO ₃ | Al ₂ O ₃ |
|-----------|------|---------------------------------------|-------------------|--------------------------------|
| wt% | 36.4 | 13.0 | 43.9 | 6.7 |

The resulted powder was subjected to hand pelletisation using 10 wt% water. The pellets were then dried at 150°C for 24 hours. The dried pellets were introduced in an alumina crucible and heated at a heating rate of 10°C/min in an induction furnace, in air, up to 1300°C, equilibrated for 2 h at maximum temperature. The material was then cooled rapidly using pressurised air. The resulting clinker was milled in a vibratory disk mill. A specific surface comparable to OPC was the goal, which resulted to be 4000 ± 200 cm²/g, measured by the Blaine method according to EN 196-6.

For producing cements, ground clinker was mixed with different amounts of gypsum (0, 10 and 20 wt%) for identifying the optimum amount needed for the control of the early age hydration reactions. The hydration products were identified using XRD analysis at 28 days of hydration. Mortar samples were prepared according to EN 196-1. As observed in the preliminary tests the setting time was rather short; therefore 2 min mixing time as well as 4 min mixing time (as specified in EN 196-1) were used for comparison.

Results and Discussion

The chemical composition of BR obtained by XRF is given in Table 2.

Table 2: Chemical composition of the bauxite residue used in the experiments

| Oxides | Fe ₂ O ₃ | Al ₂ O ₃ | CaO | SiO ₂ | TiO ₂ | Na ₂ O | Other | L.O.I. |
|--------|--------------------------------|--------------------------------|-----|------------------|------------------|-------------------|-------|--------|
| wt% | 47 | 23 | 9 | 9 | 6 | 3 | <3 | 11 |

In terms of mineralogy the main phases in BR were: hematite (29 wt%), diaspore (14 wt%), katoite (9 wt%), cancrinite (6 wt%), gibbsite (5 wt%) and an amorphous content (22 wt%). Minor phases include boehmite, calcite, goethite, kaolinite, rutile and quartz. As regards the mineralogy of the sulfo-ferroaluminate clinker, the results show that, iron-rich ferrite (C₆AF₂) phase (40 wt%), ye’elimite (C₄A₃Ŝ -25 wt%) and β-C₂S (approx. 10 wt%) were the main phases formed. Anhydrite (CŜ),

tricalciumaluminate (C_3A) and quartz are also present in minor quantities. Both, ferrite and ye’elimite, are expected and desired crystalline phases in CSFA cements. Interesting to note is that in the produced clinker, ferrite phase was found in a higher quantity compared to a typical CSA cement, where typically ye’elimite is the main mineral phase⁵.

The compressive strength results after 3, 7 and 28 days of cement mortars made with different amounts of gypsum addition are given in Figure 1. It is notable that an increase in the gypsum addition leads to a strength decrease. The optimum gypsum additions seemed to be between 0 and 10 wt%; the results are comparable considering the standard deviation. The setting time was short in both mortars with and without gypsum addition thus the mixing time was reduced, in order to be able to cast. For this series, only samples with 10 wt% gypsum addition were developed. Figure 2 shows that for 2 min mixing time the compressive strength attained was higher. The shorter mixing time allowed casting of a still-liquid paste, which led to a denser macrostructure with less entrapped air (Figure 3). High strength was already developed at early age, typical for CSA cements.

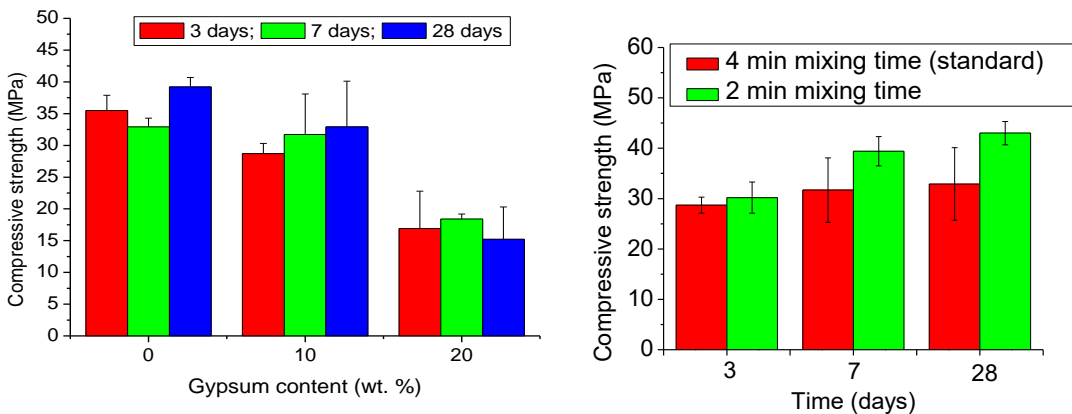


Figure 1: Compressive strength results for mortars with different gypsum additions and 4 minutes mixing

Figure 2: Compressive strength results for mortars with 10 wt% gypsum additions and different mixing times

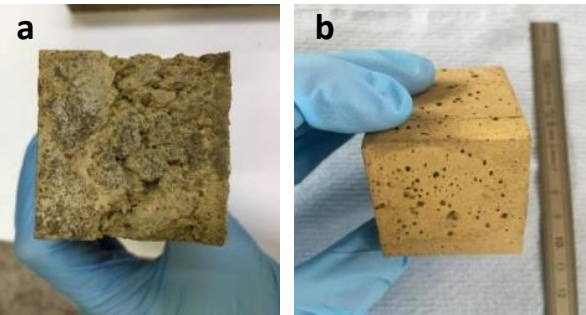


Figure 3: Mortar samples with: a) 10 wt% gypsum addition and 4 min mixing, b) 10 wt% gypsum addition and 2 min mixing

XRD analyses after 28d of hydration suggested the formation of monosulfate (AFm), vaterite, semi-crystalline gibbsite and minor ettringite. No ye'elimite was detected, indicating the complete dissolution and hydration, while ferrite was still present. The addition of gypsum slowed down the reaction of brownmillerite, which was detected in higher amounts compared to the reference clinker, while ye'elimite was also in this case completely consumed. The formation of ettringite was promoted, but a small content of gypsum was still present, indicating either an initial excess in the blend, or secondary formation as hydration product. Neither vaterite nor monosulfate formation were detected.

Conclusions

A CSFA clinker with about 40 wt% BR used as raw material was developed. The main phases in the clinker were a Fe-rich ferrite (C_6AF_2 , 40 wt%), ye'elimite ($C_4A_3\hat{S}$; approx. 25 wt%) and β - C_2S (approx. 10 wt%). Mortars were subsequently made, where the clinker was mixed with variable amounts of gypsum. When no gypsum was added, the obtained mechanical properties were similar to OPC CEMIII 52.5R at 3d and comparable to OPC CEMIII 42.5R at 28d of hydration. Mortars with 10 wt% gypsum and 2 min mixing time presented 3d strength comparable to OPC CEMIII 52.5 and 28d strength comparable to OPC CEMIII 42.5R. Ettringite formation was the main hydration product in presence of gypsum. Ferrite was still detected in all samples at 28d of hydration. The results are promising and there is a number of realistic actions to be explored that can further improve the performance of the mortars.

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