

FROM BAUXITE RESIDUE TO CALCIUM SULFO-FERROALUMINATE CEMENT: STUDY OF THE CLINKERIZATION AND HYDRATION KYNETICS

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ABSTRACT

The present study aims to offer a better understanding of the clinkerization and hydration processes of calcium sulfo-ferroaluminate cements prepared with large amounts of bauxite residue. In order to achieve that, four clinkers were designed and fired at a temperature of 1250 °C. Their clinker phase compositions were determined by X-ray diffraction and quantified by Rietveld analysis. The resulting clinkers were ground as-is to produce cement. The hydration kinetics of the resulting cements were studied by a combination of setting time determination and in-situ x-ray diffraction technique. The experimental results suggest that it is feasible to produce calcium sulfo-ferroaluminate cement with bauxite residue as the main component being the resulting material a fast-setting cement with reasonable mechanical properties.

INTRODUCTION

Every year more than 150 MT of bauxite residue (BR) are produced during the alumina extraction in the Bayer process ^[1]. From this amount, most of it is stored in legacy sites or landfilled and only a small part of this amount (2 – 3 wt%) is used by other industries in their production processes.

Over the years, the preparation of construction materials has been proved as an interesting way for the alumina industry to make profitable products while allocating large amounts of this waste ^[2]. Amongst the large variety of building materials ^[4-6], calcium sulfo-ferroaluminate (CSFA) cement seems a promising path to allocate large quantities of BR ^[7]. This is due to the fact that CSFA clinker chemistry is favorable to the BR chemical composition, which maximizes its allocation while targeting the obtention of ye'elimite ($\text{Ca}_4\text{Al}_{6-x}\text{Fe}_x\text{O}_{12}\text{SO}_4$) as well as cementitious iron-bearing phases ^[8].

However although calcium sulfoaluminate cement is a known material with a well-established production, its iron-rich counterpart (CSFA) needs further research. Mainly, because the use of large amounts of iron will affect the phase assemblage of the calcium aluminate phases as well as their properties (e.g. hydration kynetics, setting time, mechanical strength, etc.). In the present study, we aim to give further insight in both of these questions.

MATERIALS AND METHODS

Bauxite residue was supplied by Aluminium of Greece, while limestone and gypsum were provided by TITAN Cement S.A. The raw materials were dried at 105 ± 5 °C for 48 h and later milled to a particle size below 250 µm. The chemical composition of the raw materials can be found in the **Table 1**.

Table 1. Chemical composition of the raw materials (in wt%).

	Bauxite residue	Limestone	Gypsum
SiO ₂	4.1	1.2	0.6
Al ₂ O ₃	22.5	0.5	0.1
Fe ₂ O ₃	47.2	0.3	0.1
CaO	9.8	54.1	33.1
MgO	0.1	1.2	2.3
Na ₂ O	1.6	0.0	n.d.
SO ₃	0.5	0.1	43.3
TiO ₂	5.8	0.0	n.d.
LOI	10.0	42.0	19.1

LOI: loss on ignition; n.d.: not determined.

In order to prepare clinker the raw materials were blended according to the compositions in **Table 2**.

Table 2. Raw meal composition (in wt%).

	Bauxite residue	Calcined limestone	Gypsum
BR55L20G25	55	20	25
BR55L25G20	55	25	20
BR65L15G20	65	15	20
BR65L20G15	65	20	15

The resulting powder was mixed with water in a 5/1 ratio to prepare pellets of approximately 1.5 cm diameter. The pellets were later dried for 48 h at 105 ± 5 °C. After this drying step, the samples were placed in an open platinum crucible to be fired in an electric furnace. Starting from a temperature of 800 °C, it was raised to a rate of 10 °C/min up to 1250 °C and held for 30 minutes. After this isothermal step, the fired samples were left to cool down inside the furnace and taken out when the oven temperature was approximately 20 °C. After this, the produced clinker samples were milled down to a Blaine surface of 4000 ± 200 cm²/g, ready for the experiments.

For X-ray diffraction (XRD), the clinkers were blended with 10 wt% ZnO (internal standard) in a McCrone micromill using isopropanol as grinding agent. The XRD analysis was performed in a D8 Advance (40 kV and 40 mA, monochromatic CuK α radiation, measurement range 5-70° 2 θ , step size 0.02° and step time 0.5 s). The phase determination was done with Diffrac.Eva V4.1.1 software and the quantification was performed using Topas version 5 software based on the normalized Rietveld method ^[9].

Setting time was determined following the EN 196-3:2016 specifications. The in-situ XRD was taken using a D2 Phaser (30 kV and 10 mA, monochromatic CuK α radiation, measurement range 5-35° 2 θ , step size 0.02° and step time 0.2 s) on cement pastes with 0.5 water/cement ratio. A special holder and plastic film were used to protect the sample from any water loss during the experiment.

Finally, the mechanical strength was obtained following the guidelines of the standard EN 196-1:2018. Mortar samples were prepared using a cement:sand:water ratio of 1:3:0.5 and casted on 40x40x160 mm³ moulds. During the first 24 hours the samples were stored in a humidity chamber and after that demoulded and moved later to the curing tank prior testing.

RESULTS AND DISCUSSION

The clinkers produced were studied by XRD technique and the experimental results can be found in

Table 3.**Table 3.** Crystal phase quantification for clinkers (in wt%).

Phase	Chemical Formula	BR55L20G25	BR55L25G20	BR65L15G20	BR65L20G15
Ye'elimite	Ca ₄ Al ₆ O ₁₂ SO ₄	29	27	17	28
Perovskite	CaTiO ₃	27	25	12	25
Anhydrite	CaSO ₄	10	7	8	3
Srebrodolskite	Ca ₂ Fe ₂ O ₅	5	17	3	4
Brownmillerite	Ca ₂ AlFeO ₅	3	7	2	5
Magnetite	Fe ₃ O ₄	3	2	2	2
α' l belite	Ca ₂ SiO ₄	0	2	0	0
β belite	Ca ₂ SiO ₄	0	0	4	3
γ belite	Ca ₂ SiO ₄	2	1	6	1
Aluminate c	Ca ₃ Al ₂ O ₆	7	9	4	5
Gehlenite	Ca ₂ Al ₂ SiO ₇	1	0	15	8
Unknown		14	2	28	17

Ye'elimite, the main phase targeted for this type of cement, was successfully produced in all the clinkers (17 – 29 wt%). Anhydrite was also found in the samples (3 – 10 wt%) which suggests that an excessive amount of gypsum was initially supplied in the raw meal. The Ti element seems to form exclusively perovskite (12 – 27 wt%) which is an inert phase that will not contribute later with hydrated phases. Regarding the Fe, a certain amount of brownmillerite (Ca₂AlFeO₅), srebrodolskite (Ca₂Fe₂O₅) and magnetite (Fe₃O₄) was found in the samples (7 – 26 wt%). Nonetheless, due to the large amount of Fe₂O₃ supplied initially with the raw meal it cannot be discarded that part of the iron is present in the crystal lattice of other phases.

Moreover, thanks to the use of an internal standard it was determined that an important amount of clinker (2 – 28 wt%) was “unknown”. When this unknown phase was analyzed with Diffra.Eva software, it was identified as SFCA phase (Ca_{2.3}Mg_{0.8}Al_{1.5}Si_{1.1}Fe_{8.3}O₂₀)^[10]. This phase is not found traditionally in cement clinkers and it should be further studied in future stages.

After the clinkers phase analysis, samples were ground to study the hydration process in cements. Starting with the setting time, the study shows that the cements possess fast setting properties (**Figure 1**). The initial setting time was 12 min for BR55L20G25, 11 min for BR55L25G20, 16 min for BR65L15G20 and 15 min for BR65L20G15. Regarding the final setting time, it was 17 min for BR55L20G25, 14 min for BR55L25G20, 25 min for BR65L15G20 and 23 min for BR65L20G15.

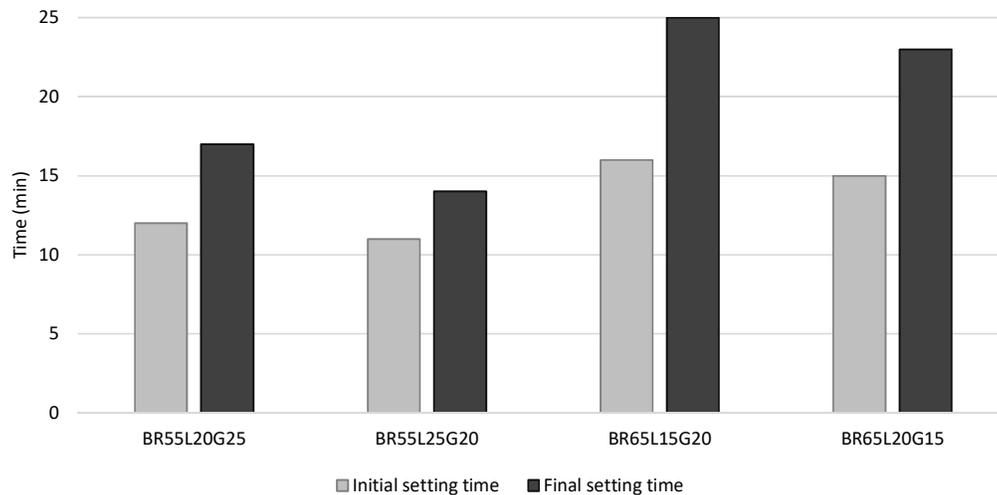


Figure 1. Setting time of cements.

The XRD in-situ (**Figure 2**) shows the evolution of the crystallographic phases during the first 6 hours of hydration. Gypsum peaks appeared at 11.5°, 20.7° and 29.0°. However, gypsum was not present amongst the clinker phases which implies the fast re-hydration of the anhydrite phase between the water addition and the start of the experiment (approximately 4 minutes). Ye'elimite peaks were observed at 23.6° and 33.6° during the first 2 – 3 hours of the test.

Regarding the hydration products, ettringite is the main one which was clearly visible in 9°, 15.7° and 25.4°. Finally, a constant peak was seen during the whole experiment in 33.1°. This can be attributed to the perovskite (CaTiO_3) or the aluminat ($\text{Ca}_3\text{Al}_2\text{O}_6$).

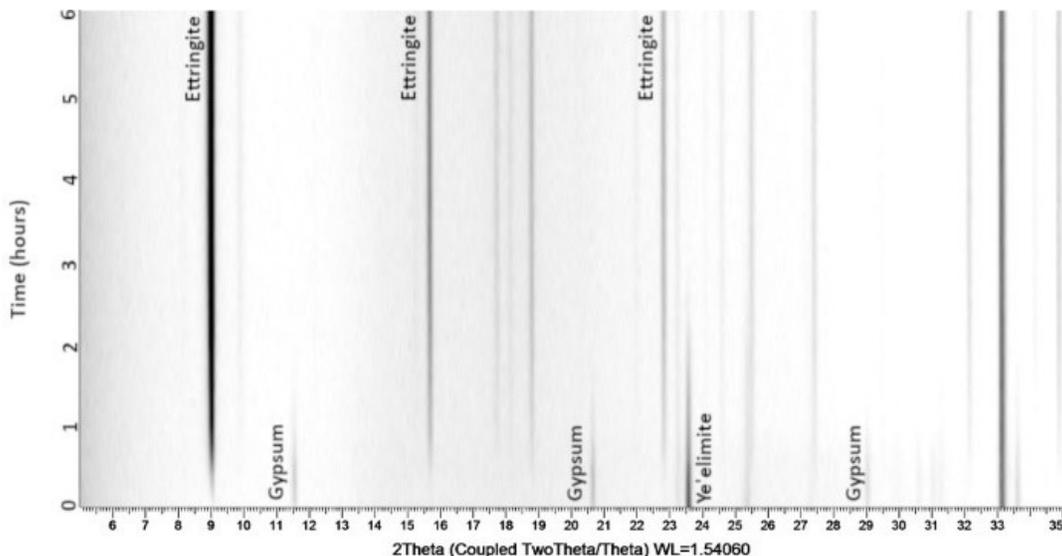


Figure 2. BR55L20G25 XRD in-situ for the first 6 hours of paste hydration.

Finally, the compressive strength was taken only for 3 samples (BR55L20G25, BR55L25G20 and BR65L20G15) and the results can be seen in the **Figure 3**. This is due to the fact that 24 hours after being submerged in water, the sample BR65L15G20 was destroyed due to expansion pressure. The remaining 3 samples reached after 28 days a mechanical strengths of 29.1 MPa for BR55L20G25, 24.2 MPa for BR55L25G20 and 26.3 MPa for BR65L20G15. This is related to the ye'elimite content, showing a higher mechanical strength those samples with higher ye'elimite content.

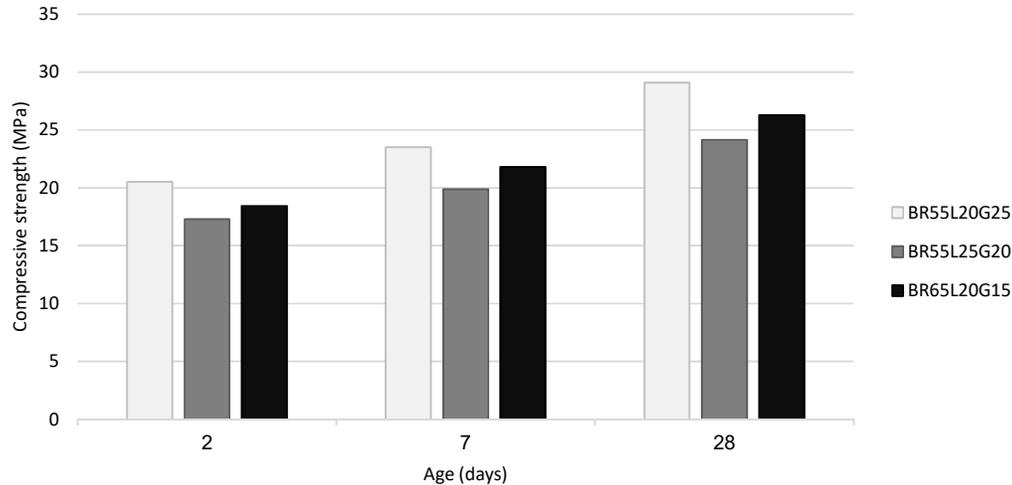


Figure 3. Compressive strength of mortars.

CONCLUSIONS

The study of 4 hydraulic binders prepared with high amounts of bauxite residue was shown herein. The research started analyzing the phase composition of those clinkers fired at 1250 °C. The successful production of typical CSFA phases (ye’elinite, brownmillerite and aluminat) as well as the presence of a calcium-sulfate source (anhydrite) pushed this research forward.

The resulting clinkers were later milled and their hydration behavior was analyzed with different methods. The setting times showed that a fast setting process was happening in the samples (up to 25 min) suggesting that these materials would be suitable for quick repair purposes. In-situ XRD showed some of the hydration processes happening in the pastes. First, the re-hydration of the anhydrite into gypsum that happens in the first minutes, between water mixing and the start of the experiment. Also, gypsum consumption is observed approximately in the first hour of the experiment, while ye’elinite it is still present during the first 2 – 3 hours. Ettringite formation happens fast and it is visible almost after 30 minutes from the start of the experiment. On top of that, a constant peak probably attributed to perovskite or aluminat, is seen at 33.1° during the whole experiment.

Finally, the mechanical strength of the mortars was obtained at 2, 7 and 28 days. The prisms were kept under water according to the European standard, but one of the samples was destroyed due to expansions during the first 24 hours submerged (BR65L20G15). The remaining samples showed that mechanical strength is strongly linked to the ye’elinite content in the clinker (achieving almost 30 MPa in the case of BR55L20G25).

Overall, the production of calcium sulfo-ferroaluminat cements making use mainly of bauxite residue was a success. This cements, showed fast setting properties and moderate mechanical strength. Such cements could be used for fast repair purposes. However, for next stages of this research the control of the setting time will be address as well as studying mechanisms to improve the compressive strength.

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