Characterization of a New Sintered Calcium Aluminate Cement

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Traditionally, calcium aluminate cements (CACs) are produced by fusion or sintering using precursor sources of high alumina and limestone with acceptable grades of impurities. The main impurities are silica, ferrites, magnesia, titania and alkalis. Due to the production conditions and raw materials compositions, CACs can be obtained with different proportions in the crystalline phases, being the main ones CA, CA_2 and $C_{12}A_7$, where CA is generally the major phase, being primarily responsible for the compressive strength of the CACs. As the fusion processing costs are considerably high, it´s presented the characterization of an Intermediate-Purity CAC produced by sintering of a bauxite and lime mixture in a rotary kiln resulting in a cement with suitable workability and setting time, in addition to good refractoriness and mechanical resistance. It was obtained CA as major phase with quantification performed by the Rietveld method (XRD/RM).

Introduction

Since the development of the calcium aluminates till recent applications and performance studies it has passed approximately 170 years. Such technology is widely known in the refractory industry in which these materials are commonly referred as calcium aluminate cements (CACs) [1]. The CACs can be classified according to their purity, including a wide range of compositions [2, 3]:

- The low purity CACs contains 39 to 50% Al_2O_3, with specific gravity and refractoriness corresponding to a range of 3,05 to 3,25g/cm³ and 1350°C, respectively
- The intermediate purity CACs contains 50 to 70% Al_2O_3, with specific gravity and refractoriness corresponding to a range of 2,95 to 3,10g/cm³ and 1410 to 1450°C, respectively
- The high purity CACs contains 70 to 90% Al_2O_3, with specific gravity and refractoriness corresponding to a range of 3,00 to 3,30g/cm³ and 1760°C, respectively

These cements are produced in several countries by using bauxite and/or alumina and limestone as raw materials, suitably homogenized in stoichiometric proportions, fused or sintered, and then crushed and milled to a fine powder with less than 5% retained on the 325 mesh [4]. The temperature in the fusion process usually ranges from 1450°C to 1550°C [5]. If the fusion process is performed by electric arc furnaces (electrofusion) the temperature reaches values higher than 2000°C. In the sintering process the temperature typically reaches the range between 1315 and 1425°C [6, 7].

Differences in the final product are caused by different chemical and mineralogical compositions of the raw materials and their size distribution in addition to the sintering/fusion conditions, such as the furnace atmosphere and the heating/cooling rate. For example, a reducing atmosphere of the furnace will mainly affect the clinker color, due to the reduction of Fe_2O_3 to FeO and a very fast cooling rate reduces the initial compressive strength, due to the lower crystallinity of the CAC. On the other side, a slow cooling rate will usually lead to a shorter setting time of the CAC [8].

The knowledge of the mineral phases present and their quantities is essential for the development, production and use of the CACs since all the properties of these materials are closely related to the phases obtained in the process and their proportions. CACs can be composed of a great number of phases depending on the C/A ratio, where C corresponds to CaO and A to Al_2O_3. The main phases present in commercial CACs are calcium monoaluminate, CA (CaO. Al_2O_3), calcium dialuminate or grossite, CA_2 (CaO.$2Al_2O_3$), mayenite $C_{12}A_7$ ($12CaO.7Al_2O_3$) and gehlenite C_2AS ($2CaO.Al_2O_3.SiO_2$) [2, 3], as observed in the ternary equilibrium phase diagram (Fig. 1).

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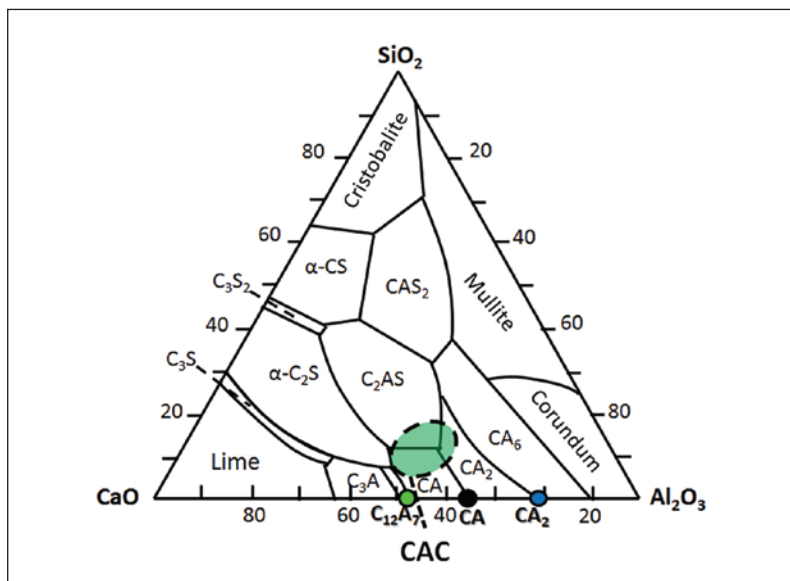**Fig. 1** CaO.Al$_2$O$_3$.SiO$_2$ ternary equilibrium phase diagram [adapted from 8 and 9].

The calcium aluminate (CA) is the most important crystalline phase in the CAC system because it is the main phase with 40 to 70%w and develops the highest compressive strength between the phases of the system. Although taking some time to start setting, there is a quick hardening after the initial setting. Furthermore, CA presents a high melting point (MP) of around 1600°C [1, 2, 8].

The calcium dialuminate (CA$_2$) usually corresponds to more than 25%w of the CACs composition. This phase has an excessively long setting time, with relative low compressive strength after 24 hours. CA$_2$ is the phase of the CAC with the lowest thermal expansion coefficient (4,4x10^{-6} °C^{-1}, from 20 to 1400°C) and higher refractoriness (decomposition at 1750°C). Its setting time is accelerated in the presence of CA, while the opposite is not valid [2, 11, 12].

The mayenite (C$_{12}$A$_7$) is frequently maintained at low concentrations (<10%w) because of its quick hydration. The mayenite amount usually increases when the C/A ratio increases and it can be used to accelerate the setting time of different other cements. In relation to the other phases mentioned, C$_{12}$A$_7$ has the lowest refractoriness (MP = 1390°C) [2, 12, 13].

The gehlenite (C$_2$AS) has reduced or no tendency to hydraulic setting unless in contact with lime or when in the non-crystalline form. When present in high concentrations it limits the refractoriness (MP = 1590°C) and the compressive strength of the CACs at higher temperatures. The amount of C$_2$AS quickly increases when the silica content is higher than 5%w, impacting negatively the setting time of the cement [2, 8, 13] and impairing its compressive strength since its thermal expansion coefficient is different to the other constituents of the CACs leading to micro-cracks formation.

When used in castables CACs can promote [1, 9, 14]: fast strength development even at low temperatures; working time at low temperatures; refractory performance with strength to support temperature fluctuations and good resistance to a wide range of aggressive chemicals at high temperatures.

Experimental Procedure

The production of the calcium aluminate cement (CAC) utilized a Brazilian gibsitic bauxite with high alumina content and a special lime source with reduced amount of impurities. Both raw materials were dried, homogenized, milled and granulated before sintering in a rotary kiln using temperatures over 1350°C. After sintering, the clinker was ball milled and the cement was submitted to several evaluations. Fig. 2 summarizes the production process of the CAC.

Sampling was proceeded following ABNT NBR ISO 8656-1 [15] standard and the CAC was characterized chemically and mineralogically. The cement had also its water ratio on the paste (W/Cp) and on the castable (W/Cc) evaluated. The setting time was measured by the Vicat needle, the specific area was evaluated by Blaine and the refractoriness evaluated by Orton cone. The castable had also its compressive strength measured at 24 hours, after a drying process at 110°C for 36 hours and after a heat treatment at 815°C and 1400°C for 4 hours.

The chemical composition was determined by X-ray fluorescence spectrometry (XRF-1800, Shimadzu), with sample preparation by the glass bead method in a fusion machine (HA-HF 16/2, Herzog). The mineralogical composition was analyzed by X-ray powder diffraction (XRD-6000, Shimadzu), with CuKα radiation scanning 2θ region from 14° to 70°, using the Rietveld method (RM) of crystalline structure refinement to evaluate the unit cell parameters and quantify the crystalline phases of the CAC through the GSAS software [16]. The water/cement ratio of the cement (W/Cp) and the setting time was determined by a Vicat needle according to ABNT NBR 9997 [17]. The water/cement ratio of the cement (W/Cc), the working time and the compressive strength were determined by using procedures developed internally [18]. To prepare the castable it was utilized a brown fused aluminum oxide
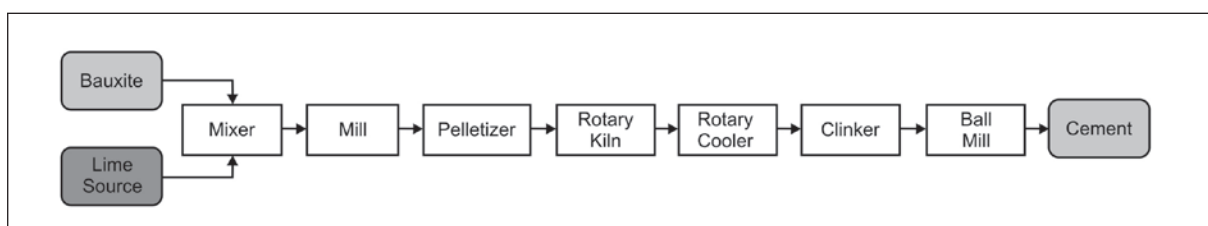

Fig. 2 Flowchart for the CAC production

(ALOTAB) as aggregate in different grit sizes. The castable formulation is present in the Tab. 1. The specific surface area was quantified by the Blaine method according to NBR 16372 [19] and the refractoriness was determined by the Orton pyrometric cone equivalent (PCE).

Results and Discussions

According to the chemical composition achieved (Tab. 2), this cement can be classified as an intermediate-purity CAC. It is also noted the low alkalis concentration and the low magnesium oxide content (<1%) will improve the castable properties.

The mineralogical composition (Fig. 3) confirms the main phases expected for the CAC, having calcium monoaluminate (CA) as the major phase (70,3%) and mayenite ($Ca_{12}A_7$) in low concentration (5,2%). As secondary phases the mineralogical evaluation shows calcium dialuminate (CA_2) and gehlenite (C_2AS) obtained at similar concentrations of 11,0% and 13,5%, respectively. In addition to this, the X-ray diffractogram indicates good crystallinity of the cement.

The iron and magnesium are not explicitly shown in the mineralogical composition because of their solubility in the C_2AS as indicated in the literature [1]. Lea points out a solubility of 3 to 5% of Fe^{3+} in CA_2 [8]. Furthermore, the CA can contain up to 4,8% of Fe^{3+}. Additionally, Robson affirms that the hydraulic activity of the CA is improved by iron admixture and Kurdowski mentions that the compressive strength of the CA doped with Fe_2O_3, and particularly with $SiO_2 + Fe_2O_3$ mixture, is considerably higher than the CA paste without these admixtures [1, 13, 20].

The refinement of crystalline structures by RM suggests the solubility of iron ions in CA and CA_2 phases noted as an increase in the volume of the unit cell of these phases with monoclinic symmetry caused by the substitution of Al^{3+} by Fe^{3+} in the tetrahedron of AlO_4. In comparison to the standard unit cells, the CA phase passed from 1069,4 to 1072,2$Å^3$, while the CA_2 phase passed from 596,0 to 598,8$Å^3$. A slight expansion was also noted in the tetragonal phase C_2AS from 299,1 to 300,3$Å^3$. The Fig. 4 shows the crystalline structure of the CA and CA_2 phases, highlighting the AlO_4 tetrahedrons.

The low results of water/cement ratio of the cement (W/Cp) and of the castable

Tab. 1 Refractory castable formulation (weight proportion)

Product	Proportion (%)
ALOTAB 4/10	32
ALOTAB 8/20	16
ALOTAB 20/40	10
ALOTAB 35/70	8
ALOTAB 70/140	4
ALOTAB – TPF II	12
Cement	18
total	100

Tab. 2 Chemical composition (%)

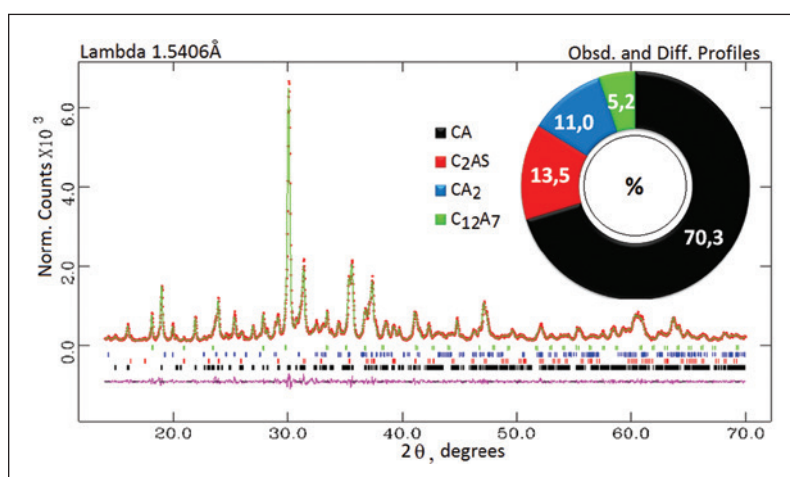| Al_2O_3	CaO	SiO_2	Fe_2O_3	MgO	TiO_2	K_2O+Na_2O
57,5	34,5	3,49	3,30	0,57	0,24	0,08

Fig. 3 Rietveld graphic and mineralogical composition of the CAC after XRD characterization
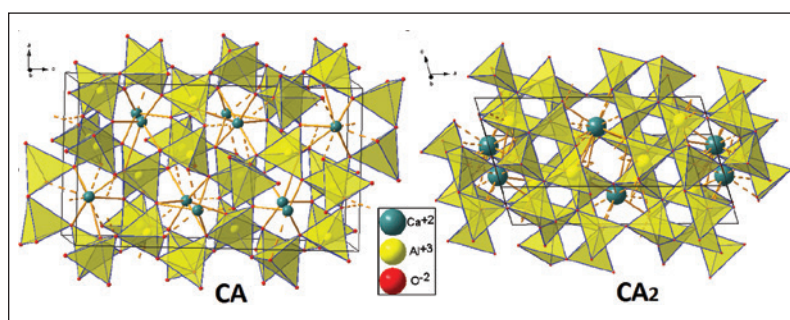

Fig. 4 Crystal structure of CA and CA_2 phases

Tab. 3 Water/cement ratio of the cement (W/Cp) and of the concrete (W/Cc) and specific surface area

W/Cp	W/Cc	Specific Area (cm²/g)
0,29	0,0746	5143

(W/Cc) (Tab. 3) could be responsible for a good expectation of the compressive strength [14]. This same table shows the specific area demonstrating the fineness
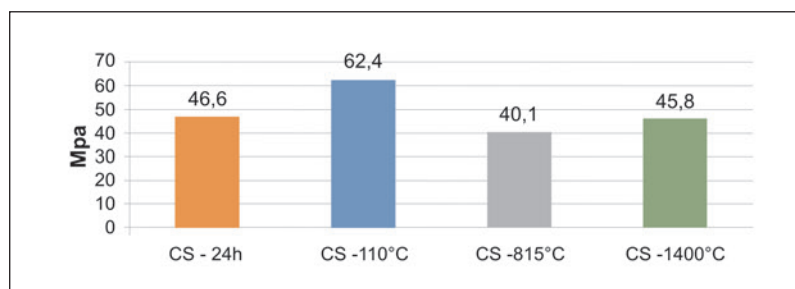
Fig. 5 Compressive strength (CS) after 24 hours at room temperature (CS – 24h), after drying at 110°C for 36 hours (CS – 110°C) and after thermal treatment at 815°C and 1400°C for 4 hours (CS – 815°C and CS – 1400°C, respectively)
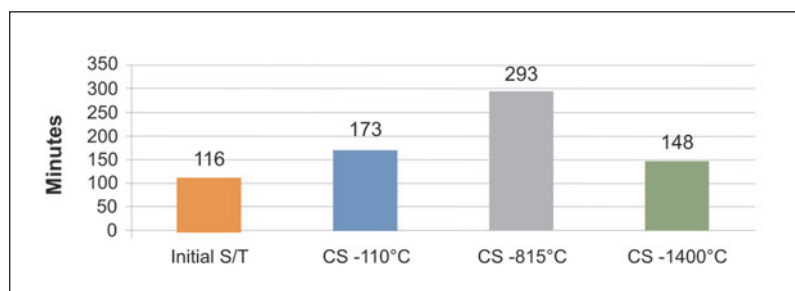

Fig. 6 Setting time and workability of the CAC

of the CAC obtained by ball milling.

The good compressive strength over 30 MPa (Fig. 5) in all conditions is due to the high CA content, combined with the high specific area. According to Nelson [14], CACs compressive strength between 225°C and 1000°C is mainly controlled by the water/cement ratio. C_3AH_6 is the only stable hydrated calcium aluminate phase at temperatures under 225°C. At higher temperatures, the water content starts to drop and $C_3AH_{1,5}$ is the phase present at 275°C. Above this temperature, decomposition of $C_3AH_{1,5}$ happens with the liberation of C (free lime). Between 550 and 950°C, recrystallization occurs resulting in C and $C_{12}A_7$, improving the strength over these temperatures till the softening point. These mechanisms explain the results observed in Fig. 5.

Initial, intermediate and final setting time (S/T) as well as the workability of the CAC (Figure 6) prove that this particular CAC is suitable for use in refractory aplications. These results showed that the low $C_{12}A_7$ was beneficial to the cement properties.

Ultimately, the refractoriness determined by Orton pyrometric cone showed a plastic deformation between 1398 and 1430°C (Orton cone equivalent between 14 and 15).

Conclusions

The intermediate-purity CAC produced by sintering presented a low water/cement ratio (W/Cp = 0,29), adequate working time (148 minutes) and setting time (S/T of 173 minutes), good refractoriness (between 1398 and 1430°C) and high compressive strengths. These properties indicate a good performance of the CAC, in which SiO2 and Fe2O3 impurities of around 3,5% each do not impact negatively in the properties of a refractory castable.

Acknowledgements

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