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Effect of Al_2O_3/SiO_2 ratio on ye'elimite production on CSA cement

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HIGHLIGHTS

- Effect of Al_2O_3/SiO_2 ratios over the CSA clinker compressive strength was determined.
- Gehelenite vs ye'elimite as function of Al_2O_3/SiO_2 and temperature was studied.
- Correlation between mechanical strength and released heat was established.
- A new correlation between CSA strengths and polymorphs of ye'elimite was established.

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ABSTRACT

Many raw materials have not been considered for the production of CSA cement due to their SiO_2 content, which affects both the formation and composition of the crystalline phases of the CSA cement, competing for the available aluminum and calcium, thus affecting the ye'elimite content and the performace of CSA cement as well. This work analyzes the effects of the Al_2O_3/SiO_2 (A/S) ratio on the mechanical properties of a series of formulations of CSA cements evaluated at two different temperatures (1250 and 1300 °C). In these formulations a limit of chemical composition was determined to reach percentages of ye'elimite that allow to produce a CSA cement with good performance, taking advantage of available raw materials in high ratios in the nature. Among the most relevant findings, the determination of the minimum and maximum limits in the A/S ratio in order to maximize the ye'elimite content, is highlighted. In addition, correlations between the higher strengths and shorter setting time and higher hydration heat fluxes with the greatest ye'elimite content, were determined. Both the effect of the ratio of ye'elimite polymorphs present on the cement and the effect of the greater A/S ratio on the fluid and hardening performance of CSA cement were identified.

1. Introduction

CSA cements have been widely studied by scientists and industrial level cement producers [1–3] since the 70s. Particularly, during the last decade, the studies have been deeper and more specialized in aspects of the crystalline structure, hydration kinetics, among others CSA characteristics. Due to the benefits and advantages associated with the lower CO_2 emissions of CSA cement (~35%) in comparison to Portland cement [4] and its adaptability to the modern industrial cement process production [5], this cement has been considered to be included into the cement portfolio of different comertial products, with high interest from both the environmental and functional point of view. Due to those potential characteristics this cement has been known under the generic name of "third cement series" [6], as an alternative for Portland cement [7,8].

On the other hand, it is important to highlight that the research carried out by different scientists have strongly focused their work on both the mineralogical composition of CSA cements and the effects on the hydration process as well [7–9]. Furthermore, some aspects regarding the crystalline composition in CSA cement have been studied and how the crystalline compound called ye'elimite, as the main phase of CSA cement, features different hydration kinetics if compared to Portland cement crystalline compounds and consequently differences over their hydration kinetics. Ye'elimite remarkably shows some advantages on its hydration speed which are associated with the high early strength reached by this kind of materials and also its faster setting time [9,10]. These features encourage researchers to investigate even more

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and understand the CSA cement characteristics and how to improve the CSA cement production process by using different raw materials widely available in the world. Those characteristics can attract the concrete end-users of cement in order to use it as a new product with better performance at early ages (precast, pavements, others). Due to its potential uses, the relevance of the scaling production process of CSA from laboratory to industrial, adapting and using the same Portland cement installations, it becomes even more interesting [11]. The importance of looking after the chemical formulation balance between alumina and silica in order to control the quality of CSA clinker is relevant due to the inhibition reactions occurring during the ye'elimite formation [12]. Depending on the silica content it can promote the formation of other crystalline compounds during the CSA clinker process, like gehlenite, which competes with ye'elimite [13] during the solid to solid reactions in a kiln. Those characteristics of alumina and silica equilibrium represent a fundamental chemical aspect that must be controlled during an operational industrial process; a condition for CSA cement production process should be reached. It is a matter not just from the chemical point of view but for the economically and environmental point of view as well, by using natural raw materials available and affordable from the cement industry.

The CSA cement can be manufactured both from synthetic materials and/or natural raw materials [14,15], but CSA cement has also been produced industrially in different countries, i.e. China, Italy, Australia [16]; however, producers and previous researches have not reported the oxides ratios nor the operational conditions required to obtain a specific CSA cement with a particular mineralogical composition. This work seeks to identify the range for the oxide ratio between alumina and silica (A/S), which has a strong influence on ye'elimite formation at an industrial level [17]. Nowadays, the CSA cement production worldwide offers an opportunity for the market [18]. The idea is to produce a CSA clinker with certain crystal composition by using materials available in nature in high quantities for users and moreover for scientists and cement producers in order to take advantages of its properties, and look forward to advance towards improvement of its environmental benefits and product benefits, in a short period of time, by using this alternative cement [7].

2. Materials and methods

Starting from raw materials and to cover a wide range of the Al_2O_3/SiO_2 ratio in order to identify its impact on the production of ye'elimite, six raw mix were formulated. Two bauxites and two limestones, one of high purity and the other one of intermediate composition, were used and a single source of gypsum of high purity and quarzt-sericitic schist was used as a source of silica. The range evaluated was $2 < Al_2O_3/SiO_2 < 6$, in which six levels were established. Each mixture was clinkerized at 1250 °C (samples identified with odd numbers) and 1300 °C (samples identified with even numbers). An experimental design is proposed for the evaluation of the variables of interest. Subsequently, the quantification of the mineral phases of the sintered material and the preparation of the CSA cement from the CSA clinkers is performed, for this purpose the necessary stoichiometric gypsum is calculated so that the hydration of the available yeelemite in each cement react completely. A microcalorimetry test is carried out to identify the qualitative characteristics of the hydration of the different cements. Afterwards, 4 of the formulated cements are selected, looking for the most extreme behaviours in terms of the content of yeelemite, they are reproduced in a larger amount to finally evaluate the behavior of said cements both in fresh and hardened state.

2.1. Raw materials

Chemical analysis of the raw materials was carried out by X-ray fluorescence, using a PANalytical AXIOS by fused bead analysis. The mineralogical analysis of the raw materials was done with a diffractometer X'pert Pro MPD of PANalytical with copper radiation $CuK_\alpha = 1.54059$ Å, in theta/theta or Bragg-Brentano configuration. The Reading was taken at 45 kV and 40 mA. The data were collected between 5 and 90° (2Theta), with a pitch of 0.0167° and an accumulation time of 40 s. For the identification of the minerals, the High Score Plus software and the ICSD 2011 database were used. Table 1 shows the main chemical and mineralogical components of each raw material.

As for the bauxites the mineralogical analysis is quite consistent with the chemical analysis because bauxite 2 (intermediate) has a greater content of quartz, in this bauxite, andradite ($Ca_3Fe_2Si_3O_{12}$) was also identified which would explain the greater content of calcium in this material as well as corundum. Common to both bauxites was the presence of kaolinite as an accessory mineral. The two limestones can be considered of high purity being calcite the main constituent mineral accompanied by quartz in smaller proportion. The source of sulphate is mainly calcium sulphate dihydrate or gypsum, followed by bassanite and to a lesser extent anhydrite, Table 1 shows the sum of the sulphate sources. Minority minerals include calcite and quartz were found in the gypsum sample. Finally, as a source of silicon the schist was used, consting mainly on quartz and in smaller percentage micas and some minerals typically methamorphic.

2.2. Elaboration of CSA raw mix

The materials were crushed, dried and ground separately to obtain a retained between 10 and 12% in 170 (90 μm) mesh, meal-like granulometry for the industrial production of Portland clinker [19]. For each raw mix design, the materials were weighed separately and homogenized dry using a Hobbart mixer for 5 min. Regarding the design of the CSA mix, they were formulated according to the composition of the raw materials presented in Table 1, a minimum content of 40% for CaO and 30% of Al_2O_3 and establishing as objective function the different Al_2O_3/SiO_2 ratios. The Solver tool

Table 1
Chemical and mineralogical characterization of raw materials.

	Bauxite 1	Bauxite 2	Limestone1	Limestone2	Schist	Gypsum
Chemical						
L.O.I.	26.50	23.55	42.68	42.80	5.57	21.19
SiO_2	10.16	19.63	1.95	0.31	76.21	3.37
Al_2O_3	58.11	46.48	0.39	0.21	3.84	1.00
Fe_2O_3	1.25	1.84	0.09	0.02	6.01	0.39
CaO	0.72	4.62	53.80	55.92	2.59	30.83
MgO	0.06	0.56	0.70	0.49	4.43	0.19
Na_2O	0.16	0.20	0.13	0.10	0.20	0.15
K_2O	0.00	0.09	0.02	0.00	0.19	0.11
SO_3	0.30	0.49	0.21	0.07	0.22	42.63
Cr_2O_3	0.04	0.03	0.00	0.00	0.03	0.00
Mn_3O_4	0.00	0.01	0.01	0.00	0.21	0.01
P_2O_5	0.06	0.07	0.03	0.09	0.22	0.02
TiO_2	2.50	2.19	0.02	0.02	0.18	0.05
Mineralogy						
Quartz	10.91	22.85	3.50		59.80	
Gibbsite	76.61	54.52				
Corundum	0.51	4.68				
Calcite			96.07	99.85		6.50
Gypsum						90.93
Kaolinite	5.23	7.00				
Hematite	1.36	0.75				