



Properties of low temperature belite cements made from aluminosilicate wastes by hydrothermal method



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ABSTRACT

The aim of this study is the synthesis at low temperature (1000 °C) of reactive belite cement, rich in reactive C₂S phases (α'_L and/or β -C₂S), starting from aluminosilicate wastes (oil well drilling mud and hydraulic dam sludge) and hydraulic lime dust recovered from bagging workshops. A hydrothermal treatment of the raw cement mixture was performed in an alkaline solution of KOH (0.6 M), with heating at 100 °C for 4 h under atmospheric pressure and continuous agitation. The burning of the hydrothermal mixture at 1000 °C produced reactive belite cements containing between 79% and 86% of C₂S (α'_L and/or β polymorphs), the rest being C₁₂A₇ (5–8%), C₄AF (7–11%) and free lime (2%). The cements were characterized by X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), microprobe, and laser granulometry. The hardening evolution of belite cement pastes and mortars was followed by thermo-gravimetric analysis (TGA), setting time and compressive strength. The results showed a rapid production of hydrates (C–S–H/C–A–S–H, calcium aluminate hydrates and portlandite), with a fast setting time (reaction of C₁₂A₇) and compressive strength evolution that led to these cements being classified in the 32.5 category according to EN 197-1.

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1. Introduction

The formation of alite (Ca₃SiO₅), the main component of clinker, produces large amounts of CO₂ compared to the formation of belite (Ca₂SiO₄). Increasing the amount of belite in cement thus leads to a great reduction of CO₂ emissions. Moreover, the use of industrial by-products rich in lime, silica and alumina, such as calcium fly ashes, as raw materials to produce belite cement, leads to the a significant reduction of CO₂ emissions [1,2].

Recently, various studies have approached the manufacture of belite cement at low temperature, around 1000 °C. Among cements with high belite contents, those containing mainly C₂S, C₄A₃S, C₃S and C₄AF phases have been reported by many researchers [3–9]. The usefulness of these cements in improving the mechanical and chemical performance of materials may increase when they are incorporated into ordinary belite cement that hardens slowly at early and medium ages [6,9–12]. Other researchers have used fly ashes as an alternative that can produce reactive belite cement

with low energy consumption by using hydrothermal treatment [1,13–17].

Ordinary belite clinker is characterized by low hydraulic reactivity, which limits its use. Improving this reactivity is currently one of the concerns of researchers in this field. Reactive belite clinker contains the reactive phases of C₂S, a mineral that can exist in six polymorphic forms depending on the temperature and pressure of their formation [18]. Three polymorphs: α'_H , α'_L and β_H -C₂S, have a reactivity similar to that of alite [19,20]. However, γ -C₂S is chemically stable, while α -C₂S and β_L -C₂S show moderate reactivity [21]. The reactive phases are very unstable and can easily transform into poorly reactive phases during clinker cooling. Some methods for obtaining the reactive belite phases and improving belite's hydraulic activity have been developed in recent decades. These methods involve the use of chemical activators and structure stabilizers of reactive C₂S phases [19,22–27] for the synthesis of reactive belite by means of a hydrothermal process [4,5,17,28–30].

The present work is a contribution to the field of eco-efficient cement manufacturing, its aim being the low-temperature synthesis of a belite cement having high hydraulic reactivity, close to that of ordinary cement. To achieve this objective, the hydrothermal method was used with a raw mixture of low lime saturation factor (LSF = 70). The raw mixture was composed of industrial wastes: oil

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well drilling mud and hydraulic dam sludge as silica sources, and lime dust collected from bagging workshops to compensate for the CaO deficit. These wastes constitute a true ecological problem in their areas of production.

According to a previous study [17], the hydrothermal method used by other researchers [2] for synthesizing belite cement with calcium fly ash can be modified to optimize the synthesis parameters [17]. Therefore, the hydrothermal treatment temperature was set at 100 °C (instead of 300 °C) and atmospheric pressure was used (instead of a high pressure of 1.4 MPa). The alkaline NaOH solution was also replaced by KOH [17], which reduced the molarity from 1 M to 0.6 M and the stirring time from 5 to 4 h. This method with these operating conditions was used for the first time on a mixture of aluminosilicate waste. Previous uses concerned fly-ash mixtures of excessive fineness favorable to the hydrothermal treatment. Burning the raw mixture at 1000 °C led to the formation of reactive belite phases (α'_1 and β -C₂S) in cement without the appearance of alite. Other phases, such as calcium aluminates, could be found in the finished product.

The paper shows the physicochemical and mineralogical characteristics of the mineral wastes used and the reactive belite cements obtained by the hydrothermal method, together with their hydraulic reactivity measured by different methods (XRD, TGA, physical and mechanical tests).

2. Experiments

2.1. Sample testing

The chemical compositions of raw materials, raw mixtures and synthesized clinkers were determined by X-ray Fluorescence (XRF) using a Philips PW 1404 X spectrophotometer. X-ray Diffraction Analysis (XRD) with a Siemens D5000 diffractometer equipped with a variable slit opening and using Co K α radiation was employed to characterize the raw materials, the hydrothermal mixtures and the belite cements, as well as to control the reaction of belite in the cement pastes. The amount of free lime in belite cements was determined by a conventional glycerin–alcohol test. The specific surface area of belite cements was determined by the Blaine and BET methods and their particle size distribution by laser granulometry (Mastersizer 2000). The morphology and texture of belite crystals were examined by Scanning Electron Microscopy (Philips XL30), after covering the sample grain (≈ 5 mm of diameter) by graphite. The chemical composition of this phase (C₂S) was measured by scanning electron microprobe analysis on a Camebax electron microscope. For this analysis, the sample was introduced in araldite and, after 24 h of hardening, the disk was polished by hand with moderate pressure on a low-speed lap with a low nap lap wheel covering for about 1 min per stage using a series of 6, 3, 1 and 0.25 μ m diamond disc and propylene glycol as a polishing lubricant. The sample surface was covered with gold under vacuum. The thermogravimetric analysis (TGA), performed in air on a Setaram Labsys thermoanalyser with a heating rate of 5 °C/min up to 1000 °C, was used to follow the cement paste hardening. The setting time test was measured on belite cement pastes to study their hydraulic reactivity, by using a Vicat needle on a mini-tapered mold 30 mm in diameter and 15 mm high. The mechanical test according to standard EN-196-1 was used to determine the compressive strength of the belite cements obtained.

2.2. Raw materials

The materials used in this study were Algerian industrial wastes, namely drilling mud (DM) from the oil wells of Hassi

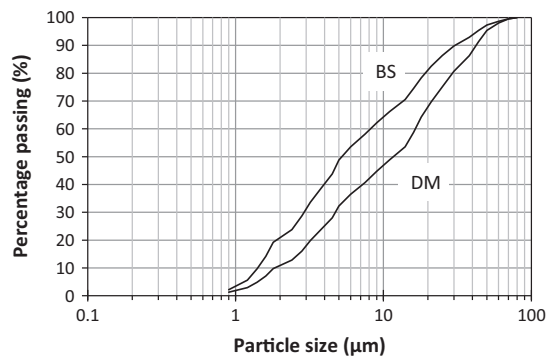


Fig. 1. Particle size distribution, determined by laser granulometry, of the materials used (drilling mud and dam sludge).

Messaoud, hydraulic dam sludge (BS) from Fergoug and slaked lime dust (LD) from bagging workshops, recovered as dust settling in the soil when putting in bag the hydrated lime at the end of the production line. After drying to constant weight in a drying oven at 105 °C, the raw materials were crushed to 80 μ m and homogenized. The particle size distribution of both crushed wastes, determined by laser granulometry, is given in Fig. 1 and shows grains ranging from 80 μ m to less than 1 μ m, with a mean diameter of 5 μ m for BS and 13 μ m for BS for DM. The chemical compositions of the raw materials, determined by X-ray Fluorescence (XRF), are given in Table 1.

The mineralogical compositions of DM, BS and LD were determined by X-ray diffraction (Fig. 2). The drilling mud and dam sludge were mainly composed of quartz and calcite, with other minerals such as montmorillonite (in DM), micas (in DM and BS), kaolinite (mainly in BS), plagioclase feldspars (mainly in DM) and dolomite (in BS). Both materials probably also included a small amount of amorphous phase, characterized by a diffusion hump between 4.7 and 2.8 Å (22 – $37^\circ 2\theta$). Slaked lime dust (LD) contained portlandite with a small amount of calcite resulting from lime carbonation during storage.

Ordinary CEM I 52.5N cements from the Martres plant of the Lafarge company – France and CEM I 42.5N-CRS from the CiBA plant of Lafarge-Algeria, were used as references in this study (chemical composition in Table 1) to evaluate the hydraulic reactivity of the synthesized belite cements. The mineralogical compositions of the two ordinary cements are given in Table 2. CEM I 42.5N was a sulfate resistant cement (SRC), with low C₃A and gypsum contents.

2.3. Synthesis procedure

To obtain belite cement without C₃S, the CaO/SiO₂ molar ratio in the raw mixture must be equal to 2, according to the C₂S stoichiometry, which is equivalent to a lime/silica mass ratio of 1.87. Raw mixtures were calculated on this basis. The first was composed of 51.12% of dam sludge with 48.88% of lime dust, and the second contained 38.16% of drilling mud with 61.84% of lime dust. The lime saturation factor (LSF)¹ [31] was 67% for the dam sludge–lime dust mixture and 69% for drilling mud–lime dust.

A hydrothermal synthesis process at normal pressure (1 atmosphere) was used in this study, as already developed in a precedent work [17]. Hydrated precursors were prepared from raw mixtures composed of lime dust and the siliceous materials mentioned above. The dry mixture was put into an alkaline solution of KOH (0.6 M) at a liquid to solid ratio of 5 (as stated in [17]). The liquid

¹ Lime Saturation Factor (LSF) = $\frac{100\% \text{CaO}}{2.8\% \text{SiO}_2 + 1.1\% \text{Al}_2\text{O}_3 + 0.7\% \text{Fe}_2\text{O}_3}$

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