

Valorization of glass and shell powders in the synthesis of Belitic clinker

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Abstract. In recent years, waste recycling has become a key issue in construction materials science for achieve the goal of sources of raw materials. The aim of this study is to use waste glass as source of SiO₂ oxide and mussel shells consisting essentially of calcium carbonate as starting materials to synthesize belite rich cement. The elaborated clinker is chemically and structurally related to β -Ca₂SiO₄, by heat solid state activation. After grinding, the raw materials are mixed and heated up to 1050°C. The samples are characterized by X-ray diffraction (XRD) and Fourier Transformed Infrared spectroscopy (FT-IR). The mechanical strength of some sample was measured for 28 and 72 days. The results show the different mineralogical stapes of formation of clinker, the state reaction method allows the elaboration of a cementitious material by a simple heat treatment at relatively low temperature and low release of CO₂. The hydration products are also identified by XR diffraction at 2, 7, 28 and 72 days.

1 Introduction

Each year, a large amount of coast shell is being picked up around all the costs sea and oceans of the world, also many factories produce a high amount of waste glass. These wastes become a serious environmental problem. The best solution to overcome the environmental impact of these wastes is to reuse them. Many researchers prove the benefit derived from reusing various waste materials, such as, fly ash [1], paper sludge ash [2], clay aggregate [3], tire crumb [4], siliceous and aluminous materials, as well as some natural pozzolanic materials [5] in the production of cement clinkers, and it has been proposed that these wastes have high potential for being alternative raw materials [6]. The use of by-products or residues generated from other activities seems to be a good approach to solve both economic and environmental problems related to cement production [7].

The use of shells and waste glass are widely studied in literature in many fields. Shells are used to improve mechanical proprieties of mortar [1], monetite [8] and engineering properties of controlled low-strength materials [9]. Shells also used to synthesis bioactive Hydroxyapatite [10]. Waste glass can be utilized in the elaboration of cement and concrete [11], can impact cement hydration [12], and can be used also to improve and enhancing durability of mortar [5] and to reduce and minimize cement content in rendering of mortar [13]. These studies proved that the use of coast shell and waste glass in cement can improve the mechanical properties

and durability of elaborated cements by beneficially influencing the material microstructure.

The syntheses of β -Ca₂SiO₄ in moderately low temperature (< 1400°C) attract a lot of interest of many researchers In recent years. The total or partial replacement of conventional Portland cement by belite cement presents many positive aspects, such as energy and raw material reducing and savings as well as the possible higher durability [7].

Belite is one of the essential components of the Portland cement. It constitutes 15 to 30 wt. % of clinker and Exists in five forms: α , α'_H , α'_L , β and γ [14, 15]. The β form is metastable under 500 °C but is hydraulically active. However, the γ stable form at ambient temperature is inactive towards water reaction. The α , α'_H , α'_L forms are stabilized at room temperature by the incorporation in their structures of foreign ions [15, 16]. The belite phase C₂S is generally present in the β form at room temperature [15, 17].

The seashells were composed of Ca as the essential metal with a small amount of Mg, Al and Si. Generally, Ca should present in the seashells as CaCO₃ [18], similar to that for other shells resumed in researches [19]. Like marine clam mussel is an aquatic bivalve mollusk. It characterize by two shells connected by a hinge-like muscle [19]. Mussel shells are considered as a calcium-rich resource that can be utilized to produce calcium oxide [20]. This latter can be utilized in several different ways in environmental technologies [21].

Glass is resulting from fusion of several inorganic mineral raw materials, which after undergoing a process

of controlled freezing becomes a hard, homogeneous, amorphous and isotropic material [22]. With the exception of Al₂O₃ and CaO, the rates of the main constituents of different types of glass are similar [23]. For soda lime glass is characterized by an approximately composition: 70% of silica, 13–17% Na₂O and 10% CaO [24]. However, glass has a composition that favors the development of pozzolanic reactions [25]. Furthermore, conferring to the chemical requirements in ASTM C 618 glass can be considered as a pozzolanic-cementitious material [26].

In this work, we have used mussel shells and glass which predominantly composed respectively of calcium carbonate and silica as starting materials in elaboration of dicalcium silicate C₂S by solid state reaction at 1050°C without any stabilizers.

2 Materials and method

2.1 Materials

Dicalcium silicate powder (C₂S) was elaborated by solid state reaction of the mixture of mussel shells and glass powders as starting material. The mussel shells are gathered from the coast of the Atlantic Ocean of Rabat-Morocco, then dried and finely milled (<40 μm). Glass powder is gotten by crushing the White glass beverage bottles and cups glass (<40 μm). In Table 1, the chemical composition of the starting materials shows that mussel shell contained a huge amount of calcium oxide 55.24 % by weight. It also contained a littler amount of impurities, primarily in the form of silicon, sodium, aluminum and magnesium oxides. The loss on ignition of 43.51 % was ascribed to the loss of carbon dioxide due to the partial decomposition of calcium carbonate. White Glass comprises basically of silicon 72.49 % and lime 11.98 %. Other minor elements as aluminum and sodium oxides are detected.

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

Oxides	Mussel shells	Glass
SiO ₂	0,35	72,49
Al ₂ O ₃	0,12	1.50
Fe ₂ O ₃	0.08	0.17
CaO	55.24	11.98
MgO	0.08	0.51
SO ₃	0.20	0.32
K ₂ O	0.02	0.17
TiO ₂	0.00	0.03
Na ₂ O	0.08	2.76

P ₂ O ₅	0.04	0.01
LOI*	43.51	9.97

2.2 Method

After crushing and grinding, shell and glass powders are mixed with a proportion of 68 %wt and 32 %wt respectively, then heated up to 500 °C for 24 h followed by milling with ethanol after quick removal from the furnace. This procedure was repeated by increasing the temperature until reaching a heat treatment of 1050 °C for 4 h in which we have gotten a C₂S phase. Table 2 shows the following heat treatment of the raw materials.

Table 2: Heat treatment of mixed materials

Temperature °C	500	600	700	800	1050
Time	24	24	12	8	4

The heated sample was performed with a Siemens D5000 diffractometer operating with 40kV and 20mA, equipped with a copper anticathode and a secondary monochromatic ($\lambda = 1.5406 \text{ \AA}$). The powder is further characterized by Infrared (FT-IR) which is used to study the functional groups having in the synthesized powder. The FT-IR spectra were obtained on the region of 400-4000 cm⁻¹.

After this, the synthesized C₂S was hydrated with water to solid ratio of W/S = 0.5, and then stored at the room temperature (21 ± 1°C). A mineralogical characterization was performed on hydrated C₂S powder with different curing time. On the other hand, cylindrical paste (diameter 15 mm × height 30 mm) based on C₂S were prepared with W/S = 0.5. Afterwards, specimens were stored in a moisture room at 21 ± 1°C until the days of mechanical determinations (28 and 72 days). The compressive strength was obtained on cylindrical samples with the DY22 machine. The average of three values was obtained.

3 RESULTS AND DISCUSSION

3.1 Characterization of synthesized C₂S

Figure.1 shows the X-ray diffraction patterns of the synthesized powders. The obvious sharp peaks and low backgrounds suggest that the C₂S (S1) powder is highly crystalline. The corresponding reflections have been indexed using the Diffraction Data (ICDD)-Card No. 01-070-0388 (JCPDS) that are assigned to the β-C₂S Phase with small peaks of Wollastonite-2M, corresponding to JCPDS card No. 00-027-0088.

Figure 2 shows the FT-IR spectra of the synthesized powder at 1050°C. The main bands corresponding to the silicate groups are due to the SiO_4^{4-} tetrahedral. According to Puertas et al [27], the absorption bands of different polymorphs of dicalcium silicate are assigned to (ν_1) (symmetric stretching) located around 800-900 cm^{-1} , (ν_3) (antisymmetric stretching) are typically located around 800-1000 cm^{-1} and those of (ν_4) (the triply degenerated out of plane bending) located around 400-500 cm^{-1} .

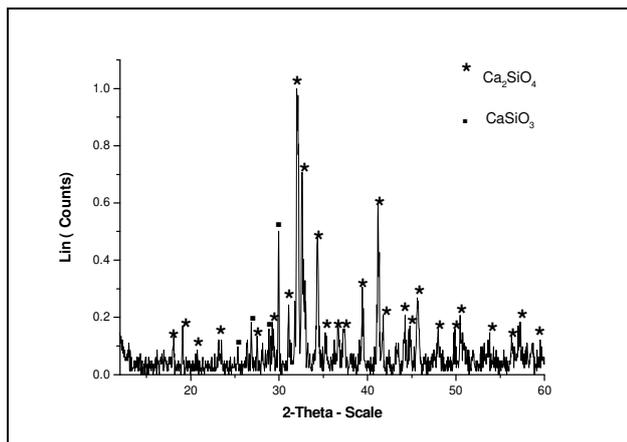


Fig. 1. XRD pattern of C_2S powder synthesized at 1050 °C

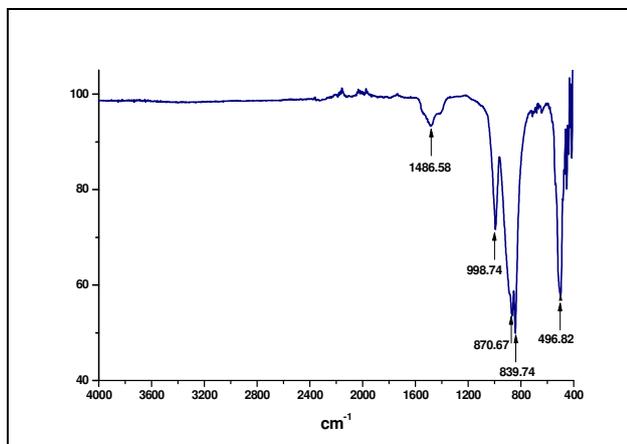


Fig. 2. FTIR spectra of C_2S powder synthesized at 1050 °C

3.2 Mineralogical analysis of hydrated C_2S

Figure.3 shows the evolution of hydrated C_2S powder with different curing time. In general, the intensity of C_2S peaks decreases with the curing time from two days to 72 days. Besides, we notice that the growth of hydrated products showed a variety of C-S-H phases as Clinotobermorite $\text{Ca}_5(\text{Si}_6\text{O}_{17})(\text{H}_2\text{O})_5$, Reinhardbraunsite $\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$ and Suolunite $\text{Ca}_2\text{Si}_2\text{O}_5(\text{OH})_2 \cdot \text{H}_2\text{O}$ after two days of hydration and then

increased with the curing time. The hydration of synthesized C_2S during time shows the formation of the crystallized C-S-H compounds which increase and become more abundant after 72 days. On the other hand, the portlandite appears with a low intensity. This can be explained by the known mechanism of this phase whose the hydration of C_2S is slow and contributes to the creation of long-term resistance [28]. It is reported that the quantity of portlandite produced by C_2S hydration is one third the amount from the C_3S hydration in a pure clinker [29].

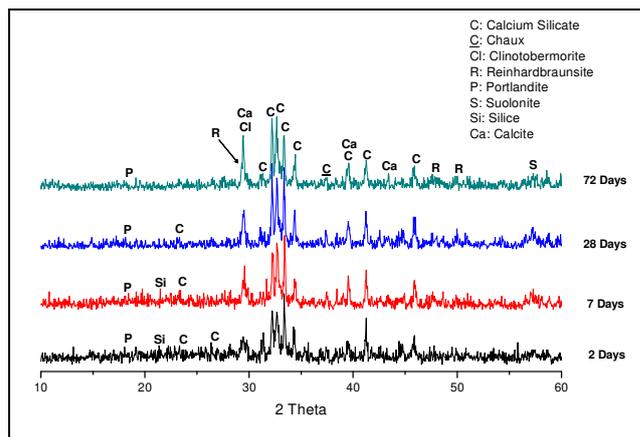


Fig. 3. XRD patterns of hydrated C_2S powder

3.3 Compressive strength

Cylindrical samples are tested with compressive tests after 28 and 72 days of curing. The obtained results are summarized in Table 3.

Table 3: Compressive strength (MPa) at 28 and 72 days

Curing time (days)	28	72
Compressive strength (MPa)	0.625	7.695

The results showed that the compressive strength was improved from 28 to 72 days with a value of 0.625 to 7.695 MPa. It is noted that the strength development for the pure clinker minerals is not similar [30, 31]. The C_2S hydrates sluggish and contributes mostly to later age strength. A complete hydration of 30% at 28 days was reported for C_2S , and 90% completion at one year [29]. This means that the strength increases gradually with time and can reach high final values after one year.

CONCLUSION

This paper demonstrate the feasibility of using mussel shell as a source of calcium carbonate and waste glass as source of silica as starting materials to synthesize

belite rich cement by heat solid state activation. After grinding, the raw materials are mixed and heated up to 1050°C.

The result show that the elaborated clinker is chemically and structurally related to β -Ca₂SiO₄, with a good mechanical strength, which prove that the state reaction method allows the elaboration of a cementitious material by a simple heat treatment at relatively low temperature and low release of CO₂.

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