Cement and Concrete Research 39 (2009) 559–565

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Synthesis of belite cement clinker of high hydraulic reactivity

Larbi Kacimi [a,*], Angélique Simon-Masseron [b], Souria Salem [c], Abdelhamid Ghomari [d], Zoubir Derriche [a]

[a] Laboratoire de Génie des Procédés, Département de Chimie, Université des Sciences et de la Technologie d'Oran, B.P. 1505, El-M'nouar, U.S.T. Oran, Algeria
[b] Laboratoire des Matériaux à Porosité Contrôlée, CNRS UMR 7016, Université de Haute-Alsace, 3, rue Alfred-Werner, F-68093 Mulhouse cedex, France
[c] Département d'Architecture, Faculté de Génie Civile, USTO-Oran, Algeria
[d] Département de Chimie, U.A.I.B., Route de Belahcel, Mostaganem, Algeria

ARTICLE INFO

Article history:
Received 11 September 2006
Accepted 14 February 2009

Keywords:
Belite
Clinker
Reactivity
Mineralizer
Clinkerization

ABSTRACT

This study is concerned with the increase of the cooling rate of belite clinker, by using the water quenching for the chemical stabilization of reactive belite, which improves the hydraulic properties of this clinker. The addition of adequate mineralizers, as NaF and Fe_2O_3, contributes to the improvement of the clinker properties obtained at low burning temperature. X-ray fluorescence spectroscopy, X-ray diffraction analysis and optical microscopy were used to determine the chemical and mineralogical compositions of this clinker. The samples were analyzed by means of a scanning electronic microscope connected with an energy-dispersive X-ray spectrometer to detect the composition of the belite phase and its morphology. Physical and mechanical properties of this clinker cement were determined. The results show that the belite clinker obtained at 1150 °C, with lime saturation factor 0.67, is characterized by a great hydraulic reactivity, similar to that of the ordinary alite clinker. The addition of 2% of NaF and the water quenching improved the chemical, mineralogical and structural properties, while improving the cement hydraulic properties.

1. Introduction

The Portland cement clinker manufacture requires a large amount of heat energy, which is about 3100 MJ/ton clinker [1–3]. This energy is necessary to get the cement raw mixture into a temperature exceeding 1450 °C that allows the alite phase to form, which determines the required cement quality [4]. One approach to the reduction in energy consumption in the cement production is to reduce the lime saturation factor (LSF) of the raw mixture. This leads to an increase in belite amount and a decrease in alite phase content in the clinker [3,5]. The reduction of the $CaCO_3$ content in the raw mixture to produce belite-rich cement decreases the energy demand by 15–20% for a lime saturation factor of 80–85% [6]. But the mechanical strength of belite cements is very low because of the slow hydration of belite phase. This strength can be increased by using a number of techniques. These include the mechanical activation of belite [7], the stabilization of more reactive forms of belite [8] and the use of hydrothermal techniques to produce material with a very high specific area [9].

In recent times, much attention has been given to the development of belite–sulfoaluminate cements, leading to energy saving because they can be synthesized at low temperature (1300–1350 °C). One of such cements containing the main phases C_2S, $C_4A_3S^*$, C_4AF and CS^* was developed and reported by many researchers [10–17]. Nevertheless, so that these cements can be useful, they should be incorporated with other products, to improve their mechanical and chemical strengths [14,18–25]. These products are partially belite cements and their hydraulic reactivity is lower than that of ordinary cement, in particular at early age. Moreover, the high sulfate content in their minerals limits their application fields.

Other researchers studied the use of fly ashes as alternative secondary raw materials for synthesizing reactive low-energy belite cement, by using the hydrothermal treatment as synthesis method [9,26–32]. The dehydration of various phases of fly ash mixture, by controlled heating at 700–800 °C, gave rise to the highly reactive belite phases (α and β-C_2S) [29,30]. The fly ash belite cement showed a better behavior than traditional belite cement, but it cannot substitute the ordinary Portland cement because its hydraulic reactivity remains relatively lower, in addition to its low sulfate resistance which is due to the high alumina content (15–16%) and the absence of portlandite [29,30,32]. The manufacture of this cement, in spite of its low burning temperature, requires high energy due to the high content of water in the raw mixture. Moreover, the use of fly ash of low abundance, as raw materials does not allow its production on industrial scale.

The chemical stabilization of the reactive forms of belite can be carried out by using many elements, of which the stabilizing effect is related to the stabilizer amount and its nature. The presence of various proportions of stabilizers in C_2S lattice leads to the formation of reactive solid solutions [33]. The recent studies show the preference for K_2O, Na_2O, SO_3, B_2O_3, Fe_2O_3, Cr_2O_3 and BaO [8,34–37]. These substances, although they make the belite phase relatively less

* Corresponding author. Tel.: +213 70 50 09 83; fax: +213 41 42 15 81.
E-mail addresses: kacimi20002000@yahoo.fr (L. Kacimi), A.Simon@univ-mulhouse.fr (A. Simon-Masseron), zinaisalem@yahoo.fr (S. Salem), belkey@hotmail.com (A. Ghomari).

0008-8846/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2009.02.004

Table 1
Chemical compositions (wt.%) of raw materials.

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	LOI[a]
Limestone	55.59	0.26	0.11	0.11	0.31	0.01	0.01	0.01	43.55
Marl	13.86	45.70	11.39	4.88	3.79	0.14	2.23	0.37	17.56

[a] LOI: loss on ignition.

reactive at early age, can be more effective at prolonged time by improving the mechanical strength. The relationship amongst the phase composition, cooling rate and alkali content in belite has been studied by other authors [35,36]. The results of these studies show that for the clinker of LSF 75–80%, the stability of α' phase corresponds to both high content of alkalis and fast cooling. The synthesis of reactive belite cement through chemical stabilization was also studied by other researchers, by using stabilizers like NaF, Li_2CO_3, TiO_2, and MnO [38,39] on the one hand, and different raw materials [40,41] on the other. These studies are now at a level of scientific curiosity and no detailed reviews are made here. According to these researches, chemical stabilization did not make it possible to obtain a belite clinker with great hydraulic reactivity at early age, in spite of the high burning temperature (more than 1200 °C).

Our contribution to this extensive investigation lies in the synthesis of complete belite clinker, without trace of alite phase, characterized by high hydraulic reactivity similar to that of alite clinker. This occurs by using mineralizers and structure stabilizers (NaF, Fe_2O_3) in a mixture of natural raw materials (limestone and marl) and fast cooling by quenching water. This reactive belite cement, of low lime saturation factor (LSF lower than 70%), can be obtained at low burning temperatures (less than 1200 °C) by the addition of these mineralizers known by their great chemical activity.

2. Experimentation

2.1. Sample preparation

The development of clinker formation was studied mainly on the basis of free lime contained in the burned samples. It is the most widely used procedure because the calcium oxide, initially formed by dissociation of $CaCO_3$, is gradually consumed by the clinker phases. The formation of the latter will be complete when the free lime rate (CaO) tends to zero.

To obtain a belite clinker, two raw mixtures were prepared with CaO/SiO_2 ratio of 2 and 2.4, in addition to one third of 2.9 to manufacture an alite clinker for the comparison. These mixtures are made of limestone and marl with percentages determined by calculation, according to each ratio. After crushing separately, to 100 μm, the raw materials and homogenization in a mixer for 20 min, the mixture (6 g) was put in a platinum crucible and introduced into a muffle furnace with a heating rate of 30 °C/min. The sample was maintained at the desired burning temperature for 30 min, then cooled quickly by quenching in water and crushed to 100–200 μm. The clinker obtained is analyzed by the traditional method, glycerin–alcohol, at the laboratory of Zahana factory, according to the European standard (NE-2-1-015-1984), in order to determine the residual free lime content.

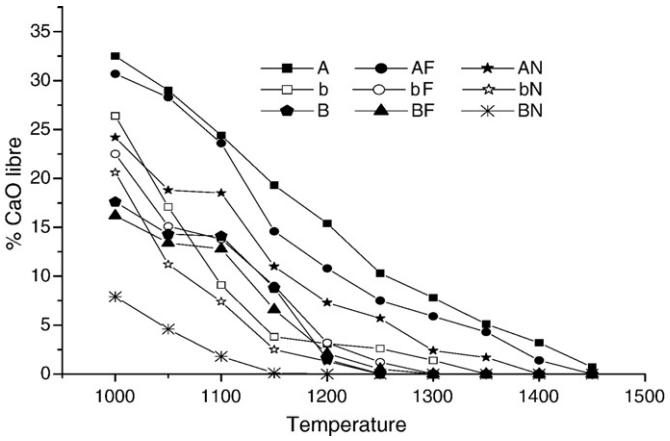

Fig. 1. Burning process of synthesized clinkers.

2.2. Sample testing

The chemical composition of raw materials, mixture and synthesized clinkers were determined by X-ray fluorescence (PW 1404X). The mineralogical composition of the studied clinkers was determined from the optical microscope observations, by using the polished section method, and their crystallized phases were identified by X-ray diffraction with Philips PW 1710 diffractometer equipped with a variable slit opening using Cu Kα radiation. The scanning electron microscope (Philips XL30) was used to study the mineral morphology, in particular the belite phase, and the chemical composition of this phase (C_2S) was determined by scanning electron microprobe analysis on a Casting type (CAMEBAX) electron microscope.

Hydration heat and compressive strength tests of the belite clinker cements have been carried out according to French standards (NF P15-461 and NF P15-451). These cements were prepared at Zahana factory, in accordance with standardized method (NF P15-301) used in the industry.

2.3. Raw materials characterization

The chemical compositions, determined by X-ray fluorescence, of the raw materials (limestone and marl) used to prepare the clinker raw mixtures, are reported in Table 1.

The chemical compositions, determined by X-ray fluorescence, of the clinker raw mixtures with various CaO/SiO_2 ratios, are given in Table 2.

In order to activate the reactions of the clinker mineral formation and consequently, decrease its clinkerization temperature by improving the belite hydraulic reactivity, two mineralizers (NaF and Fe_2O_3) were added to the raw mixtures with percentages of 2 and 4% respectively. The synthesized clinkers are: alite clinker (A), alite clinker with 2% of NaF (AN), alite clinker with 4% of Fe_2O_3 (AF), belite clinker (b), belite clinker with 2% of NaF (bN), belite clinker with 4% of Fe_2O_3 (bF), completely belite clinker (B), completely belite clinker with 2% of NaF (BN) and completely belite clinker with 4% of Fe_2O_3 (BF). The CaO/SiO_2 ratios of the alite, belite and completely belite clinkers are

Table 2
Chemical compositions (wt.%) of different raw mixtures.

Mixture with C/S	% of materials		Chemical composition								
	Limestone	Marl	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	LOI[a]
2.9	68.5	31.5	42.38	14.64	3.68	1.62	1.41	0.05	0.12	0.71	35.32
2.4	63.5	36.5	40.36	16.85	4.23	1.85	1.58	0.06	0.14	0.82	34.06
2.0	58.5	41.5	38.27	19.12	4.79	2.1	1.75	0.06	0,16	0.93	32.76

[a] LOI: loss on ignition.