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

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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.

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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).

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

Material	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	SO$_3$	K$_2$O	Na$_2$O	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$_2$CO$_3$, 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$_2$O$_3$) 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.

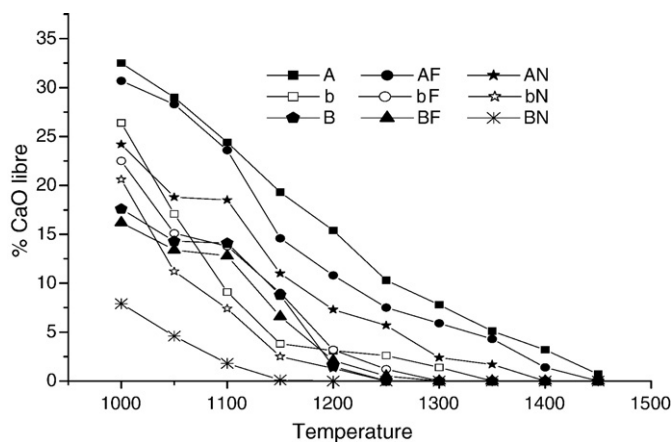## 2. Experimentation

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$_2$S) 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$_2$O$_3$) 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$_2$O$_3$ (AF), belite clinker (b), belite clinker with 2% of NaF (bN), belite clinker with 4% of Fe$_2$O$_3$ (bF), completely belite clinker (B), completely belite clinker with 2% of NaF (BN) and completely belite clinker with 4% of Fe$_2$O$_3$ (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$_2$O$_3$	Fe$_2$O$_3$	MgO	SO$_3$	Na$_2$O	K$_2$O	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.

Table 3
Chemical compositions of the synthesized clinkers.

Clinker	Burning temperature (°C)	Chemical composition								
		CaO_f	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	LSF[a]
A	1450	0.7	65.27	22.68	5.2	2.61	2.26	0.17	1.31	0.94
AF	1450	0	63.15	21.47	5.52	6.10	2.2	0.18	1.15	0.91
AN	1350	0.7	64.36	22.3	5.55	2.60	2.10	0.16	1.24	0.94
b	1350	0	61.18	25.34	6.75	2.62	2.4	0.24	1.18	0.79
bF	1350	0	58.65	24.50	6.23	6.67	2.32	0.14	1.20	0.76
bN	1250	0	60.0	25.16	6.4	2.81	2.35	0.19	1.26	0.79
B	1300	1.0	56.82	28.57	7.03	3.24	2.62	0.20	1.38	0.67
BF	1250	0.5	54.74	27.42	6.78	6.7	2.48	0.19	1.30	0.65
BN	1150	0.8	55.78	27.68	7.1	3.16	2.50	0.21	1.35	0.67

[a] LSF: lime saturation factor.

2.9, 2.4 and 2 respectively. The belite clinkers were cooled by water quenching.

3. Results and discussion

3.1. Study of the clinkerization process

The clinkerization process of clinker mixtures is followed by the decrease of the free lime content in the clinker with the increase of the burning temperature. The results are illustrated in Fig. 1.

The burning temperature of alite clinker (A) is highest (1450 °C). This temperature decreases with the addition of 4% of Fe_2O_3 and advantage with 2% of NaF. The belite clinker is characterized by a lower burning temperature, in particular the clinker rich in belite (B), with $CaO/SiO_2 = 2$, which can be obtained at 1150 °C only by the addition of 2% of NaF (Fig. 1).

Obtaining a belite clinker at low temperature is possible, in particular by the addition of mineralizers, but the clinker quality remains to be examined by comparing it with the ordinary alite clinker. This constitutes the remainder of this study.

3.2. Mineralogical study of the synthesized clinkers

3.2.1. Chemical composition of clinkers

The chemical compositions, determined by X-ray fluorescence, of the synthesized clinkers are reported in Table 3.

The lime saturation factor (LSF) decreases with the reduction in CaO/SiO_2 ratio in the clinker, because of the decrease in CaO content and the increase in SiO_2 content. The addition of 4% of Fe_2O_3 lowers this factor and increases the ferric oxide content in the clinker. The amount of the other components varies consequently, in particular CaO and SiO_2. The effect of NaF addition on the clinker chemical composition is not considerable.

Table 4
Mineralogical compositions of the studied clinkers.

Clinker with C/S	% additive	Burning temperature (°C)	Cooling mode	% Alite	% Belite	% IP
2.9	0	1450	Air-cooling	55	27	18
	4% Fe_2O_3	1450		54	25	21
	2% NaF	1350		55	28	17
2.4	0	1350	Air-cooling	27	56	17
	0	1350	Water quenching	28	56	16
	4% Fe_2O_3	1350		26	55	19
	2% NaF	1250		28	57	15
2	0	1300	Air-cooling	0	76	24
	0	1300	Water quenching	0	78	22
	4% Fe_2O_3	1250		0	77	23
	2% NaF	1150		0	78	22

Table 5
Chemical composition of the belite phase in belite clinkers.

Belite clinker	Cooling mode	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	SO_3	CaO/SiO_2
Ordinary	Air-cooling	63.92	34.28	0.52	0.12	0.16	/	/	1.87
B	Water quenching	63.7	34.02	1.11	0.30	0.55	0.13	0.18	1.87
BF	Water quenching	62.72	33.84	1.53	0.41	1.10	0.19	0.20	1.85
BN	Water quenching	58.44	32.56	2.40	1.31	2.03	2.11	1.14	1.79

3.2.2. Mineralogical compositions of the studied clinkers

Mineralogical analysis of various clinkers, by using the polished section method, determined the mineral content: alite ($3CaO \cdot SiO_2$ or C_3S), belite ($2CaO \cdot SiO_2$ or C_2S) and the interstitial phases (IP) as tricalcium aluminate ($3CaO \cdot Al_2O_3$ or C_3A) and tetracalcic aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ or C_4AF). The results are given in Table 4.

According to the mineralogical analysis of the various synthesized clinkers (Table 4), the mixture of $C/S = 2.9$ gives an alite clinker, while for 2.4 and 2.0, belite clinkers are obtained, the second being completely belite clinker and does not contain any trace of alite.

Mineral content in each clinker do not change with the mineralizer addition or the cooling mode. The mineralizer addition allows decreasing the mineral formation temperature without influencing their amount in the clinker.

The completely belite clinker, obtained at low temperature (1150–1250 °C), is deprived of alite and rich in belite. This is owing to the weak lime saturation factor (FSC) which does not exceed 0.67 (Table 3). The addition of NaF leads to decrease the clinker burning temperature to 1150 °C.

3.2.3. Chemical composition of the belite phase in belite clinkers

To study the effect of the mineralizer and the cooling mode (water quenching) on the belite activity, and consequently the belite clinker obtained at low burning temperature (1150–1250 °C), the chemical composition of this phase has been determined by EDAX coupled with scanning electron microscope. The results are reported in Table 5.

The CaO/SiO_2 ratio in belite decreases by the addition of the mineralizer; the smallest ratio is recorded by the addition of NaF. This mineralizer decreases strongly the CaO content and slightly the SiO_2 content, which explains the reduction of this ratio in the belite phase. Moreover Al_2O_3, Fe_2O_3, Na_2O, MgO and SO_3 contents increase in NaF–clinker belite. This is explained by the Ca substitution by Mg, Na, S and Si by Al and Fe [18,33,42,43]. The insertion of these elements in the
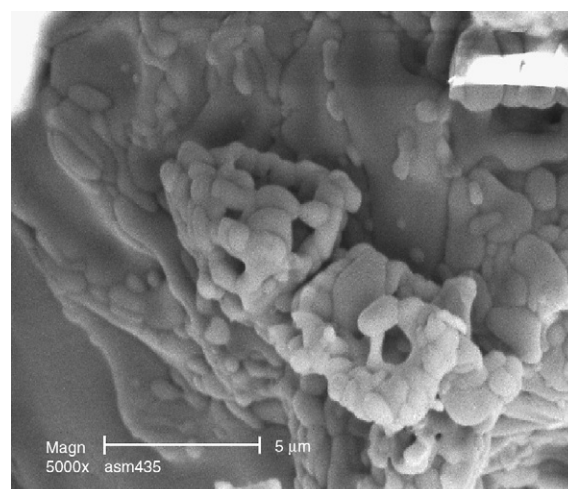
Fig. 2. Ordinary belite clinker morphology (air-cooling).

Fig. 3. Belite clinker morphology (cooling by water quenching).
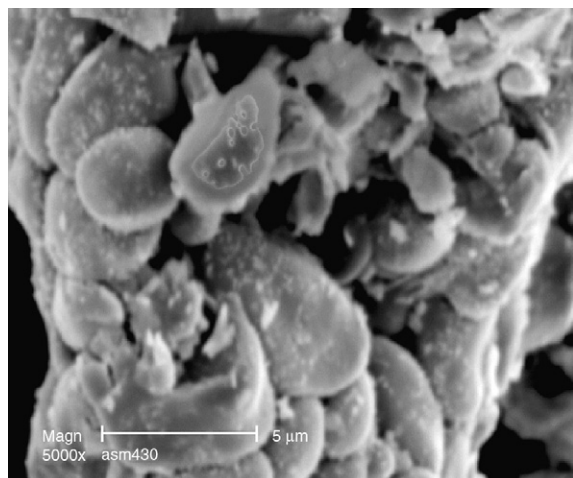
belite structure is also probable [25,33,43], which is deduced from the difference between the elements content in belite of ordinary clinker and that of quenching cooling clinker (B). The substitution of Ca^{2+} or Si^{4+} ions, as well as the inclusion of foreign ions in the crystal lattice, leads to a rise in the disorder state of lattice and consequently, in a rise in the entropy of system which supports the maintenance of high temperature forms of belite phase (α, α' and β) at ambient temperature [33,43]. The clinker air cooled contains less foreign elements which can be preserved in the structure of the belite cooled quickly by quenching with water [25,33,43].

The effect of Fe_2O_3 addition on the belite chemical composition is lower than that of NaF.

3.3. Structural and morphological properties of belite clinkers

Belite clinkers cooled by water quenching, of lime saturation factor 0.67 (C/S = 2.0), with or without mineralizer, are retained to study their morphological and structural properties. The ordinary belite clinker is used for comparison.

3.3.1. Characterization of belite clinkers by scanning electron microscopy

The belite morphology of various belite clinkers was examined by scanning electron microscopy (Figs. 2–5).

The ordinary belite clinker, air cooled, presents a bad form of belite phase (non regular form of crystals, without clear separation from the liquid phase) with small crystal size (Fig. 2). Fast cooling, by
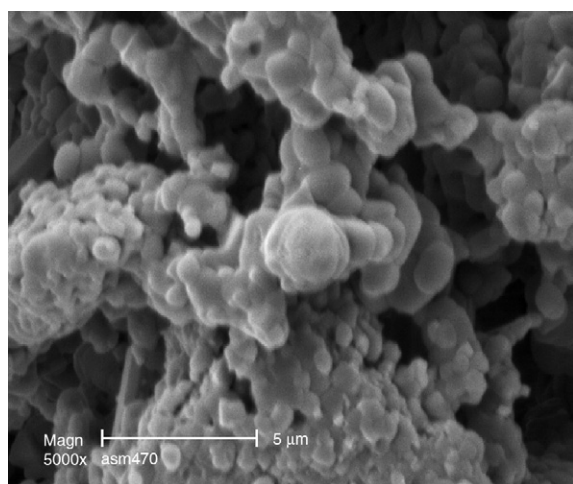
quenching water, of this clinker allows to improve the belite morphology and to increase its crystal size (Fig. 3). The use of Fe_2O_3 as mineralizer in the clinker synthesis plays a negative role on the belite formation (incomplete formation of the belite phase), in spite of the fast cooling by quenching water. This clinker is characterized by small crystal size with bad form (Fig. 4). The addition of NaF in the belite clinker mixture improves the belite formation, which has a regular morphology with large crystal size (Fig. 5). This morphology is improved by the quenching with water, which preserves the belite structure of high temperature.

3.3.2. Characterization by X-ray diffraction

The XRD patterns (Figs. 6–9) do not present any alite characteristic peak, which confirms the belite character of these clinkers. Thus, the free CaO absence testifies to the clinkerization at low burning temperatures (<1250 °C) without decomposition of the calcium silicate phases during cooling.

The XRD patterns of belite clinkers cooled by water quenching (Figs. 7–9), with and without mineralizer, show that the belite phase is well crystallized in beta form (β-C_2S) which has a strong hydraulic reactivity. This is proven by the presence of much intense peaks of beta belite phase. The presence of C_2SA is also shown, which is a belite solid solution, characterized by its great hydraulic reactivity because of its disturbed crystalline structure of low symmetry [42]. The NaF-clinker (Fig. 9) contains a new belite variety, noted down as β^*-C_2S ($d_{hkl} = 2.6473$). This phase, which appears in clinkers obtained by very fast cooling, is characterized by a higher chemical activity similar to α'_H [34,44].

C_3A and C_4AF are not present in the belite clinkers, in spite of the high alumina content in their mixtures and the iron oxide presence in the Fe_2O_3-clinker. This is related to the fast cooling starting from the melting point of these phases, which prevents their crystallization [25,31].

The main interreticular distances of belite crystal lattice in the belite clinkers are reported in Table 6.

The results show that the interreticular distances of the belite phase in the quenching clinkers are larger than that in the ordinary belite clinker (Table 6). This is due to the incorporation of foreign elements, fixed in its structure by water quenching (Table 5), which increases the crystal cell parameters of the belite phase and improves its chemical activity [25,45,46].

The interreticular distances in NaF–clinker belite are smaller than that of the other quenching clinkers. This is owing to Ca^{2+} substitution, of larger diameter (1.06 A°), by smaller diameter ions Mg^{2+} (0.78 A°) and Na^+ (0.98 A°), which reduces the crystal cell parameters of the belite phase and, consequently, increases the

Fig. 4. Fe_2O_3–belite clinker morphology (cooling by water quenching).
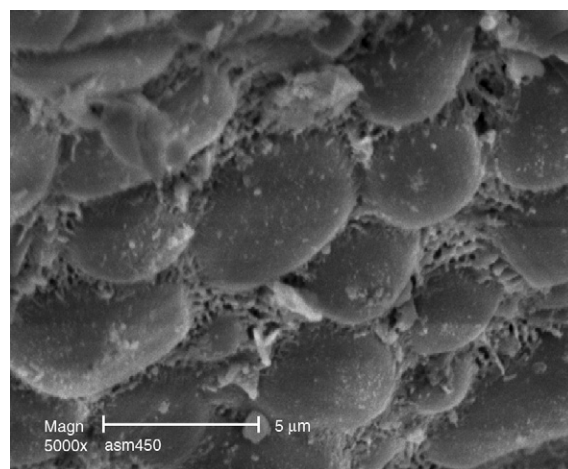
Fig. 5. NaF–belite clinker morphology (cooling by water quenching).
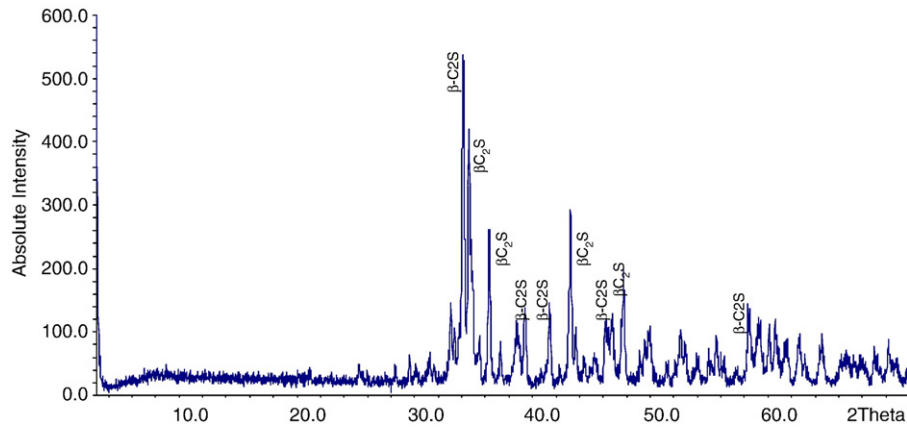
Fig. 6. X-ray pattern of belite clinker cooling with air.
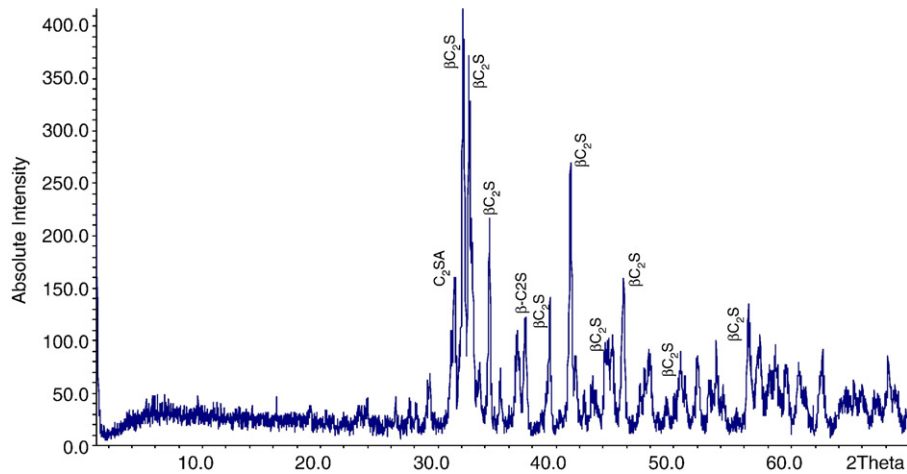
Fig. 7. X-ray pattern of belite clinker cooling by water quenching.

stability of the belite reactive structure during the cooling process [25]. The important number of β-belite peaks confirms its adequate crystallization, which could improve its hydraulic properties [25,47].

3.4. Hydraulic properties of studied clinkers

To determine the physical and mechanical properties of the clinker cements, great amounts of clinkers are synthesized to carry out the hydration and hardening tests. The cement, composed of 95% of syn-thesized clinker and 15% of natural gypsum, was crushed to a specific area of 3600 cm^2/g and mixed for 30 min, according to the standard (NF P15-301). The alite clinker was taken as a control sample in this study.

3.4.1. Hydration heat

The hydration heat is one of the most important properties for practical use and the cement activity evaluation. C_3S and C_3A hy-dration are characterized by high heat release in comparison with C_2S

Fig. 8. X-ray pattern of Fe$_2$O$_3$–belite clinker cooling by water quenching.

Fig. 9. X-ray pattern of NaF–belite clinker cooling by water quenching.

and C_4AF. In this study, this property was determined by the dissolution method, according to the French standard NF P15-461 [48]. The results are reported in Table 7.

The hydration heat of NaF–belite clinker is very appreciable; it is similar to that of alite clinker (Table 7). This is due to the very quick cooling mode (water quenching), which allows to stabilize the reactive belite phases (β^*-C_2S, β-C_2S and C_2SA), known by their high hydraulic reactivity [34,42,44]. Thus the disturbed belite structure, by the presence of impurities in its crystal lattices (Table 5), leads to improve its hydraulic activity, hence the high heat release in comparison with the ordinary belite [18,25,42,45,46]. The NaF addition leads to stabilize the reactive structure of belite [38,39,49].

The low hydration heat value at an early age (2 days) is due to the absence of crystallized C_3A in this clinker (Fig. 9).

3.4.2. Compressive strength

Test specimens of mortars (40 mm × 40 mm × 160 mm) with water/cement ratio of 0.5 and an aggregate/cement ratio of 3, according to standard EN 196-1 [50], were produced from cements of studied clinkers. The results of compressive strengths are given in Table 8.

The compressive strength of belite clinker cement is lower than that of control cement (alite clinker cement) at early ages. After

7 days, the strength evolution speed of water-quenching clinker cements increases, particularly the NaF-clinker which presents a value at 28 days similar to that of alite clinker (Table 8). This is owing to the disturbed belite structure, its lower crystalline symmetry, the presence of impurities in its structure, its large crystal sizes, the crystallization and stabilization of its reactive phases: β-C_2S, β^*-C_2S and C_2SA [25,34,42,44]. These characteristics lead to the improvement of the hydraulic reactivity of this belite clinker obtained at low burning temperature (1150 °C).

4. Conclusion

The industrial manufacture of belite clinker at 1150–1250 °C could be realized by the addition of 2% of NaF or 4% of Fe_2O_3, but the obtained clinker has no adequate mechanical performances. The quick cooling, using the water quenching, leads to improve the hydraulic properties by the stabilization of the reactive belite structure (β-C_2S and C_2SA) at ambient temperature.

The NaF addition as mineralizer improves the formation and stabilization of the reactive belite at 1150 °C only. NaF-clinker contains, in addition to the habitual phases, a new variety β^*-C_2S. This variety, generating a great number of inclusions by substitution or insertion, is characterized by disturbed crystal structure of low symmetry, which improves its hydraulic reactivity. Thus, NaF contributes to the stabilization of this belite phase during cooling by water quenching, which leads to the improvement of cement quality.

Physical and mechanical tests carried out on the cement mortars of NaF–belite clinker show that the hydration heat and compressive strength evolve quickly to reach values, at 28 days, similar to those of alite clinker.

Obtaining a belite clinker, characterized by a great hydraulic reactivity similar to that of alite clinker, is possible by burning a raw mixture containing 2% of NaF at 1150 °C and cooling quickly by water quenching.

Table 6
Main interreticular distances of belite crystal lattice in belite clinkers.

Belite clinker	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7
Ordinary	2.8511	2.7807	2.7416	/	/	2.6003	2.1812
B by water quenching	2.8607	2.7934	2.7544	2.7277	/	2.6180	2.1937
BF by water quenching	2.8558	2.7851	2.7473	/	/	2.6070	2.1900
BN by water quenching	2.8538	2.7836	2.7456	2.7195	2.6473[a]	2.6043	2.1873

[a] β^*-C_2S.

Table 7
Hydration heat of studied clinkers.

Clinker	Hydration heat (cal/g)		
	3 days	7 days	28 days
Alite clinker	71	83	92
Ordinary belite clinker	15	25	40
B by water quenching	30	53	71
BF by water quenching	18	33	48
BN by water quenching	63	79	87

Table 8
Compressive strength of studied clinker cements.

Cement of	Compressive strength (MPa)		
	2 days	7 days	28 days
Alite clinker	16.92	33.25	43.18
Ordinary belite clinker	1.43	4.17	15.97
B by water quenching	6.26	16.57	34.78
BF by water quenching	1.63	7.86	16.43
BN by water quenching	8.63	27.89	41.26

The production of this clinker leads to a decrease in the burning temperature by about 300 °C, with increasing the production efficiency and decreasing the fuel consumption. This reactive belite clinker, of low lime saturation factor (0.67 instead of 0.94), allows to decrease the limestone amount from 68.5 to 58.5. This decrease of about 10% of $CaCO_3$ in the raw mixture allows to:

– preserve the limestone field, particularly in countries poor on this material;
– substitute high $CaCO_3$ content by low $CaCO_3$ content limestone;
– reduce the energy consumption by decreasing the decarbonation heat;
– reduce the CO_2 and NO_x emissions.

The substitution of alite clinker by reactive belite clinker leads to the improvement of the long-term strength, by decreasing the Ca$(OH)_2$ amount formed during the cement hydration, and consequently increases the concrete durability.

Acknowledgments

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