37. Elaboration of belite cement with low environment impact.

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Abstract The objective of this work is to valorise the discharges (rejections) of the Boukhedra iron ore mine (east of Algeria) as raw materials for the elaboration of the cement raw. The study concerns the development of different types of low impact environmental belite cements whose raw are exclusively mine rejections. The use of a low CaO / SiO2 ratio and the combination of quick cooling of clinker with adequate NaF and LiF mineralization in association with $CaSO_4$, has led to the production of belite cement with high hydraulic reactivity comparable to that of ordinary Portland cements. The used mineralization plays also a positive role in improving performance in terms of firing of the raw, by lowering the clinker process temperatures of these cements, thus, enabling an additional gain in terms of environmental impact and energy consumption. This mineralization and the low LSF of these cements allows obtaining them at low burning temperatures 1150 °C and 1100 °C for the cement with 2%LiF. This is 350 °C lower to ordinary Portland cement. The addition of $CaSO_4$, NaF and LiF to the clinkers makes the improvement of its clinkering possible. The effect of LiF seems to be the most significant followed by NaF and finally, $CaSO_4$

Keywords Belite Cement, mineralizer, Environment, low energy, evaluation of rejection

1 Introduction

The cement industry is one of the major energy consumers and an important producer of CO_2 in the world. The cement subsector consumes approximately 12-15% of the total industrial energy use; it releases CO_2 into the atmosphere as a result of fossil fuels burning and this to produce the needed energy for the cement manufacturing process. The cement industry contributes about 7% of the total worldwide CO_2 emissions (Ali et al 2011). This study focuses on the development and characterization of low impact environmental belite cement with mechanical performances, compared to that of the alite cements (Portland). The cements produced are derived from very low lime saturation factor (LSF), with the aim of minimising the required firing temperature for the correct crystallisation of these cements (Bouzidi 2015). It is possible to considerably reduce CO_2 emissions during the clinker process, thanks to the low lime saturation factor of the belite cement sand, since most of these emissions occur during the decarbonisation of $CaCO_3$ and during the firing of the clinkers (Barecelo et al. 2013). In addition to the environmental impact reduction of these cements, reducing the lime saturation factor allows significant energy savings while feeding the furnaces. The low level of lime, necessary for the preparation of the raw belite cement, allows the incorporation of several discharges from the industry in the composition of their raw (Guerrero et al. 1999, Goñi et al. 2000).

Completely belite cements, without trace of alite, can be obtained with a CaO / SiO_2 ratio equal to 2 and maximising the benefits, derived from the production of this type of cement, is made possible. Thus, the belite becomes the major component of these cements, whereas it usually represents only 15 to 20% of the composition of the Portland clinkers (Hewlett 2003). The belite is characterized by a slow hydration which limits the mechanical performances, especially at young age. Although these performances become more consistent over the longer term, they make the belite cements incompatible with use, as a replacement for Portland cements (El-Didamony et al. 2012, Chatterjee 1996).

Numerous methods exist to try to enhance the mechanical performance of these cements, by improving the hydraulic reactivity of the belite phases which compose them, (Popescu et al. 2003, Kacimi et al. 2010, Rajczyc et al. 1992, Gies and Knöfel 1986, Mathur et al. 1992, 1987, Singh et al. 1992, Majling et al. 1990).

In this study four different mineralizations (2% NaF, 2% LiF, 1% NaF + 1% $CaSO_4$, 1% LiF + 1% $CaSO_4$), in combination with quick cooling were used to try to stabilise the most reactive forms (β, α'L, α'H and α) (Chatterjee 1996, Zhang et al. 2012) and to optimise their hydraulic reactivity by improving the morphology of the belite crystals (Kacimi et al. 2009). The used mineralisation plays also a positive role in improving performance in terms of firing of the raw, by lowering the clinker process temperatures of these cements, thus, enabling an additional gain in terms of environmental impact and energy consumption (Kacimi et al. 2006, 2006).

2 Methods

2.1. Raw materials

The raw materials used to carry out this study, both for the preparation of the raw of the Belite cements and for those of the cements used as reference, are derived exclusively from the iron mine of BOUKHADRA (East of Algeria). Large quantities of these materials are released during operation of the mine. The accumulation of these materials creates stability problems that jeopardize the sustainability of the operation of the mine. The used materials were selected on the basis of their chemical and mineralogical compositions to use them as raw materials for the production of belite cement.

2.2. Operating mode

The different stages of the manufacturing process of the synthesized cements are presented in Fig. 1
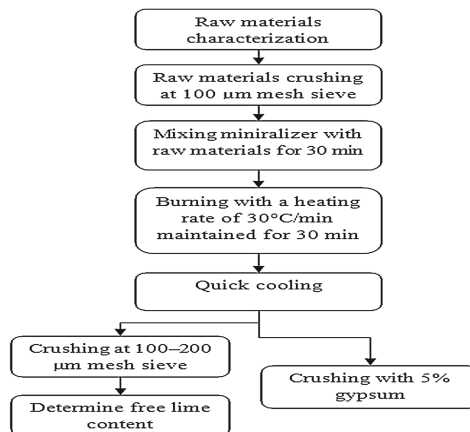

Fig.1 Processing stages of the synthesized clinkers

Two types of mixtures were prepared thanks to the combination of the marl and the limestone of Boukhadra mine. The first mixture has a ratio $CaO / SiO_2 = 2.9$, for the preparation of alite cement (Portland), which will be used as reference. The second mixture with a CaO / SiO_2 ratio $= 2$ will give belite cements. The latter mixture will receive the various mineralizations: NaF, LiF and their association with $CaSO_4$ known to favour the formation of the belite (Gies and Knöfel 1986). The use of these additions will allow the preparation of belite cements, the performances that are discussed in this study. Two belite cements, one quickly cooled and the other one slowly cooled, are also produced to aid in understanding the effects of quick cooling on the characteristics of belite cements. Table 1

presents a summary of the various cements prepared during this study, as well as the type of mixture and the cooling method used for their preparation.

Table 1 The different produced clinkers

Designation	Type	CaO/SiO₂	Mode of cooling	Mineralizers
A	Alite	2.9	Quick cooling	/
B	Belite	2	Slow cooling	/
B'	Belite	2	Quick cooling	/
B1	Beilte	2	Quick cooling	2% NaF
B2	Beilte	2	Quick cooling	2% LiF
B3	Belite	2	Quick cooling	1% NaF +1% CaSO₄
B4	Belite	2	Quick cooling	1% LiF +1% CaSO₄

The chemical composition of the various prepared mixtures is presented in Table 2

Table 2 Chemical composition of the different produced raw mixtures

Ratio Cao/SiO₂	% of raw materials		Chemical composition of the different mixtures (%wt)								
	Marl	Limestone	CaO	SiO₂	Al₂O₃	Fe₂O₃	MgO	SO₃	Na₂O	K₂O	LOI*
2,00	23,91	76,09	40,41	20,20	4,34	1,70	0,21	0,28	0,04	0,56	32,26
2,90	16,62	83,38	44,16	15,23	3,28	1,44	0,20	0,30	0,04	0,39	34,96

*LOI = Loss on ignition

3 Results and Discussion

3.1 **Study of the clinkering by determination of free lime**

Fig.2 shows the percentage of free lime contained in the cement samples synthesized at different firing temperatures. Free lime contained in a clinker sample is usually considered as a good indicator of the quality and completion of its clinkering (Chaterjee 1996, Zhang et al. 2012).
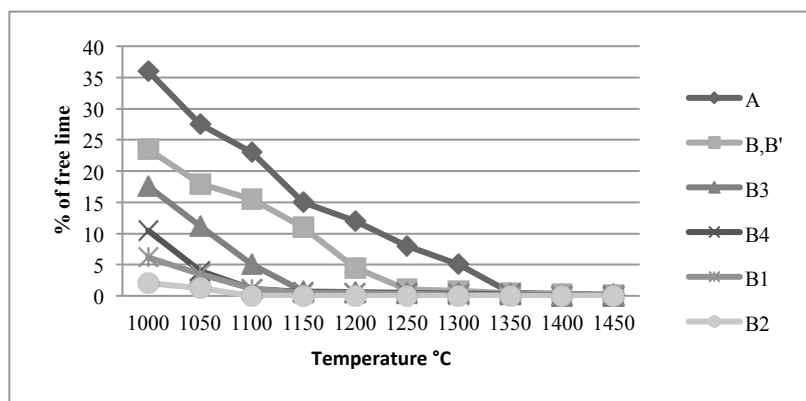
Fig.2 Percentage of free lime contained in the synthesized clinkers

With a clinkering temperature of 1450 °C, the alite cement (A) has the highest firing temperature of all the synthesized clinkers. By reducing the CaO / SiO$_2$ ratio from 2.9 to 2, the clinkering temperature decreases to 1300 °C for ordinary belite cements without mineralisation (B, B'). The use of additives in the raw of the belite clinkers reduces more the clinkering temperature to reach 1150 °C. The lowest clinkering temperature (1100 °C) is recorded for clinker B2 with 2% LiF as an addition.

3.2 Chemical composition of produced clinker

The chemical composition of the synthesized clinkers is shown in Table 3.

Table 3 Chemical composition of the various synthesised clinker

Clinke	Burning	CaO	SiO$_2$	Al$_2$O	Fe$_2$O	Mg	SO	Na$_2$	K$_2$	LOI
A	1450	64,2	23,2	5,27	5,15	0,54	0,2	0,09	0,3	0,93
B	1300	61,6	26,6	7,38	2,41	0,52	0,3	0,06	0,3	0,79
B'	1300	61,4	26,8	7,37	2,44	0,43	0,3	0,07	0,3	0,76
B1	1150	60,0	26,7	7,18	2,43	0,45	0,3	1,21	0,3	1,21
B2	1100	59,6	28,3	7,46	2,44	0,70	0,3	0,06	0,3	0,67
B3	1150	60,1	27,1	6,83	2,40	0,41	1,1	0,74	0,3	0,88
B4	1150	59,5	27,5	7,25	2,39	0,75	1,0	0,08	0,3	1,11

*LOI = Loss on ignition

The composition of the raw strongly influenced the composition of the corresponding clinkers. Thus, the low CaO / SiO$_2$ ratio in the raw of belite cement clinkers, compared to the raw material of the alite clinker, gave result to a decrease in CaO levels and an increase in the SiO$_2$ content in the belite clinkers. The use of CaSO$_4$ as an additive in the growths of clinkers B3 and B4 led to an increase in the SO$_3$ content in these clinkers. Similarly for the Na2O content that increased in clinkers where NaF was used as an addition.

3.2 Mineralogical composition of produced clinker

3.2.1 Polished section method

Table 4 Mineralogical composition of the produced clinkers

Clinker	% Alite	% Belite	% Interstitial phases
A	56	25	19
B	0	76	24
B'	0	77	23
B1	0	76	24
B2	0	77	23
B3	0	77	23
B4	0	76	24

Clinker obtained from the raw with a CaO/SiO_2 ratio = 2.9 (Clinker A) is composed of alite (C_3S) belite (C_2S) and interstitial phases, such as aluminate (C_3A) and Tetracalcium aluminoferrite (C_4AF). The clinkers obtained from the raw with a CaO / SiO2 = 2 ratio (belite clinker) are composed of belite (C_2S) and interstitial phases, without any trace of alite (Table 4).

3.2.2 Mineralogical analysis by X-ray diffraction

 The X-ray diffraction spectra of the synthesized belite clinkers are shown in Fig.3. Several high-intensity peaks of the β-C_2S and $\alpha'L$-C_2S phases of belite can be distinguished in these spectra, phases that are known for their high hydraulic reactivity (Quillin 2001). This adequate crystallisation of the belite phases should improve their hydraulic reactivity (Kacimi et al. 2009, Quillin 2001, Emanuelson et al. 2003). The clinkers B3 and B4 contain the new form of β^*-C_2S belite, characteristic of a very rapid cooling. This new form of belite is characterized by a high hydraulic reactivity, comparable to that of the $\alpha'H$-C_2S phase [Chaterjee 1996, Kacimi et al. 2009, Von and Lamp 1989). The DRX spectra also show the absence of characteristic peaks of the free lime (CaO) and the γ-C_2S belite phase. The absence of free lime confirms the good clinkering of the cements, at the chosen temperature for each one. The absence of γ-C_2S is due to rapid cooling that prevented the polymorphic transformation of C_2S: $\beta \rightarrow \gamma$ from occurring [Kacimi et al. 2009, Quillin 2001, Raina and Anakiraman1998, Ichikawa and Kanaya 1997).

The C index defined by G. Goswami and al. 1991, as an indicator of the clinkering conditions and the degree of crystallisation of the clinker phases, is calculated for synthesized belite clinkers. The results obtained are shown in Table 5. The clinker B has the highest C value among the synthesized clinkers, reflecting a lower degree of crystallisation of the belite phases. Quick cooling plays a positive role in improving the degree of crystallisation of belite; the clinker B' which has been quickly cooled, has a lower C-value than the clinker B which has been cooled slowly. The use of the various mineralizations has played a positive role in the improvement of the belite clinkers crystallisation; clinkers B1, B2, B3 and B4 have very low C indexes (less than 1.1 and very close to 1). This is the indicator of perfect crystallisation.

Table 5 C index values of the synthesized clinkers

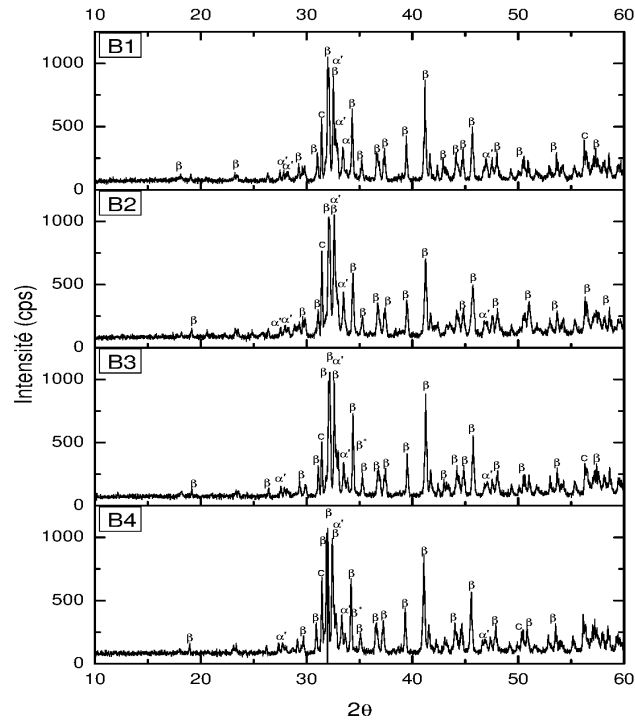| Clinker	C index
B	1.20482458
B'	1.15324129
B1	1.04026038
B2	1.00343623
B3	1.08483261
B4	1.09323034

Fig.3 XRD pattern of the produced clinkers (β: β-C$_2$S; α': α'L-C$_2$S; C: C$_2$AS)

3.3 Characterization of the Clinkers by SEM coupled to EDX

The morphology of the belite phase and its chemical composition in synthesized belite clinkers, were studied using a scanning electron microscope coupled to EDX. The obtained results are shown in Table 6 and Fig.4.

Tableau 6 Chemical composition of the Belite phase in the different produced clinkers

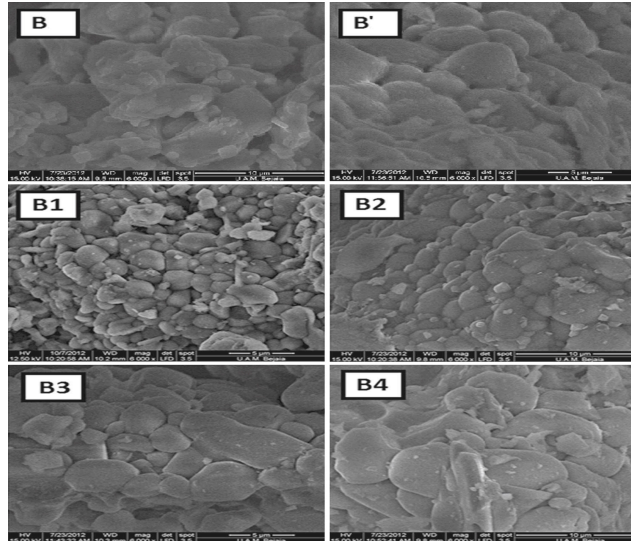| Belite	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	SO$_3$	Na$_2$O	K$_2$O	Li
B	63.47	33.28	1.55	0.78	0.06	0.47	0.08	0.31	/
B'	62.97	33.41	1.67	0.96	0.09	0.42	0.12	0.36	/
B1	60.43	32.04	2.52	1.55	0.38	0.63	1.79	0.66	/
B2	61.25	32.13	2.56	1.55	0.59	0.61	0.32	0.69	0.30
B3	59.79	31.96	2.63	1.56	0.35	1.72	1.27	0.72	/
B4	60.34	31.89	2.68	1.57	0.63	1.63	0.36	0.71	0.19

/ : Not detected

Fig.4 Belite morphology of the synthesized clinkers

The belite morphology phase in the clinker B is irregular, without any clear distinction between the liquid and solid phases. For the clinker B', the morphology is more regular; the quick cooling has improved the morphology phase by allowing preservation of the high temperatures structure and thanks to the inclusion of foreign elements in its structure (Kacimi and al. 2009). The clinkers B1, B2, B3 and B4 are characterized by regular round shaped crystals of belite, clearly distinct from the liquid phase. This is due to additions that have improved the crystallisation of the belite and decreased the clinkering temperature (Bouzidi 2015). The round shapes of the belit crystals have a small size which does not exceed 10 μm. These characteristics should improve the hydraulic reactivity of these belite phases (Kacimi and al. 2010). EDX analysis show that the belite does not contain fluoride in its composition, even in cases where fluoride has been used as an additive. These results can be explained by the strong attraction of F- for interstitial oxygen, the belite possessing oxygen only in the Si-O bond; makes it difficult to include F-ions in its structure (Tran and al. 2009).

3.4 Determination of compressive strength

The compressive strengths of the synthesized cements are presented in fig.5. The tests were carried out in accordance with European standards EN 196-1 (2005), of the mortar specimens (40 mm × 40 mm × 160 mm) with a water/Cement ratio = 0.5.
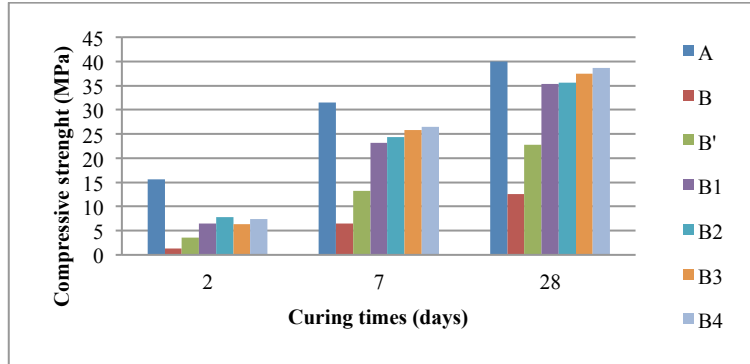
Fig.5 Compressive strength of the produced cements

The slowly cooled cement (B) has the lowest strength at all ages, of all tested cements. The higher strength, of the quick cooled cement (B'), is an indicator that this mode of cooling improves the hydraulic reactivity of this type of cement. The use of additives improves considerably this reactivity, in view of the mechanical strengths obtained for these cements and which have the highest early strength of all the tested belite cements. The cements with LiF as additive (B2, B4), presented a greater strength at young age compared to other belite cements, due to the presence of lithium which is known as an accelerator for setting and hardening cements (Gu an Beaudoin 1993, Matusinovic and Curlin 1993). However, the compressive strengths of belite cements remain lower than that of the alite cement.

3.5 Determination of the heat of hydration

The heat hydration of the various synthesized cements is presented in Fig.6.
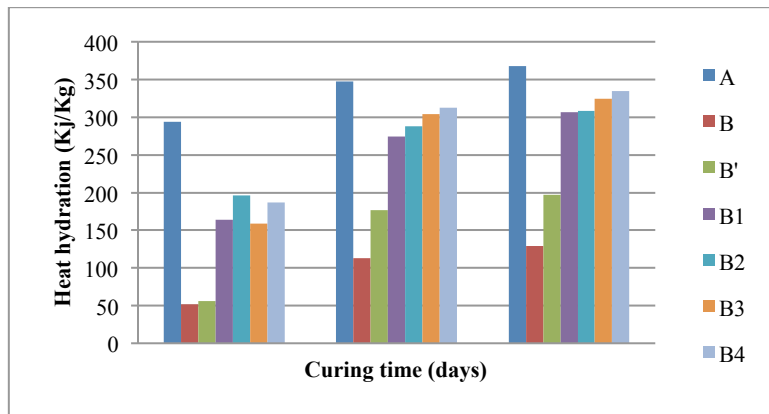

Fig.6 Heat hydration of the produced cements

The tests were carried out in accordance with the French standards NF P 15-461 (1984) at 2, 7 and 28 days. The results of the heat hydration tests, carried out on the synthesized cements, are in agreement with the results of the compressive strength tests. The slowly cooled cement (B) presented the lowest results at all ages. The cement (B'), where no addition was used and which was quickly cooled, obtained higher results than (B). Nevertheless, these results remain low compared to cement with mineralisation (B1, B2, B3, B4). The latter, in turn, have weaker results than the alite cement (A). These differences in the heat hydration, between the belite cements (B1, B2, B3, B4) and the alite cement decrease with time, starting from the 7th day.

3 Conclusions

The production of belite cement with high hydraulic reactivity, comparable to that of alite cement, is possible by the association of quick cooling, an adequate mineralization and its association with $CaSO_4$. This mineralisation and the low LSF of these cements allows obtaining them at low burning temperatures 1150 °C and 1100 °C for the cement with 2%LiF. This is 350 °C lower to ordinary Portland cement. The addition of $CaSO_4$, NaF and LiF to the clinkers makes the improvement of its clinkering possible. The effect of LiF seems to be the most significant followed by NaF and finally, $CaSO_4$. With a low CaO/SiO_2 ratio of these belite cements and the combination of additions, this clinkering temperature was lowered about 300 to 350 °C compared to the alite cement, thus considerably reducing the energy consumption and greenhouse gas emissions during manufacturing.

Belite cements have been obtained at temperatures ranging from 1100 to 1150 °C with characteristics that meet the requirements of French standard NF P 15-301 (1994) for cements Portland class 32.5.

The low CaO/SiO_2 ratio of these belite cements, their low clinkering temperature and their high hydraulic reactivity make these cements ecological. In addition to preserving limestone deposits, they also save energy and significantly reduce greenhouse gas emissions. These qualities are likely to contribute to reducing the environmental impact in cementitious production.

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