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C_3A polymorphs related to industrial clinker alkalies content

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Abstract

The C_3A crystalline structure in Portland clinkers is basically determined by the incorporation of alkali-oxides and is also function of the cooling rate, both actions have a combined effect on the changes in reactivity of clinkers. Industrial clinkers have been found to contain cubic or orthorhombic forms of aluminate, alone or in combination; the monoclinic modification has not been observed. The aim of this research is to evaluate the different polymorphs of C_3A present on industrial clinkers produced with different amounts of sodium and potassium oxide in the raw mix. The optical microscopy was useful to distinguish the different kinds of C_3A based on their crystal features. The SEM (scanning electron microscopy)-EDS analysis was used on the chemical characterization of the C_3A. An accurate quantification of the phases, including proportions of C_3A polymorphs, could be achieved using X-ray diffraction with Rietveld refinement. The quantification was confirmed by chemical selective dissolution applied in samples for which the refinement indicated almost only one type of C_3A polymorph. Finally, correlations between alkalies contents, Na_2O and CaO for white cement clinker and K_2O and CaO for grey clinker suggest partial substitution of CaO and incorporation of Na_2O or K_2O in the vacant site of the cubic C_3A leading to the formation of the orthorhombic phase.

Keywords: Clinker; Alkalis; X-ray diffraction; Petrography; SEM

1. Introduction

This paper shows the relationship of raw mixes with different amounts of potassium and sodium oxides and the C_3A crystals formed on different industrial clinkers from a white cement and a grey cement factory. The C_3A content and crystal modifications of various commercial clinkers were studied using X-ray diffraction with Rietveld method for phases quantification, with some support of microscopy methods.

White Portland clinker is composed of three basic oxides (CaO, Al_2O_3 and SiO_2) and minor components such as Na_2O, K_2O, SO_3, etc. The main and obvious difference with respect to grey cement is colour, which represents a decisive criterion to evaluate the quality. To achieve the required whiteness level, the content of colouring elements (Fe, Mn, Cr, Ti, etc.) in raw mixtures must be strictly controlled.

Grey clinker is mainly composed by alite (40% to 70% in weight), which is a substituted impure form of tricalcium silicate, C_3S ($3CaO.SiO_2$, or Ca_3SiO_5). Other phases present are belite (C_2S or $2CaO.SiO_5$) in weight proportions of 10% to 20%, aluminate (C_3A or $3CaO.Al_2O_3$) with 5% to 10% and ferrite (C_4AF or $4CaO.Al_2O_3.Fe_2O_3$) around 10% in weight. Common minor phases are free lime (CaO) and periclase (MgO). White clinker is mainly composed by alite, belite, aluminate and minor phases. The Table 1 shows the typical chemical compositions of phases in Portland cement clinkers [1].

Pure C^3A does not exhibit polymorphism. It is cubic, with $a = 1.5263$ nm, space group Pa3a; the structure is built from Ca^{2+} ions and rings of six AlO_4 tetrahedra [2]. It can incorporate Na^+ by substitution of Ca^{2+} with inclusion of a second Na^+ ion in an otherwise vacant site, thus, giving solid solutions of general formula $Na_{2x}Ca_{3-x}Al_2O_6$ [3,4]. The substitution occurs without change in structure up to a limit of about 1% Na_2O, higher degrees lead to a series of variants of the structure (Table 2). In the absence of other substituents, the upper limit of Na_2O is 5.7%.

The cubic phase normally consists of uniform, small, xenomorphous to rectangular crystals (1 to 60 μm), usually isotropic in cross-polarized light, colorless (in white cement) to tan and brown under transmitted light in ordinary Portland cement. It reflects grey on unetched polished surfaces and etches blue to blue-grey in distilled water and potassium

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Table 1
Typical chemical compositions of phases in Portland cement clinkers (wt.%) [1]

Phase	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_2O_3	Fe_2O_3
Alite[a]	0.1	1.1	1.0	25.2	0.1	0.1	0.1	71.6	0.0	0.0	0.7
Belite[a]	0.1	0.5	2.1	31.5	0.1	0.2	0.9	63.5	0.2	0.0	0.9
Aluminate (cubic)[a]	1.0	1.4	31.3	3.7	0.0	0.0	0.7	56.6	0.2	0.0	5.1
Ferrite[a]	0.1	3.0	21.9	3.6	0.0	0.0	0.2	47.5	1.6	0.7	21.4
Aluminate (orthorhombic)[b]	0.6	1.2	28.9	4.3	0.0	0.0	4.0	53.9	0.5	0.0	6.6
Aluminate (low Fe)[c]	0.4	1.0	33.8	4.6	0.0	0.0	0.5	58.1	0.6	0.0	1.0
Ferrite (low Al)[d]	0.4	3.7	16.2	5.0	0.0	0.3	0.2	47.8	0.6	1.0	25.4

[a] Typical values for an ordinary Portland cement clinker with 1.65% MgO, 3.1% Fe_2O_3 and molar $SO_3/(K_2O+Na_2O)<1.0$. For clinkers not fitting these conditions, the compositions of the phases may differ significantly from those given in the table, as explained in the text.

[b] Orthorhombic or pseudotetragonal forms, present in some clinkers high in alkalies. Na/K ratio varies with that of clinker.

[c] Tentative composition for aluminate phases in white cement clinkers.

[d] Values for the ferrite phase in a typical sulfate-resisting clinker (MgO, 2.1%; Al_2O_3, 3.8%; Fe_2O_3, 4.7%). Compositions of other such clinkers may vary considerably [1].

hydroxide, either in white or grey cement. The orthorhombic phase, known as alkali aluminate, is colorless to dark in thin section, and, in polished section, turns blue with water and potassium hydroxide, as does cubic C_3A [5]. The orthorhombic modification is also known as the prismatic, dark interstitial material, and is sometimes pseudotetragonal. It can arise only if sufficient alkali is available, but its formation appears to be favored also by rapid cooling and by bulk compositions potentially able to yield a relatively high proportion of aluminate [1].

Regourd and Guinier [3] presented an XRD powder pattern of material from which the silicate phases had been removed, showing a splitting of the strong peak at 33.3°2θ into a strong singlet at approximately 33.2° and a weaker, close doublet at 32.9–33.0° (Fig. 1B); the 33.3°, 47.7° and 59.4° peaks can be distinguished from the principal alite and belite peaks. The unit cell parameters were A = 1.0874 nm, B = 1.0860 nm, C = 1.5120 nm. Another clinker, in which the aluminate was pseudotetragonal, gave a strong singlet peak at 33.2° and a weaker singlet at 33.0° (Fig. 1C), and the cell parameters were A = B = 1.0867 nm, c = 1.5123 nm.

In the Rietveld method [6] applied to XRD, a theoretical pattern is calculated and fitted to an observed powder diffractogram in several refinements until the calculation describes the observed pattern as closely as possible. The calculation of a theoretical powder pattern requires crystal structure information about the phases to be quantified. The accuracy of the quantification is directly dependent upon the quality of the structural and instrumental parameters. Overviews concerning the application of the Rietveld method to clinker phase analysis have been more recently given [7–11].

Table 2
Modifications of the C_3A structure of general formula $Na_{2x}Ca_{3-x}Al_2O_6$ [1]

Approximate Na_2O (%)	Compositional range (x)	Designation	Crystal system	Space group
0–1.0	0–0.04	C_I	Cubic	Pa3
1.0–2.4	0.04–0.10	C_{II}	Cubic	$P2_13$
2.4–3.7	0.10–0.16	$C_{II}+O$	–	–
3.7–4.6	0.16–0.20	O	Orthorhombic	Pbca
4.6–5.7	0.20–0.25	M	Monoclinic	$P2_1/a$

Takeuchi and Nishi [4] studied the structures of cubic, orthorhombic and monoclinic C_3A, and found that C_3A can occur in clinkers with impurities of Na, Fe, Si, etc. The orthorhombic and monoclinic structures are very similar, so that the C_3A forms are commonly the cubic and monoclinic models only. The crystal structure of Na-substituted C_3A was refined by Rietveld method in experimental clinker [12]. Synthetised cubic and orthorhombic Na-substituted C_3A were refined as single phases and mixtures, showing a very precise quantification. Modified structural data of Mondal and Jeffery [2] and Nishi and Takeuchi [13] were used respectively for cubic and orthorhombic C_3A.

2. Methods

Clinkers from two Portland cement factories operating with dry manufacturing technology were used in this study, one produces grey cement and the other produces white

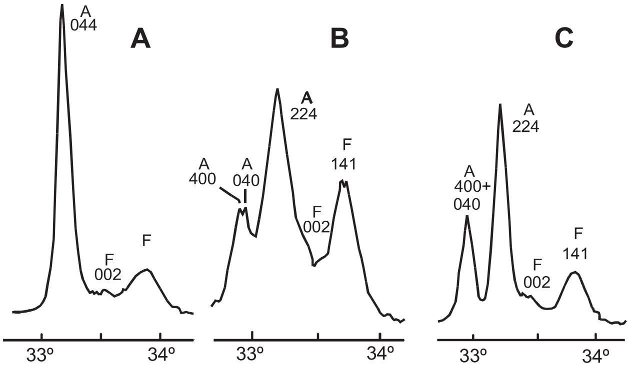

Fig. 1. Portions of XRD powder patterns of clinkers containing (A) cubic, (B) orthorhombic and (C) pseudotetragonal modifications of the aluminate phase. Peaks marked A and F are due to aluminate and ferrite phases, respectively [1].

Table 3
Basic data of the two studied cement factories

Data	Grey cement factory	White cement factory
Kiln length	49.0 m	68.0 m
Kiln diameter	3.6 m	3.4 m
Cooler	Grate cooler	Water vapour cooler
Production	1500 t clinker/day	370 t clinker/day

cement. The two factories have raw materials containing alkalies, the white cement raw material was normally enriched in Na_2O and the common clinker have high K_2O contents on the raw feed. The basic plant data for the two factories are indicated in the Table 3.

Different fuels were used to produce the different clinkers. The white one was produced with oil. The grey clinker was produced with different fuel mixes where small amounts of natural coal were used combined with petroleum coke, which have higher SO_3 weight percentage in comparison with the other fuels. The different fuels used on clinker production of the studied samples and their basic characteristics are shown on Table 4.

The grey clinker samples were produced with the same raw materials but with different fuels mix. White clinker samples were produced with different raw materials but always with the same fuel on the process. Two white clinker samples were produced with a silicate rock in the raw material composition with addition of gypsum in the kiln, and the others were produced with fine quartz enriched raw materials without gypsum addition.

2.1. Optical microscopy

The reflected optical microscopy (Zeiss microscope, model Axioplan 2) was used to qualify the different clinker samples. It permitted to distinguish the different kinds of C_3A based on their crystal features and also identified if the cubic C_3A was alone, associated with orthorhombic C_3A, or if there was only orthorhombic phase. Sample preparation was that traditionally applied for microscopic phases studies, and the polished section surfaces were etched by NH_4Cl, to highlight the silicates, and with a potassium hydroxide solution with sucrose, for interstitial phase recognition.

2.2. SEM-EDS analysis

The SEM (scanning electron microscopy) analysis of about 30-mm diameter carbon coated samples was performed on a *Leo* electron microscope model Stereoscan 440. X-ray spectrometry was used to obtain the clinker phases chemical microanalysis, with EDS system coupled to the SEM. For each analysed phase at least five measurements were done considering the presence of the most common oxides (CaO, Al_2O_3, SiO_2, Fe_2O_3, MgO, Na_2O, K_2O, SO_3 and Mn_2O_3). The literature shows that the alkalies and SO_3 are preferentially incorporated by the belite crystals [14,15], and the C_3A phase incorporates K_2O and Na_2O leading to the stabilization of the prismatic phase when in higher contents [15]. To verify the alkalies incorporation in the belite and C_3A, some crystals of these phases were selected to the microanalysis.

Table 4
Different Fuels used in the studied factories

Parameters	Grey clinker		White clinker
	G1 and G2	G3 and G4	
Fuel	coal	coal + pet coke	oil
SO_3	0.05%	5.31%	0.8%

Table 5
Chemical composition of raw mixes (wt.%)

Components	G1–G4 range	W 1	W 2	W 3	W 4
SiO_2	13.56–13.63	15.04	15.15	15.56	15.36
Al_2O_3	3.43–3.51	3.54	3.23	2.92	2.87
Fe_2O_3	2.17–2.19	0.09	0.10	0.10	0.10
CaO	43.22–43.30	44.26	44.33	44.91	45.46
MgO	0.84–0.89	0.21	0.19	0.12	0.13
SO_3	0.12–0.13	0.81	0.84	0.11	0.01
Na_2O	0.24–0.27	1.08	0.89	0.04	0.08
K_2O	0.72–0.73	0.19	0.34	0.10	0.09
LSF	98.80–99.70	95.00	95.75	95.39	97.85
SM	2.39–2.42	4.17	4.55	5.15	5.17
AM	1.58–1.60	39.33	33.30	29.20	28.70

Oxides–X-ray spectometry.

2.3. X-ray diffraction

The samples were reduced to powder in an agate ball mill and mounted in 10 g holder by hydraulic pressing. The measurements were carried out in the range of 10 to 80°2è with a step size of 0.02°2è and a counting time of 2 s/step. The powder diffraction analysis (XRD) were done with a

Table 6
Chemical composition of the different clinkers studied

	Grey cement clinkers				White cement clinkers			
Components	G1	G2	G3	G4	W1	W2	W3	W4
SiO_2	21.89	22.27	20.85	21.15	23.29	23.38	23.43	24.25
Al_2O_3	5.54	5.28	5.01	5.16	5.50	4.95	5.51	4.71
Fe_2O_3	3.35	3.12	3.22	3.28	0.15	0.17	0.16	0.18
CaO	65.21	64.41	63.52	64.33	67.50	67.64	69.47	70.29
MgO	0.99	1.36	1.47	1.53	0.37	0.31	0.29	0.33
SO_3	0.29	0.86	2.04	1.39	1.10	1.01	0.32	0.16
Na_2O	0.33	0.41	0.54	0.52	1.43	1.13	0.12	0.05
K_2O	1.04	1.02	1.10	1.07	0.18	0.31	0.09	0.02
Mn_2O_3	nd	nd	nd	nd	0.03	0.03	0.03	0.02
LSF	93.15	91.21	95.7	95.4	94.00	94.71	96.21	95.54
SM	2.46	2.65	2.53	2.51	4.12	4.57	4.13	4.86
AM	1.65	1.69	1.56	1.57	36.67	29.12	34.44	26.17
Free lime	1.02	1.08	0.83	1.53	0.90	1.40	0.93	2.34
Alkalies equivalent[a]	1.01	1.08	1.26	1.22	1.55	1.33	0.18	0.06

[a] (0.658 × K_2O)+(1,000 × Na_2O).

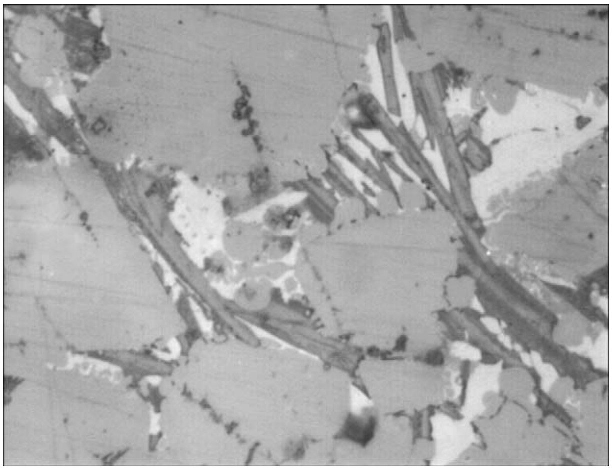

Fig. 2. Orthorhombic C_3A formed with high K_2O percentages. Sample G2; magnification: × 1000.

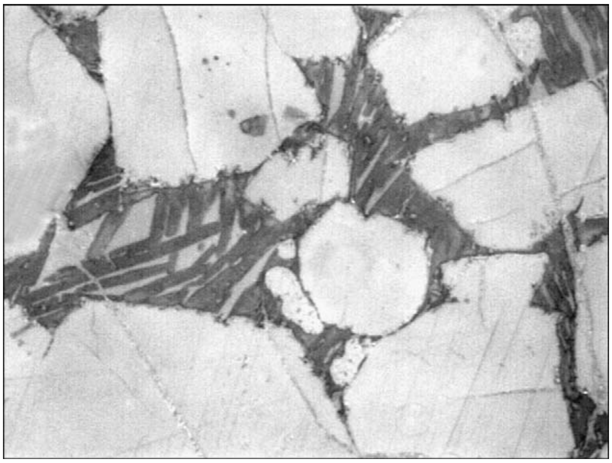

Fig. 3. Orthorhombic C_3A formed with high Na_2O percentages in the raw mix. Sample W1; magnification: × 1000.

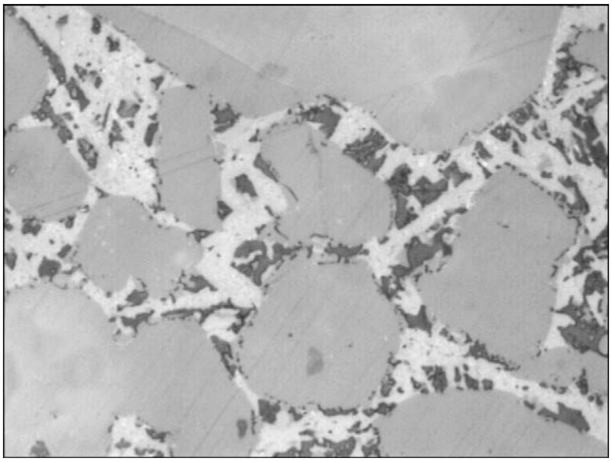

Fig. 4. Cubic C_3A formed with lower K_2O percentages and higher SO_3 content from the fuel. Sample G4; Magnification: × 1000.

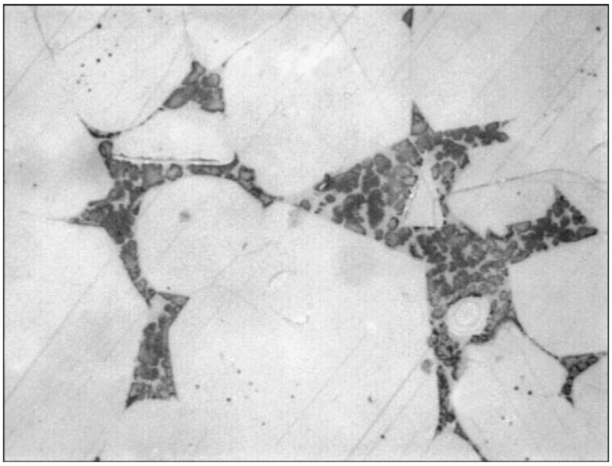

Fig. 5. Cubic C_3A formed almost without Na_2O in the raw mix. Sample W3; magnification: × 1000.

broad focus CuKá tube anode, applying 40 kV/40 mA under configuration of 1/2° divergent slit, graphite monochromator, 0.2 mm receiving slit and proportional detectors. The

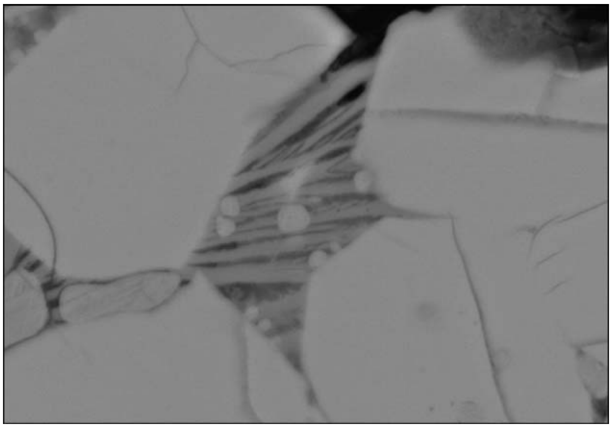

Fig. 6. SEM image of orthorhombic C_3A formed with high Na_2O percentages. Sample W1; magnification: × 3000.

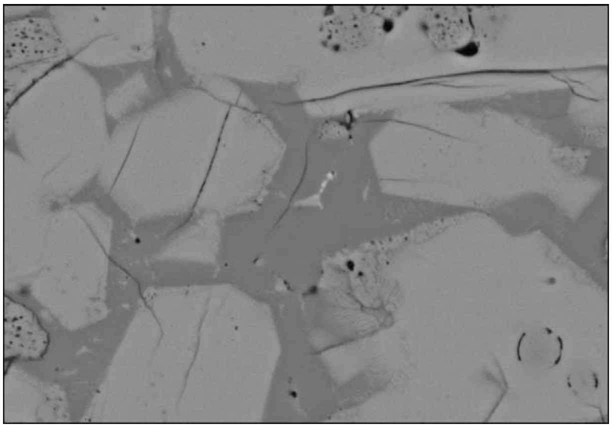

Fig. 7. SEM image of cubic C_3A formed with very low Na_2O percentages. Sample W3; magnification: × 2000.

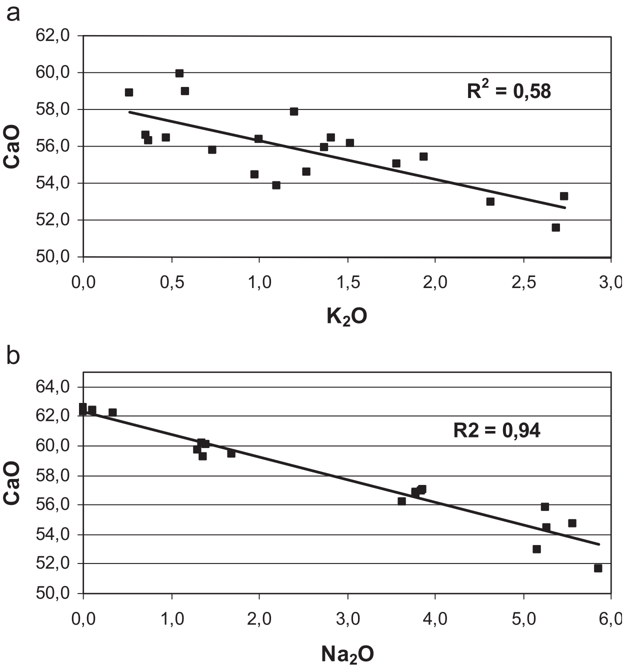

Fig. 8. (a) Correlation of K_2O and CaO obtained by SEM-EDS microanalysis of C_3A phases that are remarkable in the grey samples. (b) Correlation of Na_2O and CaO obtained by SEM-EDS microanalysis of C_3A for white cement.

recorded X-ray diffractograms were saved as computer files and can be loaded directly into Rietveld program for further analysis, as necessary.

The Rietveld refinement, based on comparison of an observed X-ray pattern and a pattern calculated from structure data of each phase, was deemed successful when the residual error was minimized by the refinement of global and structural parameters. Structural data of alite [16], belite [17], C_4AF [18], cubic C_3A [2], orthorhombic C_3A [13], free lime and periclase were used for refinement and quantification.

Data sets were refined by the Rietveld method using GSAS software [19]. The background was fitted with a Chebyshev function with four terms. The peak profiles were modelled using a pseudo-Voight function with one Gaussian and Lorenzian coefficient. The lattice constants, the phase fraction, and the coefficient corresponding to the zero-point correction were also refined. The goodness of the fit is evaluated as χ^2, whose values are generally around 3.5, and as Rwp (weighted residuals), with values close to 0.1.

3. Results

The grey raw mix samples showed high K_2O and low Na_2O contents, the silicate material used in the raw mix increased the potassium levels. The white cement raw mix showed higher percentages of Na_2O in the first sample, with decreasing values in the W4 sample direction, due to the different type of silicate rock used in the raw mix of the samples W1 and W2, while the samples W3 and W4 were produced with low Na_2O from siliceous enriched raw materials. The raw mix chemical compositions are shown on Table 5. These were sampled 1 h prior to sampling the studied clinkers. Due to the gypsum presence in the raw mix, the W1 and W2 samples were enriched in SO_3 compared with others.

3.1. Clinker chemical composition

The grey clinker samples presented similar results with high K_2O contents shown for all samples. The differences among the analysed samples can be observed in the SO_3 levels that increase from the first to the last sample.

White clinkers analysis showed clearly the reduction of Na_2O content from the first to the last sample; reproducing the raw mixes conditions. To guarantee the alkali-equivalent close to 1, some gypsum percentages were added in the process making the reduction on sulfur contents in clinker notable from the W1 to the W4 sample. Comparing the raw materials and clinker compositions (Table 6), it is evident that sulfur came from another source. Due to the reduced Fe_2O_3 in the white cement raw mixes, its clinker AM is higher than in the grey samples. The major AM are presented in the W1 and W2 samples and the lower are presented in the G3 and G4 samples.

3.2. Optical microscopy

The photomicrographs present the different C_3A formed in the samples of grey and white cements. The first shows the orthorhombic C_3A of sample G2 produced with higher percentages of K_2O (Fig. 2), and higher percentages of Na_2O in the case of the sample W1 (Fig. 3). Both figures present a prismatic interstitial material, which became blue to dark on potassium hydroxide and water etching. The belite and alite crystals are identified by their morphology. The Fig. 4 shows the C_3A of sample G4, formed in presence of almost the same amounts of K_2O from the three other grey samples,

Table 7
Chemical microanalysis obtained in SEM-EDS (wt.% range value for five points)

Phase	Component	G1	G2	G3	G4	W1	W2	W3	W4
C_3A	Na_2O	1.3–1.8	1.4–2.0	1.0–2.0	0.6–1.2	5.2–5.9	3.6–3.9	1.3–1.7	0.0–0.3
	K_2O	1.3–2.7	1.2–1.8	0.6–1.7	0.3–0.6	0.2–0.3	0.2–0.4	0.0–0.8	0.1–0.2
	CaO	51.6–55.4	55.0–57.8	53.9–58.9	56.3–60.0	51.7–55.8	56.2–57.0	59.3–60.2	62.2–62.6
Belite	SO_3	tr	tr	0.4–0.6	0.4–0.6	0.7–1.2	0.7–1.0	0.0–0.5	0.0–0.0

Tr—trace.

Table 8
Phases composition based on Rietveld Method (wt.%)

Components	Grey cement clinker				White cement clinker			
	G1	G2	G3	G4	W1	W2	W3	W4
Alite	69.5 (0.2)	66.3 (0.2)	68.9 (0.2)	66.9 (0.2)	77.6 (0.2)	66.2 (0.2)	73.1 (0.2)	67.9 (0.2)
Belite	13.6 (0.6)	16.6 (0.5)	13.7 (0.6)	14.0 (0.5)	13.1 (0.6)	24.1 (0.5)	16.4 (0.6)	24.4 (0.5)
C_3A-cubic	–	1.3 (0.3)	2.2 (0.3)	5.1 (0.2)	–	–	7.5 (0.3)	6.5 (0.2)
C_3A-orthorhombic	7.9 (0.2)	5.8 (0.2)	2.9 (0.2)	2.6 (0.2)	8.7 (0.2)	8.5 (0.2)	–	0.8 (0.1)
C_4AF	7.3 (0.3)	9.5 (0.3)	11.5 (0.3)	10.2 (0.3)	–	–	–	–
$C_{12}A_7$	–	–	–	–	–	–	2.6 (0.2)	–
Free lime	0.2 (0.1)	0.2 (0.1)	0.2 (0.1)	0.3 (0.1)	0.6 (0.1)	1.2 (0.1)	0.3 (0.1)	0.4 (0.1)
Periclase	1.5 (0.0)	0.3 (0.3)	0.7 (0.1)	0.9 (0.2)	–	–	–	–
Total	100	100	100	100	100	100	100	100
χ^2	3.6	3.4	3.1	3.2	4.5	3.9	4.1	2.3

(–) not detected, ( ) detection limit.

but in presence of higher SO_3 content introduced by the petroleum coke, it shows mainly cubic C_3A. The photomicrograph of the Fig. 5 shows cubic C_3A of sample W3, formed almost without Na_2O in the raw materials.

3.3. SEM-EDS analysis

In the SEM images an interstitial prismatic material could be also verified in the samples G1, G2, W1 and W2. The W1 image of Fig. 6 shows orthorhombic C_3A phase, easily recognized by the typical morphology, and Fig. 7 shows the cubic C_3A of sample W3. The images were selected from samples of white cement to better illustrate the aluminate.

The microanalysis of the grey clinker C_3A showed similar amounts of Na_2O and decreasing amounts of K_2O from the sample G1 to the sample G4. Also some SO_3 in the belite crystal structure of the samples G3 and G4 and absence of SO_3 in the G1 and G2 samples could be detected. The Fig. 8a shows some correlation between the K_2O and CaO for the grey clinker C_3A. In the white cement group of samples, the decrease of the Na_2O in the C_3A is notable from the sample W1 to W4. The SO_3 amounts in the belite decrease related with the alkalies content in the C_3A. Fig. 8b shows the correlation for Na_2O and CaO present in the white clinker C_3A (Table 7).

3.4. Clinker phases composition

The XRD analysis confirmed the phases previously identified by microscopical methods. Rietveld refinement quantified phase compositions of the samples, as shown in Table 8. The alite content in the grey cement clinker shows some variation among the samples, while the white cement clinker showed greater variation due to the LSF (lime saturation factor) differences observed. Differing from the grey cement, small quantities of $C_{12}A_7$ were observed in the white cement clinkers and are related to the very high AM in the raw mix.

Regarding the phases compositions, it is observed that all samples have high alite contents and including white clinker only the change of the raw material leading to the formation of more cubic C_3A. The raw material enriched in sodium was the responsible for the higher contents of orthorhombic C_3A in the sample W1 and W2. The free lime is not abundant in the samples and, except in the sample W3, periclase is rare. As expected, the C_4AF is not present in the white clinker samples.

The higher C_3A content in the sample G2 and W1 is related to the higher AM. The orthorhombic C_3A is abundant in the samples G1 and G2 and also in the samples W1 and W2. The samples G3, G4, W3 and W4 showed higher percentages of cubic C_3A. The C_3A forms could be recog-

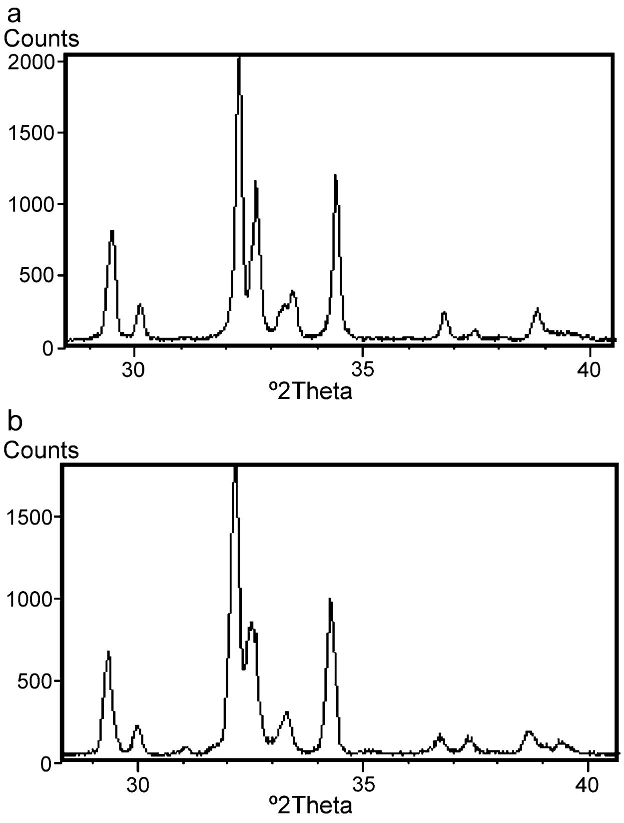

Fig. 9. (a) The observed pattern of sample W1. (b) The observed pattern of sample W3.

nized and quantified based on XRD spectrum differences, mainly related to the 33.5°2θ peak that is a doublet for orthorhombic C_3A and singlet for cubic C_3A. This is remarkable for sample W1, which consists predominantly of the orthorhombic structure and sample W3 which is predominantly a cubic structure, as shown in Fig. 9a and b, respectively.

To evaluate the Rietveld quantification accuracy, chemical selective dissolutions were done for samples W1 and W3 to obtain pure C_3A crystals, according to Takashima's method [20]. The XRD spectrum for the dissolution residues (Fig. 10a and b) confirm the differences in the peak 33.5°2è. The doublet peak in the range 32–35°2è indicates the orthorhombic C_3A in the residue of the sample W1 and the single strong peak in the Fig. 10b shows the cubic C_3A in the residue of the sample W3, confirming the Rietveld refinements results. As white cement do not have C_4AF, the C_3A phase was isolated, which is not possible for normal clinkers, as reported in Regourd et al. [21], powder pattern of material from which the silicate phases had been removed and C_3A peaks could be distinguished from the principal alite and belite peaks, however the C_4AF phase remained.

The Fig. 11a and b show clearly the decreasing in relative proportions of the orthorhombic aluminate with the increasing in the SO_3/alkalies relation, for both groups of white and grey clinkers. A clearly broken transition in C_3A relative proportions from orthorhombic to cubic phase is observed in the white cement figure, as a consequence of the change in the raw mixes that decrease the Na_2O grades. The grey cement graph shows a gradual diminution of the orthorhombic content and also a gradual increase in cubic C_3A content. In this case, the increase in the SO_3/alkalies relation was the main cause for the changes in polymorph proportions.

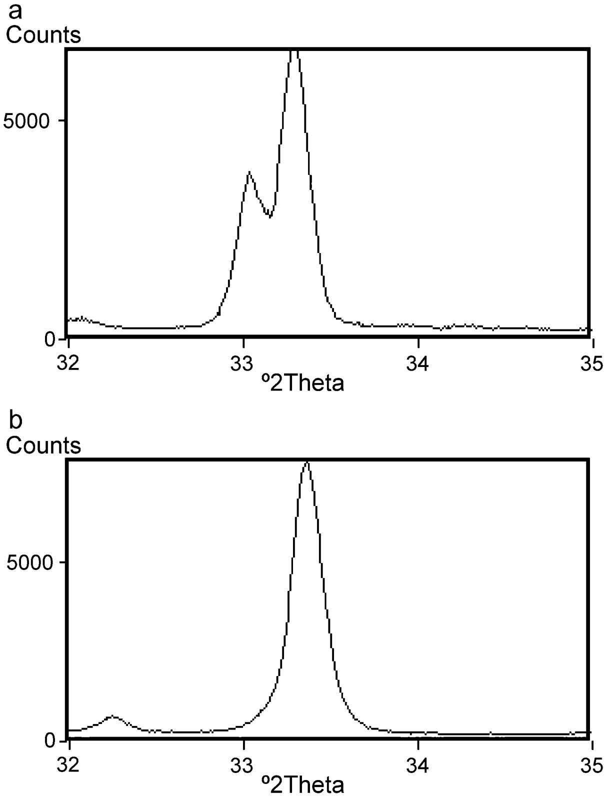

Fig. 10. (a) The doublet peak in the range 32–35°2θ indicates the presence of the orthorhombic C_3A in the residue of the sample W1. (b) The single strong peak in the Fig. 9b shows the cubic C_3A presence in the residue of the sample W3.

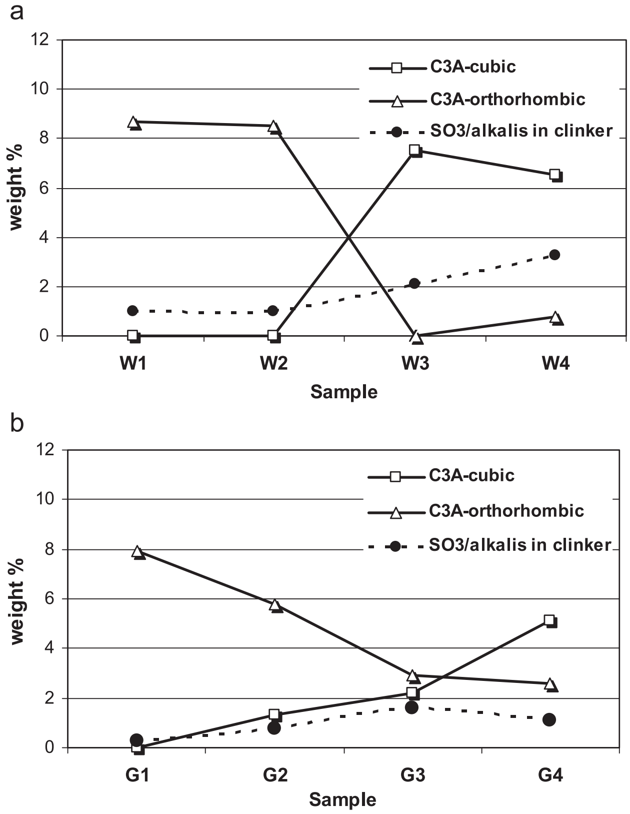

Fig. 11. Correlation of orthorhombic C_3A and SO_3/alkalies values in clinkers.

4. Conclusions

The paper shows characteristics of eight clinker samples produced in two distinct plants, with variable fuels and raw materials in systems with SO_3 content. Four samples are referred to a grey cement factory and the others to a white cement factory. Several differences were observed in the clinker phases proportions, and particularly attention was paid to consequent C_3A formation. XRD with Rietveld method became an important and accurate tool to quantify the C_3A cubic and orthorhombic polymorphs proportions in industrial clinkers.

It is expected that part of the available SO_3 is fixed in the belite crystalline structure and part reacts with the K_2O forming alkaline sulphates as minor compounds. In the samples studied a significant sulfur content was observed in belites with pet coke fuel in the process, although none sulphate phase was detected. On the other hand, in the samples without sulfur enriched fuel in the process, the belite crystals have no SO_3, as indicated by SEM-EDS microanalysis.

In the white cement the higher grades of Na_2O in the raw materials led to formation of orthorhombic C_3A. In this case, the introduction of sulfur by way of gypsum in the raw material inhibits the formation of cubic C_3A. The changing of raw materials, for a less enriched Na_2O rock, allowed the formation of cubic C_3A with acceptable quantity of orthorhombic C_3A for cement performance.

The correlations between alkalies contents, Na_2O and CaO for the white cement clinker and K_2O and CaO for grey clinker, suggest partial substitution of CaO and incorporation of Na_2O or K_2O in the vacant site of the cubic C_3A leading to the formation of the orthorhombic phase.

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