

RESEARCH ARTICLE

THE EFFECT OF GRINDING ON THE POLYMORPHIC TRANSITION OF ALITE FROM M1 TO M3 TYPE

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ABSTRACT

The polymorphism of alite (C3S) has been subjected to examination through various factors, such as the burning process and cooling. This study is centered on investigating the impact of grinding on alite polymorphism. To determine the chemical composition, X-ray fluorescence (XRF) analysis was employed. The mineralogical characterization was conducted utilizing X-ray powder diffraction (XRD), complemented by the Rietveld method. Morphological assessments of the ground clinker were carried out using scanning electron microscopy (SEM) in conjunction with EDS microanalysis. XRD analysis, performed on both gray and white cement as well as clinker, has revealed that mechanical treatment (grinding), aside from reducing particle size, actively induces the transformation of alite polymorphism from monoclinic M1 to monoclinic M3.

KEYWORDS

grinding, polymorphism, Rietveld method, alite, monoclinic M1, monoclinic M3.

1. INTRODUCTION

The main phase of white Portland cement clinker are C3S (Ca₃SiO₅), C2S (Ca₂SiO₄), C3A (Ca₃Al₂O₆) and C4AF (Ca₄Al₂Fe₂O₁₀). Alite (C3S) is the most important clinker phase in cement, since it controls mainly the initial and ultimate strength of cement. Typically, incorporated ions within the alite crystal lattice are Mg²⁺, Al³⁺ and Fe³⁺. The impurities in alite stabilize high temperature polymorphs at low temperatures (below the related decomposition temperature) (Taylor, 1997). So far, there exist seven known polymorphs between room temperature and 1070 °C: three triclinic (denoted with T), three monoclinic (M) and one rhombohedral (R) polymorph (Taylor, 1997; Bye, 1983). Due to incorporations in the alite crystal lattice, M1 and M3 polymorphs are present mostly in industrial clinker. Accurate quantitative phase analysis is one of the crucial points in every cement production process. The X-ray powder diffraction, combined with the Rietveld method, is the most recent and accurate for the quantification of the mineralogical composition of Portland clinker (Rietveld, 1969; Pritula et al., 2004, Le Saoût et al., 2011, León-Reina et al., 2009, Scarlett et al., 2001, De la Torre et al., 2001, Walenta et al., 2004, Scrivener et al., 2004, Peterson et al., 2006, Neubauer et al., 2007, Snellings et al., 2014 and Li et al., 2014).

Over the past decade, numerous studies have concentrated on refining the crystal structure of alite to facilitate precise Rietveld quantitative phase analysis of Portland clinker (De la Torre et al., 2008; Peterson et al., 2004; Zhang et al., 2011; Dunstetter et al., 2006; De Noirfontaine et al., 2006; Le Saoût et al., 2011; Mohamed et al., 2017). C3S exhibits complex polymorphism which is not yet fully understood. The most appropriate C3S-monoclinic model was chosen using the selected angular windows W1=31.5-33.5 and W2= 51-53, W3= 24.5-26.5°, W4= 26.5-28.5° and W5=36- 38, 2θcu) proposed by (Courtial et al., 2003). In order to correctly choose the alite polymorph, a detailed analysis of XRD patterns was made on windows from 31.5 to 33.5° and from 51 to 53°, as proposed in previous studies. The influence of individual ions on the structure of C3S has been

extensively studied in the past decades (Zhang et al., 2011).

In industrial clinkers, the M1 and M3 polymorphs are mostly stabilized at room temperature by the presence of sulfate or magnesium impurities respectively (Maki et al., 1978; Maki, 1982). The factors influenced the alite modification are related to the process of burning and cooling of clinker. Other factors can influence the alite modification such as chemical composition of raw meal, grain size distribution, mineral composition, contents of minor oxides (especially MgO and SO₃) and homogeneity (Stanek et al., 2002).

Grinding-induced changes include deformation, microcracking, phase transformation, and residual stresses at both surface and subsurface levels (Perry et al., 1996; Tönshoff et al., 1999; Hegeman et al., 2001; Tönshoff et al., 2001; Denkena et al., 2008, Breidenstein et al., 2013; Yanga et al., 2014; Mei Yang et al., 2017).

The present study focused on the assessment and understanding of grinding effects on the alite modification. XRD pattern was used to show the grinding effect on the alite monoclinic modification. Rietveld method was employed for the quantification of the clinkers and cements samples (white, gray). The particle size and morphology of ground clinker were determined successively by laser diffractometry and SEM equipped with EDS microanalysis.

2. EXPERIMENTAL

The clinker and the cement samples were collected from a cement plants. White clinker and cement were collected from SOTACIB (Tunisian-Andalusian White Cement Company) and gray clinker and cement were collected from Bizerte Cement Company. They were subjected to the following analysis: The chemical composition of the samples was determined by X-Ray fluorescence (XRF) spectrometry (ARL type XP 9800). The loss on ignition (LOI) of sample was measured by heating at 1050 °C for 2 hours.

A test was performed to free lime to quantify uncombined lime which,

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remains in the free state. In fact, by dissolving in ethylene glycol and lime dosing with a weak acid.

The particle size distribution of the samples was measured by laser diffractometry using a Malvern Mastersizer S equipped with a small volume sample dispersion unit. Isopropanol was used as dispersion medium. Measurements were carried out in triplicate (Snellings et al., 2014).

XRD measurements were made using a PANalytical X'Pert Pro diffractometer (Bruker D8 ADVANCE Diffractometer) in conventional Bragg-Brentano θ - 2θ with a 217.5 mm goniometer radius. The data were collected at room temperature in the 2θ range of 10° to 70° in the step of 0.02° , with an integration time of 6 sec/step. The X-ray tube was operated at 40 kV and 40 mA. The samples were prepared using the back loading technique to minimize preferred orientation effects and repacked between repeated measurements. During measurement the samples were spun around the vertical goniometer axis to improve particle statistics. The quantitative phase analysis of the XRD results was performed by Rietveld refinement using X'Pert Highscore Plus software (PANalytical B.V., version 2.2c). This software perform as follows. RQPA patterns were analysed by the Rietveld method with peak shapes were fillet by using the Voigt function.

Background was Polynomial (6 term Chebyshev) combined with a $1/X$ term. The refined overall parameters were: cell parameters, zero-shift error, W (Gaussian contribution) peak shapes. March-Dollase preferred orientation corrections were applied when necessary for alite.

The crystallographic structures used during the refinement of the clinker/cement are given in literature.

The compounds of clinkers compounds studied were examined by scanning electron microscope (JEOL JSM- 5400). Ground clinker was metalized by gold sputtering for better image definition. MEB observation aims to determine the morphology of powder destined to the XRD analysis.

3. RESULTS AND DISCUSSION

3.1 Grinding

The particle size curve of granulated clinker sample with various milling time are shown in figure 1 (Images a and b). The sample milled for 40 minutes showed a particle size of about $40\mu\text{m}$. This represents the ideal time which gives the best grinding to keep intact crystalline phases. Each sample is ground in an agate mortar and was passed through a $40\mu\text{m}$ sieve with 0% retained (Courtil et al., 2003), until a powder lower or equal size to $40\mu\text{m}$. This procedure generates a very wide distribution of particle size that appears to be in the order of 40 microns for the vast majority.

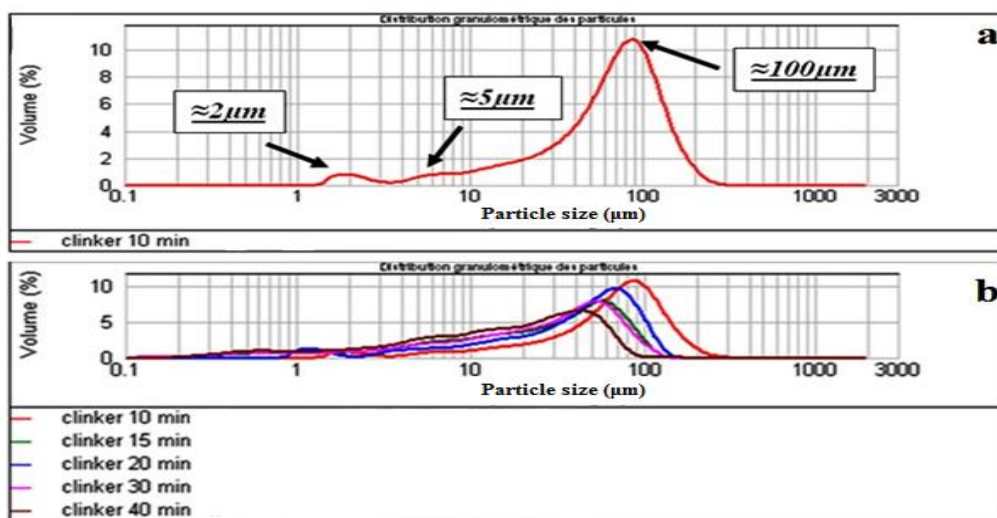


Figure 1: Particle size distribution; a: Particle size distribution curve shows a clinker sample milled 10 minutes with the number of revolutions per minute constant. b: Particle size distribution curve shows a clinker sample milled 10, 15, 20, 30 and 40 min

The SEM photograph of the clinker sample milling at $40\mu\text{m}$, show a wide distribution of particle size.

The SEM photograph of the clinker sample (figure 2) showing the maximum particle size of $40\mu\text{m}$ (milled 40 minutes), show a wide distribution of particle size. In fact, the hardness has a visible effect on the size of the resulting grinding particles. As cement contains minerals with

different hardness, C3A, C3S and C2S present the successive Hardness 6, 5.5 and 5 (Enders, 2007). Therefore, C3A present a larger particle than C3S and C2S and this devoted to the presence of alumina. Alite (C3S) is more brittle than belite due to more pronounced cleavage, grinding leads to the concentration of brittle and softer minerals (gypsum, alite) in the finer fraction and harder phases (belite) in the coarser fraction (Le Saout et al., 2011; Gutteridge, 1984).

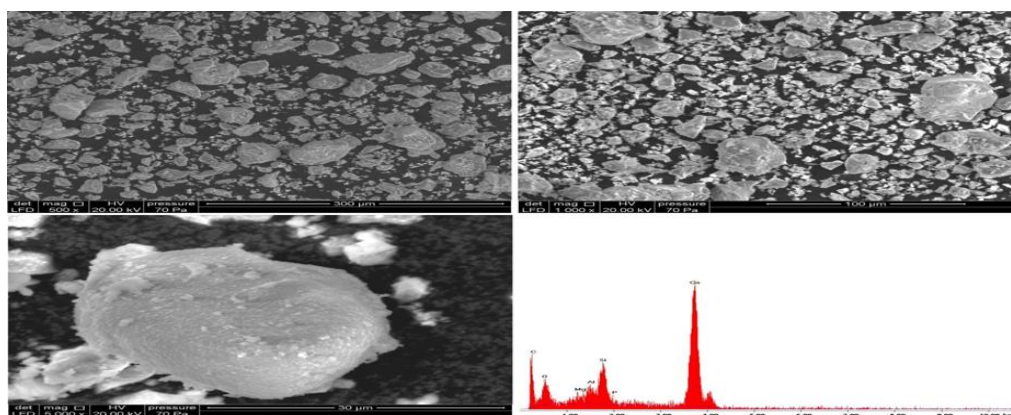


Figure 2: SEM photographs shows particles size distribution of clinker milling at $40\mu\text{m}$.

3.2 Choice of alite polymorph

Using XRD patterns, alite polymorphs were identified for the samples as follows:

- The M1 polymorph was observed in white clinkers samples (B1, B2, B3). While the M3 polymorph was identified in the

corresponding cements (CB1, CB2) (Figure 3).

- The M1 polymorph was observed in gray clinkers samples (G1, G2, G3). While the M3 polymorph was identified in the corresponding cements (CG1, CG2) (Figure 4).

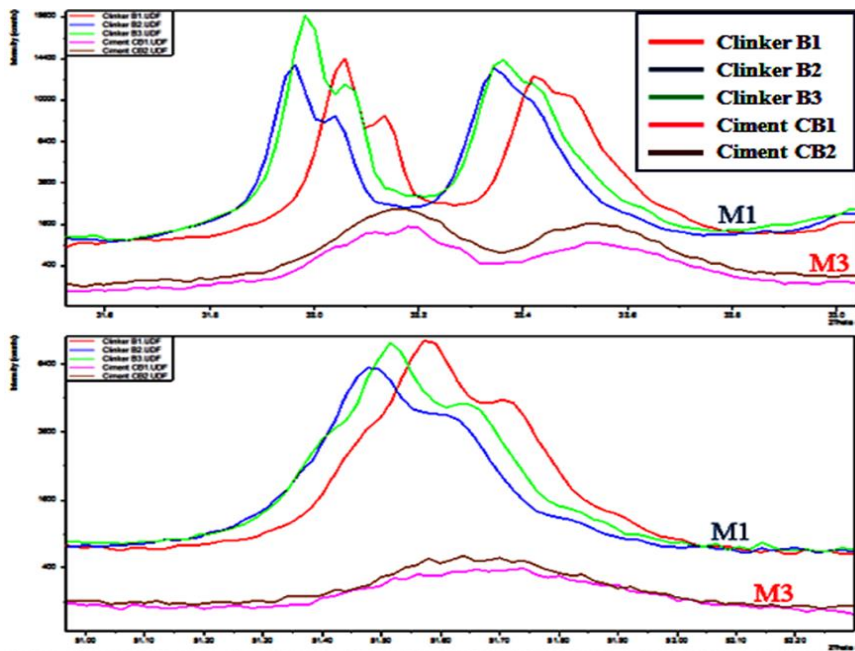


Figure 3: Two angular windows 31.5°-33.5°, 51°-53° that allow the identification of the M1 and M3 alite polymorphs (clinker)

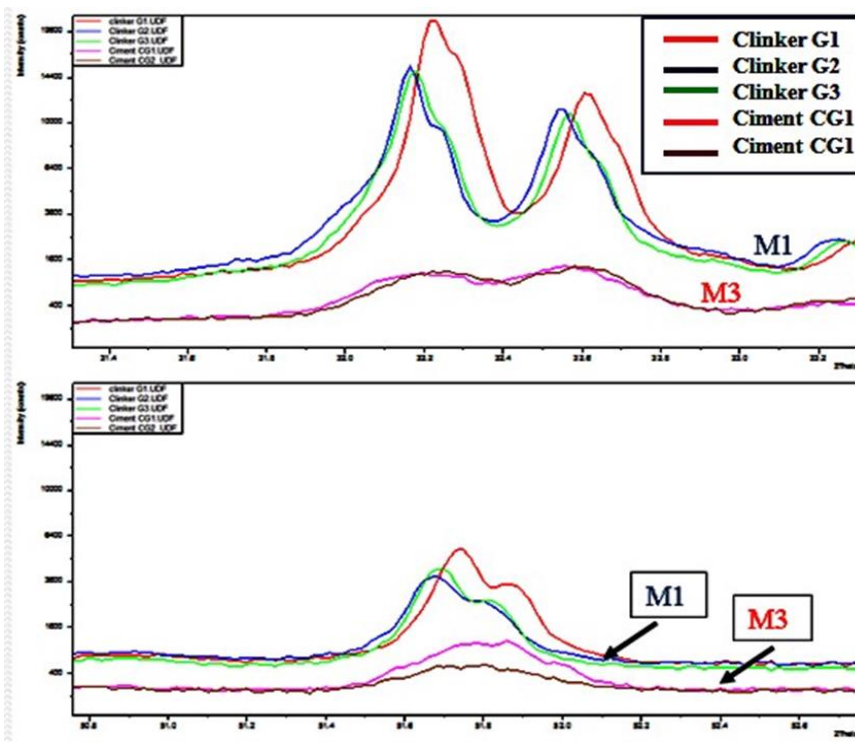


Figure 4: Two angular windows 31.5°-33.5°, 51°-53° that allow the identification of the M1 and M3 alite polymorphs (clinker)

These results suggest that mechanical treatment has probably generated a sort of instability within the crystal lattice that induced the transformation of the alite polymorph from M1-type to M3-type. In fact, mechanical stress on a crystal lattice causes distortion and deformation of the crystal structure and an increase of crystal defect sites (Baldyrev, 1993; Mercury et al., 2004; Mohamed et al., 1997).

Question: Is there any relation between the mechanical treatment (grinding) and the alite polymorphic transformation?

Two hypotheses were considered in this case; (1) Grinding when it exceeds the threshold causes the deformation and the distortion of the expected structure, which translates by the transformation of the structural model M1 to another (M3).

(2) Increasing the grinding time of clinker with additives leads to a rise in the temperature of the ground material, which causes the insertion of the ions in the crystal (MgO was found in the raw material of additives). The increase in grinding time, along with the presence of ions from additives facilitates the transformation in the crystallographic model, subsequently leading to a stabilization of the M3 phase.

3.3 Quantitative analysis

The calculated weight percent values of phases and the Rietveld conventional agreement indexes are indicated in Table 2. The first result to be emphasized is the occurrence of the alite monoclinic M1-type for all samples clinker (gray and white), with good agreements indexes (Rwp, Gof). On the other hand, in the cement samples (gray and white), alite (C3S) M3- type was presented. C3A present in the clinker and the gray cement in two polymorphs; cubic (between 1.6 and 4.6%) and Orthorhombic (between 1.6 and 4.9%). While only the cubic polymorph is present in white clinker and cement samples (7.38 and 8.7%). The CaO content varies between 0.1 and 1.07%. The comparison of these values with those determined by dosage (Table 1) shows that there is an underestimation of the free lime content by the DRX combined with the Rietveld method, indicates the increase of error with the minor phase. Others minors phases such as periclase and arcanite were taken high contents successively 6.5% and 3.3%. This abnormal elevation can be also explained by a refinement error. For the cementitious materials quantification, the amorphous content in the clinker and cement was ignored as the proved low quantity in cement clinker (Snellings, 2014).

Table 1: Chemical composition of cements and clinkers (% wt.)

	G1	G2	G3	CG1	CG2	B1	B2	B3	CB1	CB2
CaO	64.06	67.55	65.99	62.35	62.64	69.85	69.65	69.27	68.39	68.17
SiO ₂	21.43	21.97	21.49	20.98	20.5	23.42	24.47	22.28	21.47	23.13
Al ₂ O ₃	5.63	4.58	4.87	5.09	4.97	3.96	3.88	4.06	3.73	3.60
Fe ₂ O ₃	3.36	3.2	3.31	3.39	3.21	0,29	0,26	0,29	0.28	0.21
SO ₃	0.69	0.31	0.65	2.15	2.3	0,00	0.01	0,08	1.93	2.02
K ₂ O	0.59	0.3	0.59	0.46	0.4	0.13	0.16	0.14	0.2	0.18
MgO	1.12	1.34	1.1	1.32	1.05	0.27	0.31	0.29	0.47	0.02
TiO ₂	0.24	0.24	0.26	0.25	0.3	0,07	0,05	0,07	0.13	0.10
Na ₂ O	0.1	0.1	0.08	0.01	0.03	0.27	0.33	0.37	0.07	0.02
LOI	1.3	0.9	0.5	2.09	2.1	0.93	0.7	0.62	1.2	0.87
Free lime	1.07	0.47	1	0.9	1.01	0.4	0.2	0.7	1.03	0.8

LOI = the loss on ignition at 1050°C.

Table 2: Mineral Composition of the Clinkers samples and cement: Rietveld Method

Phase	G1	G2	G3	CG1	CG2	B1	B2	B3	CB1	CB2
Alite C3S (M1) (De Noirefontaine 2006)	58.3	49.8	63.0	-	-	79.48	83.87	60.15	-	-
Alite C3S (M3) (Nishi F et al 1985)	-	-	-	65.3	60.3	-	-	-	74.3	65.5
Belite β-C2S (Mumme et al 1995)	18.5	25.5	17.7	13.3	17.1	9.20	7.64	26.59	8.5	19.5
Ferrite C4AF (Colville et al 1971)	13.2	12.7	11.0	10.7	12.3	-	-	-	-	-
Aluminate -Cubic C3A (Mondal et al 1975)	2.2	-	1.6	4.7	4.0	7.38	7.60	7.38	8.1	8.7
Orthorhombic C3A(Nishi et al 1975)	2.4	2	4.9	1.7	2.3	-	-	-	-	-
Calcium oxide-lime (Huang et al 1994)	0.2	0.2	0.1	0.2	-	1.07	0.61	0.68	0.3	0.3
Periclase (Sasaki et al 1979)	0.5	3.3	0.2	-	0.3	0.18	0.27	0.23	0.2	-
Arcanite (McGinnety 1972)	4.7	6.5	1.4	1.4	1.3	-	-	-	0.2	-
Calcite (Maslen et al 1993)	-	-	-	0.2	0.6	-	-	-	5.3	3.1
Dolomite (Pilati et al 1998)	-	-	-	0.9	0.4	-	-	-	-	-
Gypsum (Pedersen et al 1982)	-	-	-	0.6	0.5	-	-	-	0.6	1.5
Portlandite (Chaix-Pluchery et al 1987)	-	-	-	0.9	0.6	2.69	-	4.97	1.4	0.9
Bassanite (Bezou et al 1991)	-	-	-	0.2	0.2	-	-	-	1.1	0.6
Rwp	8.25	6.8	8.33	11.90	10.78	10.70	11.82	11.45	19.00	15.58
Gof	9.86	6.9	8.16	3.15	2.5	3.44	1.80	4.69	3.51	3.48

Rwp, Gof: The conventional Rietveld agreement indexes of profile fitting.

3.4 Alite monoclinic transformation (M1 to M3)

The investigation needs to be focused on the grinding effect in laboratory. Figure 5 shows the XRD patterns of the B1 white clinker which was ground with an agate ball milling using varying durations of grinding (10min, 15min, 30min, 35min, 40min, 45min, 50min). Using the two identification windows of alite polymorphs (32–33 and 51– 52_ (Cu Ka), figure 6 shows that there is a gradual transition from M1 polymorph to M3- polymorphic type. The polymorphic transition of Alite from M1 to M3 was frequently studied in the literature and was promoted by several factors. In this work,

milling can be considered as a mechanical generator for Alite polymorphic transformation. As shown in Figure 6, an increase of the milling times induces changes in the alite polymorph from M1 to M3 through the mix of M1- M3. In fact, under 20 min it seen the occurrence of alite M1-type. At 25 min a mix form M1-M3 type was present in the clinker B1. With milling time of 30 min and more only M3-polymorph is present in the clinker B1. In fact, an intense grinding process is not required due to the high process related fineness of the material (Ludwig et al., 2015). This microstructure appears to be a product of recrystallization due to relatively high temperature, grinding stress, or both, which convert the previously continuous atomic structure into a myriad of minute polygonal crystalline units (Donald, 2000; Mohamed et al., 2016).

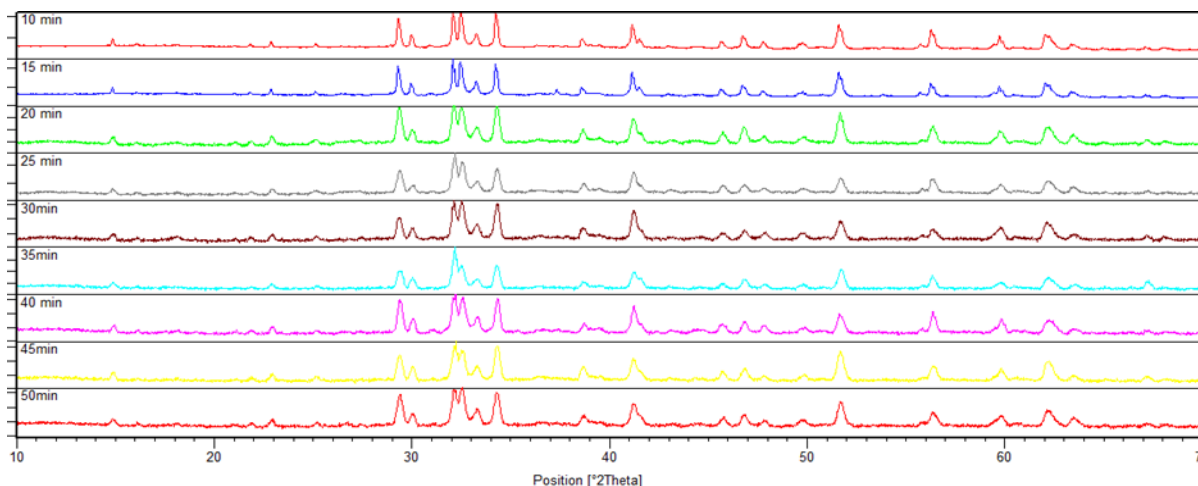


Figure 5: Clinker B1 ground at 10, 15, 20, 25, 30, 35, 40, 45 and 50 minute.

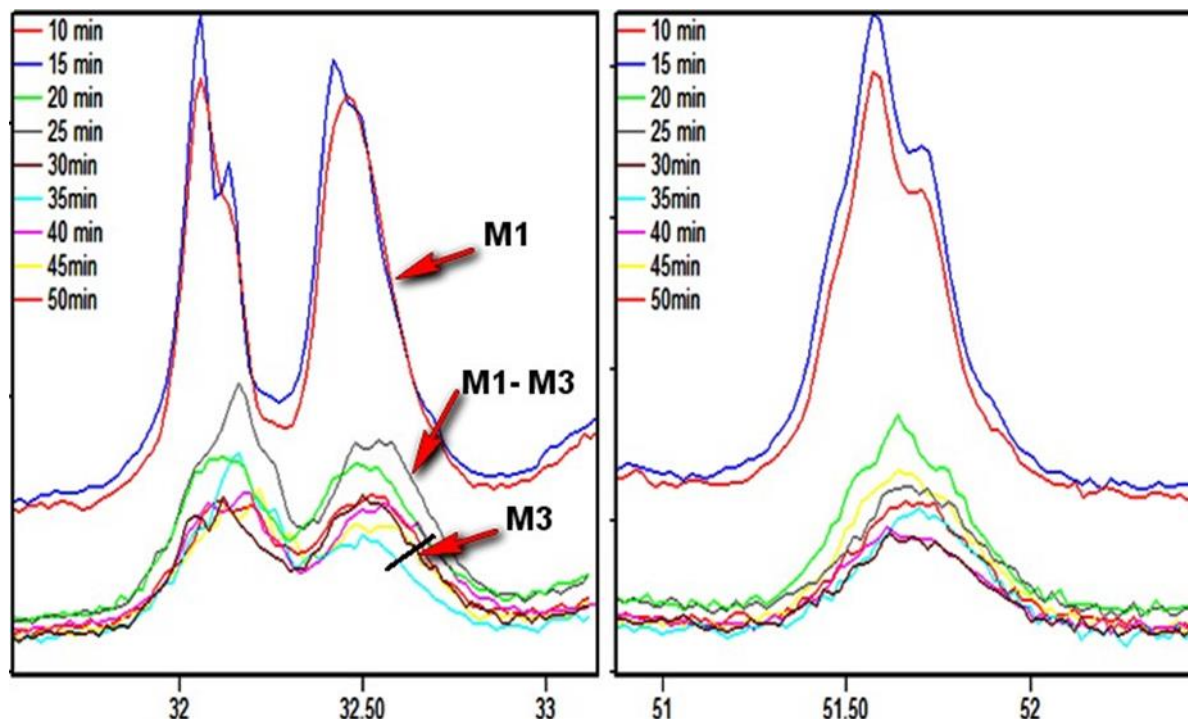


Figure 6: Two angular windows 31.5° - 33° , 51° - 53° that allow the identification of the M1 and M3 alite polymorphs (clinker)

4. CONCLUSION

It is obvious that grinding does not only influence the quantitative aspect of cement materials but it is also involved in the alite polymorphism as shown in the present work. Specifically, the grinding technique induces the transformation of monoclinic M1 alite in clinker into the monoclinic M3-type even in the absence of additives but it depends on milling times.

Furthermore, it's worth noting that the Rietveld method for quantitative analysis is highly sensitive to minor elements present in the mixture, such as arcanite, free-lime, and periclase.

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REFERENCES

- Benmohamed, M., Alouani, R., Jmayai, A., Ben Haj Amara, A., & Ben Rhaïem, H. (2016). Morphological Analysis of White Cement Clinker Minerals: Discussion on the Crystallization-Related Defects. *International Journal of Analytical Chemistry*, 2016(1), 1259094. C. H. Donald, Microscopical Examination and Interpretation of Portland Cement and Clinker, The Portland Cement Association, Skokie, Ill, USA, 2000.
- Bezou, C., Christensen, A.N., Cox, D., Lehman, M., Nonat, A., 1991. Structures cristallines de $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ et $\text{CaSO}_4 \cdot 0.6\text{H}_2\text{O}$, *C.R. Acad. Sci. Sér.*, 2 (312), Pp. 43–48.
- Boldyrev, V.V., 1993. Mechanochemistry and mechanical activation of solids. *Solid State Ionics.*, 63, Pp. 537.
- Breidenstein, A., Denkena, B., 2013. Influence of the residual stress state on cohesive damage of PVD-coated carbide cutting tools. *CIRP Annals – Manufacturing Technology*, 62, Pp. 67.
- Bye, G.C., 1983. *Portland Cement Composition, production and preparation*. 1st ed. Pergamon Press Ltd, Oxford, 1983.
- Chaix-Pluchery, O., Pannetier, J., Bouillot, J., Niepce, J.-C., 1987. Structural prereactional transformations in $\text{Ca}(\text{OH})_2$, *J. Solid State Chem.*, 67, Pp. 225–234.
- Colville, A. A., and Gelle, S., 1973. The crystal structure of brownmillerite, $\text{Ca}_2\text{FeAlO}_5$ [J]. *Acta Crystallogr.*, B (27), Pp. 2311–2315.
- Colville, A. A., Geller, S., 1972. The crystal structure of $\text{Ca}_2\text{Fe}_{1.43}\text{Al}_{0.57}\text{O}_5$ and $\text{Ca}_2\text{Fe}_{1.28}\text{Al}_{0.72}\text{O}_5$, *Acta Crystallogr.*, B (28), Pp. 3196–3200.
- Courtial, M., De Noirfontaine, M. N., Dunstetter, F., Gasecki, G., and Signes-Frehel, M. 2003. Polymorphism of tricalcium silicate in Portland cement: a fast visual identification of structure and superstructure. *Powder Diffraction*, 18 (1), Pp. 7-15.
- De la Torre, A.G., Cabeza, A., Calvente, A., Bruque, S., Aranda, M.A.G., 2001. Full phase analysis of portland clinker by penetrating synchrotron powder diffraction *Anal. Chem.*, 73 (2001) 151–156.
- De la Torre, A.G., De Vera, R.N., Cubero, A.J.M., Aranda, M.A.G., 2008. Crystal structure of low magnesium-content alite: application to Rietveld quantitative phase analysis, *Cem. Concr. Res.*, 38, Pp.1261–1269.
- De Noirfontaine, M. N., Dunstetter, F., Courtial, M., Gasecki, G., and Signes-Frehel, M., 2006. Polymorphism of tricalcium silicate, the major compound of Portland cement clinker: 2. Modelling alite for Rietveld analysis, an industrial challenge. *Cement and concrete research*, 36 (1), Pp. 54-64.
- Denkena B., Breidenstein, B., 2008. Significance of residual stress in PVD-coated carbide cutting tools. *Advanced Engineering Materials*, 10, Pp. 613.
- Dunstetter, F., De Noirfontaine, M.N., Courtial, M., 2006. Polymorphism of tricalcium silicate, the major compound of Portland cement clinker. 1. Structural data: review and unified analysis. *Cem. Concr. Res.*, 36, Pp. 39.
- Gutteridge, W.A., 1984. Quantitative X-ray powder diffraction in the study of some cementive materials, *Brit. Ceram. Proc.*, 35, Pp. 11–23.
- Hegeman, J.B.J.W., De Hosson, J.T.M., de With, G., 2001. Grinding of WC-Co hard metals, *Wear*, 248, Pp. 187.
- Huang, Q., Chmaissem, O., Caponi, J.J., Chaillout, C., Marezio, M., Tholence, J.L., 1994. Neutron powder diffraction study of the crystal structure of $\text{HgBa}_2\text{Ca}_4\text{Cu}_5\text{O}_{12+d}$ at room temperature and at 10 K, *Physica C*, 227, Pp. 1–9.
- Le Saoût, G., Kocaba, V., Scrivener, K., 2011. Application of the Rietveld method to the analysis of anhydrous cement, *Cem. Concr. Res.*, 41, Pp. 133–148.
- Leon-Reina, L., De la Torre, A. G., Porras-Vázquez, J. M., Cruz, M., Ordonez, L. M., Alcobé, X., Gispert-Guirado, F., Larranaga-Varga, A., Paul, M., Fuellmann, T., Schmidt, R., Aranda, M.A.G., 2009. Round robin on Rietveld quantitative phase analysis of Portland cements. *J. of App. Crystallogr.*, Pp. 0021-8898.
- Li, X., Xu, W., Wang, S., Tang, M., X. Shen, 2014. Effect of SO_3 and MgO on Portland cement clinker: Formation of clinker phases and alite polymorphism, *Construction and Building Materials*, 58, Pp. 182–192.
- Ludwig, H. M., Zhang, W., 2015. Research review of cement clinker chemistry, *Cem and Concr Res.*, 78, Pp. 24–37.
- M. Enders, Quantitative phase analysis, *World Cem.*, 2007, Pp.45–49.

- Maki, I., Chromy, S., 1978. Characterization of the alite phase in Portland cement clinker by microscopy II Cemento, 3, Pp. 252-274
- Maki, I., Fukuda, K., Yoshida, H., and Kumaki, J., 1992. Effect of MgO and SO₃ on the impurity concentration in alite in Portland cement clinker. *Journal of the American Ceramic Society*, 75 (11), Pp. 3163-3165.
- Maki, I., Kato, K., 1982/ Phase identification of alite in Portland cement clinker, *Cem. Concr. Res.* 12, Pp. 93- 100.
- Maslen, E.N., Strel'tsov, V.A., Strel'tsova, N.R., 1993. X-ray study of the electron density in calcite, CaCO₃, *Acta Crystallogr. B Struct.*, (49), Pp. 636-641.
- McGinnety, 1972. Redetermination of the structures of potassium sulfate and potassiumchromate: the effect of electrostatic crystal forces upon observed bond lengths, *Acta Crystallogr. B Struct.*, 28, Pp. 2845-2852.
- Mercury, J.M.R., De Aza, A.H., Turrillas, X., Pena, P., 2004. The synthesis mechanism of Ca₃Al₂O₆ from soft mechanochemically activated precursors studied by time-resolved neutron diffraction up to 1000 °C. *J. Solid State Chem.*, 177, Pp. 866.
- Mohamed, B., Haykel, G., Rabah, A., Marouene, B., Abdesslem, B. H. A., & Hafsia, B. R. (2017). Inter-comparative study of quantitative methods of industrial clinker. *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, 32, 1250-1260.
- Mohamed, B.M., Sharp, J.H, 1997. Kinetics and mechanism of formation of Monocalcium aluminate, CaAl₂O₄. *Journal of Materials Chemistry*, 7, Pp. 1595.
- Mondal, P., Jeffery, J.W., 1975. The cristal structure of tricalcium aluminate Ca₃Al₂O₆ [J]. *Acta cristallogr.*, B31, Pp. 689-697.
- Mumme, W.G., Hill, R.J., Bushnell-Wye, G., Segnit, E.R., 1995. Rietveld crystal structure refinement, crystal chemistry and calculated powder diffraction data for the polymorphs of dicalcium silicate and related phases, *Neues Jahrb. Mineral. Abh.*, 169, Pp. 35-68.
- N.V.Y. Scarlett, I. C. Madsen, C. Manias, D. Retallack, Online X-ray diffraction for quantitative phase analysis: application in the Portland cement industry. *Powder Diffr.*, 16, 2001. 71-80.
- Neubauer, J., Goetz-Neunhoeffler, F., Holland, U., Schmitt, D., Gaerberlein, P., and Degenkolb, M., 2007, July. Crystal chemistry and microstructure of hydrated phases occurring during early OPC hydration. In *Proceedings of the 12th International Congress on the Chemistry of Cement*, Montreal, Canada.
- Nishi, F., Takeuchi, Y., 1975. The Al₆O₁₈ rings of tetrahedra in the structure of Ca_{8.5}NaAl₆O₁₈, *Acta Crystallogr. B Struct.*, (31), Pp. 1169-1173.
- Pedersen, B.F., Semmingsen, D., 1982. Neutron diffraction refinement of the structure of gypsum, CaSO₄ (H₂O)₂, *Acta Crystallogr. B Struct.*, 38, Pp. 1074-1077.
- Perry, A.J., Geist, D.E., Narasimhan, K., Treglio, J.R, 1996. On the stress state in the surface of ground cemented carbide before and after metal ion implantation, *Surface and Coatings Technology*, 86- 87, Pp. 364.
- Peterson, V.K., Hunter, B.A., Ray, A., 2004. Tricalcium silicate T1 and T2 polymorphic investigations: Rietveld refinement at various temperatures using synchrotron powder diffraction, *J. Am. Ceram. Soc.*, 87, Pp. 1625-1634.
- Peterson, V.K., Ray, A.S., Hunter B. A., 2006. A comparative study of Rietveld phase analysis of cement clinker using neutron, laboratory X-ray, and synchrotron data, *Powder Diffract.*, 21, Pp. 12-18.
- Pilati T., Demartin, F., Gramaccioli, C.M., 1998. Lattice-dynamical estimation of atomic displacement parameters in carbonates: calcite and aragonite CaCO₃, dolomite CaMg(CO₃)₂, and magnesite MgCO₃, *Acta Crystallogr. B Struct.*, 54, Pp. 515-523.
- Pritula, O., Smrcok, L., Obbens D. M. T., Langer, V., 2004. X-ray and neutron Rietveld quantitative phase analysis of industrial Portland cement clinkers, *Pow. Diffrac.*, 19, Pp. 3, Pp. 232- 239.
- Rietveld, H. M. (1969). A profile refinement method for nuclear and magnetic structures. *Journal of applied Crystallography*, 2(2), 65-71. I. Maki, K. Goto, Factors influencing the phase constitution of alite in Portland cement clinker, *Cem Concr Res*, 12 (1982) (3):301-8.
- Sasaki, S., Fujino, K., Takeuchi, Y., 1979. X-ray determination of electron-density distribution in oxides, MgO, MnO, CoO, and NiO, and atomic scattering factors of their constituent atoms, *Proc. Jpn. Acad.*, 55, Pp. 43-48.
- Scrivener, K.L, Fullmann, T., Gallucci, E., Walenta, G., Bermejo, E., 2004. *Cement and Concrete Research*, 34, Pp. 1541-1547.
- Snellings, R., Bazzoni, A., Scrivener, K., 2014. The existence of amorphous phase in Portland cements: Physical factors affecting Rietveld quantitative phase analysis, *Cement and Concrete Research*, 59, Pp. 139-146.
- Stanek T., Sulovsky, P., 2002. The influence of the alite polymorphism on the strength of the Portland cement, *Cement and Concrete Research*, 32, Pp. 1169-1175.
- Taylor, H. F. W., 1997. *Cement Chemistry*. 2nd ed. Academic Press Thomas Telford: London, 1997.
- Tönshoff, H.K., Karpuschewski, B., Mohlfeld, A., Seegers, H., 1999. Influence of subsurface properties on the adhesion strength of sputtered hard coatings, *Surface and Coatings Technology*, 116-119, Pp. 524.
- Tönshoff, H.K., Seegers, H., 2001. X-ray diffraction characterization of pre-treated cemented carbides for optimizing adhesion strength of sputtered hard coatings, *Surface and Coatings Technology*, 142-144, Pp. 1100.
- Walenta, G., Füllmann, T., 2004. Advances in quantitative XRD analysis for clinker, cements, and cementitious additions, *Powder Diffract.*, 19, Pp. 40-44.
- Yang, J., Odén, M., Johansson-Jøesaarb, M.P., Llanesa, L., 2014. Grinding effects on surface integrity and mechanical strength of WC-Co cemented carbides, *Procedia CIRP* 13, Pp. 257 - 263.
- Yang, M., Guo, Z., Xiong, J., Liu, F., and Qi, K., 2017. Microstructural changes of (Ti, W) C solid solution induced by ball milling. *International Journal of Refractory Metals and Hard Materials*, 66, Pp. 83-87.
- Zhang, W., Ren, X., Ouyang, S., 2011. Development on ion substitution effect on the crystal structure and properties of tricalcium silicate, *J. Chin. Ceram. Soc.*, 39, Pp. 1666-1672.

