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Polymorphism of tricalcium silicate, the major compound of Portland cement clinker 2. Modelling alite for Rietveld analysis, an industrial challenge

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Abstract

A comprehensive quantification of the various phases of clinkers by X-ray diffraction with a Rietveld-like analysis is an important industrial challenge. Various available structural models are used for the most frequent M1 and M3 polymorphs of alite usually found in industrial clinkers, referred to as M1- or M3-based clinkers. In this paper, the effect of C_3S structural model is investigated. Four models are tested and compared using either synthetic M1 and M3 alites or M1- and M3-based clinkers. The comparison validates the available models for M1 and M3 alites and an average model, given here, derived from our recently proposed M1 structure as a catch-all model when the nature of the clinker is unknown. The latter model is meant to be used for industrial on-line quantification.

Keywords: Alite; Ca_3SiO_5; Clinker; Crystal structure; X-ray diffraction

1. Introduction

This paper is the second of a series of two. The first one was devoted to a review and a description of the various structural models available for pure tricalcium silicate or synthetic alite, with impurity contents on the order of a few percent. This second paper is meant to investigate the applicability of Rietveld analysis of X-ray diffraction data on real industrial products. The main object is the study of the effect of the choice of a given alite model on the final quantification of the multiphase compound produced in the cement kiln: the clinker.

Two distinct points of view can be considered. On one hand, a laboratory researcher is mainly interested in the relation between structure and properties: he looks for a reliable identification and subsequent quantification of the polymorph of alite present in a given clinker sample. On the other hand, an engineer working in an industrial context is mainly interested in a reliable on-line follow-up of his production, aimed at controlling the kiln. He is more concerned about the consistency of his production than about an exact knowledge of the polymorphs and will prefer a catch-all model with the minimum bias in the quantification in case of a fluctuation in the nature of the alite polymorph.

From these two points of view, two distinct questions arise:

- Q_1: for a given polymorph, what is the best structural model, i.e. the most sensitive to the real structure?
- Q_2: what is the best approximate model, i.e. the less sensitive to a possible variation of the structure?

In order to answer these questions, we investigate the effect of various models on industrial clinkers.

The paper is organised as follows. A first part deals with a rapid survey of the methods used in industry and the known studies. The second part presents the four structural models of

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alite used to refine the experimental data, the usual Nishi et al. model [1], a model slightly adapted from the literature [2] to describe the M3 alite, and two new models to describe M1 alite. The last part discusses the results and the bias introduced by the choice of an approximate model.

2. Quantification in industry: a very actual challenge

An important industrial problem is the variability of the mineralogy of clinkers which mainly depends on two factors: (i) impurities introduced either by the raw material extracted from the quarries or by the fuel and (ii) temperature effects inside the kiln and during the cooling process. These combined effects markedly influence the crystal morphology and structure of the clinker phases. Automatic control of this variability constitutes a major industrial challenge.

Up to now, the only method used in factories for on-line analysis of clinkers is X-ray fluorescence which provides an elementary analysis of the output. To go from the measured atomic concentrations to the phase concentrations, the Bogue procedure [3], later improved and usually referred to as the modified Bogue calculation [4,5] is used; together with the knowledge of the free lime content, it gives an estimate of the content of the clinker phases. The main point is that such an analysis only leads to a rough estimate of the atomic content of the phases, without any information on their polymorphic form. These results can be checked by point counting using optical microscopy which is often a powerful tool to relate the microscopic observations to the steps of the whole process. However, point counting requires a lot of time and manpower, which can neither be systematised nor be introduced in a factory.

X-ray diffraction (XRD) has been used for a long time as a complementary tool, able to provide information on the nature and possibly quantify the polymorphs. But, until the recent introduction of tractable computers and software, only specialists in their laboratories used this method, with good results, see e.g. [6,7]. The XRD quantitative analysis mainly used the internal standard method. A major difficulty arises from the high degree of overlapping of the Bragg peaks in the powder patterns of the major phases, which reduces the domain of applicability of the traditional XRD peak area measurement, based on integrated intensity ratios.

A recent method, the Rietveld analysis, is able to deconvoluate the different peaks of the diffraction pattern, provided a good structural model is known for each phase of the mixture [8]. Starting from a known structural model, structure factors and intensities can be computed.

Table 1
Structural models of alite used in literature for Rietveld analyses of clinkers

Structural model of alite	Clinker refinement study	
	(Industrial or NIST reference clinkers)	Reference
Average monoclinic structure ⟨M⟩*Am* (Mumme 1995 [2])	Industrial	Mumme 1995 [2]
	NIST (8486–8487–8488)	Taylor et al. 2000 [14]
	Industrial	de Noirfontaine 2000 [15]
	NIST (8486–8487–8488)	Pritula et al. 2003 [16]
M3 superstructure 6⟨M⟩*Cm* (*Im*) (Nishi et al. 1985 [1])	Industrial	Neubauer et al. 1997 [17]
	NIST (8486)	Stutzman and Leigh 2000 [18]
	Industrial	de Noirfontaine 2000 [15]
	Industrial	De la Torre et al. 2001 [19]
M3-like superstructures (Berliner et al. 1997 [9], De la Torre et al. 2002 [10])	Industrial	De la Torre et al. 2002 [10]
Pseudo-rhombohedral structure (Moller 1995 [11])	Industrial and NIST (8486–8487–8488)	Moller 1995 [11]
Rhombohedral structure **R** (Il'inets and Malinovskii 1985 [12])	NIST (8486–8487–8488)	Taylor et al. 2000 [14]
Triclinic structure **T** (Golovastikov et al. 1975 [13])	NIST (8486–8487–8488)	Taylor et al. 2000 [14]
Various mixtures: ⟨M⟩+R, R+T, ⟨M⟩+T, R+⟨M⟩+T	NIST (8486–8487–8488)	Taylor et al. 2000 [14]

Table 2
Structural models used for the phases of clinkers in this study

Phase	Unit cell space group	Model used	Cell parameters	Atoms (a.u.)	*Z*
Alite (C_3S)	⟨M⟩*Pc*	our model in Table 3	a=9.2952 Å b=7.0792 Å c=12.2214 Å β=116.08°	27	6
	⟨M⟩*Am*	our model in Table 4	a=9.261855 Å b=7.055248 Å c=12.418528 Å β =116.077652°	34	6
	3⟨M⟩*Pc*	our model to be submitted [22]	a=27.873 Å b=7.059 Å c=12.257 Å β =116.03°	81	18
	6⟨M⟩*Im*	model of Nishi et al. [1], without atomic splitting	a=18.517944 Å b=7.032959 Å c=36.694286 Å β =116.037842°	172	36
Belite (β-C_2S)	$P2_1/n$	Mumme et al. 1995 [23]		7	4
C_3A	*Pa3*	Mondal and Jeffery 1975 [24]		14	24
C_4AF	*Ibm2*	Colville and Geller 1972 [25]		8	4

The models used for alite were refined on synthetic alites.
The two last columns give the number of atoms in the asymmetric unit and the number *Z* of formula units per unit cell.

Table 3
⟨M⟩*Pc* structural model

Atom name	*x*	*y*	*z*	Atom (Mumme [2])
Ca1	0.00673	−0.00135	0.02101	Ca3
Ca2	0.00461	0.50018	0.00877	Ca3
Ca3	0.33163	0.46938	0.79072	Ca1
Ca4	0.34468	−0.00177	0.78102	Ca1
Ca5	0.68814	0.75656	0.48510	Ca4
Ca6	0.00432	0.72678	0.25164	Ca6
Ca7	0.33340	0.75241	0.04818	Ca5
Ca8	0.67364	0.48519	0.72551	Ca2
Ca9	0.67660	0.03480	0.73504	Ca2
O1	0.89208	0.76109	0.38270	O7
O2	0.11092	0.72811	0.10560	O8
O3	0.49178	0.74341	0.26204	O2
Si1	0.98719	0.24241	0.24612	Si1
O11	0.79454	0.26095	0.16979	
O12	0.07350	0.37868	0.18630	
O13	0.04050	0.30451	0.38624	
O14	0.04020	0.02548	0.24213	
Si2	0.65602	0.26293	0.47553	Si2
O21	0.46226	0.27026	0.40448	
O22	0.73000	0.44655	0.43940	
O23	0.71204	0.26185	0.62120	
O24	0.71976	0.07304	0.43702	
Si3	0.35057	0.25183	0.02188	Si3
O31	0.20556	0.09976	−0.02526	
O32	0.37761	0.32745	−0.09283	
O33	0.30588	0.42801	0.08584	
O34	0.51323	0.15210	0.11978	

Refined atoms parameters for M1 alite, on the basis of Rietveld refinement of X-ray diffraction data of M1 synthetic alite. For all the atoms, Biso~2 Å^2 and occupancy=1. The last column indicates the numbering of the atoms in the Mumme model [2]. Since the order of space group *Am* is higher than that of space group *Pc*, some atoms equivalent in the *Am* space group (e.g. Ca3) correspond to non equivalent atoms in the *Pc* space group (Ca1 and Ca2).

Then, modelling the line width makes it possible to compute the profile and extract the contribution of any Bragg line to the diffraction pattern. The contribution of all the Bragg lines can be added at each point of the diffraction diagram. Either instrumental parameters, such as line width, angular offsets or background or structural parameters, such as lattice parameters, atomic positions or thermal factors, can be refined in order to reproduce the experimental data. It must be noticed that the structural parameters are refined only by starting from a model. Under no circumstances is it possible to solve an unknown structure for such complex compounds, since no individual integrated intensity is available from the mixture of lines found in the diffraction patterns.

The quality of the result is monitored by various statistical agreement factors, inspection of the agreement between observed and calculated patterns, or comparison with the results of alternative methods discussed above. But, in the last case, a new and very important question is raised, concerning the relative precision of the various methods and the limits of such a comparison. Each method has its own intrinsic limitations. The amount and the scale of observation of examined material are different. The statistics of the observations and the possibility to point out the various species are different. Therefore, it is not sufficient to apply two methods or more and try to justify the possible discrepancies. It is also necessary to estimate the intrinsic precision of each method. A very complete review of all these problems is given in [7].

Concerning XRD, various structural models of alite have been used in the literature for Rietveld quantitative analyses of clinkers since 1995 (Table 1). The reliability of the refinements has been estimated both by using the agreement crystallographic factors and by comparing the quantitative analyses with other techniques (X-ray fluorescence and optical microscopy). But the available structural models of alite have not been tested and compared for the same sample and the procedure of Rietveld refinements changes from one study to another (different softwares and refinement strategies). Therefore, one cannot easily decide what part

Table 4
⟨M⟩*Am* structural model

Atom	*x*	*y*	*z*	Occ.	Biso (Å^2)	Atom (Mumme [2])
Ca1	0.35381	0.73883	0.00635	1	2.7	Ca1
Ca2	0.70492	0.26658	0.96947	1	2.7	Ca2
Ca3	0.03187	0.77133	0.23331	1	2.7	Ca3
Ca4	0.68687	0.50000	0.20076	1	2.7	Ca4
Ca5	0.35701	0.50000	0.78572	1	2.7	Ca5
Ca6	0.00869	0.50000	−0.02413	1	2.7	Ca6
O1	0.49332	0.50000	0.01106	1	3.5	O2
O2	0.92873	0.50000	0.13516	1	3.5	O7
O3	0.16384	0.00000	0.35813	1	3.5	O8
Si11 (1G)	0.03020	0.00000	0.02605	0.4	2.7	Si1
O11	−0.16430	−0.01083	−0.04115	0.4	3.5	
O12	0.09756	0.02957	−0.07468	0.4	3.5	
O13	0.08597	0.17715	0.12027	0.4	3.5	
O14	0.10156	−0.19588	0.09977	0.4	3.5	
Si12 (1D)	0.03139	0.00000	−0.02842	0.5	2.7	Si1
O15	−0.13664	0.00000	−0.15121	0.5	3.5	
O16	−0.00542	0.00000	0.08942	0.5	3.5	
O17	0.13381	−0.18807	−0.02595	0.5	3.5	
Si13 (1U)	0.01303	0.00000	−0.02795	0.1	2.7	Si1(U)
O18	0.01670	0.00000	0.10571	0.1	3.5	
O19	−0.17178	0.00000	−0.13113	0.1	3.5	
O110	0.10359	0.18807	−0.04318	0.1	3.5	
Si2 (2D)	0.67162	0.00000	0.20407	1	2.0	Si2(D)
O21	0.47688	0.00000	0.13764	1	2.0	
O22	0.73413	0.00000	0.35028	1	2.0	
O23	0.73773	−0.18807	0.16417	1	2.0	
Si31 (3U)	0.37291	0.00000	0.76266	0.9	2.7	Si3(U)
O31	0.19354	0.00000	0.65148	0.9	3.5	
O32	0.50422	0.00000	0.70846	0.9	3.5	
O33	0.39694	0.18807	0.84535	0.9	3.5	
Si32 (3D)	0.35806	0.00000	0.79262	0.1	2.7	Si3
O34	0.32682	0.00000	0.91298	0.1	3.5	
O35	0.18724	0.00000	0.67226	0.1	3.5	
O36	0.45909	0.18807	0.79262	0.1	3.5	

Refined atom parameters for M3 alite, on the basis of Rietveld refinement of X-ray diffraction data of M3 synthetic alite. The *Cm* space group can be used: swap *x* and *z* and the corresponding unit cell parameters.

Table 5

	6⟨M⟩*Im*			⟨M⟩*Am*			⟨M⟩*Pc*			3⟨M⟩*Pc*		
	R_B	R_F	wt.%	R_B	R_F	wt.%	R_B	R_F	wt.%	R_B	R_F	wt.%
A. Clinker A: M3-based												
C_3S	8.9	6.7	43.0(0.4)	9.7	6.8	47.5(0.5)	7.6	6.4	46.1(0.4)	8.2	7.0	48.2(0.4)
C_2S	12.9	6.6	20.5(0.4)	19.5	10.4	16.0(0.3)	12.9	7.1	18.4(0.3)	11.7	6.6	16.9(0.3)
C_3A	9.7	6.2	4.8(0.2)	14.0	9.7	3.7(0.1)	10.7	7.6	3.5(0.1)	11.2	7.3	3.6(0.1)
C_4AF	12.0	6.6	5.5(0.1)	13.5	8.9	5.7(0.2)	11.8	7.4	5.8(0.2)	11.6	7.1	5.6(0.2)
Al_2O_3	9.3	4.5	24.0(0.3)	8.7	4.3	24.8(0.4)	8.5	4.7	23.6(0.3)	10.0	5.1	23.3(0.3)
MgO	6.1	3.8	2.2(0.1)	6.2	3.8	2.3(0.2)	2.3	1.7	2.6(0.1)	4.2	2.5	2.4(0.1)
χ^2	12.7			18.8			12.8			12.9		
C_3S/C_2S ratio	2.1			3.0			2.5			2.9		
B. Clinker B: M1-based												
C_3S	10.6	7.3	49.0(0.5)	13.3	8.6	52.7(0.5)	9.8	7.3	53.2(0.4)	10.1	7.0	55.4(0.5)
C_2S	15.0	7.1	13.8(0.4)	17.8	9.5	11.7(0.4)	14.3	7.6	10.7(0.3)	12.3	6.4	9.7(0.3)
C_3A	9.1	6.4	6.0(0.2)	16.2	11.3	4.1(0.2)	13.1	9.4	4.5(0.1)	12.6	7.9	4.3(0.1)
C_4AF	12.2	7.1	5.5(.1)	13.8	9.0	5.3(0.2)	12.3	8.0	5.7(0.2)	11.0	6.7	5.7(0.1)
Al_2O_3	5.8	3.2	25.7(.3)	5.8	3.6	26.2(0.4)	6.3	3.9	25.9(0.3)	7.0	4.0	24.9(0.3)
χ^2	19.7			21.3			14.8			14.6		
C_3S/C_2S ratio	3.5			4.5			4.9			5.7		

Results of Rietveld refinements of X-ray data. Angular domain: $2\theta_{Cu}$=10–70°.

is played by the very choice of a given structural model on the refinement results.

In the present paper, various structural models of alite (including recent proposed models) are tested in a systematic way, with the same refinement procedure, on two clinkers: M1-based and M3-based clinkers. We discuss the fluctuations of the results of Rietveld analyses of XRD data as a function of the available parameters of the problem: the choice of the structural model, the connection with other instrumental parameters and the subsequent bias in the analyses introduced by the choice of an approximate structural model, in order to answer to the two questions raised in the introduction.

3. Experimental

3.1. Samples

Two different clinkers have been selected, one is a M3-based clinker and the second is a M1-based clinker (clinker A and clinker B). As recalled in the first paper, the amount and the nature of the impurities are not the same for the two polymorphs. The detailed chemical analyses can be found in reference [20]: the major impurities are MgO and SO_3, with 0.76 wt.% of MgO and 0.88 wt.% of SO_3 for M1-based clinker (clinker B), and 3.76 wt.% of MgO and 1.23 wt.% of SO_3 for M3-based clinker (clinker A). The clinker A was found to contain periclase.

A detailed analysis of all the Bragg lines characteristic of each M1 and M3 polymorph was made in order to determine the nature of the alite polymorphs present in these clinkers [20]. The powder X-ray diffraction data were collected with a Philips diffractometer system, in Bragg Brentano geometry (Cu radiation, λ=1.5405 Å) in the range $10<2\theta<80°$, with step intervals of 0.02° (2θ) and fixed-time counting of 10 s. Al_2O_3 was used as an internal reference. Both samples were registered consecutively with the same conditions and the same sample holder.

3.2. Structural models

For each clinker, the models of the superstructures and average structures of alite were tested (Table 2): ⟨M⟩*Pc*, ⟨M⟩*Am* for the average structural models and, 3⟨M⟩*Pc*, 6⟨M⟩*Im* for the superstructures. These models are determined from the refinements of M1 and M3 synthetic alites data, with a treatment of the silicates as rigid bodies, except for the case of the M3 superstructure[1]. The ⟨M⟩*Pc* model is our average model for the M1 alite, given in Table 3. The ⟨M⟩*Am* model is similar to the Mumme model, except for the silicates (Table 4) [21]. The 3⟨M⟩*Pc* model is our model for M1 synthetic alite [22]. The 6⟨M⟩*Im* model is similar to that of Nishi et al. for M3 alite, except for the atomic splitting, which does not significantly affect the powder diffractograms.

The C_2S phase usually found in clinkers is the β monoclinic form. The crystal structure recently proposed by Mumme et al. for β-C_2S [23] was used in our refinements. To refine the C_3A and C_4AF phases, the atomic parameters given respectively by Mondal and Jeffery [24] and Colville and Geller [25] have been used.

[1] As observed in other models with a smaller unit cell, better results are expected when using rigid body refinement of the M3 superstructure. This is not possible with the two refinement programs we used because they are limited in the number of atoms or rigid bodies.

3.3. Refinement strategy

The X-ray data were refined by Rietveld analysis using either the Fullprof [26] and GSAS [27] programs, with similar results.

In all the refinements, a pseudo-Voigt profile shape function (expressed by a weighted sum of Gaussian and Lorentzian functions) was chosen. Scale factors, instrumental values (zero, background, peak halfwidth parameters) and cell parameters were refined. Atomic positions were not refined.

All the results are presented together in Table 5A and B and Figs. 1–4. The two clinkers A and B are refined by using the four models $6\langle M\rangle Im$, $\langle M\rangle Am$, $\langle M\rangle Pc$ and $3\langle M\rangle Pc$ previously described. The crystallographic residues R_B and R_F–respectively sensitive to strong and weak Bragg lines–χ^2 and C_3S/C_2S ratio are sketched at Figs. 3 and 4. All the refinement residues are detailed in reference [20].

4. Discussion

It is now possible to answer the two questions Q_1 and Q_2 raised in the introduction: what are the structural models, which are the most and the less sensitive with respect to the real structure, respectively efficient for an identification of the alite polymorph or to a quantification without identification of the polymorph.

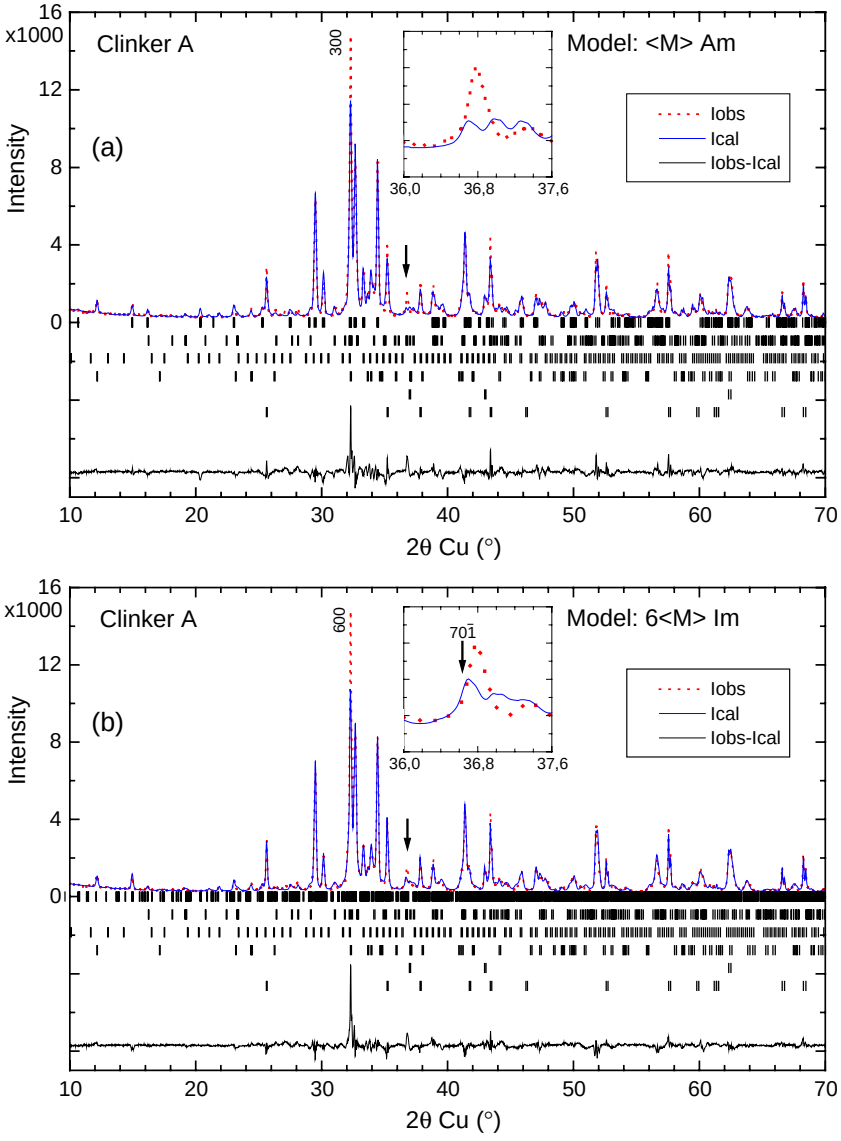

Fig. 1. Rietveld refinement of X-ray data of a sample of clinker A (M3-based), in the range $2\theta_{Cu}$=10–70°. The models used for alite are (Table 2): $\langle M\rangle Am$ average unit cell. (b) $6\langle M\rangle Im$ superstructure. The Bragg reflection markers correspond, from top to bottom, to alite, β-C_2S, C_3A, C_4AF, MgO and Al_2O_3 (internal standard). The arrow marks the characteristic superstructure Bragg line of the $6\langle M\rangle Im$ structure, magnified in the insert.

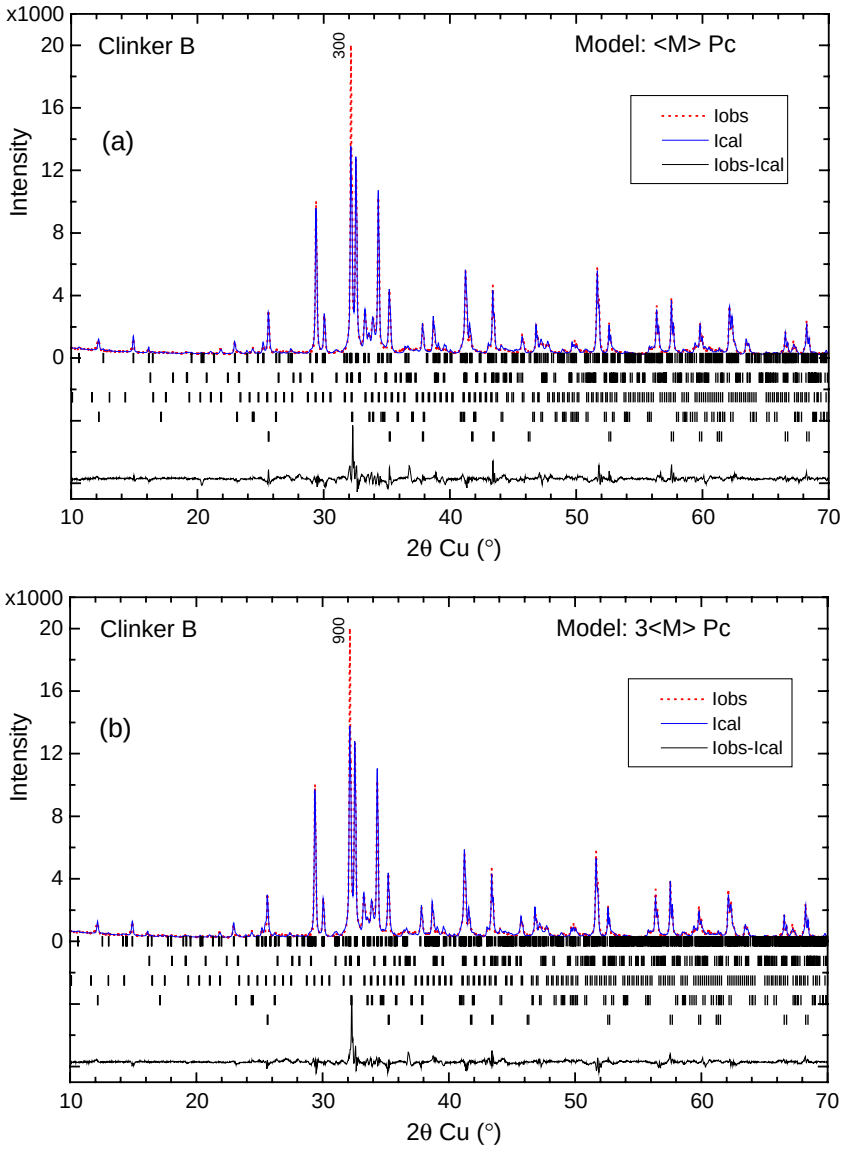

Fig. 2. Rietveld refinement of X-ray data of a sample of clinker B (M1-based), in the range $2\theta_{Cu}$=10–70°. The models used for alite are (Table 2): (a) ⟨M⟩*Pc* average unit cell. (b) 3⟨M⟩*Pc* superstructure. The Bragg reflection markers correspond, from top to bottom, to alite, β-C_2S, C_3A, C_4AF, MgO and Al_2O_3 (internal standard).

4.1. Identification approach

Question Q_1 is: what is the best model for identifying and quantifying the polymorph?

4.1.1. M3-based clinker

The distinction between the two M3-based structures, 6⟨M⟩*Im* and ⟨M⟩*Am* is clear. By examining the weak superstructure Bragg lines [20], one finds the 6⟨M⟩*Im* structure. Table 5A also shows the best refinement we obtained by using this structure. The structure ⟨M⟩*Am* is not convenient. The most characteristic superstructure Bragg lines $70\bar{1}$ of the 6⟨M⟩*Im* structure (arrow on Fig. 1) is not perfectly reproduced by the model. As mentioned in footnote 1, better results are expected with a rigid body refinement of the silicate ions. However, the superstructure is clearly identified by the Rietveld refinement due to the presence of several other Bragg lines characteristic of the 6⟨M⟩*Im* superstructure [20]; among them, the $70\bar{1}$ is fairly strong, completely isolated and well identified.

It is much more difficult to distinguish between M1-based and M3-based structure only on the basis of the crystallographic residue. Without a direct visual observation of the characteristic 6⟨M⟩*Im* Bragg lines, both M1-based models may also be retained: the 3⟨M⟩*Pc* and ⟨M⟩*Pc* models both generate Bragg lines at the 6⟨M⟩*Im* $70\bar{1}$ position, which explains the difficulty to separate them.

4.1.2. M1-based clinker

Table 5B shows the best refinements with two possible structures: ⟨M⟩*Pc* and 3⟨M⟩*Pc*. The M3-based models are here clearly excluded. The distinction between the two M1-

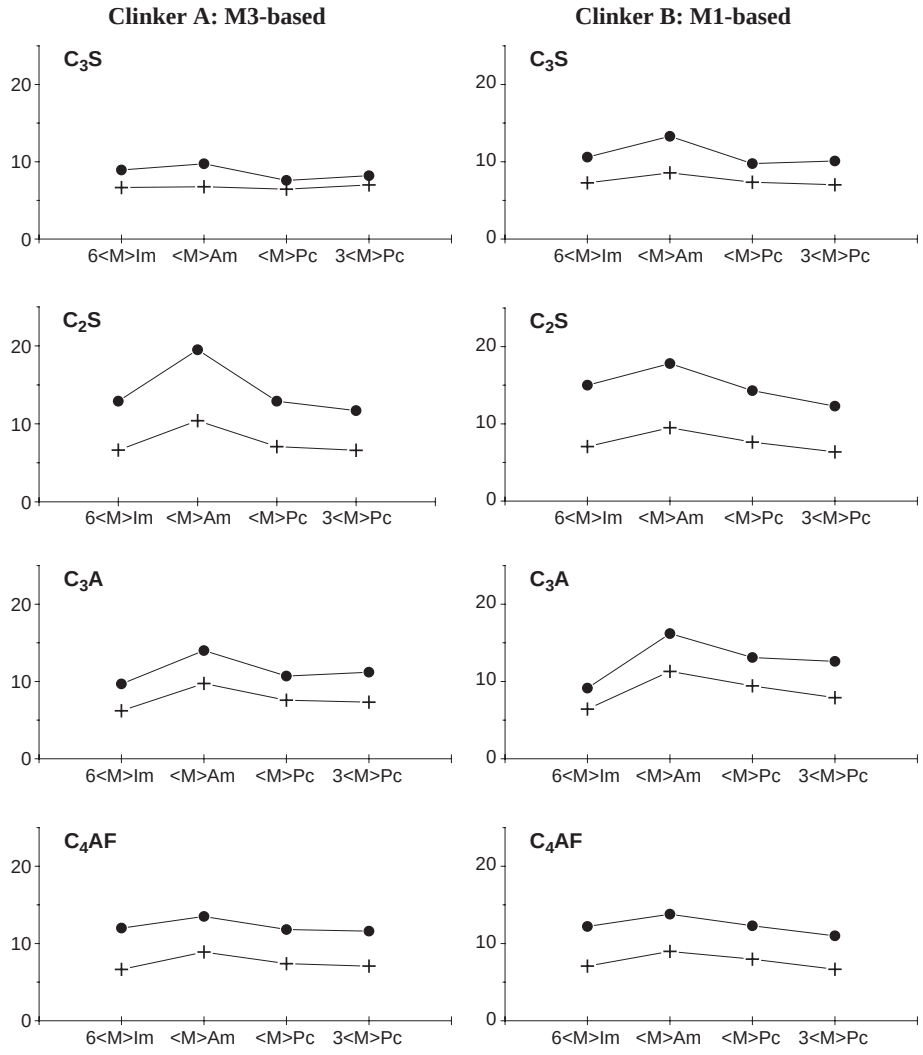

Fig. 3. Crystallographic residues R_B (circles) and R_F (crosses) for each phase of the clinker as a function of the model used to refine the C_3S phase.

based models is rather difficult: the residues are slightly better for $3\langle M\rangle Pc$, but a direct visual inspection of the diffraction pattern is in favour of $\langle M\rangle Pc$, due to the lack of the characteristic superstructure lines $21\bar{3}$ and $41\bar{3}$ of the $3\langle M\rangle Pc$ structure. In fact, these Bragg lines (at the same position) constitute the only well isolated superstructure line

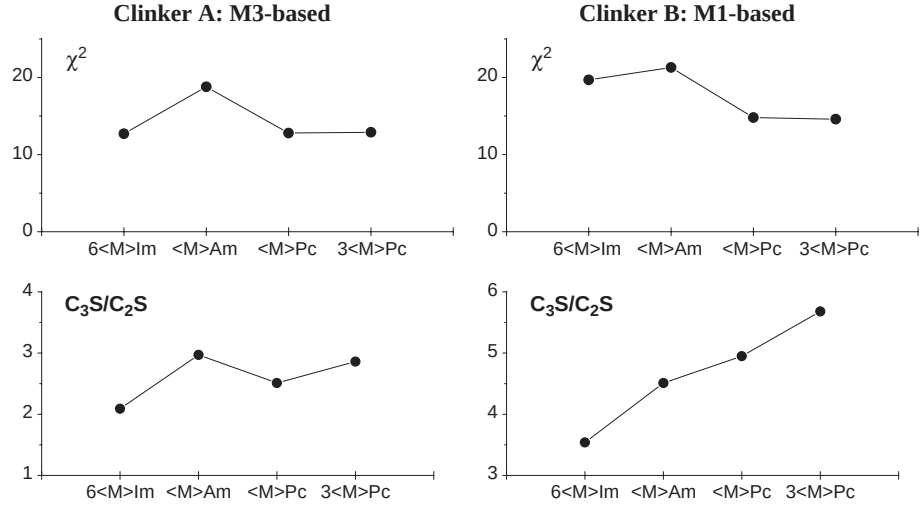

Fig. 4. χ^2 and C_3S/C_2S ratio as a function of the model used to refine the C_3S phase.

and are significantly weaker than the $70\bar{1}$ Bragg line of the $6\langle M\rangle Im$ structure. Therefore, the Rietveld refinement is not able to cut a clear distinction between these two models. For the M1 polymorph, the limit of the ability of the Rietveld refinement to point out the superstructure seems to be attained.

The answer to question Q_1 is: On the basis of the refinement residues only, it is not easy to decide which model is the best one. Additional inspection of the diffractogram and complementary chemical analyses (impurities) are necessary.

4.2. Approach without identification

Question Q_2 is: what is the most universal model, whatever the polymorph?

As already mentioned in the previous paragraph, and clearly seen on the χ^2-plot of Fig. 4, the $\langle M\rangle Am$ model is always the worst. With respect to the χ^2 values, the three other models are similar for the clinker A, whereas the $\langle M\rangle Pc$ and $3\langle M\rangle Pc$ models are similar for clinker B. If one is interested in a "universal" model, the $6\langle M\rangle Im$ model is excluded, since only valuable for clinker A.

The two remaining models $\langle M\rangle Pc$ and $3\langle M\rangle Pc$ are rather similar with respect to the χ^2 values.

If one now considers the C_3S/C_2S ratio, the approach is slightly different from that of the previous paragraph. Here, without any additional knowledge on the real structure, there is no real way to choose among the models. The most stable result with respect to the C_3S/C_2S ratio determination is expected for the model who will be located in between the two types of clinkers, in order to be able to handle any mixture.

The bias between the two clinkers and the $3\langle M\rangle Pc$ model is always the same, with a systematic overestimation of the C_3S/C_2S ratio. At the opposite, the $\langle M\rangle Pc$ model overestimates the ratio for a clinker A with $6\langle M\rangle Im$ structure and underestimates the ratio for a clinker B with $3\langle M\rangle Pc$ structure. For this reason, it clearly appears to introduce the minimal bias, especially for a mixture, where the balance of the bias may even produce a rather good estimation of the C_3S/C_2S ratio.

Another additional (but not sufficient in itself) argument for this choice is the greater simplicity of the $\langle M\rangle Pc$ model.

The answer to question Q_2 is unambiguous: the $\langle M\rangle Pc$ model is the best one.

It is now interesting to answer the following questions, already partially discussed:

a. Why is model $\langle M\rangle Pc$ able to refine both M1 and M3 alites?
   - Because models $\langle M\rangle Pc$ and $3\langle M\rangle Pc$ are very similar and
   - because the well defined superstructure Bragg lines of alite M3 are simulated by some lines introduced by the *Pc* space group and not by the *Am* space group. Therefore, model $\langle M\rangle Pc$ is fairly versatile since it generates Bragg peaks at the right place, albeit the intensities be not perfectly reproduced. For this reason, this model can be used for the treatment of the M1/M3 polymorphs mixtures often found in real industrial clinkers.

b. Why does model $\langle M\rangle Am$ always give worse results than model $\langle M\rangle Pc$ does? Part of the diffractogram ($2\theta_{Cu}$-range: 24.5° to 28.5°) is very badly reproduced for both M1 and M3 alites. The characteristic superstructure Bragg lines of the M3 alite are also very badly reproduced in the 36° to 37.5° $2\theta_{Cu}$-range.

The last question is the influence of an approximate model on the refinement parameters.

4.3. Bias introduced by the choice of an approximate model

4.3.1. Bias introduced on the quantification

Fig. 3 and Table 5 show how the choice of different models for the C_3S phase influences the crystallographic residues R_B and R_F of all the phases of the clinkers. Fig. 4 shows the effect on χ^2 and the C_3S/C_2S ratio, with the same tendency. However, the χ^2 values are dependent on the experimental conditions and cannot be used as a reliable comparison tool between distinct experiments. The crystallographic residues R_B and R_F are more interesting for such comparison.

An important point is that using an approximate model mainly modifies the residues and the compositions of the other phases, mainly the error on the ratio C_3S/C_2S (Fig. 4), up to 50%.

For the M3-based clinker, A, the examination of χ^2 only does not allow to distinguish between the $6\langle M\rangle Im$, $\langle M\rangle Pc$ and $3\langle M\rangle Pc$ models, whereas the composition is strongly affected: this clearly shows that an accurate quantification needs the use of the right $6\langle M\rangle Im$ model.

For the M1-based clinker, B, the examination of χ^2 only seems efficient to eliminate the M3-based models, but not to choose among the M1-based models.

The choice of model $\langle M\rangle Am$ mainly affects the refined models of C_2S and C_3A. In all the cases, this model is quite rejected and may be difficult to use in an industrial context without a careful control.

4.3.2. Bias introduced on the refinement parameters of alite

Fig. 5 sketches the effects of the four structural models on two very important refined parameters of the Rietveld method: the line-width HW (half-width) and the background BKG (refined with a polynomial expansion). Since the case of clinker with several compounds is more complicated due to the high number of parameters, we have chosen here the simpler case of synthetic alites M1 and M3 described in reference [20]. The best model is $3\langle M\rangle Pc$ for alite M1 and $6\langle M\rangle Im$ for alite M3. The $\langle M\rangle Am$ model, always the worst, introduces very strong bias on the line width, especially in

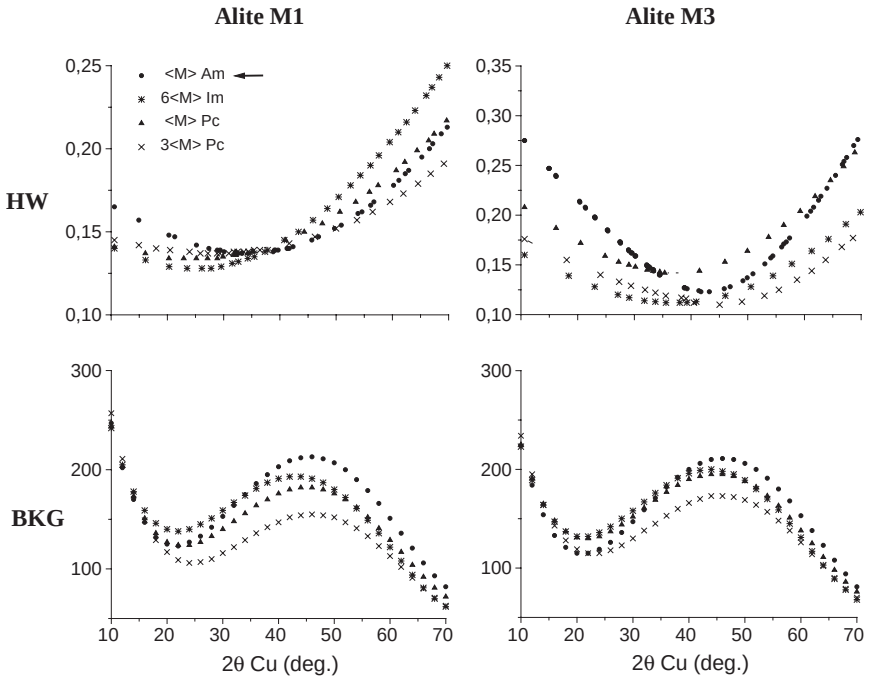

Fig. 5. Effect of the structural model on the line-width and the background for experiences and refinements made in the same conditions. Synthetic alites M1 and M3 are refined using the various models discussed in the text: $\langle M\rangle Pc$, $3\langle M\rangle Pc$, $\langle M\rangle Am$ and $6\langle M\rangle Im$. The arrow marks the worst model, the same for both alites.

the low angle range and increases the background in all the angular range. When the model does not give enough Bragg lines or lead to ill-located lines, the effect is obviously to compensate the missing lines by increases of the line-widths and of the background.

Another parameter often difficult to choose is the temperature factor B. Single crystal studies produce a distinct value for each atom. It is difficult to decide which value can be chosen in the Rietveld refinement. Fig. 6 shows the effect of the temperature factor. Each curve is related to a refinement with the same B_{iso} value for all the atoms. Three values B=0.5, B=1.5, B=2 Å^2 are chosen. These values cover quite the whole range of B values found in the single crystal experiments found in the literature for

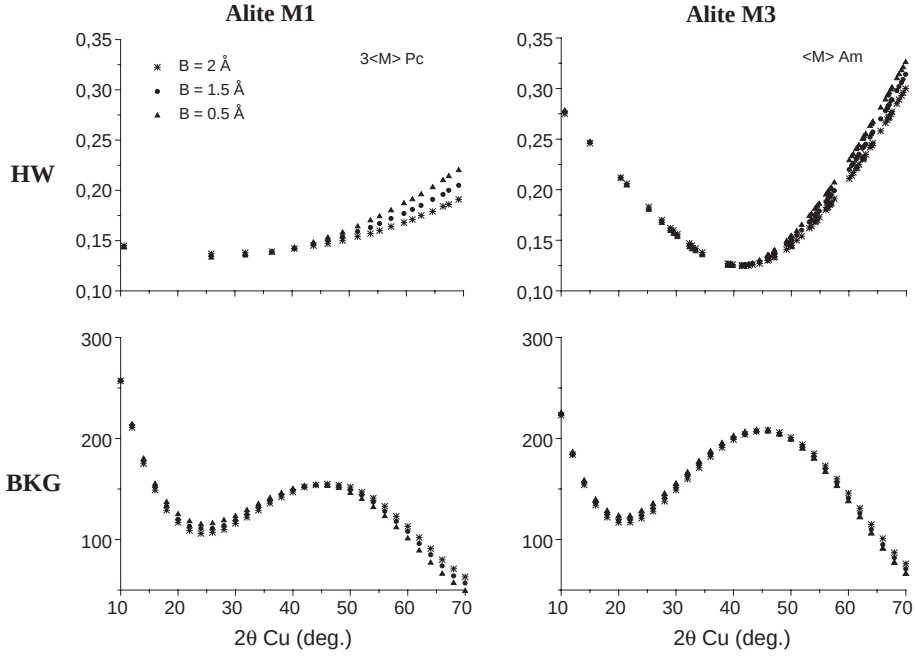

Fig. 6. Effect of the temperature factor B in two extreme cases: for the best model ($3\langle M\rangle Pc$ for alite M1) and the worst model ($\langle M\rangle Am$ for alite M3).

various alite polymorphs. Two extreme cases are shown: the best case (alite M1 with $3\langle M\rangle Pc$ model) and the worst one (alite M3 with model $\langle M\rangle Am$).

The effect of the temperature factor is "certainly" very small compared to that of the choice of the model (Fig. 5) especially for the background.

A final interesting effect is the bump[2] observed on the refined background for both alites whatever the model is. Such a bump may be induced by an inaccurate modelling of the line shape or by the process used in computing the background. Alite is not supposed to exhibit an amorphous component. In clinkers, the aluminates are sometimes suspected to contain an amorphous component. It seems fairly risky to justify a bump in the "background", whatever its actual origin, only by such an amorphous component.

5. Conclusion

- The identification of the M1 or M3 polymorph in industrial clinkers by X-ray diffraction with Rietveld analysis must be supported by an additional inspection of the X-ray diagram (see the five angular windows described in [20]). Several variations of two models for the M3 polymorph can be found in the literature. Here we propose a new model for the M1 polymorph. In fact, this model is convenient whatever the polymorph and can be used in the case of a M1/M3 mixture.
- The R_B and R_F residues (and not only the χ^2) of the various phases of the clinker must be used to select the proper M1 or M3 structural models.
- An approximate model introduces bias on the background and the line-width.
- From a practical point of view:
- in the laboratory context, a visual inspection of the adequate angular windows [20] makes it possible to choose the proper structural model
- in the industrial context, the $\langle M\rangle Pc$ model can be used whatever the real alite composition: M1, M3 or M1/M3.

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[2] Such a bump, if it really exists, may be seen as a broad diffuse ring; i.e. the (liquid-like) thick outer surface of a sphere in the reciprocal space. It may result either from an amorphous component, or from the correlation between disordered but correlated first neighbour silicates (as can be found in molecular systems). A powder XRD experiment is not able to answer such a question.

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