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Where is the iron? Clinker microanalysis with XRD Rietveld, optical microscopy/point counting, Bogue and SEM-EDS techniques

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Abstract

This paper presents the use of different techniques to assess the amounts of the main mineralogical phases in Portland cement clinker. The amounts measured by quantitative XRD analysis (Rietveld) show differences when compared to the Bogue calculation and this is particularly notable for the ferrite phase within certain clinkers. The amount of elemental substitution within the major clinker phases was determined by SEM-EDS microanalyses and the results show that defined amounts of iron oxide can be incorporated within the alite, belite and aluminate phases. Therefore even if a significant amount of the ferrite phase is expected due to the Bogue calculation, it is quite possible that less or no ferrite will be formed during clinker production.
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1. Introduction

This particular study results from previous work by Lafarge whereby the XRD Rietveld Method has been assessed as a quality control technique for the production of industrial clinkers [1,2].

There are three commonly available methods for the quantification of the phase composition of Portland cement clinker (in terms of its four major phases alite, belite, aluminate and ferrite): quantitative X-ray diffraction analysis, optical microscopy using point counting and the Bogue Method.

The European Bogue Calculation (a standard method based on the elemental composition of the clinker), calculates the potential phase composition and predicts the relative amounts of the four major clinker phases. The Bogue Method is based on simple chemical assumptions, but is not itself an analytical tool for the measurement of the actual phase composition of a real clinker [3]. This calculation can therefore give very misleading results since it assumes that equilibrium conditions are achieved during clinker production, and that the composition of the four major phases in the clinker are C_3S, C_2S, C_3A and C_4AF.[1] The Bogue Method does not account for the incorporation of foreign ions within the structures, or for the occurrence of different solid solutions. As reported by Taylor [4] the traditional clinker phases are not pure phases, but solid solutions. Typical compositions are:

- *Alite is not C_3S* but: [3(Ca 0.98 Mg 0.01 Al 0.067 Fe 0.0033)] [(Si 0.97 Al 0.03)] O_5
- *Belite is not C_2S* but: [2(Ca 0.975 K 0.01 Na 0.05 Mg 0.01)] [(Fe 0.02 Al 0.06 Si 0.9 P 0.01 S0.01)] $O_{3.9}$
- *Aluminate is not C_3A* but: [3(K 0.03 Na 0.06 Ca 2.76 Mg 0.08 Ti 0.01)] [(Fe 0.22 Al 1.6 Si 0.18)]O_6 *Cubic* [3(Na 0.292 Ca 2.792)] [(Fe0.15 Al 1.725 Si 0.125)] O_6 *Orthorhombic*
- *Ferrite is not C_4AF* but: $Ca_2(Al_XFe_{2-X})_2O_5$ — For example: Ca_2Al Fe 0.6 Mg 0.2 Si 0.15 Ti 0.05 O_5

Previous research, as reported by Taylor [4], shows that the Bogue calculation generally underestimates the alite content

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[1] Cement Chemistry notation: C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3. alite, belite, aluminate and ferrite are impure forms of C_3S, C_2S, C_3A and C_4AF and which contain minor elements substituted within the crystal structures.

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Table 1
Chemical analysis of the clinkers

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2	P_2O_5	LOI
CK1	22.78	4.22	3.61	67.07	0.24	1.41	0.02	0.40	0.00	0.06	0.39
CK2	22.47	4.30	3.56	67.34	0.25	1.41	0.02	0.39	0.03	0.05	0.38
CK3	**22.77**	**5.64**	**1.02**	**68.36**	**0.24**	**1.43**	**0.02**	**0.43**	**0.01**	**0.05**	**0.25**
CK4	22.45	5.50	0.98	68.44	0.28	1.59	0.02	0.53	0.03	0.04	0.34
CK5	22.78	4.20	3.62	67.26	0.31	0.90	0.02	0.79	0.03	0.04	0.19
CK6	22.34	4.22	3.59	67.26	0.32	0.91	0.03	0.81	0.07	0.03	0.26
CK7	22.75	5.56	1.01	68.63	0.33	0.86	0.02	0.71	0.03	0.04	0.26
CK8	22.53	5.56	0.99	69.03	0.33	0.81	0.02	0.69	0.04	0.03	0.26

and overestimates the belite content when compared to quantification by point counting and optical microscopy techniques.

Optical microscopy with point counting techniques can produce very reliable phase content results especially for alite and belite [4]. However, the quantification of the aluminate and the ferrite interstitial phases by this technique is often very difficult, due to the very small crystal size of these phases within the microstructure and thus difficulties in resolving them with an optical microscope. Additionally the chemical similarities between these two phases can give further problems especially when iron or alkali rich orthorhombic C_3A is present. This may prevent a correct differentiation between the orthorhombic aluminate phases and ferrite [1,4] since the crystal structure of ferrite is also orthorhombic and typically dendritic or prismatic in Portland cement clinkers [5].

Quantitative X-ray diffraction techniques (QXRD) can give comparable results to quantitative optical microscopy for alite and belite phases. The quantification of the aluminate and the ferrite phases is, however, more reliable with QXRD since it can overcome the resolution difficulties of optical microscopy [1,4]. Standard QXRD techniques (such as internal standard, area peak fitting) have limitations for complex multiphase materials. The problems include preferential orientation and overlapping of peaks and can lead to serious errors [4]. The recent development of Rietveld QXRD techniques eliminates or minimises many of these errors and allows for the quantification of clinker and cement phase compositions to be achieved with good levels of precision and reproducibility [1,2,6–12]. Modern Rietveld software systems account for factors such as preferential orientation, microabsorption and microstrain.

2. Experimental

Eight different Portland cement clinkers were produced in the laboratory using standard raw materials, limestone, bauxite and iron oxide. The chemical analyses of the clinkers were made by X-ray fluorescence and wet chemistry techniques (Table 1). The target phase composition of the clinkers was calculated using the European Bogue calculation [4], (Table 2). The actual phase composition of the clinkers was measured with a Panalytical X'pert MPD PRO system and quantified using the Rietveld Method (Panalytical Highscore Plus), (Table 2) with control files developed by Lafarge. The phase composition was also measured by optical microscopy/point counting techniques (Table 2).

Quantitative EDS microanalyses were made in an SEM (JEOL 5800LV) with a PGT Prism detector and an IMIX processing and quantification software. The quantification and processing method included cement based oxide reference standards, processing by phi–rho–zi and oxygen calculated by stoichiometry. The detection limit (DL) is in the order of 0.1 wt. % or less for individual elements within oxide based materials [13]. The EDS analyses were made on carbon coated polished sections of the clinker. For each clinker many different sized

Table 2
Clinker phase composition — Bogue calculation[a] and quantification by optical microscopy/point counting and Rietveld analysis

No clinker	Analytical technique	Clinker phase (wt %) C_3S alite	C_2S belite	C_3A aluminate cubic/ortho	C_4AF ferrite	Free CaO
	Bogue	65.2	16.1	5.1	11.0	•
CK1	Optical M	72.2	9.9	5.2	12.4	0.3
	Rietveld	79.4	7.5	5.1	7.9	0.1
	Bogue	68.2	13.0	5.4	10.8	
CK2	Optical M	73.7	8.8	4.7	11.3	1.4
	Rietveld	79.5	7.1	5.3	7.4	0.5
	Bogue	64.6	16.6	13.2	**3.1**	
CK3	Optical M	74.9	8.3	12.5	**2.7**	0.7
	Rietveld	82.9	4.0	3.5/8.7	**0.1**	0.8
	Bogue	68.1	13.0	12.9	3.0	
CK4	Optical M	79.2	5.0	10.0	4.5	1.5
	Rietveld	85.1	4.1	3.0/6.5	0.3	1.1
	Bogue	65.0	16.3	5.0	11.0	
CK5	Optical M	72.0	13.2	3.1	11.3	0.4
	Rietveld	72.9	13.2	6.4	7.4	0.1
	Bogue	68.2	12.6	5.1	10.9	
CK6	Optical M	69.9	11.2	4.8	12.6	1.4
	Rietveld	76.3	10.3	6.2	7.0	0.1
	Bogue	65.6	15.7	13.0	3.1	
CK7	Optical M	76.2	8.7	11.5	2.8	0.5
	Rietveld	77.5	8.3	12.7	1.3	0.1
	Bogue	69.0	12.5	13.1	3.0	
CK8	Optical M	75.4	8.5	11.3	3.0	1.6
	Rietveld	77.5	8.1	12.8	1.2	0.5

[a] The European Bogue uses the following procedure: Assume that the compositions of the four major phases are C_3S, C_2S, C_3A and C_4AF; Assume that the Fe_2O_3 occurs as C_4AF; Assume that the remaining Al_2O_3 occurs as C_3A; Deduct from the CaO content the amounts attributable to C_4AF, C_3A and free lime, and solve two simultaneous equations to obtain the contents of C_3S and C_2S. The CaO content is assumed to have been corrected for free lime.

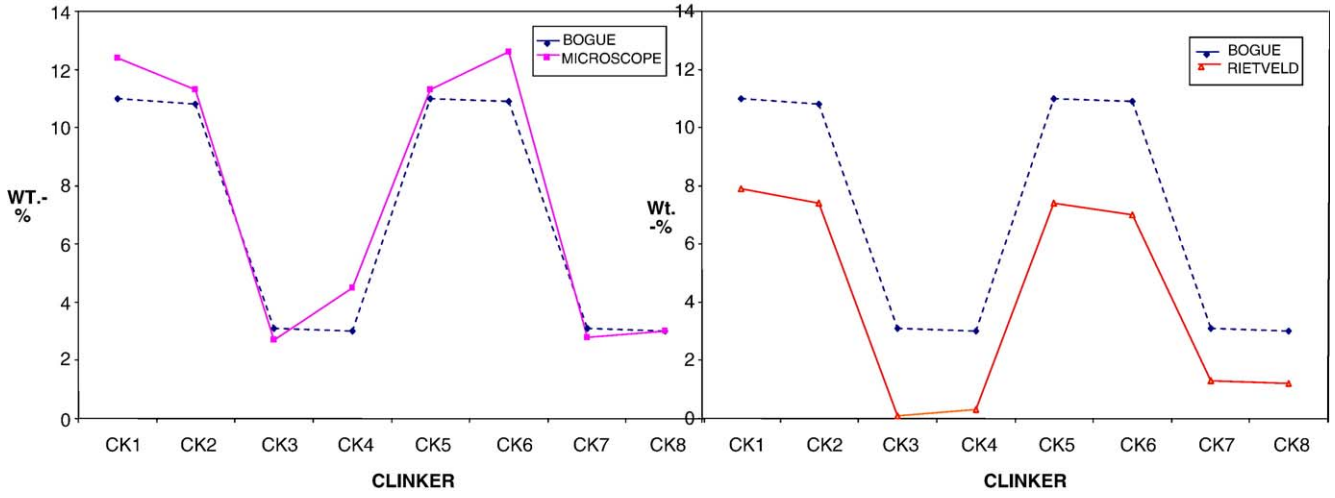

Fig. 1. Quantification of the Ferrite phase by standard Bogue calculation, Rietveld and optical microscopy techniques.

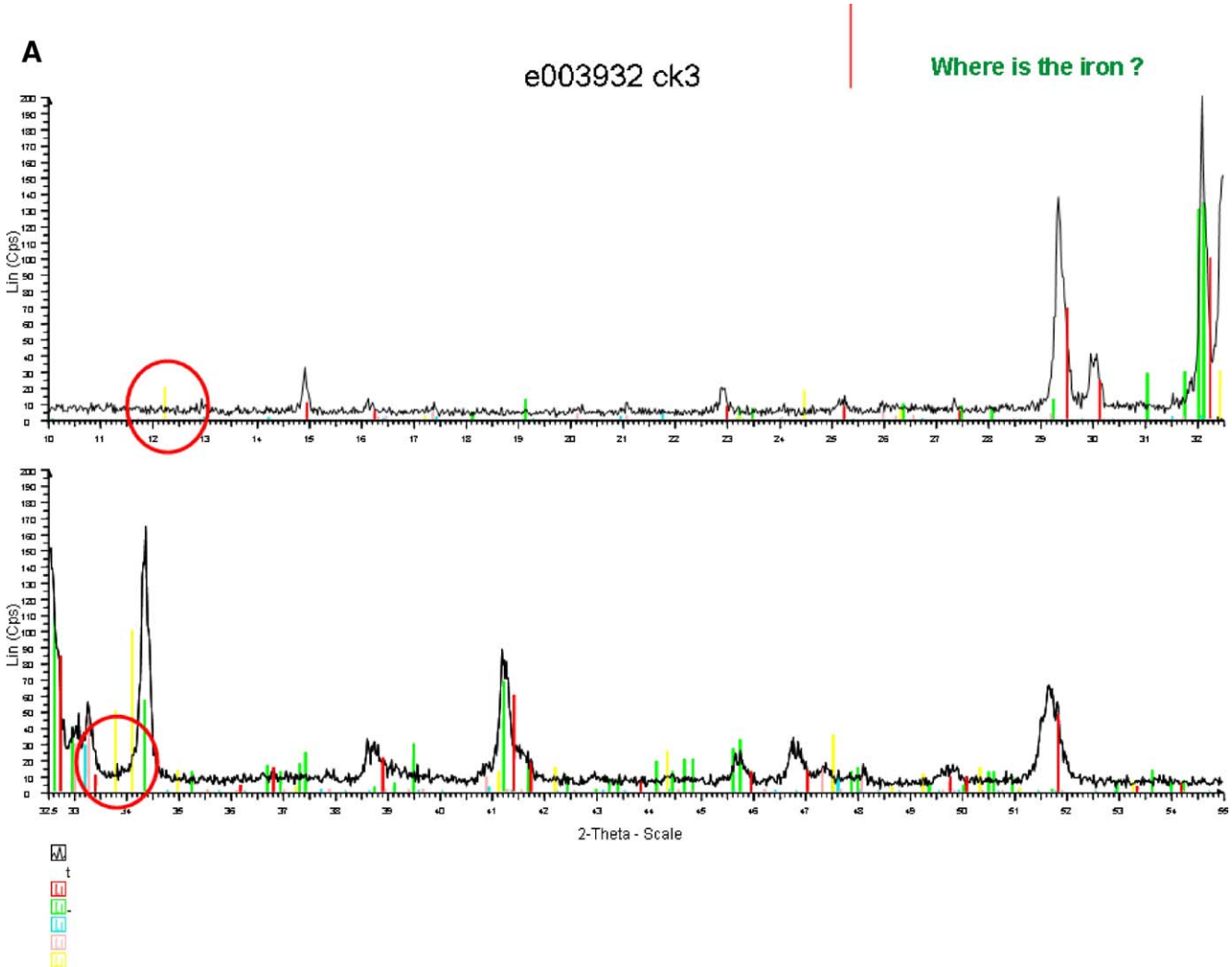

Fig. 2. a: XRD raw spectra of clinker CK3. b: XRD raw spectra of clinker CK1.

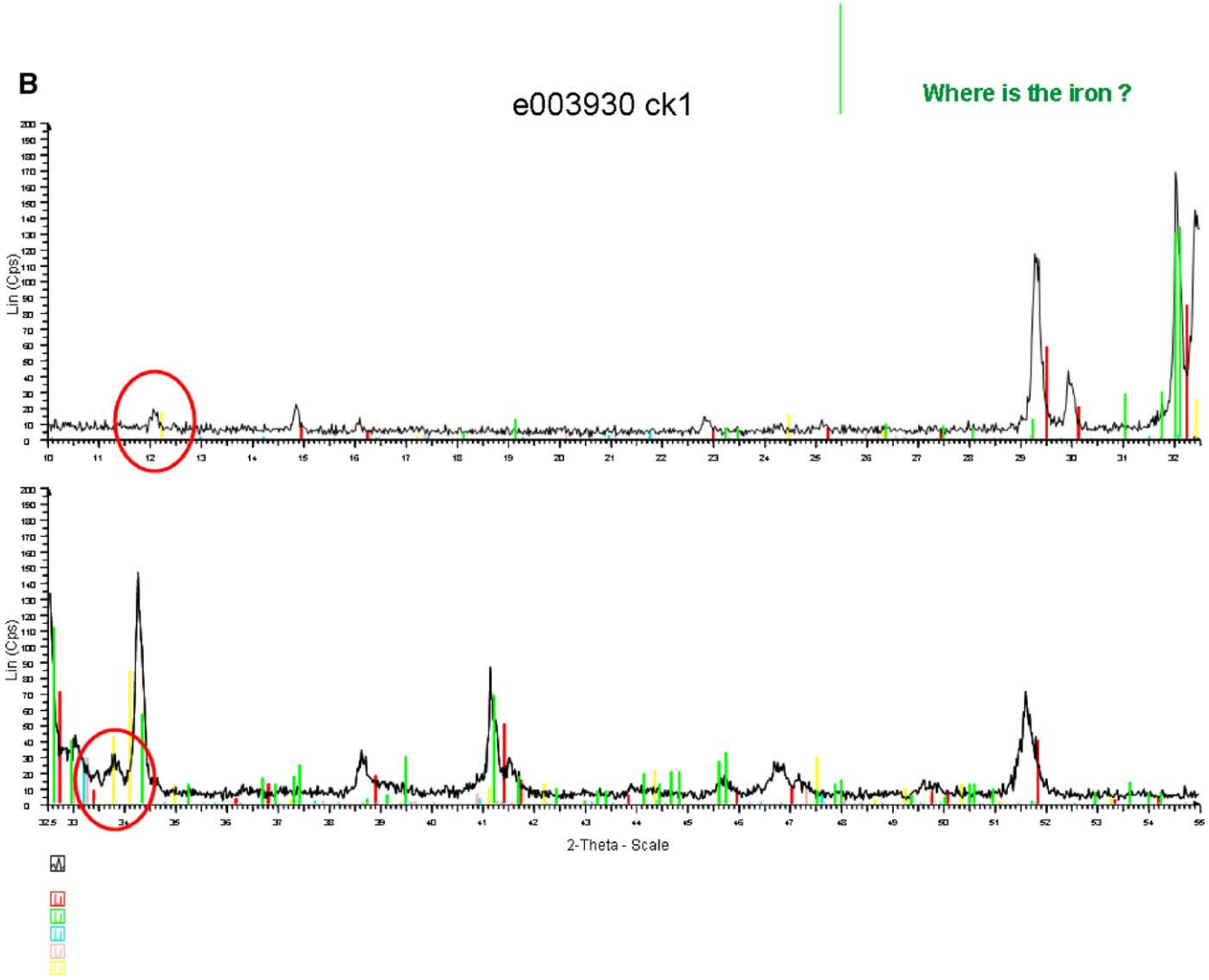

Fig. 2 (*continued*).

grains were examined and 20 spot analyses were made for each of the four major phases. The SEM operating conditions were 15 kV, beam current 1 nA. The volume of clinker phase analysed in each individual spot measurement is in the order of 1 μm^3. In this present study only the results for CK3 have been exploited and these are given in Table 4.

3. Results and discussion

The amounts of alite, belite, aluminate and ferrite for the eight laboratory clinkers as predicted by the standard Bogue Method and measured by optical microscopy and XRD Rietveld analysis show similar trends, but there are significant differences in the absolute amounts (Table 2).

For all clinkers Bogue calculates less alite and more belite than that measured by optical microscopy and point counting which agrees with previous research [4].

There is a good correlation in the amounts measured by optical microscopy and Rietveld analysis for the alite, belite and aluminate phases.

The agreement between all three approaches is good for the aluminate phase, but the Rietveld Method systematically measures 3 wt.% less ferrite phase than predicted by Bogue Method and optical microscopy. In particular,

Table 3
Typical compositions of phases in Portland cement clinkers (wt.%) according to H.F.W Taylor 2nd edition 1997 [4]

	NaO	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_2O_3	Fe_2O_3
Alite	0.1	1.1	1.0	25.2	0.1	0.1	0.1	71.6	0	0	0.7
Belite	0.1	0.5	2.1	31.5	0.1	0.2	0.9	63.5	0.2	0	0.9
Aluminate cubic	1.0	1.4	31.3	3.7	0	0	0.7	56.6	0.2	0	5.1
Aluminate ortho.	0.6	1.2	28.9	4.3	0	0	4.0	53.9	0.5	0	6.6
Ferrite	0.4	3.7	16.2	5	0	0.3	0.2	47.8	0.6	1	25.4

Table 4
Quantitative Energy Dispersive Spectroscopy (EDS) results (in wt.%) of major clinker phases for CK3

	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	0.05	0	0.92	25.08	0	0	0	73.5	0	0	0.38
S.D.	0.01	0	0.18	0.36	0	0	0	0.60	0	0	0.15
Belite	0.00	0.2	2.47	29.12	0.16	0.38	2.41	64.2	0	0.09	0.94
S.D.	0	0.07	0.29	0.41	0.10	0.26	0.24	0.56	0	0.09	0.23
Aluminate ortho.	0	0	29.45	5.12	0	0.18	4.12	57.2	0	0	3.97
S.D.	0	0	0.80	0.41	0	0.05	0.53	0.81	0	0	0.88
Aluminate cubic	0	0.3	31.95	4.97	0.42	0.05	0.82	57.05	0	0.31	4.13
S.D.	0	0.07	0.67	0.46	0.21	0.08	0.08	0.84	0	0.06	0.75
Ferrite	Crystal size is not sufficient for analysis										

according to Rietveld, clinkers CK3 and CK4 show no ferrite at all (Fig. 1).

For example the XRD raw spectra for clinker CK3 is shown in (Fig. 2a). The characteristic Ferrite peak at the 2θ angle around 12° is missing (C_4AF, Brownmillerite, ICDD (International Centre for Diffraction Data) Mineral Powder Diffraction File 30-226) which indicates the absence of ferrite in this clinker. Conversely the ferrite peak at around 12° angle 2θ is clearly visible in the XRD spectra for clinker CK1 (Fig. 2b) and in this case Rietveld calculates nearly 8 wt.% ferrite, (Table 2 and Fig. 1).

Typical elemental substitution in Portland cement clinker phases given by Taylor [4], (Table 3) shows that all of the major clinker phases can contain some Fe_2O_3 and that this is especially significant for the aluminate phases. Based on these typical values up to 1.37 wt.% of Fe_2O_3 could be incorporated in the alite, belite and aluminate phases of clinker CK3.

Our SEM study and quantitative EDS analysis of clinker CK3 show significant incorporation of minor elements within the major phases and this is notably so for the aluminate phase with high potassium and iron substitution (Table 4). Standard deviations (S.D.) relevant to each element analysed are included in Table 4. The values that we obtain are reasonably similar to the average values proposed by Taylor (Table 3).

The calculation below shows the total amount of iron incorporated in the major clinker phases of CK3 based on the SEM-EDS analyses.

0.38%	Fe_2O_3	(SEM-EDX) X 82.9 wt.%	(Rietveld) alite	0.32% Fe_2O_3
0.94%	Fe_2O_3	(SEM-EDX) X 4 wt.%	(Rietveld) belite	0.04% Fe_2O_3
3.97%	Fe_2O_3	(SEM-EDX) X 8.7 wt.%	(Rietveld) Orth. aluminate	0.35% Fe_2O_3
4.13%	Fe_2O_3	(SEM-EDX) X 3.5 wt.%	(Rietveld) cubic aluminate	0.19% Fe_2O_3
Total			0.90% of Fe_2O_3 was incorporated	

The SEM microstructural study by backscattered electron (BSE) imaging confirms the lack of ferrite and shows that the interstitial matrix (Fig. 3) is significantly different to that of a conventional industrial OPC clinker (Fig. 5).

The aluminate phase forms in large masses and is often observed as two dimensional areas of 50 μm^2. This is considered large when compared to industrial clinkers, (Fig. 5), and previous studies [4,5] where the interstitial aluminate typically forms as areas of 1 to 2 μm^2.

The aluminate phases in sample CK3 also show two distinct different crystal structures (Fig. 3), which agrees with the Rietveld analysis (Table 2). An orthorhombic form is identified

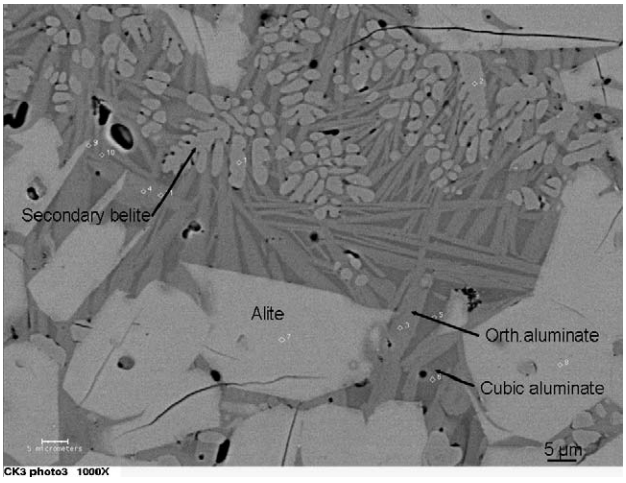

Fig. 3. BSE image of clinker CK3 showing interstitial matrix.

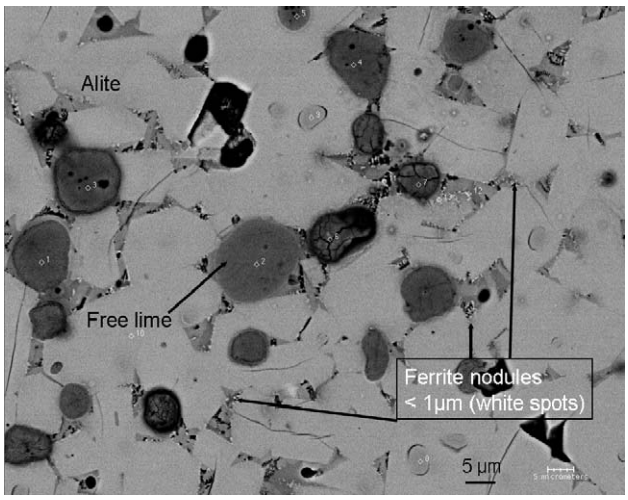

Fig. 4. BSE image of clinker CK3.

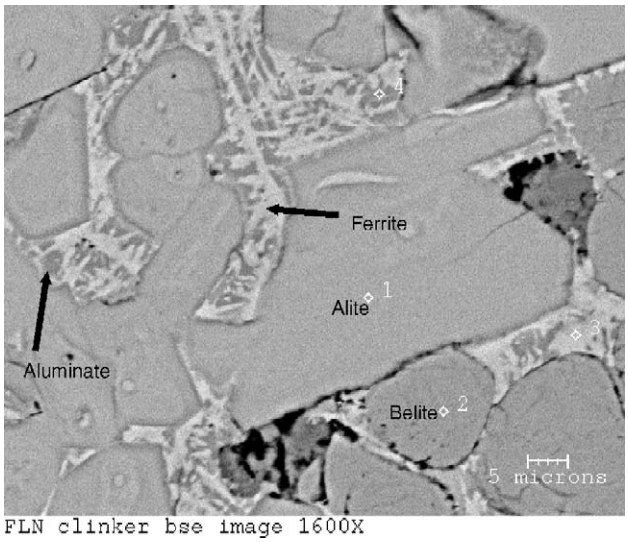

Fig. 5. BSE image showing the fine intermixing of the interstitial phases in conventional industrial Portland cement clinker.

based on its typical lath type morphology [5] — prismatic with dimensions of up to 50 μm length and 5 μm width are observed.

The EDS microanalyses of this phase show that about 4 wt.% K_2O and 4 wt.% Fe_2O_3 is incorporated within the aluminate crystal structure (Table 4) which is coherent with previous research for alkali orthorhombic aluminate [4].

The second aluminate phase identified by SEM-EDS techniques corresponds to a cubic tricalcium aluminate containing significantly less alkali 0.8 wt.% K_2O and about 4 wt.% Fe_2O_3.

Further the particular microstructure shown by the interstitial matrix in CK3 is likely to complicate the identification of the aluminate and the ferrite phases by optical microscopy and point counting techniques. In CK3 the orthorhombic and the cubic aluminate phases are observed to be intimately associated (Fig. 3). The prismatic morphology of the orthorhombic phase in combination with its location and spatial distribution within the microstructure is fairly similar to that which is normally observed by the ferrite phase in a conventional industrial Portland cement clinker (Fig. 5). The ferrite phase also showing dendritic, prismatic morphology. Therefore in this particular clinker CK3 it is possible that the alkali orthorhombic aluminate phase has been identified as the ferrite phase by optical microscopy.

In clinker CK3 the SEM study shows little ferrite phase, which is normally observed to be finely intermixed with the aluminate phase, and is coherent with the XRD Rietveld analysis. The ferrite phase observed appears with a submicron crystal size, (Fig. 4), which prevented microanalysis. For comparison, Fig. 5 shows the typical appearance (spatial distribution) of the interstitial phases in a conventional industrial Portland cement clinker.

4. Conclusion

The use of the standard Bogue calculation to predict the phase composition of Portland cement clinkers can give serious errors. SEM and EDS quantitative microanalysis of the individual clinker phases in some selected clinkers has confirmed significant substitution of secondary elements within the major phases, especially the aluminate. This factor can explain certain significant discrepancies between the phase compositions calculated from the European Bogue Method and the phase compositions given by Rietveld Method. This discrepancy is important for the major phases as well as for the interstitial phases, aluminate and ferrite (where the total amounts are relatively low).

The study shows that for certain clinkers where the amount of iron in the raw mix is very low, i.e. CK3, it is very likely that there will not be sufficient Fe_2O_3 to form any significant amount of the ferrite phase during clinker production.

XRD Rietveld analysis combined with SEM and quantitative EDS microanalysis techniques give reliable and complimentary information concerning the phase composition of Portland cement clinkers and their complex chemistry and crystallography.

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