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A comparative study of ordinary and mineralised Portland cement clinker from two different production units
Part I: Composition and hydration of the clinkers

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Abstract

Portland cement clinkers from two production units were investigated; Plant 1: ordinary clinker (P1) and clinker mineralised with $CaF_2 + CaSO_4$ (P1m); Plant 2: ordinary clinker (P2) and two clinkers mineralised with $CaF_2 + CaSO_4$ (P2m, low SO_3 and P2m′, high SO_3). The chemical composition of the clinkers was determined by X-ray fluorescence, ICP analysis, titration (free lime) and ion selective electrode measurements (F). Observed clinker parameters (LSF, SR, AR, R, wt.% MgO, F, SO_3, free lime): P1 (0.96, 2.72, 1.27, 1.04, 0.78, 0.06, 0.64, 0.71); P1m (1.03, 2.21, 1.58, 2.18, 0.87, 0.23, 1.95, 0.69); P2 (1.00, 2.66, 1.72, 0.75, 4.06, 0.20, 1.38, 1.51); P2m (1.01, 2.91, 1.96, 0.90, 3.21, 0.39, 1.72, 2.06); P2m′ (0.97, 2.70, 1.84, 1.15, 3.86, 0.42, 2.48, 0.89). The qualitative and quantitative phase compositions were characterised using X-ray powder diffraction, backscattered electron imaging, X-ray microanalysis and elemental mapping, plus optical reflection microscopy. Phases observed in all clinkers were: alite, β-belite, cubic aluminate, ferrite and free lime. Additional phases observed were: aphthitalite (P1, P2, P2m, P2m′), calcium langbeinite (P1m) and periclase (P2, P2m, P2m′). The clinker composition and texture differ more between the two plants, than between ordinary and mineralised clinker from the same production unit. Laboratory cements were prepared by mixing ground clinker with $CaSO_4 \cdot 2H_2O$. The cements were hydrated in an isothermal calorimeter at 20 °C (water/cement weight ratio = 0.5) during 33 h. After 12 h, the laboratory cement based on P1m reached a higher level of reaction than the one based on P1. The P2m and P2m′ laboratory cements had a slower reaction than the P2 cement.

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1. Introduction

More than 95 wt.% of ordinary Portland cement clinker consists of CaO, SiO_2, Al_2O_3 and Fe_2O_3. These four oxides form the main phases in clinker: alite (Ca_3SiO_5), belite (Ca_2SiO_4), aluminate ($Ca_3Al_2O_6$) and ferrite (Ca_2AlFeO_5). The minor elements either form separate phases (periclase, alkali sulfates, etc.) or are incorporated into the main clinker phases by ionic substitution [1]. It is possible to utilise the effect of the minor elements constructively, for example, the combined addition of fluoride and sulfate has positive effects on the clinkering process and on properties of the clinker, since the two species act as mineralisers [2].

An aluminium and iron oxide melt is responsible for the transport of the reactants forming alite in the clinker. A mineraliser either changes the relative thermodynamical stabilities of the clinker minerals by substitutions and/or acts as a flux. A flux decreases the viscosity and surface tension of the oxide melt and/or reduces the temperature at which the first oxide melt is formed. It thus facilitates the transport of reactants and enables the alite to form at lower temperatures. As a result of the mineralising effects, the hydraulic activity of the silicates might be modified by solid solution or by symmetry effects [3].

In addition to acting as a mineraliser, sulfate forms a separate melt at low temperatures (1000–1200 °C) compared to the oxide melt (~ 1300 °C), with which it is immiscible. This enables the silicates to form at even lower temperatures [4]. A drawback of using sulfate as a mineraliser is sulfate stabilisation of belite, which inhibits forma-

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tion of alite. However, this effect is counteracted if the addition of sulfate is combined with fluoride [5].

Improved hydraulic properties of cements based on clinker mineralised with calcium fluoride and calcium sulfate have been reported [2,4,6]. The reaction rate is lower during the first hours up to one day, but then accelerates providing higher compressive strength than corresponding ordinary clinker cement. This behaviour is explained by the high alite content in the mineralised clinker and by the substitution-stabilised rhombohedral alite, which is claimed to be more hydraulically active than monoclinic and triclinic alite [2,7,8].

The aim of the present work is to compare the compositions of ordinary clinker to the corresponding sulfate and fluoride mineralised clinker and to investigate the hydraulic activity of the clinker from two production units (Part I: Composition and hydration of the clinkers). Part II: Characteristics of the calcium silicates, focuses on the effects of sulfate and fluoride mineralisation on the silicate phases, e.g. polymorphism and substitutions [9].

2. Experimental

Ground clinker was mixed with Spektroflux 110 (66.5 wt.% lithium tetraborate, 33.5 wt.% lithium metaborate) and melted at 1000 °C in a Fluxy Classie furnace. The chemical composition was determined by X-ray fluorescence with a Philips PW 1480 spectrometer. The sodium content was determined by ICP analysis (Spectroflame ICP-AES, Spectro). Ground clinker was dissolved in ethylene glycol and the free lime content was determined by titration with HCl. The analyses were performed at Scancem Research. The fluoride content was determined at Aalborg Portland using an ion selective electrode. The phase composition was calculated according to Bogue (original version) [1]. The lime saturation factor (LSF), silica ratio (SR), aluminia ratio (AR), and the molar SO_3 to alkali oxide ratio (R) were also calculated [1].

To extract the interstitial phase from the clinker, 5 g of ground clinker was dissolved in a solution of 250 ml ethanol (99.5 vol.%) and 40 g salicylic acid (99.9 wt.%, Analar), stirred for 2 h and then filtered. The clinkers and the extracted interstitial phases were pressed onto a sample holder and investigated using a Siemens D500 X-ray powder diffractometer ($CuK_{\alpha 1}$ radiation) at Scancem Research. Each diffraction pattern covered $2\theta = 10-60°$ and was collected for 20 min totally.

Clinker grains were embedded in a low viscosity epoxy resin under vacuum, ground planar with SiC and polished with diamond powder. A thin layer of carbon was evaporated onto the samples. A JSM-840A scanning electron microscope (SEM) was used for backscattered electron imaging, for microanalysis and recording of elemental maps using energy dispersive X-ray analysis. The analyses were made at an acceleration voltage of 20 kV, with a probe current of 9 nA for imaging and microanalysis, and 60 nA for X-ray mapping. Microanalysis was performed on eight separate sulfate grains in each clinker. Polished sections of epoxy-embedded clinker grains were also etched for 15 s with nital solution (1 ml conc. $HNO_3 + 99$ ml 99.5 vol.% ethanol) and the phase composition was studied in reflection mode in an optical microscope, Olympus BH-2, at Scancem Research. A computer-controlled sample holder moved the sample along a total distance of ~5 mm, so that 2000 phase boundaries could be registered. The materials registered were alite, belite, interstitial material (including aluminate, ferrite, free lime, periclase, sulfate phases, etc.), epoxy resin in clinker pores and epoxy resin between clinker nodules. The volume percent of each material was calculated from the chord lengths and the weight percent of the clinker materials was calculated from the volume percent and the densities; 3200, 3280 and 3710 kg m^{-3} for alite, belite and interstitial material, respectively.

The clinkers were crushed in a Retsch BBO crusher and ground with a Retsch AS200 digit ball mill to a surface area of 160–188 m^2/kg. A Sympatec HELOS laser interferometer was used to determine the particle size distribution and the surface area of the samples (Table 1). The soluble SO_3 content in the clinkers (i.e. SO_3 in sulfate phases) was calculated [1,10] and the ground clinkers were mixed with $CaSO_4 \cdot 2H_2O$ (MERCK, pro analysi) so that all the laboratory cements contained 6 wt.% total soluble SO_3. Laboratory cement (10 g) was mixed with 5 ml water and then 5 g of the paste was placed in a prototype of the TAM AIR isothermal calorimeter (Thermometric) for 33 h. The reaction heat rate was recorded as a function of time. The reaction heat mainly comes from hydration of alite. The hydraulic activity of belite is expected to be very low within the time period in question. Aluminate and ferrite react immediately to form ettringite, however, this initial reaction peak has been eliminated by extrapolation but after 12–16 h renewed ettringite formation will cause a contribution to the reaction heat [1]. The high SO_3 content in the cements ensures

Table 1
Particle size distribution and surface area of the ground clinkers

	Plant 1		Plant 2		
	Ordinary	Mineralised	Ordinary	Mineralised (low SO_3)	Mineralised (high SO_3)
10% (μm)	4.53	4.14	3.73	3.56	3.85
50% (μm)	27.24	26.82	22.38	24.83	24.78
90% (μm)	65.96	65.96	61.13	64.68	66.40
Surface area (m^2/cm^3)	0.503	0.531	0.572	0.589	0.548
Surface area (m^2/kg)	160	169	182	188	174

that no conversion of ettringite to monosulfate will occur during the hydration experiments.

3. Results and discussion

Five clinkers from two production units, Plant 1 and Plant 2, were included in this study. Plant 1 uses a precalciner process; its raw material consists mainly of fine-grained chalk and fly ash. Plant 2 uses a dry process; crystalline limestone and blast furnace slag make up the main raw materials. The differences in the raw materials between the two plants are reflected in the composition of the clinkers (Table 2). Plant 1 clinkers are in the region of typical ordinary Portland clinker in wt.%; 67 CaO, 22 SiO_2, 5 Al_2O_3, 3 Fe_2O_3 and 3 wt.% minor components [1]. Clinkers from Plant 2 have a somewhat higher level of minor elements, primarily magnesium, alkali and fluorine.

Table 2

Chemical composition, Bogue calculation (original), free lime content, LSF, SR, AR, and the molar SO_3 to alkali oxide ratio (R) defined according to Ref. [1], and quantitative phase composition determined by optical microscopy

wt.%	Plant 1		Plant 2		
	Ordinary	Mineralised	Ordinary	Mineralised (low SO_3)	Mineralised (high SO_3)
CaO	67.0	66.6	64.2	65.1	62.9
SiO_2	22.2	20.0	20.3	20.5	20.4
Al_2O_3	4.55	5.53	4.83	4.66	4.90
Fe_2O_3	3.59	3.50	2.81	2.38	2.66
Mn_2O_3	0.017	0.022	0.199	0.051	0.033
TiO_2	0.208	0.274	0.254	0.134	0.146
K_2O	0.31	0.61	0.88	0.92	0.97
SO_3	0.64	1.95	1.38	1.72	2.48
P_2O_5	0.210	0.231	0.099	0.083	0.165
MgO	0.78	0.87	4.06	3.21	3.86
SrO	0.136	0.144	0.026	0.022	0.047
Na_2O	0.27	0.29	0.85	0.87	1.02
F	0.06	0.23	0.20	0.39	0.42
Σ	100.0	100.3	100.1	100.0	100.0
Bogue calculation					
C_3S	65.5	74.2	64.6	66.0	60.7
C_2S	14.2	1.3	9.4	8.9	12.7
C_3A	6.0	8.7	8.1	8.3	8.5
C_4AF	10.9	10.7	8.6	7.2	8.1
Free lime	0.71	0.69	1.51	2.06	0.89
Σ	97.3	95.6	92.2	92.6	90.8
Σ Interstitial material[a]	20.3	24.5	26.0	25.1	26.6
LSF	0.96	1.03	1.00	1.01	0.97
SR	2.72	2.21	2.66	2.91	2.70
AR	1.27	1.58	1.72	1.96	1.84
R	1.04	2.18	0.75	0.90	1.15
Optical microscopy					
Alite	64	70	76	74	67
Belite	16	3	3	3	10
Interstitial material	20	27	21	23	23

[a] Σ Interstitial material = aluminate + ferrite + free lime + minor oxides.

The processes were modified for mineralisation by the addition of calcium sulfate and calcium fluoride to the raw material (exact amounts unknown). One ordinary clinker and one mineralised clinker were supplied from Plant 1. As can be seen in Table 2, the SO_3 content was increased from 0.64 in the ordinary clinker to 1.95 wt.% in the mineralised clinker. The fluoride content was increased from 0.06 to 0.23 wt.% F. In addition, the Al_2O_3 content was increased from 4.55 to 5.53 wt.% and the LSF was increased from 0.96 to 1.03. Plant 2 supplied one ordinary clinker and two mineralised clinkers. The SO_3 content was increased from 1.38 in the ordinary clinker to 1.72 and 2.48 wt.%, respectively, in the two mineralised clinkers. The fluorine content was increased from 0.20 to about 0.4 wt.% F.

The alite phase was identified in all clinkers by the powder X-ray diffraction peaks at $2\theta \approx 51-52°$, however, the peak-to-noise ratio was too low to draw conclusions about the polymorphic state. Further experiments were undertaken to investigate this (see Part II [9]). Alite was also identified as angular crystals; light grey in the backscattered electron images recorded in the SEM, dark grey in the X-ray maps of calcium (Figs. 1 and 2) and bluish or brownish under the optical microscope. The microstructure of alite in ordinary and mineralised clinker did not differ significantly. All clinkers contained more or less subhedral alite, with the exception for ordinary clinker from Plant 1, which contained mainly euhedral alite. All clinkers also exhibited coalescence of alite crystals. The crystal size distributions of alite are presented in Fig. 3. Ideally, the average size of alite should be 15–20 μm, although it is often larger in practice [1]. The alite crystals in all samples were smaller than that usually found in Portland clinker. In Plant 1 clinkers the mean size decreased from 15 μm in the ordinary clinker to 13 μm in the mineralised clinker. In Plant 2 clinkers the mean size decreased from 17 μm in the ordinary clinker to 13 μm in the mineralised clinkers.

Monoclinic β-belite (PDF 33-302) was identified by the diffraction peak at $2\theta \approx 37°$ in all of the clinkers. Belite was also identified as rounded crystals; dark grey in the backscattered electron images recorded in the SEM and light grey in the X-ray maps of calcium. In the optical microscope, belite was observed as bluish or brownish rounded crystals rich in lamellas. It was not possible to draw any general conclusions about the difference in microstructure of belite between ordinary and mineralised clinkers. In the ordinary clinker from Plant 1, the belite crystals were evenly distributed in relation to alite. In the corresponding mineralised clinker and in all clinkers from Plant 2, belite crystals were few and existed mainly in nests, indicating (i) that the clinkering reaction had proceeded extensively in the direction of alite and (ii) that the raw mix was not homogenous. The crystal size distributions of belite are presented in Fig. 3. Ideally, the average

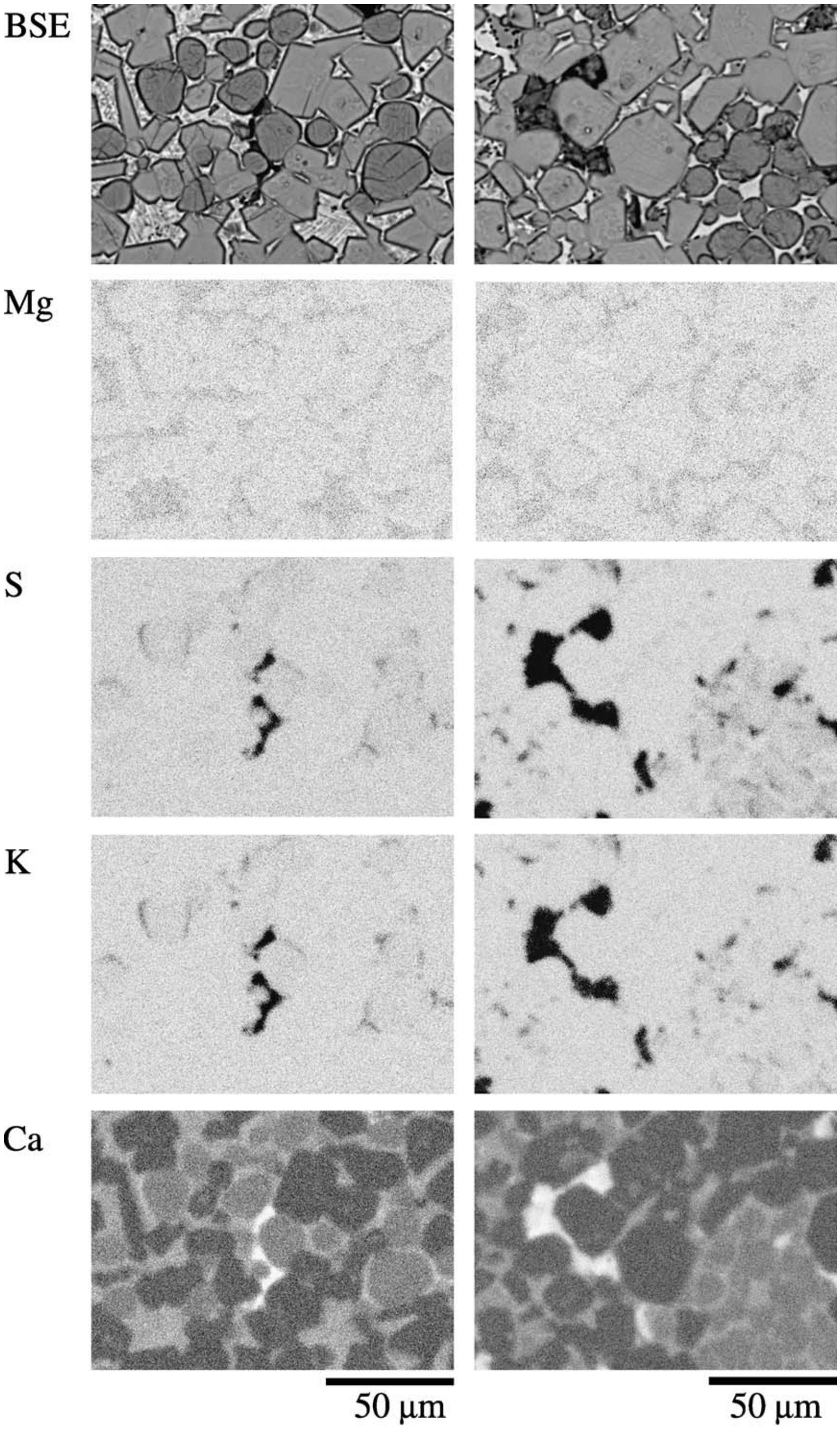

Fig. 1. Backscattered electron images and X-ray mapping of magnesium, sulfur, potassium and calcium in (left) ordinary Portland clinker and (right) mineralised clinker from Plant 1. Dark areas in the X-ray maps correspond to a high concentration of the element.

size of belite should be 15–20 μm, but as with alite, it is often larger in practice [1]. The belite crystals in all samples were smaller than usually found in Portland clinker. For Plant 1 the mean size of the belite grains decreased from 17 μm in diameter in ordinary clinker to 10 μm in mineralised clinker, and the proportion of larger crystals decreased upon mineralisation. The mean size of belite in all Plant 2 clinkers was 6 μm.

Extracted aluminate and ferrite was studied at the X-ray diffraction angle $2\theta \approx 33–34°$. The single peak at $2\theta \approx 33°$ revealed cubic aluminate (PDF 38-1429) in all of our clinkers and the double peak at $2\theta \approx 33.5–34°$ indicated

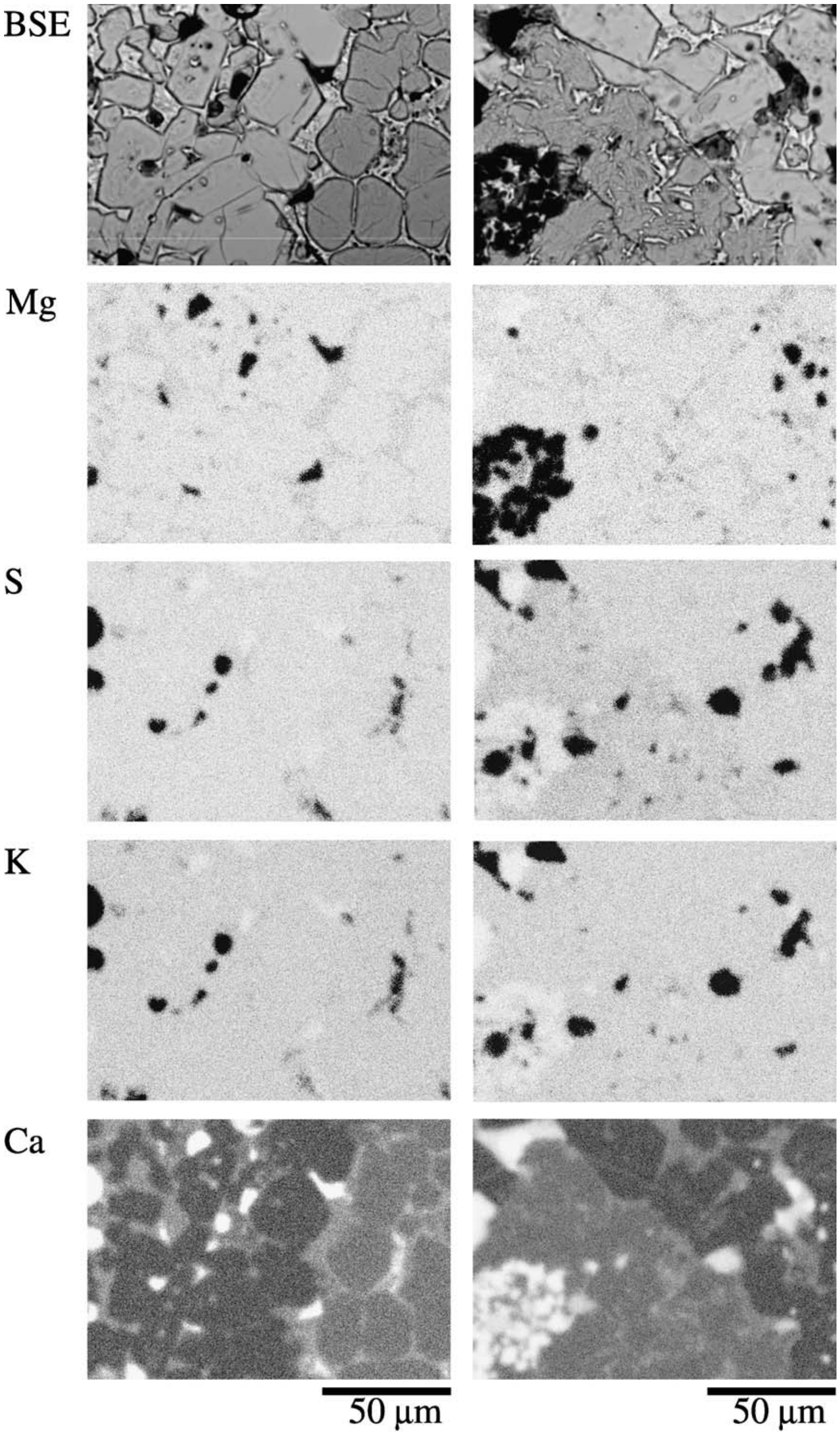

Fig. 2. Backscattered electron images and X-ray mapping of magnesium, sulfur, potassium and calcium in (left) ordinary Portland clinker and (right) mineralised clinker from Plant 2. Dark areas in the X-ray maps correspond to a high concentration of the element. Black areas in the Mg maps are periclase, MgO.

the presence of orthorhombic ferrite (PDF 30-226). Ferrite was also seen as white interstitial material in the backscattered electron images in Figs. 1 and 2. Aluminate was seen as grey areas intermixed with ferrite.

Free lime, CaO, was observed as multicoloured, rounded grains, 10–20 μm in size, in the optical microscope. It was found in the Plant 2 clinkers and in lesser amounts in the Plant 1 clinkers, consistent with the chemical analysis (Table 2).

Sulfates were observed as black areas in the optical microscope and dark grey areas in the backscattered images. The X-ray maps of sulfur coincided with the maps of

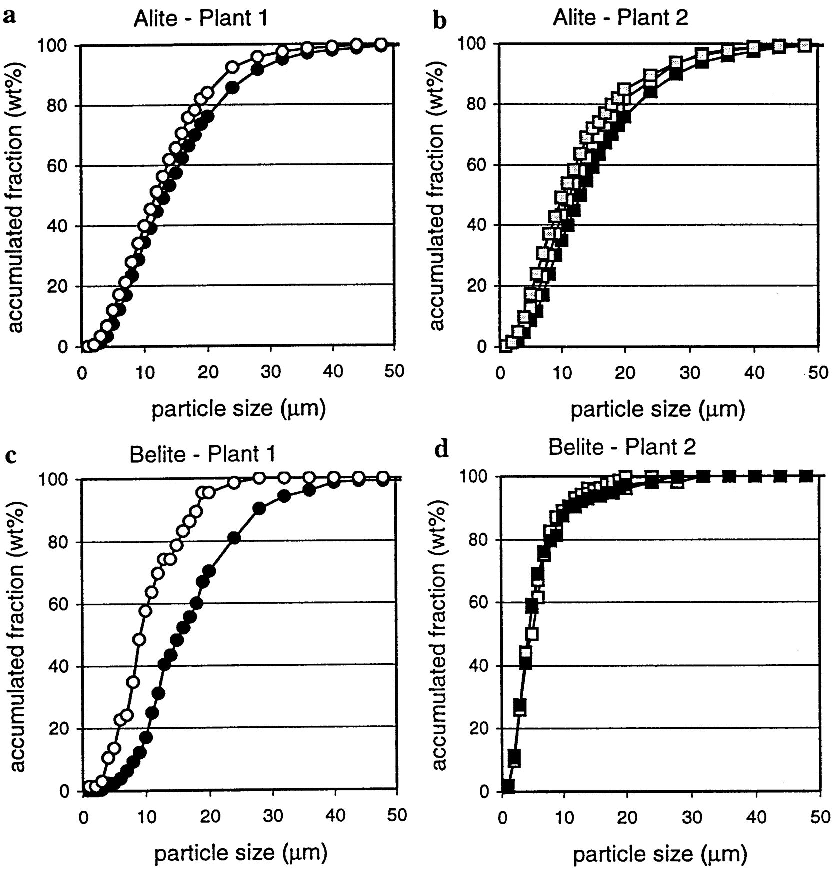

Fig. 3. Accumulated crystal size distribution determined by optical microscopy. (a) Alite in clinkers from Plant 1, (b) alite in clinkers from Plant 2, (c) belite in clinkers from Plant 1 and (d) belite in clinkers from Plant 2. The black and white circles represent ordinary and mineralised Portland clinker from Plant 1, respectively. The black, white and grey squares represent ordinary, low SO_3 mineralised and high SO_3 mineralised Portland clinkers from Plant 2, respectively.

potassium (Figs. 1 and 2), confirming the presence of potassium in the sulfate phases in all clinkers. Plant 2 clinkers were found to be richer in sulfate phases than corresponding clinkers from Plant 1. The X-ray microanalyses of the sulfate phases are presented in Fig. 4a. Aphthitalite, $(K,Na)_2SO_4$, with some substitution of calcium, was found in all clinkers except in the mineralised clinker from Plant 1. Due to the high molar SO_3 to alkali oxide ratio (R) in this clinker (Table 2), the composition of the sulfate phase corresponded to calcium langbeinite, $K_2Ca_2(SO_4)_3$, with substitutions of sodium. According to Moir [2,6], calcium langbeinite plays an important role in controlling the early hydration reactions, as it is sufficiently soluble to give set control. The sulfate phase analyses were closer to the end-compositions than expected from the empirical equations of Pollitt and Brown [10] (see Fig. 4b); aphthitalite contained less calcium than expected and calcium langbeinite contained less sodium. Mixed sulfate phases were not observed in either of the clinkers, which might possibly be an effect of the selective choice of large sulfate grains for microanalysis, in order to avoid stray radiation from the matrix.

X-ray maps of magnesium were recorded in the SEM (Figs. 1 and 2). Periclase crystallises when the bulk content exceeds 1.5–2 wt.% MgO [1,11]. In Plant 1 clinkers, the MgO content was less than 1 wt.% (Table 2) and consequently magnesium was only found in the oxide interstitial material and at a lower level in alite and belite. Plant 2 clinkers contained 3–4% MgO and were rich in periclase. Periclase in the Plant 2 clinkers was also observed in the optical microscope as grains, 5–10 µm in size, unattacked by the etchant.

The results from the Bogue calculations and optical microscopy show good accordance for Plant 1 clinkers (see Table 2). The LSF was higher in the mineralised clinker (1.03) compared to the ordinary clinker (0.96). A higher free lime content would therefore be expected, but as can be seen in Table 2, the amount of free lime was 0.7 wt.% in both clinkers. The improved burnability of the mineralised clinker can be explained by reduced viscosity and surface tension of the oxide melt [3] and by the additional liquid sulfate phase in the clinker, which enables alite to form at low temperatures (1000–1200 °C) [4]. No such improvement of the burnability caused by the sulfate and fluoride additions can be observed in Plant 2 mineralised clinkers. When comparing the Bogue calculations to the quantitative phase composition determined by optical microscopy, it is noted that the alite contents are under-

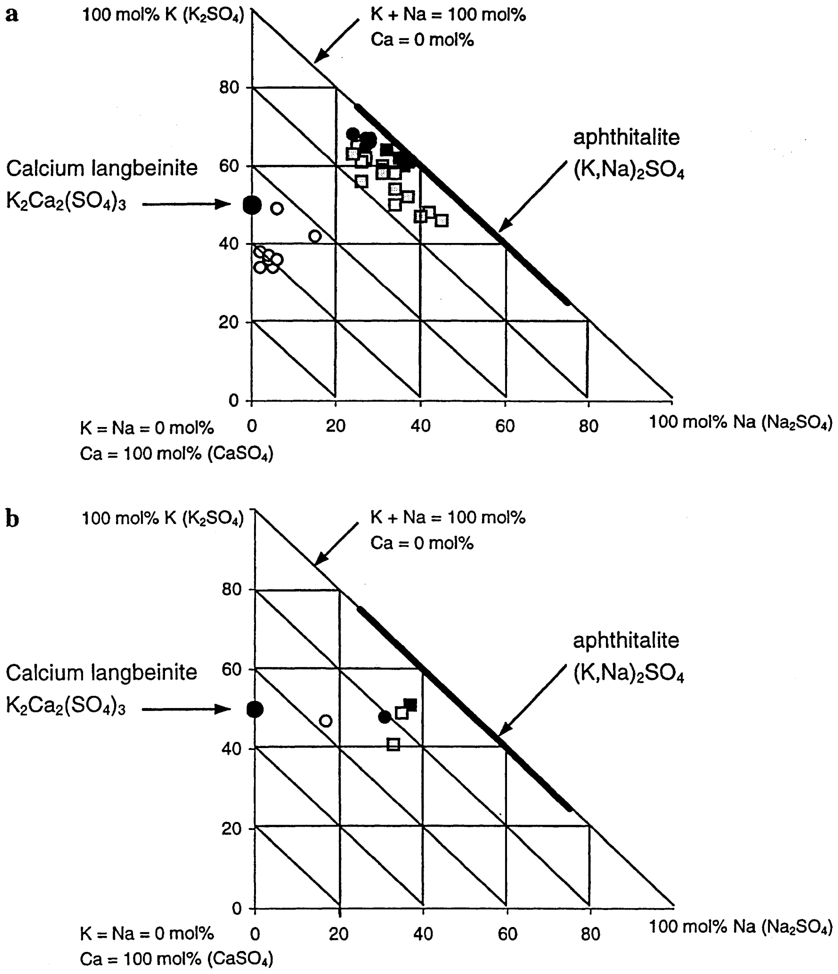

Fig. 4. (a) X-ray microanalysis of individual sulfate grains. (b) Expected average composition of the sulfates, calculated according to the empirical equations of Pollitt and Brown [10]. The mol% K, Na and Ca refer to molar percentages of cations in the sulfate phase. The black and white circles represent ordinary and mineralised Portland clinker from Plant 1, respectively. The black, white and grey squares represent ordinary, low SO_3 mineralised and high SO_3 mineralised Portland clinkers from Plant 2, respectively.

estimated by the Bogue calculations and the belite contents are overestimated for Plant 2 clinkers. The high magnesium content of the clinkers may partly explain the differences. Magnesium promotes alite formation substituting for calcium and since alite is the most calcium consuming of the two silicate phases, magnesium additions will increase the relative amount of alite compared to belite. The Plant 2 high SO_3 mineralised clinker shows better accordance between the Bogue calculations and optical microscopy, particularly for belite, despite the high level of magnesium. The high SO_3 level in this clinker increases the substitution of sulfur for silicon. Belite is richer in silicon than alite and thus the relative amount of alite compared to belite will decrease with increasing sulfur content. The combination of high magnesium level with high fluoride content already in the ordinary clinker (Table 2) has a positive impact on the burnability of Plant 2 clinkers, as also observed by Kleem and Jawed [12] and Surana and Joshi [13], and thus further mineralisation gives no improvement.

The content of soluble SO_3 (wt.%) in the clinkers was estimated according to Refs. [1,10]; Plant 1: 0.59 (ordinary), 1.37 (mineralised); Plant 2: 1.38 (ordinary), 1.65 and 2.20 (mineralised). After the addition of gypsum, the total level of SO_3 (wt.%) in the laboratory-prepared cements was calculated to be 6.05 (ordinary), 6.59 (mineralised) for Plant 1; 6.00 (ordinary), 6.07 and 6.28 (mineralised) for Plant 2. The mineralised laboratory cement from Plant 1 evolved heat slowly during the first 8 h of hydration, but thereafter the reaction rate increased and the mineralised cement reacted faster than the ordinary laboratory cement after 12 h (Fig. 5a). It should be noted that the aluminate content, according to Bogue, differs somewhat in the two samples (see Table 2) and continued ettringite formation contributes to a small part of the reaction heat. The mineralised laboratory cements from Plant 2 clinkers react slower than the corresponding ordinary cement (cf. Fig. 5b). According to the Bogue calculation in Table 2, Plant 2 clinkers have the same aluminate and ferrite content and the renewed ettringite

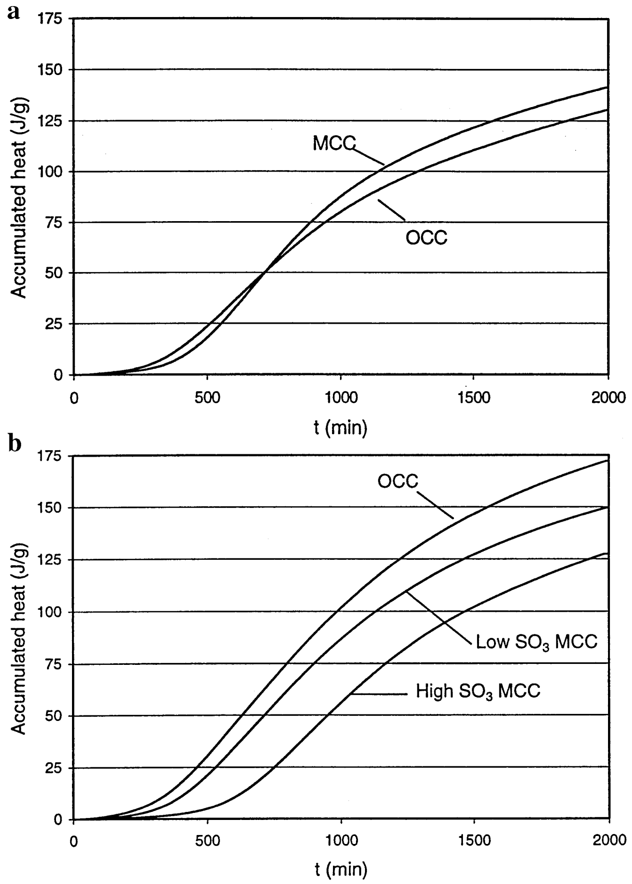

Fig. 5. Accumulated reaction heat per unit weight of dry cement recorded using ordinary clinker cements (OCC) and mineralised clinker cements (MCC) from (a) Plant 1 and (b) Plant 2.

formation can therefore be neglected. Although part of the difference in reactivity of the cements should be addressed to differences in alite content, the characteristics of the calcium silicates have an influence, as will be further explored in Part II [9].

4. Final remarks

Clinkers from Plant 1 have a typical ordinary Portland clinker composition. Clinkers from Plant 2 exhibit a higher level of minor elements, in particular fluorine, magnesium (present partly as periclase) and alkali. They are also richer in free lime and in sulfate phases than corresponding clinkers from Plant 1. The sulfate phase in the Plant 1 mineralised clinker consists of calcium langbeinite, due to its high molar SO_3 to alkali oxide ratio (R). The other clinkers contain aphthitalite. There are no general differences in the microstructure between an ordinary clinker and the corresponding sulfate and fluoride mineralised clinker. The nature of the raw mix and the overall process has a decisive influence in determining the clinker texture and composition for a specific production unit.

Two mineralising effects are observed for the Plant 1 clinkers, increased burnability and modified hydraulic activity. Despite the higher LSF in the mineralised clinker compared to the ordinary clinker, the free lime content is the same in both clinkers, due to the mineralising effect of sulfate and fluoride. Any such effects are outdone in the Plant 2 clinkers by the high levels of magnesium and fluoride in all clinkers. A cement based on the Plant 1 mineralised clinker has a lower reaction rate during the early hydration than corresponding ordinary clinker, but then accelerates to reach a higher reaction rate after 12 h. The cements based on the mineralised clinkers from Plant 2 react slower than the corresponding ordinary cement.

In Part II [9], the characteristics (ionic substitutions and polymorphism) of the calcium silicates were studied in detail to further explore the differences in reactivity of cements based on ordinary clinker and clinker mineralised with sulfate and fluoride.

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