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The influence of earth alkalis on the mineralogy in a mineralized Portland cement clinker

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Abstract

Laboratory-burned sulfur-rich Portland cement clinker has been prepared with varying amounts of MgO, SrO, and BaO. The distribution of these alkaline earth elements was analyzed with EPMA. The structural changes of the belite phase have been determined by full-pattern Rietveld X-ray diffraction. Although the belite phase did only amount to 15–25% of the total clinker mass, it was possible to follow the β to α′ transition particularly as a function of increasing SrO content. The α phase was not detected. The observed lattice parameters are close to values found in pure belite phase studies. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Crystal structure; X-ray diffraction; Ca_2SiO_4; BaO; SrO

1. Introduction

The strive to continuously optimize the composition of the raw materials for production of Portland cement clinker is still mainly a matter of trial and error. Some more general guidelines are understood, regarding relationships between chemical composition of the clinker minerals and their reactivity, but many questions remain.

Studies have reported the occurrence of either β- or α′-type belite as very important for the early development of the ultimate strength of Portland cements. It is generally acknowledged that the α′ modification is the more reactive of the two, but that compositions just leading to partial transition are superior [1].

Studies of pure or nearly pure belite systems have shown many transition conditions between the two modifications as a function of overall chemical composition and preparation conditions [2,3]. The question is to which extent these data can be used to predict transition condition in real Portland cement systems. This can be resolved if it is possible to follow the transitions also in mixed Portland cement samples where the investigations with XRD are hampered by serious overlaps from the alite phase.

The development of the Rietveld method for analyzing XRD and Neutron powder spectra has been used for several investigations of the minerals in cement. Typically these studies also have been made on pure or nearly pure minerals. This study concerns the applications of the method for evaluating the influence of the earth alkalis on the structure of belite from a sulfur and fluorine mineralized cement.

2. Background

The distribution of MgO among the clinker minerals has already been investigated by several authors [4–6]. It is well known that the amount of MgO in clinker minerals correlates linearly with the overall amount of MgO in the clinkers. The reason why the distribution of MgO is included in this investigation is to detect whether the distribution of SrO/BaO is influenced by the amount of MgO in the clinkers.

The crystal structure of pure belite or C_2S[1] is well described in the literature and only a brief review will follow. In all five polymorphs of C_2S; γ, β, α_L', α_H', and α, the structure is built up of Ca^{2+} and SiO_4^{4-} ions. The α-

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[1] Cement chemical notation where $C = CaO$ and $S = SiO_2$ is used in the text.

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form is hexagonal, the α'-forms and the γ-form are orthorhombic and the β-form is monoclinic [7]. The γ-polymorph has an olivine structure whereas the structure of the other polymorphs all are related to the structure of glaserite, $K_3Na(SO_4)_2$ [8]. Structures of the glaserite type are characterized by being built up of a central cation ideally 12 coordinated to oxygen. Six of the oxygen atoms make an elongated antiprism and the other six are situated in a hexagonal ring in the plane of the central cation. Six tetrahedral groups are bound to the oxygen atoms forming the antiprism. The apical oxygen atoms in the tetrahedral groups can point either up or down. In α-C_2S, the SiO_4 tetrahedrons have the same orientation whereas in the α'-polymorphs have the SiO_4 tetrahedrons orientated alternately up and down and in the β-polymorph the tetrahedrons are further tilted with respect to the *c*-axis [8]. Studies have shown that the α_L' and α_H' polymorphs are complex superstructures based on an ideal α' structure and a differentiation between the two polymorphs by XRD is only possible with accurate investigations [9,10]. In general, it can be concluded that only small changes are involved in the transformations and it is therefore difficult to distinguish the different polymorphs, particularly in cement.

The influence of BaO and SrO on the structure of C_2S solid solutions has been investigated by Catti et al. [2] and Udagava et al. [3]. According to Udagava et al. [3], a solid solution of $(Ca_{1-x}Sr_x)SiO_4$ will exhibit the γ-form with $x < 0.10$ and the α_L'-form with $x > 0.15$. The study only included solid solutions with x values between 0 and 0.3. Catti et al. [2] found that the β-form was stable with x between 0.04 and 0.10 and with $x > 0.92$ whereas the α'-form was stable with x between 0.10 and 0.75. With a solid solution of the composition $(Ca_{1-x}Ba_x)SiO_4$ Udagava et al. [3] found that the γ-form was stable with $x < 0.03$, the α'-form was stable with x between 0.05 and 0.10, and the α-form was stable with x between 0.20 and 0.30, the latter value of x being the maximum value in their investigations. There is no information in their paper about whether the β-form is stable with x between 0.03 and 0.05.

According to the authors' knowledge, no papers have been published concerning the distribution of SrO and BaO among the clinker minerals nor the combined influence of MgO, SrO, and BaO on the unit cell or the crystal structure of belite.

3. Experimental

3.1. Materials

A clinker with the composition shown in Table 1 was made from a mixture of chalk, sand, kaolin, pyrite ash, gypsum, and fluorspar. To adjust the composition of the clinkers $Mg(OH)_2$, $SrCO_3$, and $BaCO_3$ of reagent grade were used. The materials were homogenized and made into nodules about 2–4 mm in size, using demineralized water. The nodules were burnt at 1400°C for 1 h and cooled quickly.

Table 1
Composition of the clinker and quantitative phase composition according to Bogue calculation given in weight percent (wt.%)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Mn_2O_3	TiO_2	P_2O_5	K_2O	Na_2O	SO_3	F
66.01	22.00	4.89	3.26	0.47	0.02	0.10	0.10	0.43	0.15	2.20	0.25
SrO	BaO	Cl	LOI	Sum	LSF	SR	AR	C_3S	C_2S	C_3A	C_4AF
0.12	0.01	0.02	0.49	100.52	0.95	2.70	1.50	63.95	14.81	7.44	9.92

The loss on ignition is the mean of two analyses.

The clinkers were made with three levels of MgO and for each level of MgO there were five levels of SrO and BaO. The amounts of MgO, SrO, and BaO in the clinkers were 0.5, 1.2 and 2.0 wt.%, 0.0, 1.0, 2.0, 3.0 and 4.0 wt.%, and 0.0, 0.8, 1.6, 2.4 and 3.1 wt.%, respectively.

3.2. EPMA

The microprobe analyses were made at a TRACOR NORTHERN automatic JEOL JCXA733/superprobe with a takeoff angle at 40.0°. The acceleration voltage was 15 kV and the current intensity 15 nA. The standards used for analyzing the clinkers for the content of MgO, SrO, and BaO was Mg-olivine, cellestine, and barite, respectively, whereas for CaO and SiO_2, wollastonite and for Al_2O_3 and Fe_2O_3, corundum and Fe-olivine were used, respectively. The melt phase was analyzed as a single phase and for each phase, alite, belite and the melt phase, a number of four to nine analyses were taken in all the clinkers.

3.3. X-ray diffraction

The X-ray diffractograms were recorded at a Phillips PW 1050 vertical diffractometer using Cu Kα radiation and equipped with a graphite monochromator, automatic divergence slit and Phillips PW 3710 controlling system. The acceleration voltage was 50 kV and the current intensity 30 mA. The scan was made as a continuous scan with a step size of 0.02° 2θ and a speed of 2.5 s/step in the interval ranging from 20° to 65° 2θ.

Together with the analysis of the changes in the cell parameters of belite, a quantitative phase analysis was made from the X-ray diffractograms with a full-profile Rietveld analysis using the computer program SIROQUANT V2 (1996). The program is based on the method developed by Rietveld [11,12]. The following minerals were included in the analysis: C_3S (T_1) [13], C_2S (β) [14], C_3A [15], C_4AF [16], CaO, MgO, $SrSO_4$, and $BaSO_4$ [17]. The cell parameters for C_3S, C_3A, C_4AF, CaO, and $BaSO_4$ are slightly modified compared with the parameters given in the references. The theoretical structure of C_3S is further modified, i.e., a large number of small reflections have been removed to increase computing times. The triclinic C_3S is used in the calculations because this polymorph was found to give the most consistent results when several different clinkers were analyzed [18].

4. Results

4.1. Distribution of SrO and BaO

The results from the EPMA on the amount of SrO in the minerals were generally very consistent. So is the maximum standard deviation (S.D.) for all phases in the interval from 0.03 to 0.32 wt.% SrO for the clinkers with the lowest and highest amount of SrO, respectively. The S.D. for the amount of BaO in alite was always less than 0.13 wt.%. For belite the S.D. was in the range from 0.16 to 0.92 and for the melt phase it was in the range from 0.16 to 2.87.

The distribution of SrO and BaO are shown in Figs. 1 and 2. The data include all EPMA results no matter what the amount of MgO in the clinkers is. This means that every data point represents the average of the analysis made on the three different levels of MgO there is in the clinkers. This is done because the results for the distribution of SrO and BaO did not show any dependencies on the amount of MgO in the clinkers.

From Fig. 1, it can be seen that belite contains the highest amounts of SrO whereas alite contains the lowest amounts of SrO. The slopes of the regression lines are 0.73, 1.76, and 1.10 for alite, belite, and the melt phase, respectively. The regression coefficient is .999 for all regression lines.

From Fig. 2, it can be seen that the melt phase contains the highest amounts of BaO whereas alite contains the lowest amounts and indeed, only incorporates a very limited amount of BaO. The slopes of the regression lines are 0.21, 1.89, and 2.21 for alite, belite, and the melt phase, respectively. The regression coefficient for all regression lines is larger than .995.

4.2. Structural changes of the belite phase

The analysis with SIROQUANT generally revealed very consistent results with the *R*-factor between 3.63 and 5.34. For the influence of MgO on the unit cell of belite 2 × 3 X-ray diagrams were analyzed whereas five diagrams for each of the three levels of MgO were analyzed to evaluate the influence of SrO and BaO on the unit cell of belite.

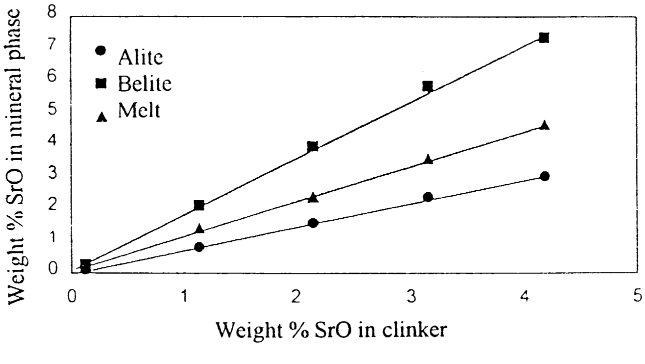

Fig. 1. The distribution of SrO among the clinker phases.

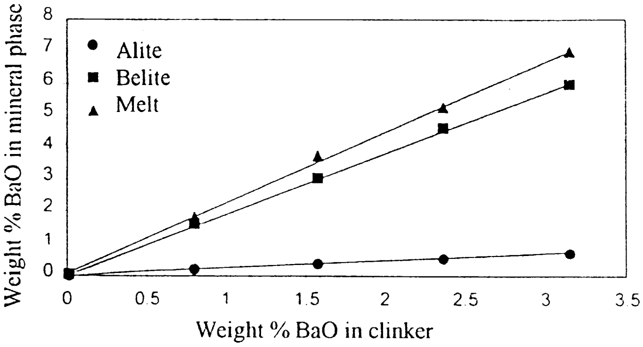

Fig. 2. The distribution of BaO among the clinker phases.

The full-profile Rietveld analysis of the X-ray diagrams revealed the following results. With the amount of MgO in belite increasing from about 0.1 to about 1.1 wt.%, the length of axis decreased with about 0.02, 0.03, and 0.04 Å from about 5.52, 6.765, and 9.34 Å for the *a*-, *b*-, and *c*-axes, respectively. The angle β was nearly constant about at 94.2°.

The influence from SrO on the lengths of the axes in the unit cell of belite is shown in Fig. 3.

Fig. 3 shows the results from the full-profile Rietveld analysis of the X-ray diagrams for the clinkers with the

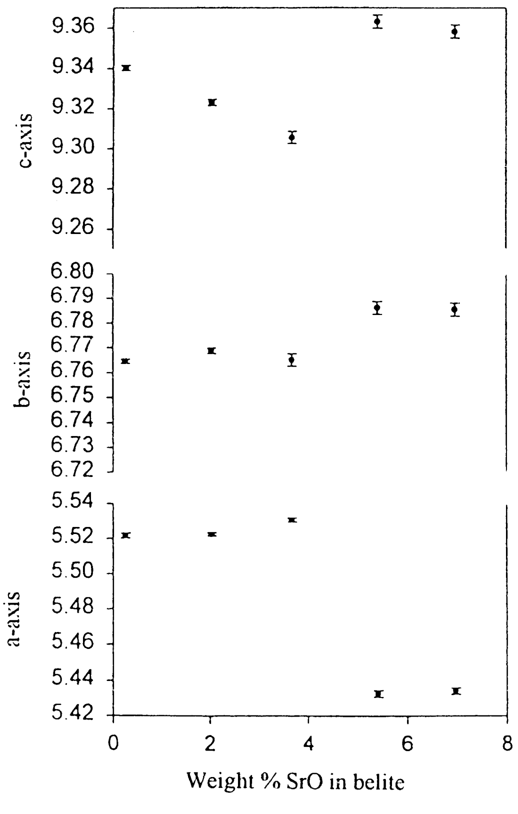

Fig. 3. The lengths of the belite unit cell axes as a function of the amount of SrO incorporated in the structure.

lowest level of MgO in the clinkers. The bar around each data point represents the S.D. The unit of the ordinate axis is in angstrom (Å). The figure shows a clear change in the length of all axes around 4 to 5 wt.% SrO in the belite. Further, the angle β changes from a value of around 94.3° to a value of around 93.1° with between 4 and 5 wt.% SrO in the belite. As a result of these changes, the volume of the unit cell falls from about 348 to about 344 Å^3.

The results from the analysis of the influence from BaO on the unit cell of belite did not show any clearly or systematic changes with increasing amounts of BaO in the belite. Further, the changes in the lengths of the axes did also show some dependency on the amount of MgO in the clinkers, which could not be explained. The results are therefore not shown.

4.3. Quantitative phase analysis

From the full-profile Rietveld analysis, the quantitative phase composition of the clinkers was also found. The amount of free CaO was barely detectable. An analysis of the amount of free CaO with glycol extraction on selected clinkers revealed that only in a clinker with the maximum amount of SrO was an increase at 0.8 wt.% in the amount of free CaO found. The amount of celestine, $SrSO_4$, did never exceed 0.2 wt.%, whereas the amount of barite, $BaSO_4$, steadily increased up till 2.2 wt.% in the clinkers containing BaO.

5. Discussion

5.1. Distribution of SrO and BaO

The analysis of the amount of SrO and BaO was generally very consistent. The relatively high S.D. for the amount of BaO in the melt phase comes from varying amounts of barite, $BaSO_4$, inhomogeneously distributed in the melt.

The distribution of SrO and BaO in Figs. 1 and 2 shows that there exists a linear relationship between the amount of SrO and BaO in the clinkers and in the clinker minerals. This is also strongly supported by the fact that the regression coefficients for the straight lines are almost 1.

5.2. Structural changes of the belite phase

The decreasing lengths in the axes of unit cell of belite with increasing amounts of MgO in the structure can be contributed to the fact that Mg^{2+} is a smaller ion compared to Ca^{2+} for which it substituted and the result is therefore to be expected. Further, investigations [4] have shown that the amount of MgO that can be incorporated in the clinker minerals is limited to about 2 wt.% MgO in the clinker. This means that the results show that no phase transformations in belite would be expected according to the incorporation of MgO in the structure.

With increasing amounts of SrO in belite, the significant changes in the lengths of the axes, shown in Fig. 3, and in the angle β, from 94.3° to 93.1°, strongly indicate a phase transformation between the β and α′-polymorph. This also agrees with the investigations made by Catti et al. [2] and Udagava et al. [3]. Note that the angle β is not equal to 90° because the program is set to refine on a monoclinic polymorph, and therefore comes out with a monoclinic unit cell!

The results from the analysis of the influence from BaO on the unit cell of belite could be hampered by the fact that there are two phase transformations with the amount of BaO in the belite increasing from 0.0 to about 6.5 wt.%. It is therefore doubtful whether the method used here can reveal which polymorph of belite is present in a given clinker or cement with different levels of BaO in the raw meal or clinker.

6. Conclusions

From the analysis of the distribution of SrO and BaO among the clinker minerals, it can be concluded that there exists a linear correlation between the amount of SrO and BaO in the clinker and in the clinker minerals, respectively. The relationship is independent on the MgO content. This conclusion is only valid for a rather limited amount of SrO or BaO in the clinker, since alite decomposes to belite and free CaO with higher amounts of SrO or BaO in the clinker [19]. The quantitative phase analysis of the clinker showed only a minor increase in the amount of free CaO in the clinker with the highest amount of SrO. This increase could be the result of either the substitution of Sr^{2+} for Ca^{2+} in the clinker minerals or a slight decomposition of alite into belite and free lime.

The full-profile Rietveld analysis of the cell parameters of belite with the computer program SIROQUANT revealed that it is possible to detect the transformation between the β and α′ polymorph of belite as a function of the content of SrO in the clinker. With the clear changes in the cell parameters between the two polymorphs, it would be expectable that it is also possible to determine which polymorph is present in a given clinker in the case where varying amounts of SrO are present in the clinker.

The full-profile Rietveld analysis of the clinker containing varying amounts of BaO did not reveal any clear results and further work is needed to evaluate whether it is also possible to determine the actual belite polymorph in clinker with BaO with the program SIROQUANT.

A further important conclusion from the full-profile Rietveld analysis of the clinker is that the sulfate in the clinkers containing BaO reacts with the BaO to form barite, which is heavily soluble. This means that the sulfate that otherwise would be at the disposal for the hydration process, is no longer available. This has obvious implications for the making of F/SO3-mineralized cements.

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