MORPHOLOGY AND CHEMICAL COMPOSITION OF MINERALS INSIDE THE PHASE ASSEMBLAGE C - C_2S - $C_4A_3\bar{S}$ - C_4AF - $C\bar{S}$ [1)] RELEVANT TO SULPHOALUMINATE BELITE CEMENTS.

JÚLIUS STRIGÁČ**, MARTIN T. PALOU, JOZEF KRIŠTÍN*, JÁN MAJLING

*Department of Ceramics, Glass and Cement, Faculty of Chemical Technology,
Slovak Technical University, 812 37 Bratislava, Slovak Republic*

* *Central Laboratory of Electron-Optical Methods, Faculty of Natural Sciences,
Comenius University, 842 12 Bratislava, Slovak Republic*

** *Present* address: *Považska Cementáreň a.s., ul. J. Kráľa 018 63 Ladce, Slovak Republic*

The paper deals with a formation of solid solutions inside the equilibrium phase assemblage C-C_2S-$C_4A_3\bar{S}$ -C_4AF-$C\bar{S}$ of the oxide system CaO-SiO_2-Al_2O_3-Fe_2O_3-SO_3. The content of minor oxides incorporated in individual phases was generally lower in comparison with data given in the literature. C_2S and $C\bar{S}$ phases form more homogeneous crystals with regard to their chemical composition than $C_4A_3\bar{S}$ and the ferrite phase. From practical consideration the stoichiometry of the ferrite phase in the given phase assemblage can be appropriately represented by a composition corresponding to C_6AF_2.

INTRODUCTION

Sulphoaluminate belite cement (SAB) is low-energy cement, being synthesised at 1200-1250 °C [1]. Its mineralogical composition in a prevalence of cases includes C_2S, $C_4A_3\bar{S}$, C_4AF, $C\bar{S}$ phases and some amount of free lime C. These phases create, however, one of the equilibrium phase assemblages inside the C-S-A-F-$\bar{S}$ oxide system. The content of free lime at usual conditions is very low (up to 1-2 %), but also the clinkers with a content of free lime up to 10 % showed good properties after hydration [2, 3]. Commercial clinkers are predominantly so designed as to contain only three principal clinker phases C_2S, $C_4A_3\bar{S}$ and C_4AF [4-6]. Nevertheless, the clinkers usually contain some amount of free lime and free calcium sulphate, so essentially they are found in the mentioned five-phase assemblage.

Up to now relatively few papers deal explicitly with the chemical composition and microstructure of SAB clinker minerals. Several authors [7-12] investigated solid solutions for only individual clinker minerals, without their relationship to the other clinker phases. Authors [4, 6, 13-16] have already studied the chemical composition of C_2S, $C_4A_3\bar{S}$ and C_4AF, but their investigation was concerned with multicomponent oxide system including Na_2O, K_2O, MgO, TiO_2, etc. The investigated clinker minerals fired at temperatures 1200 - 1300 °C were of small size (ca 1-5 μm), poorly crystallised and sometimes intergrown with neighbouring phases.

The data on chemical composition of coexisting clinker minerals C_2S, $C_4A_3\bar{S}$, C_4AF and $C\bar{S}$ are absent in the literature and we have attempted, therefore, in this work to make them available.

Solid solutions and morphology of C_2S

C_2S, important clinker mineral in Portland as well as SAB cement has been studied extensively. The authors [17] have considered that univalent and divalent ions replace Ca^{2+} and multivalent ions Al^{3+}, Fe^{3+}, S^{6+} replace Si^{4+}. For C_2S present in calcium sulfoaluminate cement it has been suggested that the principal substitution taking place may be the replacement of $3(SiO_4)^{4-}$ by $(2(AlO_4)^{5-} + (SO_4)^{2-})$ [6]. The amount of a'-C_2S increases with increasing SO_3, and Al_2O_3 in contrary to Fe_2O_3, which promotes β-C_2S formation [13].

The boundary composition of α'-C_2S at 1200 °C, saturated with Ca^{2+} and $(SO_4)^{2-}$ ions, can be represented by a formula $Ca_{1.99}Si_{0.99}S_{0.01}O_{4.00}$ (1.1 mol % $C\bar{S}$) [18]. Belites, containing a significant amount of SO_3 (3-4 %), possess a strongly distorted structure [13] and consequently manifest an improved hydration properties.

Generally, the extent of substitutions in C_2S of SAB cement is greater in comparison to C_2S of Portland cement (PC) [6]. The boundary solid solution at a temperature of the PC clinker burning is approximately 6 wt.% expressed as a sum of all impurity oxides [19]. Compositions of C_2S of the low energy cements have been given in [4, 6, 13-15]. The content of oxides varies

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[1)] $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $\bar{S} = SO_3$

in following limits, CaO: 59.96-66.70, SiO_2: 28.60-35.52, Al_2O_3: 0.10-2.49, Fe_2O_3: 0.10-2.00, SO_3: 0.10-4.10 [4, 13-15].

The crystallochemical formula of C_2S solid solution given in [6] is then as follows:

$$Ca_{1.96\pm0.06}Al_{0.11\pm0.07}Fe_{0.01\pm0.00}Si_{0.77\pm0.05}S_{0.08\pm0.02}O_4 \quad [6]$$
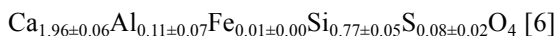
The structure of the SAB clinkers is porous; it shows the lace-like open textured structure [6]. The minerals formed at low temperature (ca 1200-1300 °C) are ill crystallised and contain large amounts of admixtures [4]. Their size is usually very small, less than 5 μm, since the clinker crystals are primarily formed by a solid state reaction [5]. C_2S present in SAB clinkers takes roughly a spherical shape [8]. It usually twins with $C_4A_3\overline{S}$ crystals. The backscattered electron images of sulphoaluminate clinkers showed that C_2S crystals form the light gray relatively coarse clusters [6].

Solid solutions and morphology of $C_4A_3\overline{S}$

The $C_4A_3\overline{S}$ belongs to the sodalite type structure [20], which has considerable tolerance for substituents. It can be considered as a structure near to the limit of the sodalite structure type stability and therefore it is sensitive to the introduced admixtures [9].

The substitution of hetero-ions in $C_4A_3\overline{S}$ consists mainly in Ca replaced by Mg and Al by Si, Fe and Ti [8]. A solid solution of Fe_2O_3 in $C_4A_3\overline{S}$ can be expressed by the formula $C_4A_{3-x}F_x\overline{S}$ [10]. The estimated maximum value of x at 1150 °C is 0.30 (7.6 wt.% Fe_2O_3) and at 1300 °C it corresponds to $x = 0.32$ (8.1 wt.% Fe_2O_3). Sodium and iron solid solution expressed by the formula $N_xC_{4-x}A_{3-y}F_y\overline{S}$ has been studied in [9]. Results suggest that the limits of solid solutions are at $x = 0.6 - 0.7$ and $y = 0.30 - 0.33$. The maximum solubility of Fe_2O_3 in $C_4A_3\overline{S}$ at 1300 °C was found to be ~ 9 wt.% [16].

The existence of completely substituted form $C_4F_3\overline{S}$, present together with $C_3F\overline{S}$ phase [14, 21, 22] was not confirmed in [13, 16, 23]. The measurements given in [13] confirmed, however, formation of solid solution of ~ 5 mol.% $C\overline{S}$ in CF. C_2F phase contained 0.3 - 1.0 wt.% of SO_3 in a solid solution [16]. According to [24] sulphoferrite phases are solid solutions of C_2F and CF with $C\overline{S}$ and their composition is variable according to the formulas $C_{(3+n)}F_3\overline{S}_n$ (from $n = 0.75$ to 1.50) and $C_{(2+m)}F\overline{S}_m$ (from $m = 0.80$ to 1.50).

The $C_4A_3\overline{S}$ phase formed at a non-equilibrium conditions of the cement manufacture is not a compound with fixed composition but a solid solution, the components of which (especially CaO) can be present in broad limits and also several hetero-ion substitution have been found to take place [8]. The industrial $C_4A_3\overline{S}$ has lower percentage of Al_2O_3 in a comparison to the stoichiometric phase but is higher for CaO and SO_3. The percentage of SO_3 depends upon a type of the rotary kiln and a possibility of the volatilised

SO_3 to be absorbed back reversibly by raw mix. The content of the oxides in industrial $C_4A_3\overline{S}$ varies in the following limits, CaO: 38.56-43.33, SiO_2: 2.80-3.19, Al_2O_3: 35.47-40.22, Fe_2O_3: 0.60-1.60, SO_3: 11.91-17.45 [8].

According to [6], contrary to previous findings, the level of substitution in $C_4A_3\overline{S}$ is low. There is no evidence of significant CaO variation from the ideal stoichiometry:

$$Ca_{4.11\pm0.04}Al_{5.60\pm0.12}Fe_{0.12\pm0.05}Si_{0.04\pm0.02}S_{1.03\pm0.05}O_{16} \quad [6]$$
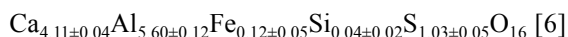
The composition of $C_4A_3\overline{S}$ given in other sources [4, 13-15] varies in following limits, CaO: 30.80-37.14, SiO_2: 0.10-3.89, Al_2O_3: 42.53-53.40, Fe_2O_3: 1.30-7.08, SO_3: 11.00-14.03.

The industrial sulpho-aluminate cement clinker can be featured as small sparse, moderately adhering particles [8]. The crystal size of $C_4A_3\overline{S}$ is less than 5 μm and the crystal appearance showed an incidence of hexagonal plates and the tetragonal polycylinder shapes. Hexagonal tabular form is typical shape for well crystallised $C_4A_3\overline{S}$ [4, 5]. The backscattered electron images of SAB clinker given in [6], showed that the $C_4A_3\overline{S}$ crystals are well shaped with an equant gray colour.

Solid solutions and morphology of C_4AF

The alumino-ferrite phase is a solid solution in series of compositions $Ca_2Fe_{2-2x}A_{2x}O_5$, where x varies from 0 to 0.7 [11], forming thus a continuous series from C_2F to C_6A_2F. The ferrite phase structure belongs to the perovskite structure type [25, 26]. Owing to the peculiarities of the perovskite structure, the ferrite phase is capable to host a great amount of admixtures, about 10-11 % at a temperature of the PC clinker burning [19]. The occurrence of octahedral and tetrahedral positions with Fe and Al promotes the variety of substitutions of these atoms.

The substitution of Si^{4+} and S^{6+} ions for Fe^{3+} or Al^{3+} ions has been studied in [26]. It has been suggested that this substitution takes place on the tetrahedral sites. The Si^{4+} ions on the tetrahedral sites play a dominant part in a change of the ferrite cementitious properties. Nonequivalent substitution of $3Si^{4+}$ for $4Fe^{3+}$ or $4Al^{3+}$ produces vacancies in the crystal lattice and brings about an introduction of the covalent bond Si-O shortened by about 10 %, causing the oxygen tetrahedra to shrink.

The substitution of S^{6+} for Fe^{3+} or Al^{3+} ions in oxygen tetrahedra seems to be of low probability due to the large difference in electronic configuration and other ionic parameters. Nonequivalent substitution of S^{6+} for $2Fe^{3+}$ or $2Al^{3+}$ would lead to a serious deformation and an unsound lattice of ferrite phase [26].

The equilibrium solubility of SiO_2 in the ferrite phase does not exceed 0.8 wt % at temperatures 1300-1380 °C [12]. In the ferrites grown under non-equilibrium conditions it reaches 1.5-2 % SiO_2. Sulphur

plays the major role in a formation of the imperfect crystals [13]. According to cited authors the large amount of sulphur is present in the lattice of the less ferrous aluminoferrite phase (C_4AF) with a composition CaO: 46.7-49.8, SiO_2: 3.5-5.4, Al_2O_3: 11.0-12.6, Fe_2O_3: 25.9-31.6, SO_3: 1.8-6.7. The high ferrous aluminoferrite phase (C_6AF_2), contains only up to 0.6 % SO_3, and has the composition CaO: 42.3-44.5, SiO_2: 3.1-4.3, Al_2O_3: 8.1-10.7, Fe_2O_3: 41.9-44.5, SO_3: 0-0.6. Higher amount of admixtures of SiO_2 and SO_3 have been measured in [4]. The ferrite phases contained:

	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3
C_6A_2F	36.18	6.91	39.25	11.34	10.66
C_4AF	37.29	6.12	19.08	26.79	6.82
C_6AF_2	35.81	7.29	8.73	27.96	0.70

It is seen from published data that the sulphur content is decreased by an amount of Fe_2O_3 in the ferrite phase. The ferrite phase exhibits large standard deviations in analytical totals of its chemical composition [6].

$$Ca_{3.57\pm0.17}Al_{0.99\pm0.60}Fe_{0.63\pm0.21}Si_{0.22\pm0.10}S_{0.18\pm0.12}O_{10} \text{ [6]}$$
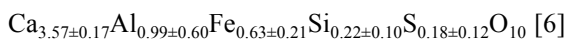
The presence of so much sulphur is surprising since sulphur is not normally a substituent in the perovskite structure. The ferrite phase had been concentrated by its selective dissolution and after which the sulphur content fell to nearly zero, thereby confirming suspicion that sulphur was not its integral constituent.

$$Ca_{4.30\pm0.15}Al_{1.23\pm0.31}Fe_{0.82\pm0.24}Si_{0.40\pm0.13}S_{0.03\pm0.01}O_{10} \text{ [6]}$$
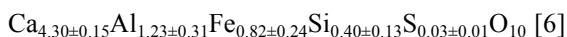
According to [26] the composition of ferrite phase in SAB cements is more ferrous than that in Portland cement.

The ferrite phase in SAB cement consists of smaller and poorer grains than in Portland cement [1, 4, 6] and the size of ferrite grains (1-2 μm) has been close to the limit of analytical detection. Backscattered electron images of SAB clinkers [6] showed that the ferrite is a bright phase and has been intergrown with other phases. The ferrite phase in the expansive cement clinker burned at temperatures below 1200 °C had the appearance of aggregates of minute crystals, but in the fused clinker it was dispersed chiefly to irregular shapes [27].

Solid solutions and morphology of $C\bar{S}$

According to [16] $C\bar{S}$ contained up to 1 wt % Fe_2O_3. In the system C-S-$\bar{S}$, anhydrite was found in a pure form, not forming solid solution [7].

The grain structure examination of anhydrite in expansive cement clinker has been performed in [27]. $C\bar{S}$ was recognised as irregular-shaped grains, without any distinct outline of crystals.

EXPERIMENTAL PART

The six SAB clinkers having the nominal phase composition: SAB1; 20 % C_2S, 20 % $C_4A_3\bar{S}$, 40 % C_4AF, 20 % $C\bar{S}$, SAB2-4; 30 % C_2S, 20 % $C_4A_3\bar{S}$, 30 % C_4AF, 20 % $C\bar{S}$, SAB5; 30 % C_2S, 20 % $C_4A_3\bar{S}$, 30 % C_6A_2F, 20 % $C\bar{S}$, SAB6; 30 % C_2S, 20 % $C_4A_3\bar{S}$, 30 % (C_2F + "C_2A"), 20 % $C\bar{S}$ (the mixture C_2F + "C_2A" was prepared using C_2F crystals, which had been obtained from K_2SO_4 flux at 1200 °C and water leached afterwards; "C_2A" was mixture of $CaCO_3$ + Al_2O_3), were selected for an experimentation.

The clinkers were prepared using analytical reagent grade $CaCO_3$, Al_2O_3, Fe_2O_3, $CaSO_4.2H_2O$ and silica gel in appropriate weight ratios. The mixtures were homogenised in an agate mortar and calcined in an electric furnace at 1000 °C for 1 hour. The calcined products were again homogenised, pelleted into short cylinders and calcined again to 1000 °C for 0.5 hour. The obtained pellets were encapsulated into Pt-tubes (diameter 5.25 mm, wall thickness 0.2 mm) by welding the ends of tubes.

The encapsulated samples were heated up to 1450 °C and hold at this temperature for 15 min. Then they were continuously cooled to 1200 °C at a cooling rate of approx. 0.6 °C/min. The samples were tempered at 1200 °C with a different soak (SAB1 without soak, SAB2, SAB5, SAB6 for 4 hours and SAB3, SAB4 for 48 hours) and next unhamperedly cooled to room temperature (sample SAB4 was air quenched from 1200 °C).

The phase composition of the products was examined by XRD using Philips powder diffractometer PW 1710 (CuKa radiation). The chemical composition of solid solutions was determined by electron probe microanalysis (EPMA) Jeol JXA 840 A. (wavedispersive analysis, accelerating potential 20 kV, electron flow 10 nA, beam focused to 1 mm). The ceramic standards have been used with known content of analysed oxides. The computation has been performed using ZAF program. The results are mean values from 15 experiments. For the EPMA study the samples were impregnated with epoxy resin, polished, coated with carbon. SEM micrographs and corresponding X-ray WDS dot maps for elements Si, Al, Fe, S were carried out by backscattered electrons.

RESULTS AND DISCUSSION

The reason of sealing the samples in platinum tubes was to prevent the loss of sulphates at high temperatures. The temperature of 1450 °C at which the samples were preliminary heated resulted in a melt quantity since whole ferrite phase was expected to be melted.

Slow cooling of the samples from 1450 °C was applied to ensure the melt assisted growth of crystals which was expected to result in their increased size and the morphology convenient for the EPMA investigation. The yielded size of clinker crystals, about 10 μm, was satisfactory for this purpose.
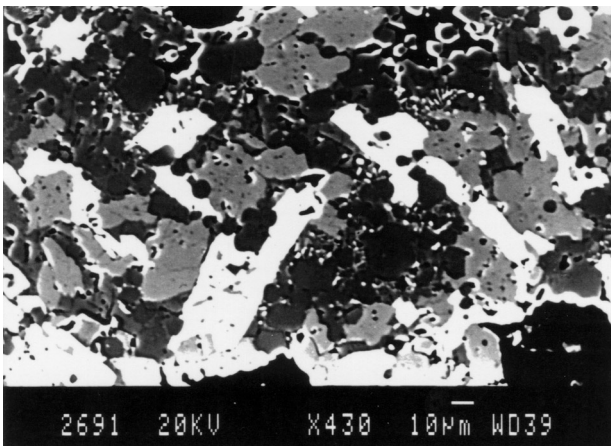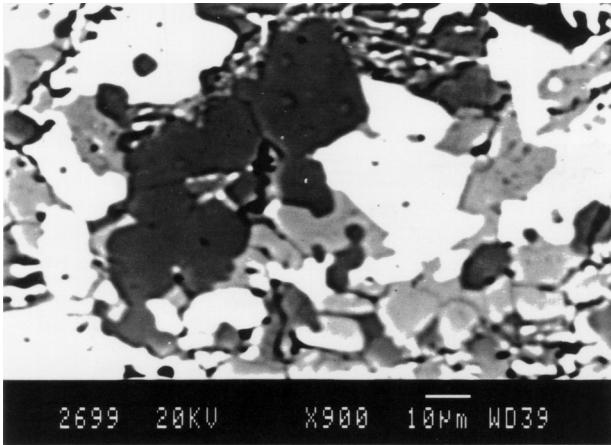
Figure 2. Backscattered SEM micrographs in the sample SAB4.

Figure 1. Backscattered SEM micrographs in the sample SAB3.

Figure 3. Backscattered SEM micrographs in the sample SAB5.

XRD analysis of the samples showed the presence of small amount of free lime besides β-C$_2$S, C$_4$A$_3$$\overline{S}$, C$_4$AF and C$\overline{S}$ respectively. The α'-C$_2$S was not identified. Free lime C was not expected to produce a solid solution, therefore its crystals were not analysed in detail. An equilibration of the clinker phases has been improved by prolonged tempering of samples at 1200 °C, which was well reflected by an increased height of their relevant XRD-peaks.

Microstructural examination

The microstructural examinations of phase distribution of the clinkers are shown in figure 1 for SAB3, in figure 2 for SAB4, in figure 3 for SAB5 and in figure 4 for SAB6 respectively; for samples SAB1 and SAB2 have been published in [28] (SAB1 in figures 1 and 2, and SAB2 in figure 3 of the work [28]).

C$_2$S, C$_4$A$_3$$\overline{S}$, C$_4$AF and C$\overline{S}$ in SEM micrographs are well identified. C$_2$S forms grey regions, irregularly shaped, with clean margins. C$_4$A$_3$$\overline{S}$ is found in angular hexagonal dark grey crystals. The ferrite phase appears as large bright crystals with irregular shapes and clear margins too. C$\overline{S}$ appears as dark grey regions with not quite well developed morphology, fuzzy margins and the crystals exhibit parallel cracks. It was difficult to
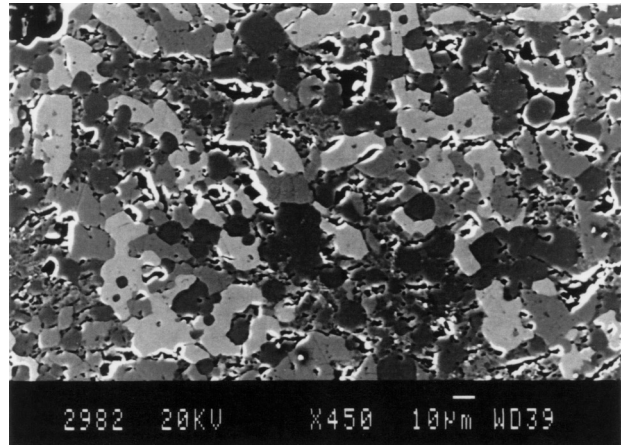

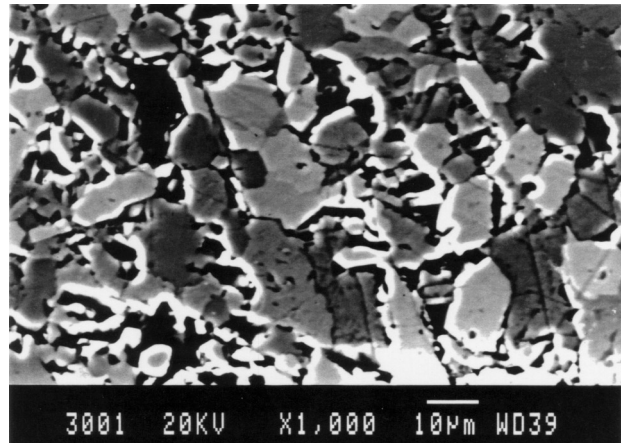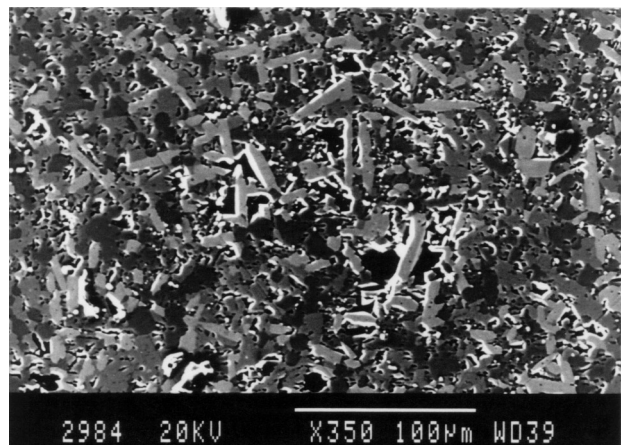Figure 4. Backscattered SEM micrographs in the sample SAB6.

find suitable large C$\overline{S}$ crystals in the clinkers such as it was shown in figure 3 of the work [28] (at the right side, bottom of the figure 3., No. 2501 [28]). The corresponding X-ray WDS dot maps for elements Si, Al, Fe and S are enclosed in [29].

The inhomogeneities were sometimes found out in $C_4A_3\bar{S}$ crystals as it is shown in figure 1. (there are at the top in the middle of the picture No. 2699).

More open textured structure was observed in the clinker SAB5 probably caused by lower amount of Fe_2O_3 given in the raw mix in comparison with the other clinkers.

C_2F crystals were admixed into the raw mix for clinker SAB6 as a template for the ferrite phase growth. In this case, the ferrite phase was shaped in needle like crystals figure 4.
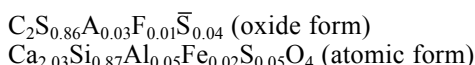
Chemical composition of clinker minerals

The chemical composition of clinker minerals from microprobe analysis is summarised in tables 1-4 for samples SAB3-6; for SAB1-2 has been already published in [28]. The tables contain arithmetic means of about fifteen analyses with maximum deviations of measurements. Table 5 contains mean composition of the phases from all samples SAB1-6.

In general, the phases contain, in a comparison to the stoichiometric composition, a slightly increased amount of CaO needed to compensate foreign admixtures. The highest deviations of microprobe measurements are observed for $C_4A_3\bar{S}$ and C_4AF phases. The presence of inhomogeneities was observed also in some crystals of $C_4A_3\bar{S}$, which is seen in figure 1.
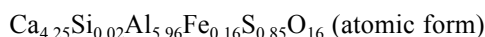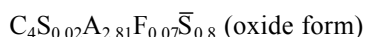
On the other hand C_2S and $C\bar{S}$ have been the most homogeneous phases with respect to the deviations in chemical composition. The deviations have decreased by longer tempering at 1200 °C; the samples SAB2 and 3. The content of admixtures presently determined is generally lower than shown by data published in literature [4, 6-10, 12-16], in spite of the high starting temperature 1450 °C used at the preparation of samples. The amounts of admixtures in the C_2S, $C_4A_3\bar{S}$, C_4AF and $C\bar{S}$ have been approximately the same for all samples SAB1-6 and their averages are given in table 5.

The composition of C_2S in the SAB1-6 samples varies in the following ranges CaO: 64.90-66.44, SiO_2: 28.93-31.04, Al_2O_3: 1.32-2.19, Fe_2O_3: 0.65-1.07, SO_3: 1.80-2.52. The average of admixtures in C_2S structure is about 1.5 % for Al_2O_3, up to 1 % for Fe_2O_3 and about 2 % for SO_3. The amounts of admixtures increase in a sequence $SO_3 > Al_2O_3 > Fe_2O_3$. The formula of C_2S composition (The data from Table 5 have been used as a source for the formula calculation) can be represented as follows (oxide form recalculated to 2 CaO; atomic form recalculated to 4 oxygens):

$C_2S_{0.86}A_{0.03}F_{0.01}\bar{S}_{0.04}$ (oxide form)
$Ca_{2.03}Si_{0.87}Al_{0.05}Fe_{0.02}S_{0.05}O_4$ (atomic form)

The composition of $C_4A_3\bar{S}$ in the samples SAB1-6 varies in the intervals CaO: 37.51-38.68, SiO_2: 0.08-0.25, Al_2O_3: 47.35-50.68, Fe_2O_3: 1.62-2.23, SO_3: 8.41-13.23. The amounts of SO_3 an Al_2O_3 vary on a relatively large scale, however, the prolonged tempering

at 1200 °C (sample SAB3) has decreased this variability. The SO_3 contents are lower than the contents published in [4, 8, 13-15]. The average of admixtures in $C_4A_3\bar{S}$ is generally low, about 0.15 % for SiO_2 and about 2 % for Fe_2O_3 in comparison with values given in [4, 8, 10, 13-16]. Especially Fe_2O_3 content is very low in comparison with its max. Solubility ~ 9 wt % reported in [10, 16]. The presence of sulphoferrite phase such as $C_4F_3\bar{S}$ was not confirmed in spite of an use of the precursor C_2F crystals in the sample SAB6. The formula of $C_4A_3\bar{S}$ composition can be expressed as follows (oxide form recalculated to 4 CaO; atomic form recalculated to 16 oxygens):

$C_4S_{0.02}A_{2.81}F_{0.07}\bar{S}_{0.8}$ (oxide form)

$Ca_{4.25}Si_{0.02}Al_{5.96}Fe_{0.16}S_{0.85}O_{16}$ (atomic form)

The composition of ferrite phase in samples SAB1-6 varies inside the specified levels of oxides, CaO: 44.22-47.75, SiO_2: 0.59-1.38, Al_2O_3: 13.75-17.24, Fe_2O_3: 34.23-39.32, SO_3: 0.09-1.04. It is seen that the ferrite phase contains an increased amount of Fe_2O_3 in comparison to C_4AF, which brings it essentially close to the C_6AF_2 stoichiometry. The amounts of Al_2O_3 and Fe_2O_3 vary on a relatively large scale namely in samples SAB1, 2 and 6. The prolonged tempering at 1200 °C (samples SAB3 and 4) has decreased this variability as in previous cases.

Since the high-ferrous ferrite phase was formed in samples, the chemical composition of raw mix for clinker SAB5 was calculated to give less ferrous phase C_6A_2F. In spite of this the high-ferrous phase has formed in this clinker too.

In a preparation of clinker SAB6, the ferrite phase has been introduced in the powder mixture as crystals C_2F. It was interesting to see, whether the formation of sulphoferrite phases as a $C_2F + C\bar{S}$ solid solution would be observed. In spite of this arrangement the high-ferrous ferrite phase has been formed. The levels of Fe_2O_3 introduced in the phases C_2S and $C_4A_3\bar{S}$, when starting from C_2F crystals, are approximately the same as in the other samples SAB1-5. It supports the idea that the ferrite phase at 1450 °C was completely melted.

All ferrite phases of studied clinkers SAB1-6 contained small quantities of SiO_2 and SO_3. The average of admixtures in ferrite phase is generally low, about 1 % for SiO_2 and about 0.5 % for SO_3, in comparison with values given in [4, 6, 13]. The value 1 % of SiO_2 slightly exceeds the equilibrium solubility of SiO_2 in ferrite phase (0.8 %) as given in [12]. About 0.5 % of SO_3 is approximately the same value as found in [6] after a selective dissolution of the ferrite phase.

The formula of ferrite phase can be represented as follows (oxide form recalculated to 4 CaO and 6 CaO; atomic forms recalculated to 10 and 15 oxygens):
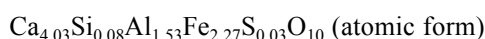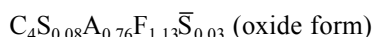
$C_4S_{0.08}A_{0.76}F_{1.13}\bar{S}_{0.03}$ (oxide form)

$Ca_{4.03}Si_{0.08}Al_{1.53}Fe_{2.27}S_{0.03}O_{10}$ (atomic form)

Table 1. Chemical analysis of clinker minerals in sample SAB 3.

		CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$
C$_2$S	(wt.%)	65.30 ± 0.06	30.93 ± 0.30	1.33 ± 0.14	0.65 ± 0.14	1.80 ± 0.25
	(mol.%)	67.75 ± 0.11	29.95 ± 0.27	0.76 ± 0.08	0.24 ± 0.05	1.31 ± 0.18
C$_4$A$_3\overline{S}$	(wt.%)	37.51 ± 1.24	0.08 ± 0.16	47.57 ± 1.13	1.62 ± 0.19	13.23 ± 1.13
	(mol.%)	50.97 ± 1.33	0.10 ± 0.20	35.56 ± 1.10	0.77 ± 0.09	12.59 ± 1.12
C$_4$AF	(wt.%)	46.18 ± 0.82	0.89 ± 0.61	15.46 ± 1.52	37.39 ± 1.06	0.09 ± 0.14
	(mol.%)	67.21 ± 0.68	1.20 ± 0.82	12.38 ± 1.26	19.11 ± 0.62	0.10 ± 0.14
C$\overline{S}$	(wt.%)	45.95 ± 0.30	0.10 ± 0.07	0.00 ± 0.00	0.26 ± 0.01	53.69 ± 0.35
	(mol.%)	54.88 ± 0.28	0.11 ± 0.08	0.00 ± 0.00	0.11 ± 0.02	44.91 ± 0.36

Table 2. Chemical analysis of clinker minerals in sample SAB 4.

		CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$
C$_2$S	(wt.%)	64.90 ± 0.35	31.04 ± 1.22	1.32 ± 0.19	0.79 ± 0.11	1.94 ± 1.16
	(mol.%)	67.43 ± 0.32	30.11 ± 1.08	0.76 ± 0.11	0.29 ± 0.04	1.41 ± 0.86
C$_4$A$_3\overline{S}$	(wt.%)	38.03 ± 1.69	0.16 ± 0.14	50.65 ± 4.50	2.23 ± 0.35	8.93 ± 5.99
	(mol.%)	52.05 ± 2.40	0.20 ± 0.17	38.13 ± 3.45	1.07 ± 0.16	8.55 ± 5.73
C$_4$AF	(wt.%)	45.06 ± 0.18	0.59 ± 0.52	17.24 ± 0.33	36.43 ± 1.01	0.67 ± 0.82
	(mol.%)	65.92 ± 0.62	0.81 ± 0.71	13.87 ± 0.27	18.72 ± 0.61	0.69 ± 0.83
C$\overline{S}$	(wt.%)	43.12 ± 0.96	1.45 ± 0.06	0.13 ± 0.02	0.45 ± 0.11	54.85 ± 1.26
	(mol.%)	51.87 ± 0.78	1.63 ± 0.03	0.09 ± 0.04	0.19 ± 0.08	46.22 ± 0.85

Table 3. Chemical analysis of clinker minerals in sample SAB 5.

		CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$
C$_2$S	(wt.%)	66.44 ± 0.86	28.93 ± 2.02	1.91 ± 1.04	0.71 ± 0.07	2.02 ± 1.12
	(mol.%)	69.10 ± 0.93	28.08 ± 1.87	1.10 ± 0.61	0.26 ± 0.02	1.47 ± 0.82
C$_4$A$_3\overline{S}$	(wt.%)	38.68 ± 1.02	0.13 ± 0.22	47.72 ± 3.58	2.12 ± 0.62	11.36 ± 4.49
	(mol.%)	52.45 ± 1.51	0.16 ± 0.28	35.59 ± 2.76	1.01 ± 0.29	10.79 ± 4.25
C$_4$AF	(wt.%)	47.75 ± 0.31	0.95 ± 0.64	16.60 ± 2.04	34.23 ± 1.22	0.46 ± 0.36
	(mol.%)	68.10 ± 0.61	1.27 ± 0.86	13.02 ± 1.60	17.14 ± 0.62	0.46 ± 0.36
C$\overline{S}$	(wt.%)	44.39 ± 0.77	0.02 ± 0.02	0.19 ± 0.10	0.38 ± 0.03	55.03 ± 0.66
	(mol.%)	53.36 ± 0.76	0.02 ± 0.02	0.13 ± 0.07	0.16 ± 0.01	46.34 ± 0.70

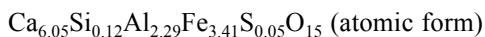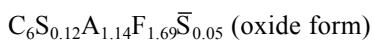Table 4. Chemical analysis of clinker minerals in sample SAB 6.

		CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$
C$_2$S	(wt.%)	65.34 ± 1.08	29.92 ± 0.64	1.37 ± 0.18	0.84 ± 0.03	2.52 ± 0.97
	(mol.%)	68.00 ± 0.96	29.07 ± 0.66	0.79 ± 0.11	0.31 ± 0.01	1.84 ± 0.71
C$_4$A$_3\overline{S}$	(wt.%)	38.39 ± 2.37	0.25 ± 0.09	47.35 ± 3.71	1.77 ± 0.47	12.25 ± 6.45
	(mol.%)	51.97 ± 3.22	0.31 ± 0.11	35.26 ± 2.78	0.84 ± 0.23	11.62 ± 6.12
C$_4$AF	(wt.%)	46.81 ± 1.23	1.06 ± 1.12	16.41 ± 4.94	34.68 ± 2.87	1.04 ± 1.67
	(mol.%)	67.12 ± 1.37	1.42 ± 1.49	12.95 ± 3.94	17.47 ± 1.36	1.04 ± 1.68
C$\overline{S}$	(wt.%)	42.85 ± 0.68	0.21 ± 0.01	1.35 ± 0.27	2.53 ± 0.87	53.09 ± 1.81
	(mol.%)	52.35 ± 0.92	0.24 ± 0.01	0.91 ± 0.18	1.09 ± 0.38	45.43 ± 1.47

Table 5. Arithmetic means of the values from tables 1-4 and tables 1 and 2 of [28].

		CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$
C$_2$S	wt %	65.52	30.02	1.59	0.81	2.07
	mol %	68.15	29.15	0.91	0.30	1.51
C$_4$A$_3\bar{S}$	wt %	38.21	0.15	48.77	1.99	10.89
	mol %	51.99	0.19	36.50	0.95	10.37
C$_4$AF	wt %	45.87	1.00	15.80	36.79	0.54
	mol %	66.66	1.35	12.64	18.81	0.55
C$\bar{S}$	wt %	44.76	0.33	0.32	0.71	53.89
	mol %	53.76	0.37	0.22	0.30	45.36

Table 6. Chemical composition of the "C-S-$\bar{S}$" phases - inhomogeneities identified in the samples SAB1, 2, 3 and 5.

		CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$
SAB1	wt %	52.62	6.66	0.57	0.60	39.57
	mol %	60.43	7.14	0.36	0.24	31.83
SAB2	wt %	59.45	24.35	4.61	6.59	5.02
	mol %	65.66	25.10	2.80	2.56	3.88
SAB3	wt %	62.09	29.67	1.30	0.95	6.00
	mol %	65.33	29.14	0.75	0.35	4.42
SAB5	wt %	61.19	26.11	5.19	0.99	6.52
	mol %	65.56	26.11	3.06	0.37	4.89

$C_6S_{0.12}A_{1.14}F_{1.69}\bar{S}_{0.05}$ (oxide form)

$Ca_{6.05}Si_{0.12}Al_{2.29}Fe_{3.41}S_{0.05}O_{15}$ (atomic form)

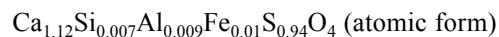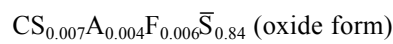The composition of C$\bar{S}$ phase in the samples SAB1-6 varies inside the following levels of oxides, CaO: 42.85-48.05, SiO$_2$: 0.02-1.45, Al$_2$O$_3$: 0.00-1.35, Fe$_2$O$_3$: 0.26-2.53, SO$_3$: 51.28-55.40. CaO and SO$_3$, its main constituents vary on a relatively large scale. The amount of CaO is continuously higher, amount of SO$_3$ continuously lower in comparison to the stoichiometric composition.

From geometrical reasons one would expect that relatively large ions (Fe^{3+}, Al^{3+} and Si^{4+}) will not enter the structure of C$\bar{S}$ at all. However the experimental results show positive contents of the mentioned ions in the structure.

The average of admixtures in C$\bar{S}$ structure is very low, 0.3 % for SiO$_2$, 0.3 % for Al$_2$O$_3$ and 0.7 % for Fe$_2$O$_3$. The highest quantities of Al$_2$O$_3$ and Fe$_2$O$_3$ admixtures have been observed in the sample SAB6 (Table 4) and of SiO$_2$ in the sample SAB4 (Table 2). This is interesting to notice that the Fe$_2$O$_3$ content in the C$\bar{S}$ structure is higher than that of SiO$_2$ and Al$_2$O$_3$ in spite of the fact, that the difference between ion size of S^{6+} and Fe^{3+} is higher than the difference between ion size of S^{6+} and Al^{3+} and Si^{4+} respectively. The quantity of Fe$_2$O$_3$ according to [16] reaches to 1 %.

The formula of C$\bar{S}$ composition can be represented as follows (oxide form recalculated to 1 CaO; atomic forms recalculated to 4 oxygens):

$CS_{0.007}A_{0.004}F_{0.006}\bar{S}_{0.84}$ (oxide form)

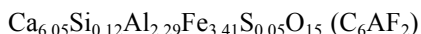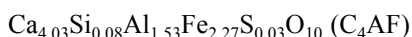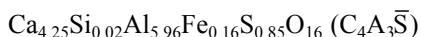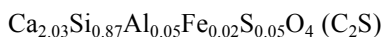$Ca_{1.12}Si_{0.007}Al_{0.009}Fe_{0.01}S_{0.94}O_4$ (atomic form)

Besides the phases treated there were found other phases - inhomogeneities "C-S-$\bar{S}$" in clinkers SAB1, 2, 3 and 5, containing CaO, SiO$_2$ and SO$_3$ as major oxides (Table 6.). The referred inhomogeneity from SAB1, found as relatively small oval inclusion in the ferrite grain, has a molar ratio CaO/SO$_3$ equal to 1.9. This ratio might indicate C$\bar{S}$ (stoichiometric CaO/SO$_3$ = 1). An increased ratio is however required to compensate for SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ admixtures. This phase is well identified in SEM micrograph of clinker SAB1 given in [28] (Figure 1 in [28]). The phase is enclosed by ferrite phase (the ferrite phase - large bright region in the middle of figure 1, picture No. 2291 [28]) and it is found nearly to the middle of the ferrite phase (small dark grey circular region; see corresponding X-ray WDS dot maps for elements Si and S published in [29]).

Another inhomogeneity "C-S-$\bar{S}$" observed was phase in SAB2, 3 and 5 samples having a molar ratio CaO/SiO$_2$ equal to 2.6, 2.2 and 2.5. These ratios might indicate C$_2$S modified with Al$_2$O$_3$, Fe$_2$O$_3$ and SO$_3$ admixtures. These phases are not considered to be related to C$_5$S$_2\bar{S}$, because of the too low content of SO$_3$ (about 6 wt %) (stoichiometric content of SO$_3$ in C$_5$S$_2\bar{S}$ is 16.66 wt %) and C$_5$S$_2\bar{S}$ is not compatible with simultaneously both C$_2$S and C$\bar{S}$.

CONCLUSION

The chemical composition of coexisting solid solutions inside the phase assemblage C-C$_2$S-C$_4$A$_3\overline{S}$-C$_4$AF-C$\overline{S}$ was determined belonging to the oxide system CaO-SiO$_2$-Al$_2$O$_3$-Fe$_2$O$_3$-SO$_3$. The pertinent samples were Pt encapsulated and cooled from 1450 °C with equilibration periods at 1200 °C. The present phases had well developed morphology and a size of crystals approximately 10 μm.

The content of admixtures entering the clinker phases as determined by electron probe microanalysis is generally lower than that corresponding to data published in the literature. C$_2$S and C$\overline{S}$ form more homogenous crystals with respect to chemical composition than C$_4$A$_3\overline{S}$ and ferrite phase. The stoichiometry of ferrite phase present under circumstances of experiments can be more adequately represented by a composition corresponding to C$_6$AF$_2$. The C$\overline{S}$ phase has usually contained less than 1.5 % of admixtures. The solid solution formulae of the clinker phases can be represented as follows:

$$Ca_{2.03}Si_{0.87}Al_{0.05}Fe_{0.02}S_{0.05}O_4 \ (C_2S)$$

$$Ca_{4.25}Si_{0.02}Al_{5.96}Fe_{0.16}S_{0.85}O_{16} \ (C_4A_3\overline{S})$$

$$Ca_{4.03}Si_{0.08}Al_{1.53}Fe_{2.27}S_{0.03}O_{10} \ (C_4AF)$$

$$Ca_{6.05}Si_{0.12}Al_{2.29}Fe_{3.41}S_{0.05}O_{15} \ (C_6AF_2)$$

$$Ca_{1.12}Si_{0.007}Al_{0.009}Fe_{0.01}S_{0.94}O_4 \ (C\overline{S})$$

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Submitted in English by the author.

MORFOLÓGIA A CHEMICKÉ ZLOŽENIE MINERÁLOV FÁZOVEJ ASOCIÁCIE C - C$_2$S - C$_4$A$_3\overline{S}$ - C$_4$AF - C$\overline{S}$ RELEVANTNEJ PRE SULFOALUMINÁTOVÉ CEMENTY

JÚLIUS STRIGÁČ**, MARTIN T. PALOU,
JOZEF KRIŠTÍN*, JÁN MAJLING

Katedra keramiky, skla a cementu, Chemickotechnologická fakulta, Slovenská technická univerzita, Radlinského 9, 812 37 Bratislava, Slovenská republika.

* Centrálne laboratóriá elektrónovo-optických metód, Prírodovedecká fakulta, Komenského Univerzita, 842 12 Bratislava, Slovenská republika.

**Považská Cementáreň a.s., ul. J. Kráľa, 018 63 Ladce, Slovenská Republika

Práca sa zaoberá tvorbou tuhých roztokov vo vnútri rovnovážnej asociácie fáz C - C$_2$S - C$_4$A$_3\overline{S}$ - C$_4$AF - C$\overline{S}$, v rámci oxidového systému CaO-SiO$_2$-Al$_2$O$_3$-Fe$_2$O$_3$-SO$_3$. Vyšetrované

fázy tvoria mineralogický základ sulfoaluminátových belitových slinkov. Vzorky boli uzatvárané do Pt kapsúl, zahrievané na 1450 °C, pomaly chladené na 1200 °C, kde boli zrovnovážňované pri rôznych časových výdržiach. Prítomné slinkové minerály mali dobre vyvinutú morfológiu s veľkosťou kryštálov okolo 10 μm, čo bolo postačujúce pre ich chemickú charakterizáciu RTG mikroanalýzou.

Prostredníctvom odrazených elektrónov sa C_2S identifikoval ako veľké šedé kryštály, $C_4A_3\overline{S}$ tvoril hranaté hexagonálne tmavošedé kryštály, feritová fáza vykryštalizovala ako veľké svetlé nepravidelné kryštály, $C\overline{S}$ tvoril tmavošedé kryštály s paralelenými priečnymi trhlinami.

Napriek zmenám vo východiskovom chemickom zložení skúmaných slinkov a taktiež rôznym časom temperovania pri 1200 °C, chemické zloženie jednotlivých fáz v rôznych slinkoch sa navzájom nelíšilo a taktiež obsah prímesí v porovnaní s publikovanými bol nižší. S ohľadom na chemické zloženie homogénnejšie kryštály tvorili fázy C_2S a $C\overline{S}$, kým u $C_4A_3\overline{S}$ a C_4AF boli namerané väčšie výkyvy v chemickom zložení. Minerály mali zvýšený obsah CaO oproti stechiometrickému, ktorý bol potrebný na kompenzáciu prítomných prímesí. Priemerný obsah prímesí v $C\overline{S}$ bol 1,5 %, pri C_2S 4,5 %, pri $C_4A_3\overline{S}$ 2 % a feritovej fáze 1,5 %. Stechiometria feritovej fázy, vychádzajúc z nameraných výsledkov by sa mohla aproximatívne vyjadriť ako C_6AF_2. Výsledky chemického zloženia slinkových minerálov môžu byť využité pri spresňovaní fázových výpočtoch podľa Bogua.