

PHASE COMPATIBILITY IN THE SYSTEMS CaO - SiO₂ - Fe₂O₃ - SO₃, CaO - Al₂O₃ - Fe₂O₃ - SO₃ AND SiO₂ - Al₂O₃ - Fe₂O₃ - SO₃

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Three quaternary oxide systems C - S - F - \bar{S}^+ , C - A - F - \bar{S} and S - A - F - \bar{S} are analysed for their subsolidus phase compatibility. The phase compatibility models of the particular systems are derived from the literature data as well as from the partial modelling of the phase compatibility relationships based on the geometrical consideration and on the own theoretical discussion. Fifteen quaternary phase assemblages have been established in the system C - S - F - \bar{S} , twenty-three in the system C - A - F - \bar{S} and six in the system S - A - F - \bar{S} respectively, which define the entire phase space of the analysed systems.

INTRODUCTION

The title oxide systems contain phases which are important in the chemistry of low energy cements such as sulphoaluminate belite (SAB) cements, most frequently with main mineralogical components C₂S, C₄A₃ \bar{S} , C₄AF, C \bar{S} and a minor amount of CaO [1].

These systems together with the systems C - S - A - F and C - S - A - \bar{S} are the subsystems of the five component system C - S - A - F - \bar{S} .

From the individual four component systems, only the system C - S - F - \bar{S} contains SiO₂ which gives rise to the necessary portland cement silicate phases C₃S, C₂S and to C₅S₂ \bar{S} potentially present in SAB cements. An attempt to make a cement in this system resulted in sulphoferrite cements [2-4] based on the mineralogical composition including C₄F₃ \bar{S} , C₃F₂ \bar{S} and C₃F \bar{S} that are the solid solutions of C₂F and CF with C \bar{S} . According to [3] the composition of the foregoing solid solutions is variable C_(3+n)F₃S_n (from n = 0.75 to 1.5) and C_(2+m)F \bar{S} _m (from m = 0.8 to 1.5). Their presence was not confirmed in the other works [5-7].

The oxide system C - S - F - \bar{S} includes four ternary subsystems C - S - F, C - S - \bar{S} , C - F - \bar{S} and S - F - \bar{S} from which the systems C - S - F [8] and C - S - \bar{S} [9] are fully described, C - F - \bar{S} is described only partially [5, 10] and S - F - \bar{S} has not been studied at all. The system C - S - F - \bar{S} has been studied in [5, 10].

The system C - A - F - \bar{S} contains three important cement clinker phases C₄A₃ \bar{S} , C₄AF and C \bar{S} present in low energy cements and the four phases C₃A, C₁₂A₇, CA and CA₂ present in calciumaluminate cements. Brownmillerite is usually from practical reasons

approximated to the stoichiometric compound C₄AF. In SAB cement the composition in its solid solution series is extended towards C₂F [11]. Equally C₄A₃ \bar{S} is considered as a stoichiometric compound in spite of the solid solution C₄(A,F)₃ \bar{S} published in [6, 7]. A study on the formation of some clinker minerals in this system was carried out in [12].

The system C - A - F - \bar{S} includes four ternary subsystems C - A - F, C - A - \bar{S} , C - F - \bar{S} and A - F - \bar{S} from which the subsystems C - A - F [8] and C - A - \bar{S} [13] are fully described C - F - \bar{S} is described partially [5, 10] and A - F - \bar{S} has not been described yet. The system C - A - F - \bar{S} has been studied in [5, 10, 12].

The system S - A - F - \bar{S} does not contain CaO which is the main chemical component of each cement and therefore this system has not been discussed from the point of cement chemistry anywhere. Its two subsystems S - A - F and S - A - \bar{S} are described in [8] and in [9] respectively. The other two subsystems, S - F - \bar{S} and A - F - \bar{S} , according to our knowledge have not been studied yet.

The aim of this work is to establish consistent compatibility (coexistence) models of the systems C - S - F - \bar{S} , C - A - F - \bar{S} and S - A - F - \bar{S} based on the published phase compatibility data, on geometrical considerations and on a minor self phase equilibrium study. Present phases are considered as stoichiometric compounds at all encountered temperatures. According to the literature, no quaternary phase is present in these systems.

† C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, \bar{S} = SO₃.

The geometrical analysis of the phase compatibility was aided by specially developed programs (unpublished) enabling us to identify the singular chemical composition of the systems i. e. those which could be linked to chemical reaction of specific types. The respective reactions of the type $A + B \rightarrow C + D$ and $A + B + C \rightarrow D + E$ have been of particular interest. The participants in the reaction schemes were single phases encountered in the systems.

The absence of relevant thermodynamic data of some phases made it impossible to predict the course of reactions on a general basis, e.g. the stable phase pairs (assemblages).

There is no definite reference temperature of the equilibrium phase compatibility defined either. This reflects the high and sometimes the very high difference in melting points of individual phases and in their thermal stability.

The phase compatibility models can be exploited in phase equilibria studies in the five component oxide system C - S - A - F - \bar{S} relevant to sulphoaluminate, sulphoferrite and sulphosilicate cements.

EXPERIMENTAL PART

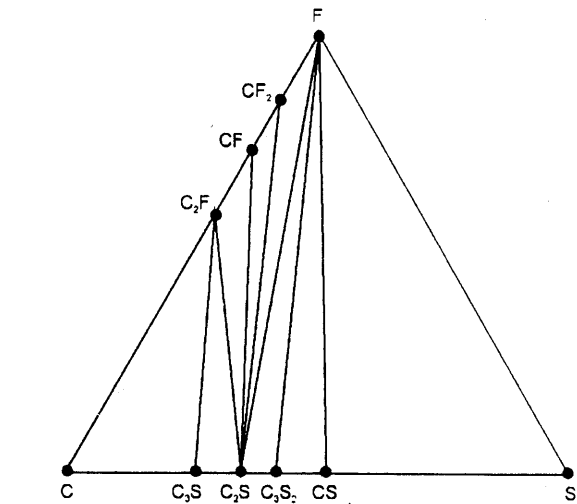
Most of the phase relationships were published in literature except for the compatibility data including phases $\bar{A}\bar{S}_3$, $\bar{F}\bar{S}_3$ and $\bar{F}\bar{A}$. The preparation of $\bar{F}\bar{A}$ was attempted using the analytical reagent grade Al_2O_3 and Fe_2O_3 . A stoichiometric mixture was homogenised in an agate mortar, pelletised and fired according to conditions given in [8] (1340 °C for 6 hours) with subsequent quenching.

REVIEW OF THE RELEVANT LITERATURE DATA, RESULTS AND DISCUSSION

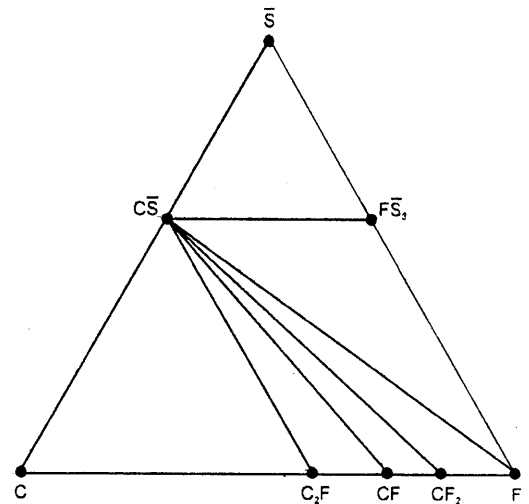
System C - S - F - \bar{S}

This system contains 9 binary phases C_3S , C_2S , C_3S_2 , CS , C_2F , CF , CF_2 , $\text{C}\bar{\text{S}}$, $\bar{\text{F}}\bar{\text{S}}_3$ and one ternary phase $\text{C}_5\text{S}_2\bar{\text{S}}$. The sulphoferrite phases $\text{C}_4\text{F}_3\bar{\text{S}}$, $\text{C}_3\text{F}_2\bar{\text{S}}$ and $\text{C}_3\text{F}\bar{\text{S}}$ have not been included in the system. The subsystems C - S - F [8] and C - S - \bar{S} [9] are fully described, C - F - \bar{S} is partially described [5, 10] except for the compatibility of $\text{C}\bar{\text{S}}$ and $\bar{\text{F}}\bar{\text{S}}_3$, but the coexistence $\text{C}\bar{\text{S}}$ - $\bar{\text{F}}\bar{\text{S}}_3$ as related to geometrical consideration must be inevitable as well as the coexistence S - $\bar{\text{F}}\bar{\text{S}}_3$ which is the only possible coexistence in the subsystem S - F - \bar{S} . In this way, all these subsystems can be taken as established (figure 1).

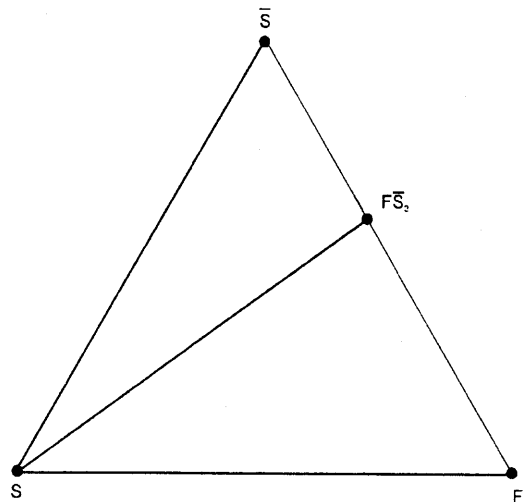
The phase relations among phases in the quaternary system C - S - F - \bar{S} were studied in [5, 10] with the establishment of the following assemblages:



a)



b)



c)

Figure 1. Diagrams of the phase compatibility in the subsystems of the system C - S - F - \bar{S} (subsystem C - S - \bar{S} was published in [9]). a) subsystem C - F - S, b) subsystem C - F - \bar{S} , c) subsystem S - F - \bar{S}

- (I) $C - C_2S - C_2F - C_5S_2\bar{S}$ [5]
 (II) $C - C_2F - CS - C_5S_2\bar{S}$
 (III) $C_2S - C_2F - CF - C_5S_2\bar{S}$
 (IV) $C_2F - CF - CS - C_5S_2\bar{S}$

The phase compatibility in this system referred to the sulphoaluminate belite cement clinker, where C_3S and $C_5S_2\bar{S}$ phases have not been included (burning temperature 1200 °C) were studied in [10]. Five 4 phase assemblages were identified:

- (V) $C - C_2S - C_2F - C\bar{S}$ [10]
 (VI) $F - C_2S - C_3S_2 - C\bar{S}$
 (VII) $F - C_2S - CF_2 - C\bar{S}$
 (VIII) $C_2S - C_2F - CF - C\bar{S}$
 (IX) $C_2S - CF - CF_2 - C\bar{S}$

Experimental results [10] showed these three 5 component assemblages $C_2S - C_3S_2 - F - C\bar{S} - C_5S_2\bar{S}$, $C_2S - CF - CF_2 - C\bar{S} - C_5S_2\bar{S}$ and $C_2S - CF_2 - F - C\bar{S} - C_5S_2\bar{S}$ from which the following new 4 phase assemblages result:

- (X) $F - C_2S - C_3S_2 - C_5S_2\bar{S}$
 (XI) $F - C_2S - CF_2 - C_5S_2\bar{S}$
 (XII) $F - C_3S_2 - C\bar{S} - C_5S_2\bar{S}$
 (XIII) $F - CF_2 - C\bar{S} - C_5S_2\bar{S}$
 (XIV) $C_2S - CF - CF_2 - C_5S_2\bar{S}$
 (XV) $CF - CF_2 - C\bar{S} - C_5S_2\bar{S}$

These 15 assemblages do not contain S , \bar{S} , C_3S , CS and FS_3 phases. Temperatures at which these assemblages were established 950 °C and 1050 °C did not enable the presence of C_3S and FS_3 . According to [14] Fe^{3+} ions together with SO_4^{2-} ions in the system $C - S - F - \bar{S}$ had no adverse effect on C_3S formation, therefore the presence of C_3S in this system below 1300 °C is prospective.

The presence of FS_3 for the sake of its low thermal stability (480 °C in the open system) is not probable.

FS_3 phase relationships were not experimentally verified. The corresponding phase relationship was solved by means of geometrical considerations.

Table 1. Phase compatibility matrix in the system $C - S - F - \bar{S}$.

Phases	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 C	-	1	1	1	0	1	1	1	0	1	1	0	1	0
2 S		-	0	0	1	1	1	0	1	1	1	0	0 ^G	1
3 F			-	1	1	0	0	0	1	1	0	0	0	0
4 \bar{S}				-	1	1	1	1	1	1	0	0	1	
5 C_3S					-	0	1	1	0	1	1	1	1	0 ^G
6 C_2S						-	0	1	0	0	0	1	1	0
7 C_3S_2							-	0	1	1	1	0	1	0
8 CS								-	1	1	1	0	1	1
9 C_2F									-	0	1	0	1	0
10 CF										-	0	0	1	0
11 CF_2											-	0	1	0
12 $C\bar{S}$												-	0 ^G	0
13 FS_3													-	1
14 $C_5S_2\bar{S}$														-

0 - denotes compatible (coexisting) phases

1 - denotes incompatible (non coexisting) phases

G - presumed geometrically

- the other phase compatibility data is taken from the literature

On the basis of these 15 assemblages of the 4 component system and on the basis of the phase compatibility in its subsystems the compatibility of the system $C - S - F - \bar{S}$ including known phases is established by geometrical consideration. The "yes or no" compatibility of phases in the $C - S - F - \bar{S}$ system is represented by means of the phase compatibility matrix given in table 1. Symbol 0 represents compatible phases and symbol 1 incompatible phases, similarly as in [10]. The data contained in the phase compatibility matrix are transfor-

Table 2. The list of the equilibrium phase assemblages in the system $C - S - F - \bar{S}$.

No.	assemblage						V_i	ΣV_i	
1	C	-	C_3S	-	C_2F	-	$C_5S_2\bar{S}$	0.025748	0.025748
2	C	-	C_2F	-	CS	-	$C_5S_2\bar{S}$	0.086365	0.112113
3	S	-	F	-	$C\bar{S}$	-	$C\bar{S}$	0.283910	0.396023
4	S	-	\bar{S}	-	$C\bar{S}$	-	FS_3	0.247423	0.643446
5	S	-	S	-	CS	-	FS_3	0.164506	0.807952
6	F	-	C_2S	-	C_3S_2	-	$C_5S_2\bar{S}$	0.011299	0.819251
7	F	-	C_2S	-	CF_2	-	$C_5S_2\bar{S}$	0.008679	0.827930
8	F	-	C_3S_2	-	CS	-	CS	0.059145	0.887075
9	F	-	C_3S_2	-	$C\bar{S}$	-	$C_5S_2\bar{S}$	0.028589	0.915664
10	F	-	CF_2	-	CS	-	$C_5S_2\bar{S}$	0.021960	0.937624
11	C_3S	-	C_2S	-	C_2F	-	$C_5S_2\bar{S}$	0.008383	0.946007
12	C_2S	-	C_2F	-	CF	-	$C_5S_2\bar{S}$	0.008871	0.954878
13	C_2S	-	CF	-	CF_2	-	$C_5S_2\bar{S}$	0.006423	0.961301
14	C_2F	-	CF	-	$C\bar{S}$	-	$C_5S_2\bar{S}$	0.022447	0.983748
15	CF	-	CF_2	-	CS	-	$C_5S_2\bar{S}$	0.016252	1.000000

med [15] into fifteen 4 phase assemblages of compatible phases (corresponding phase tetrahedra), which are listed in table 2. For each phase assemblage the relative volume V_i was calculated and a summing up of the relative volumes shows that the phase space is wholly filled by the tetrahedra with no empty space and without their superposition which implies the consistency of the phase compatibility data. The computed volumes refer to the positions of apexes of the tetrahedra given on the wt.% basis.

By comparison of the previous phase compatibility results it is seen that the assemblages (II), (III), (IV), (X), (XI), (XII), (XIII), (XIV) and (XV) are the same as the assemblages No. 2, 12, 14, 6, 7, 9, 10, 13 and 15 given in table 2. The assemblage (I) is corresponding to the assemblages No. 1 and 11 at temperatures below the temperature of C_3S formation, where C and C_2S are compatible phases. Assemblages (VI), (VII), (VIII) and (IX) correspond to the assemblages No. 6, 7, 12 and 13 in a case at which $C_5S_2\bar{S}$ is decomposed to its simpler constituents C_2S and CS and assemblage (V) corresponds to assemblages No. 1 and 11 when C_3S as well as $C_5S_2\bar{S}$ are decomposed to their simpler constituents. So the results given in the present study are confirmed by the literature data. New phase assemblages No. 3, 4, 5 and 8 containing additional phases S , \bar{S} , CS and FS_3 were established from the results given in the phase compatibility matrix. At high temperatures at which the FS_3 phase can not exist, the assemblages No. 4 and 5 should transform into a new phase assemblage $S - F - \bar{S} - CS$.

System C - A - F - \bar{S}

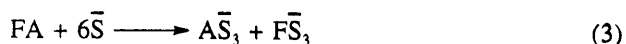
This system contains 12 binary phases C_3A , $C_{12}A_7$, CA , CA_2 , CA_6 , C_2F , CF , CF_2 , CS , FA , AS_3 , FS_3 and two ternary phases C_4AF and $C_4A_3\bar{S}$. From its subsystems C - A - F [8], C - A - \bar{S} [13] and C - F - \bar{S} (previous paragraph of this work) are fully described and the subsystem A - F - \bar{S} has not been studied yet and needs closer inspection. The subsystem A - F - \bar{S} contains phases with very different levels of their thermal stability FS_3 up to 480 °C, AS_3 up to 770 °C and FA is unstable below 1318 °C [8]. Therefore the phase relationships can be established only from geometrical consideration and a theoretical prediction.

The presence of FA phase prepared experimentally was not unambiguous probably owing to insufficient quenching. X-ray records showed mainly the presence of solid solutions $A(F)ss$ and $F(A)ss$.

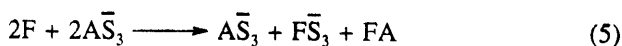
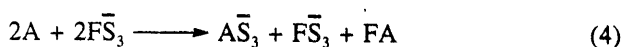
The subsystem A - F - \bar{S} has four possible solutions. Two solutions which would need coexistences A - FS_3 and F - AS_3 are not taken into account due to presumed reactions (1) and (2).



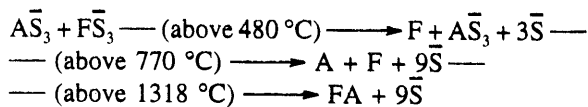
This means the coexistences $A\bar{S}_3 - FA$ and $F\bar{S}_3 - FA$ are geometrically imperative. On the other hand, $FA + \bar{S}$ at the temperatures where $A\bar{S}_3$ and $F\bar{S}_3$ are stable could react according to reactions (3).



Thermal stability of the phases $A\bar{S}_3$ and $F\bar{S}_3$ is a condition for their taking into consideration the study of the phase relationships. The reaction (1) and (2) with respect to the reaction (3) should proceed according to schemes (4) and (5).



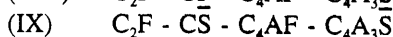
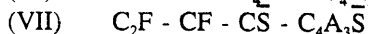
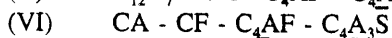
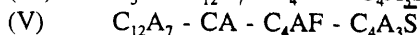
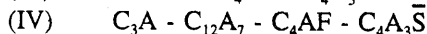
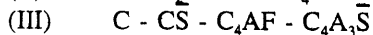
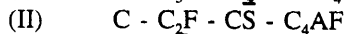
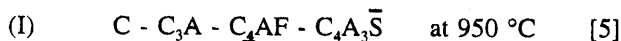
Without the relevant thermodynamic data it is difficult to decide a possible course of these reactions. From a practical point of view considering the open system, the following reaction scheme should be valid:



At the high temperatures above 1318 °C phases $A\bar{S}_3$ and $F\bar{S}_3$ will not exist and in the subsystem A - F - \bar{S} , the coexistence of $\bar{S} - FA$ phases is only possible. If we take coexistences $A\bar{S}_3 - FA$ and $F\bar{S}_3 - FA$ into consideration we should take the coexistence $A\bar{S}_3 - F\bar{S}_3$ into consideration too. This means the compatibility of the phases in all subsystems of the system C - A - F - \bar{S} is established (figure 3).

The phase compatibility of the quaternary system C - A - F - \bar{S} was studied in [5, 10, 12] with the establishment of the following compatible phases:

at 1150-1200 °C $C_4A_3\bar{S}$ coexists with C_2F and CF [12]
up to 1300 °C $C_4A_3\bar{S}$ coexists with C_4AF
at 1300-1350 °C $CS - C_4AF - C_4A_3\bar{S}$ coexist together



The assemblages (I) and (III) in relation to sulphoaluminate cement clinkers containing C_2S are stable above 1115°C [16].

The twelve 4 phase assemblages in the system $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$ relevant to sulphoaluminate belite cement clin-

compatibility matrix taking into account reactions (6) and (7), give twenty-three assemblages of compatible phases listed in table 4.

By comparison of the previously stated phase compatibility results, it is seen that assemblages (I), (II),

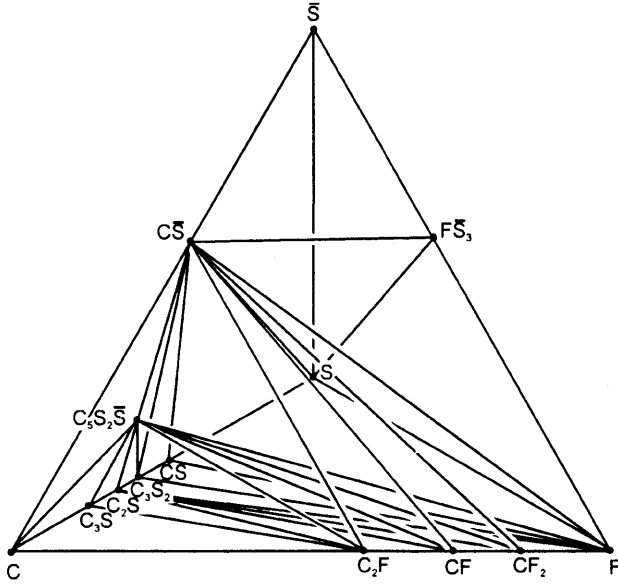
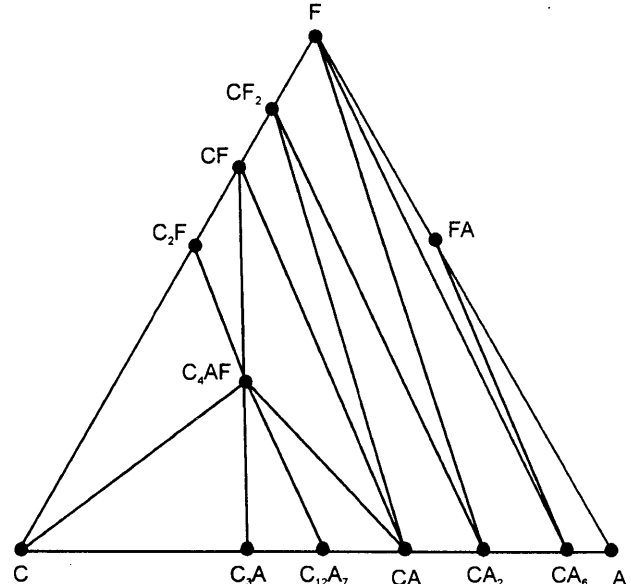


Figure 2. Diagram of the phase compatibility in the system $\text{C} - \text{S} - \text{F} - \bar{\text{S}}$.

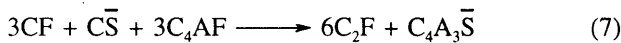
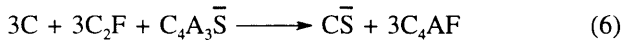


a)

ker were identified in [10]: (I), (II), (III), (IV), (V), (VI), (VII), (VIII), (IX)

- (X) $\text{F} - \text{CF}_2 - \text{CS} - \text{C}_4\text{A}_3\bar{\text{S}}$
- (XI) $\text{CA} - \text{CF} - \text{CF}_2 - \text{C}_4\text{A}_3\bar{\text{S}}$
- (XII) $\text{CF} - \text{CF}_2 - \text{CS} - \text{C}_4\text{A}_3\bar{\text{S}}$

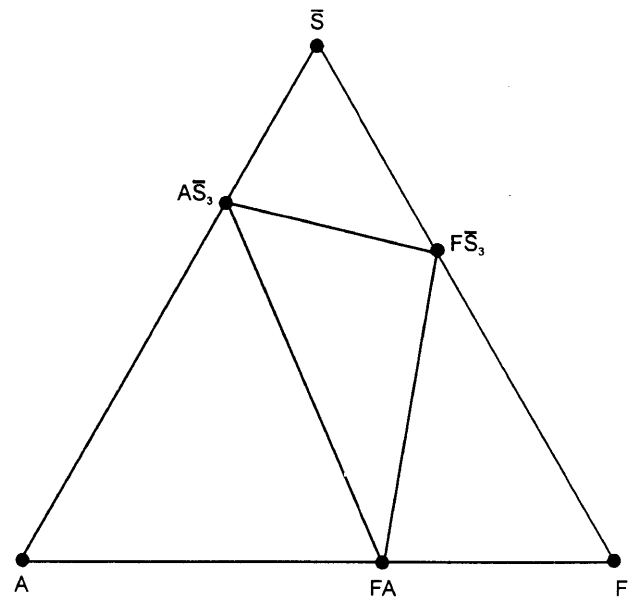
In the system $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$ the following reactions (6) and (7) were reported [5, 10].



According to the reactions (6) and (7) the phase associations $\text{C} - \text{C}_2\text{F} - \text{C}_4\text{A}_3\bar{\text{S}}$ and $\text{CF} - \text{CS} - \text{C}_4\text{AF}$ are unstable and transform to stable binary coexistences $\text{CS} - \text{C}_4\text{AF}$ and $\text{C}_2\text{F} - \text{C}_4\text{A}_3\bar{\text{S}}$.

On the basis of the known subsystems and the 12 assemblages, only the volume coexistences $\text{CS} - \text{FA}$ and $\text{FA} - \text{C}_4\text{A}_3\bar{\text{S}}$ remain unknown. Coexistence $\text{CS} - \text{FA}$ in the phase association $\text{A} - \text{F} - \text{CS}$ and coexistence $\text{FA} - \text{C}_4\text{A}_3\bar{\text{S}}$ in the phase association $\text{A} - \text{F} - \text{C}_4\text{A}_3\bar{\text{S}}$ must be inevitable as the only possibility in these phase associations related to geometric prediction.

The compatibility or incompatibility of phases in the system $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$ is given in the phase compatibility matrix given in table 3. The data contained in the phase



b)

Figure 3. Diagrams of the phase compatibility in the subsystems of the system $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$ (subsystem $\text{C} - \text{A} - \bar{\text{S}}$ was published in [9] and subsystem $\text{C} - \text{F} - \bar{\text{S}}$ in figure 1).

a) subsystem $\text{C} - \text{A} - \text{F}$, b) subsystem $\text{A} - \text{F} - \bar{\text{S}}$

(III), (IV), (V), (VI), (VII), (VIII), (IX), (X), (XI) and (XII) are the same as the assemblages No. 1, 2, 3,

14, 15, 18, 19, 20, 21, 10, 17 and 22 given in table 4. Established are however the new phase assemblages No. 4, 5, 6, 7, 8, 9, 11, 12, 13, 16 and 23 containing additional phases A, \bar{S} , CA_2 , CA_6 , FA, AS_3 and FS_3 .

At high temperatures at which the phases AS_3 and FS_3 are not stable the assemblages No. 5, 11, 13 and 23 should transform into the following phase assemblages:

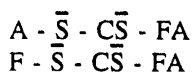


Table 3. Phase compatibility matrix in the system C - A - F - \bar{S} .

phases	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 C	-	1	1	1	0	1	1	1	1	0	1	1	0	1	1	1	0	0
2 A		-	1	1	1	1	1	1	0	1	1	1	0	0	0	1 ^T	1	0
3 F			-	1	1	1	1	0	0	1	1	0	0	0	1 ^T	0	1	0
4 \bar{S}				-	1	1	1	1	1	1	1	1	0	1 ^T	0	0	1	1
5 C_3A					-	0	1	1	1	1	1	1	1	1	1	1	0	0
6 $C_{12}A_7$						-	0	1	1	1	1	1	1	1	1	1	0	0
7 CA							-	0	1	1	0	0	1	1	1	1	0	0
8 CA_2								-	0	1	1	0	1	1	1	1	1	0
9 CA_6									-	1	1	1	1	0	1	1	1	0
10 C_2F										-	0	1	0	1	1	1	0	0
11 CF											-	0	0	1	1	1	0	0
12 CF_2												-	0	1	1	1	1	0
13 $C\bar{S}$													-	0 ^G	0	0 ^G	0	0
14 FA														-	0 ^T	0 ^T	1	0 ^G
15 AS_3															-	0 ^T	1	1
16 FS_3																-	1	1
17 C_4AF																	-	0
18 C_4A_3S																		-

- 0 - denotes compatible (coexisting) phases
- 1 - denotes incompatible (non coexisting) phases
- G - presumed geometrically
- T - forecasted theoretically
- the other phase compatibility data is taken from the literature

Table 4. The list of the equilibrium phase assemblages in the system C - A - F - \bar{S} .

No.	assemblage						V_i	ΣV_i	
1	C	-	C_3A	-	C_4AF	-	$C_4A_3\bar{S}$	0.016267	0.016267
2	C	-	C_2F	-	$C\bar{S}$	-	C_4AF	0.072477	0.088744
3	C	-	$C\bar{S}$	-	C_4AF	-	$C_4A_3\bar{S}$	0.096858	0.185602
4	A	-	CA_6	-	FA	-	$C_4A_3\bar{S}$	0.006723	0.192325
5	A	-	$C\bar{S}$	-	FA	-	AS_3	0.176487	0.368812
6	A	-	$C\bar{S}$	-	FA	-	$C_4A_3\bar{S}$	0.098947	0.467759
7	F	-	CA_2	-	CA_6	-	$C_4A_3\bar{S}$	0.017280	0.485039
8	F	-	CA_2	-	CF_2	-	$C_4A_3\bar{S}$	0.015369	0.500408
9	F	-	CA_6	-	FA	-	$C_4A_3\bar{S}$	0.004293	0.504701
10	F	-	CF_2	-	$C\bar{S}$	-	$C_4A_3\bar{S}$	0.044026	0.548727
11	F	-	$C\bar{S}$	-	FA	-	FS_3	0.096416	0.645143
12	F	-	$C\bar{S}$	-	FA	-	$C_4A_3\bar{S}$	0.063176	0.708319
13	\bar{S}	-	$C\bar{S}$	-	AS_3	-	FS_3	0.049024	0.757343
14	C_3A	-	$C_{12}A_7$	-	C_4AF	-	$C_4A_3\bar{S}$	0.005921	0.763264
15	$C_{12}A_7$	-	CA	-	C_4AF	-	$C_4A_3\bar{S}$	0.005624	0.768888
16	CA	-	CA_2	-	CF_2	-	$C_4A_3\bar{S}$	0.015529	0.784417
17	CA	-	CF	-	CF_2	-	$C_4A_3\bar{S}$	0.009356	0.793773
18	CA	-	CF	-	C_4AF	-	$C_4A_3\bar{S}$	0.014457	0.808230
19	C_2F	-	CF	-	$C\bar{S}$	-	$C_4A_3\bar{S}$	0.045002	0.853232
20	C_2F	-	CF	-	C_4AF	-	$C_4A_3\bar{S}$	0.004202	0.857434
21	C_2F	-	$C\bar{S}$	-	C_4AF	-	$C_4A_3\bar{S}$	0.019981	0.877415
22	CF	-	CF_2	-	$C\bar{S}$	-	$C_4A_3\bar{S}$	0.032583	0.909998
23	$C\bar{S}$	-	FA	-	AS_3	-	FS_3	0.090002	1.000000

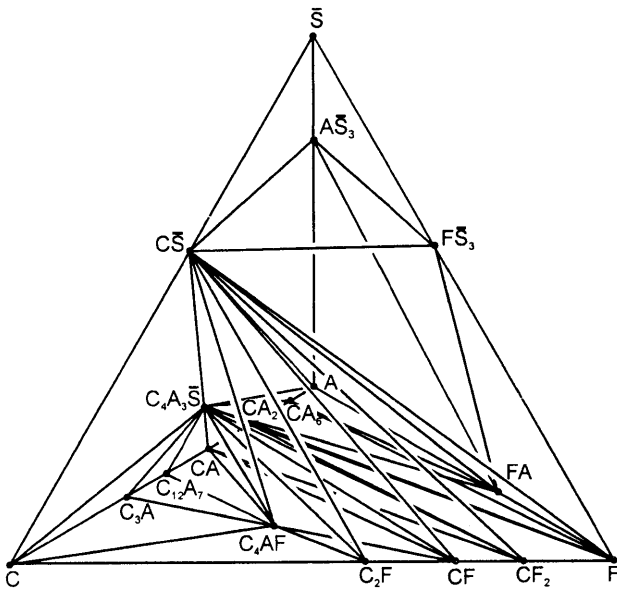


Figure 4. Diagram of the phase compatibility in the system $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$.

System $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$

This system contains only 4 binary phases A_3S_2 , FA , $\bar{\text{A}}\bar{\text{S}}_3$ and $\bar{\text{F}}\bar{\text{S}}_3$, but the establishment of the phase relationships owing to low thermal stability of $\bar{\text{A}}\bar{\text{S}}_3$ and $\bar{\text{F}}\bar{\text{S}}_3$ and simultaneously the high temperature of A_3S_2 and FA formation is practically impossible. We have tried establishing only the theoretical model of this system without its experimental study, based only on the geo-

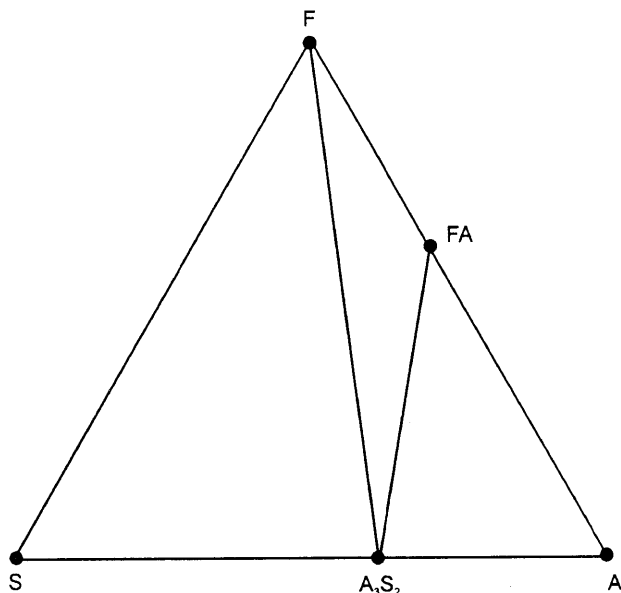


Figure 5. Diagrams of the phase compatibility in the subsystems of the system $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$ (subsystem $\text{S} - \text{A} - \bar{\text{S}}$ was published in [9], subsystem $\text{S} - \text{F} - \bar{\text{S}}$ in figure 1 and subsystem $\text{A} - \text{F} - \bar{\text{S}}$ in figure 3).

metrical considerations and the theoretical forecast in spite of a lack of the relevant thermodynamic data.

From the subsystems $\text{S} - \text{A} - \bar{\text{F}}$ is fully described [8] (figure 5), $\text{S} - \text{A} - \bar{\text{S}}$ is established on the basis of available thermodynamic data [9] and the subsystems $\text{S} - \text{F} - \bar{\text{S}}$ and $\text{A} - \text{F} - \bar{\text{S}}$ have been described in previous paragraphs of this work. While for the subsystems $\text{S} - \text{A} - \bar{\text{F}}$ and $\text{S} - \text{F} - \bar{\text{S}}$ only one solution existed in regard to the studied temperatures, for the subsystems $\text{S} - \text{A} - \bar{\text{S}}$ and $\text{A} - \text{F} - \bar{\text{S}}$ more solutions exist. The former system has two solutions and the latter one has four solutions. A combination of the last two systems depends on temperatures at which the process is performed. At temperatures, when $\bar{\text{A}}\bar{\text{S}}_3$ and $\bar{\text{F}}\bar{\text{S}}_3$ are stable in the subsystem $\text{S} - \text{A} - \bar{\text{S}}$, coexistences $\text{S} - \bar{\text{A}}\bar{\text{S}}_3$ and $\text{A}_3\text{S}_2 - \bar{\text{A}}\bar{\text{S}}_3$ should be valid. In the subsystem $\text{A} - \text{F} - \bar{\text{S}}$ in regard to coexistence $\bar{\text{S}} - \bar{\text{A}}\bar{\text{S}}_3$ either coexistences $\text{F} - \bar{\text{A}}\bar{\text{S}}_3$, $\text{FA} - \bar{\text{A}}\bar{\text{S}}_3$, $\bar{\text{A}}\bar{\text{S}}_3 - \bar{\text{F}}\bar{\text{S}}_3$ or coexistences $\text{A} - \bar{\text{F}}\bar{\text{S}}_3$, $\text{FA} - \bar{\text{F}}\bar{\text{S}}_3$, $\bar{\text{A}}\bar{\text{S}}_3 - \bar{\text{F}}\bar{\text{S}}_3$ should be valid. In fact the coexistences $\text{A} - \bar{\text{F}}\bar{\text{S}}_3$, $\text{F} - \bar{\text{A}}\bar{\text{S}}_3$ have been already ruled out in our previous discussion, therefore the coexistence $\text{S} - \bar{\text{A}}\bar{\text{S}}_3$ should be ruled out too. After this in the subsystem $\text{S} - \text{A} - \bar{\text{S}}$ there remain coexistences $\bar{\text{S}} - \text{A}_3\text{S}_2$ and $\text{A}_3\text{S}_2 - \bar{\text{A}}\bar{\text{S}}_3$, what implies the coexistences $\bar{\text{S}} - \text{FA}$, $\text{FA} - \bar{\text{A}}\bar{\text{S}}_3$, $\text{FA} - \bar{\text{F}}\bar{\text{S}}_3$ in the subsystem $\text{A} - \text{F} - \bar{\text{S}}$. It has been discussed in the previous paragraph that at temperatures when $\bar{\text{A}}\bar{\text{S}}_3$ and $\bar{\text{F}}\bar{\text{S}}_3$ are stable phases the coexistence $\bar{\text{S}} - \text{FA}$ should not be valid and this means therefore the coexistences $\text{FA} - \bar{\text{A}}\bar{\text{S}}_3$, $\text{FA} - \bar{\text{F}}\bar{\text{S}}_3$ and $\bar{\text{A}}\bar{\text{S}}_3 - \bar{\text{F}}\bar{\text{S}}_3$ are valid.

There are still more combinations in subsystems $\text{S} - \text{A} - \bar{\text{S}}$ and $\text{A} - \text{F} - \bar{\text{S}}$ but it is difficult to screen which one of them is possible without the relevant thermodynamics data. The probable sequence of the coexistences in subsystems $\text{S} - \text{A} - \bar{\text{S}}$ and $\text{A} - \text{F} - \bar{\text{S}}$ depending on the temperature needs decomposition of $\bar{\text{F}}\bar{\text{S}}_3$ phase:

conditions	subsystem $\text{S} - \text{A} - \bar{\text{S}}$	subsystem $\text{A} - \text{F} - \bar{\text{S}}$
up to 480 °C	$\text{S} - \bar{\text{A}}\bar{\text{S}}_3$, $\text{A}_3\text{S}_2 - \bar{\text{A}}\bar{\text{S}}_3$	$\text{A} - \bar{\text{F}}\bar{\text{S}}_3$, $\text{FA} - \bar{\text{F}}\bar{\text{S}}_3$, $\bar{\text{A}}\bar{\text{S}}_3 - \bar{\text{F}}\bar{\text{S}}_3$
up to 770 °C	$\text{S} - \bar{\text{A}}\bar{\text{S}}_3$, $\text{A}_3\text{S}_2 - \bar{\text{A}}\bar{\text{S}}_3$	$\text{F} - \bar{\text{A}}\bar{\text{S}}_3$, $\text{FA} - \bar{\text{A}}\bar{\text{S}}_3$
above 770 °C	$\bar{\text{S}} - \text{A}_3\text{S}_2$, $\text{A}_3\text{S}_2 - \bar{\text{A}}\bar{\text{S}}_3$	$\bar{\text{S}} - \text{FA}$, $\text{FA} - \bar{\text{A}}\bar{\text{S}}_3$
decomp. $\bar{\text{A}}\bar{\text{S}}_3$	$\bar{\text{S}} - \text{A}_3\text{S}_2$	$\bar{\text{S}} - \text{FA}$

Let us utilise the previously solved subsystems $\text{S} - \text{A} - \bar{\text{S}}$ and $\text{F} - \text{A} - \bar{\text{S}}$ at an establishment of the compatibility in the system $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$.

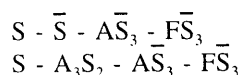
The system $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$ has only one possible "volume" coexistence $\text{A}_3\text{S}_2 - \bar{\text{F}}\bar{\text{S}}_3$ in the phase association $\text{F} - \bar{\text{S}} - \text{A}_3\text{S}_2$. The phase compatibility matrix of the system $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$ is given in table 5. The establishment of the phase compatibility in this system consists of six 4 phase assemblages listed in table 6.

Table 5. Phase compatibility matrix in the system S - A - F - \bar{S} .

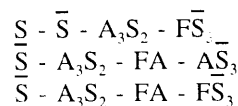
Phases	1	2	3	4	5	6	7	8
1 S	-	1	0	0	0	1	1 ^E	0 ^G
2 A		-	1	1	0	0	0	1 ^T
3 F			-	1	0	0	1 ^T	0
4 \bar{S}				-	0 ^E	1 ^T	0	0
5 A_3S_2					-	0	0 ^G	0 ^G
6 FA						-	0 ^T	0 ^T
7 \bar{AS}_3							-	0 ^T
8 \bar{FS}_3								-

0 - denotes compatible (coexisting) phases
 1 - denotes incompatible (non coexisting) phases
 E - verified experimentally in the work [9]
 G - presumed geometrically
 T - forecasted theoretically
 - the other phase compatibility data is taken from the literature

In the case when in the subsystem S - A - \bar{S} coexistences S - \bar{AS}_3 and A_3S_2 - \bar{AS}_3 are valid, the assemblages No. 2 and 5 (table 6) would transform into the following phase assemblages:

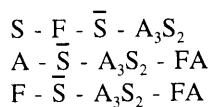


In the case when coexistences \bar{S} - A_3S_2 , A_3S_2 - \bar{AS}_3 in the subsystem S - A - \bar{S} are valid and coexistences \bar{S} - FA, FA - \bar{AS}_3 and FA - \bar{FS}_3 in the system A - F - \bar{S} are valid the assemblages No. 2, 5 and 6 would transform into the following phase assemblages:



From a practical point of view, conditions of the cement clinker firing only temperatures are interesting at which \bar{AS}_3 and \bar{FS}_3 are not stable. In this case in the

subsystems \bar{S} - A - \bar{S} and F - A - \bar{S} only coexistences \bar{S} - A_3S_2 and \bar{S} - FA are possible and system S - A - F - \bar{S} will consist of the following three assemblages:



The phase compatibility in the system S - A - F - \bar{S} remains partially undefined. Our model of the system S - A - F - \bar{S} is showed in figure 6.

The compatibility of the phases in these systems encountered together with the phase compatibility in the systems C - S - A - F [8] and C - S - A - \bar{S} [9] can be a starting point for the establishment of the phase compatibility of the 5 component oxide system C - S - A - F - \bar{S} as it will be published in [17]. The phase compatibility models can also be the starting point for the establishment of solid state phase compatibility involving solid solutions.

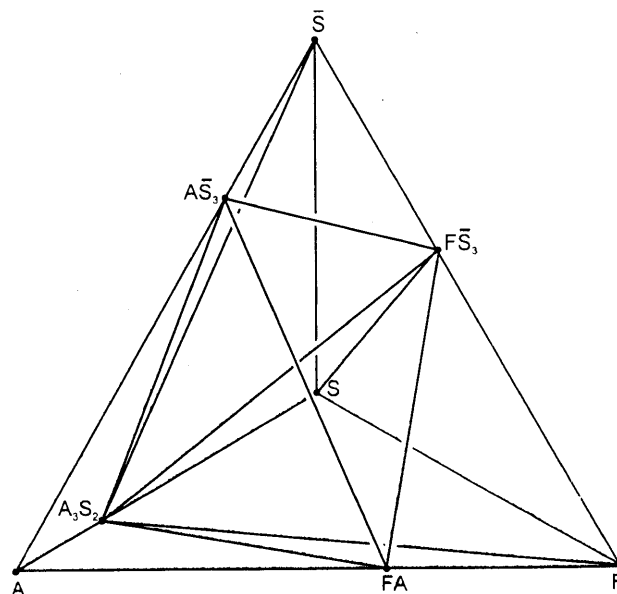


Figure 6. Diagram of the phase compatibility in the system S - A - F - \bar{S} .

Table 6. The list of the equilibrium phase assemblages in the system S - A - F - \bar{S} .

No.	assemblage							V_i	ΣV_i
1	S	-	F	-	A_3S_2	-	\bar{FS}_3	0.431240	0.431240
2	S	-	\bar{S}	-	A_3S_2	-	\bar{FS}_3	0.286720	0.717960
3	A	-	A_3S_2	-	FA	-	\bar{AS}_3	0.120837	0.838797
4	F	-	A_3S_2	-	FA	-	\bar{FS}_3	0.066014	0.904811
5	\bar{S}	-	A_3S_2	-	\bar{AS}_3	-	\bar{FS}_3	0.033566	0.938377
6	A_3S_2	-	FA	-	\bar{AS}_3	-	\bar{FS}_3	0.061623	1.000000

CONCLUSION

The phase compatibility models for the three specified oxide systems $\text{C} - \text{S} - \text{F} - \bar{\text{S}}$, $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$ and $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$ are presented based on the data scattered in the literature, geometrical consideration and the own theoretical discussion. The present phases were considered as stoichiometric ones. Theoretical models of these systems were established with fifteen 4 phase assemblages in the system $\text{C} - \text{S} - \text{F} - \bar{\text{S}}$, twenty three in the system $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$ and six in the system $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$. The results were verified by means of the summing up of volumes of individual phase tetrahedra implying the consistency of the phase compatibility models.

Phase assemblages in the systems $\text{C} - \text{S} - \text{F} - \bar{\text{S}}$ and $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$ were compared with previously published data. The system $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$ remains open, for the further experimental study.

Acknowledgement

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Submitted in English by the authors.

KOEXISTENCIA FÁZ V SÚSTAVÁCH

$\text{CaO} - \text{SiO}_2 - \text{Fe}_2\text{O}_3 - \text{SO}_3$, $\text{CaO} - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{SO}_3$
A $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{SO}_3$

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Štvorzložkové oxidové sústavy $\text{C} - \text{S} - \text{F} - \bar{\text{S}}$, $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$ a $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$ obsahujú fázy ktoré tvoria mineralogický základ sulfoaluminátových cementov, ktoré patria do triedy nízkoenergetických cementov. Analýza koexistencie fáz v sústavách zahŕňa všetky známe fázy C, S, A, F, $\bar{\text{S}}$, C_3S , C_2S , C_3S_2 , CS , C_3A , C_{12}A_7 , CA, CA_2 , CA_{62} , C_2F , CF, CF_2 , CS , A_3S_2 , FA, AS_3 , FS_3 , C_4AF , $\text{C}_5\text{S}_2\bar{\text{S}}$, $\text{C}_4\text{A}_3\bar{\text{S}}$, ktoré sa uvažujú ako stechiometrické zlúčeniny (v celom rozsahu teplôt). Modely koexistencie fáz sústav sa vytvorili na základe publikovaných údajov o fázových rovnováhach a na základe využitia čiastočného modelovania koexistencií fáz vychádzajúc z geometrických zákonitostí.

Koexistencia fáz sústav sa vyjadřila pomocou matíc koexistencie fáz, na základe ktorých sa identifikovalo 15 rovnovážnych asociácií fáz (v podobe fázových tetraédrov) v sústave $\text{C} - \text{S} - \text{F} - \bar{\text{S}}$, 23 v sústave $\text{C} - \text{A} - \text{F} - \bar{\text{S}}$ a 6 v sústave $\text{S} - \text{A} - \text{F} - \bar{\text{S}}$. Konzistentnosť modelov koexistencie fáz sa verifikovala sumáciou objemov elementárnych fázových tetraédrov.

Modely koexistencie fáz môžu slúžiť ako východisko pri definovaní koexistencie fáz päťzložkového systému $\text{C} - \text{S} - \text{A} - \text{F} - \bar{\text{S}}$.

Erratum for

"Phase compatibility in the system $\text{CaO} - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{SO}_3$ "

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Ceramics-Silikáty 42 (3), 90-98 (1998).

On page 92 in reaction (1) the values of standard Gibbs energies should be replaced with: $\Delta G^0_{1000^\circ\text{C}} = -370 \text{ kJ mol}^{-1}$, $\Delta G^0_{1200^\circ\text{C}} = -690 \text{ kJ mol}^{-1}$.

The authors apologize.