PHASE COMPATIBILITY IN THE SYSTEM $CaO - SiO_2 - Al_2O_3 - SO_3$

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The oxide system C - S - A - $\bar{S}$[+], which includes phases C, S, A, $\bar{S}$, C_3S, C_2S, C_3S_2, CS, C_3A, $C_{12}A_7$, CA, CA_2, CA_6, $C\bar{S}$, A_3S_2, $A\bar{S}_3$, C_2AS, CAS_2, $C_5S_2\bar{S}$, $C_4A_3\bar{S}$, is analysed for its phase compatibility. The phase compatibility model of the system is derived from the literature data as well as from the own experimental study and from the partial modelling of the phase compatibility relationships based on the geometrical consideration. Twenty-eight equilibrium quaternary phase assemblages have been established, which define the entire subsolidus phase space.

INTRODUCTION

The title oxide system contains a number of phases which play an important role in the chemistry of Portland, aluminate and sulphoaluminate cements. Sulphoaluminate cements (SAC) may be designed as expansive or non expansive ones and in general belong to the energy-saving types of cements. Their industrial production has been realised to date only in China [1]. The burnt product consists of C_2S, $C_4A_3\bar{S}$, $C\bar{S}$ and some CaO. The clinker can also contain the phases $C_{12}A_7$, CA and $C_5S_2\bar{S}$ [2-7]. The sequence of the reactions taking place during the firing of the clinker is given in [8-10]. As the principal minerals also gehlenite, C_2AS or even anorthite, CAS_2 can be formed in cement clinkers rich in SiO_2 [11].

Expansive cements [12] generally contain Klein's compound, $C_4A_3\bar{S}$, alite, C_3S, belite, C_2S, C_4AF, anhydrite, $C\bar{S}$ and some free lime. The sulphates in the raw mix act as a fluxing agent, so that the formation of C_3S and C_2S is essentially completed at or below 1300 °C. Occasionally silicosulphate, $C_5S_2\bar{S}$ has been detected in expansive cements. This phase may also be a dominant phase in special kinds of cement [7]. Different types of aluminate cements, next to calcium aluminates present, may contain also C_2S and a small amount of $C_4A_3\bar{S}$ [3].

The oxide system C - S - A - $\bar{S}$ includes four ternary subsystems C - S - A, C - S - $\bar{S}$, C - A - $\bar{S}$, S - A - $\bar{S}$ from which only the subsystems C - S - A [13], C - A - $\bar{S}$ [14] are fully described, subsystem C - S - $\bar{S}$ [15, 16] is only partially described (missing data concerning the C_3S - $C_5S_2\bar{S}$ coexistence (compatibility)) and the ternary subsystem S - A - $\bar{S}$ has not yet been described at all (besides the phase compatibility data of individual binary subsystems).

The system C - S - A - $\bar{S}$ has been studied only in its high lime portion [17-24] including phases (C, C_3S, C_2S, C_3A, $C_{12}A_7$, CA, $C\bar{S}$, C_2AS, $C_5S_2\bar{S}$, $C_4A_3\bar{S}$) important for cement production. The phase relationship among the low lime or limeless phases of this system have not been reported, except for an information about the compatibility of C_3S_2 and CAS_2 given in [18, 24].

The phase compatibility for the CaO - rich compositions of the $CaO - SiO_2 - Al_2O_3 - CaSO_4 - CaF_2$ system has been studied in [25]. It was interesting that a formation of C_3S was observed at temperatures as low as 1050 and 1100 °C.

The aim of our present work was to review the existing data on the subsolidus phase compatibility inside the title system and to set up a consistent model of the phase compatibility (coexistence) relationship taking the system as a whole. The literature data were supplemented by the own experimental study of phase compatibility.

The present study included all 20 known phases in the system, i.e. C, S, A, $\bar{S}$, C_3S, C_2S, C_3S_2, CS, C_3A, $C_{12}A_7$, CA, CA_2, CA_6, $C\bar{S}$, A_3S_2, $A\bar{S}_3$, C_2AS, CAS_2, $C_5S_2\bar{S}$, $C_4A_3\bar{S}$. No quaternary phase in this system has been reported in the literature.

There is no definite reference temperature of the phase compatibility study performed. This reflects the great difference in melting points of individual phases and in their thermal stability. The equilibrium phase compatibility given in the literature refers mostly to the temperature range of 950 - 1300 °C. Our experimental studies were performed at temperatures in the range of 1000 - 1200 °C.

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

On a basis of the phase compatibility data given in the literature for the single ternary subsystems it was possible to derive the alternative geometrical models of the potential phase compatibility inside the quaternary system [26-28]. All possible arrangements of phase compatibility, from a given set of phases, were considered in the corresponding computations inside the quaternary system and it was found out interestingly that the quaternary system could be divided into the variant as well as the invariant portion. The invariant portion consisted of a set of phase tetrahedra common to all models (arrangements) of phase compatibility in the system (a phase tetrahedron is a geometrical equivalent of the quaternary equilibrium phase assemblage). The phase compatibility was only experimentally checked for the invariant portion of the system. The phase compatibility alternatives in the variant portion of the system were, on the other hand, helpful in the selection of compositions for an experimental study. In this way the number of experiments identifying the phase coexistence in the quaternary system could be kept to a minimum.

EXPERIMENTAL PART

The samples for the phase equilibrium study were prepared from powder mixtures, using chemicals of the analytical reagent quality $CaCO_3$, $Ca(OH)_2$, SiO_2 (quartz--powder), SiO_2 (silica-gel), $Al(OH)_3$, $AlO(OH)$, $Al_2(SO_4)_3.18H_2O$, $CaSO_4$, $CaSO_4.2H_2O$ or presynthesised binary C_3S (1250 °C) or ternary $C_5S_2\overline{S}$ (1150 °C) and $C_4A_3\overline{S}$ (1200 °C) compounds. In one instance a wet diphasic gel, a precursor of mullite (A_3S_2 gel), was intimately mixed with the fine particle anhydrite. The powder mixtures were prepared by homogenisation in an agate mortar and dehydrated at 600 °C and decarbonized at 950 °C in an electric furnace for 0.5 hour. The homogenized mixtures were pressed to pellets at high pressure in order to support good contact between reactants and calcined again.

The pellets were encapsulated into Pt-tubes by welding the ends of the tubes. The encapsulated samples were heated in an electric furnace in the temperature range of 1000 - 1200 °C for 5 - 50 hours depending upon the composition of the mixtures.

Some experiments were repeated using an arrangement where the sample pellets were inserted into powder beds of the compatible sulphate containing phase and using experimental arrangement of the firing in SO_x atmosphere shown in [29]. As a source of SO_x atmosphere were used $C\overline{S}$, $A\overline{S}_3$, $C_4A_3\overline{S}$.

Phase analysis was accomplished by X-ray powder diffraction using Dron-2 and Philips powder diffractometer PW 1710 (Cuk_α radiation).

REVIEW OF THE RELEVANT LITERATURE DATA

Ternary subsystem C - S - A

This subsystem is the most complex and most thoroughly studied, includes 10 binary phases C_3S, C_2S, C_3S_2, CS, C_3A, $C_{12}A_7$, CA, CA_2, CA_6, A_3S_2 and two ternary phases C_2AS, CAS_2 (figure 1). The phase relations in this system are well established [13].

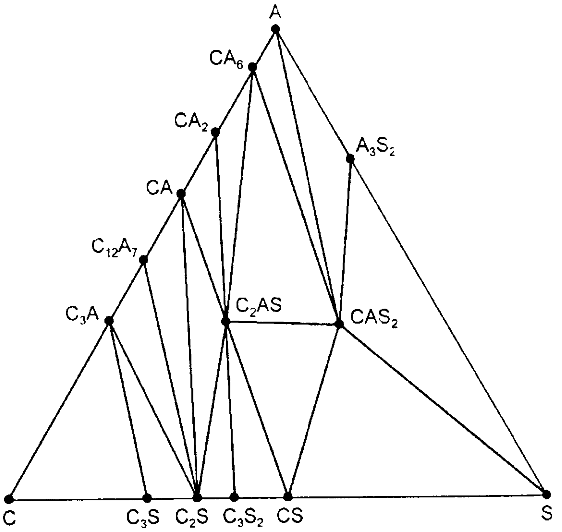

Figure 1. Diagram of the phase compatibility in the subsystem C - S - A [13].

Ternary subsystem C - S - $\overline{S}$

This subsystem with respect to the previous one, contains an additional binary phase $C\overline{S}$ and one ternary phase $C_5S_2\overline{S}$. The phase relations in this system were established [15, 16] at 1000 and 1200 °C except for the compatibility of C_3S and $C_5S_2\overline{S}$. According to [10] the thermal decomposition of $C_5S_2\overline{S}$ into C_2S and $C\overline{S}$ takes place in the temperature interval of 1180-1290 °C. A low stability limit of pure C_3S is given 1250 °C. However the experimental results [10, 15, 17] ruled out the coexistence between C_3S and $C_5S_2\overline{S}$. A tentative composition [17] for a solid solution of C_3S with Ca^{2+} and SO_4^{2-} ions, existing at 1310 °C, has been proposed as 2.9 SO_3 : 71.3 CaO : 25.8 SiO_2 (wt.%). This lies on the hypothetical join C_3S - "$C_5S_2\overline{S}$". The compatibility of C_3S and $C_5S_2\overline{S}$ has been predicted as a possibility above 1175 °C where C_3S becomes stable [19]. Our geometrical prediction says that C_3S and $C_5S_2\overline{S}$ are a compatible pair.

Coexistence of C_3S and $C\overline{S}$ has been determined at temperatures above 1290 °C [10, 15, 17] where the phase $C_5S_2\overline{S}$ does not exist. C_3S was identified [15] in annealed compositions containing up to 38 wt.% SO_3. However the coexistence of C_3S and $C\bar{S}$ is not believed to represent an equilibrium state [19]. High SO_3 content in Portland cement clinker leads to low C_3S contents [17]. The coexistence of C_3S and $C\bar{S}$ may occur only after the decomposition of $C_5S_2\bar{S}$ as well as the coexistence of C_2S and $C\bar{S}$.

A diagram of the phase coexistence in this subsystem is given in figure 2 which is supplemented with the coexistence of S and $C\bar{S}$ (given in [15] and verified by our experiments) and of C_3S and $C_5S_2\bar{S}$.

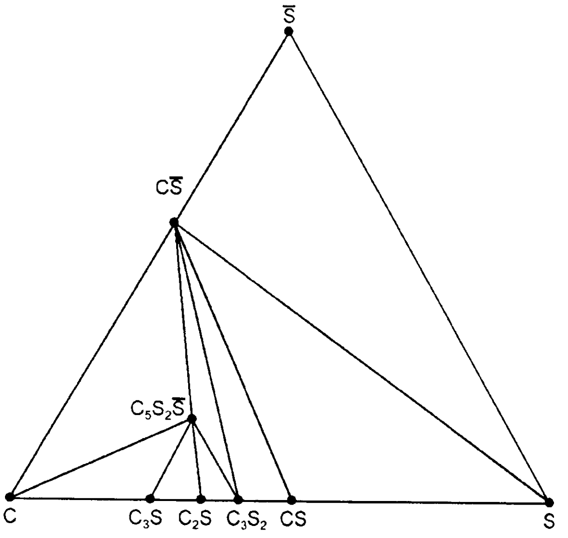

Figure 2. Diagram of the phase compatibility in the subsystem C - S - $\bar{S}$ [14].

Ternary subsystem C - A - $\bar{S}$

This subsystem introduces only one new binary phase $A\bar{S}_3$ and one ternary phase $C_4A_3\bar{S}$. The phase relations in this system are well established at 1250 °C [14] and some of them at 1350 °C [30, 31]. Its diagram of the phase coexistence is given in figure 3.

Ternary subsystem S - A - $\bar{S}$.

This subsystem introduces no new additional phase. The phase compatibility in this subsystem has not yet been reported at all. We have tried to establish the phase compatibility in spite of a very different thermal stability of the present binary phases A_3S_2 and $A\bar{S}_3$. By means of relevant thermodynamic data [32], it was possible to predict the course of the reaction (1) and in this manner to define the phase compatibility. A compatibility of A_3S_2 and $A\bar{S}_3$ is estimated from a geometrical prediction.

$$3A\bar{S}_3 + 2S \rightarrow A_3S_2 + 9\bar{S} \quad \Delta G^0_{1000\,°C} = -21 \text{ kJ mol}^{-1} \quad (1)$$

$$\Delta G^0_{1200\,°C} = -40 \text{ kJ mol}^{-1}$$

With an increase in temperature the reaction (1) is becoming more probable and therefore at 1200 °C A_3S_2 and $\bar{S}$ should be a compatible pair. Our experimental results are shown in table 1. $A\bar{S}_3$ was decomposed to γ-A at 1000 °C and SO_3 escaped from the system. The temperature of 1000 °C was not sufficient for a reaction between SiO_2 and Al_2O_3 to get mullite (A_3S_2), as well as the temperature of 1200 °C. An amorphous mullite gel was transformed into the crystalline at 1200 °C in the SO_x atmosphere.

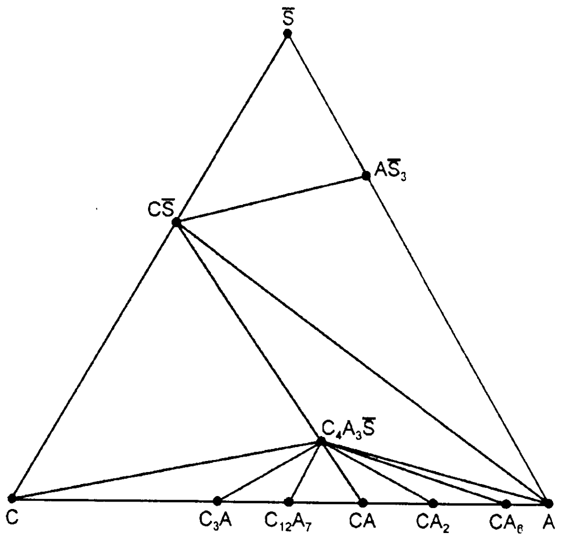

Figure 3. Diagram of the phase compatibility in the subsystem C - A - $\bar{S}$ [15].

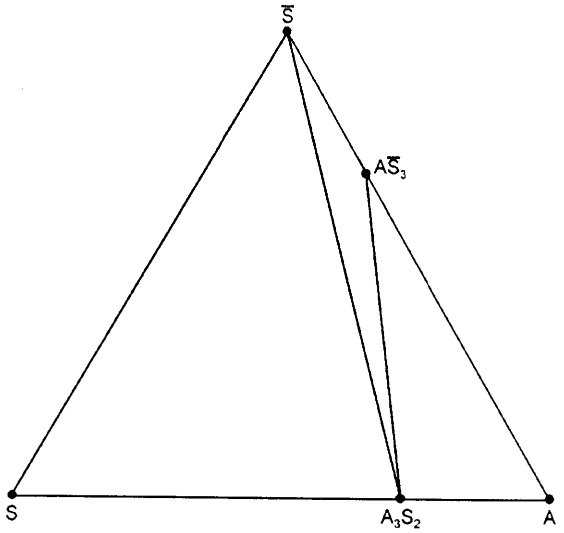

Figure 4. Diagram of the phase compatibility in the subsystem S - A - $\bar{S}$.

Table 1. Experimental results.

	reactant phases	temperature (°C)	time (hours)	product phases
1	$S + C\bar{S}$	1200	50	$S + C\bar{S}$
2	$S + \bar{S} + A\bar{S}_3$	1000	12	$S + \gamma\text{-}A$
3	$\bar{S} + A_3S_2$	1000	12	$S + \gamma\text{-}A + \alpha\text{-}A$
4	$\bar{S} + A_3S_2$	1200	12	$S + \alpha\text{-}A$
5	$\bar{S} + A_3S_2$ (gel)	1200	12	A_3S_2
6	A_3S_2	1200	12	$S + \alpha\text{-}A$
7	$C\bar{S} + CAS_2$	1200	5	$C\bar{S} + CAS_2$
8	$CAS_2 + C_4A_3\bar{S}$	1200	5	$CAS_2 + C_4A_3\bar{S}$
9	$A + C_5S_2\bar{S}$	1000	7	$\beta\text{-}C_2S + C\bar{S} + C_2AS$
10	$\bar{S} + C_2AS$	1200	12	$\beta\text{-}C_2S + CA_2 + C_2AS + CAS_2 + C_4A_3\bar{S}$
11	$CA_2 + C_5S_2\bar{S}$	1000	7	$\beta\text{-}C_2S + C\bar{S} + C_2AS$
12	$\bar{S} + CAS_2$	1200	12	CAS_2
13	$C_3S + C_4A_3\bar{S}$	1200	5	$C_3S + C_4A_3\bar{S}$
14	$C_3S_2 + C_4A_3\bar{S}$	1200	6	$S + \beta\text{-}C_2S + C_2AS + CAS_2 + C_4A_3\bar{S}$
15	$C\bar{S} + A\bar{S}_3$	1000	6	$S + C\bar{S} + A_3S_2$
16	$C\bar{S} + A_3S_2$	1200	6	$\alpha\text{-}A + C\bar{S} + CAS_2$
17	$C\bar{S} + A_3S_2$ (gel)	1200	6	$C\bar{S} + A_3S_2 + CAS_2$
18	$A_3S_2 + C_4A_3\bar{S}$	1200	6	$\alpha\text{-}A + CAS_2 + C_4A_3\bar{S}$
19	$A\bar{S}_3 + CAS_2$	1000	6	$S + \alpha\text{-}A + C\bar{S} + A_3S_2 + CAS_2$
20	$C_2AS + C_5S_2\bar{S}$	1200	5	$C_2AS + C_5S_2\bar{S}$
21	$\bar{S} + C_3S_2 + C_4A_3\bar{S}$	1200	6	$\beta\text{-}C_2S + C_2AS + C_4A_3\bar{S}$
22	$\bar{S} + C\bar{S} + A\bar{S}_3$	1000	6	$S + \alpha\text{-}A + C\bar{S} + CAS_2$
23	$\bar{S} + C\bar{S} + A_3S_2$	1200	6	$C_2AS + CAS_2 + C_4A_3\bar{S}$
24	$\bar{S} + A_3S_2 + C_4A_3\bar{S}$	1200	6	$\alpha\text{-}A + C_2AS + CAS_2 + C_4A_3\bar{S}$
25	$\bar{S} + A\bar{S}_3 + CAS_2$	1000	6	$S + \alpha\text{-}A + C\bar{S} + CAS_2$
26	$\bar{S} + S + C\bar{S} + A_3S_2$(gel)	1200	12	$\gamma\text{-}A + CAS_2$
27	$\bar{S} + S + C\bar{S} + A\bar{S}_3$	1200	12	$C_2AS + CAS_2$

At the temperatures up to the limit of the thermal stability of $A\bar{S}_3$ (770 °C in the open system), S and $A\bar{S}_3$ should be a compatible pair. The phase compatibility in this ternary subsystem is given in figure 4.

The system C - S - A - $\bar{S}$

The four component system was studied in [17-24] with an establishment of the following assemblages of the compatible phases:

C_2AS - $C_5S_2\bar{S}$ - $C_4A_3\bar{S}$ may coexist at 1200 °C [21]
C_2S - $C_5S_2\bar{S}$ - $C_4A_3\bar{S}$ coexists at 1200 - 1250 °C

(I) C - C_2S - C_3A - $C_5S_2\bar{S}$ 950 - 1150 °C [19]
(II) C - C_3A - $C_5S_2\bar{S}$ - $C_4A_3\bar{S}$
(III) C - $C\bar{S}$ - $C_5S_2\bar{S}$ - $C_4A_3\bar{S}$
(IV) C_2S - C_3A - $C_{12}A_7$ - $C_4A_3\bar{S}$
(V) C_2S - C_3A - $C_5S_2\bar{S}$ - $C_4A_3\bar{S}$
(VI) C_2S - $C_{12}A_7$ - CA - $C_4A_3\bar{S}$

Assemblage (I) is predicted to divide into two assemblages above 1175 °C:

(Ia) C - C_3S - C_3A - $C_5S_2\bar{S}$
(Ib) C_3S - C_2S - C_3A - $C_5S_2\bar{S}$

$C_{12}A_7$ - $C_5S_2\bar{S}$ and CA - $C_5S_2\bar{S}$ are incompatible pairs [19].

The phase changes in the subsystem C - CA - C_2S - $C\bar{S}$, below and above 1180 °C, were studied in [10]. The phase combination C_3A - $C_5S_2\bar{S}$ becomes unstable at temperatures above 1180 °C and converts into a new stable phase combination C - C_2S - $C_4A_3\bar{S}$ according to the reaction (2):

$$3C_3A + C_5S_2\bar{S} \rightarrow 6C + 2C_2S + C_4A_3\bar{S} \qquad (2)$$

The phase assemblages (I), (II) and (V) which are stable below 1180 °C are changed to the new phase assemblage containing C - C_2S - $C_4A_3\bar{S}$. The phase assemblages stable above decomposition temperature of $C_5S_2\bar{S}$ at 1180 °C are: (IV), (VI) and

(VII) C - C_2S - C_3A - $C_4A_3\bar{S}$
(VIII) C - C_2S - $C\bar{S}$ - $C_4A_3\bar{S}$

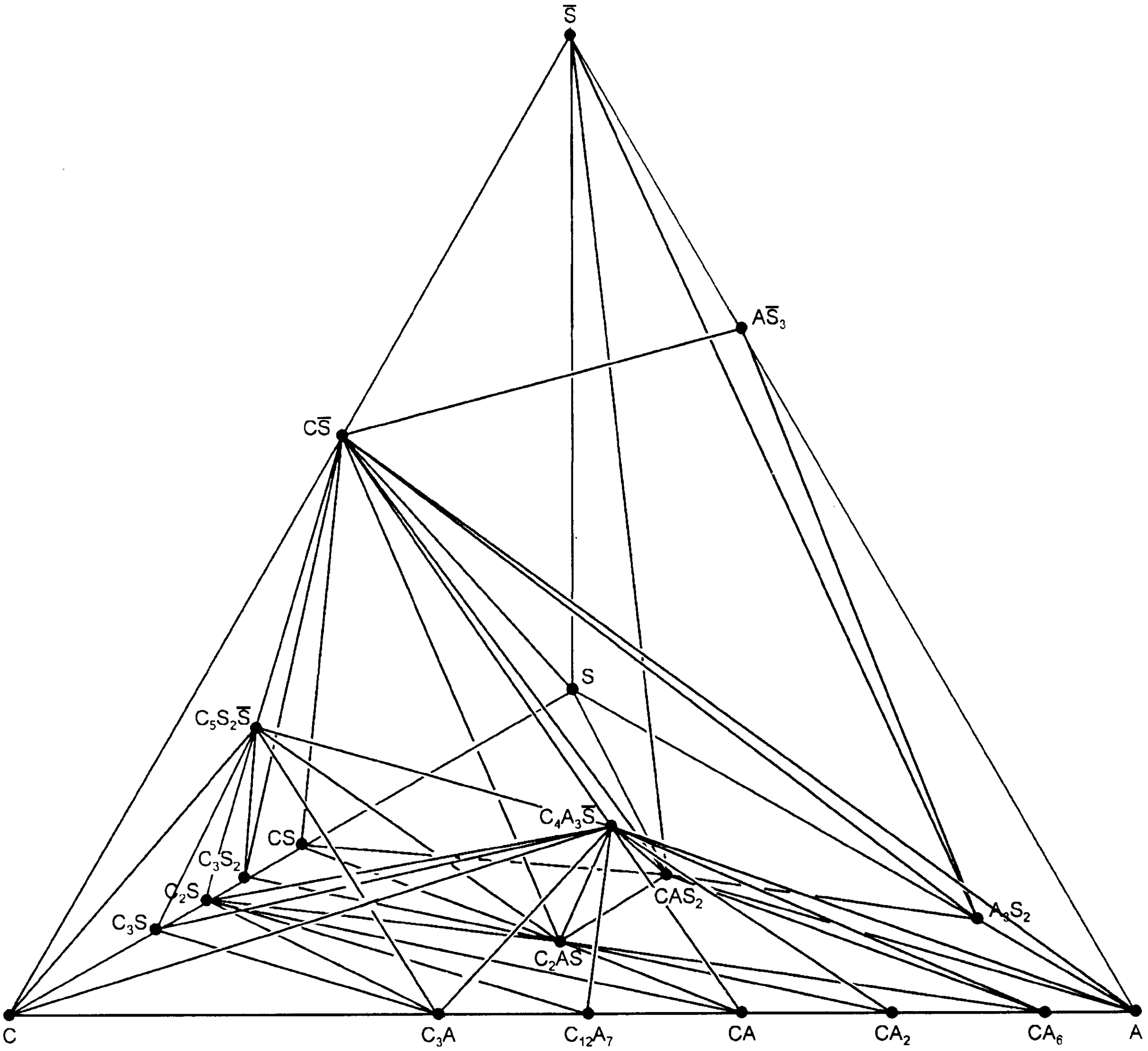

Figure 5. Diagram of the phase compatibility in the system $C - S - A - \bar{S}$.

Phase compatibility in the system $C - S - A - \bar{S}$ referred to sulphoaluminate belite cement clinker with C_2S as a key phase, where C_3S and $C_5S_2\bar{S}$ phases have not been included (burning temperature 1200 °C) were studied in [24]. The following 7 phase assemblages were identified: (IV), (VI), (VII), (VIII) and

(IX) $C_2S - C_3S_2 - C\bar{S} - C_2AS$
(X) $C_2S - CA - C_2AS - C_4A_3\bar{S}$
(XI) $C_2S - C\bar{S} - C_2AS - C_4A_3\bar{S}$

Phases C_3S_2 and $C_4A_3\bar{S}$ were predicted as an incompatible pair. A theoretical prediction and the experimental results showed that CS and $C_4A_3\bar{S}$ are an incompatible pair too [24].

According to [2] the presence of SO_3 inhibits the formation of C_2AS.

The binary relation between C_3S and $C_4A_3\bar{S}$ was studied in [10, 12, 17, 21]. According to [10] C_3S is not compatible with $C_4A_3\bar{S}$. At temperatures below 1180 °C, C_3S reacts with $C_4A_3\bar{S}$ to give phase association $C_2S - C_3A - C_5S_2\bar{S}$. Above 1180 °C, the phase association $C - C_2S - C_4A_3\bar{S}$ becomes stable. In the system $C - S - \bar{S}$, $C\bar{S}$ accelerated the formation of C_3S at a relatively low temperature of 1310 °C [15], but in the system $C - S - A - \bar{S}$ combined action of Al^{3+} and SO_4^{2-} ions prevent the formation of C_3S and C_2S forms preferentially [17]. Mineralogical composition of expansive cement burned above 1300 °C contains C_3S and $C_4A_3\bar{S}$ as the main clinker phases [12]. According to [21] C_3S and $C_4A_3\bar{S}$ do not coexist when the $C\bar{S}$ content is higher than 5 wt.%. From this and from our experiment (table 1) we have presumed, that the coexistence $C_3S - C_4A_3\bar{S}$ is possible at temperatures higher than 1300 °C (where C + C_2S may react to form C_3S). Therefore the phase association C_2S - C_3A - $C_5S_2\overline{S}$ has not been considered here as a stable one.

The addition of SiO_2 to C - A - $\overline{S}$ system may decompose $C\overline{S}$ forming thus C_2AS, β-C_2S or CAS_2, which depends on the amount of SiO_2 [18]. $C\overline{S}$ - C_2AS - CAS_2 and $C\overline{S}$ - C_2AS - $C_4A_3\overline{S}$ were identified as compatible phases. The reaction of Al_2O_3 with SiO_2 and CaO to form C_2AS is faster than the reaction to form $C_4A_3\overline{S}$. By increasing the CaO content, C_2AS decomposes completely to β-C_2S and Al_2O_3, afterwards Al_2O_3 is incorporated in $C_4A_3\overline{S}$. When the amount of CaO in the starting materials is sufficient, the addition of SiO_2 does not affect the formation of $C_4A_3\overline{S}$ and β-C_2S is formed. The samples ignited at the temperatures 1250 - 1300 °C for 2 hours showed these new phase assemblages:

(XII) S - $C\overline{S}$ - CAS_2 - $C_5S_2\overline{S}$
(XIII) S - C_2S - $C\overline{S}$ - CAS_2
(XIV) C_2S - $C\overline{S}$ - $C_5S_2\overline{S}$ - $C_4A_3\overline{S}$

These assemblages are considered as non equilibrium, because S - C_2S, S - $C_5S_2\overline{S}$, CAS_2 - $C_5S_2\overline{S}$ and C_2S - $C\overline{S}$ - $C_5S_2\overline{S}$ are not compatible pairs.

In the absence of the relevant thermodynamic data, it is not possible to predict the course of reactions, if any, between the main clinker phases and sulphates. The enthalpy of formation of $C_4A_3\overline{S}$ has been determined as 443 kJ kg^{-1} [8], but the enthalpy of formation of $C_5S_2\overline{S}$ is missing.

RESULTS AND DISCUSSION

The "yes, or no" compatibility of phases in the system C - S - A - $\overline{S}$ is represented by means of the phase compatibility matrix which is given in table 2. Symbol 0 represents compatible phases and symbol 1 incompatible phases, similarly as in [24].

Using the procedure given in [33] it can be shown that the data contained in the phase compatibility matrix gives 28 assemblages of compatible phases, which are listed in table 3. The relative volumes are given for each 4 phase assemblage (corresponding phase tetrahedra) as well as are given the cumulative volumes. The single volumes of the phase tetrahedra show that the phase space is completely and consistently filled by the tetrahedra with no empty space and no superposition of the tetrahedra that implies the consistency of the phase compatibility data. The computed relative volumes refer

Table 2. Phase compatibility matrix in the system C - S - A - $\overline{S}$.

	phases	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	C	-	1	1	1	0	1	1	1	0	1	1	1	1	0	1	1	1	1	0	0
2	S		-	1	0	1	1	1	0	1	1	1	1	1	0^E	0	1^E	1	0	1	1^G
3	A			-	1	1	1	1	1	1	1	1	1	0	0	0	0	1	0	1^E	0
4	$\overline{S}$				-	1	1	1	1	1	1	1	1	1	0	0^E	0	1^E	0^E	1	1
5	C_3S					-	0	1	1	0	1	1	1	1	1	1	1^G	1	1	0^G	0^E
6	C_2S						-	0	1	0	0	0	1	1	1	1	1^G	0	1	0	0
7	C_3S_2							-	0	1	1	1	1	1	0	1	1^G	0	1	0	1^E
8	CS								-	1	1	1	1	1	0	1	1^E	0	0	1	1
9	C_3A									-	0	1	1	1	1	1	1	1	1	0	0
10	$C_{12}A_7$										-	0	1	1	1	1	1	1	1	1	0
11	CA											-	0	1	1	1	1	0	1	1	0
12	CA_2												-	0	1	1	1	0	1	1^E	0
13	CA_6													-	1	1	1	0	0	1^G	0
14	$C\overline{S}$														-	0^E	0	0	0^E	0	0
15	A_3S_2															-	0^G	1	0	1^G	1^E
16	$A\overline{S}_3$																-	1^G	1^E	1^G	1
17	C_2AS																	-	0	0^E	0
18	CAS_2																		-	1^G	0^E
19	$C_5S_2\overline{S}$																			-	0
20	$C_4A_3\overline{S}$																				-

0 - denotes compatible (coexisting) phases
1 - denotes incompatible (non coexisting) phases
E - verified experimentally
G - presumed geometrically
- the other phase compatibility data is taken from the literature

Table 3. The list of the equilibrium phase assemblages in the system C - S - A - $\bar{S}$.

No.	assemblage							V_i	ΣV_i
1	C	-	C_3S	-	C_3A	-	$C_5S_2\bar{S}$	0.016540	0.016540
2	C	-	C_3A	-	$C_5S_2\bar{S}$	-	$C_4A_3\bar{S}$	0.012377	0.028917
3	C	-	$C\bar{S}$	-	$C_5S_2\bar{S}$	-	$C_4A_3\bar{S}$	0.073693	0.102610
4	S	-	$\bar{S}$	-	$C\bar{S}$	-	CAS_2	0.150972	0.253582
5	S	-	$\bar{S}$	-	A_3S_2	-	CAS_2	0.144728	0.398310
6	S	-	CS	-	$C\bar{S}$	-	CAS_2	0.104053	0.502363
7	A	-	CA_6	-	CAS_2	-	$C_4A_3\bar{S}$	0.004758	0.507121
8	A	-	$C\bar{S}$	-	A_3S_2	-	$A\bar{S}_3$	0.081558	0.588679
9	A	-	$C\bar{S}$	-	A_3S_2	-	CAS_2	0.033434	0.622113
10	A	-	$C\bar{S}$	-	CAS_2	-	$C_4A_3\bar{S}$	0.070024	0.692137
11	$\bar{S}$	-	$C\bar{S}$	-	A_3S_2	-	$A\bar{S}_3$	0.034622	0.726759
12	$\bar{S}$	-	$C\bar{S}$	-	A_3S_2	-	CAS_2	0.085160	0.811919
13	C_3S	-	C_2S	-	C_3A	-	$C_4A_3\bar{S}$	0.004241	0.816160
14	C_3S	-	C_2S	-	$C_5S_2\bar{S}$	-	$C_4A_3\bar{S}$	0.007153	0.823313
15	C_3S	-	C_3A	-	$C_5S_2\bar{S}$	-	$C_4A_3\bar{S}$	0.006080	0.829393
16	C_2S	-	C_3S_2	-	C_2AS	-	$C_5S_2\bar{S}$	0.004201	0.833594
17	C_2S	-	C_3A	-	$C_{12}A_7$	-	$C_4A_3\bar{S}$	0.006285	0.839879
18	C_2S	-	$C_{12}A_7$	-	CA	-	$C_4A_3\bar{S}$	0.005970	0.845849
19	C_2S	-	CA	-	C_2AS	-	$C_4A_3\bar{S}$	0.006038	0.851887
20	C_2S	-	C_2AS	-	$C_5S_2\bar{S}$	-	$C_4A_3\bar{S}$	0.005956	0.857843
21	C_3S_2	-	CS	-	$C\bar{S}$	-	C_2AS	0.021993	0.879836
22	C_3S_2	-	$C\bar{S}$	-	C_2AS	-	$C_5S_2\bar{S}$	0.010631	0.890467
23	CS	-	$C\bar{S}$	-	C_2AS	-	CAS_2	0.045598	0.936065
24	CA	-	CA_2	-	C_2AS	-	$C_4A_3\bar{S}$	0.004000	0.940065
25	CA_2	-	CA_6	-	C_2AS	-	$C_4A_3\bar{S}$	0.003786	0.943851
26	CA_6	-	C_2AS	-	CAS_2	-	$C_4A_3\bar{S}$	0.015039	0.958890
27	$C\bar{S}$	-	C_2AS	-	CAS_2	-	$C_4A_3\bar{S}$	0.026038	0.984928
28	$C\bar{S}$	-	C_2AS	-	$C_5S_2\bar{S}$	-	$C_4A_3\bar{S}$	0.015072	1.000000

to the positions of apexes of the tetrahedra given on the wt.% basis.

It was interesting to find out that the equilibrium phase compatibility in the ternary subsystems predetermines to a fair extent the phase compatibility in the four component system. The prerequisite for the corresponding analysis naturally was that no quaternary phase was present in the system, what was subsequently confirmed by the experimental study and the coexistences in the surfaces of the basic phase tetrahedra i. e. in the four 3 phase subsystems are well established. From the analysis of the phase compatibility according to [26-28] an invariant portion of the system was therefore discriminated for which the same phase compatibility was always issued, irrespective of the number of preliminary models of the phase compatibility. The rest phase space was considered as a variable part of the system with a necessity of the experimental establishment of phase equilibria and to which the experiments were predominantly directed.

The invariant portion of the system consists of two compatible phase pairs $C\bar{S}$ - CAS_2 and CAS_2 - $C_4A_3\bar{S}$ and 12 incompatible phase pairs:

A - $C_5S_2\bar{S}$ S - $C_4A_3\bar{S}$ $\bar{S}$ - C_2AS C_3S - $A\bar{S}_3$
C_2S - $A\bar{S}_3$ C_3S_2 - $A\bar{S}_3$ CA_2 - $C_5S_2\bar{S}$ CA_6 - $C_5S_2\bar{S}$
A_3S_2 - $C_5S_2\bar{S}$ $A\bar{S}_3$ - C_2AS $A\bar{S}_3$ - $C_5S_2\bar{S}$ CAS_2 - $C_5S_2\bar{S}$

Experimentally, the coexistences of $C\bar{S}$ - CAS_2 and CAS_2 - $C_4A_3\bar{S}$ and three incompatible phase pairs A - $C_5S_2\bar{S}$, $\bar{S}$- C_2AS and CA_2 - $C_5S_2\bar{S}$ were verified. Experimental results confirmed the correctness of the computing method.

The variant portion of the system implies 8 "yes or no" phase relations:

$\bar{S}$ - CAS_2 C_3S - $C_4A_3\bar{S}$ C_3S_2 - $C_4A_3\bar{S}$ CS - $A\bar{S}_3$
$C\bar{S}$ - A_3S_2 A_3S_2 - $C_4A_3\bar{S}$ $A\bar{S}_3$ - CAS_2 C_2AS - $C_5S_2\bar{S}$

From the experimental results following the coexistences $\bar{S}$- CAS_2, C_3S - $C_4A_3\bar{S}$, $C\bar{S}$ - A_3S_2 and C_2AS - $C_5S_2\bar{S}$ were confirmed and 4 relations C_3S_2 - $C_4A_3\bar{S}$, CS - $A\bar{S}_3$, A_3S_2 - $C_4A_3\bar{S}$ and $A\bar{S}_3$ - CAS_2 were the incompatible phase pairs (table 1.).

Despite the use of the sealed Pt-tubes, some loss of sulphates and perhaps of the moisture occurred. An attempt was made to verify the compatibility of phases with gaseous SO_3 phase by means of the experimental arrangement shown in [29].

The coexistence of $C\bar{S}$ - A_3S_2 was deduced from the product of the reaction between incompatible phase pairs CS - $A\bar{S}_3$ and $A\bar{S}_3$ - CAS_2 respectively fired at 1000 °C for 6 hours. At CS - $A\bar{S}_3$, the product was S + $C\bar{S}$ + A_3S_2 phase association that should be transformed according to reaction (4). But at $A\bar{S}_3$ - CAS_2, were identified S + A + $C\bar{S}$ + A_3S_2 + CAS_2 where S and A could transform into A_3S_2 as well as S and A product in the cases of reactions $\bar{S}$ + CS + $A\bar{S}_3$ and $\bar{S}$ + $A\bar{S}_3$ + CAS_2 (table 1.). In the latter two cases A_3S_2 was not identified probably because the forming pressure was lower than at Pt-encapsulated samples in order to support the transport of gaseous SO_x through the tablet from the corresponding bed getter, to compensate SO_3 escaped from the samples.

The phase associations C - C_3S - $C_4A_3\bar{S}$, S - $C\bar{S}$ - A_3S_2 and C_2S - C_3A - $C_5S_2\bar{S}$ are unstable due to the reactions (3), (4) and (5).

$$4C + 2C_3S + C_4A_3\bar{S} \rightarrow 3C_3A + C_5S_2\bar{S} \qquad (3)$$

$$4S + 3C\bar{S} + A_3S_2 \rightarrow 3\bar{S} + 3CAS_2 \qquad (4)$$

$$4C_2S + 3C_3A + C_5S_2\bar{S} \rightarrow 6C_3S + C_4A_3\bar{S} \qquad (5)$$

The relationship in the temporarily taken phase association S - $C\bar{S}$ - A_3S_2 was examined experimentally (table 1.). Besides the expected CAS_2 phase present a small amount of γ-A was also identified resulting from the incompletely reacted A_3S_2 gel.

In the C_3S_2 - $C_4A_3\bar{S}$ experiment the presence of α-CS could not be ruled out because its main diffraction peaks are superposed with diffraction peaks of the other present phases. A simultaneous presence of C_2S and CS would mean an incompleted reaction $C_2S + CS \rightarrow C_3S_2$. The presence of small amount of SiO_2 together with C_2S shows the possibility of a saturation of C_2S with SiO_2 giving C_3S_2 (table 1.). However the direct evidence of the coexistence of C_3S_2 and $C_4A_3\bar{S}$ was not reached.

If the coexistence C_3S_2 - $C_4A_3\bar{S}$ is presumed, two 3 phase associations C_2S - C_2AS - $C_5S_2\bar{S}$ and C_3S_2 - $C\bar{S}$ - $C_4A_3\bar{S}$ will have to be unstable due to reactions (6) and (7).

$$C_2S + 3C_2AS + C_5S_2\bar{S} \rightarrow 3C_3S_2 + C_4A_3\bar{S} \qquad (6)$$

$$6C_3S_2 + C\bar{S} + 2C_4A_3\bar{S} \rightarrow 6C_2AS + 3C_5S_2\bar{S} \qquad (7)$$

The assemblages No. 16 and 20 (table 3.) would transform to 3 new assemblages:

C_2S - C_3S_2 - C_2AS - $C_4A_3\bar{S}$
C_2S - C_3S_2 - $C_5S_2\bar{S}$ - $C_4A_3\bar{S}$
C_3S_2 - C_2AS - $C_5S_2\bar{S}$ - $C_4A_3\bar{S}$

By comparison of previous literature of the phase compatibility with our results it is seen that assemblages (Ia), (II), (III), (IV), (VI) and (X) are the same as the assemblages No. 1, 2, 3, 17, 18 and 19 (table 3.). The assemblages (I), (VII) and (VIII) correspond to the cases in which C_3S is decomposed into its simpler constituents with the assemblages No. 1, 13 and 14 as well as the assemblages (VIII), (IX) and (XI) correspond to the cases in which $C_5S_2\bar{S}$ is decomposed into C_2S and $C\bar{S}$ respectively with the assemblages No. 14, 16, 22 and 20, 28. The assemblages (Ib) and (V) contain the phase association C_2S - C_3A - $C_5S_2\bar{S}$ which in our case is transformed according to the reaction (5) into the coexistence of C_3S - $C_4A_3\bar{S}$ and the assemblages (Ib) and (V) are changed into three new assemblages No. 13, 14 and 15. So the results given in the present study are confirmed by the literature data.

The newly defined phase assemblages No. 4, 5, 6, 7, 8, 9, 10, 11, 12, 21, 23, 24, 25, 26 and 27 (table 3.) contain phases S, A, $\bar{S}$, CS, CA_2, CA_6, A_3S_2, $A\bar{S}_3$ and CAS_2 which were not encountered in the data in the previous 4 phase assemblages. At high temperatures at which the $A\bar{S}_3$ phase can not exist owing to its low thermal stability (in comparison with the other phases) the assemblages No. 8 and 11 should transform into the new phase assemblage A - $\bar{S}$ - $C\bar{S}$ - A_3S_2. In this way our phase compatibility model of the system C - S - A - $\bar{S}$ can be useful in studying its phase relationships including all known phases or for a study at which some of the phases e.g. $\bar{S}$, C_3S, $C_5S_2\bar{S}$, $A\bar{S}_3$ are not taken into account.

CONCLUSION

The system C - S - A - $\bar{S}$ was analysed for its phase relationships including all 20 known phases which were considered as stoichiometric compounds without thermal decomposition at all encountered temperatures. The phase subsystems of the system were analysed and completed with unknown coexistences. The phase compatibility model of the system is deduced based on literature data, on the partial modelling of the phase compatibility taking into account the geometrical reasons as well as on the own experimental study. The phase space system was divided into invariant and variant portions. The variant portion needed an experimental establishment of the phase equilibria.

As a result, twenty-eight 4 phases assemblages (tetrahedra) are identified. The phase compatibility model was verified formally by summing up of the volumes of the individual phase tetrahedra in order to show that the phase space is filled wholly and consistently by the individual phase tetrahedra without their superposition and no empty space available.

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KOEXISTENCIA FÁZ V SÚSTAVE CaO - SiO_2 - Al_2O_3 - SO_3

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Štvorzložková sústava C - S - A - $\overline{S}$ obsahuje fázy, ktoré tvoria mineralogický základ vysokohlinitých, expanzných a sulfoaluminátových cementov, prináležiacich do triedy nízkoenergetických cementov. Analýza koexistencie fáz v sústave zahŕňa všetkých 21 známych fáz $\underline{C}$, S, A, $\overline{S}$, $C_{\underline{3}}S$, C_2S, C_3S_2, CS, C_3A,_ $C_{12}A_7$,_ CA, CA_2, CA_6, $C\overline{S}$, A_3S_2, AS_3, C_2AS, CAS_2, C_5S_2S, C_4A_3S, ktoré sa uvažujú ako stechiometrické zlúčeniny (v celom rozsahu teplôt). Na základe publikovaných údajov o fázových rovnováhach, nášho experimentálneho štúdia a využitia čiastočného modelovania koexistencií fáz vychádzajúc z geometrických zákonitostí, sa vytvoril model koexistencie fáz sústavy.

Na zníženie počtu experimentov potrebných k vyriešeniu systému, bol využitý program zabezpečujúci apriorné rozdelenie študovaného systému na invariantnú a variantnú časť. Objemové vzťahy vo variantnej časti bolo potrebné experimentálne overiť.

Koexistencia fáz sústavy sa vyjadrila pomocou matice koexistencie fáz, na základe ktorej sa identifikovalo 28 rovnovážnych asociácií fáz (v podobe fázových tetraédrov). Konzistentnosť modelu koexistencie fáz sa verifikovala sumáciou objemov elementárnych fázových tetraédrov.