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Solid state compatibilities in $CaO–CaO.Al_2O_3–CaSO_4–CaF_2$ system

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The determination of the phases assemblages in equilibrium in the $CaO–CaO.Al_2O_3–CaSO_4–CaF_2$ system at 1100 °C has been performed. Four assemblages are found and one more is deduced. $3CA.CaSO_4$ appears in all compatibility tetrahedra in solid state or in melt presence. It is compatible with C_3A, $C_{12}A_7$ss, CA, $C_{11}A_7.CaF_2$ and the aluminate formed depends on Al_2O_3 and CaF_2 proportion, (cement chemistry abbreviations: C = CaO, A = Al_2O_3). *© 1998 Kluwer Academic Publishers*

1. Introduction

Modifications introduced in the $CaO–Al_2O_3$ equilibrium system by the presence of CaF_2 or $CaSO_4$ are of interest in the chemistry of cement because of their fluxing and mineralizing properties and because it contains phases involved in special cements (expansive cement type K, SR-white cement, super-sulphated belitic cements) [1–6].

The system $CaO–CaO.Al_2O_3–CaSO_4–CaF_2$ is a subsystem of the $CaO–SiO_2–Al_2O_3–CaSO_4–CaF_2$ system in which a solid state phase relationship existing in the zone rich in CaO, at 1050 and 1100 °C has been determined [7].

In the $CaO–CaO.Al_2O_3–CaSO_4$ system, the only stable ternary compound known in $3CA.CaSO_4$, which is in solid state, a compatible phase with all calcium aluminates, with CaO and $CaSO_4$ [8]. Thermal stability of $3CA.CaSO_4$ is superior to that of $CaSO_4$ [9–11], and in open system and in the temperature range of 1300–1500 °C, its decomposition obeys two kinetic mechanisms [12].

On the other hand, a ternary phase in condensed state, ($3CA.CaF_2$) and a solid solution of $C_{12}A_7$ and CaF_2 (being $C_{11}A_7.CAF_2$ the richest term of the solution) are known to exist in the $CaO–Al_2O_3–CaF_2$ system.

$3CA.CaF_2$ is compatible with $C_{11}A_7.CAF_2$, CA, CA_2, and CaF_2 [13]. CaF_2 is incompatible with C_3A, $C_{12}A_7$ and CA. Both C_3A and $C_{12}A_7$ do not have a stability field in compositions having CaF_2 higher than 5.54 wt %. $C_{11}A_7$ CaF_2 is compatible with CaO in this ternary system, and the C_3A stability field is limited by the use of compatibility $CaO–C_{11}A_7.CaF_2$.

Brisi and Rolando [14] initially, and later Massazza and Puzzuoli [15] talked about the existence of an intermediate point in the line of solid solutions $C_{12}A_7–C_{11}A_7.CaF_2$, which would partially modify the compatibilities in solid state published by Chaterjee and Zahmoidin [16]. Blanco-Varela and Giménez [17], verify the solid state compatibilities in this system, and they found the compatibilities given by Charterjee and Zahmoidin [16].

There is a discrepancy between different authors concerning the stability of $3CA.CaF_2$ in open atmosphere [18, 19] because of its high vapour pressure at synthesis temperature. However, different authors claim the possibility of synthesizing $3CA.CaF_2$ in open atmosphere if humidity is avoided [20, 21].

With regard to the $C_{12}A_7$ss, this solid solution is produced without important fluorine loss at temperatures between 900 and 1300 °C [22].

There is no quaternary compound known in $CaO–Al_2O_3–CaF_2–CaSO_4$ system. The ternary compounds are fluoraluminates and sulphoaluminates, described earlier.

The main objective of this paper is to study the solid state compatibilities in $CaO–CaO.Al_2O_3–CaSO_4–CaF_2$ system.

2. Experimental procedure

For the study of compatibilities, a previous synthesis of the existing phases in the $CaO–CaO.Al_2O_3–CaSO_4–CaF_2$ system was performed.

Those syntheses were carried out mixing RA pure chemical reactants and calcining the mixes at temperatures and times described in Table I. Several intermediate grindings were also done during the synthesis to homogenize samples and to favour reactions. The pureness of the phases was verified by X-ray diffraction (XRD).

The determination of the phase assemblages in equilibrium in the $CaO–CaO.Al_2O_3–CaSO_4–CaF_2$ system at 1100 °C has been carried out by the study of

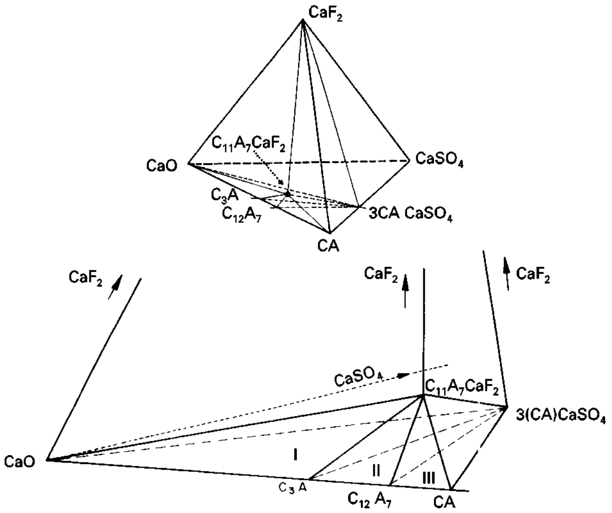

Figure 1 Partial compatibilities in CaO–Al$_2$O$_3$–CaSO$_4$–CaF$_2$ system at 1100 °C.

the pure phase mixes given in Table II. Some other mixes were done to prove the compatibilities shown in Fig. 1.

Phase mixes were homogenized in an agate mortar using ethanol as dispersant medium. The samples were homogenized and dried and then thermally treated at 1000 and 1100 °C for different times (Table II). In all thermal treatments carried out, samples were quenched in air.

Phases formed during heating were identified by XRD. The XRD equipment used was a Phillips PW-1700 X-ray tube with Cu anode worked at 40 kV and 50 mA.

In some samples, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was performed in a Mettler A-1 type thermoanalyser with air atmosphere.

TABLE I Conditions of phase synthesis

Compounds	Reactive (Molar relations)	Temperature (°C)	Time (h)
CaSO$_4$	CaSO$_4$.2H$_2$O	200	2
CaO	CaCO$_3$	1000	3
C$_3$A	3CaCO$_3$ + Al$_2$O$_3$	1350	70
C$_{12}$A$_7$	12CaCO$_3$ + 7Al$_2$O$_3$	1250	24
C$_{11}$A$_7$.CaF$_2$	11CaCO$_3$ + 7Al$_2$O$_3$ + CaF$_2$	1100	89
CA	CaCO$_3$ + Al$_2$O$_3$	1350	25
3CA.CaSO$_4$	3CaCO$_3$ + 3Al$_2$O$_3$ + CaSO$_4$.2H$_2$O	1100	50
3CA.CaF$_2^*$	3CA + CaF$_2$	1100	2–5

* Synthesized pelleting reactants at 300 MPa in vacuum.

3. Results

Solid state compatibilities study in quaternary system CaO–CaO.Al$_2$O$_3$–CaSO$_4$–CaF$_2$ in compositions with CaO/Al$_2$O$_3$ > 1 molar ratios have been carried out according to phase mixes given in Table II, heated to 1100 °C for between 5 and 20 h. Compounds identified by XRD after heating treatments are given in the same table and compatibilities obtained are represented in Fig. 1.

Mixes of 3CA.CaF$_2$ and C$_{11}$A$_7$.CaF$_2$ with CaSO$_4$ (CASF9 and CASF10 samples) heated to 1100 °C decompose, giving place to 3CA.CaSO$_4$ as the main phase. So, both fluoraluminates are incompatible with CaSO$_4$.

During heating of CASF9C$_{11}$A$_7$CaF$_2$ decomposes producing 3CA.CaSO$_4$, CaO and CaSO$_4$. CaF$_2$ was not identified probably because its proportion in the sample is under the XRD detection limit.

TABLE II Compounds identified by XRD in the CaO–Al$_2$O$_3$–CaF$_2$–CaSO$_4$ system after heating at 1100 °C

Sample	Composition	t (h)	Compounds identified by XRD
CASF3	3CA.CaSO$_4$ (47%), CA (3%) CaF$_2$ (50%)	5	CaF$_2$ (M), 3CA.CaSO$_4$ (M), C$_{12}$A$_7$ss (p)
		10	CaF$_2$ (M), C$_{12}$A$_7$ss (M), 3CA.CaSO$_4$ (m)
CASF4	CaF$_2$ (50%), 3CA.CaSO$_4$ (25%), CaO (25%)	5	CaF$_2$ (M), 3CA.CaSO$_4$ (m), CaO (m)
		10	CaF$_2$ (M), 3CA.CaSO$_4$ (m), CaO (m), C$_{11}$A$_7$.CaF$_2$ (p)
CASF5*	3CA.CaSO$_4$ (47%), CA (3%) CaSO$_4$ (30%), CaF$_2$ (50%)	5	3CA.CaSO$_4$ (M), CaSO$_4$ (m), CaF$_2$ (m), C$_{12}$A$_7$ss (p), (L)
CASF6	3CA.CaSO$_4$ (47%), CA (3%) C$_{11}$A$_7$.CaF$_2$ (50%)	5	3CA.CaSO$_4$ (M), C$_{12}$A$_7$ss (M), CA (p)
		20	3CA.CaSO$_4$ (M), C$_{12}$A$_7$ss (M), CA (p)
CASF7	3CA.CaSO$_4$ (47%), CA (3%), 3CA.CaF$_2$ (50%)	5	3CA.CaSO$_4$ (M), C$_{11}$A$_7$.CaF$_2$ (M), 3CA.CaF$_2$ (m), CA (m), CaF$_2$ (m)
CASF8	C$_{11}$A$_7$.CaF$_2$ (40%), CaO (40%), C$_3$A (17%), CaSO$_4$ (3%)	5	C$_{12}$A$_7$ss (M), 3CA.CaSO$_4$ (M), C$_3$A (m), CaO (p)
CASF9	C$_{11}$A$_7$.CaF$_2$, CaSO$_4$ (50%)	20	3CA.CaSO$_4$ (M), CaSO$_4$ (m), CaO (m)
CASF10	3CA.CaF$_2$, CaSO$_4$ (50%)	5	3CA.CaSO$_4$ (M), CaSO$_4$ (M), CaF$_2$ (p), C$_{12}$A$_7$ss (p), (L)

* 1000 °C heating temperatures.
M: XRD peak intensity is 100% or close to.
m: XRD peak intensity is higher than 10%.
p: XRD peak intensity corresponds to trace compounds.
L: Sample is melted after heating.

In sample CASF10, in which $3CA.CaF_2$ was initially present, $3CA.CaSO_4$, $CaSO_4$, CaF_2 and $C_{11}A_7.CaF_2$ were identified by XRD after heating. In this sample, a melting was produced and, $C_{12}A_7ss$, though not compatible with $CaSO_4$, crystallizes during the fast cooling process. In this sample equilibrium was not achieved.

Mixes of $3CA.CaSO_4$ and CaF_2 with 3% CA (CASF3 sample) or with 25% CaO (CASF4), were heated in air for 5 and 10 h. During the heating, $C_{11}A_7.CaF_2$ was formed in these samples. When CA is present (CASF3 samples), the appearance of this phase at 5 h is interpreted as caused by evaporation of volatile material (F or SO_3) with the subsequent composition shift towards CaO-richer regions and caused by the CaO reaction with CA and CaF_2. Then, $3CA.CaSO_4$–CaF_2 compatibility is not excluded. $CaSO_4$ absence from $3CA.CaSO_4$ decomposition verifies this interpretation. After 10 h heating, additional loss of SO_3 and a greater $C_{11}A_7ss$ formation are produced.

$3CA.CaSO_4$ compatibility with CaF_2 is verified in CASF4 sample in which heating in the presence of CaO does not give place to phase variation after 5 h. However, at long heating times (10 h), a small amount of $C_{11}A_7.CaF_2$ is produced. This $C_{12}A_7ss$ presence in the mix indicates a shift of the initial composition because of volatile component loss (SO_3).

In the case of CASF5 mix, belonging to the composition triangle $3CA.CaSO_4$–$CaSO_4$–CaF_2, the sample appears melted at 1000 °C and starting phases and $C_{12}A_7ss$ traces are identified. This compound crystallizes during the sample fast cooling and it is not in equilibrium with $CaSO_4$, which also crystallizes.

The DTA/TGA of the sample shows that a melting is produced at 925 °C; from this temperature, a weight loss is produced and the weight loss rate increases with temperature.

$3CA.CaSO_4$, $C_{11}A_7.CaF_2$ and CA mix (CASF6 sample) have been heated to 1100 °C for 5 and 20 h. After heating, starting compounds were identified by XRD. After heating of the sample CASF7 for 5 h, $3CA.CaSO_4$, $3CA.CaF_2$, $C_{11}A_7.CaF_2$, CA and CaF_2 were identified. This means that even when the sample has not reached equilibrium during heating, $3CA.CaF_2$ decomposition is produced, giving rise to CA and CaF_2. It seems that $3CA.CaF_2$ and $3CA.CaSO_4$ are not compatible.

$3CA.CaF_2$ incompatibility with $3CA.CaSO_4$ and $CaSO_4$ seems to suggest that $3CA.CaF_2$ has no stability field in this system or it is reduced to $CaSO_4$ in very low proportions, which has not been studied in this work.

CASF8 sample, which is a mix of CaO, C_3A, $C_{11}A_7.CaF_7$ and 3% $CaSO_4$ gives rise to $3CA.CaSO_4$ formation after heating to 1100 °C, this composition being in a compatibility tetrahedron CaO–C_3A–$C_{11}A_7.CaF_2$–$3CA.CaSO_4$.

Weight loss registered in these samples by TGA is produced at appreciable rate at temperatures over 1100 °C except for those compositions placed in tetrahedra where CaF_2 and $CaSO_4$ coexist, in which melting at about 950 °C is produced and important weight losses are observed.

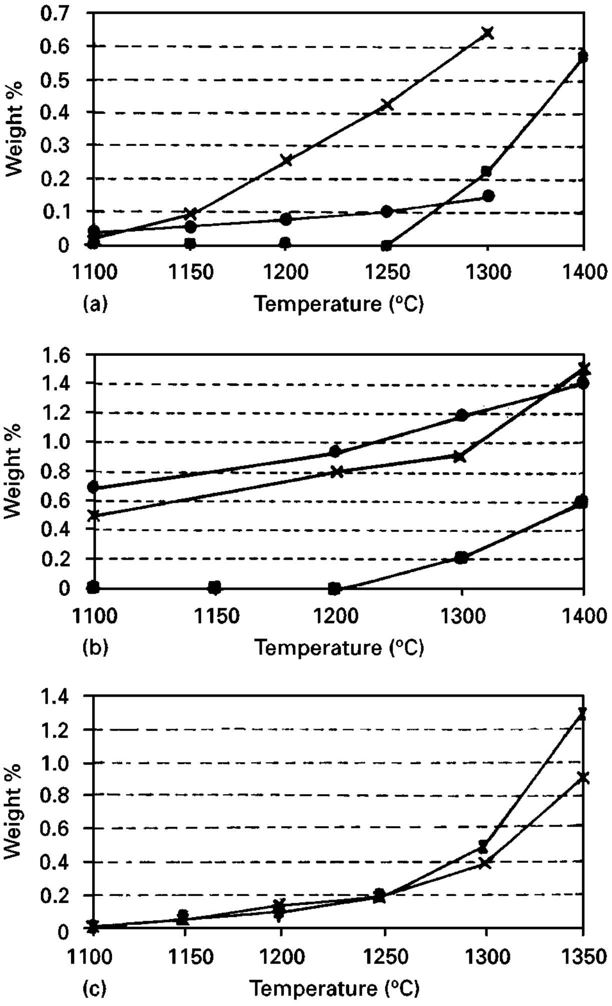

Figure 2 Weight loss of some pure compounds, and some mixes of them, versus temperature. (a) (×) $3CA.CaSO_4 + CaF_2$ (50 wt%) (■) $3CA.CaSO_4$; (●) CaF_2. (b) (×) $3CA.CaSO_4 + C_{11}A_7.CaF_2$ (50 wt%); (■) $3CA.CaSO_4$; (●) $C_{11}A_7.CaF_2$. (C) (×) $3CA.CaSO_4 + CaSO_4$ (50 wt%); (I) $CaSO_4$.

In Fig. 2a, b and c, weight losses of some pure compounds and their mixes are shown, expressed as SO_3 and/or F^-% weight lost with respect to the total SO_3 or F content. This way of expressing weight lost gives an idea of the relative stability of the mixes in relation to the pure compounds. In Fig. 2, it seems that registered lost are higher in the mixture of phases than in the pure compounds under the same dynamic heating conditions.

4. Discussion

In the references, numerous studies are found about CaF_2 or $CaSO_4$ effect on clinker formation, but nothing about both substances joint effect on phases relations in CaO–Al_2O_3 system.

Results obtained about compatibilities in CaO rich region in this system at 1100 °C are shown in Fig. 1. Compatibility tetrahedra found at 1100 °C are:

$$CaO–C_3A–3CA.CaSO_4–C_{11}A_7.CaF_2$$

$$C_3A–3CA.CaSO_4–C_{12}A_7ss$$

$$C_{12}A_7ss–3CA.CaSO_4–CA$$

$$CaO–C_{11}A_7.CaF_2–CaF_2–3CA.CaSO_4$$

Because of $3CA.CaSO_4$ and $3CA.CaF_2$ incompatibility in the tetrahedra, the following tetrahedron is deduced:

$$CA–C_{11}A_7.CaF_2–3CA.CaSO_4–CaF_2$$

Compatibility tetrahedron $CaO–3CA.CaSO_4–CaF_2–CaSO_4$ exists at 900 °C, but at 1100 °C the presence of a melt has been verified.

5. Conclusions

According to the compatibilities obtained, the following conclusions can be extracted:

1. Any aluminate, fluorated or not, gives place to $3CA.CaSO_4$ formation in the presence of $CaSO_4$.
2. $3CA.CaSO_4$ appears in all compatibility tetrahedra in solid state or in melt presence. It is compatible with C_3A, $C_{12}A_7$ss, CA, $C_{11}A_7.CaF_2$ and the aluminate formed depends on Al_2O_3 and CaF_2 proportion.
3. $C_{11}A_7.CaF_2$ is also compatible with C_3A, $3CA.CaSO_4$, CA, CaF_2 and CaO aluminates but not with $CaSO_4$.
4. Binary aluminates, C_3A and CA, are found in very limited tetrahedra in compositions with low CaF_2 concentrations.
5. $3CA.CaF_2$ stability field has not been found in the quaternary system. This might be because it is limited to the low proportions of $CaSO_4$, but this has not been studied in this work.
6. At 1100 °C the system is in the limit at which mixture weight loss begins. Heating at this temperature for a moderate period of time does not give place to important weight losses; however, for longer times, the weight loss produces a composition movement towards CaO–richer regions.
7. CaF_2 and $CaSO_4$ addition to aluminate mixes decreases melting phase appearance temperature in relation to $CaO–Al_2O_3$ system; this appearance at 951 °C being in the tetrahedron where CaF_2 and $CaSO_4$ coexist.

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