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SOLID STATE PHASES RELATIONSHIP IN THE $CaO-SiO_2-Al_2O_3-CaF_2-CaSO_4$ SYSTEM

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ABSTRACT

In this paper the effect of CaF_2 and $CaSO_4$ on the equilibrium phases in the $CaO-SiO_2-Al_2O_3$ system at 1050°C and 1100°C is presented.

The phase compatibilities in the five components system were obtained by adding increasing amounts of CaF_2 to CaO-rich compositions of the $CaO-C_2S-CA-CaSO_4$ system. The introduction of an additional component into the quaternary tetrahedron, involves the appearence of seven quinary compatibilities at 1050°C and five quinary compatibilities at 1100°C.

The quinary volume F, can be observed at 1050ºC as well as 1100ºC. It contains C_3S_{ss} in equilibrium with $CaO-C_{12}A_{7ss}$ - fluorellestadite and CaF_2. C_3S_{ss} is formed in those compositions in which all the $CaSO_4$ is combined as fluorellestadite and all the Al_2O_3 as $C_{12}A_{7ss}$. Besides, some extra CaF_2 must exist.

For those compositions rich in CaO in wich $CaSO_4/CaF_2<3$, $Al_2O_3/CaF_2<7$, $CaSO_4+Al_2O_3<10CaF_2$ and $SiO_2/CaSO_4>1$, the formation of C_3S_{ss} is produced.

Introduction

The use of mineralizers and fluxes in the cement industry is widely known. The incorporation of compounds other than those usual, in low proportions, which improve the clinkering conditions as well as decrease the maximum clinkering temperature or improve the phase formation in the clinker without altering the final properties of the product is widely used.

The mineralizing and fluxing properties of the compounds CaF_2 and $CaSO_4.2H_2O$ have already been described in the literature. Their properties are different when they are added separately or jointly in the raw materials.

It has been verified that the joint adding of CaF_2 and $CaSO_4.2H_2O$ to raw clinker materials of grey or white cement results in a decrease of the maximum clinkering temperature to 1350°C and in a clinker with a good proportion of alite. A cement with satisfactory mechanical properties therefore results (1,2,3,4,13,14).

As to the grey cement clinker, the reader is referred to the studies already conducted by Blanco et al.(1,2), Tong and Lin (3), and Ye Quing et al. (14), where the decrease of the clinkering temperature and the good properties of the molten phase are described as regards the viscosity and therefore the ion diffusion required for the formation of the alite phase. The temperature at which the molten phase appears has been determined at 1175°C (1).

In addition to CaO, C_2S and C_3S, the phases found in white clinker with added $CaSO_4$ and CaF_2 include fluorellestadite ($3C_2S.3CaSO_4.CaF_2$; here, Fell), $3CA \cdot C\bar{S}$ and $C_{11}A_7CaF_2$ (2,4). The decrease in the temperature of formation of the molten phase is mainly due to the presence of fluorellestadite.

Up to the present time, there have not been exhaustive studies of the different aspects of the influence of CaF_2 and $CaSO_4 \cdot 2H_2O$ on the formation of the phases in equilibrium or the temperature and composition at which molten phases occur, in the $CaO-SiO_2-Al_2O_3-CaF_2-CaSO_4$ or $CaO-SiO_2-Al_2O_3-Fe_2O_3-CaF_2-CaSO_4$ systems, of interest in the chemistry of cement.

In the $CaO-SiO_2-CaSO_4-CaF_2$ system the compatibilities in the solid state at 1000°C and 1150°C have been determined (5). Also in this system, it is known the temperature of occurrence of the invariant points in the $C_2S-CaSO_4-CaF_2$ subsystem and in the pseudosystem CaO-C_2S-Fell (6) where the compositions of fluorellestadite and tricalcium silicate are respectively found.

In the quaternary system $CaO-SiO_2-CaSO_4-CaF_2$, the occurrence of the alite phase has not been established at temperatures below 1250°C (5,6).

The purpose of the present investigation is to study the quinary compatibilities diagram, in a thermodynamic equilibrium, of the $CaO-SiO_2-Al_2O_3-CaF_2-CaSO_4$ system at temperatures of 1050°C and 1100°C, where the formation of white cement is possible.

The study of compatibilities within the quinary system $CaO-SiO_2-Al_2O_3-CaF_2-CaSO_4$ was carried out at 1050°C and 1100°C by addition of CaF_2 at compositions located in the compatibility tetrahedra of the $CaO-SiO_2-Al_2O_3-CaSO_4$ system existing in the zone rich in CaO.

Experimental

$CaSO_4.2H_2O$, $CaCO_3$, quartz, CaF_2 and Al_2O_3 have been used in the form of pure reagents (AR) as starting products. C_3A, C_2S, $3CA\cdot C\bar{S}$ and $2C_2S\cdot C\bar{S}$ were previously synthesized in a platinum crucible, starting from the initial reagents, at temperature of 1350°C, 1350°C, 1100°C and 1100°C, respectively, until completion of the reaction. The purity of the phases was checked by XRD.

CaO and $CaSO_4$ were obtained from the calcination of $CaCO_3$ and $CaSO_4.2H_2O$ at 1000°C and 800°C, respectively. The tetrahedra of the $CaO-SiO_2-Al_2O_3-CaSO_4$ system chosen are as follows:

T1) CaO - C_3A - $2C_2S\cdot C\bar{S}$ - C_2S
T2) CaO - C_3A - $2C_2S\cdot C\bar{S}$ - $3CA\cdot C\bar{S}$
T3) CaO - $3CA\cdot C\bar{S}$ - $CaSO_4$ - $2C_2S\cdot C\bar{S}$

Compositions in these tetrahedra T1, T2 and T3 were prepared from previously synthesized compounds in the proportions as follow:

T1.- In quaternary tetrahedron 1, the composition in % wt is: 25% $2C_2S\cdot C\bar{S}$, 23% C_2S, 26% CaO and 26% C_3A.

T2.- In quaternary tetrahedron 2, the composition in % wt is: 25% $2C_2S\cdot C\bar{S}$, 23% $3CA\cdot C\bar{S}$, 27% CaO, 25% C_3A.

T3.- In quaternary tetrahedron 3, the composition in % wt is: 20% $2C_2S\cdot C\bar{S}$, 23% $3CA\cdot C\bar{S}$, 26% CaO, 31% $CaSO_4$.

To those homogenized mixtures, CaF_2 was added in proportions of up to 5% wt. They were maintained at a controlled temperature during different periods of time. The phases present were determined by XRD and IR methods.

Results

The study of the compatibilities in the quaternary system $CaO-SiO_2-Al_2O_3-CaSO_4$ has been carried out by different authors (7,8), and there are discrepancies among them as to the temperature ranges where the compatility diagrams are valid.

According to diferente authors, the compatibility tetrahedra at temperatures comprised between 950°C, 1150°C and 1180°C, in the zone rich in CaO of the $CaO-SiO_2-Al_2O_3-CaSO_4$ system are:

- $2C_2S\cdot CS$, C_2S, CaO and C_3A (T1)
- $2C_2S\cdot CS$, $3CA\cdot C\bar{S}$, CaO and C_3A (T2)
- $2C_2S\cdot CS$, $3CA\cdot C\bar{S}$, $CaSO_4$ and CaO (T3)
- $2C_2S\cdot CS$, $3CA\cdot C\bar{S}$, C_2S and C_3A (T4)
- C_2S, C_3A, $C_{12}A_7$ and $3CA\cdot C\bar{S}$ (T5)
- C_2S, $C_{12}A_7$, CA and $3CA\cdot C\bar{S}$ (T6)

When the temperature is raised, the $2C_2S\cdot C\bar{S}$ present in tetrahedra T1, T2, T3 and T4 decomposes into C_2S and $CaSO_4$, and the following compatibility tetrahedra are then obtained:

- CaO, C_2S, C_3A and $3CA\cdot C\bar{S}$ (31)
- CaO, C_2S, $3CA\cdot C\bar{S}$ and $CaSO_4$ (32)

while T5 and T6 do not suffer any variations, with temperature.

The decomposition temperature of $2C_2S \cdot C\bar{S}$, indicated by various authors, varies from 1298°C (9) in a closed atmosphere, to 1195°C (10) in the air, to 1200°C (11) in the presence of C_3A.

The addition of CaF_2 to compositions located within the compatibility tetrahedra T1, T2 and T3 diminishes the decomposition temperature of $2C_2S \cdot CS$ down to 1100°C (15).

Compatibilities in the quinary system $CaO-SiO_2-Al_2O_3-CaF_2-CaSO_4$ at 1050°C

Table (1) gives the composition of the samples preprared for the study of the compatibilities, temperatures and calcination times as well as, the phases identified by DXR.

TABLE 1

Compounds identified through XRD of the mixtures heated at 1050°C.

SAMPLES	%wt CaF_2	t (h)	COMPOUNDS IDENTIFIED THROUGH XRD
T11	0.45	2	CaO, C_3A, $2C_2S.CaSO_4$, C_2S, $C_{12}A_7ss$
T12	1.6	2	CaO, C_2S, F ell, $C_{12}A_7ss$, $2C_2S.CaSO_4$
T13	2.5	2	CaO, C_2S, F ell, $C_{12}A_7ss$
T14	3.9	2(*)	CaO, C_2S, F ell, $C_{12}A_7ss$, C_3S
		4	CaO, F ell, C_3S, $C_{12}A_7ss$
T21	0.92	2	CaO, $3CA \cdot C\bar{S}$, $C_{12}A_7ss$, C_3A, $2C_2S.CaSO_4$,
T22	2.3	2	CaO, $C_{12}A_7ss$, $3CA \cdot C\bar{S}$, F ell, $2C_2S.CaSO_4$
T23	5.0	2	CaO, F ell, C_3S, $C_{12}A_7ss$
T31	0.4	2	CaO, $3CA \cdot C\bar{S}$, F ell, $CaSO_4$, $2C_2S.CaSO_4$
T32	2.1	2	CaO, $3CA \cdot C\bar{S}$, $CaSO_4$, F ell
T33	3.6	2	CaO, $3CA \cdot C\bar{S}$, $CaSO_4$, F ell, CaF_2

* Nom-equilibrium.

The addition of CaF_2 to the composition lying in T1 tetraedron ($2C_2S \cdot CS$, C_2S, CaO and C_3A) has been made in proportions comprised of between 0.45% and 4% wt.

The addition of 0.45% CaF_2 results in the occurrence of $C_{12}A_{7ss}$, the $2C_2S \cdot CS$ and C_2S remaining unaltered and the C_3A proportion diminishing.

The addition of 1.6 and 2.5% wt results in the occurrence of $C_{12}A_{7ss}$ and Fell, C_3A disappearing in both cases, as well as $2C_2S \cdot C\bar{S}$ when the proportion of CaF_2 was 2.5% wt.

With 3.9% CaF_2 added, tricalcium silicate is identified in addition to $C_{12}A_{7ss}$ and Fell, as in the preceding samples.

The proportion of CaF_2 added to the composition located in the compatibility tetrahedron T2 ($CaO-C_3A-2C_2S \cdot CS-3CA \cdot C\bar{S}$) has been 0.92, 2.3, and 5% wt. The sequence of occurrence of the compounds with the addition of CaF_2 is similar to that given for the previous tetrahedron. With 0.92%, the formation of $C_{12}A_{7ss}$ takes place, the proportion of C_3A in the mixture diminishing. The addition of 2.3% gives place to the formation of $C_{12}A_{7ss}$ and Fell, C_3A disappearing from the mixture; and the proportions of $2C_2S \cdot C\bar{S}$ and $3CA \cdot C\bar{S}$ diminishing. The addition of 5% CaF_2 results in the formation of Fell, $C_{12}A_{7ss}$ and C_3S, instead of the initial compounds C_3A, $2C_2S \cdot C\bar{S}$ and $3CA \cdot C\bar{S}$.

The addition of CaF_2 in proportions of 0.4, 2.1, and 3.6% wt to the composition located in tetrahedron T3 ($CaO-3CA \cdot C\bar{S}- CaSO_4-2C_2S \cdot C\bar{S}$), gives rise to the formation of fluorellestadite. For the proportion of 3.6%, the CaF_2 is identified through XRD.

The figure (1) shows the compatibilities found at 1050 C.

The introduction of an additional component into the quaternary tetrahedra of the $CaO-SiO_2-Al_2O_3-CaSO_4$ system results in the appearance of the following quinary compatibilities along the range of the compositions studied:

A.- $CaO - C_3A - C_{11}A_7CaF_2 - 2C_2S \cdot C\bar{S} - C_2S$
B.- $CaO - C_3A - C_{11}A_7CaF_2 - 2C_2S \cdot C\bar{S} - 3CA \cdot C\bar{S}$
C.- $CaO - C_{11}A_7CaF_2 - 2C_2S \cdot C\bar{S} - C_2S$ - Fell
D.- $CaO - C_{11}A_7CaF_2 - 2C_2S \cdot C\bar{S} - 3CA \cdot C\bar{S}$ - Fell
E.- $CaO - 3CA \cdot C\bar{S} - 2C_2S \cdot C\bar{S} - CaSO_4$ - Fell
F.- $CaO - C_{11}A_7CaF_2$ - Fell - $C3S_{ss} - C_2S$
G.- $CaO - CaSO_4 - 3CA \cdot C\bar{S} - CaF_2$ - Fell

Upon addition of CaF2 to compositions located within the quaternary compatibility tetrahedron T1 $CaO-C_3A-2C_2S \cdot C\bar{S}-C_2S$ of $CaO-Al_2O_3-SiO_2-CaSO_4$ system, an initial formation of $C_{11}A_7CaF_2$ starts by the reaction of CaF_2 with C_3A according to reaction:

$$7C_3A + CaF_2 \longrightarrow 10CaO + C_{11}A_7CaF_2 \qquad [1]$$

resulting in the quinary compatibility volume A.

When the addition of CaF_2 to these compositions is that required to transform the whole C_3A into $C_{11}A_7CaF_2$, the composition is found in compatibility tetrahedron 12. The addition of CaF_2 to compositions of tetrahedron 12 results in the formation of Fell by the reaction of $2C_2S \cdot C\bar{S}$ with CaF_2:

$$3(2C_2S \cdot C\bar{S}) + CaF_2 \longrightarrow 3C_2S \cdot 3CaSO_4 \cdot CaF_2 + 3C_2S \qquad [2]$$

These compositions are located within the quinary volume C.

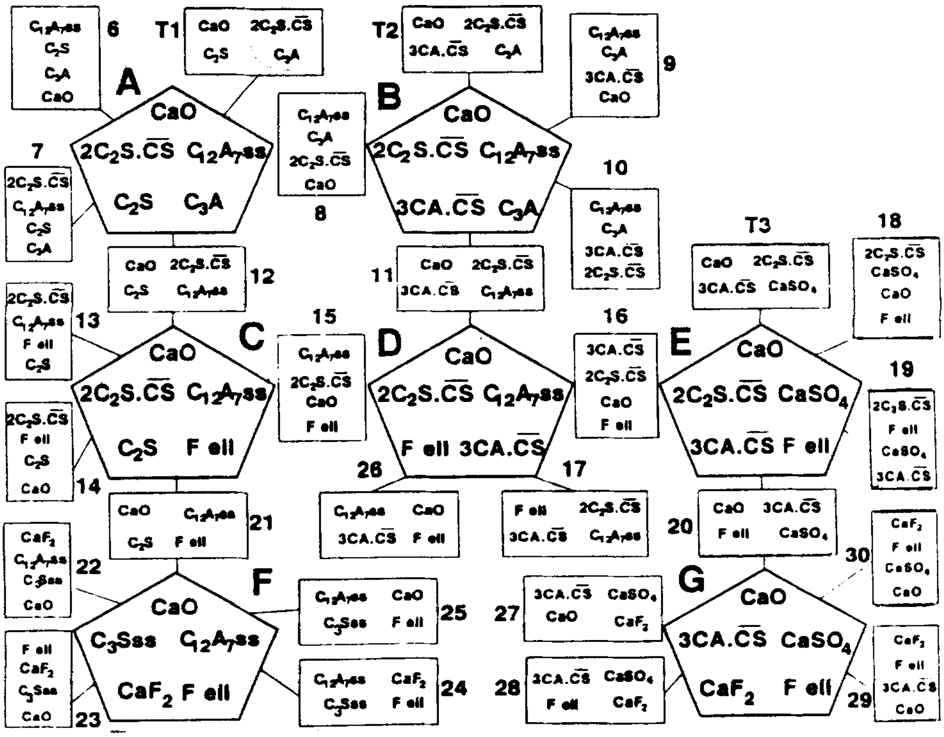

Figure 1

Quinary compatibilities at 1050°C

In the tetrahedron 21 are located the compositions of quinary compatibility volume C which contain the CaF_2 required to react with the whole $2C_2S \cdot C\bar{S}$ according to reaction (2). Further addition of CaF_2 to compositions located in this compatibility tetrahedron results in the formation of C_3S_{ss} and the composition will place itself in quinary compatibility volume F.

The addition of CaF_2 to the quaternary compatibility tetrahedron T2 $CaO-C_3A-2C_2S \cdot C\bar{S}-3CA \cdot C\bar{S}$ results in the formation of $C_{11}A_7CaF_2$ according to reaction (1), and the composition will be located in quinary compatibility volume B. When the amount of CaF_2 for transformation of C_3A is total, the composition is located within compatibility tetrahedron 11.

For the compositions proceeding from compatibility tetrahedron 11, the addition of CaF_2 gives rise to the formation of fluorellestadite and $C_{11}A_7CaF_2$, according to the following reaction (reaction [3]):

$$36CaO+21(2C_2S \cdot C\bar{S})+21(3CA \cdot C\bar{S})+23CaF_2 \rightarrow 9(C_{11}A_7CaF_2)+14Fell \quad [3]$$

These compositions are located in the compatibility volume D.

New increments in the amount of CaF_2 will result in the compositions displacing themselves towards compatibility tetrahedra 15 or 26, depending on the proportion of $3CA\cdot C\bar{S}$ in the initial composition. The study of the addition of CaF_2 to compositions located in tetrahedron 26 has no relevance, since its composition includes no silicate phase.

If the composition is located in tetrahedron 15, a higher proportion of CaF_2 will result in the displacement of the compositions towards quinary compatibility volume C, tetrahedron 14, and quinary compatibility volume F, as mentioned before.

On the other hand, adding CaF_2 to the compositions located within the compatibility tetrahedron T3 $CaO-CaSO_4-2C_2S\cdot C\bar{S}$ $-3CA\cdot C\bar{S}$; fluorellestadite is formed through reaction

$$3(2C_2S\cdot C\bar{S}) + 3CaSO_4 + 2CaF_2 \longrightarrow 2Fell \qquad [4]$$

originating the quinary compatibility volume E.

When CaF_2 is added in the amount required to consume the whole initial $2C_2S\cdot C\bar{S}$ according to reaction (4), the composition will situate itself in tetrahedron 20. Subsequent additions of CaF_2 will lead into the location of the compositions in quinary compatibility volume G.

In the event that the proportion of $CaSO_4$ in the quinary volume E is not sufficient for the formation of fluorellestadite according to reaction (4), it is possible that the composition shifts according to compatibility tetrahedron 16 and quinary D, as the CaF_2 proportion increases.

Compatibilities in the quinary system $CaO-SiO_2-Al_2O_3-CaF_2-CaSO_4$ at 1100°C

The composition and compounds identified by XRD and IR spectroscopy after heating of the samples at 1100°C are given in table 2.

Starting from compositions located in the quaternary compatibility tetrahedra of the $CaO-Al_2O_3-SiO_2-CaSO_4$, i.e. T1, T2 and T3 (Table 2), the addition of CaF_2 results in the decomposition of $2C_2S\cdot C\bar{S}$ into C_2S and $CaSO_4$ at a temperature of 1100°C.

The sample T1, of composition $2C_2S\cdot C\bar{S}$, C_2S, CaO and C_3A, after adding 0.45% of CaF_2, shows, after being heated to 1100°C over 2 hours $C_{12}A_{7ss}$ and traces of $3CA\cdot C\bar{S}$, together with $2C_2S\cdot C\bar{S}$, C_2S, CaO and C_3A. For heating times of 4 hours, CaO, C_2S, C_3A, $C_{12}A_7$ and $3CA\cdot C\bar{S}$ are identified, but not $2C_2S\cdot C\bar{S}$.

Likewise, the addition of 1.6% of CaF_2 to the T1 composition gives rise to the formation of $C_{12}A_{7ss}$, Fell and $3CA\cdot C\bar{S}$ and the disappearance of C_3A.

The addition of CaF_2 in ratios of 2.5 y 3.9% gives results similar to those obtained with the same proportions at a temperature of 1050°C. When the addition of CaF_2 is of 4% wt, tricalcium silicate is formed, together with $C_{12}A_{7ss}$ and Fell.

TABLE 2

Compounds identified through XRD of the mixtures heated at 1100°C.

SAMPLES	%wt CaF_2	t (h)	COMPOUNDS IDENTIFIED THROUGH XRD
T11	0.45	2(*)	CaO, C_2S, C_3A, $2C_2S.C\bar{S}$, $C_{12}A_7ss$, ($3CA \cdot C\bar{S}$)
		4	CaO, C_2S, C_3A, $C_{12}A_7ss$, $3CA \cdot C\bar{S}$
T12	1.6	2.5 (*)	CaO, C_2S, $C_{12}A_7ss$, F ell, $2C_2S \cdot C\bar{S}$ ($3CA \cdot C\bar{S}$)
		4.5	CaO, C_2S, F ell, $C_{12}A_7ss$, $3CA \cdot C\bar{S}$
T13	2.5	2	CaO, C_2S, F ell, $C_{12}A_7ss$
T14	3.9	2(*)	CaO, C_2S, F ell, $C_{12}A_7ss$, C_3S
		4	CaO, F ell, $C_{12}A_7ss$, C_3S
T21	0.92	2(*)	CaO, $3CA \cdot C\bar{S}$, $C_{12}A_7ss$, C_3A, C_2S, ($2C_2S \cdot C\bar{S}$)
		4	CaO, $3CA \cdot C\bar{S}$, $C_{12}A_7ss$, C_3A, C_2S
T22	2.3	2(*)	CaO, $C_{12}A_7ss$, $3CA \cdot C\bar{S}$, F ell, C_2S, ($2C_2S \cdot C\bar{S}$)
		4	CaO, $C_{12}A_7ss$, $3CA \cdot C\bar{S}$, F ell, C_2S
T23	4.3	2(*)	CaO, F ell, $C_{12}A_7ss$, C_2S, $3CA \cdot C\bar{S}$
T24	5.0	2	CaO, F ell, C_3S, $C_{12}A_7ss$
T31	0.4	2(*)	CaO, $CaSO_4$, $3CA \cdot C\bar{S}$, $2C_2S \cdot C\bar{S}$, F ell, (C_2S)
		4	CaO, $CaSO_4$, $3CA \cdot C\bar{S}$, C_2S, F ell, ($2C_2S.C\bar{S}$)
T32	2.2	2	CaO, $3CA \cdot C\bar{S}$, C_2S, F ell, $CaSO_4$, ($2C_2S \cdot C\bar{S}$)
T33	3.5	2	CaO, $3CA \cdot C\bar{S}$, $CaSO_4$, F ell, CaF_2

(*) No equilibrium
( ) Traces

The addition of CaF_2 to the compositions located in the T2 and T3 tetrahedra results in the decomposition of $2C_2S \cdot C\bar{S}$, in this case C_2S occuring as a primary phase.

Dicalcium silicate and $C_{12}A_{7ss}$ are identified for a CaF_2 ratio of 0.92% wt in the composition of the T2 tetrahedron, and C_2S, $C_{12}A_{7ss}$ and Fell for CaF_2 ratios of 2.3 and 4.3% . For a 5% ratio of CaF_2, C_3S is obtained as well.

In T3 tetrahedron compositions, the addition of CaF_2 results in the formation of fluorellestadite and C_2S.

The diagram of compatibilities in the solid state at this temperature is shown in figure 2.

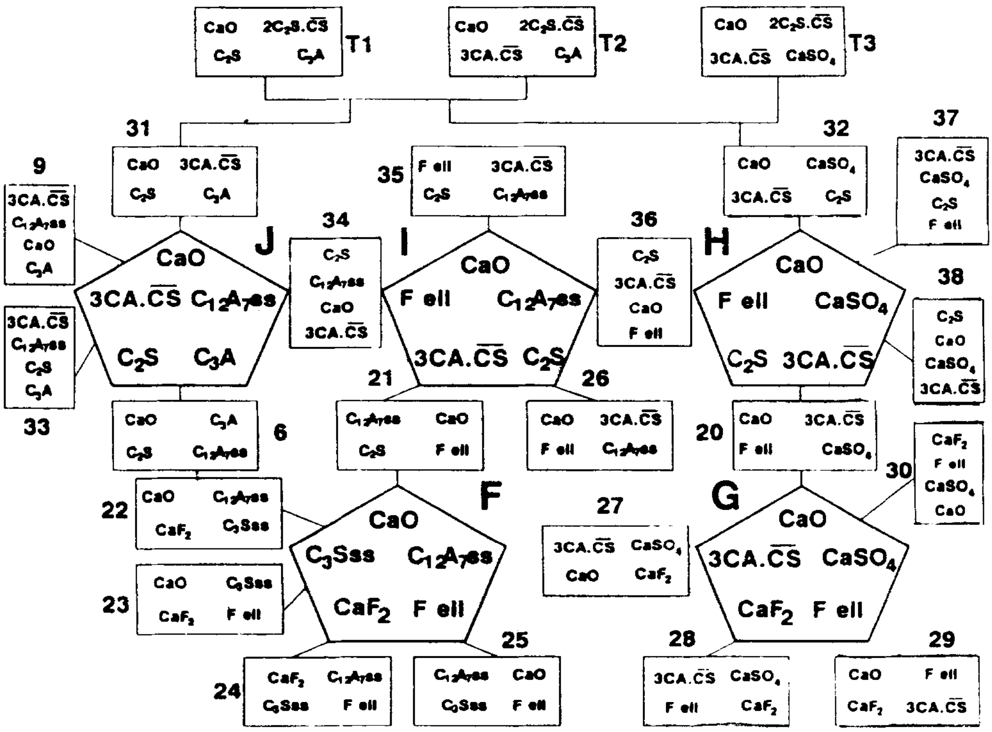

Figure 2

Quinary compatibilities at 1100°C

The quinary compatibility volumes identified at 1100°C are:

H.- CaO - $3CA\cdot C\bar{S}$ - C_2S - $CaSO_4$ - Fell
I.- CaO - $3CA\cdot C\bar{S}$ - C_2S - Fell - $C_{11}A_7CaF_2$
J.- CaO - $3CA\cdot C\bar{S}$ - $C_{11}A_7CaF_2$ - C_3A - C_2S
F.- CaO - C_2S - Fell - $C_{11}A_7CaF_2$ - C_3S
G.- CaO - $CaSO_4$ - $3CA\cdot C\bar{S}$ - Fell - CaF_2

In quaternary compatibility tetrahedra T1 and T2, in those compositions in which the ratio Al_2O_3 /$CaSO_4$ > 3, at 1100°C and in presence of fluorides, a shift towards tetrahedron 31 is produced by decomposition of $2C_2S\cdot CS$:

$$2C_2S\cdot C\bar{S} \longrightarrow 2C_2S + CaSO_4 \qquad [5]$$

as well as the reaction of C_3A with $CaSO_4$:

$$3C_3A + CaSO_4 \longrightarrow 6CaO + 3CA\cdot C\bar{S} \qquad [6]$$

The additon of CaF_2 in small proportions locates these compositions in the compatibility volume J.

When the reaction of C_3A with CaF_2 is complete, the evolution of the compositions toward another quinary compatibility volume is possible. This only happens in tetrahedron 34. The addition of CaF_2 to compositions located in this tetrahedron results in the appearance of Fell. The reaction is:

$$7(3CA\cdot C\bar{S})+7C_2S+(16/3)CaF_2+4CaO \longrightarrow (7/3)Fell+3C_{11}A_7CaF_2 \quad [7]$$

these compositions are located in quinary compatibility volume I.

When the amount of CaF_2 is sufficient for to complete reaction (6), the compositions are located in tetrahedron 21. Additions of CaF_2 to compositions in tetrahedron 21 result in the compositions shifting towards quinary compatibility volume F, with formation of the C_3S_{ss} phases.

Compositions in the quaternary tetrahedra T1 and T2, with an $Al_2O_3/CaSO_4$ ratio < 3 and those located in the compatibility tetrahedron T3, upon being heated at 1100°C and in the presence of fluorides, are transformed into tetrahedron 32 by decomposition of $2C_2S\cdot CS$ through reaction [5] and the reaction of CaF_2, C_2S and $CaSO_4$ takes place, with the formation of fluorellestadite:

$$CaF_2 + 3C_2S + 3CaSO_4 \longrightarrow 3C_2S\cdot 3CaSO_4\cdot CaF_2 \quad [8]$$

the composition shifting to quinary compatibility volume H.

In the case of compositions located in this quinary volume H, the addition of CaF_2 will result in the displacement of the composition towards tetrahedron 36, if the molar concentration of the free $CaSO_4$ is less than that of C_2S, and towards tetrahedron 20 in the opposite case. The shifting of the compositions upon increasing of the CaF_2 proportion in tetrahedron 36 will be towards quinary volume I, tetrahedron 21, and quinary compatibility volume F.

The addition of CaF_2 to compositions situated in tetrahedron 20 induces the appearance of the quinary compatibility volume G that, as already mentioned, does not experience any changes when the temperature increases from 1050°C to 1100°C.

In no case has alite been identified at these temperatures, no compositions other than those in quinary volume F.

Table 3 shows the composition of Fell mixtures heated during different periods of time at 1100°C with aluminates, and the compounds identified by XRD from these samples. The Fell mixtures and the binary aluminates C_3A, $C_{12}A_7$ and CA (QF3 to QF5) are found in accordance with the data obtained from compatibilities in the solid state in the quinary system. Fell is not compatible in any of the quinary volumes with any of these aluminates. In binary mixtures with these aluminates, the formation of $3CA\cdot C\bar{S}$ is produced, Fell descomposing. Starting the mixtures of Fell with $3CA\cdot C\bar{S}$ and $C_{11}A_7CaF_2$, the compatibility amoung these compounds in the solid state is verified.

TABLE 3

Fluorellestadite and aluminates compatibilities at 1100°C(mixes at 50% wt).

SAMPLE	COMPOSITION	t (h)	T (ºC)	XRD IDENTIFICATION
QF1	$3CA \cdot C\bar{S}$, Fell, (CA)	5	1100	$3CA \cdot C\bar{S}$, F ell, ($C_{12}A_7ss$)
QF2	$C_{11}A_7CaF_2$, F ell	5	1100	$C_{12}A_7ss$, F ell
QF3	C_3A, F ell	17	1100	C_3A, $3CA \cdot C\bar{S}$, $C_{12}A_7ss$, C_2S, CaO
QF4	$C_{12}A_7$, F ell	10	1100	$3CA \cdot C\bar{S}$, CaO, F ell, $C_{12}A_7ss$, C_2S
QF5	CA, F ell	5	1100	$3CA \cdot C\bar{S}$, CaO, C_2S

( ) traces

Discussion

Starting from the quaternary systems, the effect of $CaSO_4$ and CaF_2 on the different phases composing clinker can be known. However, now the phase relations in the $CaO-Al_2O_3-SiO_2$ system (traditionally, the diagram for cement), do change, as well as which compositions are the most adequate for a correct dosing of the raw materials, which can only be known from the phase relations in the quinary system $CaO-SiO_2-Al_2O_3-CaF_2-CaSO_4$.

In this paper, the solid state compatibilities at 1050°C and 1100°C in the quinary system $CaO-Al_2O_3-SiO_2-CaF_2-CaSO_4$ have been determined in the zone rich in CaO, where the formation of the tricalcium silicate is possible.

The solid state compatibilities show that fluorellestadite and $C_{11}A_7CaF_2$ are the phases which appear upon adding CaF_2 to quaternary compositions $CaO-Al_2O_3-SiO_2-CaSO_4$. The quinary compatibility volumes identified are:

A.-	CaO - C_3A - $C_{11}A_7CaF_2$ - $2C_2S \cdot C\bar{S}$ - C_2S	
B.-	CaO - C_3A - $C_{11}A_7CaF_2$ - $2C_2S \cdot C\bar{S}$ - $3CA \cdot C\bar{S}$	
C.-	CaO - $C_{11}A_7CaF_2$ - $2C_2S \cdot C\bar{S}$ - C_2S - F el	1050°C
D.-	CaO - $C_{11}A_7CaF_2$ - $2C_2S \cdot C\bar{S}$ - $3CA \cdot C\bar{S}$ - F ell	
E.-	CaO - $3CA \cdot C\bar{S}$ - $2C_2S \cdot C\bar{S}$ - $CaSO_4$ - F ell	
H.-	CaO - $3CA \cdot C\bar{S}$ - C_2S - $CaSO_4$ - F ell	
I.-	CaO - $3CA \cdot C\bar{S}$ - C_2S - F ell - $C_{11}A_7CaF_2$	1100°C
J.-	CaO - $3CA \cdot C\bar{S}$ - $C_{11}A_7CaF_2$ - C_3A - C_2S	
F.-	CaO - $C_{11}A_7CaF_2$ - F ell - C_3S_{ss} - C_2S	1050°C and
G.-	CaO - $CaSO_4$ - $3CA \cdot C\bar{S}$ - CaF_2 - F ell	1100°C

The initial formation of $C_{11}A_7CaF_2$ is produced by the reaction between C_3A and CaF_2. After the whole C_3A has reacted or into compositions in which it did not previously exist, the addition of CaF_2 results in the appearance of fluorellestadite.

The sequence of reactions shown implies that the formation of $C_{12}A_7ss$ is prior to the formation of Fell, in those compositions in which C_3A is present.

The formation of $2C_2S \cdot C\bar{S}$ in this system has been found; however, its decomposition temperature is 1100°C, a temperature quite below that indicated in pure state or in the binary systems with C_3A.

The solid state decomposition of $2C_2S \cdot C\bar{S}$ into $CaSO_4$ and C_2S in compositions in which C_3A is present results in the formation of $3CA \cdot C\bar{S}$, a more stable phase with a decomposition temperature above 1300°C (16 and 17).

At 1050°C, dicalcium silicate is compatible with C_3A, $C_{11}A_7CaF_2$, Fell and CaO but not with $3CA \cdot C\bar{S}$. At 1100°C, dicalcium silicate becomes compatible with $3CA \cdot C\bar{S}$ and $CaSO_4$ besides $C_{11}A_7CaF_2$ and Fell. The decomposition of $2C_2S \cdot C\bar{S}$ does modify the quinary compatibility volumes found at temperatures below 1100°C.

At a temperature of 1050°C, the alite phase has been identified as compatible in the solid state in the diagram zone poor in $CaSO_4$ and rich in CaF_2.

The formation of alite at temperatures as low as 1050°C is interpreted in the literature as due to the formation of double solid solutions of Al and F (12). In these solid solutions Al replaces Si and F replaces O ions to maintain the electron neutrality ($Al^{3+} \rightarrow Si^{4+}$; $F^- \rightarrow O^{2-}$). The general formula for these solid solutions is $Ca_3(Si_{1-x}Al_xO_{5-x}F_x)$, where x can vary from 0 to 0.169. This phase tends to be found in tempered samples, in the rhombohedric polymorphic form of C_3S.

At that temperature, the alite phase has been identified, together with $C_{11}A_7CaF_2$, C_2S, CaO and Fell in some of the samples analyzed. The compatibility $C_{12}A_7ss-C_2S-CaO$ and C_3S_{ss} is not thermodynamically possible, since, in these compositions, there are sufficient Al and F in order to complete the formation reaction of C_3S_{ss} form C_2S and CaO. This formation reaction takes place in the solid state and is kinetically limited, so that it is possible to identify these compounds in samples in which an equilibrium has not been reached. An increase in the temperature does not change the diagram zone where tricalcium silicate appears.

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