

# Influence of water chemical potential on the phase assemblages of the CaO-Al<sub>2</sub>O<sub>3</sub>-CaSO<sub>4</sub>-H<sub>2</sub>O system at 25°C

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## Abstract

In the previous calculations of phase diagrams related to cement chemistry, water was always supposed to be in excess. This can be the case during the hydration beginning but at later ages, it is known that the porosity of the cement paste is partly filled by a vapor phase depending on the outside relative humidity and the size of pores. As a consequence a new method, based on chemical potentials, was developed in order to calculate phase diagrams at different relative humidities. The methodology was applied to the CaO-Al<sub>2</sub>O<sub>3</sub>-CaSO<sub>4</sub>-H<sub>2</sub>O system at 25°C. The reported calculation indicate that calcium mono-sulfoaluminate hydrate could become a stable phase at the expense of ettringite when in contact with water vapor that relative humidity ranges approximately from 32 to 66%.

## 1- Introduction

The knowledge of the mineral phases that are stable in given conditions is important in order to assess the durability of mineral assemblages such as stones, concrete ... During the last decade, some progress have been made in order to calculate phase diagrams related to chemical systems representative to cement chemistry. Nevertheless the calculation still suffers from some approximation such as handling solid-solution, and sometimes experimental data do not agree with calculation. This may be due to unwanted experimental problems such as carbonation but also to the fact that the conditions are different but thought to be similar. A common example is the water saturation state during the experiment. Indeed the equilibrium conditions can be quite different with liquid water or with vapor water especially for hydrates containing a high number of water molecules such as ettringite.

Several methods based on thermodynamics and the attainment of an equilibrium state have been developed. The equilibrium state can be calculated by the direct calculation of the phases at equilibrium in chemical systems having several components as it was done before using the code PHREEQE [1] and its derivatives. However we need to go back to the water chemical potential and not to its activity, in order to assess the

effect of the different state of water on the hydrate stability and thus an alternative approach was used with a code named Zen+k [2] specially designed to the construction of phase diagrams.

## **2 - Zen+k software and input data for the CaO-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O system at 25°C under 1 bar of pressure**

Guy and Pla have named such a code "Zen+k" in recognition of E. A. Zen who discussed methods of prediction of structures of diagrams for systems with n components and n+2 or n+3 phases [2]. With the Zen+k software, the method is extended with n components and n+k phases, k being unspecified. The principle of the software is based on an original thermodynamic concept, affigraphy [3]. The required input data to use Zen+k are the following:

- temperature and reference pressure,
- the number of independent components and the number of phases,
- the matrix of composition,
- the status of each component (immobile, mobile or perfectly mobile).

For each phase, the matrix of composition specifies the composition according to the components and the value of the molar Gibbs energy corresponding to the temperature and the reference pressure. If variations of temperature and pressure are to be considered, the matrix of composition must be completed with the molar entropy of reference and the molar volume of each phase. The status of components follows the terminology used in Petrology, namely that a component can be "immobile", "mobile" or "perfectly mobile" [4]. The immobile components are those for which the conservation of matter applies (behavior in a closed system). For the mobile components, the conservation of matter does not apply and the chemical potential controls the spatial variation of the phases of the system (behavior in an open system). The perfectly mobile components are mobile components that are the most easily exchanged with the outside medium and, as a consequence, their chemical potential may be taken at the same value in the whole system.

For the exploration of the CaO-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O system at 25°C and 1 bar, the following phases were considered : Portlandite (Ca(OH)<sub>2</sub>), hydrogarnet (3CaO.Al<sub>2</sub>O<sub>3</sub>.6H<sub>2</sub>O), ettringite (3CaO.Al<sub>2</sub>O<sub>3</sub>.3CaSO<sub>4</sub>.32H<sub>2</sub>O), calcium monosulfoaluminate hydrate (3CaO.Al<sub>2</sub>O<sub>3</sub>.CaSO<sub>4</sub>.12H<sub>2</sub>O), C<sub>4</sub>AH<sub>13</sub> (4CaO.Al<sub>2</sub>O<sub>3</sub>.13H<sub>2</sub>O), gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O), anhydrite (CaSO<sub>4</sub>) and gibbsite (Al(OH)<sub>3</sub>).

In the composition matrix (Table 1), the Gibbs energy of reference of each phase is the Gibbs energy of formation calculated from simple chemical

elements. As the temperature and the fixed pressure of reference are those for which the system will be explored, the entropy and the molar volume of reference of each phase do not need to be considered. With T and P fixed, the Gibbs phase rule is written (Eq. 1):

$$v = c - \varphi \quad (\text{Eq. 1})$$

with  $v$ , the variance of the system,  
 $c$ , the number of independent components,  
 $\varphi$ , the number of phases.

When not known, the Gibbs energy of formation of solid phases have been calculated from solubility constants by using the values of the chemical potentials of reference of the ions given in the geochemical compilations of Shock et al. [5].

	P	E	M	H	L	N	A	G
CaO	1	6	4	3	0	4	1	1
SO <sub>3</sub>	0	3	1	0	0	0	1	1
Al <sub>2</sub> O <sub>3</sub>	0	1	1	1	0.5	1	0	0
H <sub>2</sub> O	1	32	12	6	1.5	13	0	2
g <sup>0</sup> (kJ/mol)	-896.4	-15213.6	-7784.2	-5022.5	-1153.9	-7330.0	-1321.6	-1797.8

*Symbols:* P: Portlandite ; E: Ettringite ; M: Calcium monosulfoaluminate hydrate ; H: Hydrogarnet ; L: Gibbsite ; N: C<sub>4</sub>AH<sub>13</sub> ; G: Gypsum ; A: Anhydrite ; g<sup>0</sup>: Gibbs energy of reference.

Table 1. Matrix of composition for the exploration of the system CaO-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O at 25°C under 1 bar of pressure.

### 3 – Results

#### 3.1. CaO-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O system with liquid water

In order to build the phase diagram of the CaO-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O system, the status of components is chosen as the following ; H<sub>2</sub>O will be chosen as “perfectly mobile” and its chemical potential will first be fixed at the value of the standard potential of reference (saturated medium). The phase diagram has been plotted for two different conditions ;

- CaO and SO<sub>3</sub> are declared as mobile components, and Al<sub>2</sub>O<sub>3</sub> as an immobile component (Figure 1),
- CaO and Al<sub>2</sub>O<sub>3</sub> are declared as mobile components, and SO<sub>3</sub> as an immobile component (Figure 2).

The axes of the phase diagram built with Zen+k correspond to chemical potentials. Gartner and Jennings [6] used this kind of diagram for the system CaO-SiO<sub>2</sub>-H<sub>2</sub>O. The interest of working with chemical potentials is

to obtain linear relations and to display directly the topology of the phase diagrams without the need to compute the actual concentration of aqueous species. Chemical potentials are linear combinations of the activities of the aqueous species.

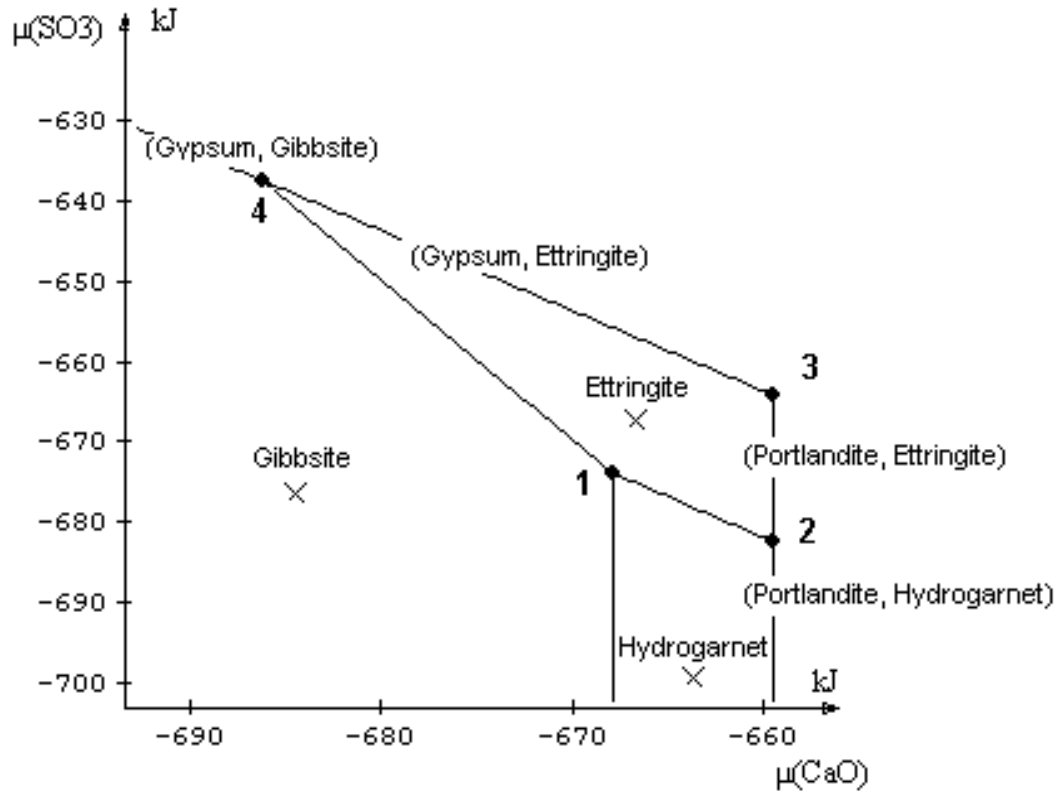


Figure 1 : Diagram ( $\mu(\text{CaO})$ ,  $\mu(\text{SO}_3)$ ) at 25°C and 1 bar, with  $\mu(\text{H}_2\text{O}) = \mu^\circ(\text{H}_2\text{O})$

The composition of the system along an univariant line is written between brackets in order to distinguish it from the domains of stability of the phases (Figures 1 and 2). The system is composed of three phases at each invariant point, in accordance with the phase rule. Indeed at an invariant point, the variance is equal to zero and as the number of independent components is 3, the number of phases at an invariant point is 3 according to Eq. 1. The invariant points of the diagrams of figures 1 and 2 are as follows:

- 1 : Gibbsite + Ettringite + Gypsum
- 2 : Portlandite + Ettringite + Gypsum
- 3 : Portlandite + Ettringite + Hydrogarnet
- 4 : Gibbsite + Ettringite + Hydrogarnet

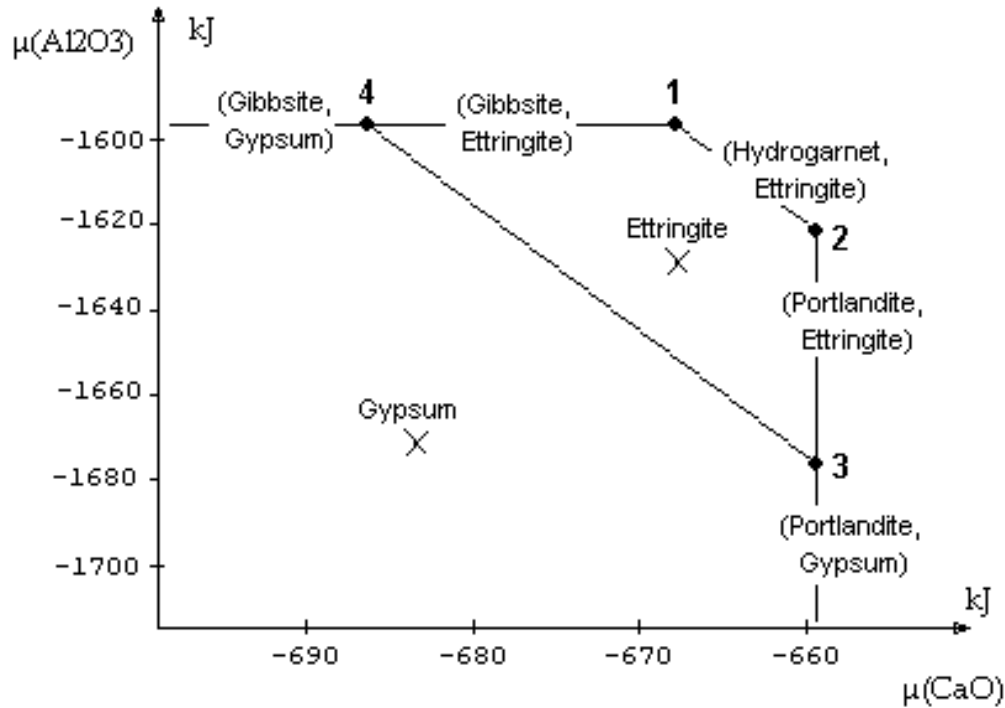


Figure 2 : Diagram ( $\mu(\text{CaO})$ ,  $\mu(\text{Al}_2\text{O}_3)$ ) at 25°C and 1 bar with  $\mu(\text{H}_2\text{O}) = \mu^\circ(\text{H}_2\text{O})$

These same invariant points were found experimentally by Jones [7], D'Ans et al. [8] and were calculated to be stable by Damidot and Glasser [9]. It is also possible to compare the numerical values of the chemical potential of these invariant points with previous investigations of the system  $\text{CaO-Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ . If the aqueous phase compositions at the invariant points given by Damidot [10] are used, it appears that the chemical potentials are very close to the values computed with Zen+k for the system  $\text{CaO-Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$  system at 25°C (Table 2).

N° inv. point	Value obtained in this work with Zen + k			Value calculated using data of Damidot [10]		
	$\mu(\text{CaO})$	$\mu(\text{SO}_3)$	$\mu(\text{Al}_2\text{O}_3)$	$\mu(\text{CaO})^*$	$\mu(\text{SO}_3)^{**}$	$\mu(\text{Al}_2\text{O}_3)^{***}$
1	-667.8	-674.1	-1596.3	-667.7	-674.2	-1596.9
2	-659.4	-682.5	-1621.5	-659.2	-682.5	-1623.0
3	-659.4	-664.2	-1676.4	-659.0	-664.0	-1678.1
4	-686.1	-637.5	-1596.3	-686.0	-637.2	-1597.0

\*  $\mu(\text{CaO}) = \mu^\circ(\text{CaO}) + 2\mu^\circ(\text{OH}^-) - \mu^\circ(\text{H}_2\text{O}) + RT \cdot [\ln(a(\text{Ca}^{2+}) \cdot a(\text{OH}^-)^2)]$

\*\*  $\mu(\text{SO}_3) = \mu^\circ(\text{SO}_4^{2-}) - 2\mu^\circ(\text{OH}^-) + \mu^\circ(\text{H}_2\text{O}) + RT \cdot [\ln(a(\text{SO}_4^{2-}) / a(\text{OH}^-)^2)]$

\*\*\*  $\mu(\text{Al}_2\text{O}_3) = 2\mu^\circ(\text{Al}(\text{OH})_4^-) - 2\mu^\circ(\text{OH}^-) - 3\mu^\circ(\text{H}_2\text{O}) + 2RT \cdot [\ln(a(\text{Al}(\text{OH})_4^-) / a(\text{OH}^-))]$

Table 2 : Chemical potentials at the invariant points in kJ/mol

### 3.2. CaO-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O system with vapor water

In this case the phase diagram of the CaO-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O system is plotted as a function of  $\mu(\text{H}_2\text{O})$  and  $\mu(\text{CaO})$ . This is possible by taking in account the activity of water in Equation (2). The calculated diagram, Figure 3, is constructed by declaring SO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> as immobile components with a molar ratio Al<sub>2</sub>O<sub>3</sub>/SO<sub>3</sub> greater than 1, which is a common situation in ordinary Portland cements. Some stable invariant points of the phase diagram of CaO-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O system with vapor water are reported on figure 3 :

- For  $\mu(\text{H}_2\text{O}) = -238.25 \text{ kJ}$  :
  - 1' : Gibbsite + ettringite + hydrogarnet + calcium monosulfoaluminate hydrate,
  - 2' : Portlandite + ettringite + hydrogarnet + calcium monosulfoaluminate hydrate,
- For  $\mu(\text{H}_2\text{O}) = -239.31 \text{ kJ}$  :
  - 3' : Gibbsite + ettringite + anhydrite + calcium monosulfoaluminate hydrate,
- For  $\mu(\text{H}_2\text{O}) = -240.01 \text{ kJ}$  :
  - 4' : Gibbsite + anhydrite + hydrogarnet + calcium monosulfoaluminate hydrate,
  - 5' : Portlandite + anhydrite + hydrogarnet + calcium monosulfoaluminate hydrate

It is interesting to note the presence of the calcium monosulfoaluminate at all these invariant points. The diagram contains other invariant points but they are not reported here because they do not concern hydrated Portland cement. We note that the number of phases at each invariant point is 4, compared to the 3 phases at the invariant points in figures 1 and 2. This difference comes from the fact that the chemical potential of the component H<sub>2</sub>O is allowed to vary, and as a consequence the variance of the system is increased by 1.

A chemical potential of water lower than the reference potential corresponds to an activity of liquid water lower than 1, thus to a relative humidity less than 100 %. One can calculate to which value of water activity and to which relative humidity a water chemical potential corresponds. At equilibrium we can write that ;

$$\mu(\text{H}_2\text{O}) = \mu(\text{H}_2\text{O})_{\text{liquid}} = \mu(\text{H}_2\text{O})_{\text{vapor}}$$

$$\mu(\text{H}_2\text{O})_{\text{liquid}} = \mu^\circ(\text{H}_2\text{O})_{\text{liquid}} + RT \ln \left( \frac{a(\text{H}_2\text{O})}{a^\circ(\text{H}_2\text{O})} \right)$$

using as reference conditions:  $T = 298.15 \text{ K}$ ,  $P = 1 \text{ bar}$ ,  $a^\circ(\text{H}_2\text{O}) = 1$  and  $\mu^\circ(\text{H}_2\text{O})_{\text{liquid}} = -237.14 \text{ kJ/mol}$ .

Moreover the following relation can be written:

$$\mu(\text{H}_2\text{O})_{\text{vapor}} = \mu^\circ(\text{H}_2\text{O})_{\text{vapor}} + RT \ln \left( \frac{f(\text{H}_2\text{O})}{f^\circ(\text{H}_2\text{O})} \right)$$

where  $f(\text{H}_2\text{O})$ , the water is fugacity of vapor.

The conditions of standard are  $T = 298.15 \text{ K}$ ,  $P = 1 \text{ bar}$ ,  $f^\circ(\text{H}_2\text{O}) = 1$  and  $\mu^\circ(\text{H}_2\text{O})_{\text{vapor}} = -228.6 \text{ kJ/mol}$  [21]. If we consider that in the system, the fugacity of water is equal to the partial pressure of water:

$$\mu(\text{H}_2\text{O})_{\text{vapor}} \approx \mu^\circ(\text{H}_2\text{O})_{\text{vapor}} + RT \cdot \ln \left( \frac{P(\text{H}_2\text{O})}{P^\circ(\text{H}_2\text{O})} \right), \text{ with } P^\circ(\text{H}_2\text{O}) = 1.$$

The chemical potential of the vapor is ;

$$\mu(\text{H}_2\text{O})_{\text{vapor}} = \mu^\circ(\text{H}_2\text{O})_{\text{vapor}} + RT \left[ \ln(h) + \ln \left( \frac{P_{\text{saturated vapor}}(\text{H}_2\text{O})}{P^\circ(\text{H}_2\text{O})} \right) \right] \quad (\text{Eq. 2})$$

with  $P^\circ(\text{H}_2\text{O}) = 1$  and  $h$ , the relative humidity, defined as:

$$h = \frac{P(\text{H}_2\text{O})}{P_{\text{saturated vapor}}(\text{H}_2\text{O})}, \text{ and } P_{\text{saturated vapor}}(\text{H}_2\text{O}) = 0.031 \text{ at } 298.15\text{K}$$

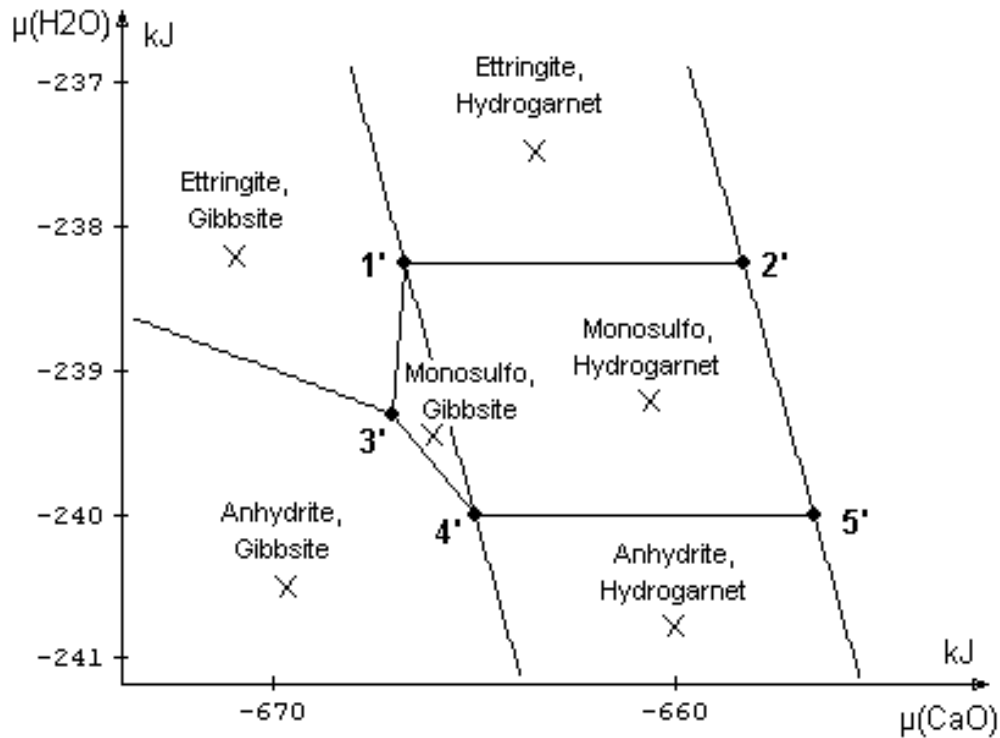


Figure 3 : Diagram ( $\mu(\text{CaO})$ ,  $\mu(\text{H}_2\text{O})$ ) at  $25^\circ\text{C}$  and  $1 \text{ bar}$

The chemical potentials are linear combinations of the type:

$$\mu(\text{CaO}) = A + RT \cdot [\ln(a(\text{Ca}^{2+}) \cdot a(\text{OH}^-)^2 / a(\text{H}_2\text{O}))]$$

$$\mu(\text{H}_2\text{O}) = \mu^\circ(\text{H}_2\text{O})_{\text{liquid}} + RT \ln(a(\text{H}_2\text{O})) = \mu^\circ(\text{H}_2\text{O})_{\text{vapor}} + RT \ln(P(\text{H}_2\text{O}))$$

This relation links the chemical potential of water to the relative humidity occurring in the porosity of a cement paste. The relative humidity

corresponding to the invariant points 1', 2', 3', 4' and 5' quoted previously is:

- $\mu(\text{H}_2\text{O}) = -238.25 \text{ kJ} \rightarrow h = 66\%$  at points 1' and 2',
- $\mu(\text{H}_2\text{O}) = -239.31 \text{ kJ} \rightarrow h = 43\%$  at points 3',
- $\mu(\text{H}_2\text{O}) = -240.01 \text{ kJ} \rightarrow h = 32\%$  at points 4' and 5'.

#### 4 – Discussion and Conclusion

Zen+k software can be used to build phase diagrams relevant to chemical systems found in cementitious systems. The calculated phase diagram corresponding to the  $\text{CaO-Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$  system at  $25^\circ\text{C}$ , 1 bar and with  $a(\text{H}_2\text{O}) = 1$ , is coherent with previous investigations. In these conditions, ettringite is a stable phase whereas calcium monosulfoaluminate is metastable.

Moreover Zen+k software allows us to calculate for the first time the  $\text{CaO-Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$  system in the presence of water vapor instead of liquid water. This last feature is very important as it is known that in normal conditions, part of the pores are filled with vapor water instead of liquid water. These first calculations indicate that calcium monosulfoaluminate could become a stable phase at relative humidity below 66%. This correspond to a slightly lower relative humidity compared to room conditions and thus it could be attained in the larger pores of old samples.

As usual with calculation, the exact values of the aqueous phase composition at equilibrium or the value of the relative humidity are not the most important point. The evolution of the system is more useful and it seems that the water chemical potential is an important parameter that has not been taken into account yet. Of course the quality of the thermodynamic database is still of primary importance. Moreover some possible improvement such as the loss of water molecules from the structure of hydrates, in particular for calcium monosulfoaluminate hydrate and ettringite [11-12], as the relative humidity decreases could be considered to refine the calculation.

Also our approach is a macroscopic thermodynamic one, as the phases are defined through their volumic properties. Thus interfacial energies are not taken into account. However in an undersaturated porous cement-based material, it is known that water molecules are adsorbed at material surfaces forming more or less continuous film depending on the relative humidity. As a consequence, another improvement would be to take into account the interfacial energies in the calculation of the chemical potential.



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