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Water chemical potential: A key parameter to determine the thermodynamic stability of some hydrated cement phases in concrete?

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Abstract

The $CaO–Al_2O_3–SO_3–H_2O$ system at 25 °C under 1 bar of pressure has been investigated with phase diagrams software (Zen+*k*) based on chemical potentials (or activities). The reported invariant points are similar to those obtained previously using equilibrium calculations. However Zen+*k* enables us to calculate systems at different relative humidities, and in conditions where water is not in excess, calcium monosulfoaluminate could be a stable phase and thus, as observed experimentally, remain for long times in an ordinary Portland cement paste.

Keywords: Ettringite; Calcium monosulfoaluminate; Phase diagram; Invariant points; Chemical potential; Activity; Relative humidity

1. Introduction

The knowledge of the mineralogical evolution of cement pastes subjected to chemical processes of deterioration such as sulfate or chloride attack, but also leaching by weakly mineralized waters at specific conditions of pressure and temperature, is very important in order to assess the durability of concrete. Several methods based on thermodynamics and the attainment of an equilibrium state have been developed. The equilibrium state can be calculated by different approaches; one of which is the direct calculation of the phases at equilibrium in chemical systems having several components. Among these codes of calculations, one distinguishes those based on the resolution of systems formulated from non linear sets of equations using equilibrium constants (WATEQ [1], MINEQL [2], PHREEQE [3], PHRQPITZ [4], CHESS [5], etc.), and codes based on an optimization algorithm allowing to minimize the total Gibbs energy of the system ([6]). Atkins et al. [7] developed CEMCHEM from the MINEQL code [2] to establish the list of stable phases resulting from the hydration of blended cements. Reardon [8] carried out a series of calculations with the PHRQPITZ code and highlighted the mineralogical modifications which occur in a cement paste in contact with sulfuric acid. Moreover, kinetic and transport modules can be added to these codes of equilibrium calculation in order to determine the mineralogical evolution as a function of time and space and mass of reactants [9].

An alternative approach, based on the construction of phase diagrams, can be envisaged. A phase diagram is the graphical representation of the regions of stability of one or several phases according to at least two thermodynamic variables. While phase diagrams are often used to represent chemical systems at elevated temperature, such as the cement clinker and steel production, their use can be extended to low-temperature chemical systems corresponding to cement paste in various environments. The interest in this approach is based on an easier understanding of complex chemical systems by appropriate use of graphical representations. Building phase diagrams using the method developed by Damidot [10], i.e. based on the PHRQPITZ code, is a lengthy process. The use of a code specially devoted to the construction of phase diagrams such as Zen+*k* [11] could be a good alternative. 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. With the

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Table 1
Input data for the exploration of the system $CaO–Al_2O_3–SO_3–H_2O$ at 25 °C under 1 bar of pressure

Temperature and pressure of reference:	25 °C (298.15 K) and 1 bar
4 constituents:	CaO, Al_2O_3, SO_3, H_2O
7 phases:	Portlandite: $Ca(OH)_2$ Hydrogarnet: $3CaO·Al_2O_3·6H_2O$ Ettringite: $3CaO·Al_2O_3·3CaSO_4·32H_2O$ Calcium monosulfoaluminate: $3CaO·Al_2O_3·CaSO_4·12H_2O$ C_4AH_{13}: $4CaO·Al_2O_3·13H_2O$ Gypsum: $CaSO_4·2H_2O$ Anhydrite: $CaSO_4$ Gibbsite: $Al(OH)_3$

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 [12]. This paper uses Zen+*k* in an investigation of the $CaO–Al_2O_3–SO_3–H_2O$ system at 25 °C under 1 bar of pressure. This system was chosen because it is relatively well understood following investigation by various authors [13–15] and also because some uncertainties still exist with respect to the stability of calcium monosulfoaluminate.

2. Method of calculation and input data for the $CaO–Al_2O_3–SO_3–H_2O$ system at 25 °C under 1 bar of pressure

The input data of 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” [16]. 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 $CaO–Al_2O_3–SO_3–H_2O$ system at 25 °C and 1 bar, the first input data (temperature and reference pressure, components and phases considered) are shown in Table 1. In the composition matrix (Table 2), 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:

$$v = c - \varphi \tag{1}$$

with

v the variance of the system,
c the number of independent components,
φ the number of phases.

A survey of the literature was done in order to define the thermodynamic database. Perkins and Palmer [17], Atkins and Glasser [18], Zhang et al. [19], Warren and Reardon [20], and Damidot and Glasser [15] propose values of solubility constant for ettringite obtained starting from solubility experiments done on ettringite produced by synthesis. Pure AFm type phases, like calcium monosulfoaluminate [18] and the C_4AH_{13}, are more difficult to synthesize and less thermodynamic data are available. However complete databases are available; either the value of Gibbs energy of formation of a phase is given directly [21] or it is deduced from a solubility constant [22]. In this paper, the database of Revertégat et al. [22] has been chosen.

The Gibbs energy of formation of solid phases have been calculated from solubility constants. For example, for ettringite, the constant of solubility resulting from [21] corresponds to the following reaction:

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \rightleftharpoons 6Ca^{2+} + 2Al^{3+} + 3SO_4^{2-} + 38H_2O$$

$K_{sp} = 5.98 \times 10^{-56}$ at $T = 298.15$ K and $P = 1$ bar [21].

Table 2
Matrix of composition for the exploration of the system $CaO–Al_2O_3–SO_3–H_2O$ at 25 °C under 1 bar of pressure

	P	E	M	H	L	N	A	G
CaO	1	6	4	3	0	4	1	1
SO_3	0	3	1	0	0	0	1	1
Al_2O_3	0	1	1	1	0.5	1	0	0
H_2O	1	32	12	6	1.5	13	0	2
g_0 (kJ/mol) [22,23]	−896.4	−15 213.6	−7784.2	−5022.5	−1153.9	−7330.0	−1321.6	−1797.8

P: portlandite; E: ettringite; M: calcium monosulfoaluminate; H: hydrogarnet; L: gibbsite; N: C_4AH_{13}; G: gypsum; A: anhydrite; g_0: gibbs energy of reference.

Table 3
Chemical potentials of reference of ions

Ionic species	Ca^{2+}	$Al(OH)_4^-$	Al^{3+}	SO_4^{2-}	OH^-	H_2O
$\mu°$ (kJ/mol)	−552.79 [23]	−1303 [22,23]	−483.7 [23]	−744.46 [23]	−157.3 [23]	−237.14 [23]

If the reference conditions are $T=298.15$ K and $P=1$ atm, the Gibbs energy of formation of ettringite can be calculated as follows:

$$\Delta G_f°(\text{Ettringite}) = 6\mu°(Ca^{2+}) + 2\mu°(Al^{3+}) + 3\mu°(SO_4^{2-}) + 38\mu°(H_2O) - RT\ln(K_{sp})$$

$$\Delta G_f°(\text{Ettringite}) = -15213.6\text{kJ/mol}.$$

The values of the chemical potentials of reference of the ions given in the geochemical compilations of Shock et al. [23] were used (Table 3).

3. Results

In order to build the phase diagram of the $CaO–Al_2O_3–SO_3–H_2O$ system, the status of components is chosen as the following; H_2O 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_3 are declared as mobile components, and Al_2O_3 as an immobile component (Fig. 1),
- CaO and Al_2O_3 are declared as mobile components, and SO_3 as an immobile component (Fig. 2).

The axes of the phase diagram built with Zen+*k* correspond to chemical potentials. Gartner and Jennings [24] used this kind of diagram for the system $CaO–SiO_2–H_2O$. 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 (see Section 4). 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 (Figs. 1 and 2).

The invariant points of the diagrams of Figs. 1 and 2 are as follows:

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

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

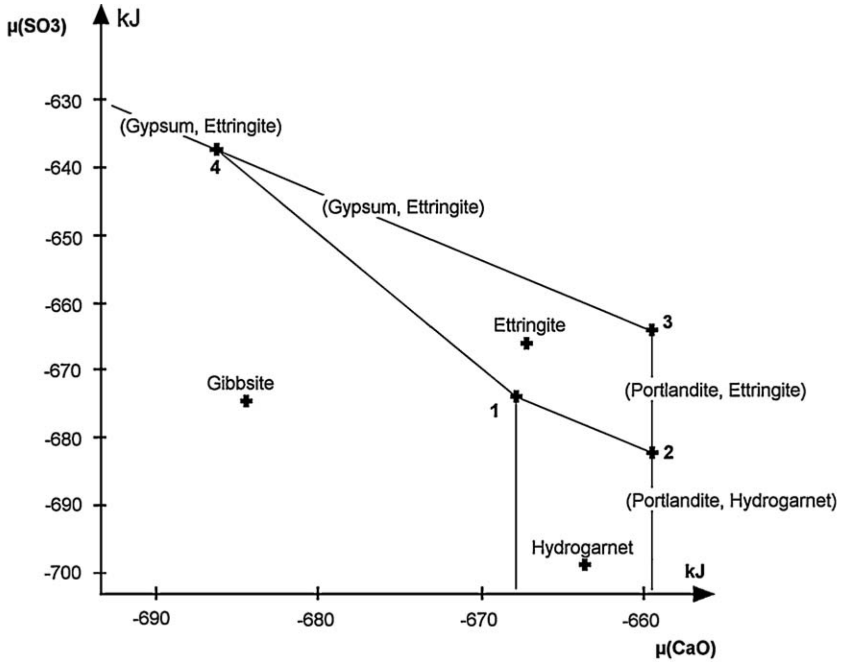

Fig. 1. Diagram ($\mu(CaO)$, $\mu(SO_3)$) at 25 °C and 1 bar, with $\mu(H_2O)=\mu°(H_2O)$. The chemical potentials are linear combinations of the type: $\mu(CaO)=A+RT[\ln(a(Ca^{2+})\cdot a(OH^-)^2)]$, $\mu(SO_3)=B+RT[\ln(a(SO_4^{2-})/a(OH^-)^2)]$. See text, Eqs. (2) and (3).

independent components is 3, the number of phases at an invariant point is 3 according to Eq. (1).

4. Comparison with previous results

These same invariant points were found experimentally by Jones [13], D'Ans and Eick [14] and were calculated to be stable by Damidot and Glasser [15]. It is also possible to compare the numerical values of the chemical potential of these invariant points with previous investigations of the system $CaO–Al_2O_3–SO_3–H_2O$. The chemical potentials of the components are actually related to the activities of the species in aqueous solution. For example, $\mu(CaO)$ can be expressed as a function of the activities of Ca^{2+} and OH^- by considering the following reaction:

$$CaO + H_2O \leftrightharpoons Ca^{2+} + 2OH^-$$

At equilibrium, the sum of the chemical potentials of the reagents is equal to that of the chemical potentials of the products:

$$\mu(CaO) + \mu(H_2O) = \mu(Ca^{2+}) + 2\mu(OH^-).$$

By supposing that the activity of water is equal to 1, i.e. $\mu(H_2O)=\mu°(H_2O)$, the following equation can be written:

$$\mu(CaO) = A + RT[\ln(a(Ca^{2+}) \cdot a(OH^-)^2)] \qquad (2)$$

using $A=\mu°(Ca^{2+})+2\mu°(OH^-)-\mu°(H_2O)$.

The chemical potentials of SO_3 and Al_2O_3 are likewise linked to aqueous species activities:

$$\mu(SO_3) = B + RT \cdot [\ln(a(SO_4^{2-})/a(OH^-))^2] \qquad (3)$$

$$\mu(Al_2O_3) = C + 2RT \cdot [\ln(a(Al(OH)_4^-)/a(OH^-))] \qquad (4)$$

Table 4
Chemical potentials at the invariant points in kJ/mol

No. invariant point	Value obtained in this work with Zen+*k*			Value calculated using data of Damidot [10]		
	$\mu(CaO)$	$\mu(SO_3)$	$\mu(Al_2O_3)$	$\mu(CaO)$ [a]	$\mu(SO_3)$ [b]	$\mu(Al_2O_3)$ [c]
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

[a] $\mu(CaO)=\mu°(CaO)+2\mu°(OH^-)-\mu°(H_2O)+RT\cdot[\ln(a(Ca^{2+})\cdot a(OH^-)^2)]$.
[b] $\mu(SO_3)=\mu°(SO_4^{2-})-2\mu°(OH^-)+\mu°(H_2O)+RT\cdot[\ln(a(SO_4^{2-})/a(OH^-)^2)]$.
[c] $\mu(Al_2O_3)=2\mu°(Al(OH)_4^-)-2\mu°(OH^-)-3\mu°(H_2O)+2RT\cdot[\ln(a(Al(OH)_4^-)/a(OH^-))]$.

using $B=\mu°(SO_4^{2-})-2\mu°(OH^-)+\mu°(H_2O)$ and $C=2\mu°(Al(OH)_4^-)-2\mu°(OH^-)-3\mu°(H_2O)$.

In each case, the ion activities can be calculated with a geochemical speciation model using adapted database.

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 $CaO–Al_2O_3–SO_3–H_2O$ system at 25 °C (Table 4). This further validates the Zen+*k* method of calculation using which is reported here [25].

5. Discussion

The results given by Zen+*k* are in agreement with previous work and, as a consequence, calcium monosulfoaluminate does not appear to be a stable phase in a saturated system. The question of the stability of this phase in hydrated cement was referred to by several authors. Atkins et al. [7] had problems to obtain pure calcium monosulfoaluminate as a small amount of ettringite was always observed. These authors deduced that the

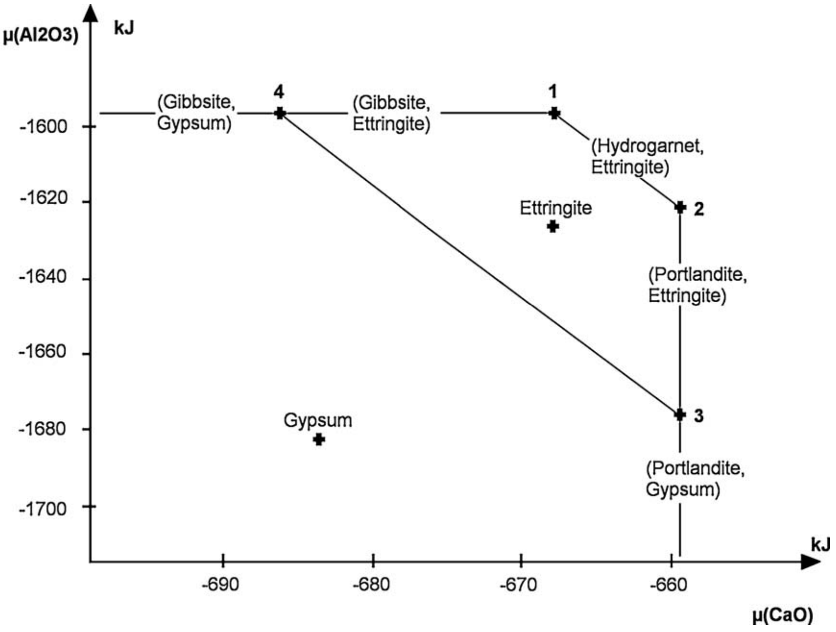

Fig. 2. Diagram ($\mu(CaO)$, $\mu(Al_2O_3)$) at 25 °C and 1 bar with $\mu(H_2O)=\mu°(H_2O)$. The chemical potentials are linear combinations of the type: $\mu(CaO)=A+RT[\ln(a(Ca^{2+})\cdot a(OH^-)^2)]$, $\mu(Al_2O_3)=C+2RT[\ln(a(Al(OH)_4^-)/a(OH^-))]$. See text, Eqs. (2) and (4).

calcium monosulfoaluminate was metastable with respect to ettringite. As a consequence, in their model CEMCHEM, calcium monosulfoaluminate is not taken into account in the database. Damidot and Glasser [15] included calcium monosulfoaluminate in their thermodynamic database and, while confirming that it is a metastable phase at 25 °C, indicated that it becomes stable at higher temperatures [26]. However these authors believed that Portland cement paste could remain for a significant time at the metastable invariant point – C_4AH_{19}, portlandite and calcium monosulfoaluminate – due to slow reaction kinetics. Warren and Reardon [20] suggested that at high pH, a portion of the sulfate ions (SO_4^{2-}) in ettringite and calcium monosulfoaluminate are substituted by hydroxyl ions (OH^-). This assumption was made in order to explain abnormally low values of solubility constant for ettringite in solutions of pH higher than 13. These variations of the solubility constant could lead to a modification of the stable assemblages of phases.

6. Water chemical potential: a key parameter for the stability of monosulfoaluminate?

In addition to these previous assumptions, we can also consider that the numerical value for the chemical potential of water could influence the presence of the calcium monosulfoaluminate in associations of stable phases resulting from the hydration of cement. This hypothesis can be tested using the Zen + *k* software by calculating the phase diagram of the $CaO–Al_2O_3–SO_3–H_2O$ system as a function of $\mu(H_2O)$ and $\mu(CaO)$. This is possible by taking in account the activity of water in Eq. (2). The calculated diagram, Fig. 3, is constructed by declaring SO_3 and Al_2O_3 as immobile components with a molar ratio Al_2O_3/SO_3 greater than 1, which is a common situation in ordinary Portland cements. Some stable invariant points of the phase diagram of Fig. 3 are:

1′: Gibbsite + Ettringite + Hydrogarnet + Calcium monosulfoaluminate
2′: Portlandite + Ettringite + Hydrogarnet + Calcium monosulfoaluminate
3′: Gibbsite + Ettringite + Anhydrite + Calcium monosulfoaluminate
4′: Gibbsite + Anhydrite + Hydrogarnet + Calcium monosulfoaluminate
5′: Portlandite + Anhydrite + Hydrogarnet + Calcium monosulfoaluminate

At these invariant points, the chemical potential of the water is:

- $\mu(H_2O) = -238.25$ kJ for the invariant points 1′ and 2′,
- $\mu(H_2O) = -239.31$ kJ for the invariant points 3′,
- $\mu(H_2O) = -240.01$ kJ for the invariant points 4′ and 5′.

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 Figs. 1 and 2. This difference comes from the fact that the chemical potential of the component H_2O is allowed to vary, and as a consequence the variance of the system is increased by 1.

It is interesting to note the presence of the calcium monosulfoaluminate at all invariant points.

The relevance of the calculated invariant points in a cement paste depends first on the possibility to attain the

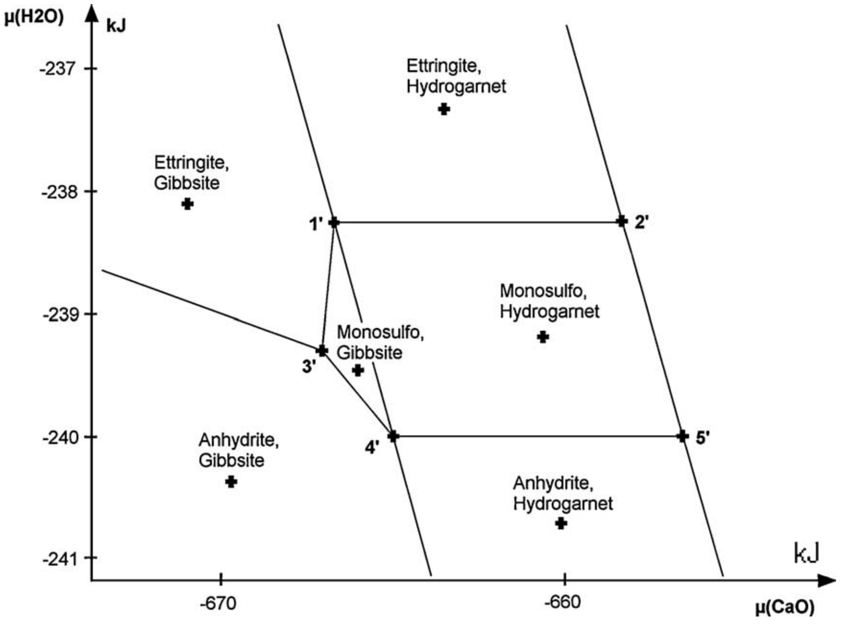

Fig. 3. Diagram ($\mu(CaO)$, $\mu(H_2O)$) at 25 °C and 1 bar. The chemical potentials are linear combinations of the type: $\mu(CaO) = A + RT[\ln(a(Ca^{2+})a(OH^-)^2/a(H_2O))]$, $\mu(H_2O) = \mu°(H_2O)_{liquid} + RT\ln(a(H_2O)) = \mu°(H_2O)_{vapor} + RT\ln(P(H_2O))$. See text.

Table 5
Composition of extracted pore solution [7]

	Na	K	Ca	SO_4^{2-}	pH
10^{-3} mol/l	87	512	0.84	1.98	13.6

calculated value of chemical potential of the water. 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%. In hydrated cement samples, water is present as molecules within the structure of hydrates, as liquid pore water and as vapor in large pores. The liquid pore water may have a high content in alkali elements (Table 5) and this may lower H_2O activity (note that the solution may not be modeled as ideal because of the interactions with surface charges of hydrates and because of all the interactions, activity of water cannot be easily calculated). It is also known that in the porous network of a cement paste maintained in dry conditions, the macro-pores are rapidly depleted in water and thus an equilibrium exists between water vapor and liquid water contained in finer pores. On the whole, the fact that the activity of water can be lower than 1 in a cement paste is thus possible. 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;

$$\mu(H_2O) = \mu(H_2O)_{\text{liquid}} = \mu(H_2O)_{\text{vapor}}$$

$$\mu(H_2O)_{\text{liquid}} = \mu^\circ(H_2O)_{\text{liquid}} + RT\ln\left(\frac{a(H_2O)}{a^\circ(H_2O)}\right)$$

using as reference conditions: $T=298.15$ K, $P=1$ bar, $a^\circ(H_2O)=1$ and $\mu^\circ(H_2O)_{\text{liquid}}=-237.14$ kJ/mol.

Moreover the following relation can be written:

$$\mu(H_2O)_{\text{vapor}} = \mu^\circ(H_2O)_{\text{vapor}} + RT\ln\left(\frac{f(H_2O)}{f^\circ(H_2O)}\right)$$

where $f(H_2O)$ is fugacity of water vapor.

The conditions of standard are $T=298.15$ K, $P=1$ bar, $f^\circ(H_2O)=1$ and $\mu^\circ(H_2O)_{\text{vapor}}=-228.6$ kJ/mol [21]. If we consider that in the system, the fugacity of water is equal to the partial pressure of water:

$$\mu(H_2O)_{\text{vapor}} \approx \mu^\circ(H_2O)_{\text{vapor}} + RT\cdot\ln\left(\frac{P(H_2O)}{P^\circ(H_2O)}\right),$$

with $P^\circ(H_2O)=1$.

The chemical potential of the vapor is;

$$\mu(H_2O)_{\text{vapor}} = \mu^\circ(H_2O)_{\text{vapor}} + RT\left[\ln(h) + \ln\left(\frac{P_{\text{saturated vapor}}(H_2O)}{P^\circ(H_2O)}\right)\right] \tag{5}$$

with $P^\circ(H_2O)=1$ and h, the relative humidity, defined as: $h=\frac{P(H_2O)}{P^\circ_{\text{saturated vapor}}(H_2O)}$, and $P_{\text{saturated vapor}}=0.031$ at 298.15 K (Rankine's equation).

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:

- $\mu(H_2O)=-238.25$ kJ $\rightarrow h=66\%$ at points 1′ and 2′,
- $\mu(H_2O)=-239.31$ kJ $\rightarrow h=43\%$ at points 3′,
- $\mu(H_2O)=-240.01$ kJ $\rightarrow h=32\%$ at points 4′ and 5′.

These values of relative humidity are lower than the experimental values reported by Andrade et al. [27] for concrete exposed under natural conditions and may not be reached in a cement paste. However, the calculations have to be improved as the loss of water molecules from the structure of both calcium monosulfoaluminate and ettringite as the relative humidity decreases is not taken into account in the matrix of composition. The number of lost water molecules can be high [28,29] and thus the impact on the calculation is also expected to be important. It is not possible at present to realize more accurate calculations because Zen+k cannot handle variable matrices of composition.

7. Influence of data input and uncertainties

The numerical values of coordinates of invariant points depend on the thermodynamic database. The value of the water chemical potential that allows the presence of calcium monosulfoaluminate mainly depends on Gibbs energy of formation of ettringite, hydrogarnet and calcium monosulfoaluminate. The calculations in this paper were made using the thermodynamic database of Revertégat et al. [22] for solid phases and the database of Shock et al. [23] for the aqueous species. By using two other databases in addition to the previous database, Babushkin et al. [21] for solids and aqueous phases, or Damidot and Glasser [15] for solids and Shock et al. [23] for the aqueous species, we note that the numerical values of Gibbs energy of formation of phases common in

Table 6
Gibbs free energy of formation from elements (ΔG_f°) of solid phases calculated with different sets of database

ΔG_f°	P	E	M	H	L	N	A	G
[22,23]	−896.4	−15 213.6	−7784.2	−5022.5	−1153.9	−7330.0	−1321.6	−1797.8
[15,23]	−896.2	−15 205.3	−7781.6	−5022.2	−1153.7	–	–	−1796.8
[21]	−897.0	−15 205.7	−7778.6	−5014.1	−1153.9	–	−1320.0	−1797.4

P: portlandite; E: ettringite; M: calcium monosulfoaluminate; H: hydrogarnet; L: gibbsite; N: C_4AH_{13}; G: gypsum; A: anhydrite; ΔG_f°: Gibbs energy of formation from elements (kJ/mol).

geochemistry are similar but for the phases that are specific to hydrated Portland cement, the values are different (Table 6). The Gibbs energy of formation of ettringite ranges from -15205.3 to -15213.6 kJ/mol, which is in accordance with the range of values proposed by Perkins and Palmer [17], -15211 ± 20 kJ/mol.

The numerical values of the chemical potential of water (computed using Zen+k) and the corresponding relative humidity (Eq. (2)) of the invariant points 1′ and 2′ are:

- [22,23]: $\mu(H_2O) = -238.25$ kJ $\rightarrow h = 66\%$,
- [15,23]: $\mu(H_2O) = -238.12$ kJ $\rightarrow h = 69\%$,
- [21]: $\mu(H_2O) = -237.23$ kJ $\rightarrow h = 98\%$.

These results provide a sensitivity analysis of the method and show the influence of the precision of data upon the result. The calculated humidity varies in a large extent (from 66% to 98%) depending on the value of Gibbs energy data of the minerals (the variation of which is only of several kJ/mol). This contributes to the discussion of the previous section concerning the values of water activity and humidity that can actually be achieved in the cement.

8. Conclusion

Zen+k software appears to be a very efficient tool to build phase diagrams relevant to chemical systems found in cement paste. The calculated phase diagram corresponding to the CaO–Al_2O_3–SO_3–H_2O system at 25 °C, 1 bar and with $a(H_2O) = 1$, is coherent with previous investigations. In these conditions, ettringite is a stable phase whereas calcium monosulfoaluminate is metastable.

Moreover Zen+k allows us to explore the system when $a(H_2O) < 1$, especially when water vapor is present 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 low relative humidity conditions. This would support the presence of calcium monosulfoaluminate in old Portland cement pastes and that ettringite is more often reported in voids where the presence of water coming from the environment can sometimes be expected. However the value of the calculated humidity greatly depends on the quality of the thermodynamic database that is used. Thus projects such as the Common Thermodynamic Database Project [30] are important to have a better homogeneity of the results obtained by thermodynamic calculations. Another possible improvement is to take into account the loss of water molecules of the hydrates as functions of both relative humidity and temperature. Indeed the combination of these two parameters may have an important effect on cement paste subjected to heat curing that may subsequently suffer from delayed ettringite formation.

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