Thermodynamic stability of thaumasite in the CaO-SiO$_2$-CaCO$_3$-Al$_2$O$_3$-CaSO$_4$-H$_2$O closed system at 25 ºC

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1.- INTRODUCTION

Thaumasite, whose general formula is CaSiO3·CaSO4·CaCO3·15H2O, is one of the few minerals to contain octahedrally coordinated silicon [1]. Its origin in cementitious environments is attributed to sulphate attack by ions either external to or existing internally in the material. Initially, thaumasite formation was associated with sulphate attack under harsh temperatures (under 15 ºC, and particularly between 0 and 5 ºC) and relative humidities [2-4]. Recently, however, thaumasite has been reported to appear at ambient temperature, in both laboratory tests [5,6] and real situations [7].

Taken together, the structural similarity between ettringite and thaumasite [1,8] and the octahedral coordination of Al in the former initially suggested that thaumasite might form from ettringite in a process involving substitution of silicon for aluminium. The non-existence of any continuous solid solubility between the two phases [9], however, would appear to rule out such a hypothesis. Nonetheless, while thaumasite forms in the absence of aluminium [10], that process is generally agreed to be enhanced by the presence of Al [11-12], even though its exact role is not understood.

Thaumasite formation is surrounded by many unknowns, some of the most prominent being formation temperature, the role of aluminium, the effect of the type and concentration of the sulphate ion and so on. A satisfactory understanding of the thermodynamics of the process may help establish the variables that favour thaumasite formation, with a view to preventing that process and the damage it occasions.

The CaO-SiO$_2$-Al$_2$O$_3$-CaCO$_3$-CaSO$_4$-H$_2$O system contains several subsystems, according to previous calculations by a number of authors [13-26]. Blanco-Varela et al. synthesized pure thaumasite [10], measured its solubility and calculated its solubility product, determining that it is stable in the CaO-SiO$_2$-CaCO$_3$-CaSO$_4$-H$_2$O system and certain regions of the CaO-SiO$_2$-Al$_2$O$_3$-CaCO$_3$-CaSO$_4$-H$_2$O system [25]. Damidot et al. [27]

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measured thaumasite solubility and calculated the composition of the invariant points in the $CaO-SiO_2-Al_2O_3-CaCO_3-CaSO_4-H_2O$ system. Thaumasite solubility was found to be one order of magnitude higher by [27] than [25], an indication that the range of stability of this phase in the system differs widely from author to author. The present study aimed to determine thaumasite thermodynamic stability in the $CaO-SiO_2-CaCO_3-Al_2O_3-CaSO_4-H_2O$ closed system at 25 ºC as well as to analyze the role of aluminium – in the form of ettringite, AH_3 or C_3AH_6 – in thaumasite formation.

2.EXPERIMENTAL

The PHREEQCI program (version 2) was run to perform the speciation and solubility constant calculations for thaumasite and determine the saturation and speciation rate of the different phases of the systems studied. This version of the application features capabilities, among others, for kinetically controlled reactions, solid solution and gas equilibria, and fixed-volume gas phase modelling.

Table 1 Dissociation reactions and constants for the phases present in the $CaO-SiO_2-CaCO_3-Al_2O_3-CaSO_4-H_2O$ closed system at 25 ºC

Phase	Dissociation reaction	Log K
$Ca(OH)_2$	$Ca(OH)_2 + 2 H^+ = Ca^{+2} + 2 H_2O$	22.815
$CaCO_3$	$CaCO_3 = CO_3^{-2} + Ca^{+2}$	-8.41
CSH(0.8)	$Ca_{0.8}SiO_{2.8}:H_2O+1.6H^+=0.8Ca^{+2}+H_4SiO_4 - 0.2H_2O$	11.08
CSH(1.1)	$Ca_{1.1}SiO_{3.1}:H_2O + 2.2H^+ = 1.1Ca^{+2} + H_4SiO_4 + 0.1H_2O$	16.72
CSH(1.8)	$Ca_{1.8}SiO_{3.8}:H_2O + 3.6H^+ = 1.8 Ca^{+2} + H_4SiO_4 + 0.8H_2O$	32.60
SiO_2	$SiO_2 + 2H_2O = H_4SiO_4$	-2.85
AH_3	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	7.228
C2ASH8	$Ca_2Al_2SiO_7 \cdot 8H_2O + 10H^+ = 2Ca^{2+} + 2Al^{3+} + H_4SiO_4 + 11H_2O$	49.67
HGSi low	$Ca_3Al_2Si_{0.3}O_{6.6} \cdot 5.4H_2O + 12H^+ = 3Ca^{2+} + 2Al^{3+} + 0.3H_4SiO_4 + 10.8H_2O$	76.07
HGSi high	$Ca_3Al_2Si_{0.8}O_{7.6} \cdot 4.4H_2O + 12H^+ = 3 Ca^{2+} + 2Al^{3+} + 0.8H_4SiO_4 + 8.8H_2O$	72.52
C_3AH_6	$Ca_3Al_2O_6:6H_2O + 12H^+ = 3Ca^{2+} + 2Al^{3+} + 12H_2O$	78.66
mCA	$Ca_4Al_2CO_9 \cdot 11H_2O + 12H^+ = 4 Ca^{2+} + 2Al^{3+} + CO_3^{2-} + 17H_2O$	69.86
Gypsum	$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$	-4.60
Ettringite	$Ca_6Al_2S_3O_{24}H_{12} \cdot 26H_2O + 12H^+ = 6Ca^{2+} + 2Al^{3+} + 3SO_4^{2-} + 38H_2O$	55.223
Thaumasite	$Ca_3SiCSO_{13}H_6 \cdot 12H_2O + 2H^+ = 3Ca^{2+} + H_4SiO_4 + CO_3^{2-} + SO_4^{2-} + 14H_2O$	-7.73

The following information is needed to perform these calculations:

a) Identity of all the phases that can be formed from the system components
b) The solubility equilibrium equation defined in terms of the ionic species and the solubility product for each of the above compounds
c) The charge balance equation for the solution defined in terms of the ionic species.

The program database contains information on the solubility or dissociation product of all the phases in the systems studied. The thaumasite data were entered into the base. Pure thaumasite synthesized as described elsewhere [10, 28] was used to calculate solubility. Pursuant to the methodology described in [28], a $logK_{dis}$ value of -7.73 was computed for the following thaumasite dissociation:

$$Ca_3SiCSO_{13}H_6 \cdot 12H_2O + 2H^+ = 3Ca^{2+} + H_4SiO_4 + CO_3^{2-} + SO_4^{2-} + 14H_2O$$
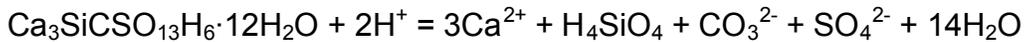
Table 1 gives the dissociation reactions and the values of the related constants used in the thermodynamic calculations.

3.- RESULTS AND DISCUSSION

At 25 ºC, the $CaO-SiO_2-Al_2O_3-CO_3-SO_4-H_2O$ system comprises four subsystems:

a) $CaO-SiO_2-Al_2O_3-CO_3-H_2O$
b) $CaO-SiO_2-Al_2O_3-SO_4-H_2O$
c) $CaO-SiO_2-SO_4-CO_3-H_2O$
d) $CaO-Al_2O_3-SO_4-CO_3-H_2O$

The first five-component sub-system – $CaO-SiO_2-Al_2O_3-CO_3-H_2O$ – in turn consists of three four-component subsystems: i) *$CaO-SiO_2-Al_2O_3-H_2O$*, a system for which a solution has already been given [15] and in which there are nine stable phases: HG Si low($C_3AS_{0.3}H_{5.4}$); HG Si high ($C_3AS_{0.8}H_{4.4}$); CSH(I); CSH(II); SH; C_2ASH_8; C_3AH_6; CH; AH_3. Nonetheless, in keeping with the model proposed by Stronach [19], this system was recalculated here to consider three rather than two CSH gels (CSH(0.8); CSH(1.1) and CSH(1.8)). ii) *$CaO-Al_2O_3-CO_3-H_2O$*, a system not previously solved [24]. The above authors found two phases that contained the four components: monocarboaluminate (mCA) and hemicarboaluminate (hCA). The calculations performed here indicate that only one compound contains all four components: mCA. Five stable phases were identified in this system: $CaCO_3$, CH, SH, C_3AH_6 and mCA. iii) *$CaO-SiO_2-CaCO_3-H_2O$*, a system calculated by the authors of this study [23], in which there are six stable phases: CH, SH, $CaCO_3$, CSH(0.8), CSH(1.1), CSH(1.8).

Further to these data, the first subsystem, CaO-SiO_2-Al_2O_3-CO_3-H_2O, has 12 stable phases: CH; CSH(0.8); CSH(1.1), CSH(1.8), SH; AH_3; C_2ASH_8; HGSi high; HGSi low; C_3AH_6; $CaCO_3$; mCA.

The second sub-system, CaO-SiO_2-Al_2O_3-SO_4-H_2O, also has three four-component subsystems: i) *CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O,* described above; ii) *CaO-SiO$_2$-SO$_4$-H$_2$O*, described to have six components: (CH, CSH(0.8), CSH(1.1), CSH(1.8), SH and $CaSO_4 \cdot H_2O$) by Aguilera [28], whose calculations concur with those performed here. iii) *CaO-Al$_2$O$_3$-SO$_4$-H$_2$O*, with five stable phases: CH, C_3AH_6, AH_3, gypsum and ettringite; the previous calculations for this subsystem reported by [22] concur with the present findings.

Further to these data, the second subsystem has 12 stable phases: the stable silicate and aluminate phases described in the preceding system – CH; CSH(0.8); CSH(1.1), CSH(1.8), SH; AH_3; C_2ASH_8; HGSi high; HGSi low; C_3AH_6 – and two phases containing sulphates – gypsum and ettringite.

The third subsystem, CaO-SiO_2-SO_4-CO_3-H_2O, has been described in the literature [28] with data that concur with the findings reported here. This system has eight stable phases: CH; CSH(0.8); CSH(1.1); CSH(1.8); $CaCO_3$; SH; gypsum; thaumasite. In this case thaumasite contains all five components.

The fourth and final sub-system, CaO-Al_2O_3-SO_4-CO_3-H_2O, is described in the literature [26] to have eight phases: gypsum, ettringite, C_3AH_6, mCA, hCA, CH, AH_3, $CaCO_3$. This system was recalculated for the present study with the data at hand and found to have seven stable phases (CH; AH_3; C_3AH_6; gypsum; etringita; $CaCO_3$; mCA), none of which contains the five elements.

Further to these data, the CaO-SiO_2-Al_2O_3-CO_3-SO_4-H_2O system has 15 stable phases: CH; CSH(0.8); CSH(1.1); CSH(1.8); SH; AH_3; C_2ASH_8; HGSi low; HGSi high; C_3AH_6; $CaCO_3$; monocarboaluminate (mCA); gypsum; ettringite; thaumasite. None of the phases contains all six components. The system has 36 five-component invariant points where thaumasite is present and stable with all the phases of the system. These data do not concur with the findings reported by Damidot et al. [27], who considered only two types of CSH gel. Furthermore, the composition and pH found by those authors for the solution in equilibrium with thaumasite differ from the results of this study. Indeed, when the concentrations given in the Damidot [27] paper were entered into the database used in this study, calcite and thaumasite precipitated out of the solution.

Table 2 lists the 19 five-component points where ettringite and thaumasite co-exist.
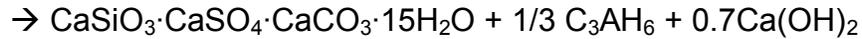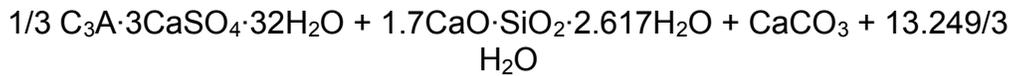
Table 2 Invariant points in the $CaO-SiO_2-Al_2O_3-CO_3-SO_4-H_2O$ system at 25 ºC where ettringite and thaumasite are both stable.

Point	Al (mol/kg)	C (mol/kg)	Ca (mol/kg)	S (mol/kg)	Si (mol/kg)	pH
CH-low-C_3AH_6-et-th	1.00e-5	1.43e-11	2.04e-2	7.64e-6	1.69e-6	12.47
CH-C_3AH_6-mCA-et-th	1.00e-5	2.85e-6	2.04e-2	7.64e-6	8.52e-12	12.47
CH-1.8-low-et-th	9.46e-6	9.40e-12	2.04e-2	7.94e-6	2.49e-6	12.47
1.1-1.8-low-et-th	1.21e-5	7.07e-12	1.794e-2	8.60e-6	3.66e-6	12.42
$CaCO_3$-mCA-CH-et-th	6.95e-6	5.93e-6	2.04e-2	9.75e-6	3.21e-12	12.47
C_3AH_6-AH_3-low-et-th	3.72e-4	4.13e-10	5.56e-3	1.11e-5	3.83e-7	11.95
1.1-high-low-et-th	1.15e-4	4.63e-12	6.87e-3	1.47e-5	1.67e-5	12.05
$CaCO_3$-et-AH_3-mCA-th	3.40e-4	6.71e-6	5.07e-3	1.48e-5	2.16e-11	11.92
C_2ASH_8-AH_3-low-th-et	3.33e-4	2.07e-11	4.96e-3	1.58e-5	6.86e-6	11.91
C_2ASH_8-high-low-et-th	2.05e-4	7.96e-12	5.65e-3	1.58e-5	1.35e-5	11.97
C_2ASH_8-1.1-high-et-th	1.53e-4	3.99e-12	5.84e-3	1.77e-5	2.24e-5	11.98
C_2ASH_8-1.1-AH_3-et-th	1.78e-4	8.30e-13	2.76e-3	1.10e-4	9.88e-5	11.65
0.8-1.1-AH_3-et-th	2.00e-5	9.75e-15	5.74e-3	4.99e-3	1.00e-3	10.68
CH-$CaCO_3$-gyp-et-th	1.34e-10	5.82e-6	3.17e-2	1.23e-2	2.25e-15	12.43
CH-1.8-gyp-et-th	1.34e-10	5.68e-15	3.17e-2	1.23e-2	2.31e-6	12.43
1.1-1.8-gyp-et-th	1.85e-10	4.49e-15	2.95e-2	1.25e-2	3.35e-6	12.37
0.8-1.1-gyp-et-th	1.73e-6	2.06e-15	1.60e-2	1.54e-2	7.82e-4	10.54
0.8- AH_3-et-th-gyp	7.34e-6	2.96e-15	1.60e-2	1.54e-2	1.38e-3	10.22
$CaCO_3$-AH_3-gyp-et-th	7.42e-6	7.16e-6	1.57e-2	1.56e-2	5.79e-13	10.23

There are 19 points in the system at which ettringite and thaumasite are both thermodynamically stable within a wide range of sulphate ion concentrations (7.64e-6 - 1.56e-2 mol/kg). Both phases are stable with all the phases in the system except SH. When sulphate concentration is greater than 4.99e-3 mol/kg, gypsum begins to appear in the medium, where the three phases co-exist when sulphate concentration is very high (1.23e-2-1.54e-2 mol/kg). All three phases are stable in the presence of CSH gels providing there is no calcite in the medium.

At 25 ºC, there are a further 17 points in the $CaO-SiO_2-Al_2O_3-CO_3-SO_4-H_2O$ system where thaumasite forms in the absence of ettringite, an indication that thermodynamically speaking, ettringite is not requisite to thaumasite formation. When ettringite decomposes, the aluminium adopts the form C_3AH_6 and/or AH_3. Table 2 shows that both phases are stable with thaumasite and ettringite in the presence of a hydrogarnet (HGSi low) at a sulphate concentration of 1.11e-5mol/kg and an aluminium concentration of 3.72e-4mol/kg. Ettringite becomes unstable when the aluminium concentration rises slightly to 3.73e-4 mol/kg, at which point the stable phases in the system are: C_3AH_6-AH_3-HGSilow-mCA-th; in other words, thaumasite is stable with different aluminium compounds.

Assuming the following reaction:

$$1/3 \ C_3A \cdot 3CaSO_4 \cdot 32H_2O + 1.7CaO \cdot SiO_2 \cdot 2.617H_2O + CaCO_3 + 13.249/3 \ H_2O$$

$$\rightarrow CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O + 1/3 \ C_3AH_6 + 0.7Ca(OH)_2$$

Bellman [29] calculated the change in the Gibbs free energy for thaumasite formation from ettringite, CSH gel and calcite to be +3.2KJ/mol. This value barely fell within the margins of error defined for the author's thermodynamic calculations, however, suggesting that this finding needs to be confirmed. The thermodynamic calculations performed here verified that thaumasite always precipitates in the following cases:

$CaCO_3$-CSH (-et-H_2O)
$CaCO_3$-CSH(1.1)-et-H_2O
$CaCO_3$-CSH(1.8)-et-H_2O
$CaCO_3$-CSH(0.8)-CSH(1.1)-et-H_2O
$CaCO_3$-CSH(1.1)-CSH(1.8)-et-H_2O

This is an indication that thaumasite formation is thermodynamically favoured in cements containing CSH gel, $CaCO_3$ and ettringite and that therefore the process is controlled by kinetic factors.

The PHREEQC program was used to calculate the sulphate concentration required for thaumasite to form at different solution pH values.

The equilibrium concentration of thaumasite was calculated in an aqueous solution whose pH was gradually modified. These data are shown in Figure 1, where the sulphate concentration values are given in the form $pSO_4^{2-} = -\log [SO_4^{2-}]$. The curve was fitted to a second degree polynomial with a fairly good correlation coefficient ($R^2 = 0.9967$). The sulphate concentration needed for thaumasite to precipitate declined (pSO_4^{2-} rose) with increasing pH up to values of nearly 12, after which it remained practically constant; from pH = 13, however, the sulphate concentration required for thaumasite to exist began to climb again (pSO_4^{2-} declined).
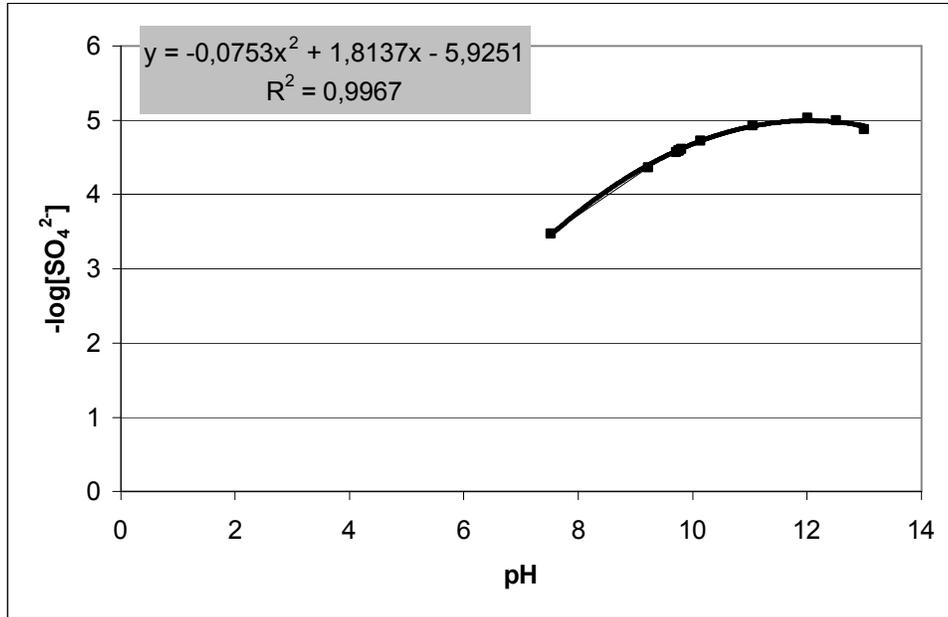
Figure 1.- Solution pH versus sulphate ion (pSO_4^{2-} = $-log[SO_4^{2-}]$) concentration required for thaumasite to precipitate

4.- CONCLUSIONS

The chief conclusions of this paper are:

1.- Thaumasite is thermodynamically stable across a wide range of sulphate ion concentrations (1.02e-11-1.56e-2).

2.- Thaumasite is stable with all the phases in the system: CH; CSH(0.8); CSH(1.1); CSH(1.8); SH; AH_3; C_2ASH_8; low HGSi; high HGSi; C_3AH_6; $CaCO_3$; monocarboaluminate (mCA); gypsum; ettringite. In addition, thaumasite is present in the 36 five-component invariant points of the system studied.

3.- Thaumasite and ettringite together are stable with all the phases in the system except SH. Both phases are stable with CSH gels when the medium is calcite-free.

4.- Ettringite is not thermodynamically necessary for thaumasite to form.

5.-Thaumasite is thermodynamically stable with aluminium-rich phases: ettringite, AH_3 and C_3AH_6.

5.- ACKNOWLEDGEMENTS

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