

## Conditions for Thaumasite formation

T. Schmidt<sup>1</sup>, B. Lothenbach<sup>1</sup>, K.L. Scrivener<sup>2</sup>, M. Romer<sup>1</sup>,  
D. Rentsch<sup>1</sup>, R. Figi<sup>1</sup>

<sup>1</sup>*Empa, Dübendorf, Switzerland*

<sup>2</sup>*EPFL, Lausanne, Switzerland*

### Abstract

The formation of thaumasite was investigated with the progressive equilibrium approach (PEA). The approach experimentally simulates the conditions of various levels of sulfate uptake in hardened cement pastes and determines the equilibrium composition of the pore solution and the solid phases to be approached after an interaction time of several months. The investigated cement pastes were analysed by XRD and <sup>29</sup>Si CP/MAS NMR, while the solutions were analysed for Na, K, Ca, hydroxide, sulfate and carbonate. The results show that thaumasite formation is favoured by lower temperatures (8 °C) as well as by high sulfate concentrations (10-20 wt% SO<sub>4</sub><sup>2-</sup> by weight cement paste) and high pH values (13) in the presence of calcite. The analytical results were compared with the results of a thermodynamic modeling. Thaumasite was only found under conditions where it has been predicted to form as a stable phase.

### 1 Introduction

Conventional sulfate attack in mortars and concretes involves the formation of expansive sulfate phases like ettringite (3CaO·Al<sub>2</sub>O<sub>3</sub>·3CaSO<sub>4</sub>·32H<sub>2</sub>O) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). However, in cements and concrete containing a source of carbonate, the formation of thaumasite (CaSiO<sub>3</sub>·CaCO<sub>3</sub>·CaSO<sub>4</sub>·15H<sub>2</sub>O) can be observed.

In recent years thaumasite formation has been studied and some primary risk factors have been identified [1]. It has been confirmed that the thaumasite form of sulfate attack (TSA) requires a source of calcium silicate, sulfate and carbonate ions, excess of humidity and low temperatures [1, 2].

It has been suggested that thaumasite is more stable at lower temperatures since silicon tends to adopt the octahedral co-ordination found in thaumasite more easily with decreasing temperatures [1]. Nevertheless, thaumasite is formed also at temperatures around 20 °C. Diamond [3] reported thaumasite formation in buildings in Southern California.

Beside the temperature aspect TSA was found in cement systems with high and low  $C_3A$  contents [4, 5, 6].

Limestone addition was found to influence the phase assemblage. In the presence of calcite monocarbonate forms as stable AFm phase instead of monosulfate [7]. Bellmann [11] assumed that monosulfate can react to form thaumasite with C-S-H since monosulfate is metastable in the presence of calcite. Other sources of carbonate potentially favouring thaumasite formation were found to be carbonate containing aggregates [1] or carbonate bearing ground water [8].

Portlandite might be involved indirectly in thaumasite formation as it supports gypsum formation in case of high sulfate concentrations [5] or calcite during the carbonation [9, 10]. Thaumasite formation is not suppressed by the consumption or absence of portlandite [11].

Investigations on the stability and formation of thaumasite have shown that it was formed either with high amounts of gypsum added to the cement [12] or through interaction between limestone blended Portland cement and sulfate enriched solutions [13]. It was claimed that thaumasite is not stable in the presence of monocarbonate and that thaumasite can only form at sulfate concentrations high enough to form gypsum [14]. According to Juel [14] gypsum and calcite cannot coexist in the presence of thaumasite. In contrast Bensted et al. [16] found that ettringite and the C-S-H phase leads to thaumasite formation in the presence of calcite and gypsum.

It was analysed that pH values above 12 enhance thaumasite formation whereas pH below 11 led to gypsum formation during sulfate attack [15].

The present investigation uses the progressive equilibrium approach PEA to evaluate experimentally the mechanisms of thaumasite formation and to compare the experimental results with the thermodynamic calculations.

## **2 Concept of Progressive Equilibrium Approach (PEA)**

A new concept – the progressive equilibrium approach (PEA) – is used to investigate the chemical aspects of a sulfate attack. It relies on a chemical gradient which can be found in real situations in concrete structures which undergo an external sulfate attack over durations of more than 20 years [10]. The chemical gradient is due to a diffusive mass exchange involving external sulfate. The PEA defines and subsequently simulates fixed chemical zones.

These zones are defined as subsystems (A-E) with different chemical compositions. The concentration of sulfate ions varies from high in subsystem A (near surface) to low in the subsystem E (unaffected, sound concrete). In this paper, test conditions according to sulfate performance tests (high sulfate concentration) are investigated.

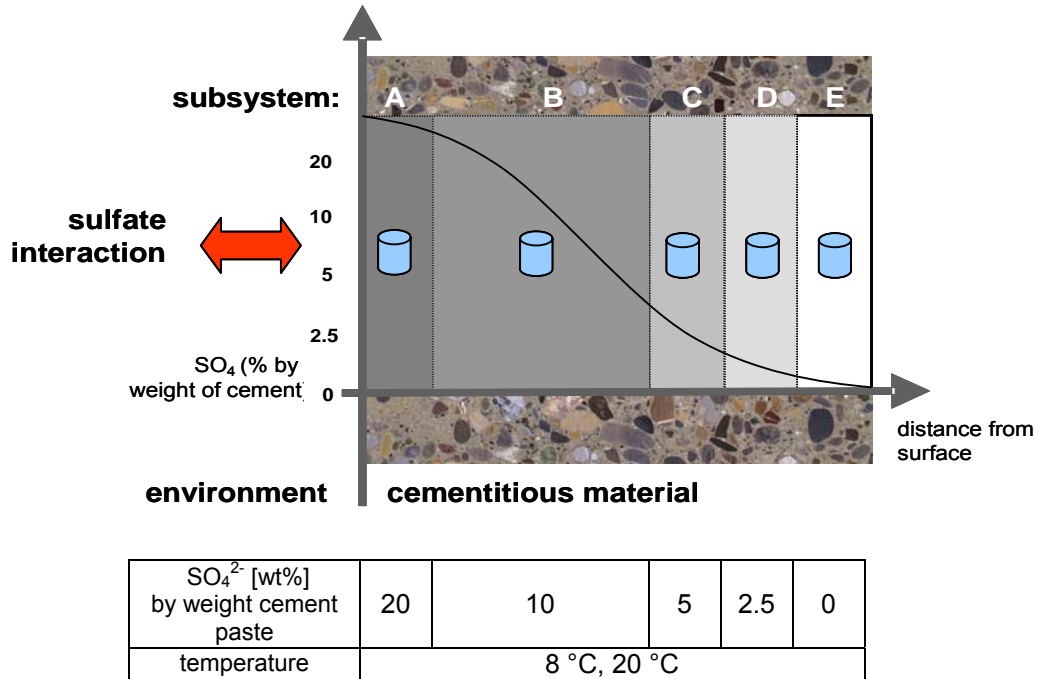


Fig. 1: Schematic illustration of the progressive equilibrium approach

To study the influence of sulfate concentration on thaumasite formation crushed cement paste samples were used in batch experiments as closed subsystems. Through chemical reactions with the solution, new hydrate phase assemblages are formed until equilibrium is reached. Since the time to attain equilibrium is not known, the subsystems were examined after 3 and 9 months. At equilibrium it can be assumed that the solution surrounding the cement paste is identical to the pore solution and in equilibrium with the hydrate phase assemblage. The analysis of the solid and liquid phase composition were compared with the calculations from the thermodynamic model and especially the determined amounts of thaumasite were compared with calculated data.

### 3 Thermodynamic Model

The thermodynamic modeling is carried out using the Gibbs free energy minimization program GEMS [17] to calculate the concentration of the dissolved species as well as the type and amount of solid phases precipitated. Chemical interactions involving solids, solid solutions and aqueous phase compositions are considered in the system.

Thermodynamic data for aqueous species as well as for the solids were taken from PSI-GEMS thermodynamic dataset. Solubility products for

cement minerals and compilation of the sulfate phases present at 8 °C and 20 °C were taken from Lothenbach and Winnefeld [18]. The solubility product of thaumasite is taken from the work of Macphee [19].

The hydrate phases considered in the model are C-S-H, portlandite, ettringite, thaumasite, monosulfate, monocarbonate, hemicarbonate,  $\text{FH}_3$  ( $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ), calcite, gypsum and hydrotalcite. As input, the composition of the laboratory cements was used. The model considered the degree of hydration at the beginning of the exposition to be 90% for all clinker phases and a certain amount of alkalies bound in the C-S-H phase.

It should be noted that in the experiments presented here, in many cases thermodynamic equilibrium has not yet been reached, while thermodynamic calculations predict the composition of the system at equilibrium. The calculations serve to predict the phase stabilities and phase composition in the subsystems resulting from sulfate interaction depending on variable calcite amounts in the cement systems.

#### 4 Experimental

The PEA concept was tested experimentally on hydrated cement pastes which were prepared from industrial cement clinkers representing sulfate resistant Portland cement, HS, and ordinary Portland cement, OPC, as given in Tables 1 and 2.

Table 1: Composition of the clinker and limestone filler used [wt%]

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	CO <sub>2</sub>	LOI
HS	19.7	4.8	7.3	62.9	1.6	1.1	0.15	0.82	0.1	0.30
OPC	21.4	4.8	2.8	65.6	1.7	0.9	0.16	0.73	0.2	0.27
Filler	0.08	0.17	0.03	55.6	0.29	0.01	0.01	0.01	43.7	43.7

Table 2: Phase composition of the clinker using Bouge calculation

	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
HS	64	9	0.4	22
OPC	68	10	8	9

Pure analytical gypsum was used to adjust the appropriate sulfate content for the HS (SO<sub>3</sub> = 1.90 wt%) and OPC (SO<sub>3</sub> = 2.96 wt%) clinker. To study the effect of limestone on thaumasite formation the cements were blended by adding 5 wt% (H2, P2) and 25 wt% (P3) calcite as filler. The cement pastes were produced at a water/binder ratio of 0.35 and fabricated as prisms of 40x40x160 mm<sup>3</sup>.

After demoulding, the prisms were cured for 56 days in saturated limewater before crushing the hydrated cement paste (0.5 – 2 mm) to enhance the specific surface available for the sulfate interaction.

The crushed cement paste (10 g dried at 40 °C) was immersed in aqueous reaction solution (70 ml) as shown in Fig. 2. For the modification of the subsystems (A – D) adequate amounts of Na<sub>2</sub>SO<sub>4</sub> were dissolved in deionised water (reaction solution) before immersion of the cement paste.

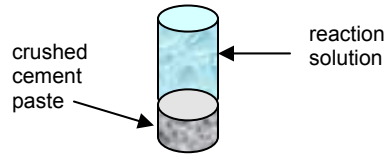


Fig. 2: Subsystem for PEA

Table 3: Clinker type, limestone addition and sulfate content of experimental setup

Clinker type	Filler [wt%]	Cement system	Subsystem SO <sub>4</sub> <sup>2-</sup> [g/l] by mass of cement paste				
			A	B	C	D	E
HS	0	<b>H1</b>	20.4	10.2	5.1	2.5	-
	5	<b>H2</b>	19.4	9.8	4.8	2.4	-
OPC	0	<b>P1</b>	19.3	9.7	4.8	2.4	-
	5	<b>P2</b>	19.3	9.6	4.8	2.4	-
	25	<b>P3</b>	15.4	7.7	3.9	1.9	-

The PEA experiments were processed as closed subsystems (sealed plastic containers) at 8 °C and 20 °C and shaken frequently. The amount of sulfate added to each subsystem is given in Table 3. For the analysis of the experiments the subsystems were filtered dividing the aqueous solution from the solid residue under vacuum using a 45 µm Nylon membrane filter. The pH was determined immediately by a pH electrode using a part of the undiluted solution. For further analysis 9 ml of 6.5% HNO<sub>3</sub> solution was added to 1 ml of solution and stored at 5 °C till further analysis. The concentration of sulfate, Ca, K and Na were determined using ICP-OES and carbonate was determined as total inorganic carbon. The solid residue was immersed in acetone and the samples then dried for 2 days at 40 °C. The samples for X-ray diffraction (XRD) and <sup>29</sup>Si cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) were ground to ≤ 40 µm and stored in a desiccator at 20 °C.

## 5 Results and Discussion

The phase assemblages of selected experiments (i.e. those containing thaumasite) identified by XRD and  $^{29}\text{Si}$  CP/MAS NMR are shown in Table 4 together with the analysed composition of the pore solutions. The quantities of thaumasite found by  $^{29}\text{Si}$  CP/MAS NMR are shown in Fig. 3. It was found that thaumasite forms only in subsystems A and B, at higher contents of sulfate in the system. Thaumasite could be identified in samples where 5 and 25 wt% of limestone was present in cement, both with low  $\text{C}_3\text{A}$  (H2) and high  $\text{C}_3\text{A}$  (P2, P3) content. Beside thaumasite, ettringite, calcite as well as gypsum were generally identified. The phase assemblages identified are in general agreement with those predicted from the model as shown in Table 4.

Table 4: Phase assemblage identified by XRD and  $^{29}\text{Si}$  CP/MAS NMR and pore solution composition after a reaction time of 9 months

sample	Phase assemblage		Solution composition [mmol/l]						
	predicted	Identified	S	C	Ca	K	Na	pH	
H2/A	8 °C	Ett Th	G↓ Ett Th Cc	50.9	0.4	4.6	13.6	421.9	13.0
H2/B		Ett Th Cc	G↓ Ett Cc	29.6	0.2	6.6	13.8	200.1	12.9
P2/A		Ett Th	G↓ Ett Th Cc	76.4	0.2	4.6	10.5	426.3	13.0
P2/B		Ett Th Cc	G↓ Ett Th Mc Cc	26.5	0.2	5.2	10.2	182.7	13.0
P3/A		Ett Th Cc	G↓ Ett Th Cc	53.0	0.2	3.5	6.9	334.9	13.0
P3/B		Ett Th Cc	G↓ Ett Th Mc Cc	17.1	0.2	4.6	6.9	152.2	12.9
H2/A	20 °C	Ett Th	G↓ Ett Mc Cc	53.0	0.4	4.9	14.1	435.0	13.0
P2/A		Ett Th	G↓ Ett Th Cc	78.0	0.3	4.6	10.5	426.3	13.0
P2/B		Ett Th Cc	G↓ Ett Th Mc Cc	28.1	0.2	3.5	6.9	334.9	13.0
P3/A		Ett Th Cc	G↓ Ett Th Cc	56.1	0.2	3.9	6.9	343.6	13.0
P3/B		Ett Th Cc	G↓ Ett Th Cc	18.7	0.2	4.5	7.2	152.2	13.0

Portlandite and C-S-H present in all samples, Abbreviations: Cc = calcite; Mc = monocarbonate; Ett = ettringite; Th = thaumasite; G = gypsum; ↓ decreasing with time; S = sulfate; C = carbonate

As shown in Fig. 3, thaumasite is detectable after 3 months of sulfate interaction at 8 °C which is due to the fact that thaumasite is favoured and more stable at lower temperatures [9, 11, 19]. At 20 °C only very little amounts of thaumasite could be detected even after 9 months of sulfate interaction. The amounts of thaumasite formed at 8 °C (P2/A, B; P3/A, B) were significantly higher than the amounts of thaumasite formed at 20 °C (P2/A, B; P3/A, B).

Clearly, thaumasite formation starts earlier in the presence of limestone filler, and is accelerated at 8 °C in Portland cement. The differences in the amounts of thaumasite formed with 5 wt% or 25 wt% limestone in the cement system comparing P2/A, B and P3/A, B at 8 °C are small.

Obviously thaumasite formation chemically is not or only slightly enhanced by increasing the amount of limestone in the cement.

As shown in Fig. 3 and 4, thaumasite was detected in all subsystems where it has been predicted to be a stable phase. The differences in the phase assemblages between calculated and measured data show that equilibrium conditions have not been reached after 9 months of sulfate interaction. Beside that also the predicted amounts of thaumasite are not reached after 9 months, indicating that thaumasite formation occurs slowly as a deterioration product.

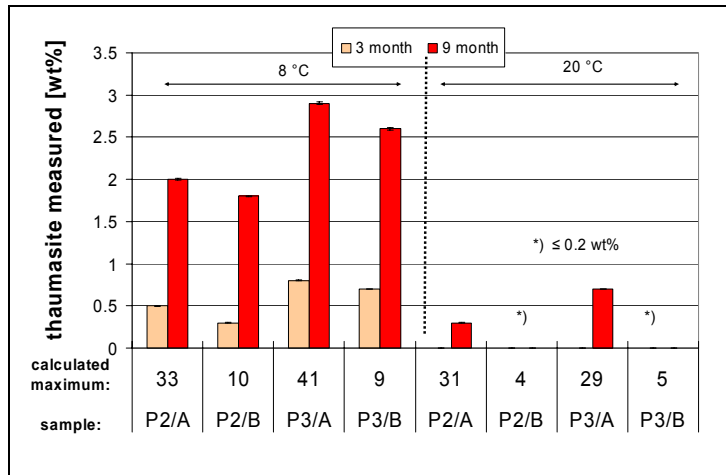


Fig. 3: Quantities of thaumasite in % by weight cement paste calculated and determined by <sup>29</sup>Si CP/MAS NMR

Thermodynamic calculations indicate that in the long term at equilibrium all calcite in the pastes with 5 wt% limestone addition will be consumed for the formation of thaumasite (Table 4, Fig. 4b). That indicates that in cement systems with less than 5 wt% limestone addition the calcite is the limiting factor for the maximum extent of thaumasite formation whereas in the case of 25 wt% limestone addition sulfate is the limiting factor. According to the model even small amounts of thaumasite are predicted in cement systems without limestone addition as shown in Fig. 4a. That can be explained by the fact that cement clinker itself contain approximately 0.2 % CO<sub>2</sub> (Table 1) which is stoichiometric sufficient to form < 3 wt% thaumasite at high sulfate concentrations. Such small amounts of thaumasite however cannot be detected experimentally. Beside the clinker other sources of carbonate for thaumasite formation can be aggregates and and/or carbonate bearing ground waters [8].

The reactions in the experimental setup used, are not completed. After 9 months there are both reacted (outer) and unreacted (inner) part of the crushed cement paste particles in the subsystems. This leads to mixed analysis and differences between calculated and determined data as shown in Table 4 and Fig. 4.

The experimentally observed phase compositions generally agree with the modeled phase composition. In cement systems without limestone addition, monosulfate and traces of hemicarbonates were determined to be

stable AFm phases. In agreement to the model small amounts of carbonate from the clinker as mentioned above lead to the formation of hemicarbonate beside monosulfate as stable AFm phases as shown in Fig. 4a, E. The addition of limestone to the cement system chemically influences the formation the AFm phase composition and leads to the formation of monocarbonate as shown in Fig. 4 b, E. Both predictions agree with the hypothesis of Kuzel and Pöllmann [7] in that hemicarbonate and/or monocarbonate were observed in the presence of carbonate during hydration.

Another effect of limestone addition is the dilution effect in cement systems. The additional carbonate leads to the formation of less ettringite, portlandite and C-S-H in the cement as shown in Fig. 4 comparing subsystems 4a, E; 4b, E and 4c, E.

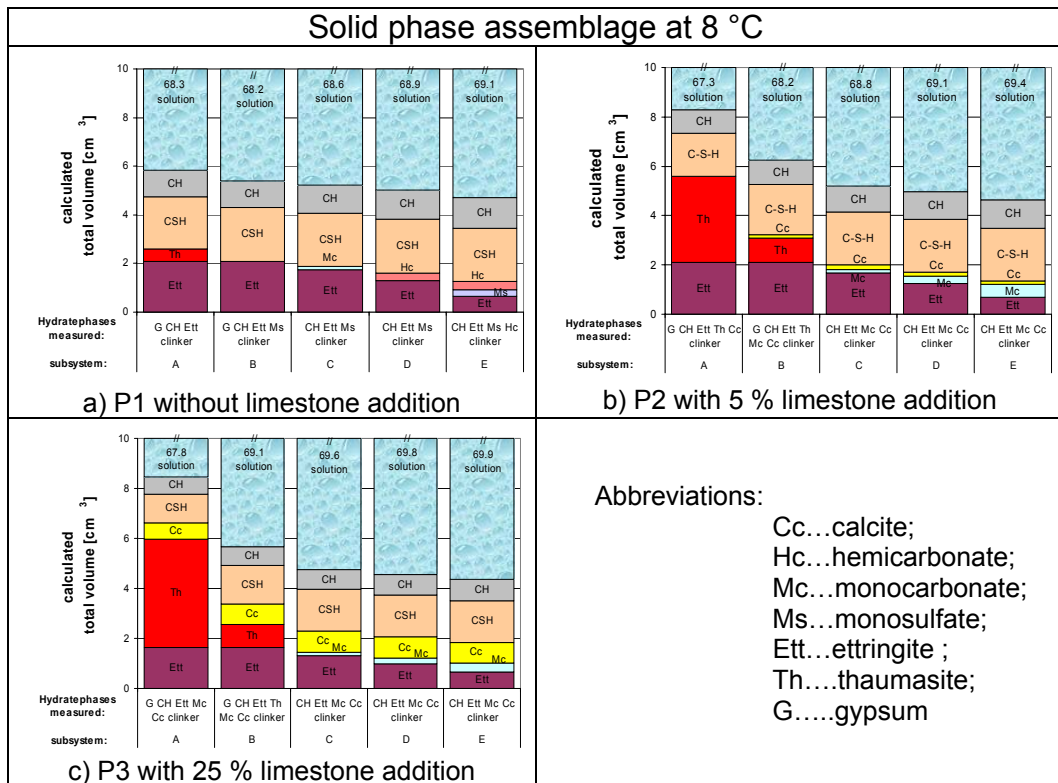


Fig 4: Experimental and calculated data of the solid phase assemblage identified by XRD and <sup>29</sup>Si/MAS NMR

If sulfate is progressively added to the subsystems moving from subsystem E to A more ettringite is formed at the expenses of the AFm phases monosulfate, monocarbonate and hemicarbonate until all available aluminate from the clinker has reacted as shown in Fig. 4. When more sulfate is added to the subsystem thaumasite starts to form in limestone containing cement systems at the expense of calcite, C-S-H and CH. In subsystems with high sulfate concentrations (Fig. 4, subsystems A,B) the formation of gypsum was observed while the thermodynamic calculations predict that all sulfate available should be present at equilibrium as



ettringite and thaumasite. However, the XRD results show a decrease of the gypsum peak between 3 and 9 months. Thus gypsum forms parallel to thaumasite at high sulfate concentrations and later acts as a source of sulfate ions required for the precipitation of thaumasite.

Portlandite was present in all subsystems investigated as shown in Fig. 4. With increasing sulfate contents portlandite is consumed by the formation of AFt phases (ettringite, thaumasite) and gypsum. The resulting release of hydroxide ions in the pore solution leads to a measured increase of the pH in the pore solution as shown in Fig. 5.

Generally, the increase of solid volume with the increasing sulfate content in the subsystems is due to the formation of secondary sulfate phases as shown in Fig. 4. However a simple increase in solid volume does not necessarily imply that expansion occurs [20].

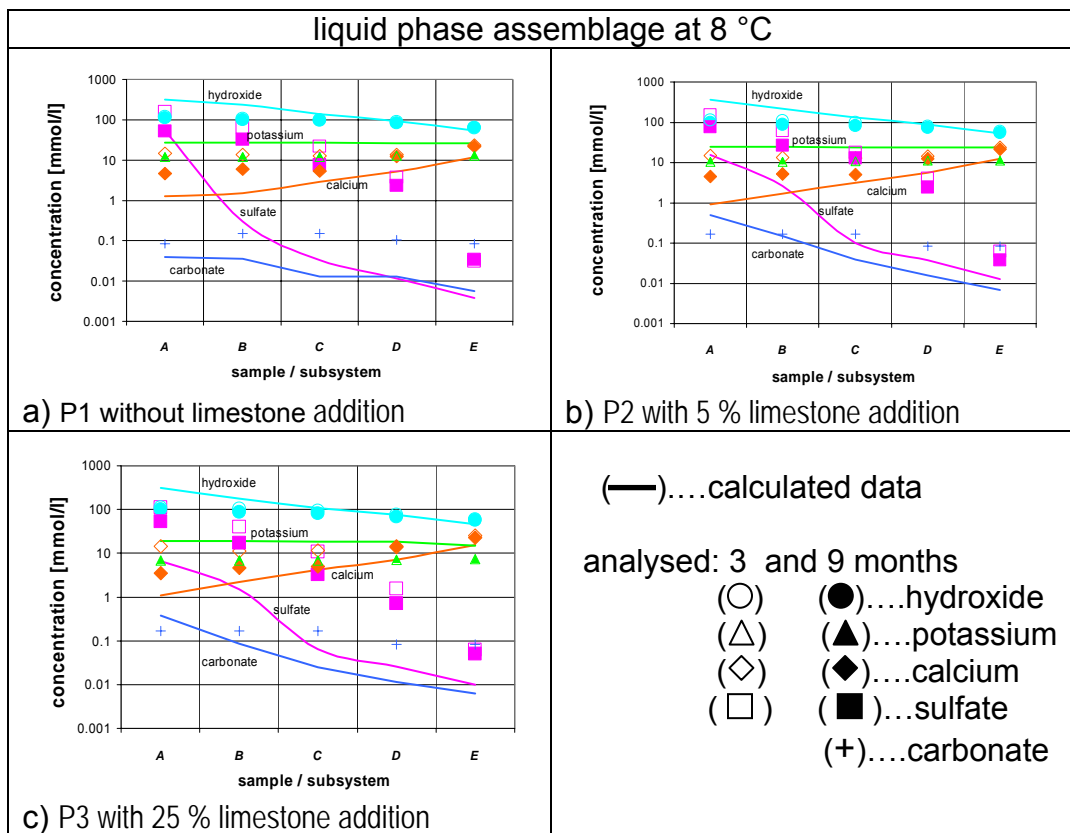


Fig. 5: Experimental and calculated data of the pore solution

The calculated and measured compositions of the solutions are shown Table 4 and Fig. 5. The trends of the measured ion concentrations over time indicate movement to the predicted equilibrium concentrations. Only subsystems without sulfate addition are found to be close to the calculated equilibrium conditions. Obviously the consumption of sulfate due to the formation of ettringite and thaumasite takes longer and is not finished after 9 months of sulfate interaction.

The transformation of monocarbonate into ettringite with increasing sulfate content releases carbonate into the pore solution thus resulting in slightly higher carbonate concentrations in the pore solution.

## **6 Conclusions**

The experimental results show that between 10 to 20 wt%  $\text{SO}_4^{2-}$  by weight cement paste are necessary to form thaumasite. Secondary gypsum forms parallel to thaumasite at high sulfate concentrations. In the experiments secondary gypsum was initially formed as the transformation of the existing hydrates into thaumasite proceeds only slowly. Later on the secondary gypsum acts as a source of sulfate needed for the precipitation of additional thaumasite.

Low temperatures ( $8^\circ\text{C}$ ) favour thaumasite formation since significantly higher amounts of thaumasite were found even after relatively short time of sulfate interaction. The results further show that both cement systems with low and high  $\text{C}_3\text{A}$  can be affected by thaumasite formation as long as they contain a source of carbonate.

Limestone addition influences the mineralogy of the AFm phases: monocarbonate is present instead of monosulfate. Chemically, it is also a source of carbonate necessary to form thaumasite. In cement systems with 5 wt% limestone addition the calcite is the limiting factor whereas in the case of 25 wt% limestone addition sulfate limits the amount of thaumasite formed.

The progressive equilibrium approach PEA used to investigate the chemical aspects of a sulfate attack is a good tool for simulating various levels of sulfate uptake due to an external sulfate attack. The experimental data correspond well with the thermodynamic calculations from the model used.

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