

VOLUME STABILITY OF CAC-CaSO₄- CaCO₃-H₂O SYSTEMS DURING DRYING

L. BAQUERIZO and T. MATSCHEI

Innovation, Holcim Technology Ltd, Im Schachen,
5113 Holderbank, Switzerland

K. SCRIVENER

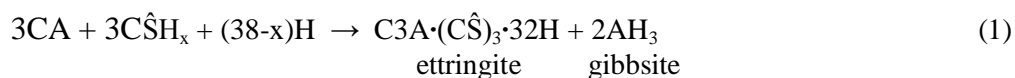
EPFL STI CCMX-GE MXG 232 (Bâtiment MXG) Station 12,
CH-1015 Lausanne, Switzerland

SUMMARY: Cement hydrates and their chemically bound water content are sensitive against changes in relative humidity and temperature. This may cause specific solid volume changes affecting dimensional properties of hydrated cement paste such as shrinkage, swelling and expansion, and therefore impact the performance and also the transport properties of cementitious materials. In the present paper we present preliminary results on the study of hydration states of the main crystalline cement hydrates found in hydrated Calcium Aluminate Cements (CAC) – CaSO₄ – CaCO₃ systems when exposed to different drying conditions. The techniques used to measure water content and volume of crystalline cement hydrates as well as thermodynamic properties associated to these changes are described. A first attempt to thermodynamically model volume changes of a cementitious system during drying is shown.

Keywords: AFm and AFt phases, hydration states, thermodynamic modelling, volume stability

INTRODUCTION

One important application of calcium aluminate cements nowadays is its use as a component in mixed binder systems containing different amounts of Portland cement and calcium sulphate. These blended systems are used for special applications such as self-levelling compounds floors, tile adhesives or fixing mortars^[1]. These mixtures can be fluid for a few hours and then harden quickly mainly due to the formation of ettringite^[2] according to the reaction^[1]:



This reaction consumes considerable amounts of water and decreases rapidly the Relative Humidity (RH) during drying, which make these mixtures very good as floor-levelling compounds^[1]. But an often neglected phenomenon which can influence

shrinkage, swelling and expansion in cementitious materials is the sensitivity of individual cement hydrates, e.g. ettringite, and their water content against changes in relative humidity and temperature, which may cause specific solid volume changes and impact the porosity, performance and transport properties of cementitious systems. Varying hydration states of cement hydrates may have a direct impact on the specific density/volume of cement paste, e.g. the volume of some hydrates can change as much as 20% during drying^[3]. Crystalline cement hydrates such as Alumina Ferrite -mono and -triphases (AFm and AFt) commonly found in the system mentioned in this study show different hydration states depending on the external temperature and relative humidity (RH)^[4-16]. Water molecules are incorporated in the interlayer in AFm phases or in the interchannel in AFt phases. In the case of AFm phases different types of interlayer water can be identified: water molecules which are strongly bound to the calcium cations of the main layer, and space filling water molecules which are easily removable upon increase of temperature or decrease of RH^[17].

The aim of this paper is to show that a decrease in the water chemical potential of a cementitious system (decrease of RH) can lead to changes of the hydration states of crystalline cement hydrates (AFm and AFt phases) commonly found in CAC blended with CaSO₄ and CaCO₃. For these systems thermodynamic properties of the different hydration states of monosulfoaluminate (Ms), monocarboaluminate (Mc) and ettringite (Ett) have been derived (the used abbreviation is shown in parenthesis). The characterization techniques used in this work will be more extensively described in an upcoming paper by Baquerizo et al.^[18].

MATERIALS AND CONDITIONING

All chemicals used were analytical grade reagents. The precursor used in the synthesis of AFm and AFt phases was tricalcium aluminate C₃A, which was prepared from a 3:1 molar ratio of CaCO₃ and Al₂O₃ at 1400°C. Anhydrite CaSO₄ was prepared by dehydration of gypsum in a muffle furnace at 550°C overnight. CaO was obtained by decarbonation of CaCO₃ at 1000°C overnight. Double distilled CO₂ free water was used in the synthesis of the hydrates. Details about the preparation of the hydrated cement phases can be found in^[19]. Once purity has been confirmed by XRD, the initially wet hydrates were vacuum filtered under N₂ atmosphere in a glove box and aged at 25°C (20 months) inside hermetic glass bottles equilibrated at different RH with the aid of salt solutions^[20]. RH was continuously monitored with embedded RH sensors.

METHODOLOGY

A complete description of the methodology and characterization techniques used to derive the stability range and thermodynamic properties of the different hydration states will be described in^[18]. Nevertheless a short description of the methods follows:

X-Ray Diffraction (XRD) and thermogravimetric analysis (TGA)

XRD and TGA were carried out on hydrated phases dried at different RH in order to determine the volume of the crystal and the water content of the samples to finally calculate their density, which was then introduced in the thermodynamic database.

Humidity buffer technique

This Method is used to determine the relative humidity (RH) value at invariant points, i.e. at which a spontaneous desorption/adsorption process occurs on a hydrated phase at a specific temperature. The approach of the method is to make a mixture of two different hydration states of a single cement hydrate, e.g. Ms12 and Ms10.5, inside a small container (HDPE small bottles) and record the RH at which the system reaches equilibrium. Since the system is closed and there is no exchange of water with the exterior the RH inside must be the one at which the two phases are in equilibrium. With this value of RH one can calculate the Gibbs free energy of reaction for a specific change of hydration state:

$$\Delta G_r^\circ = -RT \ln (K) \quad (2)$$

We can also calculate the enthalpy of reaction using the van't Hoff's equation:

$$\partial(\ln K)/\partial(1/T) = -\Delta H_r^\circ/R \quad (3)$$

Sorption balance ^[21]

This tool can continuously measure the mass of a small sample (5-100mg) while it is exposed to a pre-selected RH program. This method was used to determine changes in hydration states and cross check the results obtained with the humidity buffer technique.

Sorption microcalorimeter ^[22]

This technique provides the possibility to continuously scan the water activity over the sample and extract both the sorption isotherm and the sorption enthalpy from the same measurement during water adsorption. The measured enthalpy of reaction of a change of hydration state, e.g. Ms10.5+1.5H₂O→Ms12, can be compared to the value obtained with the humidity buffer technique and this data is then introduced in the thermodynamic model.

RESULTS

Table 1 summarizes the observed hydration states of cement hydrates introduced into the thermodynamic database ^[23]. The related invariant points at which a desorption/absorption process happens will be published in an upcoming paper. It has to be noticed that some of the used data in this paper are preliminary and need further validation. More detailed results on other AFm and AFt phases will be published elsewhere.

Table 1. Different hydration states of crystalline cement hydrates introduced in the database ^[23]

Hydrates	Hydration states
Monosulfo aluminate	Ms14 - Ms12 - Ms10.5 - Ms9
Monocarbo aluminate	Mc11 - Mc9
Ettringite *	Ett32 - Met9

*Preliminary results

Fig. 1 and 2 show experimental results on the interaction of monosulfoaluminate (Ms) and air buffered by salts at different relative humidities. Initially the sample was vacuum filtered and then exposed to dry conditions (desorption), while during adsorption monosulfate was preconditioned at 8% RH for 20 months and later exposed to increasing RH during 2 months. As a consequence of the sample treatment several hydration states of monosulfoaluminate can be observed in XRD patterns (in Fig. 1) upon drying and rewetting as function of RH at 25°C. The water content of the individual samples was measured by TGA and sorption balance (not shown here). Fig. 2 summarises the volume changes of monosulfoaluminate versus RH with the corresponding enthalpies measured by sorption microcalorimeter. The hysteretic behaviour observed in Fig. 1 is represented by dashed-line in Fig. 2. The Gibbs free energy of the changes of hydration states were calculated according to Eq. (1) using results obtained during adsorption.

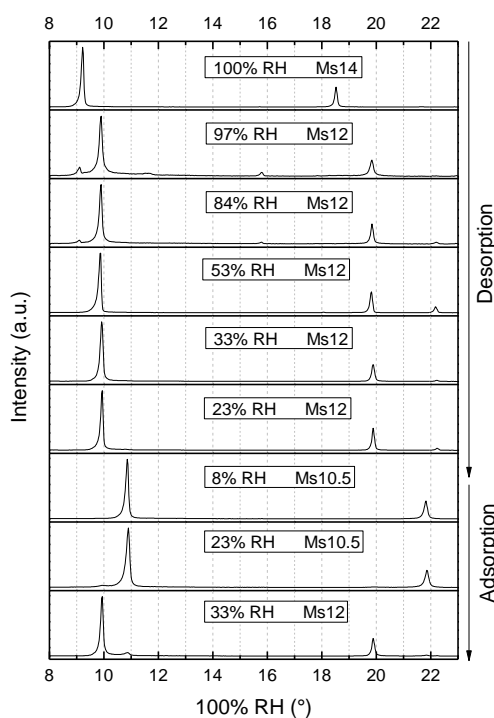


Fig. 1: XRD patterns of monosulfoaluminate dried at different RH at 25°C

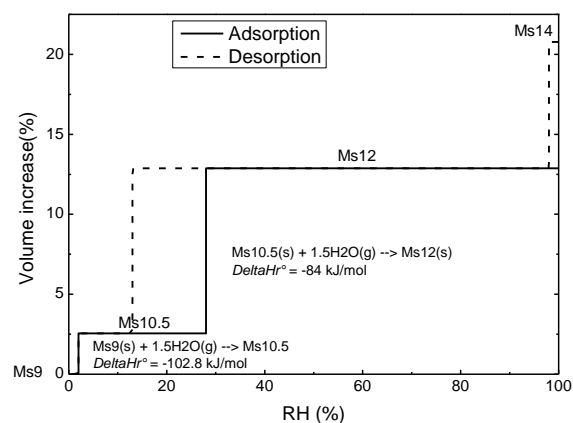


Fig. 2: Phase diagram volume changes of monosulfoaluminate vs RH at 25°C and enthalpies of reaction.

The ettringite structure remains unchanged during drying until 8%RH (see XRD patterns in Fig. 3a, however our sorption balance and sorption calorimetry results (not shown here) indicate that during desorption this hydrate starts to decompose approximately at 2% RH at 25°C until it reaches an estimated water content of 9 H₂O moles close to zero % RH, which here is called Met9 (for metaettringite, a decomposition product of ettringite [14]) but during adsorption Met9 slowly rehydrates first to Met12 (from 0% to 60% RH approximately) then to Ett32 at >60% RH. As the true reason for this non-ideal sorption behaviour is not yet clarified in the current (dehydration) model we have therefore only introduced two hydration states, Ett32 and Met9 [23]. This hysteretic behaviour was also observed in ettringite samples aged during 30 days at 80°C and different RH as shown in Fig. 3b; once the sample is decomposed at 4.5% RH in order to recrystallize ettringite

the RH must be increased to values much higher than the decomposition one, in our case up to 79% RH which is in agreement with observations by Zhou and Glasser^[15].

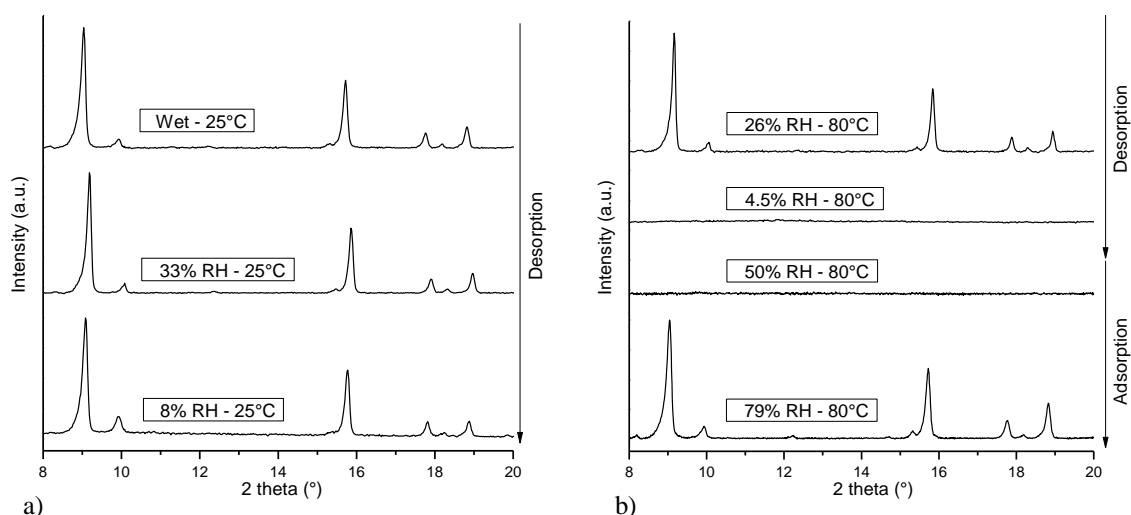


Fig. 3: XRD patterns of ettringite dried at different RH at a) 25°C and b) 80°C

THERMODYNAMIC MODELLING

GEMS-PSI^[24], a software package including a GEM (Gibbs free energy minimisation) solver, a built-in thermodynamic database^[25] complemented with a cement database^[26,27] and a graphical user interface, was used for the thermodynamic simulations. Thus for every change of hydration state of the studied phases, e.g. Ms14 → Ms12 + 2H₂O, the enthalpy of reaction and Gibbs free energy of reaction were introduced into a user-defined project database in the software. To simulate drying the system CaO-Al₂O₃-SO₃-CO₂-H₂O was chosen. The initial model mixture contained mono calcium aluminate (CA), anhydrite (C^S) (resulting SO₃/Al₂O₃=0.546 molar bulk ratio), and varying amounts of calcite at 25°C.

Hydration reactions

The amount of solids was kept constant (100 g) and reacted with 80 g water. A diagram of the specific volume changes of the hydrated mixture with respect to calcite content can be found in the Annex. The formation of solid solutions was omitted. During hydration of CAC gibbsite or aluminium hydroxide (AH₃ in cement notation) is reported to precipitate as a poorly crystalline hydrate^[1,28], however different hydration states of gibbsite were not considered in this study due to a lack of available data.

Drying

Hydrate phase assemblages *A* and *B* in Annex, with 0% and 6.2% of calcite respectively, were selected as initial hydrated systems for the drying modelling. Drying in the simulation was carried out by increasing removal of water until a RH of zero was reached. The investigated systems were:

- System A: monosulfoaluminate (Ms14), ettringite (Ett32) and Gibbsite (Gbs)
- System B: monocarboaluminate (Mc11), ettringite (Ett32) and Gibbsite (Gbs)

During drying modelling we found that some of the hydration states observed in our experimental results are metastable with respect to other phase assemblages. These metastability features of the individual phases relevant to the systems studied in this paper are summarised in Table 2. Experimentally we did not see a transformation of metastable phases into thermodynamically more stable phase assemblages involving a nucleation/recrystallization step. For that reason we introduced several metastability constraints in the calculations in order to obtain the metastable AFm/AFt phases with lower hydration states at 25°C.

Table 2. Thermodynamic stability of changes of hydration states at 25°C (Taken from ^[23])

Dehydration reaction ^{I)}	Thermodynamically stable ^{II)}	Metastable with respect to:
Monosulfoaluminate Ms14→Ms12 Ms12→Ms10.5 Ms10.5→Ms9	Yes Yes No	C ₃ AH ₆ +anhydrite at < 16% RH ^{III)}
Monocarboaluminate Mc11→Mc9	No	C ₃ AH ₆ + calcite at < 32% RH ^{III)}
Ettringite Ett32→Met9	No	Ms12+anhydrite at < 45% RH ^{III)}

^{I)} Index number next to the abbreviation of hydration states denotes the total water content of the phase ^{II)} with respect to the chosen dehydration reaction ^{III)} not seen in practice

Modelled volume changes upon drying on the systems *A* and *B* are shown in Fig. 4 and 5. Changes of specific solid volume as function of RH are presented in Fig. 4. Dehydration happens stepwise at specific RH representing invariant points where the RH is fixed due to phase rule restrictions. At this critical RH two hydration states of the same cement hydrate coexist and buffer the humidity. It has to be noticed that the addition of calcite and the formation of monocarboaluminate and ettringite will enhance the dimensional stability of a hydrated cement paste and makes it less sensitive to humidity variations as shown in the calculations for System *B*.

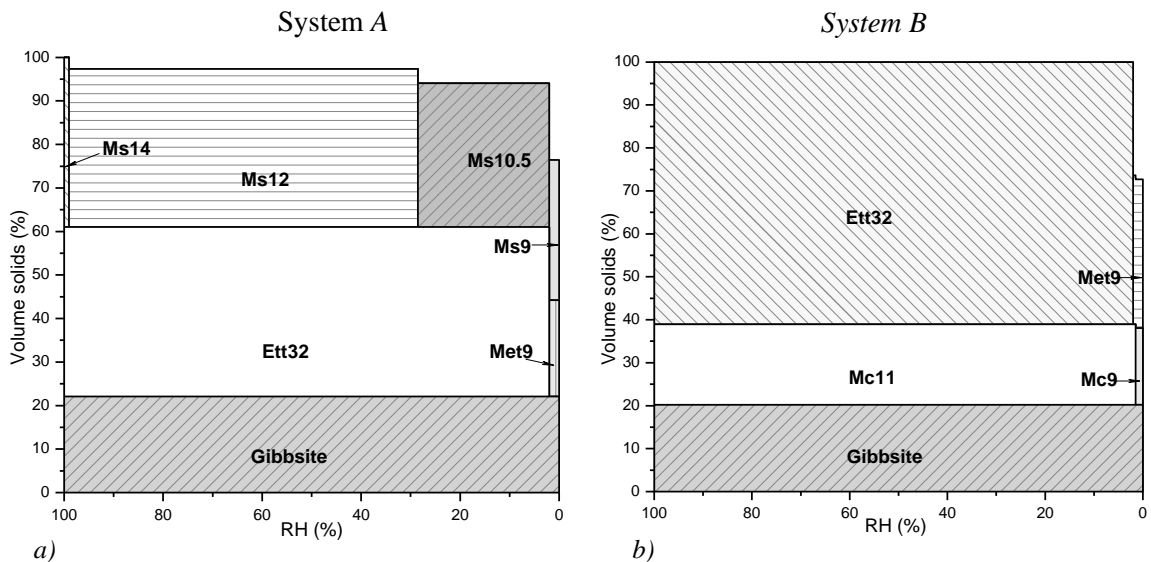


Fig. 4: Calculated volume phase assemblages with respect to changes in RH at 25°C in the Systems *A* and *B*.

In Fig. 5 the volume of the system with respect to water removed from the solid phase assemblage is shown. Specific solid volume of the hydrated paste may decrease at constant RH due to the buffering effect mentioned before. Due to the presence of monocarboaluminate and ettringite system *B* is the most stable phase assemblage, from which we can only remove water and initiate decomposition at very low humidities (<2% RH), whereas monosulfoaluminate loses already part of its interlayer water at <99% RH ^[23] (Fig. 5 system A).

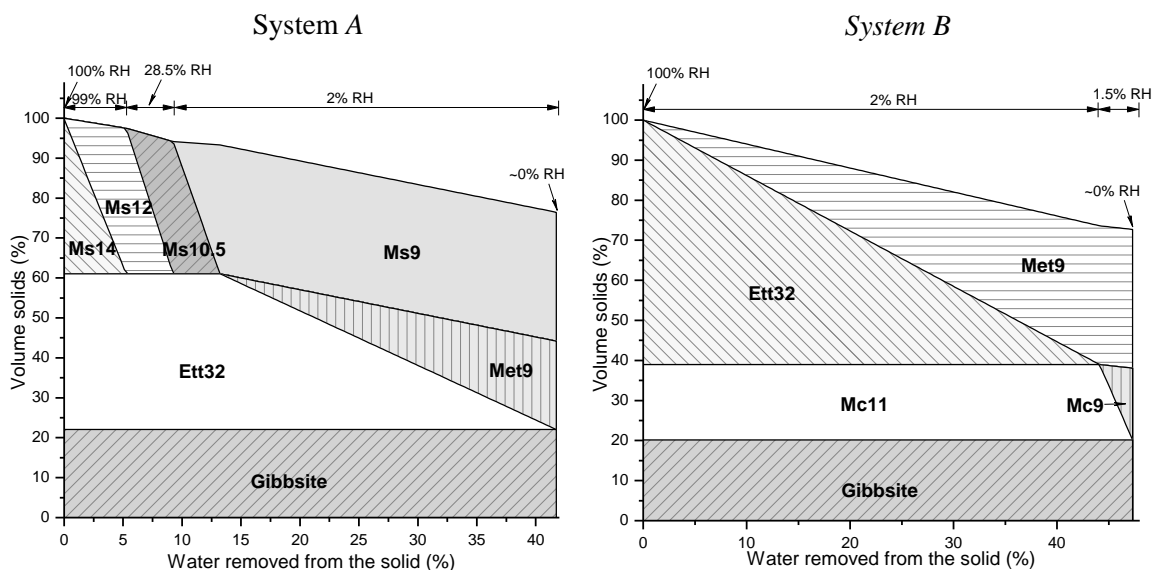


Fig. 5: Calculated volume phase assemblages with respect to increasing removal of water from the solid at 25°C in the Systems A and B

DISCUSSION

It was shown that the addition of limestone i.e. in form of calcite has potential to improve the dimensional stability of CAC-CaSO₄ systems when subjected to drying. Thermodynamic calculations indicate that crystal water can only be removed at relative humidities < 2% from blends containing limestone due to the thermodynamic stability of ettringite and monocarboaluminate at RH > 2%. The practical implications however have to be shown in application based test methods including also the impact of changing microstructure and porosity constitution. Nevertheless the calculations indicate that the addition of small amounts of limestone filler (≤5-8%) to CAC-CaSO₄ blends does not only slightly improved the water binding capacity (as shown in earlier publications ^[19]) but also enhance its dimensional stability.

During drying modelling we faced some problems with respect to the thermodynamic stability of the different hydration states: some of the studied phases with lower hydration states seem to be thermodynamically metastable with respect to other phases, e.g. Mc11 should decompose to C₃AH₆ and calcite at < 32% RH but in our tests we have not seen the formation of new phases. Further investigation of solid-state dehydration reactions are therefore needed to address the metastability problems observed in the simulations of the lower hydration states.

ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under grant agreement 264448. We would like to thank Holcim Technology for actively promoting cement research. We thank Lars Wadsö and Mahsa Saeidpour from Lund University for their support and advice with sorption microcalorimetry and sorption balance tests.

REFERENCES

- [1] Newman J and Choo BS. *Advanced Concrete Technology. Constituent Materials*. Chapter 2. Elsevier, 2003.
- [2] Seifert S, Neubauer J and Goetz-Neunhoeffler F. Application of two-dimensional XRD for the characterization of the microstructure of self-leveling compounds. *Powder Diffr.*, Vol. 24, 2009, pp 107-111.
- [3] Baquerizo L, Matschei T and Scrivener K. *The impact of water chemical potential on the hydration states of Monosulfoaluminate*. 31th Cement and Concrete Science Conference, PP9, London, 2011.
- [4] Pöllmann H. *Characterization of Different Water Contents of Ettringite and Kuzelite*. Proc. XII International Congress on the Chemistry of Cement, 8–13 July, Montreal, Canada, 2007.
- [5] Taylor H.F.W. *Cement Chemistry*, 2nd edition. Thomas Telford, London, 1997.
- [6] Schwiete H E and Ludwig U. *Crystal structures and properties of cement hydration products (hydrated calcium aluminates and ferrites)*. 5th ISCC, Vol 2, 1968, 67-71.
- [7] Kaprálik I and Hanic F. *Phase relations in the subsystem $C_4A_3\bar{S}-C\bar{S}H_2-CH-H_2O$ of the system $CaO-Al_2O_3-C\bar{S}-H_2O$ referred to hydration of sulphoaluminate cement*. *Cem. Concr. Res.* 19, 1989, pp 89-102.
- [8] Kuzel H J. *Initial Hydration Reactions and Mechanisms of Delayed Ettringite Formation in Portland Cements*. *Cement and Concrete Composites* 18, 1996, pp 195-203.
- [9] Pöllmann H. *Die Kristallchemie der Neubildungen bei Einwirkung von Schadstoffen auf hydraulische Bindemittel*. PhD-Thesis, University of Erlangen-Nuernberg, 1984.
- [10] Fischer R and Kuzel H J. *Reinvestigation of the system $C_4A.nH_2O - C_4A \cdot CO_2 \cdot nH_2O$* . *Cem. Concr. Res.* 12, 1982, pp 517-526.
- [11] Robert M H. *Calcium Aluminate Hydrates and Related Basic Salt Solid Solutions*. 5th ISCC, Vol 2, pp 104, 1970.
- [12] Francois M, Renaudin G and Evrard O. *A Cementitious Compound with Composition $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$* , *Acta Cryst.* C54, 1998, pp 1214-1217.
- [13] Renaudin G, Francois M and Evrard O. *Order and disorder in the lamellar hydrated tetracalcium monocarboaluminate compound*. *Cem. Concr. Res.* 29, 1999, pp 63-69.
- [14] Zhou Q, Lachowski E E and Glasser F P. *Metaettringite, a decomposition product of ettringite*. *Cem. Concr. Res.* 34, 2004, pp 703-710.
- [15] Zhou Q and Glasser F P. *Thermal stability and decomposition mechanisms of ettringite at 120°C*. *Cem. Concr. Res.* 31, 2001, pp 1333-1339.
- [16] Renaudin G, Filinchuk Y, Neubauer J and Goetz-Neunhoeffler F. *A comparative structural study of wet and dried ettringite*. *Cem. Concr. Res.* 40, 2010, pp 370-375
- [17] Pöllmann H, Runcevski T and Dinnebier R. *Synthesis and characterization of layered carbonated Calcium Aluminate Hydroxi Carbonate Hydrates*. IV International Workshop on Layered Materials, Campinas, SP, Brazil, 2012.
- [18] Baquerizo L, Matschei T, Scrivener K, Saedipour M, Thorell A and Wädso L. *Methods to determine hydration states of cement hydrates*. In preparation.

- [19] Matschei T, *Thermodynamics of Cement Hydration*. PhD Thesis, University of Aberdeen, 2007.
- [20] Greenspan L. *Humidity fixed points of binary saturated aqueous solutions*. J. Res. Nat. Bur. Standards. Sect. A 81, 1977, pp 89–96.
- [21] Wadsö L and Markova N. *Comparison of three methods to find the vapor activity of a hydration step*. European Journal of Pharmaceutics and Biopharmaceutics, 51, 2001, pp 77-81.
- [22] Wadsö L Markova N. A method to simultaneously determine sorption isotherms and sorption enthalpies with a double twin microcalorimeter. Review of Scientific Instruments 73, 2002, pp 2743-2754.
- [23] Baquerizo L, Matschei T, Scrivener K. *Impact of water activity on volume stability of cement hydrates*. Conference water transport in cementitious materials, Guildford – UK, 2013. Submitted
- [24] Kulik D, Berner U, Curti E. *Modelling chemical equilibrium partitioning with GEMS PSI code*. PSI Scientific report 2003, Vol. IV, pp 109-122, <http://gems.web.psi.ch>
- [25] Hummel W, Berner U, Curti E, Pearson F J, Thönen T. *Nagra/PSI Chemical Thermodynamic Data Base 01/01*. Universal Publishers, Parkland, Florida, USA, 2002.
- [26] Matschei T, Lothenbach B, Glasser F. Thermodynamic properties of Portland cement hydrates in the system CaO-Al₂O₃-SiO₂-CaSO₄-CaCO₃-H₂O. Cem. Concr. Res. 37, 2007, pp 1379-1410.
- [27] Lothenbach B, Matschei T, Möschner G, Glasser F. Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement. Cem. Concr. Res. 38, 2008, pp 1-18.
- [28] Gosselin C. *Microstructural Development of Calcium Aluminate Cement Based Systems with and without Supplementary Cementitious Materials*. PhD Thesis, EPFL, 2009.

ANNEX

Calculated specific volume changes of a hydrated model mixture consisting of CA, CaSO₄ (SO₃/Al₂O₃=0.546 molar bulk ratio) in dependence of changing calcite content at 25°C.

