

IMPACT OF WATER ACTIVITY ON VOLUME STABILITY OF CEMENT HYDRATES

L.Baquerizo¹, T. Matschei¹, K.Scrivener²

¹ Innovation, Holcim Technology, Switzerland. ²EPFL-LMC, Switzerland.

1. Introduction

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 [1] and may thus strongly affect the porosity and performance of a cementitious system. Crystalline cement hydrates such as Alumina Ferrite -mono and -triphases (AFm and AFt) show different hydration states depending on the exposure temperature and relative humidity (RH) [2]-[14]. 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 [15].

Thermodynamic properties of the different hydration states of monosulfoaluminate (Ms), ettringite (Ett), hemicarboaluminate (Hc), monocarboaluminate (Mc) and hydroxy-AFm (OH-AFm) have been studied (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. [16].

2. Materials and conditioning

Details about the preparation of the hydrated cement phases and tricalcium aluminate C₃A can be found in Ref. [20]. 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 [21]. RH was continuously monitored with embedded RH sensors.

3. Methodology

A complete description of the methodology and characterization techniques used to assess the stability range and thermodynamic properties of the different hydration states will be described in [16]. The developed multi-method approach includes: X-ray diffraction (XRD), thermogravimetric analysis (TGA), humidity buffer technique, sorption balance [22] and sorption microcalorimeter [23].

4. Results

Table 1 gives a summary of the observed hydration states of cement hydrates which were introduced into the thermodynamic database. The related invariant points, including phase transformation and critical RH will be published in an upcoming paper. It has to be noticed that some of the data are preliminary and need further validation. For example in the case of Ettringite our sorption balance and sorption calorimetry results show that during desorption this hydrate starts to decompose at around 2% RH at 25°C until it reaches an approximate water content of 9 H₂O moles at <2% RH, which here is called Met9 (for metaettringite, a decomposition product of ettringite [12]) but during adsorption Met9 slowly rehydrates first to Met12 at > 2%RH then to Ett32 at >60% RH. As the true reason for this non-ideal sorption behaviour is not yet clear we have therefore only introduced two hydration states, Ett32 and Met9 in the current (dehydration) model.

Table 1. Different hydration states of crystalline cement hydrates introduced in the database

Hydrates	Hydration states
Monosulfoaluminate	Ms14 - Ms12 - Ms10.5 - Ms9
Monocarboaluminate	Mc11 - Mc9
Hemicarboaluminate *	Hc12 - Hc11.25 - Hc10.5 - Hc9
Hydroxy-AFm *	OH-AFm19 - OH-AFm13 - OH-AFm11 - OH-AFm9.5
Ettringite *	Ett32 - Met9

*Preliminary results

5. Thermodynamic modelling

For the thermodynamic simulations GEMS-PSI [17] was used together with a modified cement database [18][19]. Thermodynamic data of the different hydration states of the cement hydrates were obtained by introducing the related Gibbs free energies and enthalpies of reaction estimated from our experimental data. To simulate drying the system $\text{CaO-Al}_2\text{O}_3\text{-SO}_3\text{-CO}_2\text{-H}_2\text{O}$, which is relevant to OPC and limestone blended cements, was chosen. The initial model mixture contained C_3A , portlandite (CH), calcium sulfate ($\text{SO}_3/\text{Al}_2\text{O}_3=1$ molar bulk ratio), and varying amounts of calcite at 25°C . The amount of solids was kept constant (100 g) and reacted with 90 g water. A diagram of the specific volume changes of the hydrated mixture with respect to calcite content is based on previous calculations by Matschei [20] and can be found in Fig. 1. Initially the formation of solid solutions was omitted but will be discussed later.

- Modelling of the drying behaviour

Due to their differing AFm-AFt mineralogy hydrate phase assemblages A, B and C in Fig. 1, with 0%, 7% and 13.2% of calcite respectively, were selected as initial hydrated systems for the drying modelling. Drying was simulated by continuously removing water from the assemblages until a RH of zero was reached. The investigated systems were:

- System A: monosulfoaluminate (Ms14) and portlandite (CH)
- System B: ettringite (Ett32), hemicarboaluminate (Hc12) and portlandite (CH)
- System C: ettringite (Ett32), monocarboaluminate (Mc11) and portlandite (CH)

One objective of the thermodynamic modelling part is the validation of experimental results with respect to the observed phase transformations and hydration state changes upon drying of the solids. During modelling we encountered that some of the experimentally observed hydration states are metastable with respect to other phase assemblages. These metastability features of the individual phases are summarised in Table 2. As indicated most of our experimental results did not indicate a transformation of metastable phases into thermodynamically more stable phase assemblages involving a nucleation/recrystallization step. Therefore we introduced several metastability constraints in the calculations and assumed the persistence of metastable AFm/AFt phases with lower hydration states at 25°C .

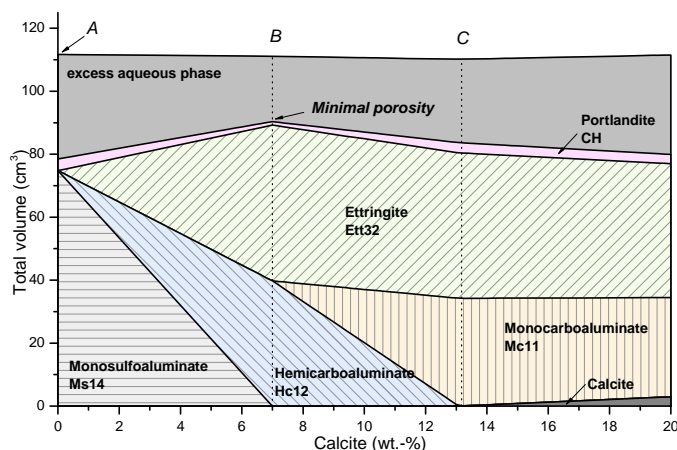


Fig. 1. Calculated specific volume changes of a hydrated model mixture consisting of C_3A , portlandite and with fixed sulfate ratio ($\text{SO}_3/\text{Al}_2\text{O}_3=1$, molar bulk ratio) in dependence of changing calcite content at 25°C [20].

Table 2. Thermodynamic stability of changes of hydration states at 25°C ¹⁾

Dehydration reaction	Thermodynamically stable ²⁾	Metastable with respect to:
Monosulfoaluminate		
Ms14-->Ms12	Yes	
Ms12-->Ms10.5	Yes	
Ms10.5-->Ms9	No	$\text{C}_3\text{AH}_6 + \text{anhydrite}$ at $< 16\% \text{ RH}$ ³⁾
Monocarboaluminate		
Mc11-->Mc9	No	$\text{C}_3\text{AH}_6 + \text{calcite}$ at $< 32\% \text{ RH}$ ³⁾
Hemicarboaluminate		
Hc12-->Hc11.25 ⁴⁾	Yes	
Hc11.25-->Hc10.5	No	$\text{C}_3\text{AH}_6 + \text{Mc11} + \text{CH}$ at $< 62\% \text{ RH}$ ³⁾
Hc10.5-->Hc9	No	$\text{Hc11.25} + \text{C}_3\text{AH}_6 + \text{Mc11} + \text{CH}$ at $< 62\% \text{ RH}$ ³⁾
Hydroxy-AFm		
OH-AFm19-->OH-AFm13	No	$\text{C}_3\text{AH}_6 + \text{CH}$ at $\leq 100\% \text{ RH}$
OH-AFm13-->OH-AFm11	No	$\text{C}_3\text{AH}_6 + \text{CH}$ at $\leq 100\% \text{ RH}$
OH-AFm11-->OH-AFm9.5	No	$\text{C}_3\text{AH}_6 + \text{CH}$ at $\leq 100\% \text{ RH}$
Ettringite		
Ett32-->Met9	No	$\text{Ms12} + \text{anhydrite}$ at $< 45\% \text{ RH}$ ³⁾

¹⁾ Index number next to the abbreviation of hydration states denotes the total water content of the phase ²⁾ with respect to the chosen dehydration reaction ³⁾ not seen in practice ⁴⁾ exact invariant point needs further investigation

Calculated volume changes during drying of the systems A, B and C are shown in Fig. 2. Fig. 2 a, b and c present the evolution of specific solid volume as function of RH. We can see that dehydration happens stepwise at *critical RH* stability limits of the phase assemblages, 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 similar as *conventional drying agents*. Another important finding is that the addition of calcite and the formation of carboaluminates and ettringite will enhance the dimensional stability of hydrated cement paste and makes it less sensitive to humidity fluctuations, which appears to be relevant for limestone blended cements.

In Fig. 2 d, e and f a different way of presentation was chosen. Here we enforce a removal of water from the system. It is important to note that due to the buffering effect the specific solid volume may decrease at constant RH, as the fractions of coexisting low and high hydration state phases are impacted by the removal of water. Due to the presence of monocarboaluminate and ettringite system C is the most stable phase assemblage, which only decomposes at very low humidities (below 2% RH) whereas monosulfoaluminate loses already part of its interlayer water at <99% RH.

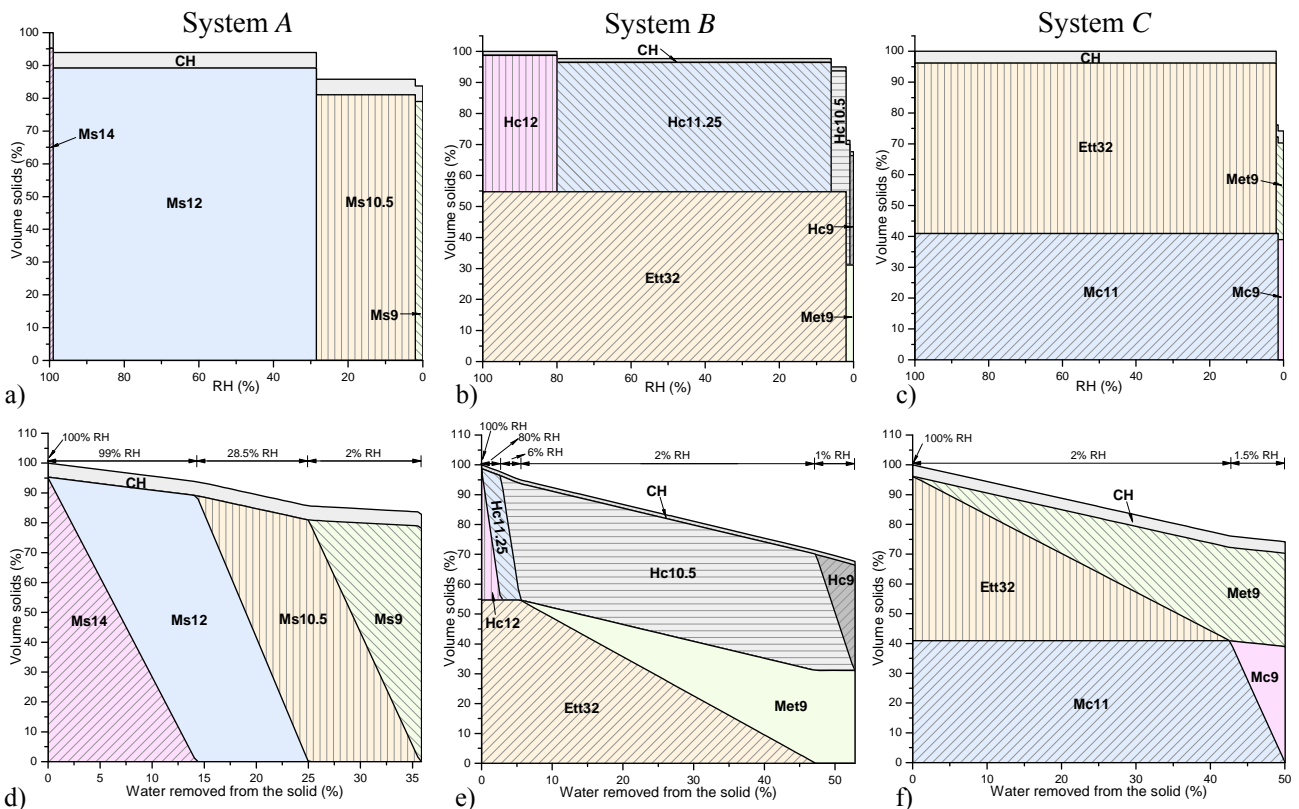


Fig. 2. Calculated volume phase assemblages with respect to changes in RH (a, b and c) and increasing removal of water from the solid (d, e and f) at 25°C in the Systems A, B and C.

6. Discussion

- Drying

This study showed that, as a consequence of their varying hydration states, AFm phases can act as *humidity buffers* in hydrating cement paste. Thus the sorption/desorption capacity of AFm rich systems may influence the resulting internal water activity gradient of a hydrated binder exposed to severe drying conditions. For OPC based systems it is however important to take the impact of C-S-H on water activity buffering into account in further studies.

It was further shown that *calcite rich systems are the most stable* upon drying due to the persistence of monocarboaluminate and ettringite with respect to dehydration. Thus hydrated limestone blended cements are likely to have slightly improved volume stability compared to pure OPC systems.

During modelling we have encountered some problems with respect to the *thermodynamic stability of the hydration states*. Some of the phases with lower hydration states are thermodynamically metastable with respect to other phases below certain critical RH values. e.g. Ms10.5 should decompose to C₃AH₆ and

anhydrite at < 16% RH. Practically we however never observed the formation of new phases. Further analysis and literature review of solid-state dehydration reactions is needed in order to understand why some cement hydrates do not decompose in the course of drying (AFm phases) and why others such as ettringite do decompose [12].

Another important point to consider is the varying sensibility of hydrate phases against *sample preparation procedures* involving a drying step. Vacuum drying for example is a common practice for the preparation of samples for MIP (mercury intrusion porosimetry), XRD, BET surface area measurements, etc. Water rich hydrates e.g. ettringite will significantly lose water at RH < 2% and its solid volume will shrink more than 40% (calculated with lattice parameters shown in [12]) which will lead to wrong results regarding porosity, specific surface and composition analysis of ettringite rich systems. Other drying methods e.g. D-drying, P-drying and oven drying may cause similar problems. Therefore it is important to know the mineralogical and chemical features of the hydrate system before choosing the right sample preparation technique.

- Solid solutions

Experimentally we have seen that Ms14 is the observed hydration state when synthesized with excess of water. Moreover Kuzel [6] showed that Ms14 remained as persistent hydration state in a wet stored Portland cement sample after 310 days of hydration. In some cases however we observed the formation of Ms12 even at > 97% RH. The reason for this is not clear. We suspect that additional stabilisation of Ms12 may be caused by a partial substitution of OH in the structure, for example Pöllmann generally reported lower hydration states for monosulfoaluminate solid solutions stored under wet conditions [7]. Further analysis is necessary to explore the role of solid solution formation during drying and wetting.

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 the Sorption Microcalorimeter and Sorption Microbalance tests.

REFERENCES

- [1] Baquerizo, L., Matschei, T., Scrivener, K., 31th Cem and Conc Science Conf (2011) PP9 London.
- [2] Pöllmann, H., XII International Congress on the Chemistry of Cement (2007), Montreal.
- [3] Taylor, H.F.W., Cement Chemistry, 2nd edition. Thomas Telford (1997) London.
- [4] Schwiete, H.E.; Ludwig, U., 5th ISCC, Vol 2 (1968) 37-67.
- [5] Kaprálik, I., Hanic, F., Cem. Concr. Res. 19 (1989) 89-102.
- [6] Kuzel, H.J., Cem. Concr. Compos. 18 (1996) 195-203.
- [7] Pöllmann, H., PhD-Thesis (1984) University of Erlangen-Nuernberg.
- [8] Fischer, R., Kuzel, H.J., Cem. Concr. Res. 12 (1982) 517-526.
- [9] Robert M.H., 5th ISCC, Vol 2 (1968) 104-117.
- [10] Francois, M., Renaudin, G., Evrard, O., Acta Cryst. C54 (1998) 1214-1217.
- [11] Renaudin, G., Francois, M., Evrard, O., Cem. Concr. Res. 29 (1999) 63-69.
- [12] Zhou, Q., Lachowski, E.E., Glasser, F.P., Cem. Concr. Res. 34 (2004) 703-710.
- [13] Zhou, Q., Glasser, F.P., Cem. Concr. Res. 31 (2001) 1333-1339.
- [14] Renaudin, G., Filinchuk, Y., Neubauer, J., Goetz-Neunhoeffler, F., Cem. Concr. Res. 40 (2010) 370-375
- [15] Pöllmann, H., Runcevski, T., Dinnebier, R., IV International Workshop on Layered Materials (2012) Campinas, SP, Brazil.
- [16] Baquerizo, L., Matschei, T., Scrivener, K., Saeidpour, M., Thorell, A., Wadsö, L., Methods to determine hydration states of cement hydrates, in preparation.
- [17] Kulik, D., Berner, U., Curti, E., PSI Scientific report 2003, Vol. IV, 109-122, <http://gems.web.psi.ch>
- [18] Matschei, T., Lothenbach, B., Glasser, F., Cem. Concr. Res. 37 (2007) 1379-1410.
- [19] Lothenbach, B., Matschei, T., Möschner, G., Glasser, F., Cem. Concr. Res 38 (2008) 1-18.
- [20] Matschei, T., Thermodynamics of Cement Hydration, PhD Thesis, University of Aberdeen, 2007.
- [21] Greenspan, L., J. Res. Nat. Bur. Standards. Sect. A (81), 1977, 89-96.
- [22] Wadsö, L., Markova, N., Eur. J. Pharm. Biopharm. 51 (2001) 77-81.
- [23] Wadsö, L., Markova, N., Rev. Sci. Instrum. 73 (2002) 2743-2754.