

P13: Impact of mineralogy on the water balance of cement paste

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1.- Introduction

It is generally accepted that concrete shrinkage, swelling and expansion strongly depends on the constitution of the internal microstructure, the related porosity and the exposure conditions. On the other hand an often neglected phenomenon is the **sensitivity of individual cement hydrates and their water content** against changes in relative humidity and temperature, which **may cause specific solid volume changes and impact the performance** and transport properties of cementitious materials. The present project studies the changes of the water content of cement hydrates exposed to different external conditions and its potential influence on specific solid volumes and thus porosity. A thermodynamic model will be developed in order to explain the de/re-hydration process of these hydrates as well as the coexisting phases in a cement paste equilibrated in different environments.

2.- Cement hydrates

Cement paste is composed of different hydration phases. The main cement hydrates are:

- **Calcium-Silicate-Hydrate (C-S-H)** (50-60% by volume of paste): C-S-H can be described as nearly X-ray amorphous, nanocrystalline solid with foil-like or fibrillar morphology. There are different hydration states of C-S-H known. Until today however we lack a consistent model which describes the response of C-S-H to different RH and temperature quantitatively.
- **Portlandite or Calcium hydroxide (CH)** (15-25% by volume): Portlandite appears as crystalline hydrate with hexagonal morphology and is easy detectable by XRD. Its water as well as its stoichiometric composition is fixed. Therefore portlandite is not sensitive to changing RH of the environment.
- **Alumina Ferrite -mono and -triphases (AFm and AFt)** (15-20% by volume): AFm phases have a layered double hydroxide structure and are therefore known to be sensitive to changing RH. AFt phases are ettringite type phases with hexagonal channel-column structure. AFt is known to dehydrate if exposed to high temperatures and potentially low humidities.

3.- Synthesis and aging of pure cement hydrates

In order to study water content of cement hydrates we need to target a phase pure synthesis. The following phases were prepared using analytical grade reagents mixed with water at a w/s of 10 or 20 (phase dependent). **Purity** was confirmed by XRD (Formula in cement notation):

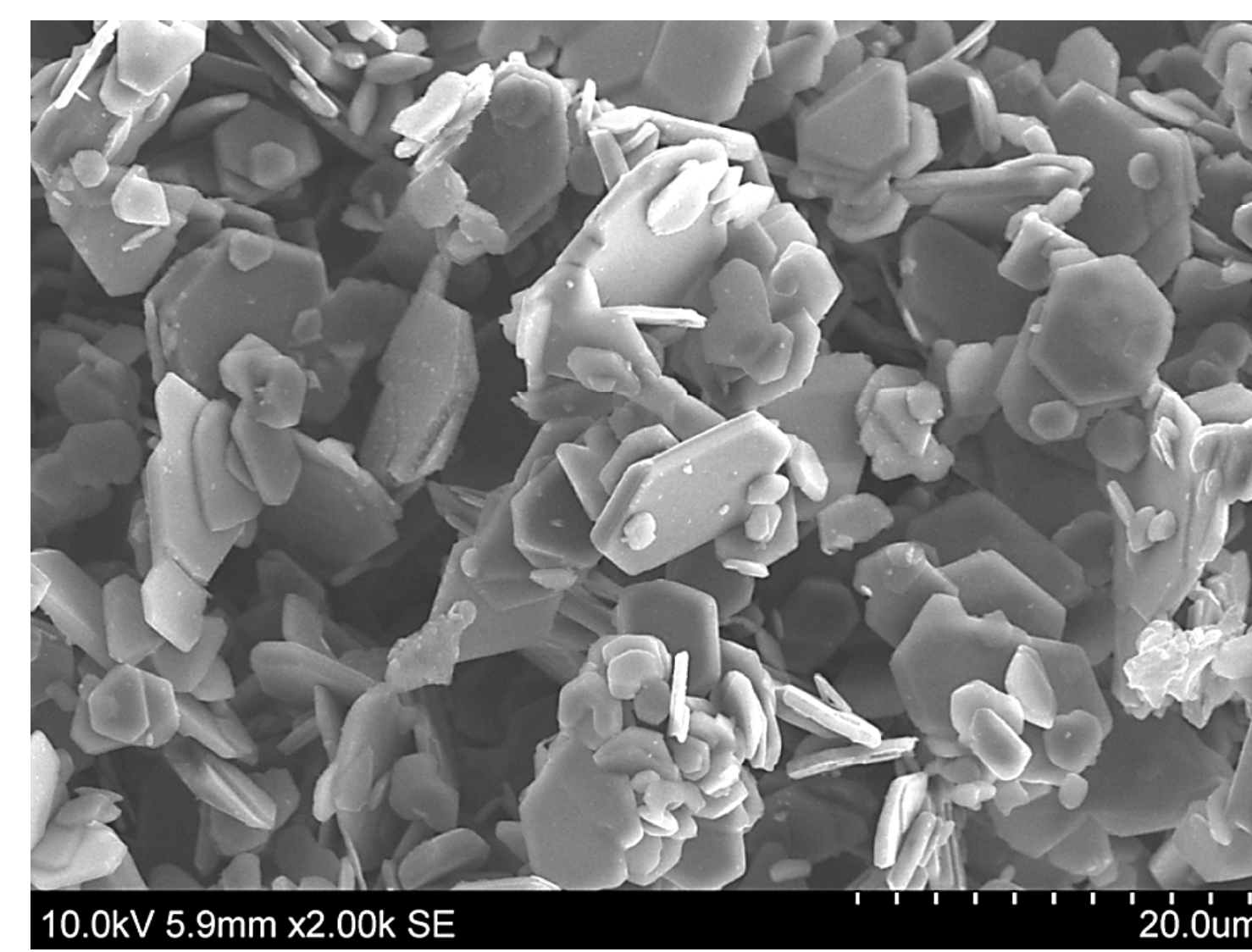


Fig. 1. SEM picture of pure synthesized Monosulfoaluminate

> AFm phases:

- C_4AH_{19} Hydroxy-AFm (OH-AFm)
- $C_2A\dot{S}H_8$ Strätlingite (Str)
- $C_4A\dot{C}H_{11}$ Monocarboaluminate (Mc)
- $C_4A\dot{C}_{0.5}H_{12}$ Hemicarboaluminate (Hc)
- $C_4A\dot{S}H_{14}$ Monosulfoaluminate (Ms)(Fig.1)

> AFt phases:

- $C_4A\dot{S}_3H_{32}$ Ettringite (Ett)



Fig. 2. Glass bottles equilibrated at 5°C and different RH with salt solutions. Pure synthetic samples are aged inside for several months before testing.

4.- Results

Our results show that there are **hydrates which present a high sensitivity to changes in temperature and RH**, being OH-AFm and Ms the most sensitive phases and Mc the most stable. Volume (measured with XRD) and water content (measured with TGA) of **AFm phases at 25°C as function of RH** are shown below. The index denotes the water content of the phases.

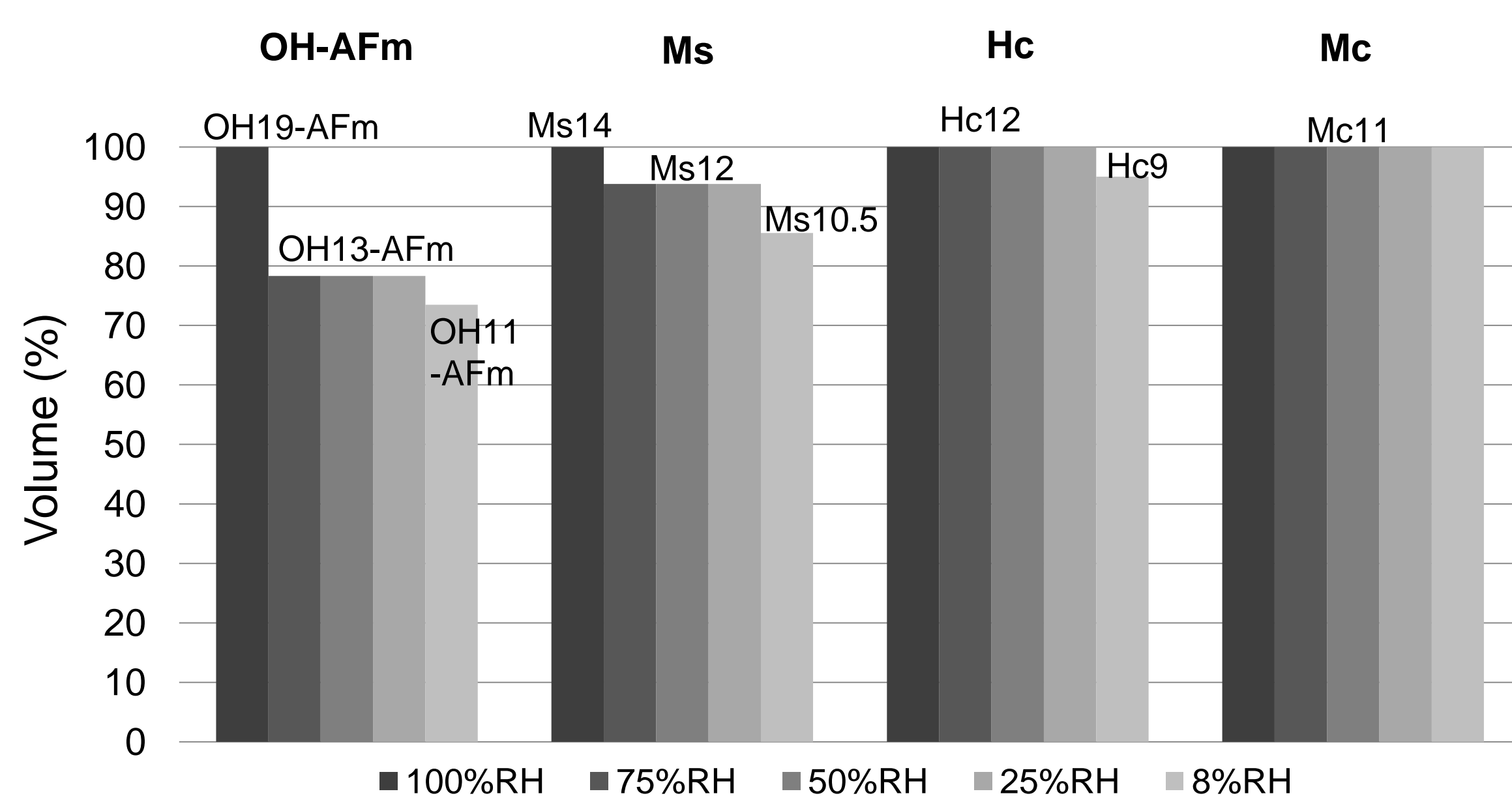


Fig. 3. Volume changes of some AFm phases at 25°C as function of RH.

The **impact of the re-hydration** of one stable (Mc) and one sensitive phase (Ms) is shown below. The samples were aged at 8%RH for several months, then compacted and exposed to 97%RH for several days. Mc shows no dimensional changes, while the Ms sample collapses due to increase of its volume caused by absorption of water (Ms10.5→Ms12).

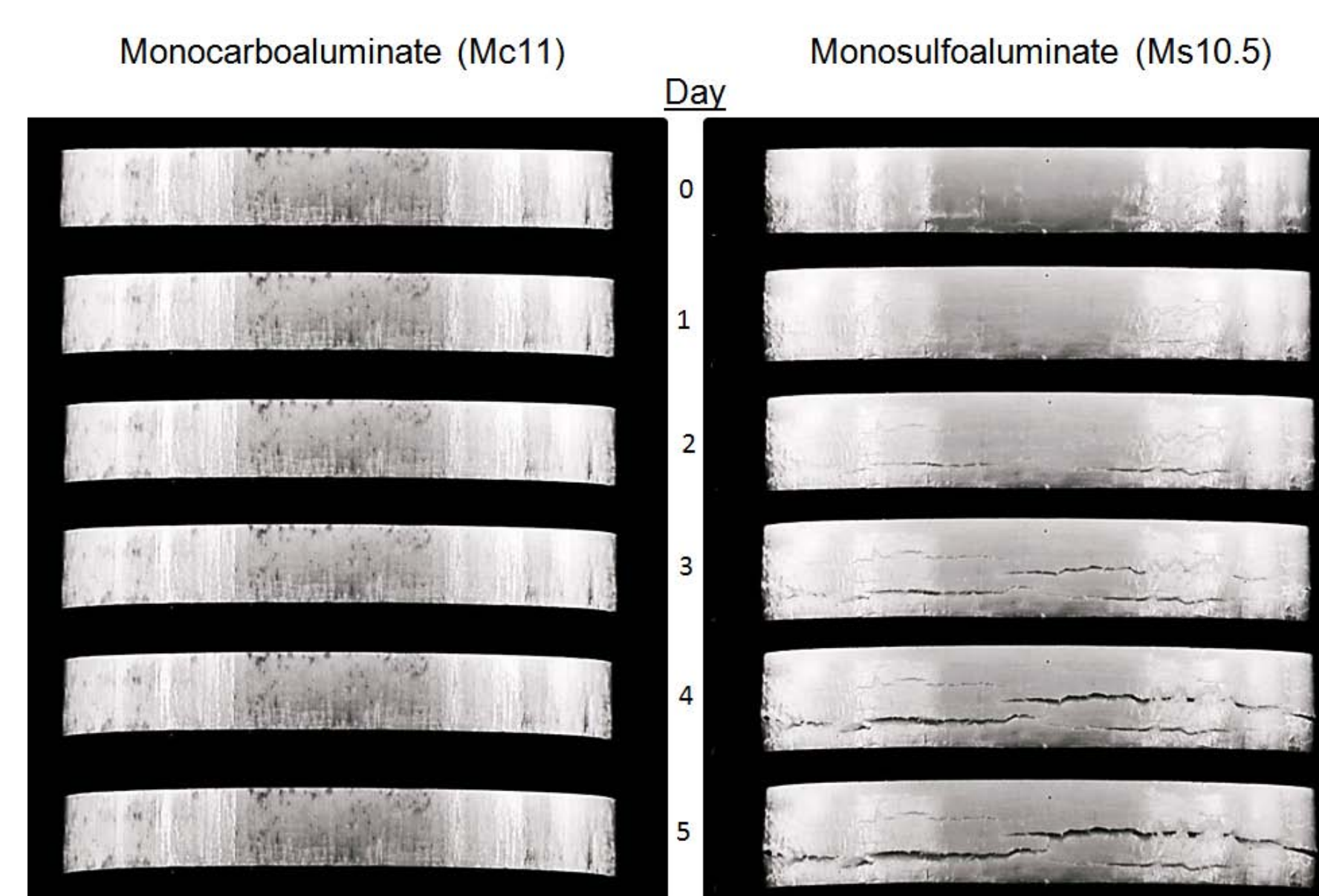


Fig. 4. Compacted Mc and Ms samples (initially aged at 8%RH) exposed to 97%RH

As can be seen **volume changes due to re-hydration** (expansion) of sensitive hydrates can lead to **cracking and collapse** of the compacted sample.

The water content of the different phases at 5°C and 50°C and varying RH will be studied, as well as the impact of de-hydration (shrinkage) in the volume stability of compacted samples.

5.- Thermodynamic modelling

We will use the **water chemical potential approach** to predict hydration states of cement pastes. Under atmospheric conditions $\mu(H_2O)$ is defined as follows:

$$\mu(H_2O) = \mu_{H_2O(l,T)} + RT \ln(a(H_2O))$$

with $\mu_{H_2O(l,T)}$ as chemical potential of liquid water as function of temperature and $a(H_2O)$ as activity of water which can be linked to RH at a given water vapor pressure p and known saturation vapor pressure of water p^0_w according to Raoult's law by: $a(H_2O) = p/p^0_w = RH/100$

Some researchers have used the water chemical potential $\mu(H_2O)$ to determine the stability of some hydrates in cement paste. Albert et al. [2] showed that the stability of monosulfoaluminate increases with reducing water chemical potential, which means a decrease in RH (Fig. 6).

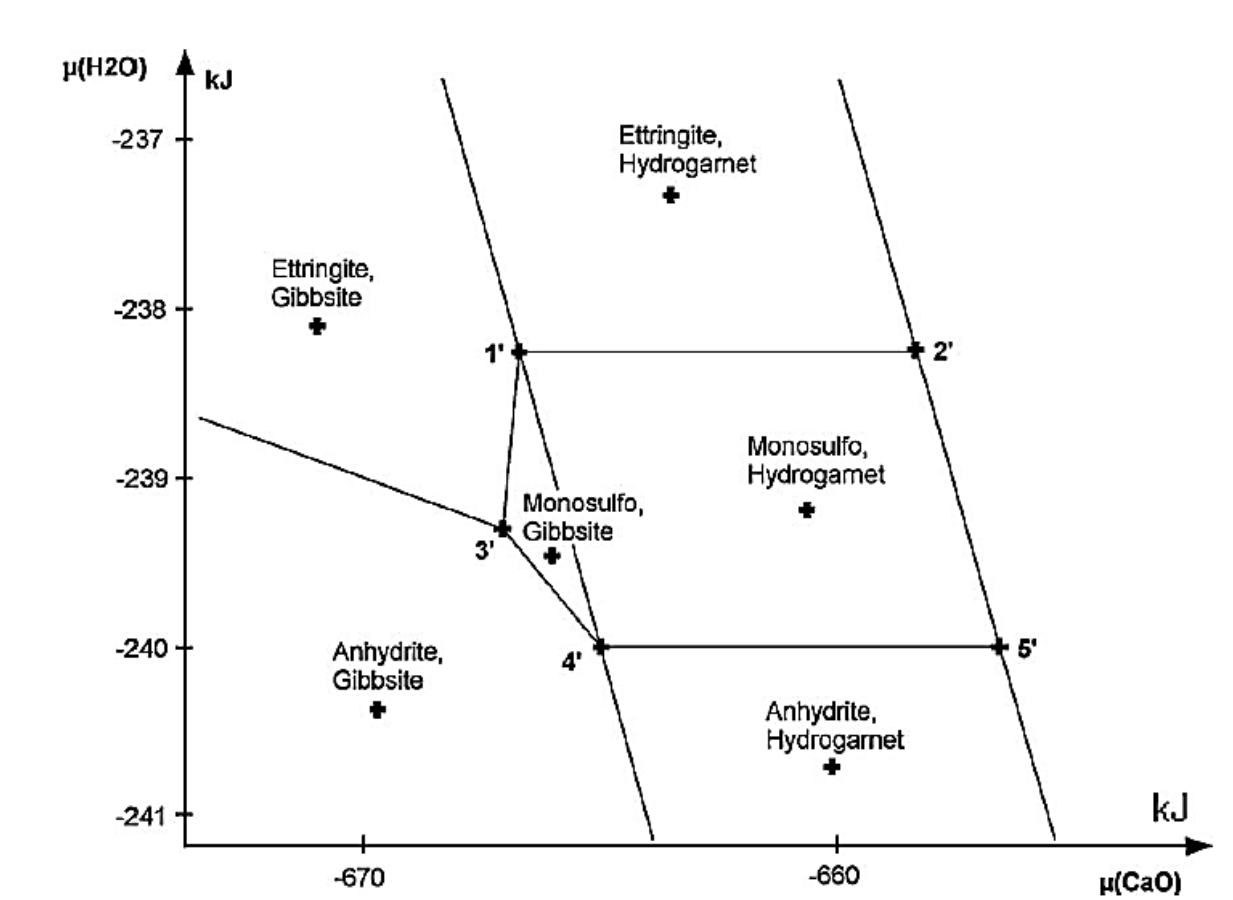


Fig. 6. Diagram ($\mu(CaO)$, $\mu(H_2O)$) at 25°C and 1 bar, showing Monosulfate between 32% and 66% RH [2].

Many available thermodynamic models have been developed in order to explain the phase assemblage of cement hydrates at different temperatures and with mineral additions (Fig. 5). Nevertheless these models are restrained to saturated conditions and do not predict mineralogy and porosity of cementitious systems at $RH < 100\%$ as function of temperature.

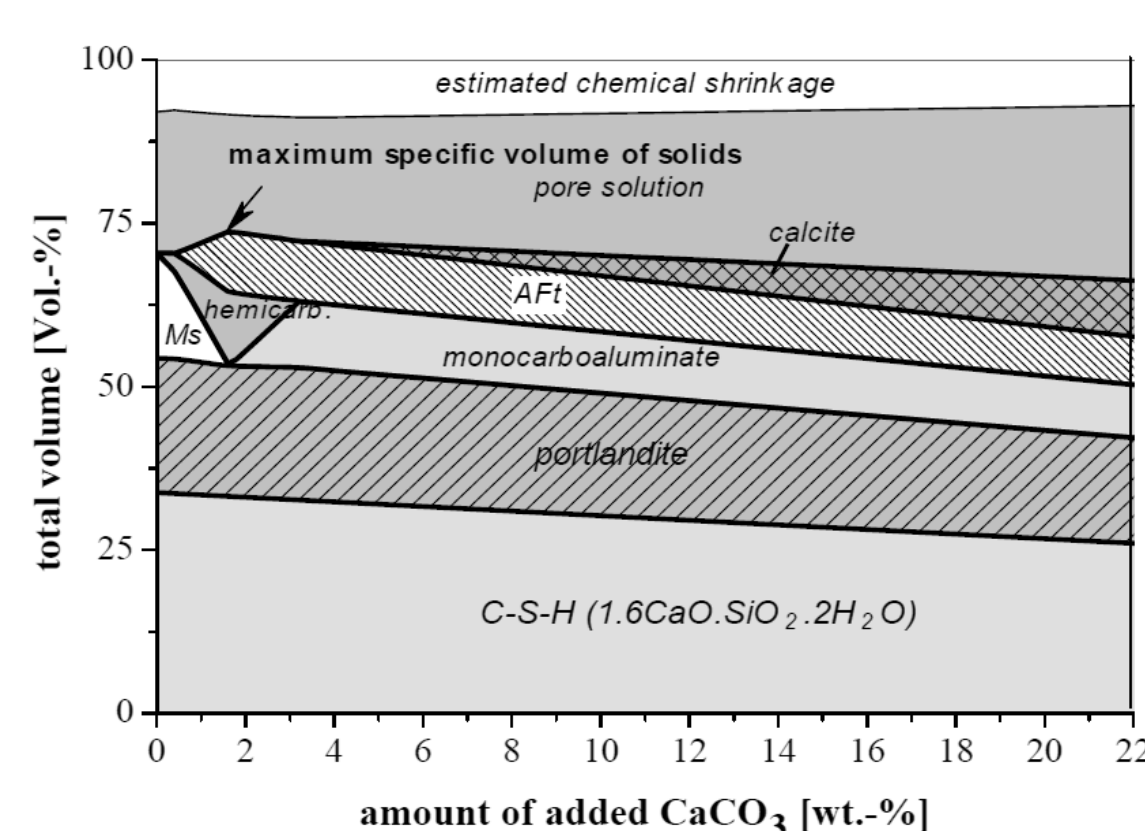


Fig. 5. Modelled volume changes of hydrate phases and pore solution of a hydrated cement with fixed sulfate ratio ($SO_3/Al_2O_3 \sim 0.7$) in dependence of carbonate contents [1].

6. Further Research

Our preliminary results show that the water content in AFm phases follows a function of temperature and relative humidity (RH). As a consequence the specific solid volume of phases like monosulfoaluminate and hydroxy-AFm may change $> 20\%$. On the other hand the water content of carboaluminates varies only marginally. This shows **potential to engineer hydrate phase assemblages which are less sensitive to changing exposure conditions** e.g. wetting-drying, which may positively impact the performance of cements. In addition to AFm phases the water content of ettringite and C-S-H will be studied as well as the impact of changing hydration states of the cement phases on total porosity. A thermodynamic model will be developed in order to predict the hydration states of cement phases as function of water chemical potential.

Abbreviations

XRD: X-ray diffraction
TGA: Thermo gravimetric analysis
DTG: Differential thermogravimetry
FTIR: Fourier transform infrared spectroscopy

DSC: Differential scanning calorimetry
DVS: Dynamic vapor sorption
RH: Relative humidity
T: Temperature

NMR: Nuclear magnetic resonance
SEM: Scanning electron microscope
ESEM: Environmental SEM

C: CaO
S: SiO₂
A: Al₂O₃

Š: SO₃
Ĉ: CO₂
H: H₂O

References

1. Matschei, T., *Thermodynamics of Cement Hydration*, PhD Thesis, University of Aberdeen, 2007
2. Albert, B., Guy, B., Damidot, D., *Water chemical potential: A key parameter to determine the thermodynamic stability of some hydrated cement phases in concrete?*, Cem. Concr. Res. 36, 2006, 783-790.