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

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A native of Ecuador, Luis Baquerizo got his MS in Materials Science and Engineering at the Polytechnic University of Catalonia, Spain, and at the Luleå University of Technology, Sweden, in 2010. He started to work at Holcim on Feb. 1st, 2011.

Project description

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.

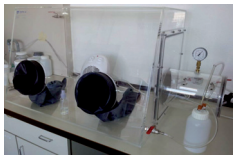
Project results

Methodology

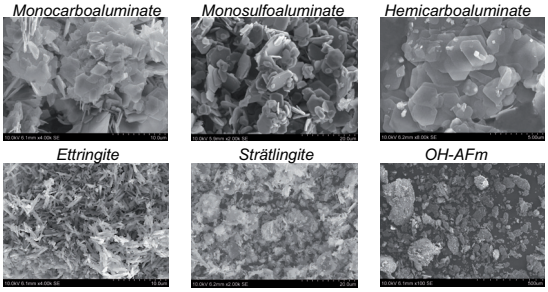
Synthesis of crystalline hydrated phases at high w/s using analytical grade reagent

Aging and conditioning of samples inside glass bottles equilibrated at different RH and T with salt solutions

Preparation of samples inside a glove box **prior characterization** to avoid carbonation



Synthetic cement hydrates

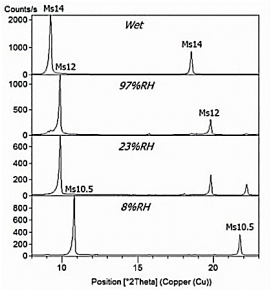


Characterization Techniques and results

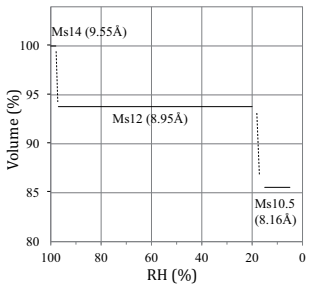
In this section different characterization techniques are shown and we analyzed the results obtained for Monosulfoaluminate (Ms). The following tests have also been done for all the synthesized phases at 25°C. XRD and TGA have been carried out for the samples conditioned at 50°C. The testing of the samples aged at 5°C is still remaining.

X-Ray Diffraction (XRD)

Measurement of the basal space and lattice parameters to calculate **volume** of the lattice.



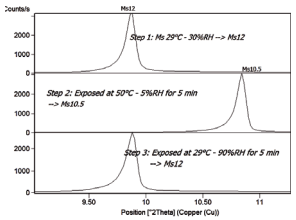
*XRD patterns of Ms14 dried at **25°C** and different RH's.*



Volume changes of Ms as function of RH at 25°C.

XRD – Humidity chamber

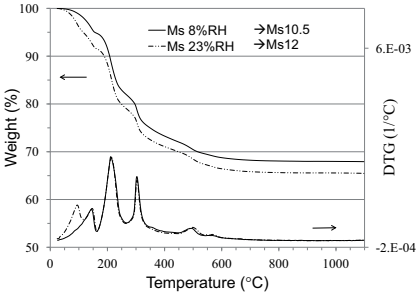
In situ changes of interlayer space when exposed to different T and RH



XRD patterns of reversible volume changes of Ms12 at different exposure conditions.

Thermogravimetric analysis (TGA)

Measurement of **water and CO_2 content**

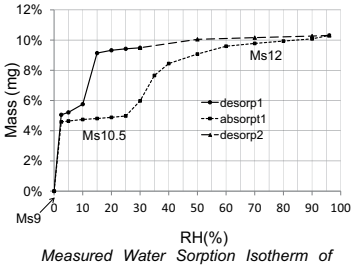


*TGA of Ms dried at **23% and 8%RH at 25°C** showing a water loss that correspond to Ms12 and Ms10.5 respectively.*

Collaboration with Transcend project 6, Mahsa Saeidpour and Lars Wädso, Lund University)

Dynamic Vapor Sorption (DVS)

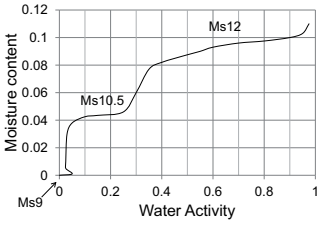
In situ measurement of the mass of **water ad(ab)sorbed or released** with respect to dynamic changes of RH.



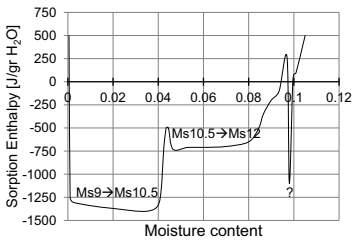
Measured Water Sorption Isotherm of dried Ms

Sorption Calorimetry (SORPCAL)

Measurement of the heat of ad(ab)sorption processes in previously dried samples to **calculate sorption isotherms and enthalpies of rehydration**



Calculated Sorption Isotherm with SorpCal , showing qualitatively and quantitatively similar results obtained experimentally with DVS

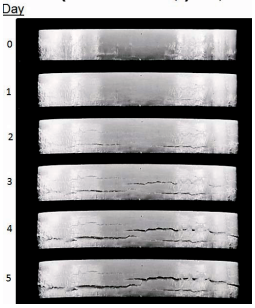


Calculated Sorption enthalpy with SorpCal

Calculated Heat of Absorption

Ms9 → Ms10.5	Ms10.5 → Ms12
= -1350 J/gH_2O	= -680 J/gH_2O
= -68.53 kJ/mol H_2O	= -56.45 kJ/molH_2O

Crystal Swelling (camera test)



The impact of re-hydration on Monosulfoaluminate (Ms) is shown above. The sample was aged at 8%RH for several months as a powder, then compacted and exposed to 97%RH for several days. The sample collapses due to swelling of the crystals caused by absorption of water (Ms10.5→Ms12).

ACKNOWLEDGMENTS: 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 Group Support Ltd. for actively promoting cement research, especially the Innovation Function and the Analytical Lab of the Materials Technology Department.

Project results

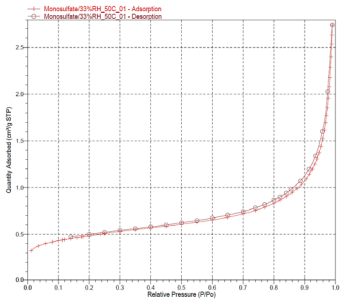
N_2 BET measurements in synthetic hydrates

BET measurements were carried out with a ASAP 2020 Surface Area and Porosity Analyzer

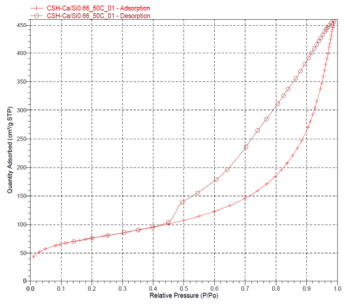
No remarkable hysteresis is observed in the crystalline phases

BET surface area of AFm and AFt phases is much lower compared to C-S-H

Sample	BET surface area [m2/g]
Monosulfoaluminate	1.55
Monocarboaluminate	5.14
Hemicarboaluminate	2.72
Strätlingite	17.01
Ettringite	6.14
C-S-H 0.66	266.58



N_2 Sorption isotherm of Ms



N_2 Sorption isotherm of C-S-H 0.66

Identification of invariant points – Calculation of Heat of desorption/absorption

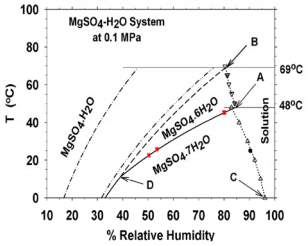
A method was developed in order to determine the exact invariant point (RH value) at which a desorption/absorption process occurs at a specific temperature.

Apart of being an important experimental data, it will allow us to **calculate the enthalpy of desorption/absorption in pure hydrated phases**, in order to **simulate the phase assemblage and change in total porosity of a cementitious system exposed at different drying conditions**

Validation of the method: MgSO4 – H2O system

1. Prepare a mixture of two hydration states of the same salt in a closed container, seal it and record the RH when equilibrium is reached at minimum 3 temperatures:

2. Superpose the observed invariant points (red dots in the graph) over an existing T vs RH phase diagram of the studied salt [1]:



3. Calculate the enthalpy of **desorption/ absorption using the Van't Hoff equation** for the studied absorption/desorption process:

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

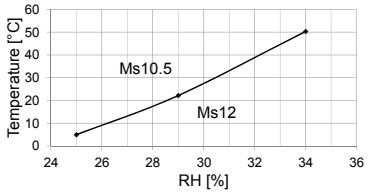
$MgSO_4 \cdot 7H_2O(s) = MgSO_4 \cdot 6H_2O(s) + H_2O(g)$

ΔG_r° [kJ/mol]	ΔH_r° [kJ/mol]	Reference
10.15	60.14	This study
10.13 ± 0.07	59.72 ± 0.76	Chou and Seal [1]
10.89 ± 1.4	59.95	DeKock [2]

Example: Monosulfoaluminate

Calculate the enthalpy of the following absorption process: $Ms10.5 + 1.5H_2O = Ms12$

1. Prepare a mix of Ms12 + Ms10.5
2. Measure the invariant points at 3 Temperatures



3. Calculate the ΔH_r

$Ms12(s) = Ms10.5(s) + 1.5H_2O(g)$

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

$\ln K = \ln[a(Ms12) \cdot a(H2O)^{1.5} / a(Ms10.5)]$

ΔH_r**= - 49.05 kJ/mol**

Measured Enthalpy with SORPCAL

ΔH_r**= -56.45 kJ/mol**

What I am planning to do for the remaining time

- Finish XRD tests of samples at 50°C
- Start the XRD test of samples at 5°C in the humidity chamber to avoid condensation
- Invariant point measurements of all the hydrated phases at 3 different temperatures: 5°C, 25°C, 50°C
- Comparison between the measured enthalpies with SORPCAL and the calculated with the Invariant point method in all the synthetic hydrates
- Derivation of a thermodynamic database of hydration states of cement hydrates
- Development of a thermodynamic model capable of predicting the phase assemblage (mineralogy) and change in porosity of a cementitious system exposed at different drying conditions

Outstanding questions

- CSH density as function of RH and Temperature?
- Hysteresis in water sorption isotherms of crystalline materials. Why it happens in some of them?
- Hysteresis in N_2 sorption isotherms of crystalline materials. Why it is not significant?
- Kinetics issues in absorption/desorption of water in crystalline cement hydrates
- Swelling pressure due to absorption of water
- Which software package is capable of thermodynamic modelling at water activities below 1 (unsaturated conditions)?

References

1. Chou, I.M., Seal II, R.R., 2003c, Determination of epsomite-hexahydrite equilibria by the humidity-buffer technique at 0.1MPa with implications for phase equilibria in the system MgSO4-H2O, Astrobiology 3, 619-630.
2. DeKock, C.W., 1986, U.S. Bureau of Mines Information Circular 9081: Thermodynamics Properties of Selected Transition Metal Sulphates and Their Hydrates, U.S. Bureau of Mines, Washington , DC.

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