

## MODERN *IN-SITU* XRD INVESTIGATIONS ON C<sub>3</sub>S - C<sub>3</sub>A - GYPSUM SYSTEMS

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The origin of cement, employed as a binding material, can be attributed to the Romans who found that a mixture of lime and crushed volcanic tuffs was able to set under water, the resistance being increased with time in a way completely different to any other material. Since ancient times, a huge amount of different kinds of cements have been produced to satisfy the request of different mechanical behaviors. To deeply understand the mechanisms that lead to the development of mechanical strength, the reaction kinetics occurring during the hydration process must be known. Nowadays, we can affirm that cement research has set many important results but despite of this “long-time story”, a lot of improvements are required to better understand the mechanisms involved in the hydration process.

Cements mixed with water are complex systems undergoing critical chemical and physical changes during the hydration process. A unique hydration model able to explain the controlling mechanisms is the main purpose of cement research, but the physical-chemical parameters involved are actually too many. To partly overcome the chemical complexity of common cement materials, simplified cement systems are often used for research purposes. This PhD thesis is part of a wide-range research project that is aimed to investigate the fundamental reactions occurring during the hydration process of cement. The project involves 3 different partners: NIST (National Institute of Standards and Technology), W.R. GRACE and University of Padua. Our part of the project was to collect X-ray powder diffraction patterns on hydrating cement pastes, using the Rietveld method for quantitative phase analysis.

Three simplified cement systems formed by the synthetic phases tricalcium silicate Ca<sub>3</sub>SiO<sub>5</sub> (C<sub>3</sub>S), tricalcium aluminate Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (C<sub>3</sub>A) and a varying amount of gypsum CaSO<sub>4</sub>·2H<sub>2</sub>O (C $\check{S}$ H<sub>2</sub>) were investigated by means of laboratory *in-situ* X-ray powder diffraction (XRPD) and isothermal calorimetry (IC) in order to evaluate dissolution-precipitation kinetics (Table 1). The main hydration products detected by means of XRPD were ettringite, hemicarboaluminate, portlandite, Ca-Si hydrates (C-S-H): the same occurring in real cements.

Table 1 - Resume table of measured samples and experimental techniques significant data.

Mix	C <sub>3</sub> S Mass ratio	C <sub>3</sub> A Mass ratio	Gypsum Mass ratio	Meas. Time (h)	XRPD	IC
MIX 1	80	20	2.3	27	- Raw materials blended by NIST - w/c=0.5	- 20 °C 23 °C 26 °C 32 °C
MIX 2	80	20	4.3	83	- Cap 0.3mm - T = 23 °C - Δt <sub>meas</sub> : 20 min	- w/c=0.5  - T=23 °C
MIX 3	80	20	6.3	106		

While isothermal calorimetry gives an insight into the development of heat flow during hydration, laboratory *in-situ* XRPD offers the possibility to determine the evolution of crystalline phases as a function of hydration time (Fig. 1). The focusing capillary geometry guarantees the insulation of the sample and the combination with a high-sensitivity position sensitive detector permits fast measurements, suited for the kinetics analysis (Fig. 2).

A clear correlation between *in-situ* XRPD data and isothermal calorimetry data can determine the contribution of each crystalline phase to the heat release during hydration (Fig. 3). A first attempt on calculating the theoretical released heat is based on the evolution of the Rietveld scale factors and the reaction enthalpy values of the ongoing dissolution/precipitation reactions. In particular, the theoretical released heat is the sum of the derivatives of dissolving or precipitating phases multiplied by their respective dissolution or precipitation enthalpy (1).

$$\begin{aligned} \frac{dQ}{dt} = & \frac{dn_{C_3S}}{dt} \cdot \Delta H_{dissC_3S} + \frac{dn_{C_3A}}{dt} \cdot \Delta H_{dissC_3A} + \frac{dn_{Gypsum}}{dt} \\ & \cdot \Delta H_{dissGypsum} + \frac{dn_{C-S-H}}{dt} \cdot \Delta H_{precC-S-H} + \frac{dn_{CH}}{dt} \cdot \Delta H_{precCH} \quad (1) \\ & + \frac{dn_{Ettringite}}{dt} \cdot \Delta H_{precEttringite} + \frac{dn_{Hemicarb}}{dt} \cdot \Delta H_{precHemicarb} \end{aligned}$$

The derivative of the mole number for each phase is given by the derivative of the Rietveld scale factor multiplied by the number of formula units present in the unit cell (Merlini *et al.*, 2007) (2).

$$\frac{dn_i}{dt} = \frac{dSF_i}{dt} \cdot Z_i \quad (2)$$

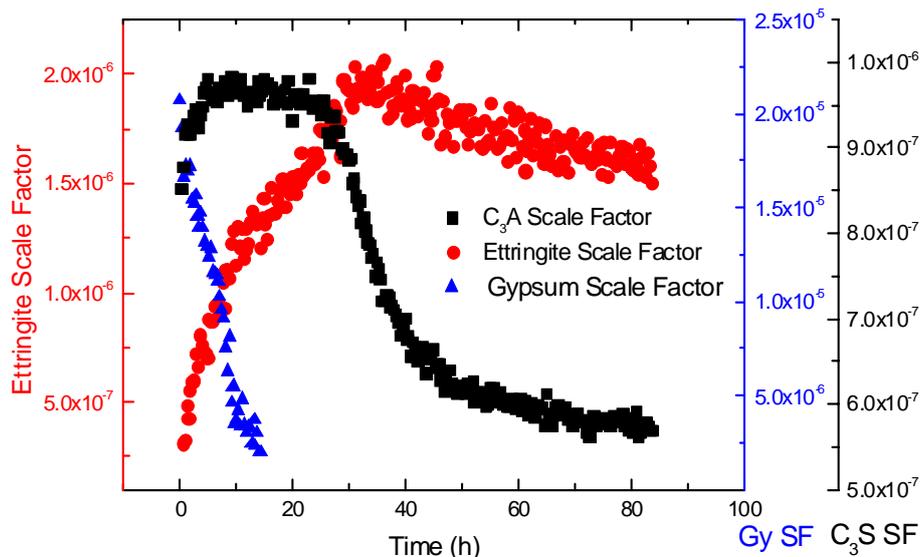


Fig. 1 - Correlation between C3A-gypsum dissolution and simultaneous ettringite precipitation.

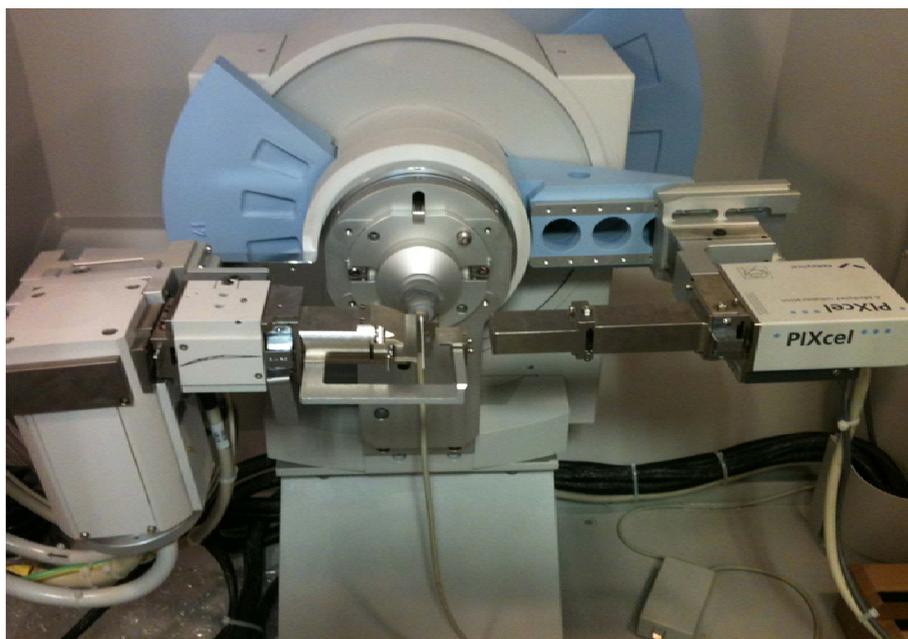


Fig. 2 - Instrument setup for laboratory *in-situ* X-ray powder diffraction (XRPD). From left to right: X-ray tube, focusing Si-W mirror, boron-glass capillary and position-sensitive detector.

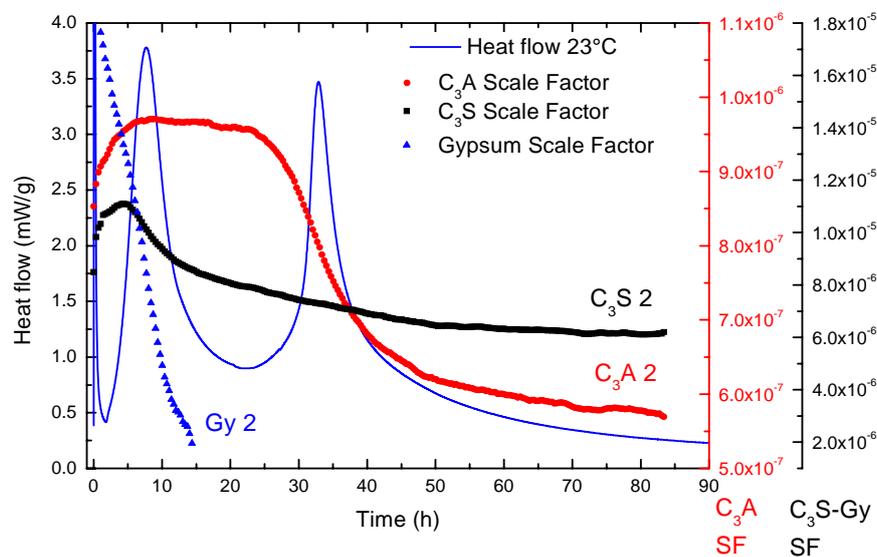


Fig. 3 - Correlation between dissolving phases and the released heat flow.

The agreement between the measured and the calculated heat flow is significant for mix 2 (Fig. 4) and mix 3 (Fig. 5), probably because the scale factors of each phase are well calculated. The calculation of a theoretical heat flow is particularly useful for those samples that cannot be prepared for a calorimetric experiment (*i.e.*, when the amount of material is too low).

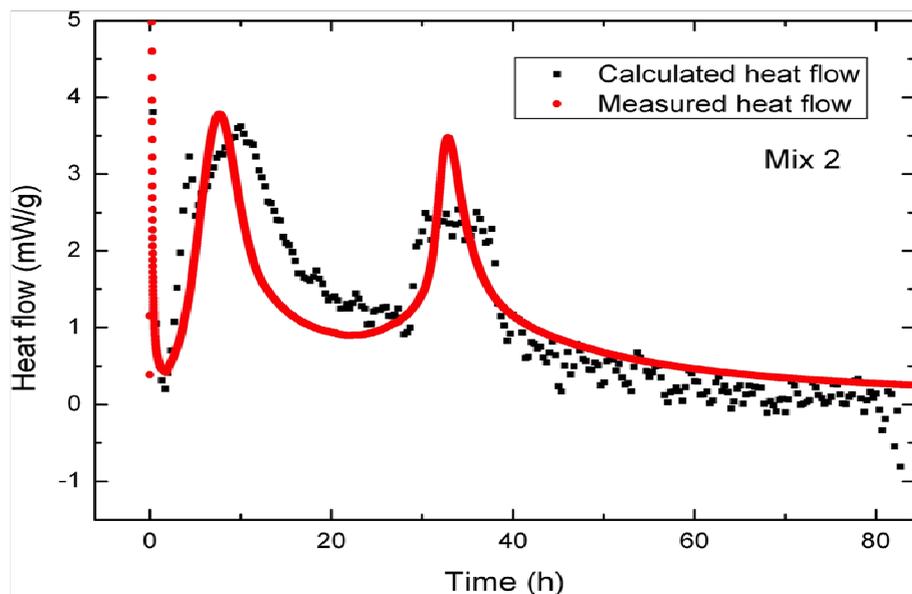


Fig. 4 - Comparison between measured (red dots) and calculated heat flow (black squares) for mix 2.

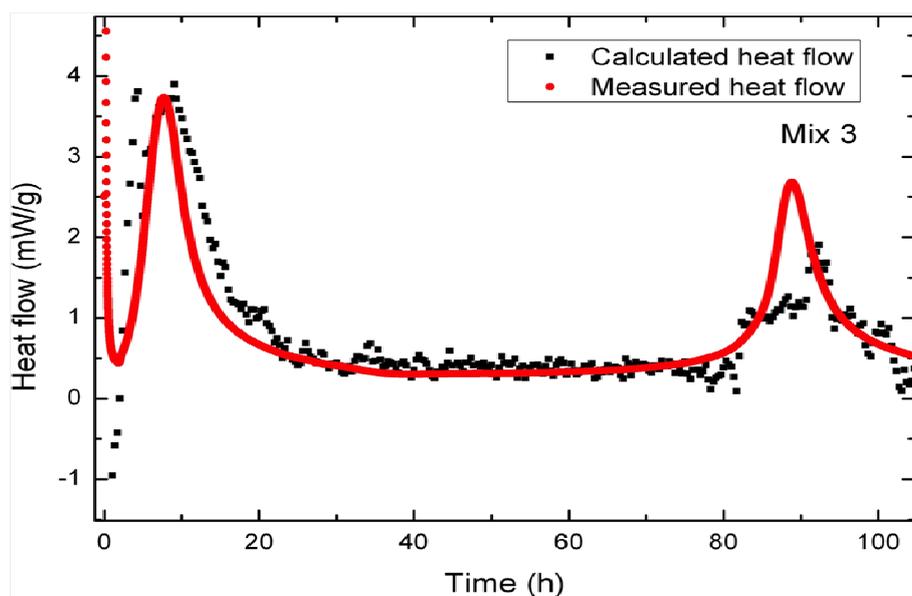


Fig. 5 - Comparison between measured (red dots) and calculated heat flow (black squares) for mix 3.

The obtained experimental data will serve as reference data for testing the reliability of numerical modeling (HydratiCA) performed on the same systems. The software has been tested and returned satisfactory results for further simplified systems, such  $C_3S$ -Gy. Nevertheless, the software is still under a development stage and improvements have to be planned for  $C_3A$ -Gy systems before testing more complex blends.

#### REFERENCES

Merlini, M., Artioli, G., Meneghini, C., Cerulli, T., Bravo, A., Cella, F. (2007): The early hydration and the set of Portland cements: *In situ* X-ray powder diffraction studies. *Powder Diffr.*, **22**, 201-208.