ESRF	**Experiment title:** **Influence of superplasticizers on the kinetics of hydration of Portland cements**	**Experiment number**: CH-1221
Beamline: BM08	**Date of experiment**: from: 07/04/2002 to: 11/04/2002	**Date of report**:
Shifts: 12	**Local contact(s)**: Carlo Meneghini	*Received at ESRF:*

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Report:

The rheological and mechanical properties of a cement depend on the chemical reactions occurring during the hydration process; in fact nucleation and growth of the hydrate phases play an important role in determining the texture of the hydrate paste. Inorganic or organic additives, like naphtalene-sulphonates and acrylic polymer based superplasticizers used in this study, influence the kinetics of the chemical reactions.
Our experiments consisted in time-resolved powder diffraction study on in-situ hydrated cement paste, in order to follow some chemical reactions occurring during the first 6-7 hours.
Samples of ordinary Portland Cement (OPC) were contained in a glass capillary; water or solution containing additives, were injected by a peristaltic pump. To increase the kinetics of the system, the specimen was manteined at a temperature of 40 °C by an hot air heater.
Data were collected by a translating image plate, to achieve an appropriate time resolution.

The reactions occurring in the first hours during the hydration af a Portland cement are schematically [1-2]:

Al-phases (mainly C3A, C4AF) + gypsum + H2O - > ettringite (C3A*3CaSO4*32H2O) (1)
C3S + H20 - > C-S-H + CH (2)
Ettringite + C3A - > Afm phases (C3A*CaSO4*10-14H2O) (3)

Reaction (3) occurs when no more Ca-sulphate is available in the system.

Fig. 1 shows the diffractograms obtained by integration of image plate related to the isothermal hydration of OPC at 40 °C.
The integrated area of the Bragg peacks, scale factor and the calculated weight fractions obtained by profile fitting and Rietveld method on the X-ray diffractograms, were used to follow the kinetics of the chemical reactions involved (fig 2).
Fig. 3 shows the amount of ettringite formed in time in systems in contact with pure water and solutions of commercial naphtalene sulphonate and acrylate based superplasticizer in different concentrations and, for comparison, with solution of an Al-sulphate based accelerating agent.

The higher amount of ettringite in the first stages of the process in system containing superplasticizer could be related to the different morphology and density of the gel initially formed and finally to the rheological behaviour of the cement paste. The different rate of ettringite formation in all systems with superplasticizer, suggest the possibility that these additives could be adsorbed on the surface of this phase and that they control the diffusion of ions through the gel formed during the hydration process. The occurrence of Afm phase after 5 hours in the system hydrated with naphtalene sulphonate plasticizer, reveal the possibility of the presence of an amorphous phase, sometimes called 'organo-mineral phase', rich in polymers and sulphates, limiting the availability of sulphate in the system.

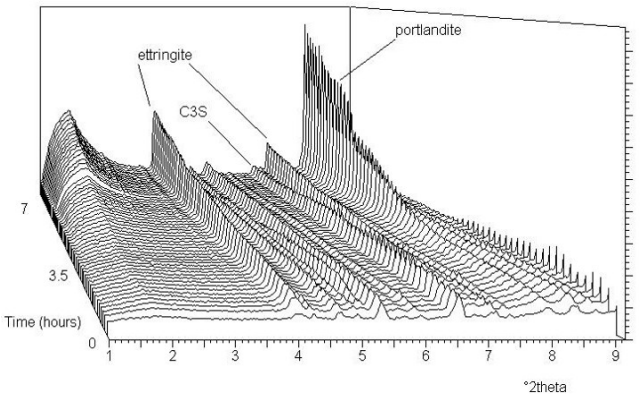

Fig.1 – XRPD patterns obtained by integration of the image plate. The experiment is related to the i situ hydration of OPC at 40 °C

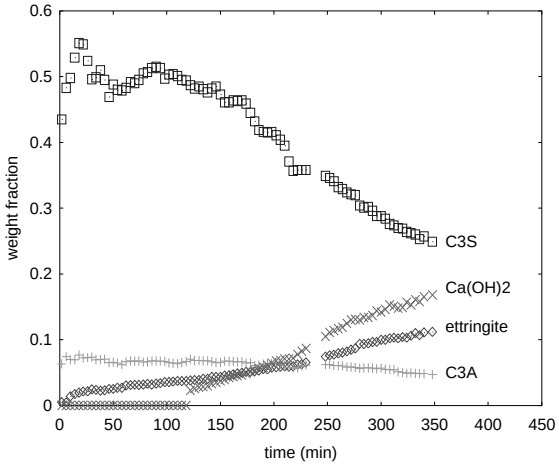

Fig. 2 – Plot of the calculated weight fraction of some clinker and hydrated phases from Rietveld refinements, using the GSAS software [3].

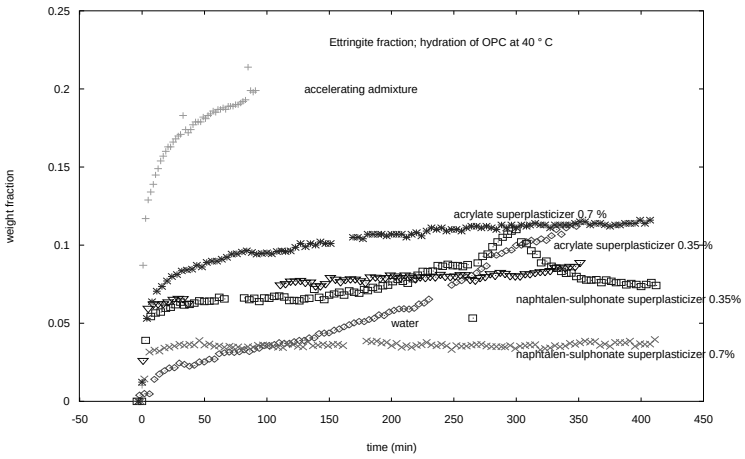

Fig. 3 – Plot of the Ettringite calculated weight fraction during hydration of OPC with different admixtures

REFERENCES

[1] Taylor, H.F.W. (1990). Cement Chemistry, Academic Press, New York

[2] Bensted J. & Barnes P. Ed.(2001). Structure and Performance of Cements, 2nd Ed., Spon Press, London & New York

[3] Larson A.C. & Von Dreele R.B. (1988). Los Alamos National Laboratory Report LAUR 86-748