




## Experiment Report Form

 <b>ESRF</b>	<b>Experiment title:</b> Pozzolanic reaction mechanisms in zeolite- Portland cement mixtures using in situ synchrotron X-ray powder diffraction	<b>Experiment number:</b> MA-1055
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 23/04/2010 to: 26/04/2010	<b>Date of report:</b> 21/01/2011
<b>Shifts:</b> 9	<b>Local contact(s):</b> Adrian Hill	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b>  Ruben Snellings*, Gilles Mertens*, Rieko Adriaens* Dept. of Earth and Environmental Sciences, KULeuven, Belgium		

### Report:

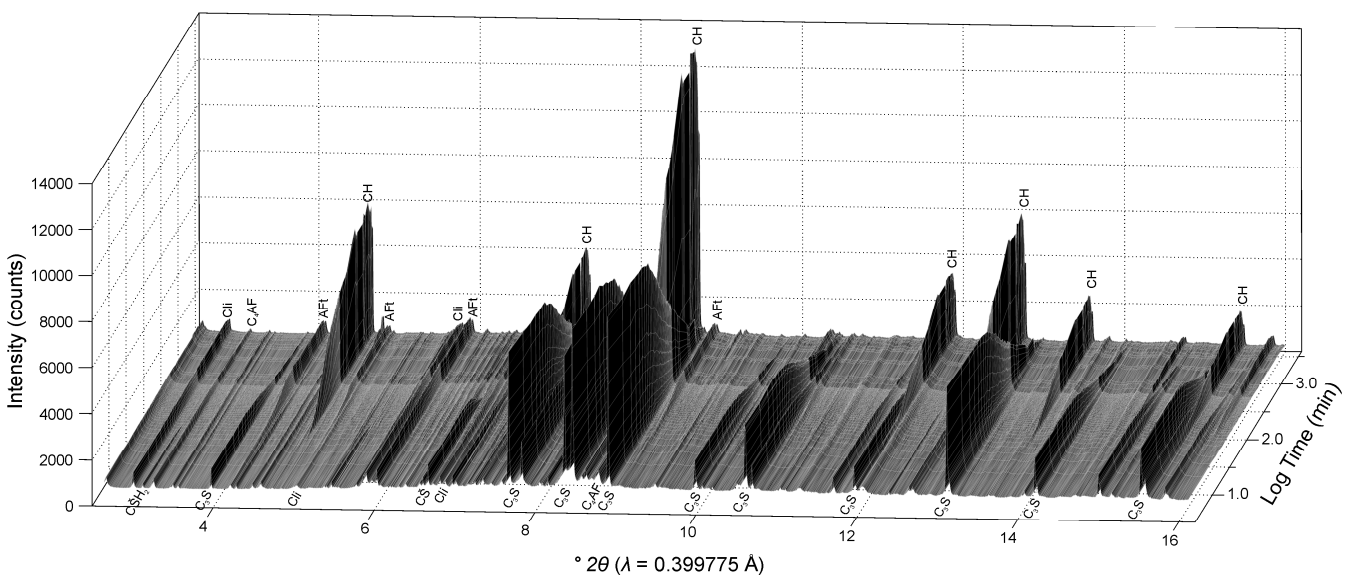
### Introduction

Addition of fine materials with an elevated specific surface has been observed to accelerate the hydration of the main clinker phases by providing additional nucleation centres for reaction products, thereby lowering the concentrations of dissolved species at the disintegrating surface (e.g. Massazza, 2001; Korpa et al., 2008). Moreover, the concentration of active surface sites is linked to the density of point, linear, and planar defects in a mineral (Juilland et al., 2010). Zeolites of high crystallinity, i.e. containing large domains exempt of planar defects, and low defect density were observed to be less pozzolanically reactive and did not accelerate the hydration of the clinker minerals to the same extent as zeolitic material of lower crystallinity (Snellings et al., 2010). This could indicate that a relationship might exist between the crystallinity of a material and its surface properties that furnish nucleation sites or govern the susceptibility to dissolution. In this study, the effect of material crystallinity on cement hydration has been investigated by mixing a zeolite and a quartzite material with similar particle size distributions but very different crystallinity indices with Portland cement.

In practice, the utilization of highly-reactive pozzolans of elevated fineness such as finely ground zeolitites or microsilica necessitates the utilization of water reducing agents, so-called superplasticisers, in order to obtain optimal binder strength performance without compromising the initial fluidity or workability of the mix. However, the adsorption of the organic superplasticiser molecules to the surface of both cement and pozzolan particles may alter the early hydration of the blended cements profoundly (Chandra, 2002). Therefore, this investigation intends to extend the findings of earlier research by in situ synchrotron X-ray diffraction on the hydration of zeolite blended cements to mixtures containing a polycarboxylate ester (PCE) superplasticiser.

## Results

A comparison was made between the early-age hydration of cements blended with micronized zeolite and quartzite powders. The Portland cement replacement in the mixes was 30 %, and the effect of introducing a superplasticiser to lower the required water to solid ratio was assessed. The cement pastes were hydrated at 40 °C and monitored in situ by time-resolved synchrotron X-ray powder diffraction combined with Rietveld quantitative phase analysis. Fig. 1 shows a stack of synchrotron X-ray powder diffraction (SR-XRPD) patterns for the zeolite blended cement.

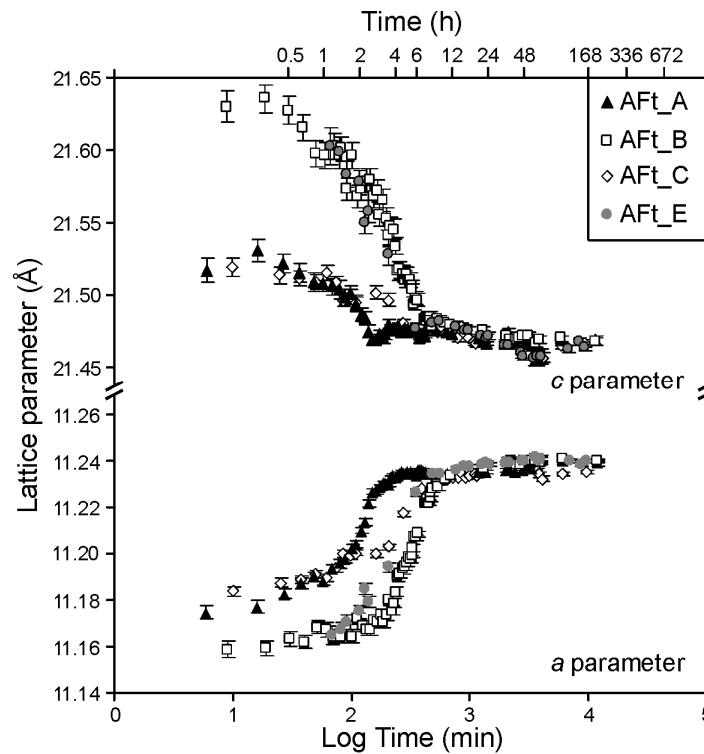


**Fig. 1.** Stack of synchrotron beam current decay corrected time-resolved SR-XRPD data for the zeolite blended cement (paste A) up to 48 hours of hydration. The main reflection positions in the 2–16° 2θ region are indicated (Cli : clinoptilolite). The intensities of the anhydrous cement phases decrease sharply and the formation of crystalline (AFm, AFt and CH (Ca(OH)<sub>2</sub>)) hydration products is noticeable.

The quantitative evolution of phase weight fractions showed that the addition of the zeolite tuff advanced both the onset of setting and accelerated the hydration rate of the main C<sub>3</sub>S cement component. Blending with the quartzite powder of similar fineness did not affect the onset of setting and hydration rate. Reduction of the water to solid ratio by introduction of the superplasticiser had a retarding effect on the hydration of the zeolite-blended cement over the early hydration period up to 3 days.

The hydration products of the clinker silicate phases in zeolite-blended cements are Ca(OH)<sub>2</sub> (CH, cement chemistry notation) and the calcium-silicate-hydrate (C-S-H) phase. The accelerated hydration of the C<sub>3</sub>S phase was paralleled by the precipitation of CH and C-S-H. During the first 48 h of hydration a linear relationship exists between the amount of C<sub>3</sub>S consumed and the amount of CH formed. After this period, in the zeolite-blended cement pastes, the linear relationship was lost due to the consumption of CH in the pozzolanic reaction. In the reference cements and the quartzite-blended cement the linearity was retained over the entire period of experimentation. In both the CH as the C-S-H phases structural evolutions during hydration were identified. The analysed trends were very similar to the results reported in a previous study (Snellings et al., 2010).

The AFt or ettringite reaction products, formed promptly after the addition of water to the mixtures, underwent a crystal structural modification over the induction period up to 4 to 6 hours of reaction (Fig. 2). The continuous contraction of the *c*-cell parameter and expansion of the *a*-cell parameter towards the ideal values for AFt or ettringite might reflect the structural adaptation of the AFt to the changing pore fluid chemistry. The observed structural changes were less pronounced in the zeolite blended cement indicating that a modification of the pore fluid chemical composition by zeolite cation exchange of surface adsorption of dissolved species on the zeolite particles can affect the AFt structural evolution.



**Fig. 2.** Evolution of the AFt lattice parameters during the first hours of reaction in mixtures A (zeolite Portland cement), B (Portland cement), C (zeolite:Portland cement:superplasticiser) and E (quartzite:Portland cement). The utilization of zeolite as a blending component significantly shifts the AFt lattice parameters compared to the quartzite blended and reference Portland cements. This could point to a modification of the aqueous phase composition by zeolitic cation exchange content or adsorption on active surface sites of the zeolite grains.

## References

- Chandra S. (2002) Properties of concrete with mineral and chemical admixtures. Pp 140-185 in: *Structure and Performance of Cements* (J. Bensted & P. Barnes, editors). Spon Press, London.
- Juilland P., Gallucci E., Flatt R. & Scrivener K. (2010) Dissolution theory applied to the induction period in alite hydration. *Cement and Concrete Research*, **40**, 831-844.
- Korpa A., Kowald T. & Tretting R. (2008) Hydration behaviour, structure and morphology of hydration phases in advanced cement-based systems containing micro- and nanoscale pozzolanic additives. *Cement and Concrete Research*, **38**, 955-962.
- Snellings R., Mertens G., Cizer Ö. & Elsen J. (2010) Early age hydration and pozzolanic reaction in natural zeolite blended cements: Reaction kinetics and products by in situ synchrotron X-ray powder diffraction. *Cement and Concrete Research*, **40**, 1704-1713.
- Massazza F. (2001) Pozzolana and Pozzolanic Cements. Pp 471-635 in: *Lea's Chemistry of Cement and Concrete* (P.C. Hewlett, editor). Butterworth-Heinemann, Oxford.