



**Experiment title:**

Kinetics of crystallisation and diffusion in ceramic hydrogeological systems

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CH-1118

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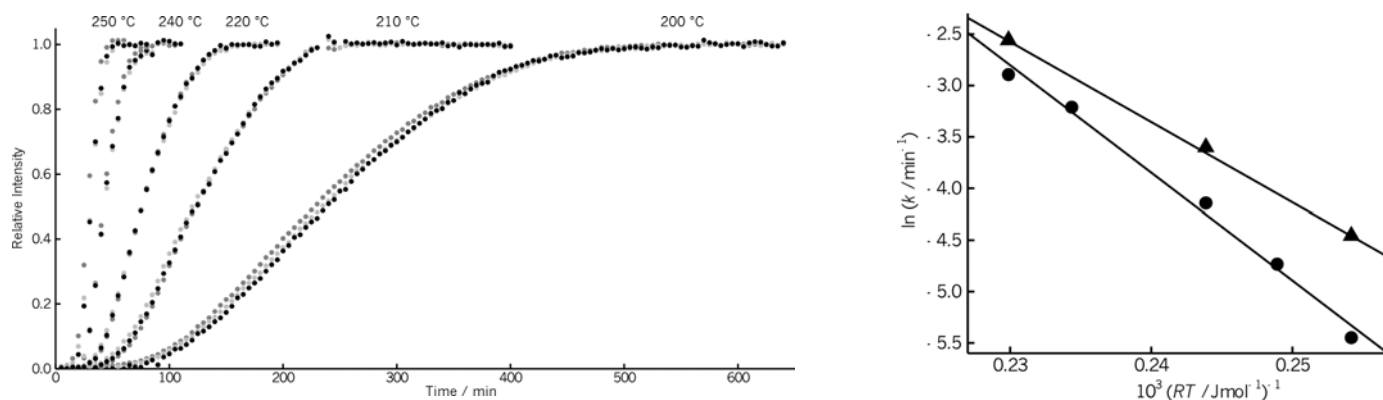
**Report:**

The aim of this experiment was to obtain high quality *in situ* kinetics data from time-resolved energy-dispersive diffraction (EDD) experiments that require high energy photons and/or spatial discrimination within the active sample: Three experimental systems were proposed:

1. the hydrothermal pre-crystallisation of pure and Ce/La-doped zirconia under autoclave conditions;
2. the kinetics of hydrothermal crystallisation of a zeolite in the vicinity of an alumina ceramic substrate;
3. determination of the kinetics of diffusion of a tracer solution through a prototype calcite rock.

In this report we will discuss the results on Nos.1 and 3, the data from No.2 having already been subsumed by a previous report (HS1258).

**Hydrothermal pre-crystallisation of pure and Ce-doped zirconia under autoclave conditions**



**Figure 1:** *left;* Example of normalised (zirconia) crystallisation plots, 200-250°C, using *in situ* EDD peaks at 59.9 keV, 97.8 keV and 113.9-115.2 keV. *right;* Standard Arrhenius plots,  $\ln [k]$  versus  $1/T$ , for pure (●) and cerium-doped (▲) zirconia crystallisations; the latter indicates a significantly lowering in the activation energy ( $2\theta$ -angle =  $4.0^\circ$ ; acquisition time = 300 s).

The preliminary results obtained on the crystallisation of zirconia from zirconium hydroxide showed no significant variation with sampling position across the autoclave cell diameter. Spatial discrimination was therefore not important for this particular experiment. However, the high energy white beam was crucial since the absorbing nature of the cell and sample (2 mm steel walls, 10 mm zirconium hydroxide/zirconia) reduced the EDD patterns to effectively zero intensity for photon energies below 50 keV. Above 50 keV, high quality data were obtained with negligible differences between the normalised integrated intensities for different reflections (Fig.1). These results have been averaged to yield a single best crystallisation plot,  $\alpha(t)$ , for each temperature, which is then fitted to an Avrami rate equation of the form:

$$\alpha(t) = 1 - \exp[-k(t - t_0)^n]$$

where  $t$  is time and  $t_0$  is the effective start time. A non-linear least-squares fit to this equation yields optimal Avrami parameters ( $k, n$ ) of which  $k$ , the crystallisation rate, can be used in an Arrhenius plot to obtain (from the slope) an activation energy,  $E$ , for the crystallisation process. The Arrhenius plots (Fig.1-right) yields  $E$ -values of 105(7) and 78(5) kJ/mol, respectively, for pure  $ZrO_2$  and  $Ce_{0.2}Zr_{0.8}O_2$ . We can be confident from these data that this lowering, 27(9) kJ/mol, in the activation energy with Ce-doping is real and is now the subject of some discussion (Lupo *et al.*).

### Determination of the kinetics of diffusion of a tracer solution through a prototype calcite rock

A new technique has been developed for the measurement of simultaneous diffusion of different ions through saturated rock. Particular interest in model chalk samples (Fig.2) stemmed from the need to assess the impact of chemical species entering the environment through porous chalk aquifers. The technique (Fig.2) involves contact between a constant (circulating) solution and one face of the chalk block ( $5 \times 10 \times 15 \text{ mm}^3$ ) while performing energy-dispersive fluorescence/diffraction measurements from regions along a 1D-grid perpendicular to the entry face; this arrangement is designed to be analogous to real interfaces that occur between a mobile solute along saturated fractures within an aquifer or at the wall of a borehole during drilling.

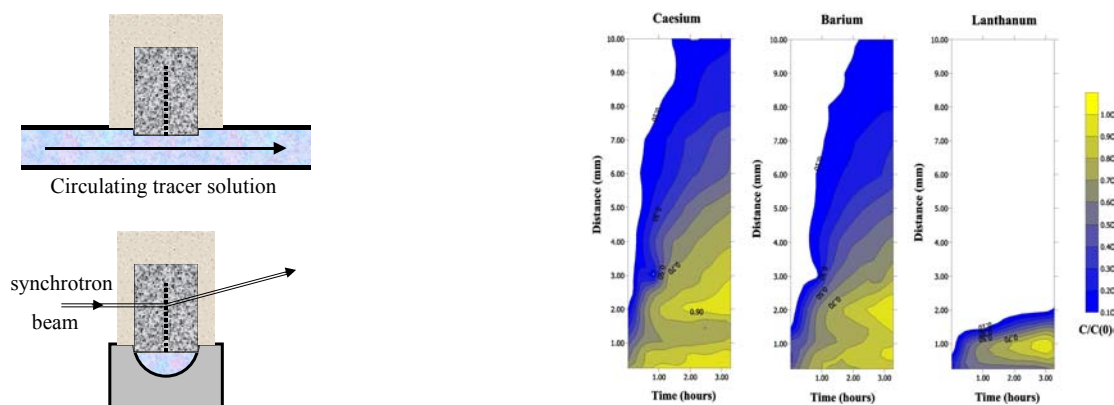


Figure 2: *left*; Schematic of the experimental arrangement (vertical grid points were 125  $\mu\text{m}$  apart). *right*; Diffusion (distance-time) plots obtained for Cs, Ba and La ions in model chalk.

Fig.2 shows data obtained for simultaneous diffusion by caesium, barium and lanthanum ions, these three having been chosen for their progressively changing valence states. Mean bulk diffusion coefficients have been obtained from these data (Betson *et al.*), showing a much lower diffusion coefficient for lanthanum and correlated diffusion behaviour for Ca and Ba. Such information, obtained non-destructively, points to a new method for examining diffusion processes for solutes under hydro-geological conditions.

### Publications

- 1 Lupo, F., Cockcroft, J.K., Barnes, P., Stukas, P., Vickers, M., Norman, C. & Bradshaw, H., "Hydrothermal crystallisation of doped zirconia: an *in situ* X-ray diffraction study", *Phys. Chem. Chem. Phys.*, in press (2004).
- 2 Betson, M., Barker, J., Barnes, P., Atkinson, T., Jupe, A., "Porosity Imaging in Porous Media using Synchrotron Tomographic techniques", *Transport in Porous Media*, in press (2004).
- 3 Betson, M., Barker, J., Barnes, P. & Atkinson, T., "Use of Synchrotron Tomographic techniques in the measurement of Porosity and Diffusion parameters for Solute Transport in Groundwater Flow", *Transport in Porous Media*, submitted (2003).