ESRF	**Experiment title:** Space/time-resolved crystallisation processes during synthesis of ceramic/zeolite material	**Experiment number**: HS1258
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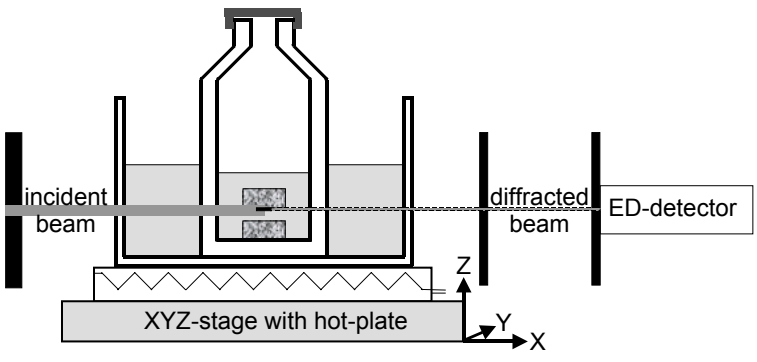
Report:

The aim of this experiment was to exploit spatially-resolved *in situ* energy-dispersive diffraction (EDD) to search for crystallisation gradients occurring during materials synthesis. The energetic well-defined ID09 white beam was an essential component, to gain penetration through the synthesis cell and for re-positioning of the beam to within microns relative to the sample. This has been the most ambitious application so far of tomographic EDD (known as *TEDDI*[1]). Three kinds of experiments were attempted: (1) growth of thin zeolite membranes; (2) hydrothermal crystallisation of a zeolite; (3) hydrothermal crystallisation of zirconia. The first two of these proved to be far more successful in respect of discovering crystallisation gradients, and are therefore reported here; the third was completed in a subsequent experiment (CH-1118).

1. Zeolite membrane growth:



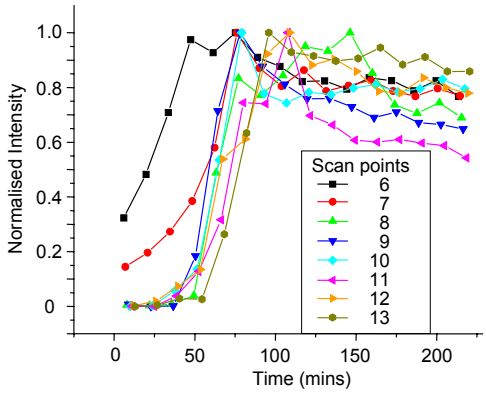


Figure 1: *left;* Schematic of the experimental arrangement (incident slits, 50 μm square; diffraction slits, 20 μm square; diffracting 2θ-angle = 4.005°; scan points Nos. 1 and 13 are reference points and Nos. 2-12 are spaced 50 μm apart. *right;* Membrane growth (points 6,7) is some 50 mins. ahead of the bulk synthesis (points 8-13) (after Hooper *et al.*[2] and reproduced by permission of the PCCP Owner Societies).

This was a challenging experiment given the required precision in temperature (98±1°C) and scan-position (microns) and that the autoclave hydrothermal/autoclave requires transmission of the X-ray beam through glassware, paraffin oil, alumino-silicate gel and α-alumina (no usable diffracted signal below 40 keV); the 1D sampling grid took ~13 minutes per cycle and was repeated continuously throughout the experiments which lasted for several hours. The crystallisation curves show that zeolite 4A membrane (points 6 and 7) forms first followed, after a delay of ~50 minutes, by the bulk synthesis (points 8-13). These latter scan points are also suggestive of a travelling crystallisation front, from the membrane outwards (there being no observable infiltration into the support itself) since crystallisation appears progressively later with increasing distance from the membrane.

2. Bulk hydrothermal crystallisation of a zeolite:

The aim of this experiment was to observe whether crystallisation gradients could be detected in a well-controlled model hydrothermal cell containing a ceramic support platform. To maximise the number of data points on each crystallisation curve, the sampling points were reduced to 3 key positions illustrated in Fig.2:

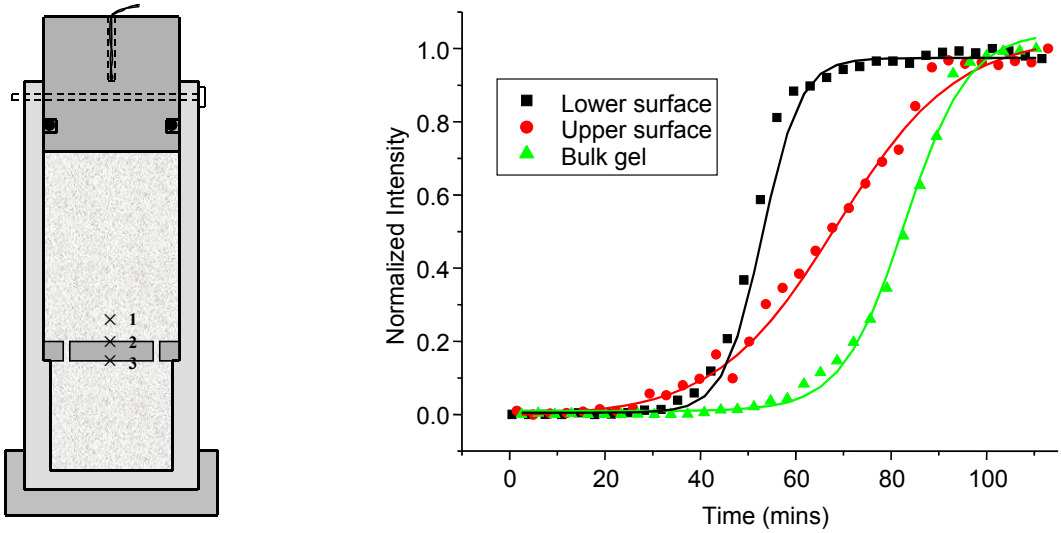


Figure 2: *left;* Schematic of the cylindrical sealable autoclave cell used to monitor zeolite 4A crystallisation at three locations - "1" is in the bulk gel, "2" is on the upper and "3" is on the lower surface of the support platform. *right;* Typical set, of 3 crystallisation plots at 95°C, showing a fastest growth on the lower surface (after Hooper *et al.*[2] and reproduced by permission of the PCCP Owner Societies).

These experiments identified some clearcut conclusions:

- Observed crystallisation rates are always fastest on the lower ceramic surface;
- The lower substrate surface realises the most regular temperature-dependent kinetics;
- Crystallisation rates can be increased by pre-seeding.

These observations can be interpreted in terms of a mechanical instability of the product settling on the upper surface during slow spinning of the hydrothermal cell, followed by transfer and re-feeding of the crystallites to the lower substrate surface.

The overall conclusion from both experiments is that tomographic diffraction analysis shows that, in spatial terms, hydrothermal/autoclave synthesis is far more complex than realised. Significant crystallisation gradients have been found within the synthesis environment as a result of a number of factors including substrate seeding, surface texture, gravity, substrate spinning and eddy currents. It is anticipated that many more xamples will be uncovered and the longer term objective is to map out crystallisation gradients for a range of synthesis modes and autoclave cells, and to feed back this information into the design of more versatile and efficient synthesis systems.

Publications:

1 Barnes,P. *et al., Nondestr. Test. & Eval.* 17, 143-167 (2001).
2 Hooper,D. *et al.*, *Phys. Chem. Chem. Phys.,* 5(21), 4946 - 4950 (2003).
3 Barnes,P. *et al.*, "Energy-Dispersive (Powder) Diffraction", *J. Res. Nat. Inst. Stand. & Techn.,* in press.