

MS40 Operando and in situ crystallographic studies

MS40-03

In situ PXRD studies of Cs-ion exchange in the zeolite chabazite

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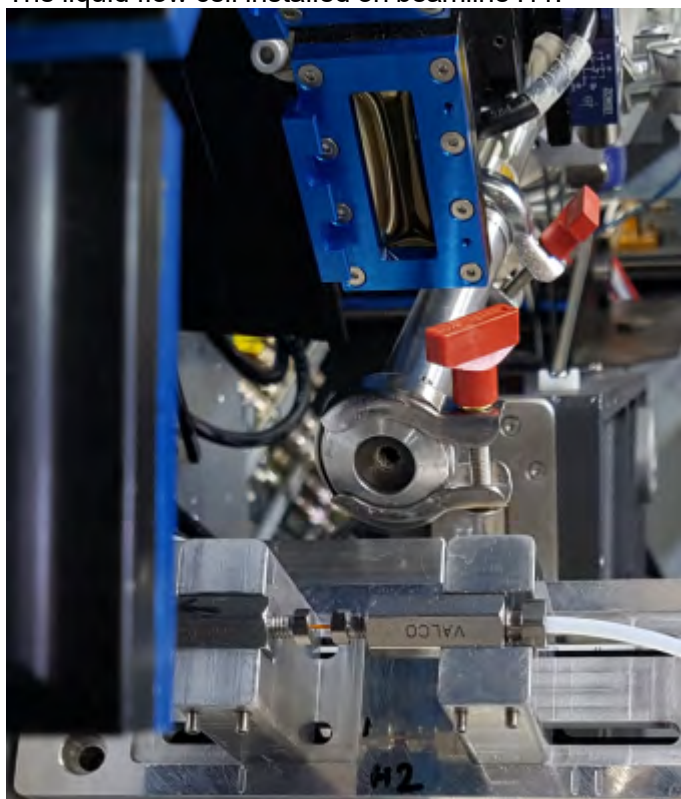
Abstract

The removal of relatively long-lived radionuclides such as ¹³⁷Cs ($t_{1/2} = 30.2$ years) from aqueous nuclear waste streams, or from aqueous environments contaminated with nuclear waste, is of high importance. A favoured option for the removal of radioactive cations are zeolites: porous crystalline aluminosilicates adopting framework structures comprising corner-shared [SiO₄] and [AlO₄] tetrahedra, with exchangeable cations occupying the hydrated pores and cages of the framework. Chabazite is a particular zeolite that is efficacious in the selective removal of aqueous Cs⁺ by ion exchange and has been applied in decontamination efforts at Fukushima.^[1] The crystallographic positions occupied by extraframework cations, such as Na, K and Cs, within the chabazite crystal structure are well established when the material contains exclusively one type of cation,^{[2][3]} however, the mechanism by which ion exchange occurs in these materials has not been previously probed despite the inherent advantages to enhancing the understanding of this process. Very few *in situ* PXRD studies have been reported on structural changes in solids as they contact solutions under flow, owing to the specialised sample environment required, the need for synchrotron sources to provide high counting statistics and appropriate detectors to permit rapid acquisition of high-quality datasets. Nevertheless, this approach has been successfully employed previously to reveal mechanistic information on ion exchange processes.^[4] In this study, PXRD patterns have been collected, on beamline I11 at the Diamond Light Source synchrotron, on chabazite samples as ion exchange occurs, facilitated by a liquid flow cell (Fig. 1.) which elutes a desired solution through the sample as data is recorded *in situ*. Cs-ion exchange has been studied for two chabazite samples, one containing sodium (Na-CHA) and the other potassium (K-CHA). Time-resolved changes observed in PXRD patterns as Cs-ion exchange proceeds are highlighted in Fig. 2, which shows changes in the (0 -2 -2) reflection during the experiment. Through applying Rietveld refinement to the *in situ* datasets, time-resolved structural changes are observed as the constitution of extraframework cations changes within the zeolite, providing a mechanistic understanding of how Cs-ion exchange occurs in these materials.

References

- ^[1] T. Tsukada, K. Uozumi, T. Hijikata, T. Koyama, K. Ishikawa, S. Ono, S. Suzuki, M. S. Denton, R. Keenan and G. Bonhomme, *J. Nucl. Sci. Technol.*, 2014, **51**, 886 – 893. (n.b. 'chabazite' is referred to by the less common term 'herschelite' in this publication)
- ^[2] M. Calligaris, A. Mezzetti, G. Nardin and L. Randaccio, *Zeolites*, 1986, **6**, 137 – 141.
- ^[3] A. Alberti, E. Galli, G. Vezzalini, E. Passaglia and P. F. Zanazzi, *Zeolites*, 1982, **2**, 303 – 309.
- ^[4] A. J. Celestian and A. Clearfield, *J. Mat. Chem.*, 2007, **17**, 4839 – 4842.

The liquid flow cell installed on beamline I11.



Changes in 0-2-2 reflection for K-CHA with time

