



**Experiment title: Methodological Study by Anomalous Diffraction of the Precise Location of two Cations In Zeolites Under Working Conditions**

**Experiment number:**  
02-02-188

<b>Beamline:</b> D2AM	<b>Date of experiment:</b> from: 27/06/02 to: 01/07/02	<b>Date of report:</b>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr Jean-Louis HODEAU	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

**PhD student Hervé PALANCHER\* (Institut Français du Pétrole – IFP)**

**Dr Christophe PICHON\* (IFP)**

**Dr Jean-François BERAR\* (CNRS)**

**Dr Jean-Louis HODEAU\* (CNRS)**

**Dr John LYNCH\* (IFP)**

**Mrs Bernadette REBOURS\* (IFP)**

### Introduction

The experiments reported here are part of a long term project (Palancher's PhD) dedicated to the methodological study by anomalous diffraction of the precise location of cations in zeolites in the presence of multi-component adsorbed phases.

The industrial and scientific background is based on optimisation and development of new molecular sieves (such as X, Y or A zeolites) for high performance processes for separation and purification of hydrocarbon isomers. In such molecular sieves, adsorption properties and, more precisely, selectivity and capacity of adsorption can be correlated with the distribution of charge compensating cations.

Preliminary measurements performed at room temperature, with pre-treated (dehydrated) samples (SrX and SrRbX) sealed in capillary holders (state 1) have shown the strong sensitivity of AWAXS to the distributions of cations ( $\text{Sr}^{2+}$  and  $\text{Rb}^{+}$  respectively) (see ref. [1] and [2]). Moreover an appropriate analytical method (optimisation of the beam optics, the data collection strategy and the detection system) has been established.

The aim of this experiment was to study *in situ* the evolution of the cation distribution in the same samples (SrX and SrRbX) under various hydration and temperature conditions as well as the validation of the experimental set-up.

12 shifts on BM2 were allocated by the CRG Committee.

### Experimental set-up

In order to control the composition of the atmosphere surrounding the sample and its temperature, a cell (based on ref. [3]) has been designed and built.

The sample, in a quartz glass capillary, was kept fixed by two glass wool plugs, to avoid sample displacements during gas circulation. The capillary was mounted between two Swagelock Tees using graphite ferrules for good tightness. The Tees were screwed onto an aluminium support placed on a sliding block. Aluminium tubing (1/16 in.) connected Swagelock fittings to gas admission or extraction. The whole cell was mounted on standard goniometer head. Thanks to a motor (not represented in figure1) placed behind goniometer head, oscillations of approximately  $\pm 55^\circ$  ( $^\circ 2\theta$ ) could be used to maximise the number of crystallites orientations sampled.

The heating system consisted of an hot air blower placed close to the sample capillary. Temperatures up to  $210^\circ\text{C}$  in the capillary could be reached. The temperature gradient is less than 5% over a 2 mm zone along the capillary whereas the synchrotron beam width could be evaluated to 1 mm.

## Diffraction experiments

In these experiments, SrX and SrRbX (with equal numbers of Sr<sup>2+</sup> and Rb<sup>+</sup> cations) were analysed. Two different parameters (temperature and degree of hydration of the flushing gas) can influence the rate of hydration of the sample. Four experimental conditions have been chosen :

1. Hydrated at room temperature and no flushing gas (state 2)
2. T : Room temperature and as received N<sub>2</sub> (as flushing gas) (state 3)
3. T : Room temperature and N<sub>2</sub> dried by use of a moisture filter (as flushing gas) (state 4)
4. T = 210°C and N<sub>2</sub> dried by use of a moisture filter (as flushing gas) (state 5).

Comparing data from the sample with a high degree of hydration (state 2, DRX laboratory data) and a low degree of hydration (state 1), reflections which are very sensitive to hydration were identified. Their evolution during the dehydration process enabled us to assess that an equilibrium state had been reached. The dehydration from state 2 to state 5 on SrX and from state 2 to 3 on SrRbX have been studied.

In spite of the presence of water molecules in the zeolite framework which could be located near cationic sites in high symmetric positions (on [111] axes) (see ref. [4]), the anomalous effect is strong enough to be able to locate both cations, even in the most hydrated state (state 3).

The sample SrRbX has been studied in state 2 at 5 energies in order to quantitatively evaluate data quality. Due to time limitations, data at 3 energies were collected for SrRbX in state 3 and SrX in the states 4 and 5.

Figure 3 points out the efficiency of the *in situ* cell in obtaining samples (SrX in this case) with modified degrees of hydration. Several stable intermediate states have been identified and the influence of Rb<sup>+</sup> on the behaviour of Sr<sup>2+</sup> cations has been clearly observed.

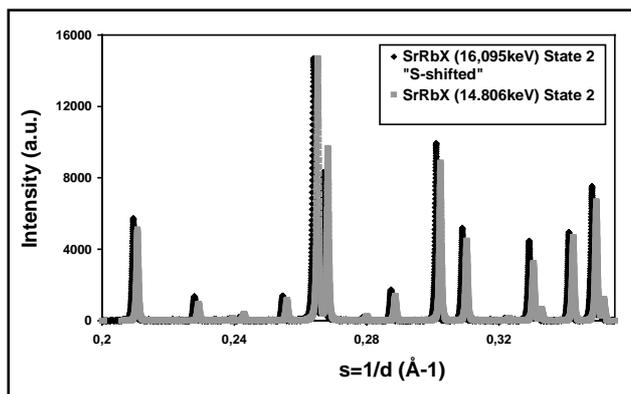
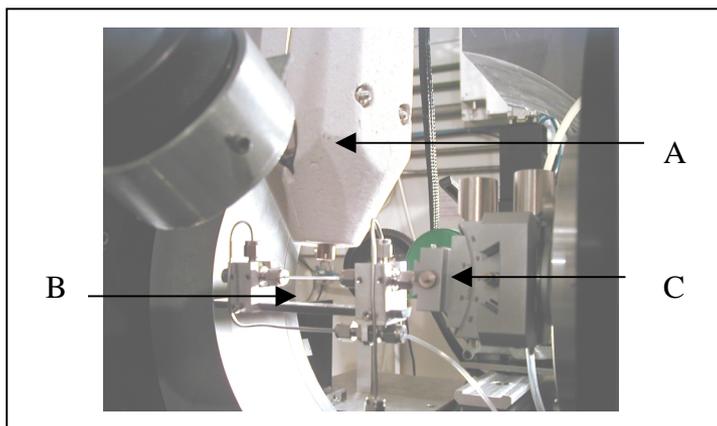


Figure 1: Picture of the experimental set-up which consists of an air blower (A), the in-situ cell enabling the control of the atmosphere surrounding the sample (B) and a standard goniometer head (C).

Figure 2: Detail of X-ray diagrams for SrRbX at the state 2 recorded on D2AM beamline at 14.806 and 16.095 keV.

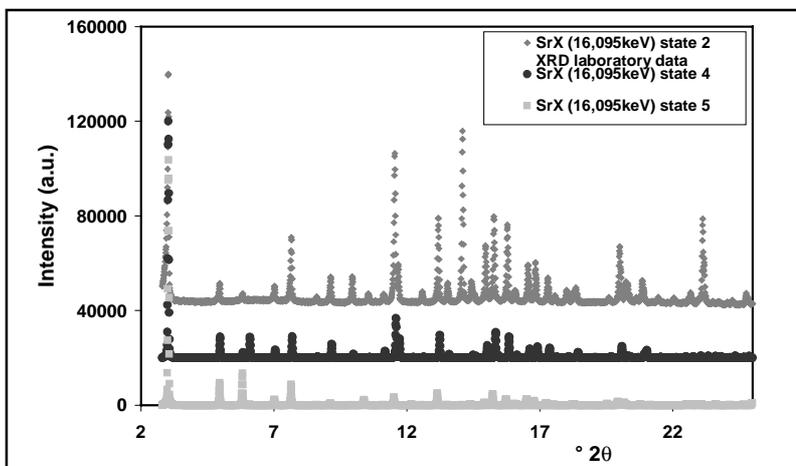


Figure 3: X-Ray diagrams of SrX at 16.095 keV at different states of hydration : state 2, 4 and 5.

- [1]: experimental report CH1216, C. Pichon, J.F. Béar, J.L. Hodeau, H. Palancher, J. Lynch, B. Rebours, 2002.  
 [2]: experimental report CRG 02-02-188, C. Pichon, J.F. Béar, J.L. Hodeau, H. Palancher, J. Lynch, B. Rebours, 2002.  
 [3]: P.Norby, C.Cahill, C.Koleda and J.B. Parise, *J.Appl. Cryst.* (1998) 31, 481-483.  
 [4]: C. Pichon, Thesis, Bourgogne University (1999).