ESRF	**Experiment title: Methodological Study by Anomalous Diffraction of the Precise Location of two Cations Into Zeolites Under Working Conditions**	**Experiment number**: 02-02-188
Beamline: D2AM	**Date of experiment**: from: 17/02/02 to: 19/02/02	**Date of report**: 28/02/02
Shifts: 6	**Local contact(s)**: Dr Jean-Louis HODEAU	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Christophe PICHON* (Institut Français du Pétrole – IFP)

Dr Jean-François BERAR* (CNRS)

Dr Jean-Louis HODEAU* (CNRS)

PhD student Hervé PALANCHER* (IFP)

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 two cations into zeolites under multi-component adsorbed phases.
The industrial and scientific background is based on optimisation and developing 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.

At a first milestone of the project and prior to attempting *in situ* studies, we wanted to determine the optimal conditions and the precision of the localisation of two cations among the different crystallographic sites of X or Y zeolite. The perfecting of an appropriate analytical method will require:

- Optimisation of sample preparation and holding as a function of composition and X-ray energy.
- Optimisation of beam optics for anomalous diffraction (in particular use of filters).
- Optimisation of data collection strategy (number of X-ray energies vs precision of the data).
- Optimisation of detection system for good statistics, good resolution and suppressing fluorescence.

3 shifts were allocated by the ESRF's Committees in order to prove the technique (proposal code CH1216). 6 supplementary shifts allocated by CRG's Committees were also used in this aim (proposal code 02-02-188).

This preliminary experiments were performed by studying the structure of two systems involving strontium-rubidium cation couples. A SrX and a SrRbX zeolites were studied. These experiments were performed at room temperature and without hydrocarbon atmosphere, with the pre-treated (dehydrated) samples sealed in capillary holders.

Diffraction experiments

In the first set of experiments, SrX and the same solid with 20% of the Sr exchanged by Rb (SrRbX) were analyzed. Data were collected on hydrated and dehydrated solids, the latter at different energies (near and far from absorption edge) to assess the efficiency of anomalous scattering in determining cation distributions in the case of two cations.

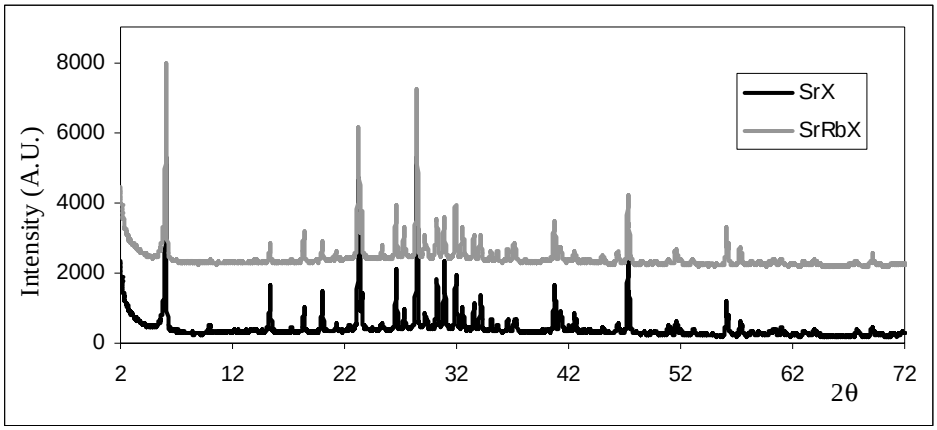

Fig. 1 : X-ray diagrams for hydrated SrX and SrRbX
(recorded on a D501 Siemens diffractometer using $K\alpha_1$ and $K\alpha_2$ copper radiations)

Whilst the hydrated samples are fairly similar (see fig. 1), the dehydrated samples of SrX and SrRbX are very different (see fig. 2), showing a strong effect of the second cation even at low exchange fractions. Because Sr and Rb are close in atomic number, only AWAXS was able to show which cations are affecting which diffraction peaks (see fig. 3). The refining of the data is still in progress.

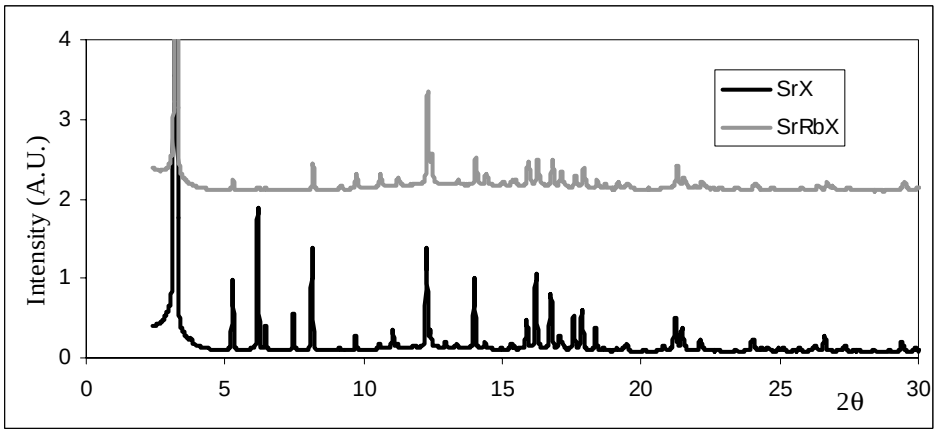

Fig. 2 : X-ray diagrams for dehydrated SrX and SrRbX
(recorded on D2AM beamline at 15.192keV)

Note that the Sr and Rb EXAFS collected at the same time are similar and show weak oscillations (see fig. 4) probably due to a mixture of cation-oxygen distances. The angular ranges most affected by each cation were determined and duplicate measurements performed to quantify the precision.

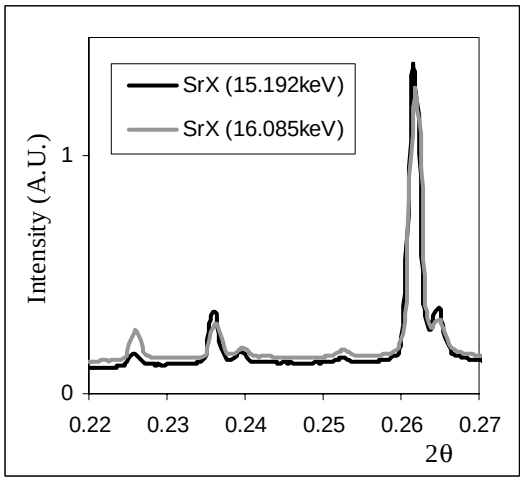

Fig. 3 : detail of X-ray diagrams for dehydrated SrX recorded on D2AM beamline at 15.192 and 16.085keV

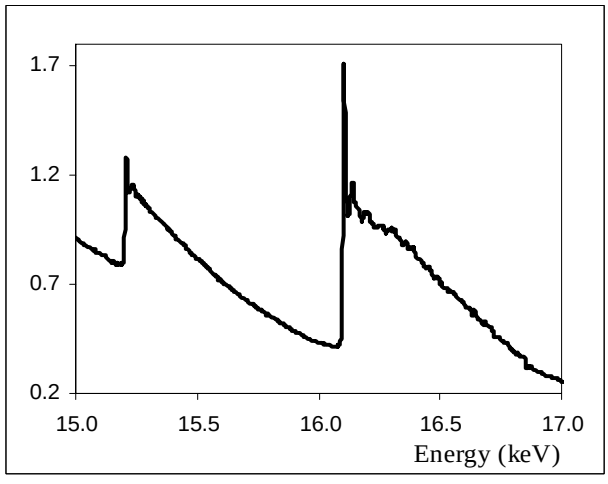

Fig. 4 : XAS spectra of SrRbX
(recorded on D2AM)