



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application**:

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Checking gas hydrate prediction software using experimental cage fillings	<b>Experiment number:</b> CH-2630
<b>Beamline:</b>	<b>Date of experiment:</b> from: 23/07/2008 to: 28/07/2008	<b>Date of report:</b> 10/12/2009
<b>Shifts:</b>	<b>Local contact(s):</b> Michela Brunelli	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> * <b>Prof Dr Werner F Kuhs</b> GZG Abt.Kristallographie, Universität Göttingen * <b>Andrzej Falenty</b> as above * <b>Dr M.Mangir Murshed</b> as above		

**Report:** Gas hydrates are non-stoichiometric inclusion compounds in which small molecules are engaged into a host framework of water molecules. For the most common structures (called type I and type II, both of them cubic) two types of water cages exist, usually referred to as small and large cages. The cage-fillings can be predicted with a statistical thermodynamic theory established by van-der-Waals & Platteeuw in 1959 and refined further over the years. A critical test for the predictive power of the various existing approaches is the comparison with experimental data of the cage fillings of gas hydrates produced at various conditions of pressure (gas fugacity) and temperature. Diffraction is the only general method to access the cage occupancies of small and large cages individually and on an absolute scale. The purpose of this proposal was to check existing predictions of cage fillings with the experimental numbers established by synchrotron powder diffraction on ID31. Synchrotron powder diffraction appeared as the most promising tool as it allows for disentangling the parameter correlations between cage occupancies and atomic displacement parameters by measuring up to high scattering angles.

24 samples were prepared in Göttingen, filled into quartz capillaries and mounted onto a magnetic sample holder ready to go onto the rotation stage of ID31. The samples were transported in a dry Moover dewar and transported by car to Grenoble. The cryo-stream cooler was set to low temperature and the samples quickly transferred to the sample stage. The wavelength was set to 0.403027Å (calibrated with a NIST Si standard). Data collection typically proceeded up to a  $2\Theta$  angle of 65° (in some cases 100°) in steps of 0.005°. The amount of sample in the capillary varied slightly along the capillary (NB: It should be noted that the filling of the capillaries under liquid nitrogen conditions was not a minor job). Thus - before setting the scans for various positions along the capillary – the most promising parts were identified by short pre-scans. Data collection then proceeded with a typical speed of 2°/ min for usually 3 to 5, exceptionally up to 15 positions. The capillary spinning during data collection was set to 2000-3000 rpm. For the following Rietveld analysis the data of the different scans for one sample were averaged. The results of the Rietveld refinements using GSAS are shown in Tab.1; Fig.1 shows two typical diffraction patterns and the Rietveld fit.. In the table the formation conditions of the gas hydrate, the weighted profile R-factor, the cubic lattice constant  $a$  as well as the so-called hydration number (which reflects the overall gas composition) is given for all studied samples.

**Table 1 Results of the Rietveld refinements**

gas hydrate	T <sub>Syn.</sub> [K]	P <sub>Syn.</sub> [bar]	f <sub>Syn.</sub> <sup>1</sup>	R <sub>wp</sub> / d	a [Å]	hydration.- number	number of scans
Xe-H <sub>2</sub> O, sl	268.15	3	2.94	6.33/1.695	11.867705(9)	6.345(12)	3
Xe-H <sub>2</sub> O, sl	268.15	6	5.75	10.27/0.494	11.87474(5)	6.269(32)	4
Xe-H <sub>2</sub> O, sl	268.15	10	9.27	9.57/1.278	11.87512(2)	6.276(15)	9
Xe-H <sub>2</sub> O, sl	268.15	20	17.15	7.04/1.105	11.87805(2)	6.208(10)	3
CO <sub>2</sub> -H <sub>2</sub> O, sl	268.15	15	24	7.39/0.996	11.84826(2)	6.345(30)	2
CO <sub>2</sub> -H <sub>2</sub> O, sl	268.15	30	23.3	6.82/0.750	11.85178(2)	6.288(19)	3
CO <sub>2</sub> -H <sub>2</sub> O, sl	271.15	30	13.4	4.71/1.34	11.85197(1)	6.277(14)	9
CO <sub>2</sub> -H <sub>2</sub> O, sl	185	0.266	-	9.31/1.100	11.86081(15)	6.32(26) <sup>2</sup>	2
CO <sub>2</sub> -H <sub>2</sub> O, sl	190 <sup>3</sup>	0.36	-	14.00/1.825	11.85626(9)	6.13(9) <sup>2</sup>	2
CO <sub>2</sub> -D <sub>2</sub> O, sl	190 <sup>3</sup>	0.36	-	11.04/1.470	"	"	2
CO <sub>2</sub> -D <sub>2</sub> O, sl	190	0.36	-	10.51/1.673	11.85800(10)	6.09(9) <sup>2</sup>	3
CO <sub>2</sub> -D <sub>2</sub> O, sl	195	0.505	-	8.95/0.539	11.86081(4)	6.080(24) <sup>2</sup>	3
CH <sub>4</sub> -H <sub>2</sub> O, sl	268.15	35	32	8.27/0.822	11.85474(2)	6.035(20)	3
CH <sub>4</sub> -H <sub>2</sub> O, sl	268.15	60	52	8.90/0.616	11.85627(2)	5.942(25) <sup>2</sup>	3
CH <sub>4</sub> -H <sub>2</sub> O, sl	268.15	100	78	15.29/0.363	11.85448(11)	5.94(4) <sup>2</sup>	3
CH <sub>4</sub> -H <sub>2</sub> O, sl	268.15	150	105	8.53/0.820	11.85484(4)	5.968(22) <sup>2</sup>	3
CH <sub>4</sub> -D <sub>2</sub> O, sl	271.15	35	32	4.80/1.363	11.85808(2)	5.98(6)	5
CH <sub>4</sub> -D <sub>2</sub> O, sl	271.15	60	52	7.95/0.826	11.85688(2)	6.016(20)	9
CH <sub>4</sub> -D <sub>2</sub> O, sl	271.15	100	79	12.89/0.251	11.85661(6)	5.94(4) <sup>2</sup>	3
CH <sub>4</sub> -D <sub>2</sub> O, sl	271.15	150	107	8.92/0.487	11.85770(4)	5.920(21) <sup>2</sup>	3
N <sub>2</sub> -D <sub>2</sub> O, sII	258.15	150	141	9.58/0.936	17.11651(5)	5.818(17)	3
N <sub>2</sub> -H <sub>2</sub> O, sII	258.15	150	141	7.95/0.630	17.11735(5)	5.759(17)	3
N <sub>2</sub> -H <sub>2</sub> O, sII	271.15	150	145	8.54/0.727	17.11961(5)	6.133(19)	3
N <sub>2</sub> -H <sub>2</sub> O, sII	271.15	200	194	7.69/0.722	17.11428(4)	5.865(14)	11

<sup>1</sup> fugacities for Xe-hydrate are calculated by CSMHyd (version 1998); other fugacities are taken from "International thermodynamic tables of the fluid state" (IUPAC: Angus *et al.*, 1976, 1978, 1979)

<sup>2</sup> filling of large cages is fixed at 100%, error estimated

<sup>3</sup> same sample, but 2 diffractograms refined together

The experiments were in the end fully satisfactory and the expected information on the cage fillings were obtained; typical standard deviations for the cage filling were well below 1%. The results are of sufficient quality to check thermodynamic prediction programs. However, various problems occurred on the way and slowed down the data analysis. Firstly, the quartz capillaries contributed a very pronounced background which had to be subtracted manually; All other analytical methods implemented into GSAS for describing the background were unsatisfactory. Secondly, some of the (competing) structural models available in literature were not compatible with the diffraction data, in particular for the molecular disorder of CO<sub>2</sub> in CO<sub>2</sub>-hydrate. This has been resolved now thanks to the data from ID31. Lastly, the nominal temperature of 90 to 100K for the sample position in the cryo-stream was found to be incorrect; after tedious cross calibrations with the lattice constants of ice Ih (our own HASYLAB synchrotron data) and those of CO<sub>2</sub> hydrate (neutron HRPD time-of-flight data from literature) we find temperatures at the sample position in the range of 115-145 K. Thus the actual sample temperatures are bound with some uncertainty without a proper calibration; the ice Ih calibration could not reliably be applied to all samples as some had very little ice. Yet, the structural results of this experiment are certainly worth publishing and this is in progress now.

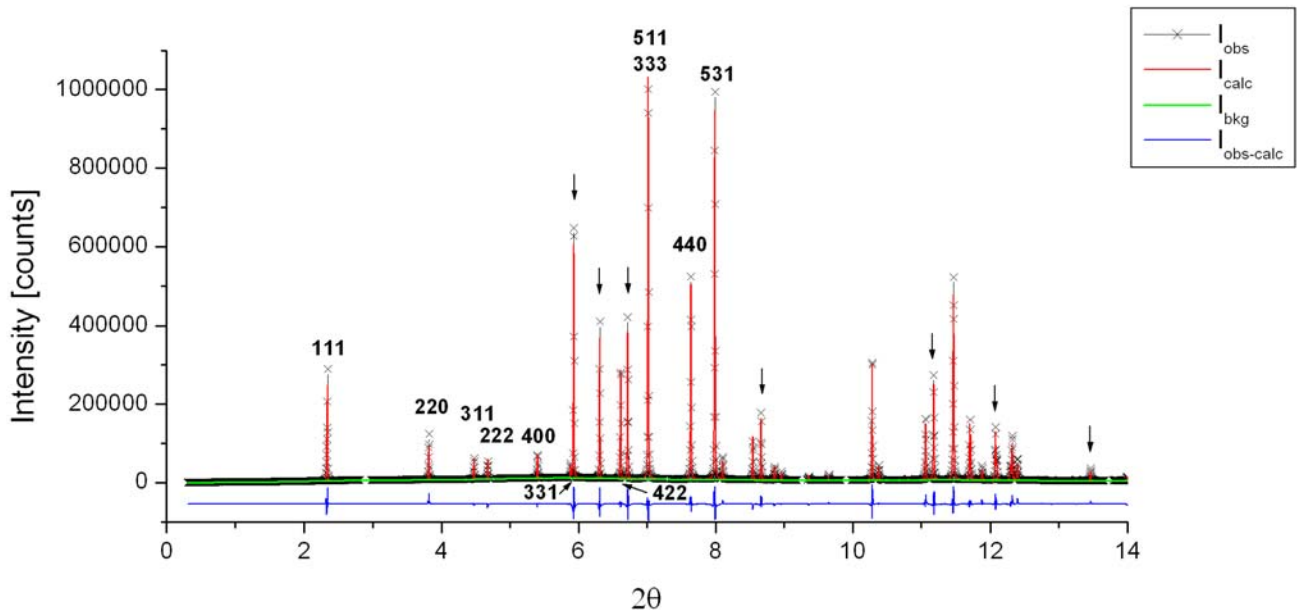
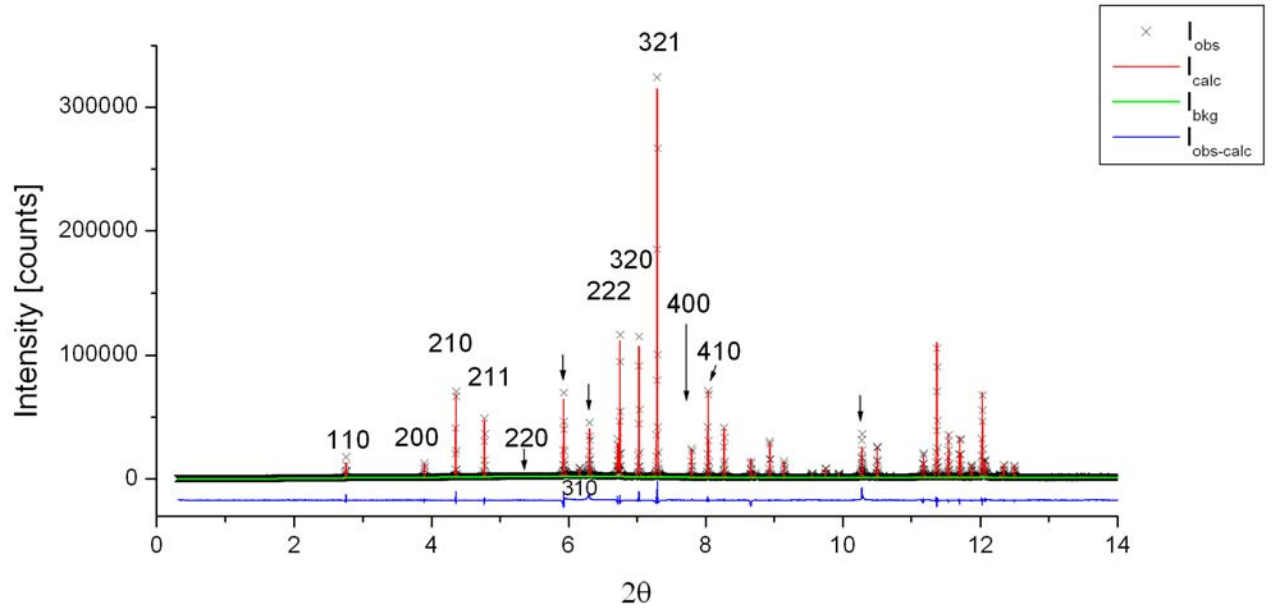


Fig.1 (top) Rietveld refinement result for deuterated CH<sub>4</sub>-hydrate formed at 150bar and 271.15K; (bottom) dito for H<sub>2</sub>O-N<sub>2</sub>-hydrate formed at 200bar and 271.15K.