Experimental report

08/11/2021

Proposal: CRG-2932 **Council:** 4/2021

Title: Methane hydrate formation in clay/sand matrix: towards a reproduction of Black Sea natural sediments.

Research area: Physics

This proposal is a new proposal

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Samples: Illite + sand
Natural black sea sediments

Instrument	Requested days	Allocated days	From	To
D1B	2	2	01/07/2021	02/07/2021
			08/10/2021	09/10/2021

Abstract:

The abstract is in the scientific case pdf file.

Methane hydrate formation in clay/sand matrix: towards a reproduction of Black Sea in lab.

D1B – CRG 2932

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Objectives of the proposal. This neutron diffraction experiment aimed at completing the ongoing investigation on the effect of clay matrix and ionic strength on the kinetics of formation of gas hydrates in sediment matrix surrogates made of silica sands and clay. Diffraction measurements on pre-made samples with different defined times of pressurization before neutron diffraction (with duration between 6 months and few hours) combined with previous D20 results (exp. 5-22-786) are key to have a complete overview on the formation of gas hydrate in the various clay/sand matrices mimicking natural conditions (thermodynamics and sedimentology) of the Black Sea geological site. At a larger scale, the objective is to evaluate the implication of gas hydrates in geo-hazards and on the volume of greenhouse gas potentially reaching the atmosphere.The results will contribute to the progress of Charlène Guimpier's and Constant Agnissan's PhD research at the frontier between physical-chemistry and geochemistry.

Work carried out during the experiment. During the experiment, 18 samples were investigated. Methane hydrates were synthesized at the laboratory prior the experiment in three different matrices: Illite, natural sediments collected in Black Sea during the cruise GHASS in 2015 and a mixture of Illite and Montmorillonite. For each matrix, 6 times of pressurization were applied. The samples were pressurized with CH_4 at 200 bar during 1, 7, 14, 30, 75 and 110 days at constant temperature T=282K and then stored in liquid nitrogen until analyses (so-called ex-situ samples in the following).

Hydrates samples were cold-transferred into the orange cryostat. The diffractograms were collected every 3 minutes at 150K during ~2 hours (λ=2,52Å).

Main results obtained. The collected results during the experiment offer us new information on the formation kinetic of the methane hydrate in clay/sand matrix by analyzing the evolution of characteristic Bragg peak of methane hydrate and ice as a function of the pressurization duration. The fraction of water converted into hydrate phase is very low (less than *ca.* 1%) for the sample pressurized during one day. This result was expected, D20 *in-situ* neutron diffraction experiments showed the absence of Bragg peak after more than 3 hours of pressurization for

the methane hydrates synthesized in these matrices. After 75 days of pressurization, the fraction of methane hydrate has increased. In the Illite matrix, the fraction of water converted into hydrates is still very low (less than *ca.* 30%). This result would confirm the impeding effect of Illite clay on the formation of gas hydrates (coherent with D20 experiment). In the natural sediments from Black Sea, the amount of hydrate in the sample is higher, more than 70%. Knowing that this sediments contains ~55% d'Illite, the presence of other chemical species may improve the formation kinetics of methane hydrate. Thus, formation in these matrices occurs on timescale of several days with a low conversion rate while the formation of methane hydrate into montmorillonite clay occurs in less than 15min, reaching an almost complete conversion in less than one hour.

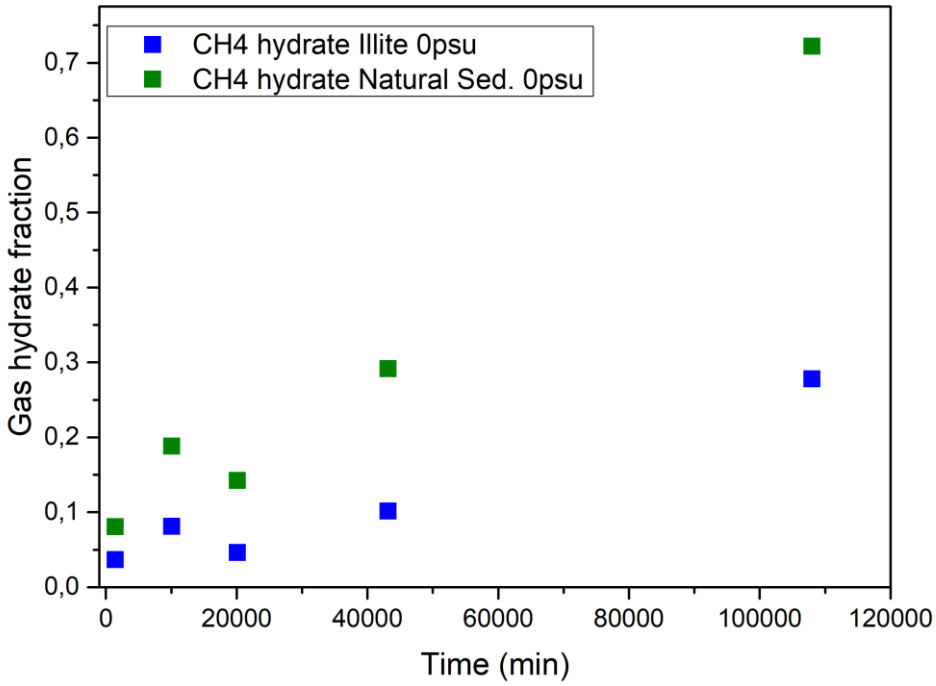

Figure. Comparison of Methane hydrate fraction in Illite and the natural sediments from the Black Sea at different times of pressurization.

Future work and pursue of the project. Deeper analysis will be performed to quantify the cage occupancy for the various sedimentary matrix through Rietveld refinement and to investigate any variability of the hydrate cell parameters depending on the nature of the sedimentary matrix. This experiment provides invaluable information on "artificial" hydrate bearing sediments. The combination of these results with the experiments of Inelastic Neutron Scattering (IN1 – Exp. 7-05-528 & 7-05-548) should provide new information to better understand the formation of gas hydrates mimicking natural conditions (thermodynamics and sedimentology), keeping the same objective of having a better estimation of gas storage capacity in ocean floor.