Experimental report

17/09/2018

Proposal:	**CRG-2447**	**Council:**	4/2017
Title:	Grain sizes and mineral compostioneffect on clathrate hydrate formation		
Research area:			

This proposal is a new proposal

Main proposer:	**Morgane LEMAIRE**
Experimental team:	Arnaud DESMEDT Bertrand CHAZALLON Morgane LEMAIRE Claire PETUYA
Local contacts:	Vivian NASSIF

Samples: D_2O
SiO_2
Fe_2O_3
Al_2O_3
CO
CO_2
$CaSiO_2$
$NaSiO_2$

Instrument	Requested days	Allocated days	From	To
D1B	7	7	18/06/2018	25/06/2018

Abstract:

CRG-2447 (18/06/18 – 26/06/18)

Scientific Report – PhD Morgane Lemaire

Purpose of the CRG

The aim of the proposal was to allow the applicant to work on the high-resolution neutron two-axis powder diffractometer (D1B) in order to investigate the influence of some surrogates of sediment on the clathrate hydrate formation. Indeed, numerous studies have been made to understand the influence of the surrogates but using artificial minerals without considering the chemical composition of the surrogate. In this work, kinetic of clathrate hydrate formation has been studied using different mineral's chemistry (feldspar sodium, potassium, alkaline and silica) in relation to two reference sediments: coarse sand and silt-fine sand. This work was carried out as part of the ANR MI2C and is part of the PhD program of M. Lemaire and C. Métais.

Work carried out during the CRG and main results obtained

Ten samples were pressure-controlled using the ILL gas pressure cells. In the cell, different kinds of chemical surrogates (Na, Ca, K, SiO_2) with different granulometry (under 60 μm and 160-280 μm) were put with deuterium oxide, without exceeding the saturation of the surrogate. First, the samples were cooled from 270K to 230K in order to form the ice, then they were heated to 270K where 30 bar of CO_2 were applied to engage the clathrate hydrate formation. A diffractogram was recorded every five minutes for eleven hours to follow the clathrate hydrate kinetic of formation.

These experiments showed that the clathrate hydrate kinetic of formation was mostly controlled by the chemical composition of the surrogate (Fig. 1 and Fig.2). In this case, the adsorption time is faster with the small granulometry, explained by the increase of the specific surface for the clathrate hydrate formation. Indeed, in the two experiments, the kinetic changes with the chemical composition of the surrogate. When the surrogates are charged with alkaline like calcium, it increases the induction times while the diffusion is reached faster than with a silicate surrogate.

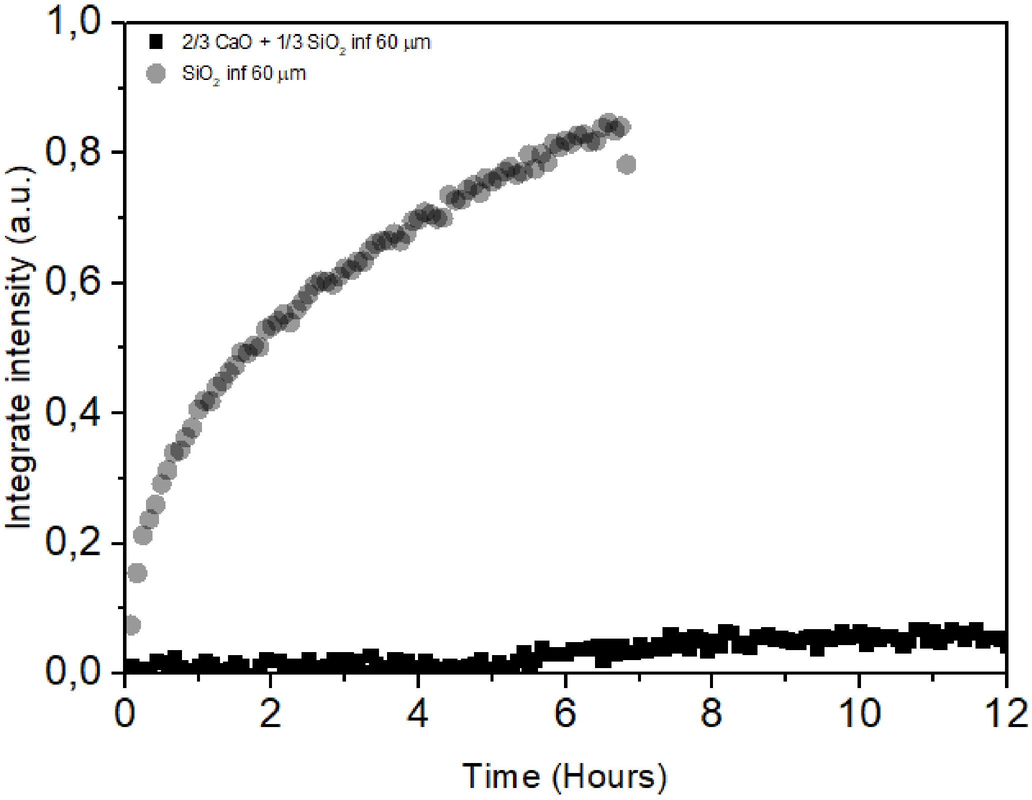

Figure 1: Formation kinetics of carbon dioxide clathrate hydrate with calcium silicate surrogate (dark square) and silica surrogate (dark circle) for a granulometry less than 60 μm.

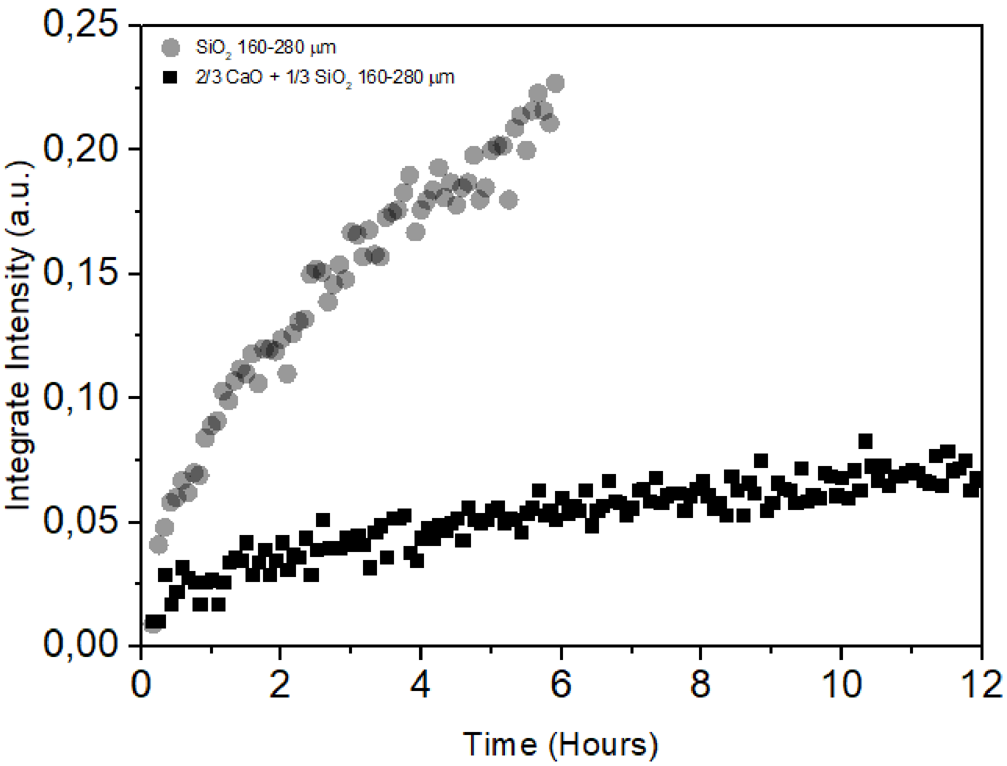

Figure 2: Formation kinetics of carbon dioxide clathrate hydrate with calcium silicate surrogate (dark square) and silica surrogate (dark circle) for a granulometry less than 160 - 280 µm.

In both cases (<60 mm and 160-280 mm), it was not possible to form clathrates hydrates with alkaline like sodium or potassium. With these two surrogates, we observed a reaction on the cell leading to a liquefaction then a solidification of the surrogate, preventing the gas from spreading through the surrogate. That could be due to the mobility and a greater reactivity of the alkaline molecules. The sodium and calcium molecules in the surrogates could react with the deuterium oxide and the carbon dioxide to form hydroxides. This reaction could act like an inhibitor of the clathrate hydrate formation.

Coming Work

This work shows the impact of the chemical composition of the surrogate on the clathrate hydrate formation. It will be a part of the understanding of the influence of the surrogate, gathering the kinetics, the selectivity and the diffusion problematic on this clathrate hydrate formation. This progress will be published and presented at conferences. We also intend to submit a proposal in the next ILL proposal round to further understand the inhibitor reaction created with the hydrophilic alkaline surrogate like sodium, by proposing the study of the kinetics of formation but with different gases like nitrogen. This future work will complement the previous one.