

A LABORATORY PROTOCOL FOR THE ANALYSIS OF NATURAL GAS HYDRATES

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ABSTRACT

For a number of years the NRC group has been working on a laboratory protocol for the analysis of gas hydrate that has been recovered from various natural sites. The expectation was that a comprehensive set of techniques would become available for the general use of hydrate researchers around the world. With the current set of available techniques a good picture of natural gas hydrates can be obtained, although the emerging complexity of the hydrate-mineral system still demands additional work. Here we present a suite of techniques that will take a researcher from preservation techniques to hydrate occurrence, gas/water/sediment ratios, gas and isotope analysis, P-T behaviour, structure, composition, degree of water conversion to hydrate, hydrate homogeneity and decomposition behaviour. As more detailed studies become possible a variety of more subtle features are revealed, for instance the role of minor gas components in hydrate stability, decomposition behaviour and heterogeneity in structure and composition.

Keywords: Gas hydrates, NMR, Raman, diffraction, Calorimetry, stability, composition, decomposition

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INTRODUCTION

One of the key elements in coming to terms with the various issues involving natural gas hydrate is to understand it as a mineral system. This means that, as for other minerals, a number of properties may be quite specific to the location where they are found. There are a number of features that distinguish hydrates from most other mineral systems. For instance, hydrate becomes unstable once it is removed from its pressure-temperature stability zone where it is found in nature. What is more, hydrates, as clathrates, are non-stoichiometric, and since all known naturally occurring hydrates have at least two kinds of cavities which may or may not be completely filled, compositions and cage occupancies are variable [1, 2, 3]. Further, hydrates are labile, that is, their composition reflects not only the conditions during the initial formation process, but also this also changes if the nature of the fluids in contact with the hydrate change with time. This can lead to heterogeneity in composition and structure on a variety of scales [4, 5]. Sediment composition and particle (pore) sizes also play a key role in hydrate formation and accumulation, and in establishing the degree of water saturation and the level of conversion to hydrate [6].

HYDRATE RECOVERY

Careful attention to hydrate recovery from natural sites is a first and essential part of the laboratory characterization of natural gas hydrates, and this starts in the field. Unless pressure coring methods are used, decomposition of some hydrate is inevitable, although self preservation often helps the cause [7]. Since cores decompose from the outside in, the best hydrate samples will be found in the center of the core. For characterization of the hydrate phase, it is sufficient to store recovered core sections in liquid nitrogen as rapidly as possible upon recovery for transfer to the laboratory [8]. If sediment structure is to be preserved as well, far more elaborate techniques are required as the cores should not be frozen.

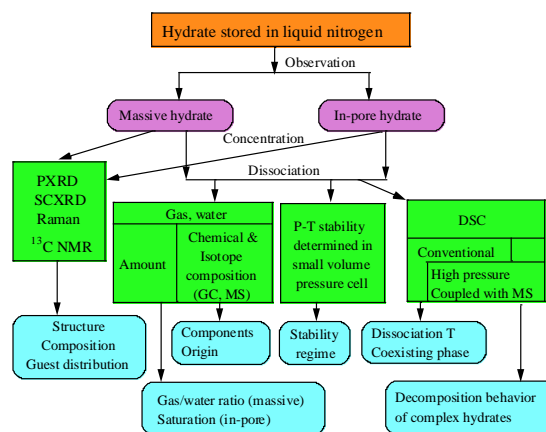


Figure 1. General scheme for the laboratory analysis of recovered natural gas hydrate samples.

HYDRATE CHARACTERIZATION

A general scheme of the laboratory analysis of natural gas hydrate and the information that becomes available is given in Fig. 1.

Macroscopic

When recovered core sections reach the laboratory, a close examination, either by eye or microscope, of the sample cooled in liquid nitrogen will often reveal the hydrate which then can be classified according to its appearance – massive, nodules, veins, etc. If there is only pore hydrate, often invisible to the naked eye, a bubble test will reveal the presence of hydrate and the amount of hydrate can be assessed by the vigour of the gas release.

If sufficient sample is available, quantitative measurements can be carried out on the amount of gas, water and solids. This will give the water saturation and, eventually, the level of conversion of water to hydrate can be estimated once the nature of the hydrate is known. Before such an analysis is carried out, it is important to remove any adsorbed gas, for instance, the N_2 gas that remains on the surface of the samples after storage in liquid nitrogen. Exposing the sample to a dynamic vacuum at $\sim 120K$ is sufficient to remove adsorbed gas, and under these conditions the hydrate will not decompose. If enough hydrate is present, the hydrate can be placed in a small-volume pressure cell and after removal of air and adsorbed gas it is

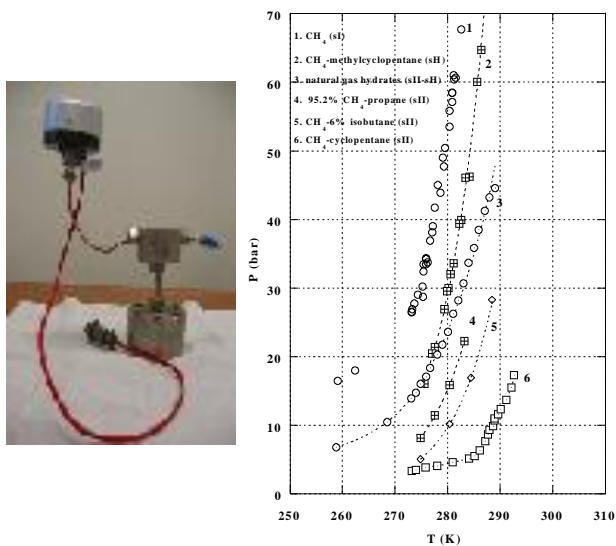


Figure 2. Left -small pressure vessel for temperature-programmed decomposition of hydrate; Right - data obtained – curve 3 is for mixed sII – sH hydrate from Barkley Canyon, Cascadia.

possible to follow the pressure-temperature behaviour of the hydrate by heating the sample in increments. After each heating step, the pressure in the cell is allowed to come to equilibrium, thus mapping out a P-T stability zone for the hydrate (Fig.2). The gas from decomposed hydrate can be captured and subjected to composition analysis by GC-MS as well as high resolution mass spectrometry for isotope analysis to give information on the origins of the gas. The sediment should be examined to determine mineralogy, particle and pore sizes and water content. Once the structure and composition of the hydrate are known, the degree of conversion of the water to hydrate can be calculated.

Microscopic

Hydrate characterization requires a determination of both the hydrate structure and composition, as these materials are non-stoichiometric and they may contain a variety of guest molecules distributed over different sites. The appropriate techniques include various powder diffraction (usually X-ray) methods to give the structure and unit cell parameters and spectroscopic methods to measure cage populations. For many recovered natural hydrates it is possible to isolate enough hydrate for study by several techniques. In cases where only pore hydrates are present it sometimes is possible to crush the hydrate/sediment composite in liquid nitrogen and harvest the finely powdered hydrate that rises to the top of the sediment for further study.

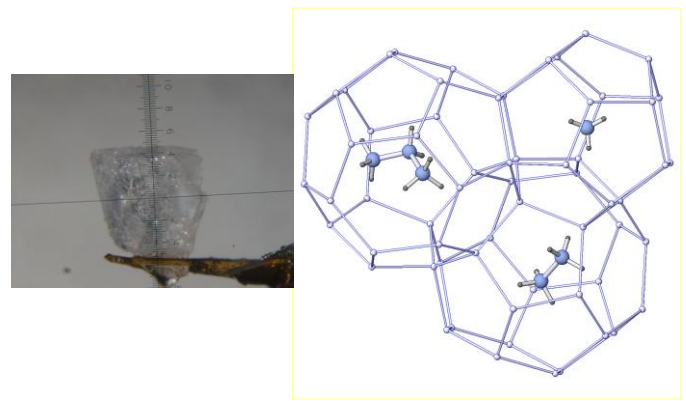


Figure 3. Single crystal of sII hydrate found in a recovered core from Cascadia – Bullseye vent (left); Structure determined by single crystal diffraction (SCD), showing location of methane, ethane and propane. Butane and isobutene were also found to be present from GC –MS, but in quantities too small to be seen by SCD (< 5% of the guest in the sII large cage)

Although powder diffraction usually yields only the unit cell parameters of the various phases present, recent work has shown that, with some assumptions, hydrate cage occupancies can be obtained in the case of simple hydrates (generally not more than one type of guest/cage) [9]. As well, in some circumstances it is possible to find single crystals of hydrate in recovered core samples [10]. Excellent structural information is available in such cases (Fig.3). For example, the structure of a sI methane hydrate crystal was refined to an R value of an order of magnitude better than for laboratory prepared crystals. Presumably this was possible because annealing of the crystal on a geological time scale removed the defects usually encountered in samples prepared in the laboratory. However, if there are a variety of guests distributed over one of the cage sites there are limits on how low cage occupancies can be before their signatures are lost in the noise.

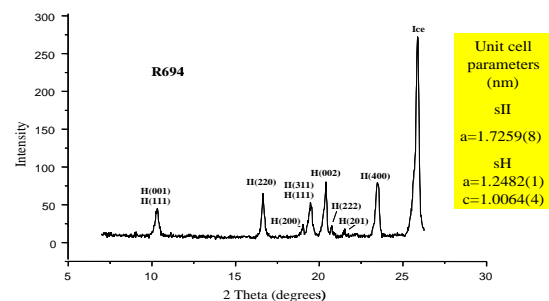


Figure 4. Detail of powder X-ray diffraction pattern of mixed sII-sH hydrate from Barkley Canyon, Cascadia

Similarly, if mixed phases are present it is necessary to examine the powder patterns carefully in order to track the minor component. Fig. 4 shows that some reflections needed to be indexed as sH hydrate with sII being the major component. A useful innovation in the study of hydrates is the availability of a sample cell for *in-situ* high pressure work. Not only is it possible to follow hydrate formation by PXRD, but also processes such as hydrate decomposition.

^{13}C NMR and Raman spectroscopy have been developed to provide information on both hydrate structure and cage occupancies (Fig. 5) [1][2][3][4][11]. Each technique has its advantages and disadvantages, including ease of use and the capital investment required. An important distinction between the two lies in the actual sampling of the hydrate: NMR gives an average over the bulk of the sample – usually from tens to a few hundred mg, whereas Raman gives a localized response from a spot of a few microns in diameter on the surface. NMR spectroscopy is inherently quantitative, as it counts the number of spins of a certain type, each at a characteristic chemical shift. The Raman spectrum is more difficult to interpret and the line intensities depend on the cross section for Raman scattering. This means that quantitative analysis requires calibration of Raman with another technique such as NMR. On the other hand, the spot analysis of natural hydrates by Raman is able to give information on sample homogeneity. A recent application in this area is that of Raman mapping [4]. A sI hydrate recovered by IODP 311 containing mainly methane and a small quantity of H_2S , indicating that the latter can be present either in a mixed $\text{CH}_4/\text{H}_2\text{S}$ hydrate or isolated H_2S and CH_4 hydrates.

Differential Scanning Calorimetry of recovered samples is another technique that can give information on the nature of the hydrate present by following the differential thermal input during decomposition of the hydrate. Quantitative measurement of the thermal events is not trivial as the mass and heat capacity of the sample may

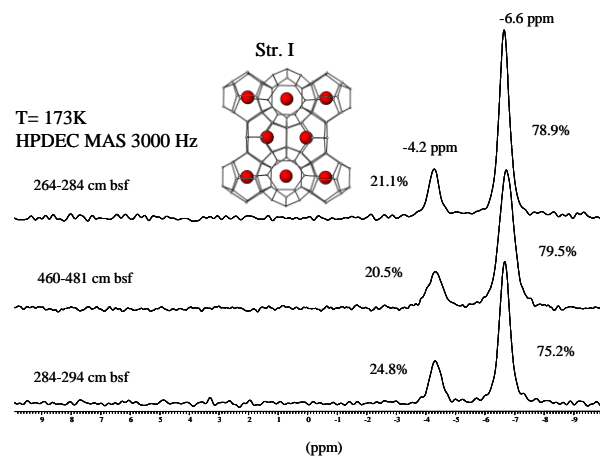


Figure 5. ^{13}C NMR spectrum of a sI methane hydrate samples recovered from a cold vent field, Barkley canyon, showing the signal of methane in small and large cages.

change when gas evolves during decomposition. However, sometimes by comparing the thermal profile of different samples, including synthetic ones, can give some valuable insight into the nature of the hydrate. Figure 6 shows that pure methane and H_2S hydrates have very different thermal profiles during decomposition, reflecting their different stabilities. The natural samples contain up to a percent of H_2S , yet the traces show remarkably different thermal profiles. Some (marked with arrows) show a two step process, others a single step, suggesting that the samples with the marked traces have distinct regions of hydrate – perhaps pure methane hydrate as well as mixed $\text{CH}_4\text{-H}_2\text{S}$ hydrate [5].

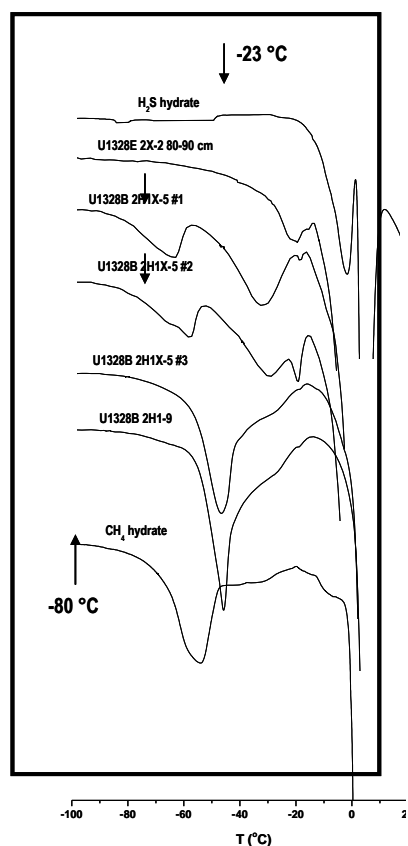


Figure 6. Differential Scanning Calorimetry traces of *sI* hydrates pure H₂S hydrate (top) samples recovered by IODP 311 and pure methane hydrate (bottom).

Technique	Information
1. Visual observation	Hydrate morphology
2. Bubble test	Presence of hydrate
3. Temperature programmed decomposition in small pressure cell	P- T stability curve
4. Gas capture– (from 3) GC – MS Isotope analysis	Gas composition Origin of gas
5. Water content of sediment	Pore saturation
6. Sediment particle/pore sizes	
7. Total gas measurement	Provisional estimate of water conversion to hydrate
8. Powder X-ray diffraction	Structure of hydrate, unit cell
9. Single crystal X-ray diffraction	Structure and composition of hydrate
10. Raman spectroscopy	Composition of hydrate Sample heterogeneity
11. NMR spectroscopy	Structure and composition of hydrate, cage occupancies
12. Results from 5 – 11,	Amounts of hydrate, water conversion
13. Differential scanning calorimetry	Thermal hydrate decomposition characteristics
14. High pressure calorimetry – mass spectrometry	Thermal hydrate decomposition and produced gas identification – simulated field conditions

Table 1 Summary of techniques and information

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