



Investigation of the 'Memory Effect' of THF-Hydrate Formation on Different Surfaces

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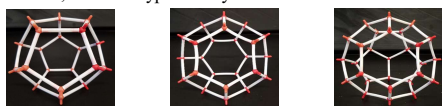
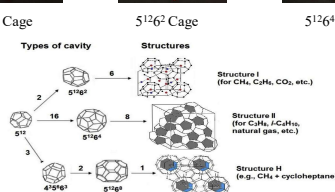
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Introduction

Clathrate hydrates: Clathrate hydrates are composed of guest molecules of liquid or gas trapped in cages of water under high temperature and low pressure. Different guest molecules, based on their sizes, form different sizes and shapes of cages and therefore, different types of crystals.



Clathrate hydrates spontaneously form in oil and gas pipelines, thereby clogging them. This can be a significant environmental hazard. On the other hand, hydrates themselves are a source of energy and have the potential to serve as efficient energy/gas storage medium. Thus, there is significant interest in characterizing the stability and formation conditions of hydrates.

Memory Effect: Clathrate hydrates tend to have a "memory effect", which is the ability of these molecules to form with greater efficiency when prepared from melted clathrate hydrates than being prepared from freshly prepared solution.

Why do clathrates exhibit Memory Effect?

1. Residual Cage Structure Hypothesis.
2. Local Concentration Hypothesis
3. Surface Imprint Hypothesis

However, nucleation of crystals is a stochastic process, so we need to make a large number of observations to understand the memory effect.

Experimental Objective and Hypothesis

This project examines the memory effect of clathrate hydrate by using clathrate hydrates prepared from tetrahydrofuran (THF, C_4H_8O). Freezing point of THF is 4.6 °C. The hypothesis is that THF hydrates will have a higher probability of formation when they are prepared from melted sample of previously formed hydrates than freshly prepared solution, which is the evidence of memory effect. To test the surface imprint hypothesis, memory effect of THF clathrate hydrates will be tested on various surfaces to compare the difference in rate of hydrate formation in them.

Sample Preparation

- 1:17 molar ratio of THF:Water was mixed and filtered
- Solution was frozen in the fridge
- It was then put in the sample holder disk with a repeating pipette

Experimental Setup

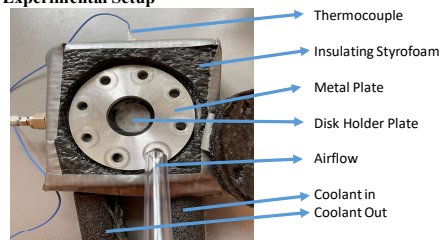


Fig: Apparatus Setup

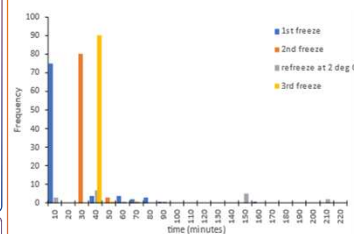
Building Sample Holder Disks

- CNC machine was used to build disks
- Diameter of disks is 1 inch, 92 holes in each disk



Fig: Sample Holder Disks

Experimental Procedure and Results



- 91 samples in aluminum disk were kept at 2 degree Celsius where nothing froze
- Samples were cooled at -15 degree Celsius and then kept at 2 degree Celsius to check if they were hydrates, since THF should freeze at any temperature below 4 degrees Celsius, but ice cannot form at 2 degrees Celsius. Process was repeated three times.
- No sample melted at 2 degrees after 1st freeze, showing clathrate formation. All samples first melted after 2nd freeze and then some of them refroze, which might be due to melting of ice first and then formation of clathrate hydrates.
- No samples melted after 3rd freeze showing clathrate formation in all samples.

Experiment Images



Both frozen and melted samples in earlier Teflon disk built by Jake Perkins



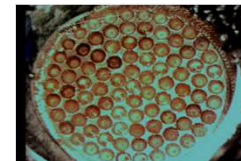
Melted samples in aluminum disk



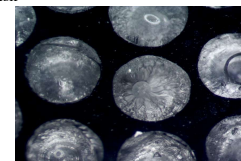
Melted samples in white Teflon disk



Both melted and frozen samples



Melted and frozen samples in copper disk



Clathrate formation in aluminum disk

Future Work

- Experiment using disks made from various materials
- Analyze the data from current experiment
- Improve temperature controlling and recording method

References

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