

## EXPERIMENTAL OBSERVATIONS OF HYDRATE FORMATION IN A CONVECTION TANK

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**Summary** Experiments were carried out to study the hydrate formation in water and the refrigerant R141b ( $\text{CH}_3\text{CCl}_2\text{F}$ ) contained in a convection tank. Experiments were performed both in the quiescent and convection mode. A thin hydrate film forms on the interface between the two fluids after seeding. Then a mushy layer forms above the hydrate film and grows in time. In a test tank with copper sidewalls, hydrates also grow from these walls at a faster rate than those at the interface. Under the convection mode, growth of hydrates in the mushy layer is very much affected by the convection current.

### INTRODUCTION

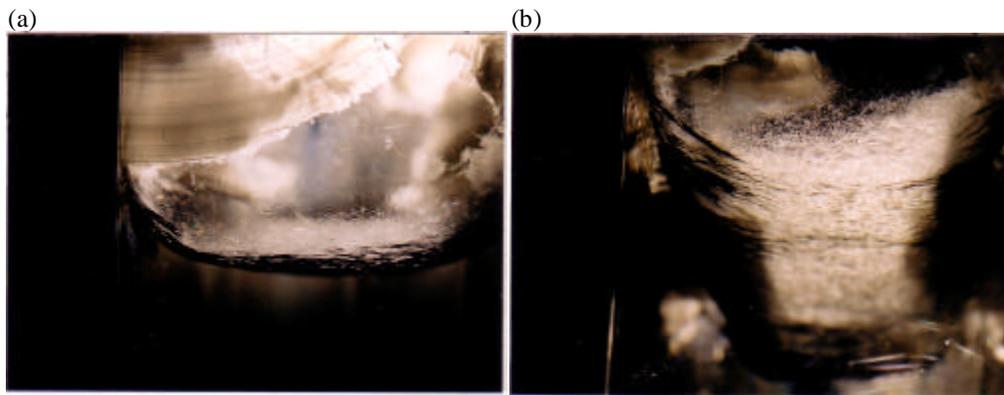
Clathrate hydrates are crystalline compounds formed by cage-like structure of hydrogen bonded water molecules enclosing a guest molecule of a hydrate forming substance. Many substances such as gases and fluorocarbon refrigerants are hydrate formers. Hydrates of  $\text{SO}_2$  was discovered by Priestley in 1790, and that of chlorine gas independently by Davy in 1811. Natural gas hydrates became industrially important in 1930's when they were found to form blockages in gas pipelines, thus prompting much research in their formation and dissolution, see recent reviews of Makogan [1] and Sloan [2]. Ohmura et al [3] were the first to perform experiments on hydrate formation on a drop of liquid R141b immersed in water. Kato et al [4] studied hydrate formation on a jet of R141b entering into a flowing water stream. Kobayashi et al [5] and Ito et al [6] made microscopic observations of the growth of R141b hydrates. We have carried out experiments to study the growth of such hydrates in a convection tank.

### EXPERIMENTAL APPARATUS AND PROCEDURE

Our experiments were carried out in two different test tanks both were 3cm wide. The first tank has 9.5cm square sidewalls made of chrome-plated copper, with passages provided for the circulation of fluids from two different constant-temperature baths. All other walls were made of Plexiglas. The other tank is smaller and is made of Plexiglas throughout with 5cm square sidewalls equipped with coolant passages. Both tanks are well insulated by polystyrene boards. The test procedure is to fill the lower half of the tank with liquid R141b (heavier and hydrophobic) and the upper half with water. After the fluids have been cooled to the desire temperature, a slurry consisting of water and tiny hydrate particles prepared beforehand is introduced in the water to initiate hydrate formation process. The growth of the hydrate layer is recorded by photographs at regular intervals up to 24 hours.

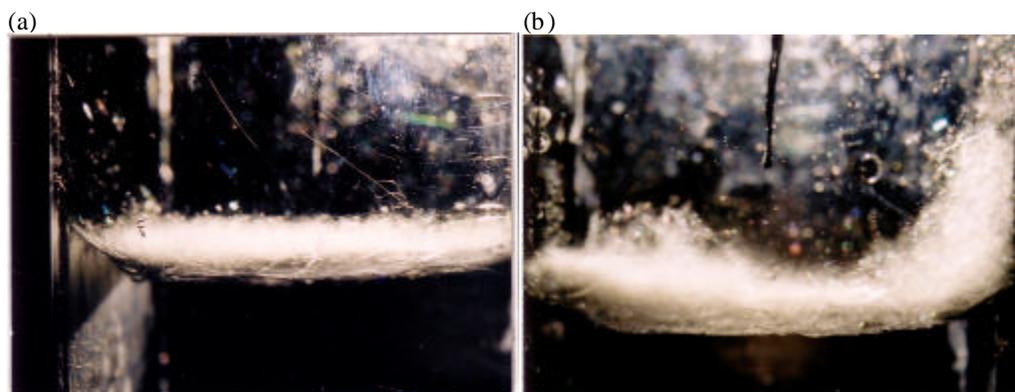
### RESULTS

The first experiment was carried out in the tank with copper sidewalls at a quiescent state of  $2^\circ\text{C}$  with R141b and water pre-saturated with R141b. Hydrates formed into a film on the interface soon after seeding. Thereafter hydrates continued to form and they appeared as a mushy layer consisting of tiny crystal whiskers immersed in water just above the interfacial film. No growth of hydrates appear on the under side of the film. At the same time, hydrates started to grow from the two copper sidewalls with a growth rate much larger than that at the interfacial film. The hydrates grown from the walls were similar to the methane hydrates observed by Makogon (1997). No growth was observed from the Plexiglas walls. Two hours after seeding, hydrates grown from the sidewalls reached the middle of the tank and the hydrate mushy layer became thicker as shown in a head-on view of the interface, Fig. 1a. The view from below at the same time, Fig. 1b, clearly shows the nature of the crystals in the mushy layer above the interface and the comparatively smooth crystal surface below the interface. Experiments with plain water and R141b under the same conditions show similar results except the growth rate is slower. In order to study the growth at the interface clearly, the next two experiments were conducted in the all Plexiglas test tank.



**Fig. 1** Experiment in tank with copper sidewalls at 2°C quiescent state 2 hrs after seeding. (a) Head-on view of the interface. Note hydrate mushy layer above interfacial hydrate film, and growth from the sidewalls. (b) View of interface from below showing loose crystal structure of the mushy layer.

Experiment 2 was conducted at 2°C in quiescent state with plain water. The interfacial hydrate crystal film formed quickly after seeding. The hydrate mushy layer above the interface grew in time, at 5 hours after seeding; its thickness was approximately 4mm as show in Fig. 2a. It can be seen from this photo that the mushy layer thickness is quite uniform, and that there is no hydrate formation at either of the sidewalls.



**Fig. 2** Experiments in all Plexiglas tank. (a) Interfacial hydrate layer at 5 hrs after seeding under 2°C quiescent state. (b) Convection state with 3.3°C at left and 1.9°C at right with counterclockwise circulation. View of the hydrate interfacial layer at 4 hrs after seeding.

Experiment 3 was a convection experiment with the left wall at 3.3°C and the right wall at 1.9°C. Circulation in the water is counter-clockwise. A photo taken at 4 hours after seeding is shown in Fig. 2b, and the effect of convection is clearly visible. Not only the hydrates were nonuniformly distributed with large accumulations along the right wall and at the foot of the left wall, but also the hydrate growth rate, as compared to the previous experiment, was enhanced by convection. The results of these experiments show that convection has an important effect on the growth of hydrates.

## References

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