

# Production of Natural Gas Hydrate by Using Air and Carbon Dioxide

Yun-Ho Ahn, Hyery Kang, Dong-Yeun Koh, Huen Lee

**Abstract**—In this study, we demonstrate the production of natural gas hydrates from permeable marine sediments with simultaneous mechanisms for methane recovery and methane-air or methane-air/carbon dioxide replacement. The simultaneous melting happens until the chemical potentials become equal in both phases as natural gas hydrate depletion continues and self-regulated methane-air replacement occurs over an arbitrary point. We observed certain point between dissociation and replacement mechanisms in the natural gas hydrate reservoir, and we call this boundary as critical methane concentration. By the way, when carbon dioxide was added, the process of chemical exchange of methane by air/carbon dioxide was observed in the natural gas hydrate. The suggested process will operate well for most global natural gas hydrate reservoirs, regardless of the operating conditions or geometrical constraints.

**Keywords**—Air injection, Carbon dioxide sequestration, Hydrate production, Natural gas hydrate.

## I. INTRODUCTION

HOW can we efficiently and safely exploit the tremendous amount of natural gas stored as gas hydrate underneath the surface of the earth? This serious task remains an urgent challenge, but fortunately recent field trials for natural gas hydrate (N.G.H.) production have suggested a hopeful new prospect for using gas hydrates as energy resources. The estimated technically-recoverable global volume of N.G.H. is roughly  $\sim 3 \times 10^{13} \text{ m}^3$  which is close to the amount of shale-gas ( $\sim 2 \times 10^{13} \text{ m}^3$ ) in the United States deposits [1], [2]. In 2012 and 2013, there were two field production tests. One onshore field trial was carried out in 2012 on the Alaska North Slope in the United States of America to investigate the potential of  $\text{CH}_4$  -  $\text{CO}_2$  replacement [3]. The first offshore field trial was attempted in 2013 in the Eastern Nankai Trough in Japan, where the depressurization technique was adopted [4], [5]. Meanwhile, in Korea, two Ulleung Basin Gas Hydrate (U.B.G.H.) Drilling Expeditions were carried out (2007 and 2010), and they confirmed the existence of considerable amounts of N.G.H. in the deep-sea sediments there [6]-[8]. A U.B.G.H. field production test is scheduled for mid-2015 at the sites (U.B.G.H. 2-6) with geological conditions providing the greatest potential [8].

The currently proposed technologies for marine N.G.H. production are generally derived from standard methods used in conventional oil and gas industries. These take advantage of the driving potential of differences in temperature, pressure and

chemical potential, which cause significant changes in the conditions within N.G.H. reservoirs. Thermal stimulation causes vacillation between N.G.H. formation and dissociation temperatures ( $\Delta T$ ), depressurization shifts the reservoir pressure to much lower than N.G.H.-formation pressure ( $\Delta P$ ), and inhibitor injection alters the chemical environment ( $\Delta \mu$ ) of the N.G.H. to inhibit the stable formation of gas hydrates [9]. However, these methods all raise serious concerns about repercussions such as slope failure and seabed ecosystem destruction [10], which must be minimized through scientific breakthroughs. A  $\text{CH}_4$ -replacement mechanism driven by  $\text{CO}_2$  injection has recently been suggested as a plausible new approach to production [11], [12]. It has the potential of being a nondestructive means by which energy production and carbon dioxide sequestration might be achieved simultaneously. However, under the harsh conditions of naturally occurring gas hydrate sites, injected  $\text{CO}_2$  gas readily transforms to a liquid state, slowing and weakening its soaking and migration. Undesirable fluctuation between the two  $\text{CO}_2$  phases (gas and liquid) makes injection and diffusion very unstable which leads to a low replacement rate and recovery yield. To overcome such weaknesses, in previous reports, we proposed the use of a gaseous mixture of  $\text{N}_2$  and  $\text{CO}_2$  [13]-[15]. The overall recovery of methane was greatly improved by specific attack of  $\text{CH}_4$  molecules in sI-S cages with added  $\text{N}_2$  molecules. In a field production test on the Alaska North Slope in 2012, the  $\text{CO}_2/\text{N}_2$  injection method was adopted as the main process and was successfully performed [3].

At this stage, we note that each N.G.H. reservoir around the globe has its own distinctive geological characteristics, and that these need to be fully examined to determine compatible production techniques. These N.G.H. geological characteristics also vary with formation depth and are determined by reservoir pressure and temperature. For example, the temperature and pressure ranges around 278 K and 7 MPa on the Alaska North Slope. The N.G.H. site in the Nankai Trough of Japan is located at a depth near 1000 m and  $\sim 287$  K. In the U.B.G.H. site, the ranges of temperature and pressure are 288-293 K and 20-22 MPa, respectively. The pressure exerted on an N.G.H. site is determined by the hydraulic pressure exerted by the water column (depth), but the surrounding temperature may be much higher than expected because of a geothermal gradient beneath the N.G.H. layer. The two exchange approaches using  $\text{CH}_4$  -  $\text{CO}_2$  and  $\text{CH}_4$  -  $\text{CO}_2/\text{N}_2$  are to a certain degree adaptable, but in reality, we still need to develop a more feasible approach to deal with huge amounts of N.G.H. In this work, we demonstrate an N.G.H. production method using air and  $\text{CO}_2$ /air. It is known that  $\text{N}_2$  and  $\text{O}_2$  gases can play a role in breaking down methane

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hydrates because of the chemical potential difference ( $\Delta\mu$ ) between their gas and solid phases [16]-[18]. Earlier such methods for replacement and dissociation were only considered for use in systems with very dilute methane hydrates [13]-[18]. Accordingly, a continuous supply of fresh air into the N.G.H. can make it melt completely. However, this cannot be recommended because in this case, the methane concentration in the recovered gas becomes quite small, requiring additional separation facilities. The use of pure air contributes to methane production by N.G.H. melting, but the key issue arises as we further extend the systems with concentrated methane hydrates or injection of  $\text{CO}_2$ -enriched air ( $\text{CO}_2/\text{air}$ ). To address in detail the process of releasing methane from N.G.H. with air or  $\text{CO}_2/\text{air}$ , we defined the new variable 'critical methane concentration' (C.M.C.), which consists of the number of methane and injected molecules, and performed experiments to reveal the mechanisms involved (Fig. 1 A).

## II. EXPERIMENTAL MATERIALS AND METHODS

### A. Sample Preparations and Gas Injection Procedures

Water of ultrahigh purity was obtained from a Millipore purification unit.  $\text{CH}_4$  and air ( $\text{O}_2$  21 mol% and  $\text{N}_2$  balance) gas were purchased from the Special Gas Company (Daejeon, Republic of Korea), with a stated minimum purity of 99.95 mol%. The apparatus for hydrate formation and gas injection was designed to monitor the status of the fluids via a high-resolution video camera. A high pressure cell was equipped with two sight quartz windows for visual observation. It had an internal volume of  $50\text{ cm}^3$  and a working pressure of 40 MPa. The cell was placed inside a refrigerated water-ethanol mixture bath (RW-2025G; JEIO Tech). The pressure of the system was measured by a pressure transducer with an uncertainty of  $\pm 0.01\%$  in a range of 0 to 35 MPa. In order to eliminate the heating effect of the entering air, it was cooled in the same bath used with the targeted gas hydrates for 5 h. The precooled air was injected using a micro-flow syringe pump (ISCO, model 260D) operated in a constant flow mode. The methane gas in the gas-hydrate reactor was exchanged for air gas for 30 seconds, which was deemed to be long enough for the methane gas to be replaced by the air gas.

### B. Raman Spectroscopy

For Raman measurements we used the Horiba Jobin Yvon LabRAM HR UV/Vis/NIR high resolution dispersive Raman microscope in which a CCD detector was equipped and cooled by liquid nitrogen. Samples were kept at 77 K during measurements. The excitation source was an Ar-ion laser emitting a 514.53 nm line. The laser intensity was typically 30 mW.

### C. Powder X-Ray Diffraction

The XRD patterns were obtained using a Rigaku D/max-IIIC diffractometer with  $\text{CuK}\alpha$  as a light source ( $\lambda=1.5406\text{ \AA}$ ) at a generator voltage of 40 kV and a generator current of 300 mA. A low-temperature stage attached to the XRD unit maintained the working temperature at 93 K, and a step-scan mode was applied ( $0.02^\circ$  step-size and 3 s per step).

### D. Gas Chromatography

The concentration of gaseous guest-molecules in the hydrate sample was measured using a Young-Lin 6000 (Young-Lin, Republic of Korea) gas chromatograph. The samples were moved to a precooled reactor ( $\sim 77\text{ K}$ ) each time, and it was evacuated using a vacuum pump. The gas phase was analyzed after being held at room temperature until the hydrate samples completely dissociated. Helium was used as the carrier gas, and the GC column was maintained at 55 kPa and 353 K.

## III. RESULTS

Up to the present, most research on N.G.H. replacement has focused on direct chemical exchange between dissimilar guest molecules, fully considering the molecular details of guest-guest and guest-host interactions in each unique hydrate structure. The sudden injection of gases such as nitrogen, oxygen and air initiates N.G.H. decomposition and proceeds to establish a new equilibrium state involving N.G.H., water and gas. We realize that air is abundant and is available at any time and at any location, which makes it the most attractive element for practical production of N.G.H. The initial stage of air injection is intended to strongly decompose the N.G.H., release the methane and finally alter the gas-phase composition around the N.G.H. Meanwhile, the guest species of nitrogen and oxygen are expected to possess strong potential for forming pure, as well as mixed, hydrates. At this point, the following issues arise and need to be addressed. First, how does air drive the N.G.H. to melt? The fresh air might have the maximum potential for decomposing N.G.H., but gradually weakens and eventually loses its methane recovery capacity at a certain methane concentration. N.G.H. 'decomposition' is considered to be a more appropriate expression than 'dissociation' because the crystalline hydrate structure must be destroyed before it can generate water and methane gas. The N.G.H. is continuously depleted until the chemical potentials of methane in both the solid N.G.H. and gas phases are equal and right after an arbitrary point, decomposition of methane hydrate stops and anomalous preservation of the methane hydrate phase occurs. Now, we define the ratio between the methane concentration in hydrate ( $n_{\text{CH}_4}$ ) and the injected gaseous air (or  $\text{CO}_2/\text{air}$ ;  $n_{\text{air}}$  or  $n_{\text{CO}_2/\text{air}}$ ) at equal chemical potentials as the 'critical methane concentration' (C.M.C.). The C.M.C. plays a central role in determining methane recovery from N.G.H. and can be influenced by complex surrounding factors such as the depth of marine N.G.H., geothermal gradient, sediment geochemistry and amount of saturated pore water.

For precise C.M.C. analysis we, above all, limited the experimental scope to the achievement of either complete or partial N.G.H. decomposition. First, we used a fixed-volume high-pressure reactor, controlling the molar ratio between methane in the N.G.H. and air ( $n_{\text{CH}_4}/n_{\text{air}}$ ) according to the initial N.G.H. amount. The temperature was fixed at 288.15 K and air was injected at 20 MPa to match closely the conditions found in the U.B.G.H. in the East Sea of Korea. When a large amount of air ( $n_{\text{CH}_4} < n_{\text{air}}$ ) was present, complete N.G.H. decomposition occurred (Fig. 1 B, left part of dotted line), thus leading to

N.G.H. depletion. Here, it becomes quite interesting to see what occurred above the C.M.C. First, we observed the incipient point of partial N.G.H. decomposition (Fig. 1 B, right part of dotted line). Thus, we identify three phenomenological stages: release of methane molecules from N.G.H., N.G.H. structure destruction via melting and increase in the concentration of gaseous methane, which are all caused by the chemical potentials of guest-molecules. Approaching the dynamic equilibrium between solid N.G.H. and gaseous air-methane, the vigorous escape of methane from N.G.H. is suppressed and eventually ceases. Accordingly, it is interesting to determine the lowest methane concentration that limits methane production from N.G.H. The complete N.G.H. decomposition at the C.M.C. can readily be confirmed visually, but above the C.M.C., a noticeable amount of N.G.H. still remains (Fig. 1 C). The continuous supply of fresh air to N.G.H. will make it possible for the gaseous phase to be in a more  $\text{CH}_4$ -dilute state, maintaining its value lower than the C.M.C., and thereby favorably leading to full decomposition of methane hydrates. However, the ultimate task is to determine the optimum methane-air ratio that could be applied to real N.G.H. fields. This requires careful consideration of many sea-bed-related complex variables, but it will take a bit more time to resolve it within the scope of feasible N.G.H. production. The N.G.H. samples remaining after sufficient exposure to air ( $n_{\text{CH}_4} \gg n_{\text{air}}$ ) have to be carefully quenched and analyzed for clear identification of solid phases that might form with the aid of air. The experimental details are presented in Section II.

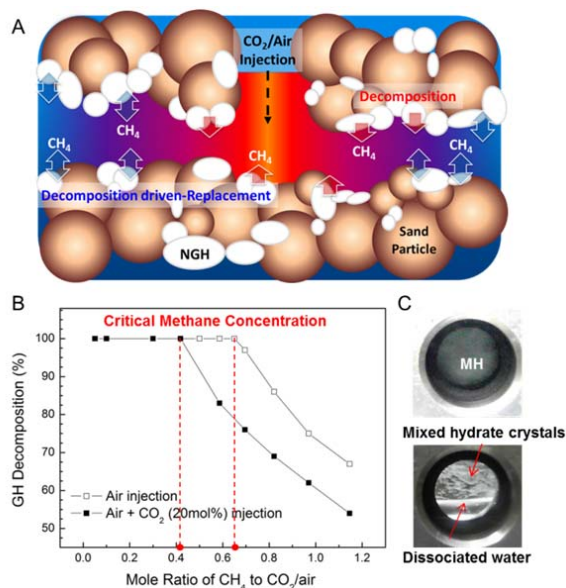


Fig. 1 (A) Schematic illustration of the described air (or  $\text{CO}_2/\text{air}$ ) driven NGH production method composed of two distinct steps: NGH decomposition caused by injected air (or  $\text{CO}_2/\text{air}$ ); subsequent decomposition driven guest exchange process, (B) Discovery of the concept of critical methane concentration (CMC) depending on the molar ratio between  $\text{CH}_4$  and injected air and  $\text{CO}_2/\text{air}$ , (C) Methane hydrate at 288.15 K and 200 bar before air injection (top), and mixed hydrate crystals coexist with water at 288.15 K after air injection above the critical concentration (bottom)

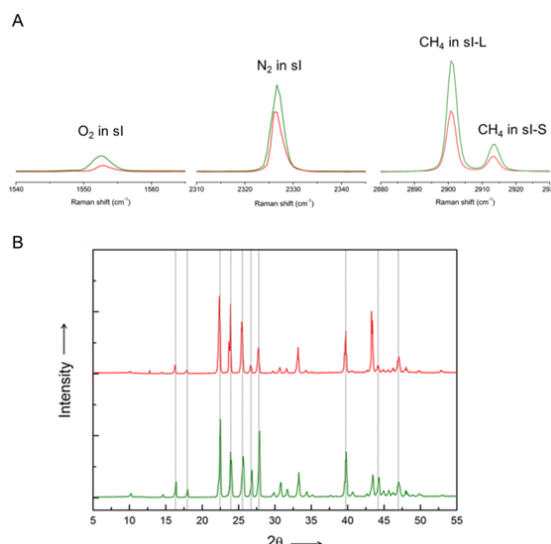


Fig. 2 (A) The Raman spectra of the mixed  $\text{N}_2+\text{O}_2+\text{CH}_4$  hydrate at 77 K. (B) PXRD patterns of each hydrate at 93 K

The Raman spectra (Fig. 2) of two samples formed from different methane-air mole ratios ( $>\text{C.M.C.}$ ) reveal that the injected  $\text{N}_2$  and  $\text{O}_2$  molecules are continuously encaged in N.G.H. until the equilibrium state is reached [9], [19]. In addition, the corresponding PXRD patterns (Fig. 2 B) confirm that a mixed hydrate structure remains in the Cubic Structure I (sl) phase. These two spectroscopic results suggest that guest-replacement is likely to occur beyond the C.M.C. The water coming from partial dissociation of the hydrate by air injection is represented as hexagonal ice (Ih) because the PXRD patterns were analyzed at 93 K. Quantitative sample analysis was conducted to find the relative contributions of the two key mechanisms, decomposition and replacement. The main peak intensities were determined by profile-matching the whole-pattern within the space group corresponding to structures Ih and sl. Stable capture of air components in sl-S and sl-L strongly implies that N.G.H. decomposition, just after gas injection, causes chemical replacement even at high temperatures, in the U.B.G.H.

Now we will focus on extending the phenomenological concept of air-based N.G.H. decomposition to the  $\text{CH}_4 - \text{CO}_2/\text{N}_2$  approach by simply using air instead of  $\text{N}_2$ . However, carbon dioxide is known to be a strong hydrate former and thus carbon dioxide mixed with air slows the N.G.H. decomposition rate. We note that carbon dioxide can replace methane stored in the N.G.H., which is greatly influenced by sediment characteristics, pressure and temperature. We further note that the C.M.C. is dramatically lowered when  $\text{CO}_2$  is added as a second guest (Fig. 1 B). When the methane- $\text{CO}_2/\text{air}$  ratio passes through the C.M.C., the inclusion of injected gases ( $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{CO}_2$ ) increases (detected by Raman spectra presented in Figs. 3 A-C). Furthermore, we tested real U.B.G.H. samples (Figs. 3 D-F) and observed trends similar to those of methane hydrates exposed to an identical methane- $\text{CO}_2/\text{air}$  ratio, confirming that the C.M.C. is universally applicable and can be used as a critical criterion for distinguishing the two core N.G.H.

recovery mechanisms, decomposition and replacement.

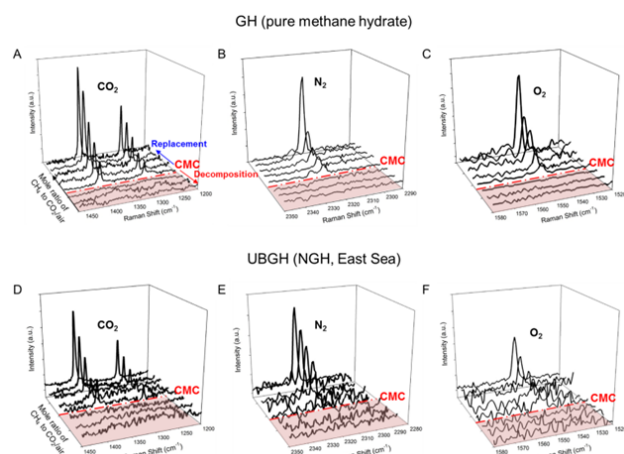


Fig. 3 Direct visualization of guest-exchange analyzed by the Raman spectra after the injection of CO<sub>2</sub>/air (20 mol% CO<sub>2</sub> and 80 mol% air) into pure CH<sub>4</sub> hydrate (A-C) and N.G.H. (D-F)

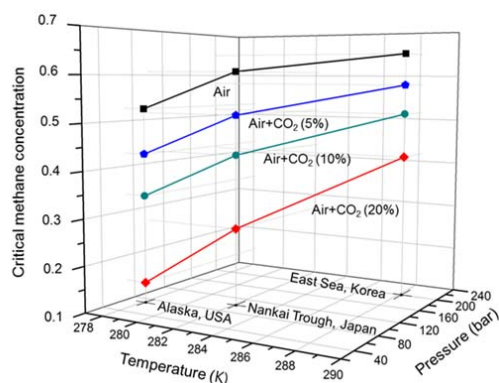


Fig. 4 CMC observed in the three representative NGH reservoirs. Black line indicates pure air injection. Blue, green and red lines indicate 5, 10 and 20 mol% CO<sub>2</sub> in air gas, respectively

Another important aspect of this research was to explore the effect of temperature and pressure on C.M.C.-related behavior. We demonstrated the potential applicability of CO<sub>2</sub>/air injection to three N.G.H. production test sites on the Alaska North Slope (USA), Nankai Trough (Japan) and Ullung Basin (Korea), and the results are shown in Fig. 4. Representative pressures and temperatures from those sites were specified for the upcoming C.M.C. analysis. To see the degree of N.G.H. decomposition, we first injected pure air into the N.G.H. and found a relatively high C.M.C. of 0.53-0.65. The C.M.C. gradually decreased as the N.G.H. pressure and temperature decreased. It is again worth noting that the injection of pure air and CO<sub>2</sub>/air can simultaneously drive the two distinct mechanisms (decomposition and replacement) needed for N.G.H. recovery. Through such a concept (combined hybrid production), we need to establish the process boundaries of the predominant mechanisms occurring in real N.G.H. fields. It is generally acceptable that hydrate replacement is accelerated when the temperature and pressure are lowered while

decomposition becomes more active at higher temperature and pressure. When 5 mol% of carbon dioxide is added to pure air, its C.M.C. shows a reduction of 10-18% compared with pure air alone, depending on surrounding conditions at the N.G.H. sites. Several more tests revealed that the C.M.C. generally decreases with increasing CO<sub>2</sub>. The lowering of the C.M.C. by the activity of carbon dioxide results in a noticeable reduction of the N.G.H. decomposition rate, and is probably linked closely to its potential for guest-exchange with methane. We thus conclude that use of high-CO<sub>2</sub> in air leads to replacement - dominant N.G.H. recovery. Here, we notice that both CO<sub>2</sub> and CH<sub>4</sub> form sI hydrates, while air composed of N<sub>2</sub> and O<sub>2</sub> forms sII structures. Thus, we need to carefully analyze the structural patterns resulting from the complex interactions of the injected guest species of CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>. Below about 3% CO<sub>2</sub> the sII hydrates prevail, according to the PXRD patterns, but above 3% CO<sub>2</sub> sI hydrate formation becomes possible. For verification of stability we measured three phase (H+L+V) equilibria using the isochoric process as presented in Fig. 5. Additionally, we observed that just a small increase in the carbon dioxide concentration in the vapor phase causes a significant increase of it in the mixed CO<sub>2</sub>/air hydrate phase.

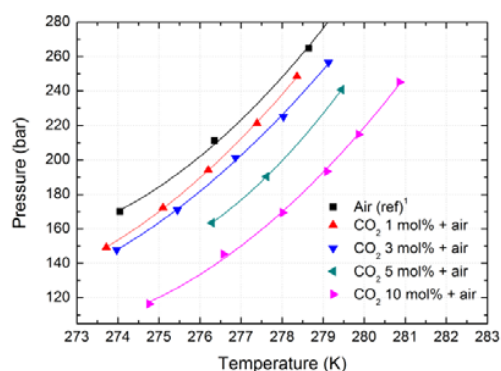


Fig. 5 H-Lw-V phase equilibrium data for the CO<sub>2</sub> + air (O<sub>2</sub> 20 mol% and N<sub>2</sub> balance) + water mixture measured at 1, 3, 5, and 10 mol% of CO<sub>2</sub>

#### IV. DISCUSSION

The most urgent task to advance N.G.H. production is to find an economically feasible means that can proceed by spontaneous, natural processes. As a major future energy resource, N.G.H. may compete with shale gas only if we can reduce the cost of primary production from large N.G.H. deposits. Depressurization has been attempted in N.G.H. field tests, most recently in the Nankai Trough (Japan). We understand that, by whatever method we choose, methane gas will be released from solid N.G.H. by melting, by decomposition or by replacement via chemical exchange. A number of strongly influential variables that drive methane extraction control the two different N.G.H. production mechanisms, while which of the two mechanisms is predominant remains to be determined.

From the insights gained from this study, we suggest a plausible strategy for extracting fuels from N.G.H. In the first

phase, CO<sub>2</sub> (transported from inland sources) and compressed air is mixed in-situ to prepare for injection into the N.G.H. layer. This 'in-situ mixing' concept allows a very effective preparation procedure for injecting gas mixtures. Liquid CO<sub>2</sub> transported from the inland sources is then mixed with compressed air captured above the production test field to produce the CO<sub>2</sub>/air gas mixture. (This is much easier than working with liquid CO<sub>2</sub>). The CO<sub>2</sub>/air gas mixture is then injected into the sediment and diffused throughout the N.G.H. layers. The first contact between the CO<sub>2</sub>/air gas mixture and the gas hydrates will induce decomposition of a certain portion of N.G.H. in the sediments. This decomposition step eventually increases the partial pressure of CH<sub>4</sub> inside the N.G.H. layer and induces a 'decomposition driven-replacement process'. The increased population of CH<sub>4</sub> molecules significantly reduces the thermodynamic barrier for replacement reactions. This replacement process enhances the geo-mechanical stability of the N.G.H. layer by forming stable hydrate lattices (Fig. 1 A). Here, we again note that the nondestructive replacement process preserves host water-lattices in the N.G.H.-bearing sediments as part of the newly formed air or CO<sub>2</sub>/air hydrates. In contrast, N.G.H. decomposition by depressurization requires large volumes of water to be displaced from the N.G.H. Furthermore, the ensuing endothermic temperature drop caused by decomposition can result in undesirable formation of secondary methane hydrate or ice in the well and near the wellbore. The chemical exchange of dissimilar guest molecules does not involve significant cooling [20], and thus the geo-mechanical stability of gas hydrate-bearing sediments is not threatened. Shallow gas-hydrate-bearing sediments (Bottom Simulating Reflector depth < 200 m) are poorly consolidated, or unconsolidated, and the hydrate provides mechanical integrity to the formation as a binding material.

We present three key aspects of our findings: 1) We defined a new factor (C.M.C.) related to the methane recovery rate from natural gas hydrates, 2) We obtained C.M.C. values for three distinct conditions (simulating three representative reservoirs) experimentally, and 3) We verified that starting decomposition leads to replacement of methane by injected CO<sub>2</sub>/air in N.G.H. According to the present outcomes, we conclude that the proposed process is likely the most efficient, nondestructive and commercially-viable means (compared to conventional ones) for onshore and offshore methane production from N.G.H., and it can be widely adapted to diverse geological conditions.

#### ACKNOWLEDGMENT

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