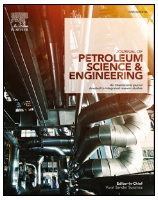
Journal of Petroleum Science and Engineering 196 (2021) 107772

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: http://www.elsevier.com/locate/petrol



Effects of soaking process on CH_4–CO_2 replacement efficiency for hydrate-bearing sediments

Jae Eun Ryou [a], Riyadh I. Al-Raoush [b], Khalid Alshibli [c], Joo Yong Lee [d], Jongwon Jung [a,*]

[a] *School of Civil Engineering, Chungbuk National University, Cheongju-si, Chungbuk, 28644, South Korea*
[b] *Department of Civil & Architectural Engineering, Qatar University, P.O Box 2713, Doha, Qatar*
[c] *Department of Civil and Environmental Engineering, The University of Tennessee, Knoxville, TN, 37996, USA*
[d] *Petroleum and Marine Research Division, Korea Institute of Geoscience and Mineral Resources, Daejeon, South Korea*

ABSTRACT

CH_4–CO_2 replacement method has the advantages of sequestering carbon dioxide and sediment stability compared to other methods such as depressurization and thermal stimulation. However, the production efficiency using CH_4–CO_2 replacement method is lower than any other method. In this study, effects of soaking process on CH_4–CO_2 replacement efficiency were determined. The soaking process was the time to close all valves for the enhancement of CH_4–CO_2 reaction which resulted in the long reaction time between the injected CO_2 and methane hydrate and consisted of the 1st and the 2nd production with soaking time after dynamic replacement. Results showed that total replacement efficiency increased with increasing number of soaking processes and more soaking time. The increasing rate of replacement efficiency in the first soaking process was higher than that in the second process. However, the soaking process showed the disadvantage that the total production time increased with increasing soaking time and process, which could result in the production cost increase. Therefore, appropriate soaking time and number of soaking processes are required to improve the replacement efficiency considering production cost.

1. Introduction

Gas hydrate as a solid compound trapped in a hydrogen bounded lattice exists under constant temperature and pressure conditions (Sloan, 1990) and has grown slowly (Jung and Santamarina, 2012). The amount of gas hydrate present in the world is about 10×10^{13} tons based on methane carbon (Boswell and Collett, 2011; Makogon, 2010; Collett et al., 2015; Milkov et al., 2004). Since this is more than the total amount of fossil fuels in the world, research on gas production from gas hydrate is necessary. CH_4–CO_2 replacement is a method of extracting methane gas of hydrate without dissociation through CH_4–CO_2 reaction by injecting carbon dioxide into the injection well (Ohgaki and Inoue, 1994). CH_4–CO_2 replacement has been found to be a method that can prevent the dissociation of gas hydrate and ground failure and deformation (Stevens et al., 2008; Jung and Santamarina, 2010; Jung et al., 2010; Espinoza and Santamarina, 2011; Cha et al., 2015; Merey et al., 2018). CH_4–CO_2 replacement method also has the advantage in that the gas hydrate layer of carbon dioxide allows for the production of methane from gas hydrate and the sequestration of carbon dioxide (Ota et al., 2005; Svandal et al., 2006; McGrail et al., 2007; Zhou et al., 2008; Jung et al., 2010). However, this production efficiency is low compared to the depressurization method. Thus, research is being conducted to increase the production efficiency of the CH_4–CO_2 replacement method.

Previous studies have determined factors influencing the production efficiency when applying CH_4–CO_2 replacement method. For example, Lee et al. (2003) has shown that gas hydrate can influence the production efficiency depending on particles size of gas hydrate and the degree of diffusion because gas hydrate performs intact CH_4–CO_2 replacement and methane diffuses through a lattice that is almost unaffected. Murshed et al. (2010) has suggested that the difference in fugacity by guest molecules can affect the production efficiency due to the generation of driving force. His suggestion is supported by results showing higher production efficiency when using liquid CO_2 than using gaseous CO_2 (Ota et al., 2005). Initial conditions of gas hydrate including pressure, temperature, and physical properties can also affect the production efficiency of the CH_4–CO_2 replacement method. Under the influence of pressure and temperature conditions and phase equilibrium, the CH_4-hydrate unstable region shows higher methane recovery than the CO_2-hydrate stable region (Zhou et al., 2008). One study has shown difference in methane recovery according to temperature and hydrate saturation by dividing zones along the boundary of CH_4-hydrate and CO_2-hydrate phase equilibrium (Zhao et al., 2015). Effects of physical properties such as gas permeability, porosity, and hydrate saturation have been reported to increase the production efficiency as

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* Corresponding author.
E-mail address: jjung@chungbuk.ac.kr (J. Jung).

https://doi.org/10.1016/j.petrol.2020.107772
Received 21 February 2020; Received in revised form 6 August 2020; Accepted 10 August 2020

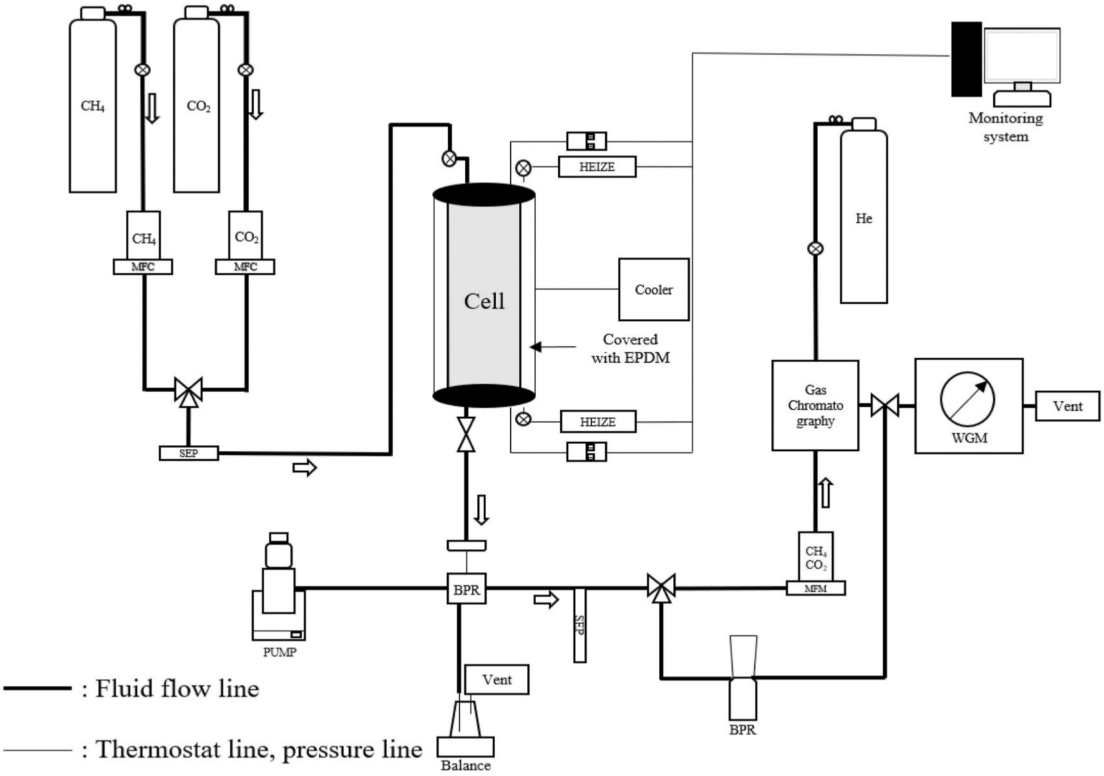

Fig. 1. Schematic diagram of the experimental setup.

permeability, porosity, and hydrate saturation increase (Mu and von Solms, 2018). Changes in the composition of gas also affect the replacement efficiency. Methane recovery can be enhanced by further replacement of gas hydrates present in the small cage while changing the composition to $CO_2 + N_2$, $CO_2 + H_2$, and CO_2 + He (Xu et al., 2018; Wang et al., 2017). Furthermore, both an inhibitor and CO_2 injection method has been introduced for the efficient recovery of methane because of the change of phase equilibrium due to an inhibitor (Jarrahian and Heidaryan, 2014; Khlebnikov et al., 2016; Heidaryan et al., 2010, 2019). Factors affecting the replacement efficiency studied include particle size of gas hydrate, difference of fugacity, initial conditions, physical properties, and gas composition. With a different approach, the soaking process time was used to determine the effect of CH_4–CO_2 replacement efficiency. Previous studies on the soaking process have examined changes in replacement efficiency with increasing soaking time (Seo et al., 2015). The objective of the present study was to explore the effects of soaking process time on CH_4–CO_2 replacement efficiency considering the production time. In addition, effects of soaking process were analyzed under various hydrate saturation and permeability conditions.

2. Materials and methods

2.1. Experimental apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. The whole apparatus consisted of four parts: a high pressure cell, a fluid injection equipment, a temperature control part, and a measuring part. The first part is a hydrate reservoir simulated cell. It was constructed to be operated at 35.46 MPa. The size of cell is 5.5 cm in diameter and 46 cm in length. A total of 11 temperature sensors were mounted along sidewalls of the high-pressure cell at regular intervals to measure the temperature of each part. The upper and lower end caps were equipped with a stainless filter of 7 μm in pore size to prevent the sample from flowing out into the flow. Also, temperature sensors and pressure transducer were connected to the cell. A cooling jacket surrounding the entire high-pressure cell was used to control the temperature of the pore system. The second part is a fluid injection equipment. Several types of fluid injection equipment have been used to control water saturation, to form gas hydrate, and to replace them with CO_2. For example, an isocratic pump and a syringe pump were used to inject distilled water to the pore system. A mass flow controller and a mass flow meter were used to control the flow rate of methane and CO_2. The third part was a temperature control part. A temperature bath circulator was used to control the internal temperature of the high-pressure cell and the temperature of the injection fluid. As a constant temperature fluid, a mixture of ethanol and water (8:2) was used. In addition, EPDM (ethylene propylene diene terpolymer) was mounted to the surface of the cell to maintain the temperature of the cell. The fourth part was a measuring part. A wet gas meter was used to measure the volume of whole gas. The wet gas meter was a positive displacement flow meter composed of a drum that was partitioned into a standard volume of space. This system could also calculate the amount of gas produced during the experiment in real time in conjunction with the system control and measurement program.

2.2. Experimental procedure

Experimental procedures consisted of sand packing, hydrate formation, and gas production due to carbon dioxide injection.

2.2.1. Sand packing

Artificial sand samples were used to simulate the hydrate reservoir. To remove impurities from the manufacturing process, an artificial sand sample was flushed with distilled water and dried in a vacuum oven for more than 24 h. The particle size of the sediment can directly affect fluid permeability which has the greatest influence on fluid capacity evaluation of the reservoir. Distribution of particle size can also influence fluid distribution inside the reservoir due to capillary pressure. Particle size distribution was measured using a laser diffraction particle analyzer

Table 1
Component analysis of the sample.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	P_2O_5
97.70	1.17	0.21	0.02	0.03	0.33	0.02	0.08	<0.01	<0.01

(Table 1).

To calculate the exact volume of the sample, density of the sample was measured with a pycnometer method. Porosity of artificial equation (1) is a formula used to calculate the porosity of the artificial sample filled in the high-pressure cell.

$$\varphi = \frac{\frac{W_w}{\gamma_w}}{\frac{W_w}{\gamma_w} + \frac{W_s}{\gamma_s}} \times 100(\%) \quad (1)$$

where γ_w is density of water [g/m^3], γ_s is density of the sample [g/m^3], W_w is weight of water [g] and W_s is weight of sample consumed during packing [g].

2.2.2. Hydrate formation

Hydrate was formed in the high-pressure cell for full-scale experiment. First, methane was injected into the cell while maintaining the flow rate. Methane was injected through the top to prevent fingering and

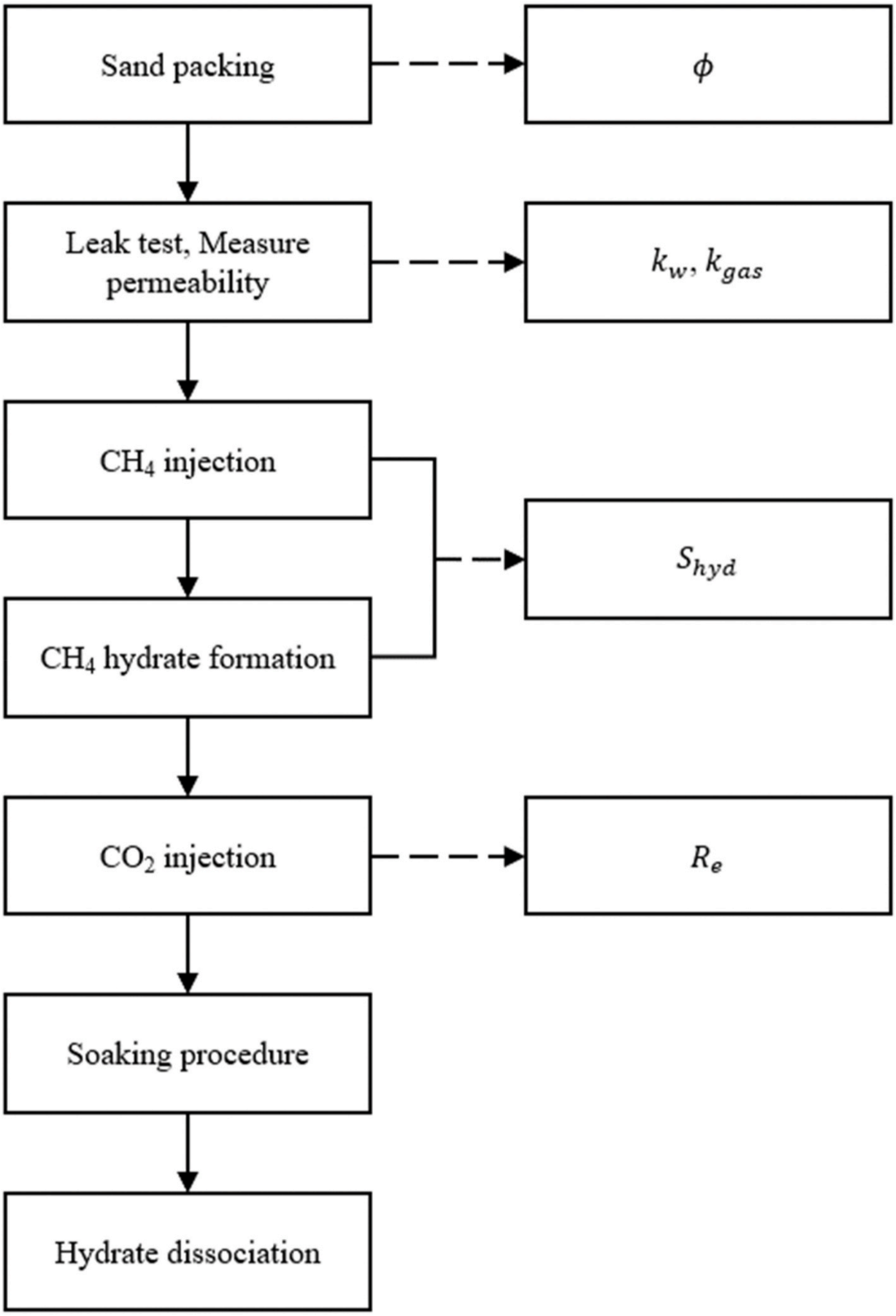

Fig. 2. Schematic diagram of the whole experimental procedure.

Table 2
Experiment condition.

Run	Temperature (K)	Pressure (MPa)	Porosity (%)	Soaking time(hr)	S_{hyd} (%)	$n_{CH_4,Total}$ (mol)	$n_{CH_4,H}$ (mol)	$n_{CH_4,G}$ (mol)
1	275.15	3.89	42.07	2	26.14	1.538	0.799	0.739
2	275.15	3.89	42.07	6	24.77	1.539	0.807	0.732
3	275.15	3.89	42.07	12	23.22	1.552	0.792	0.76
4	275.15	3.89	41.74	6	28.87	1.486	0.858	0.628
5	275.15	3.89	41.74	6	36.54	1.424	0.985	0.439
6	275.15	3.89	39.58	6	24.86	1.369	0.663	0.706

stabilize the front surface. In this process, the amount of injected methane was used to calculate the hydrate saturation formed in the simulated sediment layer. The temperature of the cell was then lowered to make gas hydrate in the high-pressure cell. Because a sudden temperature decrease may cause a heterogeneous saturated form, the temperature of the cell should be lowered gradually. In this case, the temperature of the bath circulator should be kept in consideration of the difference in the heat loss depending on temperature difference in the laboratory. In this case, the temperature inside the cell should not fall to 0 °C or below to avoid various problems caused by ice formation rather than hydrate formation. The hydrate saturation can be calculated with Equation (2) using the volume of methane in the pore volume and the pressure drop due to hydrate formation (Sakamoto et al., 2005).

$$S_H = \frac{V_i}{172} \frac{\Delta P}{P_0} \frac{T_0}{T_f} \frac{1}{AL\varphi} \tag{2}$$

where V_i is the volume injected methane gas in the pore volume [m^3], ΔP is the pressure drop [MPa] due to hydrate formation, P_0 and T_0 are the pressure [MPa] and temperature [K] in the standard state, respectively, T_f is the temperature [K] set for hydrate formation, A is the cross-sectional area [m^2], L is the length of the cell, and φ is the porosity of the sample.

2.2.3. *Gas production*

Once the injection of methane was complete, additional methane was injected to keep the operating pressure. Ten minutes later, there was no additional hydrate generation after the injection because the pressure of the cell was constant. After the above process was completed, carbon dioxide was injected into the cell for CH_4–CO_2 replacement reaction. The injection flow rate was 200 standard cubic centimeter per minute for each experiment to avoid productivity change depending on the injection flow rate. The operating temperature and pressure of the cell were kept constant at 275.15 K and 4.5 MPa, respectively, to prevent hydrate dissociation and to induce continuous replacement production. The composition of the gas produced at the injection flow rate was analyzed at intervals of 30 s. The value of CH_4 gas recovered was calculated during the production period. Replacement efficiency was calculated with Equation (3).

$$R_R = \frac{V_{CH_4,R} - V_{CH_4,G}}{V_{CH_4,H}} \times 100(\%) \tag{3}$$

where $V_{CH_4,R}$ was the recovered methane gas volume [m^3], $V_{CH_4,H}$ was the volume of hydrate [m^3], and $V_{CH_4,G}$ was the volume of free gas [m^3]. The produced gas was discharged from the mixed gas of carbon dioxide and methane when carbon dioxide was injected into the gas hydrate. Finally, the concentration of methane in the mixed gas was reduced and converged to 0%. A soaking process was then given to increase the replacement efficiency, which means the CH_4–CO_2 reaction under the constant pressure and temperature without gases (i.e., CH_4 and CO_2) flow. The soaking process was used to close all valves of the cell when methane was not produced even after continuous injection of carbon dioxide and to perform an additional replacement reaction between the already injected carbon dioxide and gas hydrates remaining in the cell. Soaking time was the period during closing valves of the cell. In this study, the starting point of soaking time began when the concentration of methane in the produced gas was less than 1%. Dynamic replacement was the process from the first production to the time before the first soaking. The 1st production refers to the process between the dynamic replacement and the first soaking time. The 2nd production refers to the process between the 1st production and the second soaking time. After the 2nd production, gas hydrates were dissociated by increasing the temperature of the cell. The overall procedure for the above-described experimental procedure is shown in Fig. 2.

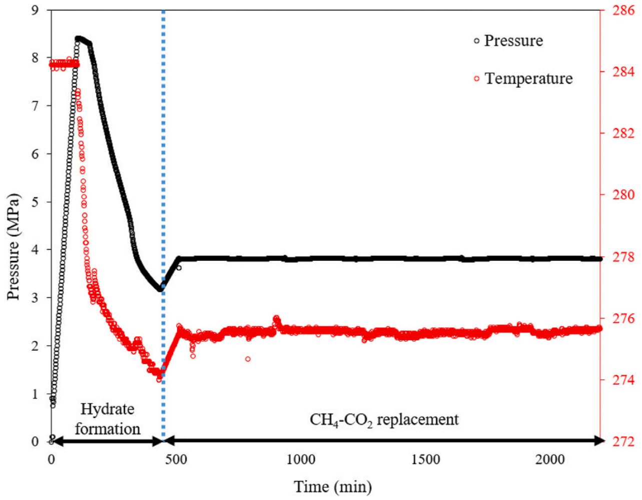

Fig. 3. Temperature and pressure changes during the whole experiment.

3. Experimental results

This work investigated effects of soaking time, hydrate saturation, and permeability on replacement efficiency. According to each experiment, the soaking time, permeability, and hydrate saturation were changed. Other conditions are shown in Table 2. Runs #1, #2, and #3 were conducted to compare the soaking effect. Runs #2, #4 and #5 were conducted to compare the hydrate saturation effect. Runs #2 and #6 were conducted to compare permeability effect. All experiments were conducted with two times of soaking process. The soaking time was the same (6 h) for Runs #2, #4, #5, and #6.

3.1. *Hydrate formation and gas production*

Temperature and pressure changes during gas hydrate formation and CH_4–CO_2 replacement reaction are shown in Fig. 3. Methane was injected to cell to form gas hydrates. Cell temperature was lowered to 275.5 K. Exothermic reaction indicating hydrate formation was observed at 300 min after injecting methane. After gas hydrate formation was completed, carbon dioxide was injected to conduct CH_4–CO_2 replacement at 430 min. Flow rate of carbon dioxide was 200 sccm (standard cubic centimeter per minute). Since then, all experiments were completed after the dynamic replacement, the 1st production, and

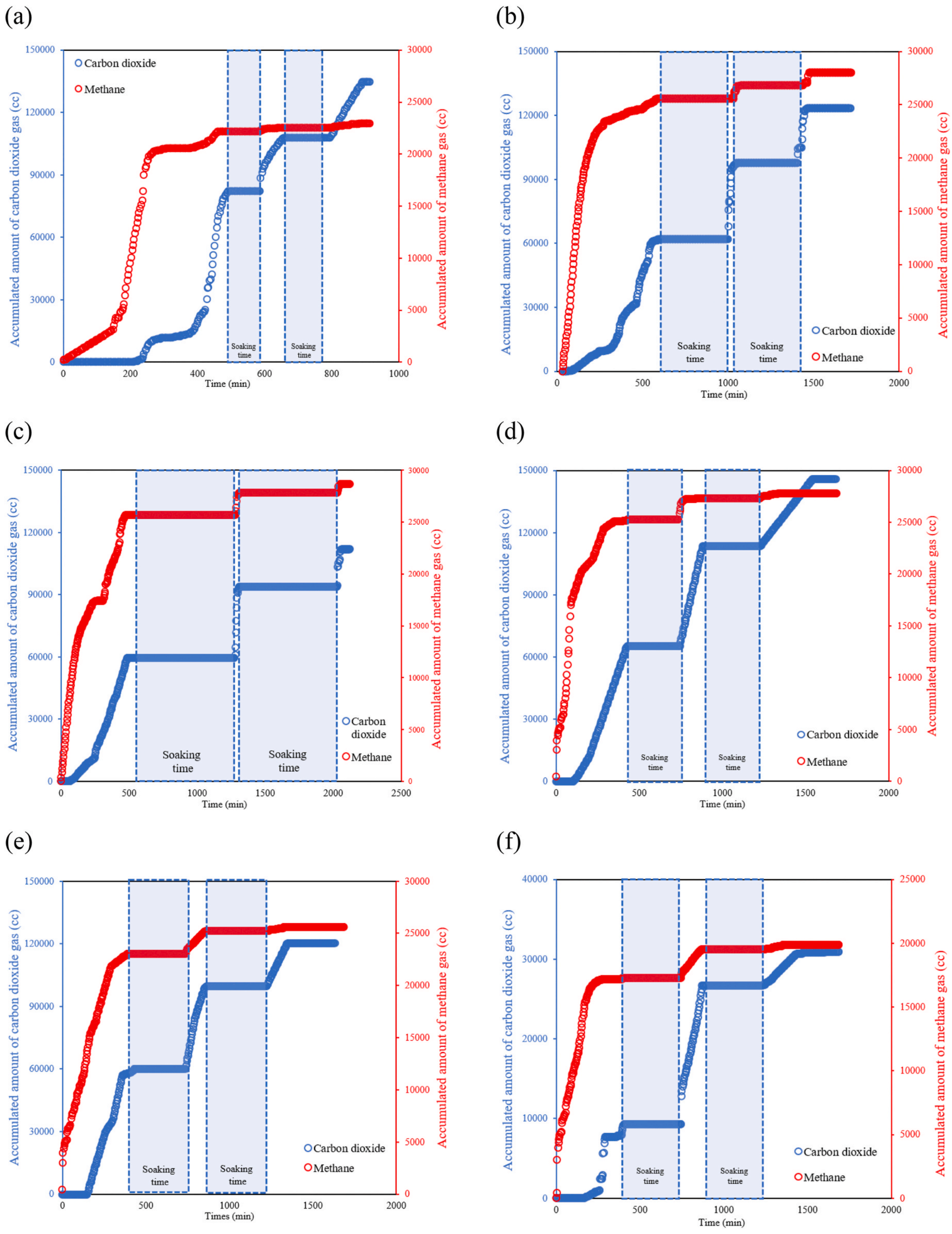

Fig. 4. Cumulated amount of gas during CH_4–CO_2 replacement: (a) 2 h soaking, (b) 6 h soaking, (c) 12 h soaking case, (d) low hydrate saturation, (e) high hydrate saturation.

the 2nd production.

Fig. 4 shows cumulative emissions of methane and carbon dioxide during CH_4–CO_2 replacement. All experiments included dynamic replacement, the 1st production, and the 2nd production with two soaking processes after carbon dioxide injection. Fig. 4(a), (b), and 4(c) show gas emissions of Runs # 1, # 2 and # 3 to confirm the soaking effect. Fig. 4(b), (d), and 4(e) show the hydrate saturation effect. Fig. 4 (b) and (f) confirm the permeability effect. Based on the above raw data, we analyzed effects of the three factors such as soaking process, hydrate saturation and permeability on the replacement efficiency. Results showed that the accumulated amount of produced methane increased with increasing time and CO_2 injection (Fig. 4).

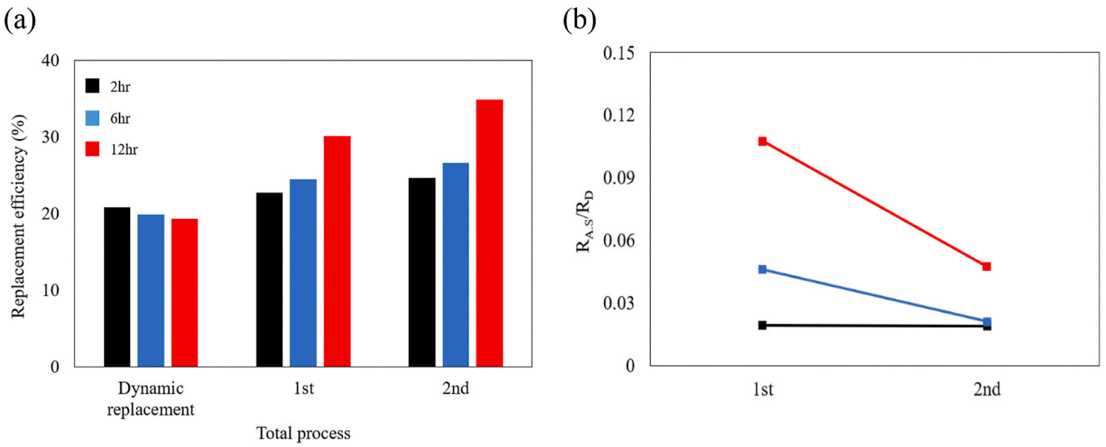

Fig. 5. Change of replacement efficiency due to soaking process. (a) Replacement efficiency according to cycle, (b) Replacement efficiency ratio after the soaking process.

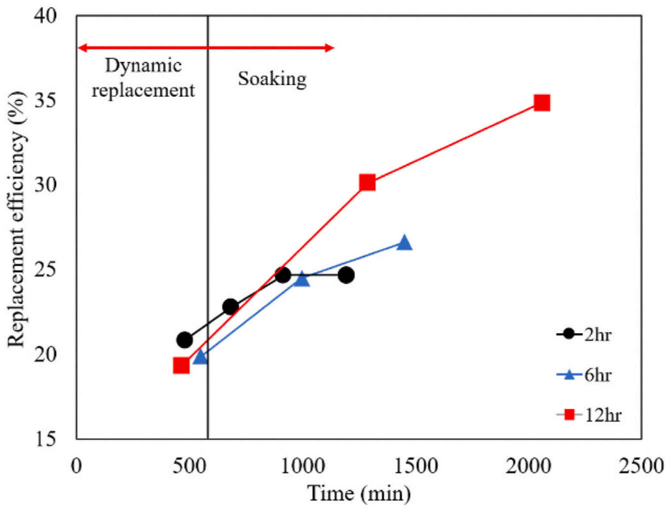

Fig. 6. Change of replacement efficiency with time.

3.2. Soaking effect

Fig. 5(a) shows the replacement efficiency of soaking time per cycle at 2 h, 6 h, and 12 h. In all cases, the replacement efficiency of the dynamic replacement which was primary production was the highest. The reason for the highest replacement efficiency in dynamic replacement was that the infiltrated carbon dioxide could act on the surface of the gas hydrate, leading to a rapid replacement reaction (Lee et al., 2014; Koh et al., 2015). Cumulative replacement in the 1st and the 2nd soaking processes tended to be proportional to the soaking time. This is because the increase of the soaking time increased the CH_4–CO_2 replacement reaction, similar to findings of a previous study (Seo et al., 2015).

Fig. 5(b) shows normalized replacement efficiency ratio by the soaking process after dynamic replacement. R_D and $R_{A.S}$(after soaking) indicate the replacement efficiency by dynamic replacement and soaking process, respectively. As a result, the increase ratio of the replacement efficiency of the 1st production tended to be higher than the increase ratio of the replacement efficiency of the 2nd production because the amount of remaining methane decreased due to many CH_4–CO_2 replacement reactions caused by the previous soaking process. Also, longer soaking time was more effective in improving the replacement efficiency.

Fig. 6 shows changes of replacement efficiency with production time. Results showed that the replacement efficiency increased with increasing soaking time and frequency. However, the production time should be considered for the production cost. Results of analysis revealed the maximum production efficiency over time. In all cases, the dynamic replacement was completed in around 500 min. When the soaking time was 2 h, the 1st production was terminated at 680 min and the 2nd production was terminated at 910 min. When the soaking time was 6 h, the 1st production was terminated at 1000 min and the 2nd

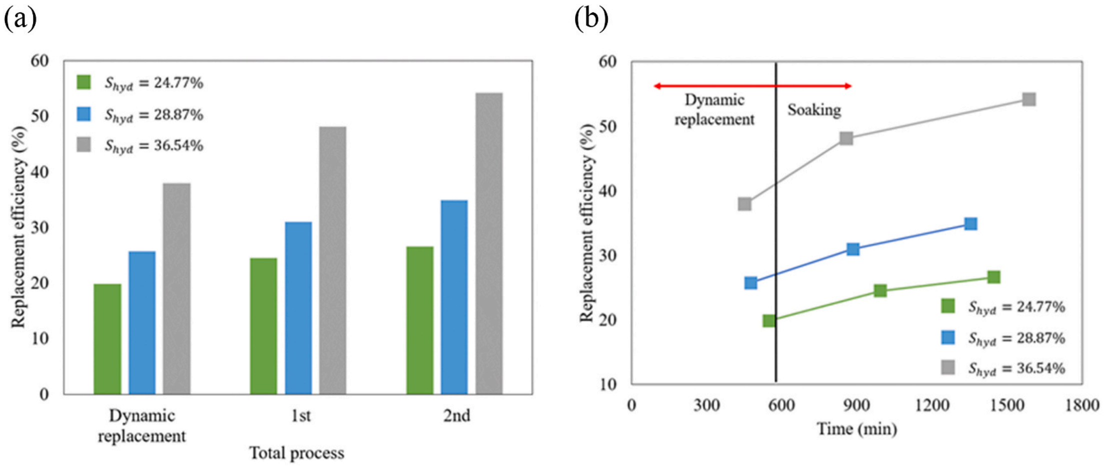

Fig. 7. Changes of replacement efficiency due to hydrate saturation. (a) Replacement efficiency according to cycle, (b) Change of replacement efficiency with time.

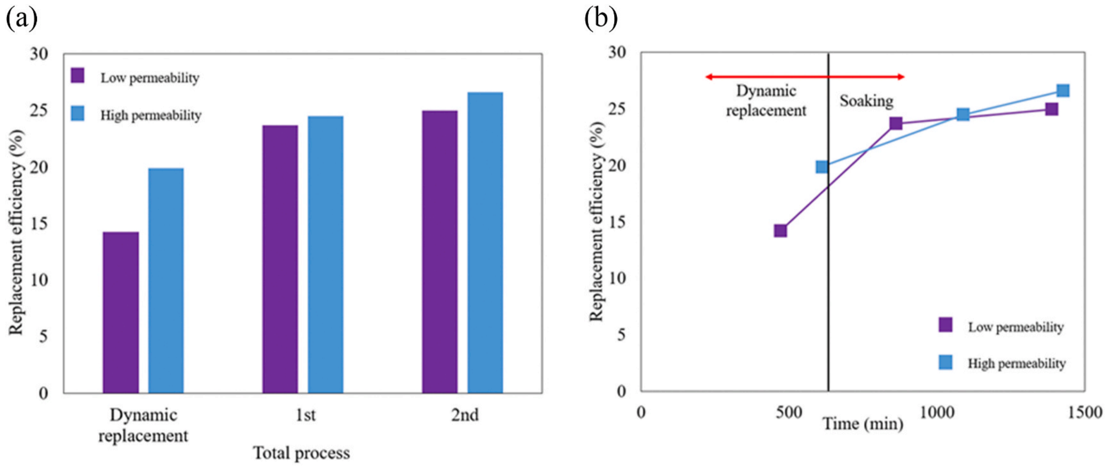

Fig. 8. Change of replacement efficiency due to permeability. (a) Replacement efficiency according to cycle, (b) Change of replacement efficiency with time.

production was terminated at 1450 min. When the soaking time was 12 h, the 1st production was terminated at 1640 min and the 2nd production was terminated at 2050 min. Results showed that: (1) all production efficiency increased with increasing time and number of the soaking process, (2) a soaking process with a soaking time of 2 h was the most effective with a production time of 0–900 min, and (3) gas production using a soaking process having a soaking time of 12 h was more efficient when the production time was more than 900 min. It implies that a short soaking time is more efficient with a limited or short production time. However, a long soaking time is better with a longer production time. Thus, the production cost should be considered to select the best soaking time.

3.3. Hydrate saturation effect

Fig. 7(a) shows replacement efficiency of each cycle by hydrate saturation. As a result, the replacement efficiency tended to increase as the hydrate saturation increased in the dynamic replacement. The lower the hydrate saturation, the greater the amount of free water resulting in the lower replacement efficiency because CO_2-hydrate was formed through the replacement reaction between the injected CO_2 and free water. This result is consistent with a previous study (Mu and von Solms, 2018). Also, the change of replacement efficiency after dynamic replacement tended to increase with higher hydrate saturation, meaning that the efficiency of soaking process increased with higher hydrate saturation. As the saturation of the hydrate increased, the efficiency of the soaking process also increased due to a large amount of hydrate remaining. Fig. 7(b) shows changes of replacement efficiency with time. The production time in the dynamic replacement period was 600 min. However, after two soaking processes, the production time increased when the hydrate saturation was high. The higher the hydrate saturation, the more the production time increased because the amount of methane emitted increased. Therefore, when hydrate saturation is high, it is judged that introducing more number of soaking processes are effective in producing the maximum efficiency over time.

3.4. Permeability effect

Fig. 8(a) shows replacement efficiency according to change of permeability. The result of dynamic replacement showed that the replacement efficiency increased with higher permeability. The replacement efficiency tends to increase due to mass transfer as permeability increases (Mu and von Solms, 2018). The difference in replacement efficiency due to soaking process in the 1st production was 10.2% when the permeability was low. It was 4.8% when the permeability was high. This was because lower permeability resulted in lower fluidity in terms of mass transfer of the injected carbon dioxide, resulting in lower replacement efficiency in the dynamic replacement when the reaction time of carbon dioxide and methane were given during soaking time, resulting in additional methane production. Fig. 8(b) shows replacement efficiency with time. Higher permeability resulted in a greater amount of CH_4–CO_2 reactions, leading to a slower termination time in dynamic replacement than lower permeability. In both cases, the 1st production time tended to be similar. However, the high permeability in the 2nd production was quickly terminated. The reason was that a relatively fast CH_4–CO_2 replacement reaction was carried out due to active mass transfer at high permeability and the residual methane was recovered quickly. The important result of the permeability effect was that the lower the permeability, the higher the efficiency of the soaking process. If the permeability is low in the field, introducing the soaking process can improve methane production.

4. Conclusions

In this study, a soaking process was induced to enhance CH_4–CO_2 replacement efficiency. This study confirmed that the soaking process could influence the replacement efficiency according to the change of hydrate saturation and permeability under various conditions. Results obtained from this study are summarized below:

Total CH_4–CO_2 replacement efficiency increased with soaking time and the number of soaking process. However, the increased ratio of replacement efficiency decreased as the soaking process progressed. A shorter soaking time was more efficient when the production time was short. It was longer when the production time was long. Thus, the soaking time and the total number of soaking process should be selected considering the production cost based on the production time.

Soaking effects of different hydrate saturation showed that both the efficiency of soaking process and production time increased as hydrate saturation increased. Thus, the soaking process can be applied in field with high saturation for higher production efficiency.

Effects of a soaking process on different permeability showed that the replacement efficiency of dynamic replacement increased with increasing permeability. However, the efficiency of soaking process was higher in the case of low permeability than that in the case of high permeability because the replacement efficiency was increased by CH_4–CO_2 replacement reaction during the soaking time.

Introducing an appropriate soaking time by understanding the amount of methane gas that can be recovered and actual conditions in the field during the introduction of the soaking process is more economical than CH_4–CO_2 replacement without a soaking process. Therefore, if soaking time is selected in consideration of production time and additional production of methane when applying the soaking process in actual field, the replacement efficiency can be improved.

CRediT authorship contribution statement

Jae Eun Ryou: Conceptualization, Methodology, Writing - original draft, Data curation. **Riyadh I. Al-Raoush:** Conceptualization, Formal analysis, Funding acquisition. **Khalid Alshibli:** Methodology, Formal analysis. **Joo Yong Lee:** Conceptualization, Data curation, Funding acquisition. **Jongwon Jung:** Conceptualization, Supervision, Writing - review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This research was made possible by an NPRP grant # NPRP8-594-2-244 from the Qatar National Research Fund (a member of Qatar Foundation). And this work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government (MSIT) (2020R1A2C101235211). Also, this research was partially supported by the Ministry of Trade, Industry, and Energy (MOTIE) through the Project “Gas Hydrate Exploration and Production Study (20–1143)” under the management of the Gas Hydrate Research and Development Organization (GHDO) of Korea and the Korea Institute of Geoscience and Mineral Resources (KIGAM). Also, this research was supported by a grant (2018-MOIS31-009) from Fundamental Technology Development Program for Extreme Disaster Response funded by Korean Ministry of Interior and Safety (MOIS).

Appendix ASupplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petrol.2020.107772.

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