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Comprehensive literature review on CH_4-CO_2 replacement in microscale porous media

Sukru Merey[a], Riyadh I. Al-Raoush[b,*], Jongwon Jung[c], Khalid A. Alshibli[d]

[a] Department of Petroleum and Natural Gas Engineering, Batman University, 07210 Batman, Turkey
[b] Department of Civil and Architectural Engineering, Qatar University, P.O Box 2713, Doha, Qatar
[c] School of Civil Engineering, Chungbuk National University, Cheongju, Chungbuk, 28644, South Korea
[d] Dept. of Civil & Env. Engineering, 325 John Tickle Building, University of Tennessee, Knoxville, TN, 37996, USA

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ABSTRACT

Gas production studies from natural gas hydrate reservoirs have been the subject of extensive research in recent years. Although CH_4-CO_2 replacement production method from gas hydrates has many advantages, the number of the studies related to this production method are less than depressurization production method studies, especially in microscale porous media. Hence, this paper presents a comprehensive literature review on CH_4-CO_2 replacement to better understand the associated processes and mechanisms in microscale porous media with emphasis on micromodel experiments, 3D imaging, other visualization testing method and pore network modelling. Moreover, the advantages and disadvantages of currently available CH_4-CO_2 replacement studies were investigated. The critical issues of the replacement method were underlined and new suggestions have been offered for future investigations.

1. Introduction

Unconventional energy resources have become very important in recent years due to the decline of conventional hydrocarbon reservoirs. Shale gas reservoirs and natural gas hydrates are the most common ones of the unconventional reservoirs in the world (Chong et al., 2016; Ritts, 2017). Feasible gas production from shale gas reservoirs is currently possible with the technological advancements in horizontal drilling and hydraulic fracturing operations. However, gas production from another unconventional gas reservoir, which is gas hydrate, is still immature and is in the stage of development (SBC, 2015; Max and Johnson, 2016).

Water (host molecules) and molecules of gases or liquids (guest molecules) form ice-like structures together at high pressure and low temperature conditions (Sloan and Koh, 2008; Liu, 2013). These ice-like structures are called “gas hydrates” if the guest molecules are in gaseous state (Carroll, 2009). Approximately 130 compounds form hydrates (Sloan and Koh, 2008). Methane (CH_4), ethane (C_2H_6), propane (C_3H_8), carbon dioxide (CO_2), nitrogen (N_2), hydrogen sulfide (H_2S), etc. can create their own gas hydrates or mixed hydrates when appropriate pressure and temperature conditions are met (Giavarini and Hester, 2011). Depending on the molecular diameter of hydrate former (guest molecule), different gas hydrate structures form: mainly structure I (sI) and structure II (sII). Structure H (sH) rarely exists in nature. Different types of cages compose each gas hydrate structure. These cages are pentagonal dodecahedron (5^{12}), tetrakaidecahedron ($5^{12}6^2$), hexakaidecahedron ($5^{12}6^4$), irregular dodecahedron ($4^35^66^3$) and icosahedron ($5^{12}6^8$). For example, pentagonal dodecahedron ($n^m = 5^{12}$) is formed from 12 (m = 12) pentagonal (n = 5) faces. Hence, n and m numbers are used to define the shape of different cages of hydrates. One sI hydrate structure consists of 2 pentagonal dodecahedron cages (small cages: 5^{12}) and 6 tetrakaidecahedron cages (large cages: $5^{12}6^2$). sII hydrate structure is larger than sI hydrate structure and they are composed of 16 small cages (5^{12}) and 8 large cages (hexakaidecahedron: $5^{12}6^4$). Finally, sH hydrate consists of 3 small (5^{12}), 2 mediums ($4^35^66^3$) and 1 large cages ($5^{12}6^8$) (Sloan, 2003; Zou, 2013). Approximately 46, 136 and 34 water (H_2O) molecules are essential for sI, sII and sH hydrates, respectively. CH_4, C_2H_6, CO_2, and H_2S establish sI hydrates and C_3H_8 and N_2 form sII hydrates (Sloan and Koh, 2008). In nature, approximately, 99% of gas hydrates is CH_4 hydrate (Kvenvolden, 1995; Max et al., 2013). Moreover, at least 95% of gas hydrates in nature are found in marine environment while the rest are found in permafrost regions (Max and Johnson, 2016).

There is a controversy about the amount of CH_4 hydrate in the

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[*] Corresponding author.

E-mail addresses: sukru.merey@batman.edu.tr, sukrumerey@gmail.com (S. Merey), riyadh@qu.edu.qa (R.I. Al-Raoush), jjung@chungbuk.ac.kr (J. Jung), alshibli@utk.edu (K.A. Alshibli).

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world but it is thought that even the most conservative estimates of the total quantity of CH_4 in CH_4 hydrates are much larger than the conventional gas resources (404 tcm) and shale gas (204 tcm–456 tcm) (Johnson, 2011; Chong et al., 2016). The magnitude of this resource can make hydrate reservoirs a substantial future energy resource. Gas production from the coarse sands saturated with gas hydrates might be feasible with current technology because porosity and permeability are high in coarse sands (Boswell, 2014; Max and Johnson, 2016; Heeschen et al., 2016; Boswell et al., 2017).

Currently, there are mainly four production methods from gas hydrate reservoirs: depressurization, thermal injection, chemical injection and CH_4-CO_2 replacement (Moridis et al., 2013; Xu and Li, 2015; Chong et al., 2016). Depressurization method is applied by reducing reservoir pressure below hydrate equilibrium pressure. It is considered that this method is the most economically viable method because no external energy is used. However, its disadvantages include a slow rate of production and the risk of reservoir subsidence (Konno et al., 2010; Huang et al., 2016). In thermal injection, mainly external heat is introduced to gas hydrate reservoirs by injecting hot water, steam or microwaves so gas hydrate equilibrium is disturbed (Liang et al., 2008; Xu and Li, 2015). The disadvantages of this method are low injection rate and low energy efficiency. Hence, for different gas hydrate reservoirs, it is suggested to combine this method with depressurization method or chemical injection method for feasible gas production (Yuan et al., 2013; Feng et al., 2015; Minagawa et al., 2015). Among four gas hydrate production methods, chemical injection method is the least preferred approach. Although chemical injection shifts gas hydrate equilibrium curve to higher pressures and lower temperatures for gas hydrate dissociation, its disadvantages are low injection rate (mostly due to low effective permeability of gas hydrates), low-cost efficiency and environmentally harmful (Moridis et al., 2013; Chong et al., 2016; Max and Johnson, 2016). CH_4-CO_2 replacement or CO_2 injection method is quite different from depressurization method, thermal injection method and chemical injection method (Ohgaki et al., 1996). Below 283.2 K, CO_2 hydrate is much more stable than CH_4 hydrate as shown in Fig. 1 (Goel, 2006). When CO_2 is injected into CH_4 hydrate reservoirs, CH_4 molecules leave their hydrate cages and CO_2 molecules fill these empty cages due to the difference in chemical potentials of both systems. CO_2 has high chemical potential in gas phase and zero in gas hydrate but CH_4 shows the opposite. This difference and initially very steep gradients drive the replacement (Xu and Li, 2015). CH_4-CO_2 replacement method in gas hydrates is advantageous due to CO_2 sequestration, low water production and low geomechanical risks (Hyodo et al., 2014).

Table 1 summarizes the advantages and disadvantages of CH_4-CO_2 replacement. The recovery of CH_4 might be up to 64% with CO_2 injection to CH_4 hydrates (Nago and Nieto, 2011). CH_4 hydrate and CO_2 hydrate are sI type of gas hydrates (2 large cages and 6 small cages). The ratio of molecular diameter of CO_2 to cavity diameter of sI hydrate structure is 1.0 for small cages and 0.834 for large cages but CH_4 easily fills both small and large cages of sI hydrate (Sloan and Koh, 2008). Consequently, CH_4-CO_2 replacement is extremely low in small cages and mostly CH_4 molecules stay in the small cages of sI hydrate (Yuan et al., 2012). Furthermore, the content of small cages remains largely immobile due to very low probability of a molecule from small cage to jump into the large cage and then reach the gas hydrate surface. The exchange has its preferred paths namely interconnected large cages. Small cages are just sinks or dead ends. After the production of approximately 64% of CH_4 from CH_4 hydrate via CO_2 injection, the mixed CH_4-CO_2 hydrate in the sediments keep the sediments geomechanically much more stable compared to other production methods (Geng et al., 2009; Hyodo et al., 2014; Liu et al., 2016). This study reviews the application of CH_4-CO_2 replacement method, the first field tests of CH_4-CO_2 replacement in Ignik Sikumi field in 2012, laboratory studies in micro scale and pore network modelling studies. However, it is also essential to review some macro-model studies and their deficits to indicate why micro-scale and pore network modelling studies are needful.

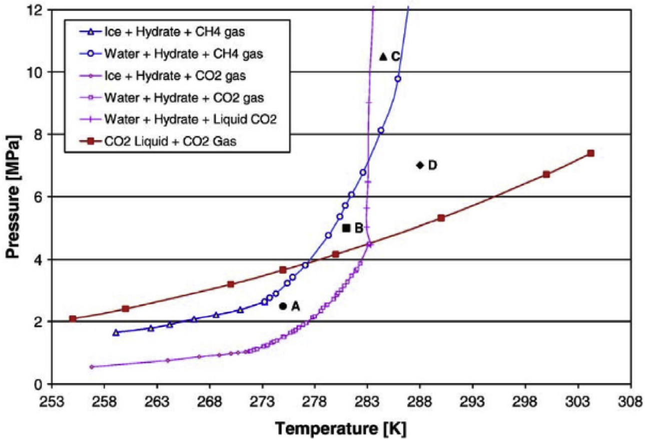

Fig. 1. Hydrate equilibrium curves of CH_4 and CO_2 (Goel, 2006).

Table 1
Advantages and disadvantages of CH_4-CO_2 replacement (Geng et al., 2009; Zhao et al., 2012; Hyodo et al., 2014; Abbasov et al., 2016; Liu et al., 2016).

Advantages	Disadvantages
A good alternative for CO_2 sequestration and gas production method	Operational difficulties for CO_2 injection (CO_2 hydrate formation) and extra cost of CO_2 injection
Less geomechanical risks in sediments	Slow injection rate due to low effective permeability of gas hydrates and slow replacement rate
Less water production	Low recovery of CH_4

2. Field study of CH_4-CO_2 replacement

The injection of CO_2 through gas hydrate reservoirs is generally a major problem because of low permeability. When high CO_2 injection pressures are observed in impermeable or low permeable gas-hydrate bearing sediments, CO_2 phase changes easily from gaseous state to liquid or supercritical state (Goel, 2006). High CO_2 injection pressure increases the possibility of formation of pure CO_2 hydrate when there is free water in the pores. As pure CO_2 hydrate is constituted instead of the CH_4-CO_2 hydrate replacement, the permeability of hydrate reservoir decreases further. In order to increase the effectiveness of CO_2 injection and to avoid the CO_2 injection problem at high pressures, 77% N_2 and 23% CO_2 mixture injection to CH_4 hydrates was suggested by University of Bergen and it was proved experimentally and also in Ignik Sikumi field pilot project (Schoderbek et al., 2013; Kvamme, 2015, 2016). During replacement processes in experimental studies, it was observed that large cages of sI hydrate filled by mostly CO_2 and small cages are filled by N_2. Thus, CH_4 recovery was increased from 64% to 85% by injecting the mixture of CO_2 and N_2. This also avoids the injection problem of CO_2 and reduces the chance of pure CO_2 hydrate formation because N_2 concentration is high. Moreover, N_2 can only create its pure sII hydrate at very high pressure (i.e. ~8.94 MPa at 281.15 K) (Sloan and Koh, 2008; Carroll, 2009). It also increases the recovery of CH_4 by replacing CH_4 in small cages with injected N_2. In another studies of Kang et al. (2014) and Ahn et al. (2015), air and CO_2 injection (flue gas) was suggested for gas production from CH_4 hydrates with the replacement mechanism because it is feasible to obtain flue gas rather than preparing CO_2/N_2 gas mixture. The efficiency of CH_4-CO_2 (20%)/air (80%) replacement in the study of Kang et al. (2014) and Ahn et al. (2015) exceeded approximately 85%.

Different from the previous pilot projects (i.e. depressurization tests) on gas hydrate reservoirs, CO_2/N_2 mixture was injected into the