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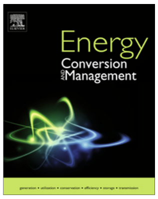

Flue gas injection into gas hydrate reservoirs for methane recovery and carbon dioxide sequestration

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ABSTRACT

Flue gas injection into methane hydrate-bearing sediments was experimentally investigated to explore the potential both for methane recovery from gas hydrate reservoirs and for direct capture and sequestration of carbon dioxide from flue gas as carbon dioxide hydrate. A simulated flue gas from coal-fired power plants composed of 14.6 mol% carbon dioxide and 85.4 mol% nitrogen was injected into a silica sand pack containing different saturations of methane hydrate. The experiments were conducted at typical gas hydrate reservoir conditions from 273.3 to 284.2 K and from 4.2 to 13.8 MPa. Results of the experiments show that injection of the flue gas leads to significant dissociation of the methane hydrate by shifting the methane hydrate stability zone, resulting in around 50 mol% methane in the vapour phase at the experimental conditions. Further depressurisation of the system to pressures well above the methane hydrate dissociation pressure generated methane-rich gas mixtures with up to 80 mol% methane. Meanwhile, carbon dioxide hydrate and carbon dioxide-mixed hydrates were formed while the methane hydrate was dissociating. Up to 70% of the carbon dioxide in the flue gas was converted into hydrates and retained in the silica sand pack.

1. Introduction

An abundance of methane (CH_4) is trapped in gas hydrates in subsea sediments [1] and permafrost regions [2], although the actual volumes of gas hydrate deposits worldwide are still arguable [3]. Gas hydrates, a type of ice-like clathrate compounds, can be decomposed if the temperature and pressure are outside their hydrate stability zone (HSZ), or the chemical equilibrium between the hydrate phase and the adjacent environment is disturbed [4]. Based on this principle, several methods were suggested for methane recovery from gas hydrates in sediments, such as depressurisation, thermal stimulation, inhibitor injection [5], and carbon dioxide (CO_2) replacement [6], or combinations of the above.

Thermal stimulation brings heat into gas hydrate deposit layers by a variety of methods such as hot brine injection, steam injection, in-situ combustion, and electromagnetic heating. Laboratory experimental results showed that about 50% of the recovered energy would be consumed to generate the required heat for heating up the gas hydrate-bearing sediment [7]. Reservoir simulation indicated that thermal stimulation appears ineffective because of huge quantity of heat loss to porous media in the hydrate layer or the geologic formations in the vicinity [8], particularly for disperse low-saturation of gas hydrate deposits [9]. The Mallik 2002 gas hydrate research well programme tested the thermal stimulation technique at in situ conditions (907–920 m below surface, 8 °C and 10 MPa) [10]. It was found that, unless the hydrate layers exhibit sufficient thickness, hydrate saturation, and permeability, it is not economically viable to heat a large mass of a hydrate-containing formation by the thermal stimulation alone [11].

Inhibitor injection shifts the gas hydrate deposit conditions out of the hydrate stability zone (HSZ) by injecting alcohol such as methanol, monoethylene glycol, and diethylene glycol. A very large volume of methanol will be needed to treat the water in the hydrate layers and to deal with the dilution by the water from hydrate dissociation as well. Moreover, injected inhibitors could pose serious risk to damage the environment for the marine ecosystem. As a result, it is believed that inhibitor injection technique on its own will not be viable for any type of gas hydrate deposits [8].

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Depressurisation method moves the hydrate reservoir conditions outside the HSZ by reducing the pressure in the gas hydrate reservoir. By comparison to the thermal stimulation technique and the inhibitor injection technique, it does not need to input additional energy or chemicals into the hydrate reservoir, therefore, is technically simple, effective, and prompt inducement to gas hydrate decomposition [12]. The depressurisation technique was successfully applied to produce methane from gas hydrate reservoirs in both onshore and offshore field tests. Messoyakha gas field in the West Siberian basin (Russia) is the only commercial production reservoirs of gas hydrates in the world, where natural gas has been produced from gas hydrate deposits since 1970s [13]. A series of scientific and engineering field trials were conducted in the Mackenzie Delta of Canadian Arctic. The Mallik 2002 gas hydrate production research well programme investigated the feasibility of gas hydrate production by thermal stimulation and depressurisation in short-term production experiments [14], while the results of the Mallik 2007/2008 programme demonstrated that natural gas can be produced from gas hydrate reservoirs by depressurisation alone [15]. Depressurisation method was also tested in the world first offshore methane recovery field trial in Nankai Trough, Japan [16]. All these hydrate sites are sandstone or marine sand reservoirs with high porosity, high permeability, and high hydrate saturation. However, Boswell and Collett estimated that such sandstone-bedded gas hydrates are only a small fraction of the total gas hydrate resources worldwide [17]. For the overwhelming majority in low-permeability sediments or disperse distribution [18] of gas hydrates, depressurisation becomes ineffective. Additionally, for the hydrate reservoirs well inside the HSZ, the reservoir pressure has to be reduced very low to be able to dissociate the gas hydrates. As a consequence, depressurisation results in huge volume of water production, sediment instability, and sand production challenges [8]. Yamamoto et al. reported that sand produced during depressurisation blocked the downhole production device and terminated the gas production of the world's first offshore trial of gas production from marine hydrate reservoirs after six days of gas flow in the Eastern Nankai Trough, Japan [19].

CO_2 replacement method is based on the fact that chemical potential of methane hydrate is higher than that of CO_2 hydrate [20]. Theoretically, CO_2 molecules have relatively high tendency to replace the methane molecules from the methane hydrate cages, which was initially proposed by Ohgaki et al. [6]. Under ideal conditions such as high specific surface areas, high permeability, good heat and mass transfer the process of CO_2 displacement process could be fast and efficient. For example, nearly all methane in methane hydrate was replaced by CO_2 in two half cylindrical sandstone cores separated with a purpose-made spacer [21]. Shin et al. found that methane-isopentane hydrates almost completely disappeared after CO_2 replacement using high-power decoupling ^{13}C NMR and Raman spectra, in a mechanically stirred reactor [22]. It was also observed that CO_2 replacement occurred quickly in fine hydrate particles that were converted from ice powers in contact with methane [23]. In practice, for example, in sediments or in-situ hydrate reservoirs, the process is constrained by a number of geologic factors such as permeability, porosity, heat and mass transfer, and secondary hydrate formation. Experimental study showed that the presence of excess water and clays resulted in slow CO_2-CH_4 exchange rate [24]. It was also reported that high saturation of gas hydrates could lead to lower percentage of CO_2 replacement [25]. The undesired CO_2 hydrate or CO_2-CH_4 mixed hydrate could clog the pores in the sediments or isolate the methane hydrate from CO_2 by forming CO_2 hydrate shells that coat on the methane hydrate crystals [26]. Recent results showed that the efficiency of CO_2 replacement technique could be improved by introduction of other gases. Masuda et al. experimentally investigated injection of a mixture of 60 mo% CO_2 and 40 mol% nitrogen (N_2) to improve the CO_2-CH_4 exchange rate and found that CO_2-CH_4 exchange ratios were about 30% for low hydrate-saturation and only 5% for high hydrate-saturation in the sand cores [27]. The experimental results from Kang et al. showed that injection of a simulated flue gas with 20 mol% CO_2 and 80 mol% N_2 increased the methane recovery ratio from 64 to 85% [28]. Kang et al. experimentally demonstrated that injection of CO_2 with air together can enhance CO_2-replacement process by decomposition-driven guest exchange mechanism [29]. Lee et al. reported the latest results showing that flue gas can be used to replace methane from structure H hydrates that was formed with methane and neohexane [30]. The first field trial of the CO_2 replacement technique was successfully conducted in the North Slope of Alaska [31]. 77% N_2 was added to the CO_2 stream to prevent secondary hydrate formation and have a high CO_2-CH_4 exchange rate [32]. Garapati et al. conducted reservoir simulation to demonstrate how addition of N2 affect the dynamic process of gas production after injection of the CO_2-N_2 mixture [33]. In about 6 weeks of gas production, in total, 23.2 ms cm (million standard cubic meters) CH_4 was produced at the well head; about 54% of the injected CO_2 was stored underground; and more than 50% of the produced methane was retained in the well until the well was further depressurised to below the methane hydrate dissociation pressure [34].

All the techniques reviewed above face challenges to be able to produce methane at an economically viable rate, although they appear technically feasible [35]. Development of novel techniques has therefore become crucial for the commercial viability of methane recovery from gas hydrate reservoirs. This work proposes direct injection of flue gas into gas hydrate reservoirs to decompose methane hydrates and recover methane from gas hydrates and simultaneously sequester the CO_2 component of the flue gas as CO_2 hydrate or CO_2 mixed hydrates in the hydrate reservoir formations. Application of the flue gas injection method could substantially enhance the feasibility of depressurisation method for severe hydrate reservoir conditions and avoid CO_2 capture burden of geologic storage of CO_2.

2. Methods

The major constituents of flue gas are nitrogen and CO_2. For example, coal-fired flue gas (post-combustion) typically contains about 12–15% CO_2 and about 80% N_2 apart from water vapour and oxygen [36]. As a concept-proof work, for simplicity, deionised water and a simulated flue gas composed of 14.6 mol% CO_2 and 85.4 mol% N_2 were used. Injection of flue gas will move the thermodynamic conditions of the gas hydrate reservoir toward lower

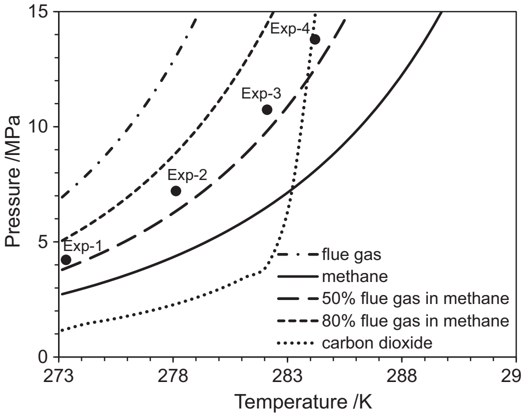

Fig. 1. Predicted shifts in methane hydrate stability zone due to injection of flue gas and the experiment conditions.