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Gas Hydrates Assessment

**Assessment of Current Technologies for Producing
Natural Accumulations of Gas Hydrate**

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Introduction

Vast quantities of natural gas are held in hydrate form in geologic reservoirs in sub-oceanic sediments and arctic permafrost zones (KVENVOLDEN, 1988; SLOAN, 1998), where conditions of high pressure and low temperature are within the hydrate stability region. In 1995, the U.S. Geological Survey (USGS) conducted a study to assess the quantity of natural gas hydrate resources in the United States and found that the estimated quantity exceeded known conventional domestic gas resources (COLLETT, 2004). Recovery of natural gas from these hydrate-bearing deposits has the potential for being economically viable (COLLETT, 2004; MORIDIS et al., 2004; CIRCONE et al., 2005), but there remain significant technical challenges in converting these natural deposits into a useable resource (COLLETT, 2004).

In conventional gas reservoirs, natural gas migrates to the recovery point via pressure gradients. For these reservoirs, the recovery rate is a function of the formation permeability and pressure gradients between the reservoir and recovery point. Natural gas recovery from hydrate-bearing deposits requires the additional energetic cost of dissociating the crystalline water lattice that forms the gas hydrate structure. A variety of methods have been proposed for producing natural gas from hydrate deposits: 1) thermal stimulation, where the temperature is increased above the hydrate stability region; 2) depressurization, where the pressure is decreased below the hydrate stability region; 3) chemical injection of inhibitors, where the temperature and pressure conditions for hydrate stability are shifted; and 4) CO₂ or mixed CO₂ and N₂ exchange, where CO₂ and N₂ replace CH₄ in the hydrate structure. Although recent estimates (MILKOV et al., 2003) put the global accumulations of natural gas hydrate at 3,000 to 5,000 trillion cubic meters (TCM), compared against 440 TCM estimated (COLLETT, 2004) for conventional natural gas accumulations, none have speculated how much gas could be produced from these vast natural gas hydrate deposits. What is needed to convert these gas-hydrate accumulations to recoverable reserves are technological innovations, sparked through sustained scientific research and development. As with other unconventional energy resources, the challenge is to first understand the resource, its coupled thermodynamic and transport properties, and then to address its production challenges.

A critical consideration for the production of gas hydrates is the thermal self-regulation of hydrate dissociation. If the hydrate-bearing reservoir is above the freezing point of the formation water then the temperature in the vicinity of dissociation will decrease, because heat flow into the region is insufficient to offset the endothermic heat of dissociation. With continued dissociation, the temperature will decrease until the hydrate is exhausted or the temperature reaches a phase boundary. In the absence of other heat sources (e.g., advective, electromagnetic), the system becomes thermally self regulating, the temperature remains constant, and the dissociation rate is controlled by diffusive heat transfer. For pressures above the quadruple point (the intersection of the hydrate stability boundary and the formation water freezing point temperature) the lower temperature limit will be that of the hydrate equilibrium boundary. For lower pressures, temperature is limited by the freezing point of the formation water. Laboratory experiments (CIRCONE et al., 2005) have shown that under these conditions that dissociation rates are not slowed by ice formation and are dependent on heat flow into the dissociation zone from the surroundings,

and the exothermic heat of formation of the ice contributes to the heat flow into the dissociation area. When the hydrate-bearing formation is below the freezing point of the formation water, however, the dissociation rates are considerably slower (CIRONE et al., 2005).

Thermal Stimulation

Gas hydrate production via thermal stimulation recently has been investigated experimentally (TANG et al., 2005) and numerically (TSYPKIN, 2000; MORIDIS, 2003, 2004; MORIDIS et al., 2004; POOLADI-DARVISH, 2004). Technologies for implementing thermal stimulation include hot brine injection, steam injection, cyclic steam injection, fire flooding, and electromagnetic heating. Steam injection, cyclic steam injection and fire flooding suffer from high heat losses and the by products of fire flooding can dilute the produced natural gas. Hot brine injection involves the injection of a saline aqueous solution at an elevated temperature into a gas hydrate bearing geologic reservoir. The energy of the injected brine is used to heat the geologic media, heat dissociated gas and aqueous phases, and dissociate gas hydrate. In general, brine flow rates yield a heating process that is dominantly advective. In addition to raising the boiling temperature of the saline solution, the dissolved salt lowers the gas hydrate dissociation temperature. Visual experiments of the dissociation process (TOHIDI et al., 2001) in glass micro-models indicate that during the dissociation process the hydrate becomes colloidal and migrates advectively with the injected brine. Production experiments of Tang et al. (2005) indicate that the efficiency of the hot brine injection production methodology is dependent on the inlet brine temperature, injection rate, and initial hydrate saturation; where the measure of efficiency is the energy ratio, defined as the ratio of combustion heat of the produced gas over the inlet heat. Tang et al. (2005) concluded that lower temperatures and injection rates yield higher recovery energy ratios, as did higher initial hydrate saturations. The downside of higher energy ratios realized through lower inlet temperatures and injection rates, however, are the lower production rates. Energy ratios for moderate to high temperatures and injection rates are on the order of 1.0, which means 50% of the recovered energy would be used to heat the injected brine. Numerical simulations of Moridis (2002; 2003) have demonstrated that the appeal of the thermal stimulation technology increases from Class 1 to Class 3 hydrate deposits. Another class of thermal stimulation technologies involves the injection of two fluids that react exothermally when mixed, such as the acidic- and basic-liquid approach proposed by Chatterji and Griffith (1998). The reaction of these two aqueous solutions would yield a hot salt solution.

Depressurization

Gas hydrate production via depressurization is considered to be the most economically promising technology (COLLETT, 2004). The Messoyakha field in northern Russia is a natural gas accumulation, containing both free gas and hydrate-bearing formations, which has been produced by simple depressurization. The sustained production of natural gas from this field is due to the dissociation of gas hydrate into an underlying free-gas formation, and has demonstrated that gas hydrates are immediately producible using conventional methods. However, production rates are ultimately controlled by heat transfer toward the hydrate dissociation region. Gas production using depressurization at the Mallik site was numerically simulated (MORIDIS et al., 2004) as part of a study to analyze various production methods. These simulations assumed a geothermal gradient of 0.03 C/m across the hydrate-bearing formation. The simulation results for a single vertical production well show temperatures dropping in response to depressurization of the formation and hydrate dissociation. The temperature decrease, however, is reversed as deeper warmer water is drawn to the well, providing the needed energy to sustain hydrate dissociation in the depressurized system. When augmented with either steam or hot methane (CH₄) gas injection from a second well, natural gas production is superior in terms of the ratios of produced gas to water and fraction of produced hydrate CH₄. Numerical depressurization studies for a one-dimensional radial confined reservoir with a central well were conducted using a linearization model (JI et al., 2001). These studies and others (HONG and POOLADI-DARVISH, 2005; SUN et al., 2005) represent depressurization in its most basic configuration. As expected, simulation results indicate that hydrate dissociation rates and associated gas production rates are controlled by the far-field reservoir pressure and tempera-

ture, via energy supplied by natural gas advected from the far field to the dissociation front. Laboratory experimental studies of gas hydrate production via depressurization (LIU et al., 2002; SUNG et al., 2003) have been limited in number and scope. Because of the thermal self-regulation of gas hydrates, pure depressurization is a viable option for natural accumulations of gas hydrates, but may suffer from slow production rates. Sustained production using depressurization additionally requires a heat source. At the Messoyakha field, that energy source is likely heat transfer into the dissociation zone via thermal conduction and advection, which ultimately controls the production rate.

Inhibitor Injection

Thermodynamic inhibitors lower the hydrate formation temperature, which can result in hydrate dissociation when injected into a gas-hydrate-bearing formation (SUNG et al., 2002). The most common thermodynamic organic inhibitors are methanol, monoethylene glycol (MEG) and di-ethylene glycol (DEG) commonly referred to as glycol. Dissolved salts (e.g., NaCl, CaCl₂, KCl, NaBr) can also be inhibitors. Whereas gas hydrate inhibitors are an effective methodology for preventing hydrate formation in engineering applications, their use in the production of natural gas hydrates is prohibitive from three perspectives: 1) environmental impact, 2) economic costs, and 3) thermal self regulation of gas hydrates.

Gas Phase Exchange

The world's energy consumption is expected to increase by 40% from 2006 to 2025, with 80% being produced using fossil fuels: oil, gas, and coal, which emit CO₂ when combusted. Over the last hundred years, the atmospheric CO₂ level has risen from 280 to 370 ppm and is continuing to increase steadily, which is of growing concern for climate change impacts. One option for mitigating the amount of anthropogenic CO₂ emitted into the atmosphere is capture and sequestration. Conventional sequestration options for CO₂ included deep saline formations, depleted or partially depleted oil and gas reservoirs, and coal beds. An additional geologic sequestration option is gas hydrates, where CO₂ is exchanged with the CH₄ in natural gas hydrate accumulations. This hydrate production technology offers two benefits: 1) reducing CO₂ emissions through sequestration as hydrates, and 2) maintaining the mechanical stability of the reservoir during production of gas hydrates.

Ohgaki et al. (1994; 1996) first advanced the concept of exchanging CO₂ with CH₄, through experiments that showed CO₂ to be preferentially clathrated over CH₄ in the hydrate phase and demonstrated the possibility of producing CH₄ gas by injecting CO₂ gas. During the exchange process, Ohgaki et al. (1996) observed that the mole fraction of CO₂ in the hydrate phase was greater than that in the gas phase. Seo et al. (2001; 2001) quantified this effect by noting that gas phase mole fractions of the hydrate formers (i.e., CH₄ and CO₂) above 40% CO₂ yielded hydrate phase mole fractions of CO₂ in the hydrate phase greater than 90%. Pure CH₄ and CO₂ form structure I (sI) type hydrates (Sloan, 1998) and their mixtures also form sI type hydrates (LEE et al., 2003). In forming mixed CH₄ and CO₂ hydrates, the CH₄ molecules occupy both the large and small cages of type sI hydrates, whereas the CO₂ molecules only occupy the large cages. Without hydrate dissociation, there is an upper limit to the substitution of CO₂ for CH₄ in hydrates. Lee et al. (2003) estimated that approximately 64% of the CH₄ could be released via exchange with CO₂. In addition to equilibrium considerations, the heat of CO₂ formation (-57.98 kJ/mol) is greater than the heat of dissociation of CH₄ hydrate (54.49 kJ/mol), which is favorable for the natural exchange of CO₂ with CH₄ hydrate, because the exchange process is exothermal (SMITH et al., 2001). Despite the considerable number of open literature publications on the CO₂-CH₄ gas exchange concept, U.S. patent applications with very similar ideas have recently been filed.^{1,2}

¹Sivaraman, A. 2005. "Process to Sequester CO₂ in Natural Gas Hydrate Fields and Simultaneously Recover Methane." Gas Technology Institute, U.S. Patent Application No. 20050121200.

²Graue; A. 2006. "Production of Free Gas by Gas Hydrate Conversion." ConocoPhillips Company, U.S. Patent Application No. 20060060356.

Neither Ohgaki et al. (1996) or Nakano et al. (1998) addressed the important issue of the kinetics of the gas exchange reaction. The first attempt to do so was performed by Uchida et al. (2001). Using a Raman spectroscopic method, they confirmed the swapping reaction at the hydrate-gas interface. Although the authors did not directly address the issue in their paper, their results suggested that the exchange mechanism was slow with induction times requiring several days. They did not address the more difficult question of the rate of CO₂ gas penetration further into bulk hydrate, beyond the first few hundred nanometers at the interface. McGrail et al. (2004) performed scanning Raman spectroscopy experiments and determined that the CO₂ penetration rate into bulk methane hydrate was only a few mm per hour.

Natural deposits of gas hydrates occur in porous media. Equilibrium conditions for hydrates differ between bulk conditions (*ex-situ*) and in porous media (*in-situ*). *In-situ* equilibrium pressures at a given temperature are greater and equilibrium temperatures at a given pressure are lower compared with *ex-situ* values. Differences between *in-situ* and *ex-situ* conditions increase with decreasing pore radius. Hydrate formation in geologic media that have a distribution of pore sizes will begin in the largest pore spaces and then continue into smaller pore spaces until the *in-situ* equilibrium condition is reached for a particular pore radius (CLENNELL et al., 1999). In addition to the equilibrium condition, porous media may affect other thermodynamic properties of hydrates. For example, in Goel's (2006) review of CH₄ production with CO₂ sequestration, a number of contrasting observations were revealed concerning the *in-situ* enthalpy of dissociation of CO₂ and CH₄ hydrates. Some research indicated that there was an increase in the heat of dissociation between *in-situ* and *ex-situ* conditions; whereas, other research indicated the opposite. Another example is the value of the lower quadruple point (ice-water-hydrate-gas) temperature and pressure for CH₄ and CO₂, and the upper quadruple point (water-hydrate-gas-liquid CO₂) for CO₂ hydrate between *in-situ* and *ex-situ* conditions; where, the *in-situ* conditions were determined for a porous media of limited pore-size distribution. In geologic media that have distribution of pore sizes, hydrates would form and dissociate over a range of temperatures and pressures according to the distribution of pore radii and accounting for the impact of salts in the residual pore water (MCGRAIL et al., 2007). The critical conclusion from Goel's (2006) review with respect to hydrates in porous media is that to understand the gas exchange technology there is a need for quantitative estimates of formation and dissociation processes in geologic media core samples.

Multiphase Exchange

Multiphase exchange of CO₂ for CH₄ was proposed by Hirohama et al. (1996). Essentially, the method is identical to that proposed by Ohgaki et al. (1996) except extending to higher pressures such that CO₂ was in the liquid state instead of gaseous. The authors reported slow conversion kinetics with liquid CO₂ and in fact had much more rapid CH₄ recovery using gaseous N₂ instead. For liquid CO₂ injection, thermodynamic conditions can either favor CO₂ or CH₄ cage occupation. This transition occurs where the pure CO₂ and CH₄ temperature-versus-pressure equilibrium functions cross with increasing pressure above the gas-liquid CO₂ phase boundary.

McGrail et al. (2004) disclosed a new approach involving injection of a microemulsion of CO₂ and H₂O into gas hydrate bearing sediments. Their enhanced gas hydrate recovery (EGHR) concept purportedly takes advantage of the physical and thermodynamic properties of mixtures in the H₂O-CO₂ system combined with controlled multiphase flow, heat, and mass transport processes to produce free gas from hydrate-bearing porous media. The microemulsion is formed with a proprietary method. The two-phase microemulsion is injected into the hydrate bearing strata at a temperature higher than the stability point of methane hydrate, which upon contacting the methane hydrate decomposes its crystalline lattice and releases the enclathrated gas. The freed gas is to be recovered at an extraction well. Sensible heat of the emulsion and heat of formation of the CO₂ hydrate provide a low grade heat source for further dissociation of methane hydrate away from the injectate plume. Conversion of the microemulsion to CO₂ hydrate occurs over time as controlled by heat transfer, diffusion, and the intrinsic kinetics of CO₂ hydrate formation. Process control is afforded by variation in the temperature of the emulsion, ratio of CO₂ and water, and droplet size of the discrete CO₂ phase.

Other Stimulation Methods

Various other stimulation methods have been discussed for gas hydrate reservoirs, including nuclear heating, downhole combustion, microwave heating, etc. However, these techniques are similar in that all are variations of thermal stimulation. One completely novel concept involves pressure pulse stimulation (PPS). The PPS method consists of applying high amplitude, low frequency pressure pulses to the producing formation using a high power PPS tool. The low frequency strain waves accelerate through the porous medium and suppress many of the advective instabilities and difficulties in aquifer cleanup. Aggressive pressure pulsing creates a porosity dilation wave, which momentarily and elastically dilates the porous media and increases the mobility of fluids to overcome capillary blockages. The PPS technique is effective in unconsolidated and consolidated sedimentary rocks exhibiting elastic properties, increases pressure, re-establishes connectivity and enhances or restores the formation permeability and a well's capacity to produce fluids (KANTZAS et al., 1994). However, no studies on the effectiveness of PPS for gas hydrate production, either alone or in combination with other methods, have been performed. Similarly, although permeability reductions in fracture networks during gas hydrate formation have been studied (NIMBLETT and RUPPEL, 2003), generation of fractures in gas hydrate reservoirs as a means of enhancing permeability and perhaps production rates has not yet received attention.

Conclusions

Estimates of vast amounts of global natural gas hydrate deposits make them an attractive unconventional energy resource. As with other unconventional energy resources, the challenge is to economically produce the natural gas. The gas hydrate challenge is principally technical. Meeting that challenge will require innovation, but more importantly, primarily scientific research to understand the resource and its characteristics in porous media. Producing natural gas from gas hydrate deposits requires releasing methane from its clathrated form. The simplest way to release methane is to dissociate the hydrate by removing it from within the hydrate stability pressure and temperature conditions. The thermal stimulation production technology effectively dissociates the gas hydrate through heating. Whether the heat source is injected steam, an exothermic reaction, or electromagnetic, the effect is to raise the temperature of the gas hydrate above the equilibrium point, causing the hydrate to dissociate. This approach, however, suffers from poor recovery efficiencies and could possibly disrupt the hydraulic and mechanical properties of the produced reservoir. The depressurization production technology dissociates gas hydrate by lowering the pressure below the hydrate stability point. The self-regulating thermal nature of gas hydrates results in lower temperatures in the dissociation region and ultimately without an additional heat source, production rates will depend on heat transport into the reservoir (e.g., geothermal gradient). Depressurization is the most economical approach, but could also disrupt the produced reservoir. The inhibitor injection technology causes hydrate dissociation by shifting the equilibrium curve, but the approach is unattractive for environmental and economic reasons. The gas exchange technology (including EHGR) releases methane by replacing it with a more thermodynamic molecule (e.g., carbon dioxide). This technology has three advantages: 1) it sequesters greenhouse gas, 2) it releases energy via an exothermic reaction, and 3) it retains the mechanical stability of the hydrate reservoir. However, the strict gas exchange approach appears, in some studies, to be limited in terms of the fraction of methane that can be produced and its rate of production. Of course, a CO₂ supply must also be available or transported to the production site. The gas exchange technology currently appears promising, but its success or failure will depend on the results of future scientific research and thorough modeling studies of reservoir production performance.

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