Gas Replacement in Clathrate Hydrates during CO₂ Injection - Kinetics and Micro-Structural Mechanism

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ABSTRACT

The replacement process in of pure sI methane clathrate powders exposed to CO₂ have been quantitatively followed by means of neutron diffraction at conditions relevant to sedimentary matrixes of continental margins. The exchange of methane with CO₂ within a crystalline lattice of gas hydrates is seen as a two-step process of (1) a fast interfacial reaction (2) followed by much slower diffusion-limited transport.

KEY WORDS: Clathrate hydrate, gas replacement, CO₂ sequestration, shrinking core.

INTRODUCTION

Gas hydrates (or clathrate hydrates, GH) (Sloan and Koh, 2008) are crystalline, ice-like compounds of hydrogen-bonded water molecules organized in the form of cages that are stabilized by small-size molecules. The majority of natural gas hydrates (e.g. of CH₄ and CO₂) crystallize in a primitive cubic lattice structure (sI) with lattice constants of about 12 Å with 2 smaller (S₁₂) and 6 larger (S₁₂₆₂) polyhedral cages in the unit cell. A second structure type crystallizes in a face-centered cubic lattice (sII) with lattice constants of about 17.2 Å with 16 smaller (S₁₂) and 8 large (S₁₂₆₂) polyhedral cages in the unit cell. The third type known to exist in nature (Ripmeester et al., 1987), hexagonal structure sIH (a=12.2 c=10.1 Å), is far more exotic; it is formed by one large (S₁₂₆₂), two medium (S₅₅₆₆), and three small (S₂₁₂) cavities that require gas molecules of two sizes (e.g. n-butane and methane) to stabilize the structure.

Clathrate hydrates are fairly widespread in nature, growing in the presence of water whenever an excess of gas fugacity allows the formation and stabilization of the structure (e.g. Kvenvolden and Lorenson, 2001; Milkov, 2004; Klauda and Sandler, 2005; Pinero et al., 2013). Typically, they are found in sedimentary matrixes of continental margins and in/below permafrost regions where they fill pore spaces frequently cementing otherwise unconsolidated sediments. Due to the microbial activity, the overwhelming majority of known natural occurrences contain nearly pure CH₄ with some minor contributions of other volatile components like CO₂, H₂S, ethane and other higher hydrocarbons (Kvenvolden, 1995; Milkov, 2005). The cage occupancy of any stable clathrate structure leads to a spontaneous gas replacement between the original compounds and the new environment. Such an exchange process attracted increasing attention in recent years as it allows for a gas recovery concomitant with the sequestration of anthropogenic CO₂ without causing any significant alterations to the original mechanical properties of the hydrate-bearing sediment. As a result, the replacement process may be nearly emission free with the advantages of both technologies and, moreover, reduced potential hazards of uncontrollable...

Recovery of this stranded gas remains technically, ecologically and economically challenging in spite of considerable progress in this area (Moridis et al., 2011). The stability of cages is provided by a sufficiently high partial fugacity of clathrate forming gas or gas mixture that remains in a dynamic equilibrium with the crystals. Gas can be extracted via the shift of p-T conditions or gas composition away from any stable clathrate structure leading to the decomposition of cages e.g. (Moridis et al., 2011; Schicks et al., 2011b; Falser et al., 2012 and references within). Since the dissociation is an endothermic process, a considerable input of energy is necessary to sustain the reaction (reviewed in: Moridis et al., 2011). On the other hand, a change in the gas composition to another one capable also of forming a stable clathrate hydrate will lead to a spontaneous gas replacement between the original compounds and the new environment. Such an exchange process attracted increasing attention in recent years as it allows for a gas recovery concomitant with the sequestration of anthropogenic CO₂ without causing any significant alterations to the original mechanical properties of the hydrate-bearing sediment. As a result, the replacement process may be nearly emission free with the advantages of both technologies and, moreover, reduced potential hazards of uncontrollable...