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Natural Gas Hydrates as CH_4 Source and CO_2 Sink - What do SO_2 Impurities do?

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The large amounts of gas hydrates stored in natural reservoirs are thought to be a promising future energy source. The recently discussed idea of methane extraction from these formations, together with the subsequent storage of CO_2 in form of gas hydrates is an elegant approach to bring forward.
A number of experiments have been performed on lab scale showing the replacement of CH_4 by CO_2 and vice versa. For instance, Graue and Kvamme (2006) demonstrated with Magnetic Resonance Images of core plug experiments the possibility of CH_4 extraction by using liquid CO_2. Laser Raman investigations of Schicks et al. (2007) showed, on the other hand, the ineffectiveness and slowness of the CH_4 exchange reaction with gaseous CO_2. After 120 hours, only 20% CH_4 were exchanged for CO_2. Natural methane hydrates which include often higher hydrocarbons tend to be even more stable than pure methane hydrates (Schicks et al., 2006).
Contrary to lab conditions, industrial emitted CO_2 contains - despite much effort to clean it – traces of impurities. For instance, CO_2 emitted from the state-of-the-art Vattenfall Oxyfuel pilot plant in Schwarze Pumpe should reach a quality of >99.7% CO_2 but still contains small amounts of N_2, Ar, O_2, SO_x and NO_x (pers. comm. Dr. Rolland).

Here we present a microscopic and laser Raman study in a p-T range of 1 to 4 MPa and 271 to 280K focussing on CO_2 hydrate formation and CH_4-exchange reaction in the presence of 1% SO_2. The experiments have been performed in a small-scale cryocell.
The Raman spectra show that CO_2 and SO_2 occupy both large and small cages of the hydrate lattice. SO_2 occurs strongly enriched in the hydrate clathrate, compared to its concentration in the feed gas which causes a strong acidification of the liquid phase after hydrate dissociation.
Our study reveals that the hydrate formation rate from impure CO_2 is similar to that of pure CO_2 hydrate but that the stability of the CO_2-SO_2-hydrate exceeds that of pure CO_2 hydrate.
The improved stability of impure CO_2 hydrate might also boost the exchange reaction with CH_4 hydrate.

These significant parameters - changes of hydrate stability and CO_2-CH_4 exchange rate as well as the acidification of the environment - have to be considered in future concepts for CO_2 sequestration combined with CH_4 recovery.

Reference:
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