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# Visualization study on the growth and occurrence patterns of CO2-SO2 mixed hydrates in porous media

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Sealing carbon dioxide (CO2) in marine sediments in the form of hydrates presents a promising approach for mitigating greenhouse gas pollution. The captured CO2 often includes other impurity gases, such as nitrogen (N2) and sulfur dioxide (SO2). It is well-established that the release of SO2 carries adverse effects on both human health and the environment. Currently, various flue gas desulfurization methods have been developed, but few methods can simultaneously achieve flue gas desulfurization and decarbonization. Consequently, the co-injection of impurity gases with CO2 into deep-sea sediments and their utilization for hydrate storage has emerged as a promising approach. While extensive studies have explored the impact of N2 on CO2 hydrate storage, the understanding of how SO2 influences the utilization of hydrate storage for CO2 remains relatively limited. In this work, we used a 2.5D microfluidic chip to characterize the pore structure of sediments in the South China Sea. Visualization studies were conducted to examine the occurrence patterns and growth habits of CO2-SO2 mixed gas hydrates under specific hydrate zone conditions (P=9 MPa, T=284.15 K) in the South China Sea under stagnant conditions. The growth and occurrence patterns of mixed gas hydrates at the pore scale were analyzed, and quantitative Raman spectroscopy was employed to investigate changes in hydrate composition within the pore space.

The results indicate that under static conditions, the dissolution and diffusion of gas are influenced by the pore structure of porous media, leading to regional differences in dissolved gas. This discrepancy can result in density variations between fluids, inducing fluid convection. This convection can place the fluid in a slightly perturbed state, facilitating the nucleation and growth of hydrates. Hydrate growth initiates from the gasliquid interface, the region with the most severe fluid disturbance, promoting hydrate nucleation. During the hydrate growth process, it was observed that hydrates preferentially grow along regions where aqueous solutions exist, occupying all pores containing solutions. After that, the hydrate film that penetrates the gasliquid interface extends into the gas phase. Due to the hydrophilicity of porous media and the high solubility of CO2-SO2 gas mixtures, the occurrence mode of mixed hydrates in the aqueous phase is typically patchy, while in the gas phase, it manifests as a mixed mode of pore-filling and load-bearing. Disparities in substance composition of dissolved substances in porous media were identified, with natural hydrate formation tending to occur in areas with higher local SO2 concentrations. Given the easier formation of SO2 hydrates compared to CO2 hydrates, the accumulation of SO2 in the fluid promotes the nucleation of mixed gas hydrates, where SO2 plays a crucial role in hydrate nucleation sites. Moreover, as SO2 is a polar molecule, its enhanced hydrophilic properties significantly improve the stability of CO2 hydrates, allowing them to remain stable and grow outside the stable domain. These findings contribute to a better understanding of the occurrence and growth mechanism of CO2-SO2 mixed hydrates in sediment pores, demonstrating the potential application of using hydrates to seal CO2-SO2.

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## Porous Media & Biology Focused Abstracts

### References

## **Conference Proceedings**

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