



Heriot-Watt University
Research Gateway

Insights into CO₂ Capture by Flue Gas Hydrate Formation: Gas Composition Evolution in Systems Containing Gas Hydrates and Gas Mixtures at Stable Pressures

Citation for published version:

Hassanpouryouzband, A, Yang, J, Tohidi Kalorazi, B, Chuvilin, E, Istomin, V, Bukhanov, B & Cheremisin, A 2018, 'Insights into CO₂ Capture by Flue Gas Hydrate Formation: Gas Composition Evolution in Systems Containing Gas Hydrates and Gas Mixtures at Stable Pressures', *ACS Sustainable Chemistry and Engineering*, vol. 6, no. 5, pp. 5732-5736. <https://doi.org/10.1021/acssuschemeng.8b00409>

Digital Object Identifier (DOI):

[10.1021/acssuschemeng.8b00409](https://doi.org/10.1021/acssuschemeng.8b00409)

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Peer reviewed version

Published In:

ACS Sustainable Chemistry and Engineering

General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Insights into the CO₂ Capture by Flue Gas Hydrate Formation: Gas Composition Evolution in Systems Containing Gas Hydrates and Gas Mixtures at Stable Pressures

Aliakbar Hassanpouryouzband¹, Jinhai Yang^{1*}, Bahman Tohidi¹, Evgeny Chuvilin², Vladimir Istomin², Boris Bukhanov², and Alexey Cheremisin²

¹ Hydrates, Flow Assurance & Phase Equilibria Research Group, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh, EH14 4AS, UK.

² Skolkovo Institute of Science and Technology, Moscow 143026, Russia

Abstract

Capturing CO₂ from power plant flue gas through hydrate formation is starting to be applied on an industrial scale. Several methods have been developed and a large number of experiments have been conducted in order to investigate ways of increasing their efficiency. However, most of them suffer from a lack of detailed kinetic studies. In this paper we present a highly accurate method to investigate the kinetics of flue gas hydrate formation. Preliminary results are detailed at three different temperatures. It has been found that more than 40% of CO₂ capture in the form of hydrates occurs after reaching the final pressure. Therefore, statistically constant pressure cannot be used as a sign of thermodynamic equilibrium. The results obtained from this study are important for optimizing CO₂ separation operations thus maximizing efficiency and reducing economic barriers. In addition, they are also useful in studying the kinetics of hydrate formation in other gas mixture systems.

Keywords: Carbon dioxide capture and storage; gas hydrate; flue gas; carbon dioxide replacement; gas separation; kinetics.

Introduction

Gas hydrates are solid, non-stoichiometric inclusion compounds consisting of an open lattice of water molecules that encage small size guest gas molecules such as nitrogen (N₂) and carbon dioxide (CO₂), etc. without chemical bonding¹. Between all potential guest molecules, CO₂ emanating from power plants² is responsible for the majority of the increasing greenhouse effect³. Accordingly, developing efficient methods for CO₂ capture is crucial in order to deal with this major environmental challenge⁴. To date, various methods that have different efficiencies at selected conditions have been developed⁵. In this regard, gas hydrate formation has been proposed as an alternative approach to separate CO₂ from power plant flue gas which mainly consists of N₂ and CO₂⁶. Furthermore, direct injection of CO₂-N₂ mixtures^{7,8} and coal-fired flue gas⁹ into methane hydrate reservoirs was proposed as a promising method

*Corresponding author: petjy@hw.ac.uk (J Yang)

for capture and geological storage of CO₂. These gas hydrate-based CO₂ capture methods are environmentally cleaner and more cost effective compared to the conventional amine-based absorbance techniques^{10,11}. Fulfilment of these methods requires the flue gas hydrate formation kinetics to be completely understood, reduction in the CO₂/N₂ ratio of the gas phase with time is the main indicator of efficiency and may even be the key factor in acceptance of these methods for use on an industrial scale. Only a limited number of investigations on this subject have been reported and the kinetics of flue gas or N₂-CO₂ hydrate formation hasn't been completely clarified. Different material and methods have been suggested to enhance the rate of gas hydrate formation¹² and the kinetics of CO₂ separation mechanism and process through hydrate formation have been investigated for systems containing CH₄, CO₂, N₂, and oxygen (O₂)^{11,13}, but little is discussed about when and how the system reaches equilibrium. Usually thermodynamic equilibrium of the gas mixture is considered to be when pressure is constant¹⁴. In this letter, experimental results are reported to show that complex hydrate formation, decomposition, and molecular exchange were still occurring in the water-CO₂-N₂ gas mixture systems when the system pressure was constant.

Materials and Methods

The kinetics of flue gas hydrate formation was studied at 3 constant temperatures using a 316 stainless steel cylindrical autoclave (maximum working pressure of 20.7 MPa, and volume of 180.1 mL), a schematic diagram of which is shown in Fig. 1. The autoclave was connected to a gas chromatograph (GC) (Varian 3600, Agilent Technologies) through an online magnetic capillary sampler system (Rolsi™) with zero dead volume. The moveable sampler was connected to the top cap and GC through a capillary tube (0.1 mm internal diameter), and heated line (T = 323.25 K), respectively. The temperature was maintained by a cryostat (Grant LTC) which pumps cooling fluid into the integral cooling jacket surrounding the cell. The system pressure and temperature were continuously monitored using a Quartzdyne pressure transducer (accuracy +/-0.0005 MPa) and a Platinum Resistant Thermometer (PRT) coated in stainless steel (uncertainty of 0.1 K), respectively, through a data acquisition device and a LabView software interface at regular time intervals. To help increase the surface contact of components, a high-

pressure stirrer (Top Industrie SA, France, model 6180300B) was fixed at bottom of the cell. Visual high pressure windows were located at each side of the autoclave to visually observe hydrate formation and discriminate it from dissolution.

40% of the autoclave was filled with deionized water generated by an integral water purification system (ELGA DV 25), following which the system was vacuumed. For simplicity, a gas mixture of 85.4% N₂ and 14.6% CO₂ (purity of 99.995 vol% from BOC Limited) was used to simulate coal-fired flue gas^{9,15}. After setting the system temperature to 294.15 K and starting stirrer, the simulated flue gas was injected continuously to reach 20.68 MPa. To control the hydrate formation the stirrer was switched off until the system reached the target temperature. After reaching the target temperature, mixing was started and flue gas hydrates were formed at a constant temperature. Throughout the process the gas composition was analysed using GC.

Fig. 2 presents the predicted¹⁶ hydrate stability zones (HSZs) of the tested gas-water systems together with the experimental temperature and pressure conditions. As can be seen experiments were conducted at 3 different temperatures, and consequently 3 different pressures (Gas law). As shown, the experiment at 273.35 K started at a pressure inside the N₂ HSZ, but the other two experiments were outside the N₂ HSZ zone. Accordingly, thermodynamically for all experiments, there was the possibility of N₂-CO₂ mixed hydrates and CO₂ hydrate formation. However, N₂ hydrate formation may occur only in the first experiment. Regarding CO₂-N₂ mixed hydrates, according to thermodynamic stabilization, N₂ will fill the small cavities and CO₂ will enter the large cavities¹⁷.

Results and Discussion

Fig. 3a shows the CO₂ in mole% in the gas phase throughout the experimental process at the set temperatures. As can be seen from Fig. 3a, initially the molar fraction of CO₂ in the gas phase reduced from 14.6% to 12.4% at 294.15 K which is mainly due to the higher solubility of CO₂ in water compared to that of N₂, moving more CO₂ into the polar phase (Fig. 4a). After cooling the system to the target temperature, the CO₂ percentage in the gas phase slightly reduced owing to further increases in CO₂ solubility with temperature reduction compared to that of N₂. For the same reason, the CO₂ fraction in the gas phase was slightly smaller in the experiments at lower

temperatures. It should be noted that, in the investigated system there is a possibility for formation of different kind of ions which are illustrated in Fig. 4d¹⁸.

After hydrate formation started, there was an initial increase in the fraction of CO₂ in the gas phase for all experiments, which is magnified in Fig. 3b. These increments infer that the CO₂/N₂ ratio in water phase was relatively higher than that in the hydrate phase at the pressures in Fig. 3b. The difference became clearer at lower temperatures. This could be plausibly justified by the fact that according to Fig. 2 showing that the first experiment was initiated at a pressure inside the N₂ HSZ and the second experiment was closer to N₂ HSZ than the third experiment, occupancy ratio of large to small cages in the formed hydrates was smallest for the first experiment and is smaller for the second experiment compared to the third one, which in turn leads to entering relatively more N₂ into hydrate phase at lower temperature given that the initial system pressure was similar. With regard to the aforementioned initial increment in the percentage of the CO₂ in the gas phase, the first hydrate crystals formed could affect the solubility of CO₂ in the water¹⁹, as the solubility of a gas in a solvent could be significantly different in the presence of other solutes in the solution. After this phase, while the system pressure continuously decreased due to hydrate formation, the CO₂ percentage in the gas phase stayed almost stable with small fluctuations, i.e., no more CO₂ appeared to go into the hydrate lattice compared to N₂. This means that in this phase the ratio of CO₂/N₂ in the forming hydrate phase was equal to the ratio in the hydrate former gas phase and water phases, demonstrating a dynamical molecule exchanging process between these phases. At pressure near to the final equilibrium pressures the molar fraction of the CO₂ in the gas phase reduced sharply. The possible reason for these changes with only small pressure changes could be attributed the fact that the initially formed hydrates with relatively low CO₂ content dissociated and new CO₂-N₂ hydrates formed entrapping more CO₂. In addition, the final slight increase in the CO₂ percentage seen in all experiments could indicate that there is an optimum pressure at each specific temperature at which more CO₂ can be captured in hydrate (by keeping the pressure constant through gas injection) than at the final pressure where dissociation of the CO₂-N₂ mixed hydrate led to an increase in the CO₂ percentage. It is worth noting that further investigation is

been in progress investigating the reasons for these final reductions and increments of the CO₂ content in the gas phase.

A physical model of different stages of experiments is illustrated in Fig. 4 to describe the kinetic process of CO₂ capture in flue gas hydrate formation. After reaching the final pressure (Fig. 4b), as can be seen from Fig. 3c, the system had not reached equilibrium and the CO₂ fraction in the gas phase was changing with time, while the pressure was almost constant (Fig. 4c). It should be noted that there were still very small fluctuations in the pressure (less than 0.14 MPa), but these very small fluctuations were commonly seen in other hydrate tests and can be considered as negligible¹⁴. The reduction of the CO₂ percentage in the gas phase suggests that at a constant pressure, the amount of CO₂ entering into hydrate should be as same as the amount of N₂ escaping from the previously formed N₂-rich hydrates. Three different mechanisms could be suggested for this behaviour, as shown in a schematic illustration in Fig. 4e-g. Initially, some of the first formed hydrates with relatively more N₂ in the hydrate phase were dissociated and new hydrates with relatively less N₂ were formed (Fig. 4e). As a side note, there could be empty cages (Fig. 4b-c) in the hydrate phase corresponding to the occupancy number, so the aforementioned secondary hydrate formation could occur by filling these cages with CO₂ molecules. Secondly, some of the hydrate cages containing N₂ were partially broken, CO₂-N₂ exchange occurred and residual rings formed new cages (Fig. 4f). A similar behaviour for CO₂/CH₄ replacement was reported in the literature²⁰. Third, CO₂-N₂ replacement in the hydrate phase occurred without dissociation of initial hydrates (Fig. 4g). There is also a similar observation for the behaviour of CO₂-CH₄ replacement after injecting CO₂-N₂ gas into methane hydrate system⁸.

The first mechanism is thermodynamically more preferable, as CO₂ tends to enter large cavities, whereas N₂ goes for small cavities¹⁷. However, the possibility of secondary and tertiary mechanisms still exist as CO₂ could go to small cavities in some circumstances²¹. What's more, two small concavities can be seen in Fig. 3c graphs for Experiments 1 and 2, which could be explained with the same reason as for the final increase in Fig. 3a. Regarding Experiment 3, lack of increment in Fig. 3c could be explained because the system was further outside the N₂

HSZ, reducing the difference in the composition of the formed hydrates at initial and final pressures. It's also confirmed that, under elevated subcooling there is possibility of hydrate formation with metastable occupancies, if the concentration of small guest molecules (such as N₂) in the hydrate phase and overall solution is comparable²². This could be another explanation for abovementioned behaviour. It should be noted that further investigation is required to deeply understand this phenomena. The HSZs at the experimental temperatures are plotted as a function of pressure against CO₂ percentage in Fig. 3a. The CO₂ concentration at the end of each experiment approached to the corresponding HSZ curve. The final CO₂ concentration is 7.1% in Experiment 1 at 273.4 K 8.2% in Experiment 2 at 275.4 K, and 8.6% in Experiment 3 at 277.1 K, suggesting lower temperatures favour more CO₂ than N₂ compared to higher temperature. Furthermore, it is clear from Fig. 3c that more than 40% of the CO₂ capture through hydrate formation occurs at final pressures and it takes longer for tests at lower temperatures to reach equilibrium compared to those at higher ones. This indicates that although CO₂ capture at higher temperatures is less efficient in terms of captured CO₂ percentage, it could have the advantages of faster capture at certain conditions (Fig. S2 in supporting information). Accordingly, temperature of the capture environment, temperature of the supplied water, energy loss for maintaining and keeping the temperature, and energy loss for the reactor's electrical part should be considered and the most economic temperature and the most economic residency time for reaction should be chosen.

Taking all of the results from this initial work into account, it is clear that, for systems containing gas mixtures, reaching constant pressure can't be considered independently as a sign of thermodynamic equilibrium and further changes in the composition of different phases can occur at the final pressure. This study substantiates the crucial role of the hydrate formation kinetics to achieve a high efficiency of CO₂ separation and storage. In addition, the observed compositional changes in both gas phase and hydrate phase for flue gas-water systems could occur in other gas mixture systems, typically water-natural gas systems, which should be closely examined if the kinetics of hydrate formation is important. Although the presented work revealed some kinetic properties of flue gas hydrate formation, it is clear that more fundamental

experiments are required for a better understanding of the observed phenomenon. These experiments could be coupled with different spectroscopy techniques such as NMR to be able to measure the composition of the hydrate phase during hydrate formation/dissociation. Moreover, effect of gas to water ratio, pressure, temperature, and different compositions on both hydrate formation and dissociation also needs to be investigated following this work.

ACKNOWLEDGMENT

This work was financially supported by the Skolkovo Institute of Science and Technology, Russia, which is acknowledged gratefully. The authors would like to thank Dr. Rod Burgass, Dr. Antonin Chapoy, and Mr. Edris Joonaki for their valuable contributions to the project, and Jim Allison for manufacture and maintenance of experimental equipment. The experiments were conducted at the Centre for Hydrate Research, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh, United Kingdom.

References

- (1) Koh, C. A. Towards a fundamental understanding of natural gas hydrates. *Chem. Soc. Rev.* **2002**, *31* (3), 157–167. DOI: 10.1039/B008672J
- (2) Stocker, T. *Climate change 2013: the physical science basis: Working Group I contribution to the Fifth assessment report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, U.K., 2014.
- (3) Parrenin, F.; Masson-Delmotte, V.; Köhler, P.; Raynaud, D.; Paillard, D.; Schwander, J.; Barbante, C.; Landais, A.; Wegner, A.; Jouzel, J. Synchronous change of atmospheric CO₂ and Antarctic temperature during the last deglacial warming. *Science* (80-.). **2013**, *339* (6123), 1060–1063. DOI: 10.1126/science.1226368
- (4) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2011**, *112* (2), 724–781. DOI: 10.1021/cr2003272
- (5) Boot-Handford, M. E.; Abanades, J. C.; Anthony, E. J.; Blunt, M. J.; Brandani, S.; Mac Dowell, N.; Fernández, J. R.; Ferrari, M.-C.; Gross, R.; Hallett, J. P. Carbon capture and storage update. *Energy Environ. Sci.* **2014**, *7* (1), 130–189. DOI: 10.1039/C3EE42350F
- (6) Kang, S.-P.; Lee, H. Recovery of CO₂ from Flue Gas Using Gas Hydrate: Thermodynamic Verification through Phase Equilibrium Measurements. *Environ. Sci. Technol.* **2000**, *34* (20), 4397–4400. DOI: 10.1021/es0011481
- (7) Park, Y.; Kim, D.-Y.; Lee, J.-W.; Huh, D.-G.; Park, K.-P.; Lee, J.; Lee, H. Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (34), 12690–12694. DOI: 10.1073/pnas.0602251103
- (8) Cha, M.; Shin, K.; Lee, H.; Moudrakovski, I. L.; Ripmeester, J. A.; Seo, Y. Kinetics of Methane Hydrate Replacement with Carbon Dioxide and Nitrogen Gas Mixture Using in Situ NMR Spectroscopy. *Environ. Sci. Technol.* **2015**, *49* (3), 1964–1971. DOI: 10.1021/es504888n
- (9) Yang, J.; Okwananke, A.; Tohidi, B.; Chuvilin, E.; Maerle, K.; Istomin, V.; Bukhanov, B.; Cheremisin, A. Flue gas injection into gas hydrate reservoirs for methane recovery and carbon dioxide sequestration. *Energy Convers. Manag.* **2017**, *136*, 431–438. DOI: 10.1016/j.enconman.2017.01.043
- (10) Hassanpouryouzband, A.; Yang, J.; Tohidi, B.; Chuvilin, E. M.; Istomin, V.; Bukhanov, B. A.;

- Cheremisin, A. CO₂ Capture by Injection of Flue Gas or CO₂-N₂ Mixtures into Hydrate Reservoirs: Dependence of CO₂ Capture Efficiency on Gas Hydrate Reservoir Conditions. *Environ. Sci. Technol.* **2018**. DOI: 10.1021/acs.est.7b05784
- (11) Babu, P.; Linga, P.; Kumar, R.; Englezos, P. A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture. *Energy* **2015**, *85*, 261–279. DOI: 10.1016/j.energy.2015.03.103
- (12) Linga, P.; Clarke, M. A. A Review of Reactor Designs and Materials Employed for Increasing the Rate of Gas Hydrate Formation. *Energy & Fuels* **2016**, *31* (1), 1–13. DOI: 10.1021/acs.energyfuels.6b02304
- (13) Linga, P.; Kumar, R.; Englezos, P. Gas hydrate formation from hydrogen/carbon dioxide and nitrogen/carbon dioxide gas mixtures. *Chem. Eng. Sci.* **2007**, *62* (16), 4268–4276. DOI: 10.1016/j.ces.2007.04.033
- (14) Tohidi, B.; Burgass, R. W.; Danesh, A.; Østergaard, K. K.; Todd, A. C. Improving the Accuracy of Gas Hydrate Dissociation Point Measurements. *Ann. N. Y. Acad. Sci.* **2000**, *912* (1), 924–931. DOI: 10.1111/j.1749-6632.2000.tb06846.x
- (15) Change, W. G. I. of the I. P. on C.; Metz, B.; Davidson, O.; Coninck, H. de; Loos, M.; Meyer, L. Working Group III of the Intergovernmental Panel on Climate Change. IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge University Press: Cambridge, U.K., 2005.
- (16) Haghghi, H.; Chapoy, A.; Burgess, R.; Tohidi, B. Experimental and thermodynamic modelling of systems containing water and ethylene glycol: Application to flow assurance and gas processing. *Fluid Phase Equilib.* **2009**, *276* (1), 24–30. DOI: 10.1016/j.fluid.2008.10.006
- (17) Dornan, P.; Alavi, S.; Woo, T. K. Free energies of carbon dioxide sequestration and methane recovery in clathrate hydrates. *J. Chem. Phys.* **2007**, *127* (12), 124510–124700. DOI: 10.1063/1.2769634
- (18) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **1973**, *77* (2), 268–277. DOI: 10.1021/j100621a026
- (19) Servio, P.; Englezos, P. Effect of temperature and pressure on the solubility of carbon dioxide in water in the presence of gas hydrate. *Fluid Phase Equilib.* **2001**, *190* (1), 127–134. DOI: 10.1016/S0378-3812(01)00598-2
- (20) Bai, D.; Zhang, X.; Chen, G.; Wang, W. Replacement mechanism of methane hydrate with carbon dioxide from microsecond molecular dynamics simulations. *Energy Environ. Sci.* **2012**, *5* (5), 7033–7041. DOI: 10.1039/C2EE21189K
- (21) Sloan Jr, E. D.; Koh, C. *Clathrate hydrates of natural gases*; CRC press, 2007.
- (22) Song, B.; Nguyen, A. H.; Molinero, V. Can Guest Occupancy in Binary Clathrate Hydrates Be Tuned through Control of the Growth Temperature?. *J. Phys. Chem. C* **2014**, *118* (40), 23022–23031. DOI: 10.1021/jp504852k

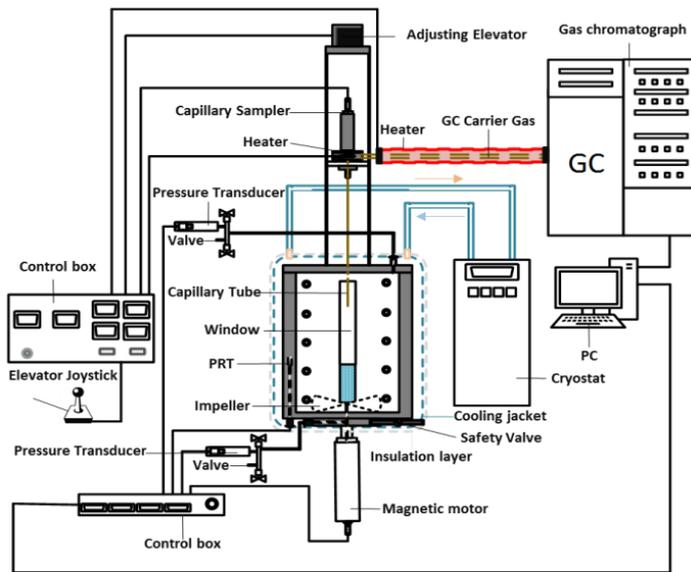


Fig. 1 Schematic of the high-pressure autoclave setup

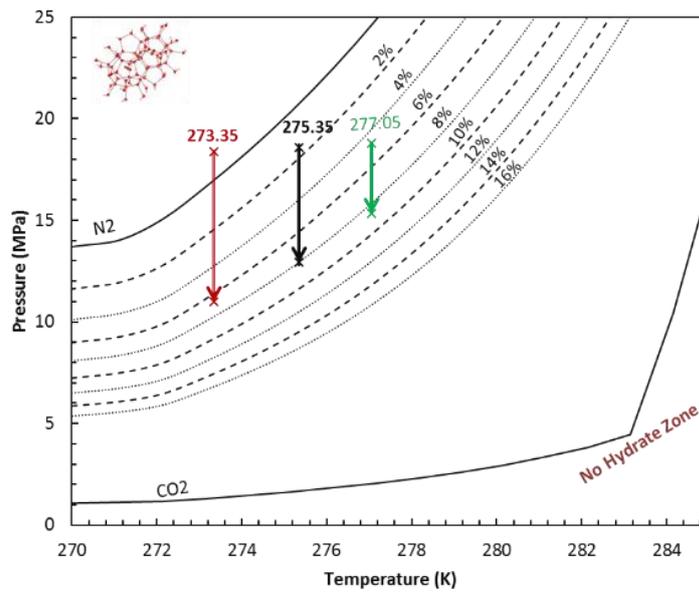


Fig. 2 The predicted hydrate stability zones of N₂, CO₂, various N₂-CO₂ combinations, and the experimental conisations

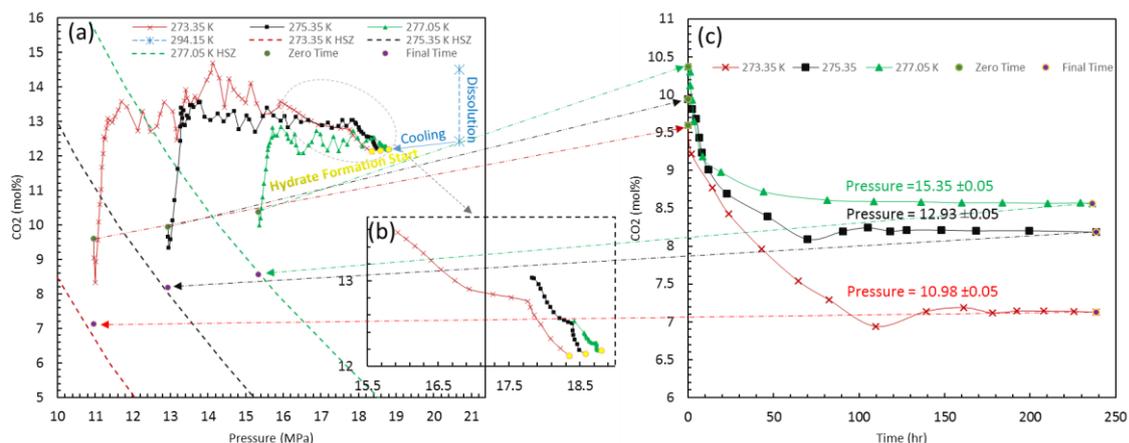


Fig. 3 (a) Variation in the CO₂ mole fraction in the gas phase versus pressure during experiments; (b) magnification of the selected part of the Fig. 3a; (c) Variation in the CO₂ mole fraction in the gas phase versus time after reaching equilibrium pressure (More detailed results can be found in Supporting Information).

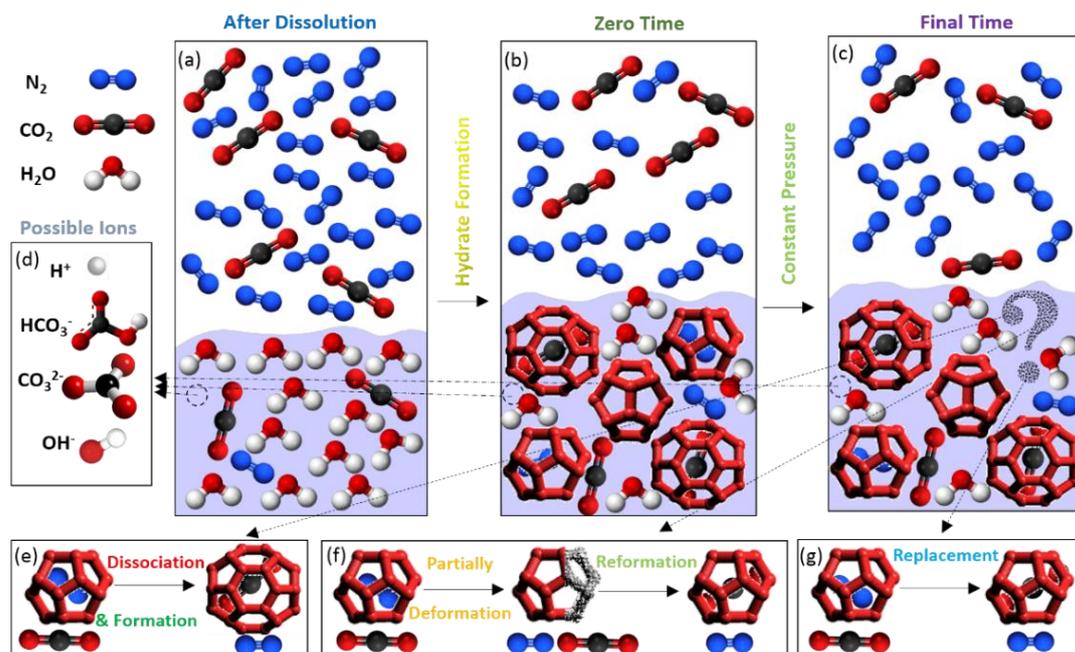
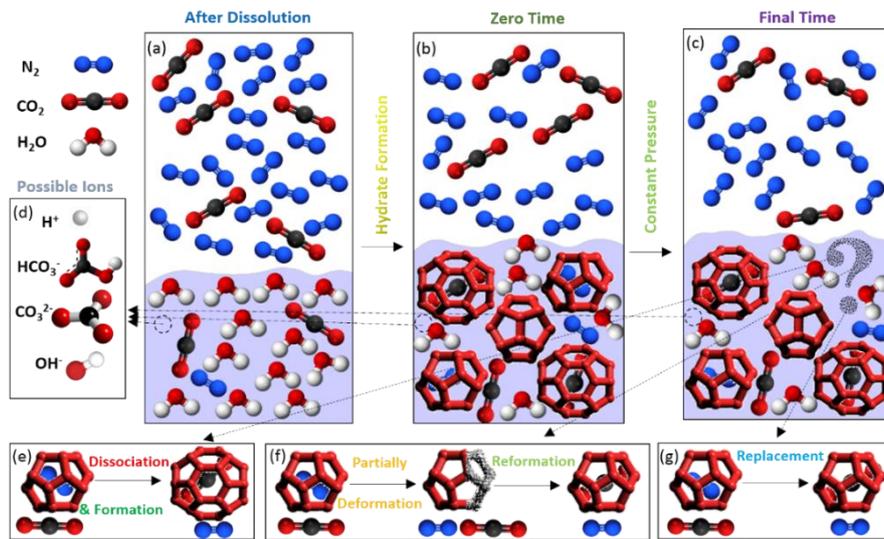


Fig. 4 Schematic illustration of the described flue gas hydrate formation experiments: (a) Dissolution of CO₂ and N₂ in water after injecting high pressure gas; (b) Formation of CO₂-N₂ hydrates after reaching to the target temperature; (c) Changing hydrate/gas phase composition after reaching final pressure; (d) Formation of different kinds of ions during experiment; (e)-(g) proposed mechanisms to explain the change in the hydrate/gas composition.

TOC



Synopsis

The compositions of both gas and hydrate phases may continuously evolve at stable pressures, understanding of which is essential for a sustainable development of hydrate-based CO_2 capture methods.