

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/262014585>

# Enhanced CO<sub>2</sub> Gas Storage in Coal

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · DECEMBER 2013

Impact Factor: 2.59 · DOI: 10.1021/ie403697q

---

CITATIONS

3

---

READS

41

## 4 AUTHORS:



Sungho Kim

Monash University (Australia)

13 PUBLICATIONS 43 CITATIONS

[SEE PROFILE](#)



Shu-Qing Hao

China University of Mining Technology

11 PUBLICATIONS 21 CITATIONS

[SEE PROFILE](#)



Yurong Qin

Guangxi University

85 PUBLICATIONS 867 CITATIONS

[SEE PROFILE](#)



X. H. Fu

China University of Mining Technology

47 PUBLICATIONS 268 CITATIONS

[SEE PROFILE](#)

## Enhanced CO<sub>2</sub> Gas Storage in Coal

Shu-Qing Hao,<sup>\*,†,‡,⊥</sup> Sungho Kim,<sup>\*,§</sup> Yong Qin,<sup>†</sup> and Xue-Hai Fu<sup>†,¶</sup>

<sup>†</sup> Key Laboratory of CBM Resources and Reservoir Formation Process Ministry of Education of China, School of Resource and Geosciences, China University of Mining and Technology, Xuzhou 221116, China

<sup>‡</sup> State Key Laboratory for GeoMechanics and Deep Underground Engineering, University of Mining and Technology, Xuzhou 221008, China

<sup>§</sup> Geotechnical and Hydrogeological Engineering Research Group, Monash University, Victoria 3842, Australia

<sup>⊥</sup> Department of Civil Engineering, Monash University, Victoria 3842, Australia

<sup>¶</sup> College of Geology and Exploration Engineering, Xinjiang University, Urumchi, Xinjiang Uygur Autonomous Region 830047, China

**ABSTRACT:** We investigate coal's performance for storing carbon dioxide (CO<sub>2</sub>) gas molecules in the form of CO<sub>2</sub> hydrates when the in situ hydrates-forming method is applied with the use of promoters. Sodium dodecyl sulfate (SDS) and pressure augmentation were adopted as a promoter for the hydrate formation in coal. The use of SDS considerably increased the rate of hydrates-forming reaction in coal. The calculated rates of the reaction in the presence of SDS reached 143.70 cm<sup>3</sup>/min at 3 MPa, and 50% of the maximum gas storage capacity was attained within 2 h. Pressure also controlled the final gas storage capacity of coal. The maximum gas storage capacity of coal under 3 MPa was 188.65 volume of CO<sub>2</sub> gas at standard temperature (273.15 K) and pressure (100 kPa) condition per unit volume of coal, as compared to 136.30 under 2.3 MPa.

### INTRODUCTION

Greenhouse gas (GHG) such as carbon dioxide (CO<sub>2</sub>) is largely believed to be a primary contributor to global warming.<sup>1–3</sup> Thus, geological GHG sequestration has recently received tremendous attention in both the scientific and industrial communities due to its potential to limit the climate change.<sup>3–5</sup> One effective technology is to store GHG in the form of hydrates, the so-called hydrates-forming method, such that the storage capacity is maximized.<sup>6–8</sup> The hydrates-forming technology has been utilized to store CO<sub>2</sub> gas within medium materials such as microporous carbons, silica gel, deep-sea sediments, and deionized water.<sup>9–12</sup> However, hydrates formation within such medium materials can be accompanied by high cost for large-scale applications and/or by environmentally hazardous side effects such as changes in seawater chemistry.<sup>4,13</sup> For example, the hydrates-forming rate in the presence of accelerating agents has been reported to be 22–56 cm<sup>3</sup>/min for various medium materials.<sup>14–16</sup>

Coal, a natural cost-effective geological medium, has been reported to be promising for geological GHG sequestration owing to its worldwide distribution and abundance.<sup>17–19</sup> Coal also has great affinity for adsorption, but the CO<sub>2</sub> has the potential for low-level leakage after placement.<sup>20–22</sup> In addition, the low rate of hydrates formation, a main obstacle to the application of the hydrates-forming technology, has been overcome by introducing an accelerating agent including sodium dodecyl sulfate (SDS) and cyclopentane.<sup>11,23–25</sup> Although carbon dioxide capture within deep unminable coal-beds has been proposed,<sup>26–28</sup> little experimental study on storing CO<sub>2</sub> gas as hydrates in coal has been reported. Coal, as a medium material seems to be useful for entrapping carbon dioxide gas in the form of CO<sub>2</sub> hydrates through the hydrates-forming method with the aid of accelerating techniques.

The objective of this study was to determine whether coal could provide desirable performance for storing CO<sub>2</sub> gas molecules in the form of CO<sub>2</sub> hydrates when the in situ hydrates-forming method is applied with the use of accelerating techniques. Two different accelerating methods were utilized: (1) use of surfactant and (2) pressure augmentation. SDS solutions were used as an accelerating agent. Two different pressures (2.3 and 3.0 MPa) were adopted to investigate the effectiveness of an increase in pressure for accelerating the in situ CO<sub>2</sub> hydrate formation. A series of laboratory experiments were performed for monitoring CO<sub>2</sub> gas storage capacity to validate the use of accelerating methods.

### MATERIALS AND METHODS

Coal used in this study was a sub-bituminous coal drilled from the no. 1 well of the Xiangxi mine in China at the depth of 525 ± 2 m. Such deep samples were used to investigate the potential for in situ CO<sub>2</sub> storage. The coal includes carbon content of approximately 75% and moisture content of 40%. Specifically, it consists of 75% carbon, 6% hydrogen, 15% oxygen, 2.8% nitrogen, and 1.2% sulfur. The CO<sub>2</sub> gas permeability of dry coal samples was  $3.95 \times 10^{-14}$  m<sup>2</sup> (~40 mD), and the porosity was 60–80%. The pore size distribution and specific surface area measured from the mercury intrusion porosimetry and low temperature nitrogen adsorption tests are shown in Table 1. The average pore throat diameter was 3.06 μm. The high pore volume and specific surface area together

Received: August 11, 2013

Revised: December 5, 2013

Accepted: December 5, 2013

Published: December 5, 2013

**Table 1.** Pore Size Distribution and Specific Surface Area of Coal Used in This Study

volume of pores ( $10^{-4}$ cm $^3$ /g) <sup>a</sup>						
VM <sub>1</sub>	VM <sub>2</sub>	VM <sub>3</sub>	VM <sub>4</sub>	VN <sub>4</sub>	VN <sub>5</sub>	VN <sub>6</sub>
96.80	22.91	117.75	51.31	0.49	1.47	0.15
specific surface area (m $^2$ /g) <sup>a</sup>						
SM <sub>1</sub>	SM <sub>2</sub>	SM <sub>3</sub>	SM <sub>4</sub>	SN <sub>4</sub>	SN <sub>5</sub>	SN <sub>6</sub>
0.05	0.34	43.95	28.00	1.50	0.32	0.03

<sup>a</sup>Measured values of eight coal samples were averaged. VM and SM denote results obtained from the mercury intrusion tests, and VN and SN denote results obtained from the low temperature nitrogen adsorption tests. Subscripts represent pore size in diameter: 1 for >1000 nm, 2 for 100–1000 nm, 3 for 10–100 nm, 4 for 5–10 nm (7.2–10 nm for M<sub>4</sub>), 5 for 2–5 nm, and 6 for <2 nm.<sup>30</sup>

with a high vitrinite reflectance coefficient ( $R_{0,\text{max}} \cong 0.62$ ) imply a great adsorption ability of the coal for CO<sub>2</sub> gas.<sup>29</sup>

A synthetic surfactant, SDS was used as an accelerating agent. It is a surface activation agent with the ability to prompt the dissolution of gas into water.<sup>23</sup> According to the stoichiometry,<sup>31</sup> a SDS solution of 300 mg/L was used. CO<sub>2</sub> gas used in this study was obtained from Yinglai Gases Co., Ltd. (Guangzhou, China). Its purity is greater than 99.99%. Distilled water made in the laboratory was used and its electrical conductivity was 0.98  $\mu\text{S}/\text{cm}$ .

The hydrates-forming reaction was processed in a self-designed instrument which includes a gas supply tank with a pressure regulator, a reaction vessel, a coolant bath, and an automated data acquisition system.<sup>24</sup> A dry coal sample of 8.0 g was soaked fully in the SDS solution or distilled water prior to testing. The weight of the SDS solution adsorbed by the coal sample was 0.49 g (0.0031 SDS wt %). The sample was placed into the reaction vessel sealed in the coolant bath in which the temperature was maintained at 273.15 K. All the air in the reaction vessel was extracted with a vacuum pump for about 2–3 h to ensure the absence of air. CO<sub>2</sub> gas as a supercritical fluid was then introduced into the reaction vessel until the pressure in the reaction vessel was reached target pressure. This injection process took a few minutes (up to less than 5 min). The variation of pressure and temperature in the reaction vessel was monitored with time. The volume of CO<sub>2</sub> gas consumed for the hydrates formation was also recorded to calculate the CO<sub>2</sub> gas storage capacity. Tests under two different pressure conditions (2.3 and 3 MPa) were performed on the SDS-saturated coal samples. Those target pressures were selected according to the results of previous research that the hydrate growth rate reaches a maximum at approximately 3 MPa.<sup>11,32</sup> No mechanical agitation was applied.

Hydrate formation can be identified in the temperature variation curve during the reaction.<sup>33,34</sup> Because the hydrates-

forming reaction is exothermic, an increase in temperature as well as a distinct drop in pressure indicates a progress of the reaction. The pressure difference between the beginning and the end of test was used to calculate the total volume of gas consumed for the hydrate formation in the reaction vessel. The calculation was made by the modified gas law as<sup>35,36</sup>

$$n = \frac{PV}{zRT} \quad (1)$$

where  $n$  is the moles of gas consumed,  $P$  is the pressure,  $T$  is the temperature,  $R$  is the universal gas constant,  $V$  is the volume of CO<sub>2</sub> gas in the vessel, and  $z$  is the compressibility factor.

## RESULTS AND DISCUSSION

**Enhanced Rate of CO<sub>2</sub> Hydrate Formation.** Real-time pressure and temperature data during the CO<sub>2</sub> hydrate formation were plotted in Figure 1. The laboratory experiment results indicate that CO<sub>2</sub> hydrates were successfully formed in the coal samples saturated with the SDS solution under both 2.3 and 3 MPa pressures. The hydrates-forming reaction entered the equilibrium stage after approximately 500 min under 2.3 MPa and after approximately 650 min under 3 MPa. In the absence of SDS, little CO<sub>2</sub> hydrate was observed over the tested time period (~800 min). The hydrates-forming reaction in coal can be classified into four stages, including the stage of induction, the stage of intense reaction, the stage of stable reaction, and the stage of equilibrium.<sup>34</sup>

In Figure 2, the reaction from the beginning to point A can be defined as the stage of induction. In this induction stage, hydrate does not form as temperature decreases to the target temperature (273.15 K). After the point A, a sharp drop in pressure was observed, while the rate of decreasing temperature became slow. Those changes imply intense hydrate formation from the viewpoint of gas consumption and the exothermic nature of the hydrates-forming reaction. The rate of hydrates-forming reaction was controlled by pressure as the induction stage ended earlier at a higher pressure (~55 min at 2.3 MPa versus ~40 min at 3 MPa). In the stable reaction stage between point B and point C, both temperature and pressure decrease slowly until they reach a steady state at point C where the equilibrium stage begins.

The rate of hydrates-forming reaction was calculated as<sup>37</sup>

$$\frac{\text{mol/mol}}{\text{min}} = \frac{\Delta n_{\text{H}_2\downarrow}/n_{\text{H}_2\text{O}}}{t} \quad (2)$$

where  $\Delta n_{\text{H}_2\downarrow}$  indicates the moles of gas consumed for hydrate formation throughout the whole experiment and  $n_{\text{H}_2\text{O}}$  denotes the moles of water in the system. The calculated rates of the reaction in the presence of SDS were 96.70 cm $^3$ /min at 2.3 MPa and 143.70 cm $^3$ /min at 3 MPa. These values are much greater than the previously reported values for other medium

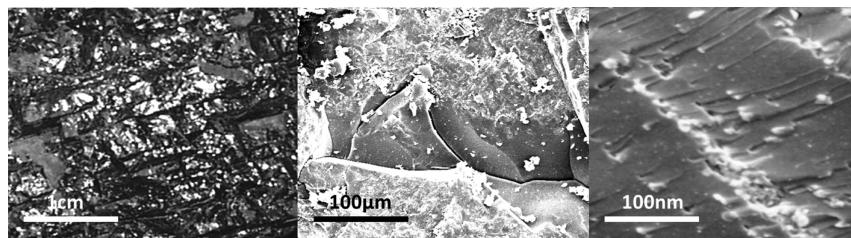


Figure 1. Porous structure of coal (from left to right, macro-crack, microcrack, and pores).

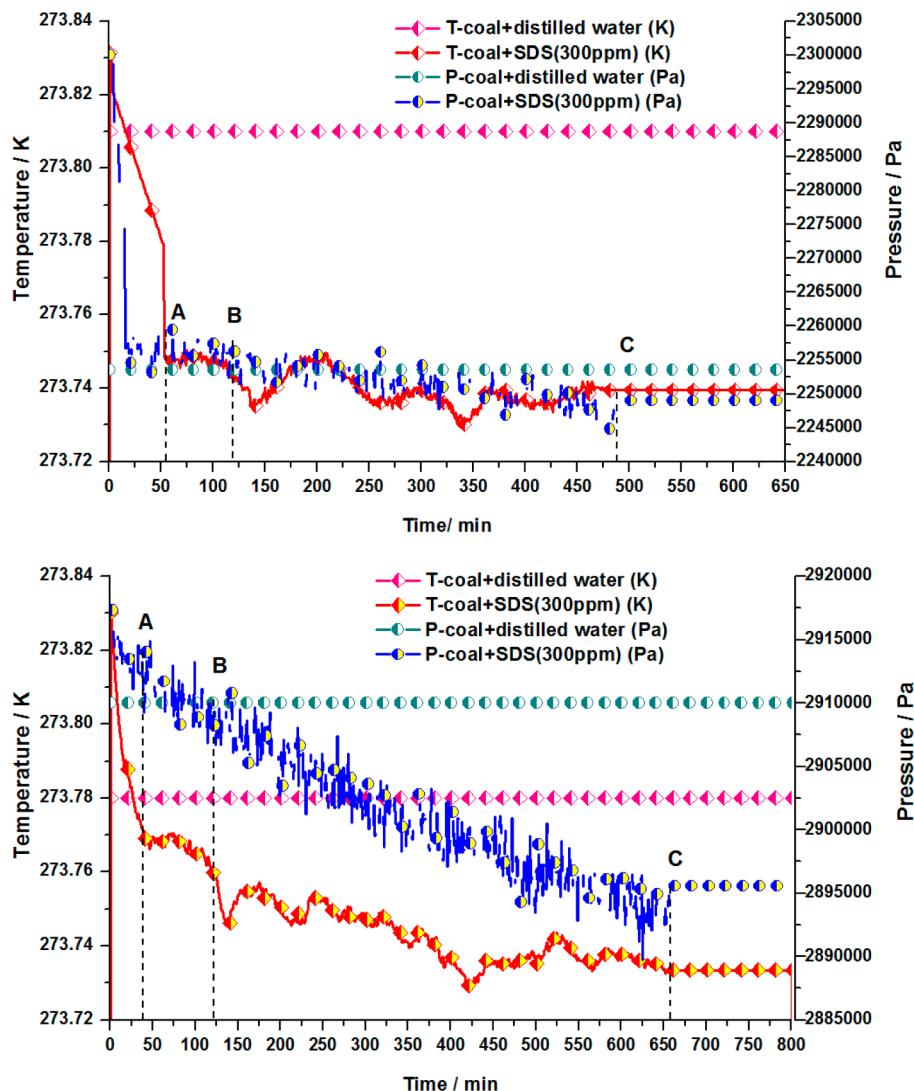


Figure 2. The variation of temperature and pressure during the hydrates-forming reaction.

materials ( $22\text{--}56\text{ cm}^3/\text{min}$ ),<sup>14–16</sup> and indicate that the addition of SDS significantly increased the rate of hydrates-forming reaction in the coal. Over the tested time period ( $\sim 800\text{ min}$ ), little hydrate formation was observed for coal samples saturated with distilled water, while a considerable amount of hydrates formed over the same time period under both 2.3 and 3 MPa. This result is in agreement with the SDS-induced enhanced rate of hydrates-forming reaction that is approximately 700 times faster than without SDS.<sup>31</sup> Although the surfactant significantly increased the reaction rate in coal, direct comparison of the rate of the reaction with SDS to that without SDS cannot be made due to unmeasurably small amount of the hydrate formation in the absence of SDS.

Pressure was an important factor controlling the rate of the reaction in the presence of SDS. The rate increased with increasing pressure ( $96.70\text{ cm}^3/\text{min}$  at 2.3 MPa versus  $143.70\text{ cm}^3/\text{min}$  at 3 MPa). This result is in good agreement with previous research in which the final gas storage capacity increased with increasing pressure.<sup>38</sup> Because the equilibrium stage was reached after  $\sim 500\text{ min}$  at 2.3 MPa and after  $\sim 650\text{ min}$  at 3 MPa, the result also implies that a larger amount of  $\text{CO}_2$  hydrates formed at 3 MPa due to the reaction over a longer time period at a higher reaction rate.

**Enhanced  $\text{CO}_2$  Gas Storage Capacity.** The volume of  $\text{CO}_2$  gas stored in a unit volume of hydrate at standard conditions is equivalent to the amount of gas consumed. The gas consumption,  $C$  can be calculated as<sup>24,33</sup>

$$C = \frac{V_{t,\text{gas}}^{\text{h}}}{V_t^{\text{h}}} \quad (3)$$

where  $V_{t,\text{gas}}^{\text{h}}$  represents the volume increment of gas in the hydrate phase over the period of time  $t$  and  $V_t^{\text{h}}$  represents the volume increment of hydrates formed. The calculated gas storage capacity was converted into standard temperature ( $0^\circ\text{C}$ ) and pressure (100 kPa) (STP) volume as

$$V_{t,\text{gas}}^{\text{h}} = 22400n_{t,\text{gas}}^{\text{h}} \quad (4)$$

where  $n_{t,\text{gas}}^{\text{h}}$  represents the volume increment of gas in the hydrate phase over the period of time  $t$ . Note that the adsorption affinity for  $\text{CO}_2$  gas onto coal surfaces is even greater than many other gas molecules. For example, the adsorbed volume of  $\text{CO}_2$  was approximately three or six times greater than that of  $\text{CH}_4$  or  $\text{N}_2$ , respectively.<sup>39,40</sup> Hence, the majority of pre-existing gases in the coal may be replaced by  $\text{CO}_2$  at the equilibrium stage.

The calculated gas storage capacity is plotted in Figure 3. The maximum volume of  $\text{CO}_2$  gas stored in unit volume of coal

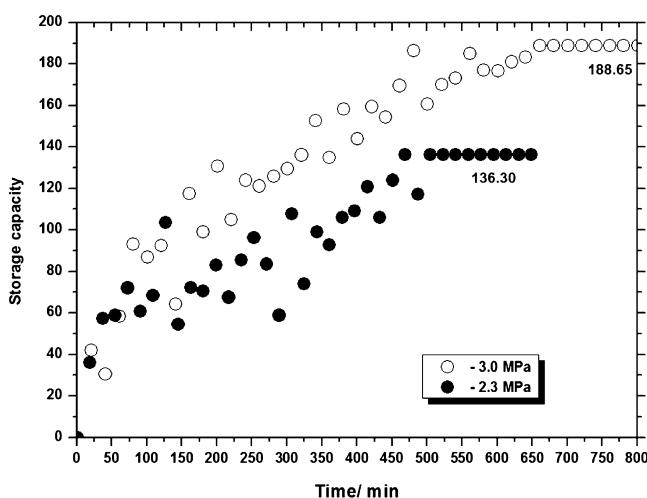


Figure 3.  $\text{CO}_2$  gas storage capacity of coal in the presence of SDS.

( $\text{CO}_2$  gas volume at STP/unit volume of coal) was 136.30 at 2.3 MPa and 188.65 at 3 MPa. The addition of the surfactant resulted in such high gas storage capacity for a relatively short time period. In addition, 50% of the maximum gas storage capacity was reached within 2 h under both pressure conditions. Note that the storage capacity was calculated on the basis of the amount of hydrates formed, therefore the fluctuation in storage capacity may be attributed to simultaneous formation and dissolution of hydrates prior to the equilibrium stage.<sup>41–43</sup>

Because hydrate formation was not observed in the absence of the surfactant, the gas storage capacity of coal with or without SDS cannot be compared in this study. Further testing is required to identify the effects of SDS on final gas storage capacity.

The high storage capacity of coal achieved in this study may be attributed to (1) the nature of coal surface and pores, (2) the use of surfactant, and (3) pressure-driven enhancement of

the hydrates-forming reaction rate. First of all, the surface of coal has been reported to have strong multipoint adsorption ability for gas molecules.<sup>20,37</sup> Such great affinity may provide the driving forces for  $\text{CO}_2$  gas molecules to enter the pores of coal and promote the hydrate formation when they are subjected to a hydrates-forming condition. As shown in Figure 1 and Table 1, the large quantity of natural pores may maximize the  $\text{CO}_2$  storage capacity of the coal. Figure 4 shows  $\text{CO}_2$  hydrates formed along the pore surface of coal. Second, the surfactant molecules improved the rate of hydrates-forming reaction.<sup>23,31</sup> It does not change the thermodynamics of the reaction, but accelerates the dissolution of carbon dioxide into water leading to the enhanced rate of the reaction. SDS is an amphiphilic molecule containing both hydrophilic and lipophilic groups. The hydrophilic group may first be adsorbed onto the structural water on the surface of coal via hydrogen bonding. The free lipophilic groups of the SDS molecule then entrap  $\text{CO}_2$  gas molecules and act as nuclei for  $\text{CO}_2$  hydrate formation. Also, it is expected that  $\text{CO}_2$  hydrates formed in coal saturated with SDS could be more stable from a viewpoint of dissociation ability. Because hydrogen bonding is dominant in the coal saturated with SDS,  $\text{CO}_2$  hydrates formed in the coal may not be easily dissociated as compared to SDS-absent coal in which the hydrates are likely bonded to the surface of coal via relatively weaker van der Waals forces.<sup>44</sup> Finally, pressure determines the final gas storage capacity because more gas molecules enter into the pores of the coal structure under a higher pressure.<sup>38</sup> The results of this study clearly exhibit that a larger amount of  $\text{CO}_2$  hydrates formed at a higher pressure.

## CONCLUSION

A series of laboratory experiments was performed to investigate carbon dioxide hydrate formation in coal. In-situ hydrates-forming technology was applied under two different pressure conditions (2.3 and 3 MPa) with the addition of surfactant, sodium dodecyl sulfate (SDS). The results support that the high carbon dioxide ( $\text{CO}_2$ ) gas storage capacity of coal was reached through in situ hydrates-forming technology within a relatively short period of time. It proves that coal can be a

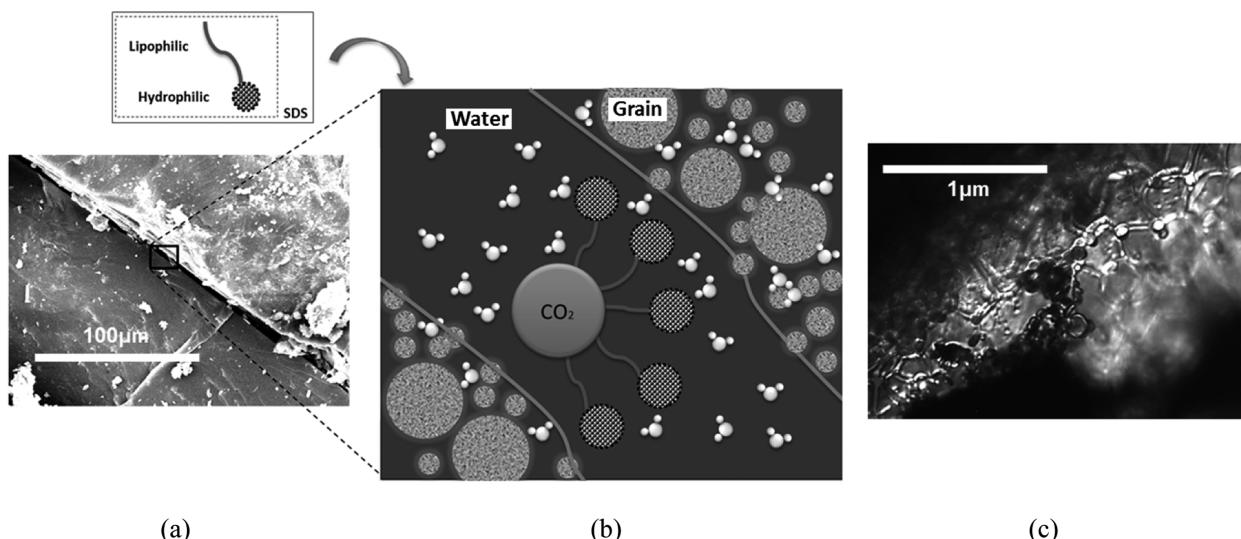


Figure 4.  $\text{CO}_2$  hydrate formation: (a) scanning electron microscopy image, (b) schematic of SDS-bridged interaction of  $\text{CO}_2$  within the coal pore, and (c)  $\text{CO}_2$  hydrates formed along the surface of a coal pore.

beneficial medium material for storing CO<sub>2</sub> gas when the accelerating methods are deliberately chosen and utilized.

The use of SDS significantly increased the rate of hydrates-forming reaction in coal. The calculated rates of the reaction in the presence of SDS were 96.70 cm<sup>3</sup>/min at 2.3 MPa and 143.70 cm<sup>3</sup>/min at 3 MPa, whereas little hydrates formed in the absence of SDS over the tested time period (~800 min). Pressure also played an important role in accelerating the final gas storage capacity of coal. Under a pressure of 3 MPa, the maximum gas storage capacity of coal was 188.65 volume of CO<sub>2</sub> gas at STP conditions per unit volume of coal. In addition, 50% of the maximum gas storage capacity was attained within 2 h in the presence of SDS.

## AUTHOR INFORMATION

### Corresponding Author

\* (S.-Q.H.) E-mail: haoshuqing@cumt.edu.cn. Tel: +61-470426585. (S.K.) E-mail: edward.kim@monash.edu.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This study was supported by National Natural Science Foundation of China (51104145, 40730422), China Postdoctoral Science Foundation (2011M501282, 2012T50500), the Fundamental Research Funds for the Central Universities (2012QNA64, 2013XK06), Jiangsu Province Postdoctoral Science Foundation (1102087C), 2011 ministry of Housing and Urban-Rural Construction Scientific Technology Scheme Project (2011-K5-18), State Key Laboratory for GeoMechanics and Deep Underground Engineering open foundation (SKLGDUEK0911), National Program on Key Basic Research Project (973 Program: 2009CB219605), Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and the China Scientific Council Overseas Studying Supporting Foundation (2011832443).

## REFERENCES

- (1) Lashof, D. A.; Ahuja, D. R. Relative contributions of greenhouse gas emissions to global warming. *Nature* **1999**, *344*, 529–531.
- (2) Thomas, R. K.; Kevin, E. T. Modern global climate change. *Science* **2008**, *302* (5651), 1719–1723.
- (3) Goldberg, D. S.; Kent, D. V.; Olsen, P. E. Potential on-shore and off-shore reservoirs for CO<sub>2</sub> sequestration in Central Atlantic magmatic province basalts. *Proc. Natl. Acad. Sci.* **2000**, *107* (4), 1327–1332.
- (4) Seibel, B. A.; Walsh, P. J. Potential impacts of CO<sub>2</sub> injection on deep-sea biota. *Science* **2001**, *294* (5541), 319–320.
- (5) Schrag, D. P. Storage of carbon dioxide in offshore sediments. *Science* **2009**, *325* (5948), 1658–1659.
- (6) Brewer, P.; Peltzer, E.; Friderich, G.; Yamane, K.; Aya, I. Experiment on the ocean sequestration of fossil fuel CO<sub>2</sub>—pH measurement and hydrate formation. *Mar. Chem.* **2000**, *72*, 83–93.
- (7) Tajima, H.; Yamasaki, A.; Kiyono, F. Energy consumption estimation for greenhouse gas separation processes by clathrate hydrate formation. *Energy* **2004**, *29*, 1713–29.
- (8) Duc, N. H.; Chauvy, F.; Herri, J. M. CO<sub>2</sub> capture by hydrate crystallization—a potential solution for gas emission of steel making industry. *Energy Convers. Manage.* **2007**, *4*, 1313–22.
- (9) House, K. Z.; Charles, D. P. S.; Harvey, F.; Lackner, K. S. Permanent carbon dioxide storage in deep-sea sediments. *Proc. Natl. Acad. Sci.* **2006**, *103* (33), 12291–12295.
- (10) Park, J.; Seo, Y. T.; Lee, J. W.; Lee, H. Spectroscopic analysis of carbon dioxide and nitrogen mixed gas hydrates in silica gel for CO<sub>2</sub> separation. *Catal. Today* **2006**, *115* (1–4), 279–282.
- (11) Zhang, J.; Lee, J. W. Enhanced kinetics of CO<sub>2</sub> hydrate formation under static conditions. *Ind. Eng. Chem. Res.* **2009**, *48*, 5934–5942.
- (12) Liu, Y.; Wilcox, J. Effects of surface heterogeneity on the adsorption of CO<sub>2</sub> in microporous carbons. *Environ. Sci. Technol.* **2012**, *46* (3), 1940–1947.
- (13) Barry, J. P.; Buck, K. R.; Lovera, C. F.; Kuhn, L.; Whaling, P. J.; Peltzer, E. T.; Walz, P.; Brewer, P. G. Effects of direct ocean CO<sub>2</sub> injection on deep-sea meiofauna. *J. Oceanogr.* **2004**, *60*, 759–766.
- (14) Linga, P.; Kumar, R.; Englezos, P. Gas hydrate formation from hydrogen/carbon dioxide and nitrogen/carbon dioxide gas mixtures. *Chem. Eng. Sci.* **2007**, *62*, 4268–4276.
- (15) Lee, H. J.; Lee, J. D.; Linga, P.; Englezos, P.; Kim, Y. S.; Lee, M. S.; Kim, Y. D. Gas hydrate formation process for pre-combustion capture of carbon dioxide. *Energy* **2010**, *35*, 2729–2733.
- (16) Lamorena, R. B.; Kyung, D.; Lee, W. Effect of organic matters on CO<sub>2</sub> hydrate formation in Ulleung basin sediment suspensions. *Environ. Sci. Technol.* **2011**, *45*, 6196–6203.
- (17) Romanov, V. N.; Yeonsoong, T. A.; Kleinman, R. CO<sub>2</sub> storage in shallow underground and surface coal mines: challenges and opportunities. *Environ. Sci. Technol.* **2009**, *43* (3), 561–564.
- (18) Zhang, D. F.; Cui, Y. J.; Liu, B.; Li, S. G.; Song, W. L.; Lin, W. G. Supercritical pure methane and CO<sub>2</sub> adsorption on various rank coals of China: experiments and modeling. *Energy Fuel.* **2011**, *25* (4), 1891–1899.
- (19) Silva, P. N. K. D.; Ranjith, P. G. Advanced core flooding apparatus to estimate permeability and storage dynamics of CO<sub>2</sub> in large coal specimens. *Fuel* **2013**, *104*, 417–425.
- (20) Krooss, B. M.; Busch, A.; and Gensterblum, Y. High-pressure adsorption of methane, carbon dioxide and their mixtures on coals. International Workshop Present Status and Perspective of CO<sub>2</sub> Sequestration in Coal Seam; Japan Forum on CO<sub>2</sub> Sequestration in Coal Seam. Japan, 2002; pp 23–38.
- (21) Bae, J. S.; Bhatia, S. K. High-pressure adsorption of methane and carbon dioxide on coal. *Energy Fuel.* **2006**, *20* (6), 2599–2607.
- (22) Ottiger, S.; Pini, R.; Storti, G.; Mazzotti, M. Measuring and modeling the competitive adsorption of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> on a dry coal. *Langmuir* **2008**, *24* (17), 9531–9540.
- (23) Kalogerakis, N.; Jamaluddin, A. K. M.; Dholabhai, P. D.; and Bishnoi, P. R. Effect of surfactants on hydrate formation kinetics. SPE International Symposium on Oilfield Chemistry; New Orleans, LA, USA; 1993.
- (24) Yang, L.; Fan, S.; Wang, Y.; Lang, X.; Xie, D. Accelerated formation of methane hydrate in aluminum foam. *Ind. Eng. Chem. Res.* **2011**, *50* (20), 11563–11569.
- (25) Alberti, M.; Pirani, F.; Lagana, A. Carbon dioxide clathrate hydrates: Selective role of intermolecular interactions and action of the SDS catalyst. *J. Phys. Chem. A* **2013**, DOI: 10.1021/jp3126158.
- (26) Gunter, W. D.; Gentzis, T.; Rottenfusser, B. A.; Richardson, R. J. H. Deep coalbed methane in Alberta, Canada: A fuel resource with the potential of zero greenhouse gas emissions. *Energy Convers. Manage.* **1997**, *38*, S217–S222.
- (27) Wildenborg, T.; Lokhorst, A. Introduction on CO<sub>2</sub> geological storage—Classification of storage options. *Oil Gas Sci Technol., Rev. IFP.* **2005**, *60* (3), 513–515.
- (28) Warwick, P. D.; Zhu, Z. New insights into the nation's carbon storage potential. *EOS, Trans. Am. Geophys. Union* **2012**, *93* (26), 241–242.
- (29) Mastalerz, M.; Gluskoterb, H.; Ruppa, J. Carbon dioxide and methane sorption in high volatile bituminous coals from Indiana, USA. *Int. J. Coal Geol.* **2004**, *60* (1), 43–55.
- (30) Hodot, B. B. *Outburst of Coal and Coalbed Gas*; China Industry Press: Beijing, 1966; p 318 (Chinese Translation).
- (31) Zhong, Y.; Rogers, R. E. Surfactant effects on gas hydrate formation. *Chem. Eng. Sci.* **2000**, *55* (19), 4175–4187.
- (32) Chen, G. J.; Sun, C. Y.; and Ma, Q. L. *The Science and Technology of Gas Hydrates*; Huaxue Industrial: Beijing, 2008; pp 300–360.

- (33) Kumar, A.; Sakpa, T.; Linga, P.; Kumar, R. Influence of contact medium and surfactants on carbon dioxide clathrate hydrate kinetics. *Fuel* **2013**, *105*, 664–671.
- (34) Su, K.; Sun, C.; Yang, X.; Chen, G.; Fan, S. Experimental investigation of methane hydrate decomposition by depressurizing in porous media with 3-dimension device. *J. Nat. Gas Chem.* **2010**, *19* (3), 210–216.
- (35) Perry, R. H.; Green, D. W.; Maloney, J. O. *Perry's Chemical Engineering Handbook*; McGraw-Hill: NY, 1984.
- (36) Smith, J. M.; van Ness, H. C.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*; McGraw-Hill: NY, 2001.
- (37) Linga, P.; Kumar, R.; Lee, J. D.; Ripmeester, J.; Englezos, P. A new apparatus to enhance the rate of gas hydrate formation: Application to capture of carbon dioxide. *Int. J. Greenhouse Gas Control* **2010**, *4* (4), 630–637.
- (38) Cui, Y.; Li, Y.; Zhang, Q.; Jiang, W. The characteristic curve of methane adsorbed on coal and its role in the coalbed methane storage research. *Chin. Sci. Bull.* **2005**, *50*, 86–92.
- (39) Ohga, K. Fundamental test of CO<sub>2</sub> sequestration in coal seams and CH<sub>4</sub> displacement. International Workshop, Present Status and Perspective of CO<sub>2</sub> Sequestration in Coal Seam: Japan Forum on CO<sub>2</sub> Sequestration in Coal Seam; 2002; pp 1–9.
- (40) Chen, G. J.; Guo, T. M. A new approach to gas hydrate modelling. *Chem. Eng. J.* **1998**, *71* (2), 145–151.
- (41) Kamath, V. A.; Holder, G. D. Dissociation heat transfer characteristics of methane hydrates. *AIChE J.* **1987**, *33* (2), 347–350.
- (42) Sugaya, M.; Mori, Y. Behavior of clathrate hydrate formation at the boundary of liquid water and a fluorocarbon in liquid or vapor state. *Chem. Eng. Sci.* **1996**, *51* (13), 3505–3517.
- (43) Kneafsey, T. J.; Tomutsa, L.; Moridis, G. J.; Seol, Y.; Freifeld, B.; Taylor, C. E.; Gupta, A. Methane hydrate formation and dissociation in a partially saturated core-scale sand sample. *J. Petrol. Sci. Eng.* **2007**, *56*, 108–126.
- (44) Alexeev, A. D.; Feldman, E. P.; Vasilenko, T. A. Methane desorption from a coal-bed. *Fuel* **2007**, *86* (16), 2574–2580.