GHGT-11

Mineral dissolution/precipitation during CO_2 injection into coal reservoir: A laboratory study

Ferian Anggara[a,b*], Kyuro Sasaki[a], and Yuichi Sugai[a]

[a]Department of Earth Resources Engineering, Kyushu University, 744, Motooka, Nishiku, Fukuoka 819-0395, Japan
[b]Department of Geological Engineering, Universitas Gadjah Mada, Jl. Grafika No.2, Yogyakarta 55281, Indonesia

Abstract

CO_2 Supercritical Fluid Extraction (SFE) has been performed on Kushiro coal. The results showed there were slightly changes in major metal oxide due to mineral dissolution/precipitation during CO_2 injection. To predict mineral dissolution/precipitation in the field scale and for long geologic period of time, numerical simulations using GMG-GEM simulator were carried out. The numerical simulation was only focused on the calcite that showed to dissolve in the near injection well area (higher pressure) as well as to precipitate at some distance from the injection well when injection of CO_2 was stopped.

Keywords: coal; CO_2-SFE, calcite dissolution/precipitation; numerical simulation.

1. Introduction

Geological storage is become one of the best options to reduce CO_2 emission in the atmosphere. One of the options discussed among many researchers is CO_2 injection on to coal seam as one of the best site for geological CO_2 storage. This option is considered as safe and effective method for permanently storing CO_2 with added value of enhancing coal bed methane production (CO_2-ECBMR).

When CO_2 is injected into reservoir, three interdependent conceptually distinct processes govern which are: CO_2 migration as a buoyant immiscible fluid phase, direct chemical interaction of this rising plume with ambient saline waters, and its indirect chemical interaction with aquifer and cap-rock minerals through the aqueous wetting phase. Each process is directly linked to a corresponding trapping

---

* Corresponding author. Tel.: +8192 802 3329; fax: +8192 802 3329.
E-mail address: ferian@mine.kyushu-u.ac.jp

mechanism: immiscible plume migration to hydrodynamic trapping, plume-water interaction to solubility trapping, and plume-mineral interaction to mineral trapping [1].

In case of CO_2-ECBMR, geochemical reactions between dissolved CO_2 and coal reservoir can lead to porosity and permeability changes. During injection of CO_2, there are hydrocarbon leaching [2] as well as mobilizing mineral matter [3]. Furthermore, neither calcite dissolution nor subsequent precipitations are likely to occur with CO_2 injection [4]. Calcite precipitation (mineral trapping) is very desirable as CO_2 is immobile and sequestered in a form that is harmless to the environments. But, calcite precipitation also gives negative effect on coal permeability. In contrast, calcite dissolution may compensate permeability reduction due to coal swelling induced by CO_2 adsorption. Hence, our research objectives are to determine mineral dissolution/precipitation in the supercritical condition and to simulate calcite dissolution/precipitation in the coal reservoir.

2. Samples and Methods

2.1. Samples

The samples used in the experiments were obtained from Kushiro underground coal mining. Actually, Japanese coal is characterized by high volatile matter and hydrogen content than Euramerican late Paleozoic coal beds of comparable rank [5]. Our samples also showed high volatile matter (38.6%) with 5.4 % moisture and 26.7 % ash content. As a reference for coal properties examination before and after exposure to supercritical CO_2 (SCCO$_2$), SARM-19 was used. Detail of coal properties used in this study was presented in Table 1.

Table 1. Physical properties of coal samples.

Component	Petrographic analysis					Proximate analysis (wt.%, adb)				Ultimate analysis (wt.%, adb)		
Sample	V	L	I	MM	R_0	A	M	VM	FC	C	H	N
KS01	75	7	1	17	0.48	26.7	5.4	38.6	29.3	53.99	4.92	0.94

* V: vitrinite (%); L: liptinite(%); I: inertinite(%); MM: mineral matter(%); R_0: vitrinite reflectance
  A: ash; M: moisture; VM: volatile matter; FC: fixed carbon; C: carbon; H: hydrogen; N: nitrogen

2.2. CO$_2$ Supercritical Fluid Extraction (SFE)

Powdered coal sample (<60 mesh and 60-250 mesh) were tested in supercritical CO_2 extraction with 15 MPa pressure and variation in exposure time and temperature. The ISCO SFX 220 supercritical fluid extraction (SFE) system was used to conduct geochemical experiments. The SCCO$_2$ extraction were conducted at 15 MPa and 50 °C, roughly corresponding to a depth of 1 km. Solvent trap containing chilled (9 °C) hexane or water is used in the solvent trap to precipitate any hydrocarbon that may extracted. The SFE program consisted of a 15-minute static (no-flow) step followed by 60-minute or 180-minute dynamic (flow) step. Schematic diagram of SFE experiments is shown in Figure 1.

Coal properties were measured before and after exposure to SCCO$_2$ using XRF for major metal oxide as well as ultimate analysis. Characteristics of leachates from geochemical reaction were analyzed using gas chromatography analysis.
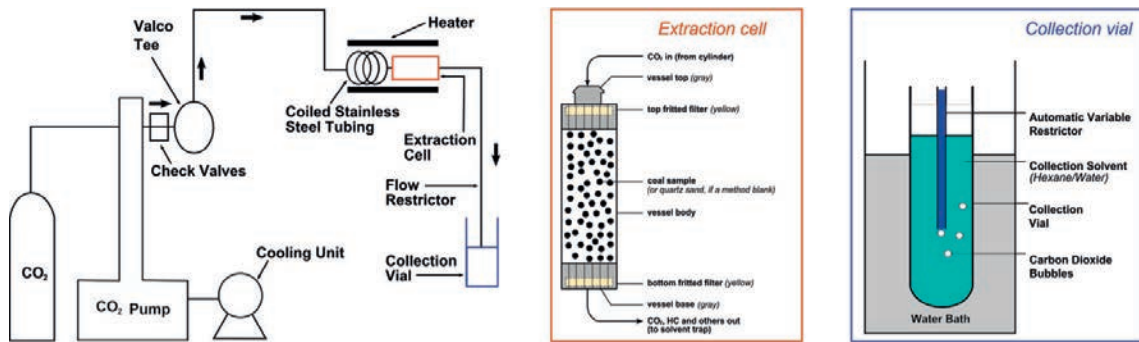
Fig. 1. Schematic diagram of CO_2 SFE apparatus.

2.3. Numerical Simulation

Based on [4], in the higher pressures encountered near the injection well may cause calcite, if it is present in the reservoir rock, to dissolve. If calcite does dissolve into the water, a second reaction may occur elsewhere in the reservoir. As water flow towards a production well, the pressure will be less than one near the injection well, and any dissolved calcite may then precipitate if the right conditions exist.

During CO_2 injection, CO_2 dissolves in aqueous phase, which is represented by Equation 1.

$$CO_2 (g) <=> CO_2 (aq) \qquad (1)$$

where CO_2 (g) and CO_2 (aq) denote the CO_2 in the gas phase and the aqueous phase, respectively.

Near the injection well where higher-pressure encounter, CO_2 dissolves in the formation water to form carbonic acid (H_2CO_3) and tend to dissociate into hydrogen ion and bicarbonate.

$$CO_2 + H_2O <=> H^+ + HCO_3^- \qquad (2)$$

$$H^+ + CaCO_3 <=> Ca^{2+} + 2 HCO_3^- \qquad (3)$$

When the CO_2 pressure drop in the some distance from the injection well, the presence of substantial amount of calcium or bicarbonate water (Eq. 4) may cause calcite to precipitate.

$$CO_2 + H_2O + Ca^{2+} <=> CaCO_3 + 2H^+ \qquad (4)$$
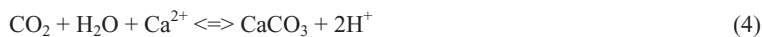
To address this phenomenon for long geologic period of time, we used CMG GEM-GHG for modeling of simultaneous geochemical sequestration. The simulator is applied to simulate the migration of CO_2 (g) and CO_2 (aq), the dissociation of CO_2 (aq) into HCO_3^- and its subsequent conversion into carbonate mineral [6].

A three dimensional model of homogenous aquifer with properties shown in Table 2 was used to simulate CO_2 behavior when CO_2 is injected to coal reservoir for long geologic time period. The reaction (1), (2), (3), and (4) were used and the properties was based on [6] and CO_2SFE experimental results.

In case of CO_2-ECBM, injection of CO_2 should be terminated when CO_2 proportion in the production well more than 20 %. Anggara et al. [7] showed that after 25 years, CO_2 is included in the production gas

more than 20%. Based on this data, CO_2 injection was conducted for 25 years in the grid block (2,2,1) and simulation was continued for 750 years.

Table 2. Aquifer properties for simulation

Cartesian grid	30 X 30 X 10
Grid size	
x-direction	27
y-direction	27
z-direction	1
Depth to top of aquifer (m)	900
Porosity (fraction)	0.3
Permeability (md)	2
Initial pressure (kPa)	8100
Temperature (°C)	50

3. Results and discussions

3.1 Ultimate and XRF analysis

The selected pressure-temperature conditions were selected to simulate CO_2 sequestration scenarios in coal reservoirs at depth of 1 km. Coal properties were measured before and after exposure to $SCCO_2$ using ultimate analysis as well as XRF for major metal oxide.

Ultimate analysis was performed on coal samples before and after experiments in order to study any changes in the principal chemical element in the coal samples. Table 3 lists the ultimate analysis results where slightly decrease in the Carbon (C) was found. CO_2SFE may make mobilize low molecular weight alkanes and polycyclic aromatic hydrocarbon (PAH) in the coal bitumen [2].

Table 3. Ultimate analysis of pre and post-treated coal samples with $SCCO_2$

Sample	Ultimate analysis (%, daf*)								
	C			H			N		
	Pre	Post		Pre	Post		Pre	Post	
		1 h	3 h		1 h	3 h		1 h	3h
KS-1(<60 mesh)	53.99	53.32	52.70	4.92	4.89	4.75	0.94	0.95	0.89
KS-1 (<60-250 mesh)	60.23	61.53	57.99	5.39	5.26	5.18	1.07	1.09	1.05
SARM-19	50.79	50.72	n.d	3.22	3.15	n.d	1.32	1.30	n.d

*daf = dry ash free basis. Pre and post are before and after induced by $SCCO_2$, respectively.

XRF analyses from bulk coal sample were conducted using 20 mm pellet. Changes in the major metal oxide from coal composition based on XRF analysis are listed in Table 4. The results indicate that mineral matter was slightly mobilized during CO_2-SFE experiments.

Due to the small amount of sample and exposure time, the changes of major metal oxide was to close to make meaningful comparison. Nevertheless, the mobilization of carbonate mineral (CaO and MgO) was observed.

Substantial hydrocarbon was assumed mobilized from the weight changes in our experiments. Changes in the total weight with geochemical reaction were well observed within average around less than 2 % for 1 hour treatment (Table 4).

Table 4. Changes in major metal oxide with geochemical reactions for 1 hour and 3 hours exposure to CO_2.

Samples Components	KS-1(<60 mesh)			KS-1 (<60-250 mesh)			SARM-19	
	Before	After		Before	After		Before	After
Major metal oxide (%)		1 h	3h		1 h	3h		(1 h)
SiO_2	13.34	13.83	13.94	11.62	13.18	15.56	14.41	14.85
Al_2O_3	6.60	6.91	6.86	5.92	6.65	7.93	7.59	8.05
Fe_2O_3	1.79	1.79	1.80	1.79	1.80	1.81	1.81	1.80
TiO_2	0.39	0.37	0.41	0.37	0.4	0.40	0.35	0.35
CaO	1.01	0.90	1.00	0.90	0.90	0.89	1.41	1.37
MgO	0.26	0.25	0.25	0.25	0.25	0.24	0.19	0.19
Na_2O	0.27	0.24	0.22	0.24	0.27	0.28	0.29	0.29
K_2O	0.34	0.39	0.35	0.29	0.34	0.37	0.24	0.24
Change in weight (%)	1 hour		3 hours	1 hour		3 hours	1 hour	
	1.79		3.28	1.68		2.75	1.45	

3.2 CO_2 distribution and calcite dissolution/precipitation

In case of drainage area by CBM production, there are actually 80, 160 and 320 acre schemes that depend on the geological condition and exploration scenario. In this study, numerical simulation was conducted on 160 acre area for 25 years of CO_2 injection and the simulation was carried out for 750 years to predict CO_2 behavior in the reservoir condition for long geologic period of time. Figure 2 showed distribution of CO_2 saturation for 1, 5 and 25 years after start of injection.
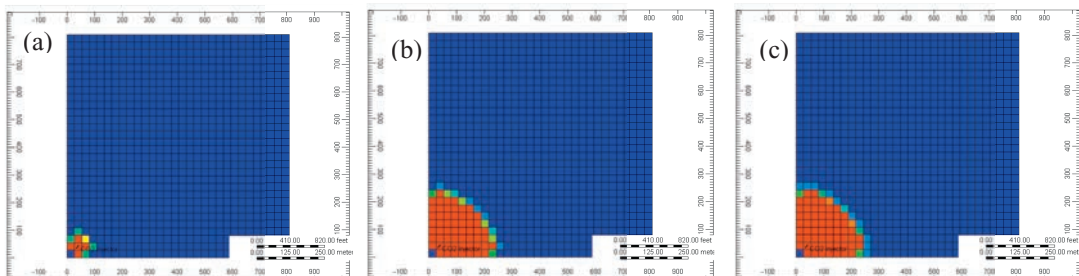

Figure 2. Distribution of CO_2 saturation for (a) 1, (b) 5, and (c) 25 years after start of injection

By convention, calcite dissolution and precipitation are represented by negative and positive values of mole numbers, respectively. The numeral simulation results showed the evolution of CO_2 dissolution in the reservoir that promote calcite dissolution in the near injection well. After injection of CO_2 was stopped and the pressure became less, any dissolved calcite was precipitated (Figure 3).

It should be noted that buffering reaction may happen when there is other dissolved component in the water [4]. The presence of substantial amounts of calcium or bicarbonate in the formation water (products in Eq. 4), as would occur if calcite had been dissolved near the injection well, may cause calcite to

precipitate from the water (the reverse of Eq. 3) when the CO_2 pressure drops at some distance from the injection well bore. Distribution of HCO_3^- saturation after injection of CO_2 is shown in Figure 4.
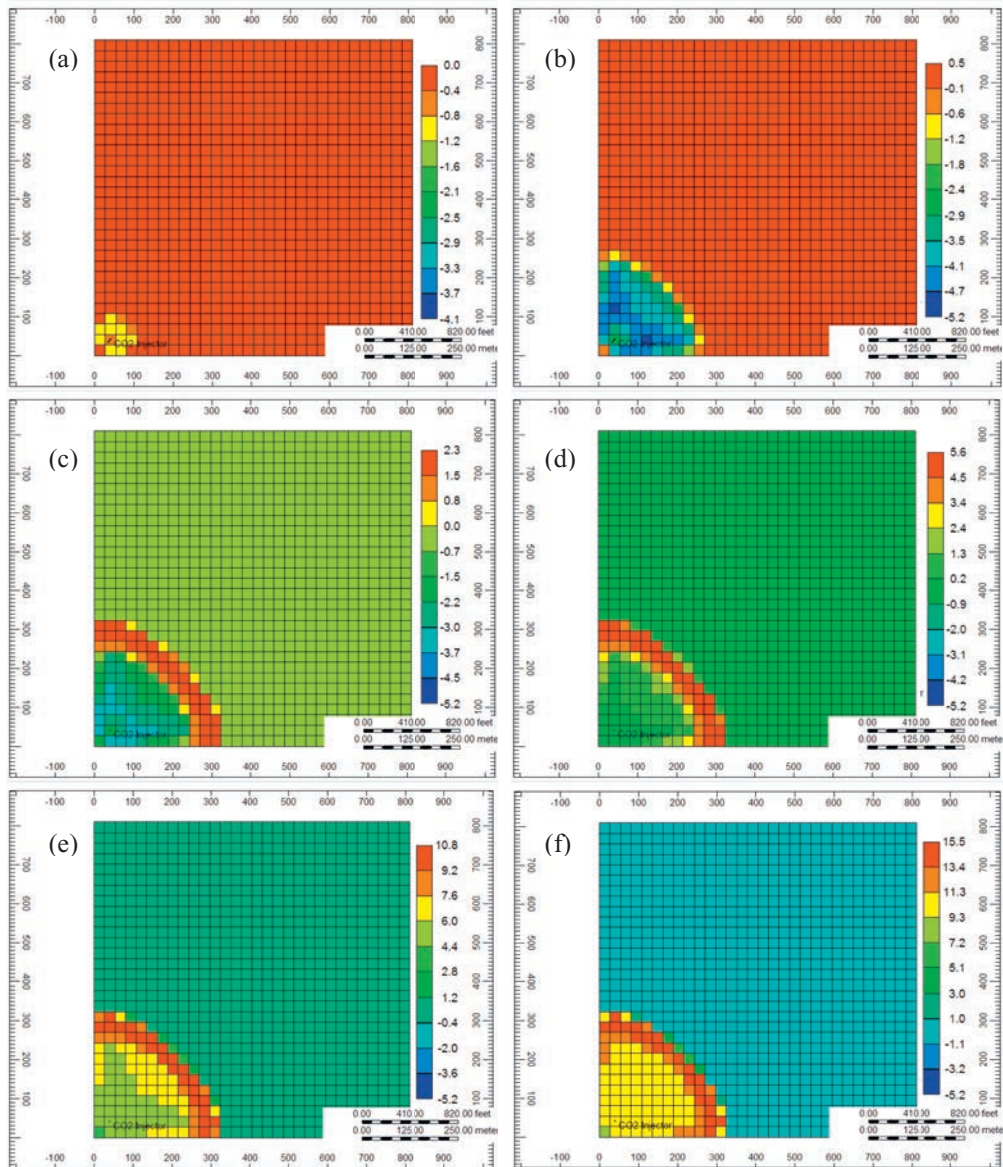

Figure 3. Calcite precipitation/dissolution due to CO_2 injection: (a) 1, (b) 25, (c) 100, (d) 250, (e) 500, and (f) 750 years.
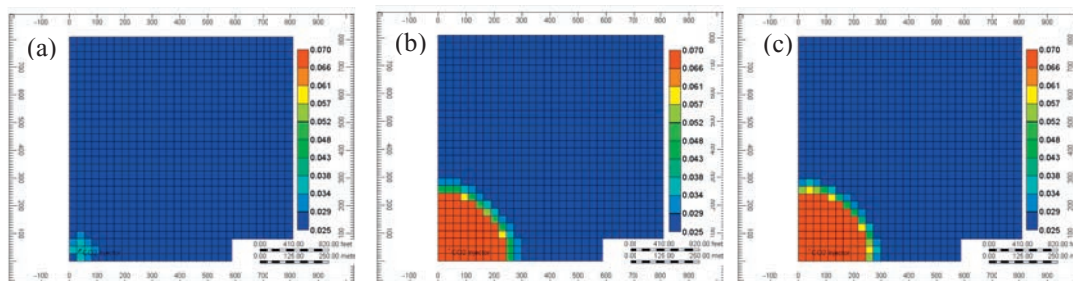
Figure 4. Distribution of HCO_3^- saturation after injection of CO_2: (a) 1, (b) 250, and, (c) 750 years.

In order to gain continuous benefit from the mixture of $SCCO_2$ and H_2O, Massaroto [3] suggested to use a system whereby water was allowed to flow with the CO_2 through the coal formation, at least in the near-well bore reservoir region. This should maximize the effect of mineral matter dissolution and thus increase both permeability and micro-porosity for extra adsorption.

4. Conclusions

In this study, it was observed that mineral matter in coal is dissolved and mobilized during CO_2SFE experiments. Moreover low molecular weight alkanes and PAH may also mobilize from the coal bitumen.

Based on the numerical simulation, calcite dissolution, not precipitation was found during injection of CO_2. It may compensate permeability reduction caused by coal swelling induced by CO_2 adsorption. After CO_2 injection was stopped and pressure dropped in some distance from injection well, calcite was precipitated. This phenomenon is very desirable for CO_2 sequestration since it is harmless to the environment.

Further research work is recommended to characterize the extractable material after CO_2SFE experiments and to simulate other minerals that may exist in the coal sample.

References

[1]   J. W. Johnson, J. J. Nitao, and K. G. Knauss, "Reactive transport modeling of CO2 storage in saline aquifers to elucidate fundamental processes, trapping mechanisms and sequestration partitioning," *Geological storage of carbon dioxide*, vol. 223, pp. 107–128, 2004.
[2]   J. J. Kolak and R. C. Burruss, *An organic geochemical assessment of CO2-coal interactions during sequestration*. US Department of the Interior, US Geological Survey, 2004.
[3]   P. Massarotto, S. D. Golding, J. S. Bae, R. Iyer, and V. Rudolph, "Changes in reservoir properties from injection of supercritical CO2 into coal seams–A laboratory study," *International Journal of Coal Geology*, vol. 82, no. 3–4, pp. 269–279, 2010.

[4]   L. K. Smith and S. R. Reeves, "Scoping Equilibrium Geochemical Modeling to Evaluate the Potential for Precipitate Formation when Sequestering CO2 in San Juan Basin Coals," *Topical Report, Contract No. DE-FC26-00NT40924, US DOE, Washington, DC (October 2002)*, 2002.

[5]   R. Takahashi and A. Aihara, "Characteristic nature of sedimentation and coalification in the Tertiary system of the Japanese Islands," *International journal of coal geology*, vol. 13, no. 1–4, pp. 437–453, 1989.

[6]   L. Nghiem, P. Sammon, J. Grabenstetter, and H. Ohkuma, "Modeling CO2 Storage in Aquifers with a Fully-Coupled Geochemical EOS Compositional Simulator," 2004.

[7]   F. Anggara, K. Sasaki, H. Amijaya, Y. Sugai, and L. D. Setjadji, "CO2 injection in coal seams, an option for geological CO2 storage and enhanced coal bed methane recovery (ECBM)," in *Proc., Indonesian Petroleum Association, Thirty-Fourth Annual Convention & Exhibition*, 2010, p. 16.