Influence of Carbonated Water-rock Interactions on Enhanced Oil Recovery in Carbonate Reservoirs: Experimental Investigation and Geochemical Modeling

Mai SHIMOKAWARA †1), ‡2),*, Elakneswaran YOGARAJAH ‡2), Toyoharu NAWA †3), and Satoru TAKAHASHI †1)

†1) Technology Dept., Oil & Gas Upstream Technology Unit, Japan Oil, Gas and Metals National Corp. (JOGMEC), 1-2-2 Hamada, Mihama-ku, Chiba 261-0025, JAPAN
‡2) Div. of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, JAPAN
†3) Hokkaido University, Kita 8, Nishi 5, Kita-ku, Sapporo 060-0808, JAPAN

(Received May 19, 2018)

Recently, the use of carbonated water injection has been considered for enhanced oil recovery (EOR), and it provides a great potential for reducing CO2 emissions. Both laboratory and field applications on EOR using carbonated water injection have been reported, and various mechanisms have been suggested for oil recovery. However, the interaction between the carbonated water and rock and its influence on EOR remains unclear. Therefore, the objective of this study was to evaluate the carbonated water-rock interactions through core flooding experiments and using an advective-reactive transport model. The experimental results pertaining to permeability of the core sample, and effluent pH value and calcium concentration were presented as a function of the amount of injectant. The effect of oil present in the core sample, ageing, and kind of injectant, on the interaction and oil recovery were analyzed. The results showed that calcite in the carbonate rock dissolved owing to its interaction with carbonated water; this increased the porosity, and thus, the permeability of the rock, and effluent pH value and calcium concentration also increased. The simulation results for effluent calcium concentration and pH agree well with experimental data, indicating the applicability of the model for further understanding the interactions in the carbonate reservoir.

Keywords
EOR, Carbonated waterflooding, Mineral dissolution, Calcite, Permeability

1. Introduction

Carbon dioxide (CO2) injection is an attractive EOR technique that allows not only the improvement of oil recovery but also the protection of the environment owing to the reduction in the amount of CO2, which is recognized as one of greenhouse gases1,2). The key for successful CO2 injection is to achieve miscibility that maximizes local displacement of oil by CO23,4). Another key is to improve sweep efficiency because gas injection has a relatively low sweep efficiency owing to gravity segregation induced by the low density of injectant5). To improve the sweep efficiency, some injection strategies have been proposed, and water-alternating CO2 injection is frequently applied to oil field6,7). During this process, not only CO2 is dissolved with oil to achieve miscibility but it is also dissolved with water, leading to the formation of carbon-dioxide-saturated water, that is, carbonated water.

Carbonated water injection is also recognized as an EOR technique. Various laboratory scale studies have been conducted since 19408-12). Core flooding experiments using a sandpack were performed by Menteclaire Research and the results demonstrated that the residual oil decreased by 15% PV if carbonated water was injected8). Core flooding experiments using freshly sampled cores were also performed, and the results showed that after carbonated water injection, the residual oil saturation reduced by 2-26% PV, as compared to the values for water flooding. Johnson et al. performed carbonated water injection in tertiary mode using sandpack9). The increase in oil recovery was between 15% and 25%. Martin performed experiments using carbonated water, and the results showed an increment of 12% oil recovery10). He also investigated the effects of oil recovery on the carbonation level of carbonated water and API oil gravity. Holm conducted core flooding experiments using carbonated water and CO2 slug, and the results demonstrated an additional oil recovery of 20% in the case of carbonated water injection as compared to that in water flooding11). Dong et al. conducted sandpack flood experiments
using distilled water and carbonated distilled water\textsuperscript{22}. They concluded that carbonated water injection recovered substantially more oil than distilled water did, and carbonated water could remobilize oil droplets in tertiary mode whereas the recovery factor in carbonated water injection was greater than that in distilled water injection at the same injection pore volume in secondary mode.

The first commercial field application of carbonated water, called the K&S project, was implemented in 1958\textsuperscript{15}–\textsuperscript{16}. The K&S project was located 10 miles north of Bartlesville, OK. The project involved 35 injectors and 24 producers spaced on regular 10-acre five-spot pattern. The target formation was the Bartlesville sand of Pennsylvanian age at 1250 ft. The small water injection started in 1953. The extended water injection and CO\textsubscript{2} injection started in February and April 1958, respectively. Before initiation of the commercial project, conventional water flooding and carbonated water flooding tests were conducted. The residual oil saturation in water flooding was 21.4 % whereas that in carbonated water injection was 11.4 %. In the field production, the injectivity was substantially improved and a peak of 73,000 bbl per month of oil was recovered from water-out areas of the reservoirs during carbonated water injection.

Another field application of carbonated water was in the Domes Unit\textsuperscript{17}. The carbonated water injection started in 1961, followed by the primary development phase, in which the cumulative oil production was 1,225,000 bbl from the total unit area while using a water injection scheme. Water and liquefied carbon dioxide were separately injected using different tubing strings and mixed at the bottom of the well before they entered the formation. The amount of carbonated water injected was estimated to be approximately one-third of the pore volume affected by the well. The total fluid production rate increased rapidly and reached its maximum value after approximately eight months of injection. Peak oil production was observed four months after injection.

Many researchers have investigated the mechanisms behind carbonated water injection that lead to improved oil recovery\textsuperscript{18}; this method is based on a Buckley-Leverett linear flow model considering the effects of oil viscosity reduction and oil swelling. Pope indicated a Buckley-Leverett solution for carbonated water flooding\textsuperscript{19}. The water saturation profile in this case depended on the relative permeability curves of oil and water and the partition coefficient, which denotes the ratio of CO\textsubscript{2} concentration in oil phase to that in water phase\textsuperscript{19}. Sohrabi et al. concluded from the results of the experiments that the main mechanisms involved were CO\textsubscript{2} dissolution in the oil causing oil swelling and viscosity reduction, evolution of solution gas from the oil due to dissolution of CO\textsubscript{2}, and wettability alteration\textsuperscript{20}. Sayegh et al. conducted core flooding tests using cores from the Cardium Formation, which are basically sandstone cores, with carbonated water\textsuperscript{21}. The results showed that permeability decreased initially and then increased gradually up to 70-85 % of the original permeability. Furthermore, microscopic examination indicated that fine migration occurred, resulting in permeability reduction. Klause et al. conducted core flooding tests on Beaverhill Lake cores, which are obtained from limestone reservoirs, with carbonated water\textsuperscript{22}. The results showed variations in permeability. In some experiments, they observed increasing permeability whereas others observed decreasing permeability. Microscopic observation indicated that dissolution textures were caused by etching and erosion, and fines were released during the flooding process. They noticed that most core samples used in these experiments were contaminated with the drilling fluid and this might have affected the results. Nunez et al. investigated the effects of carbonated water injection on dolomite porous media\textsuperscript{23}. The experimental system in their work allowed the comparison of the effects of carbonated water to those of mineral dissolved-carbonated water. The results showed that the permeability decreased gradually with carbonated water injection although porosity tended to increase, possibly associated with rock dissolution; in contrast, permeability decreased with the use of mineral dissolved-carbonated water owing to precipitation of the mineral. As mentioned above, some researchers discussed the interactions between carbonated water and rocks. However, the interactions have not been clearly explained.

Carbonated water reduces the pH of aqueous solution, and thus, it can possibly dissolve the carbonated rocks composed primarily of calcite and dolomite. The dissolution and precipitation (in case of a reversible reaction) of carbonate minerals in the presence of carbonated water may affect multi-phase flows in carbonate rocks. In this study, core flooding experiments were performed considering various conditions such as the presence or absence of oil and ageing, using carbonated distilled water and carbonated sea water. The core sample and effluent properties were analyzed before and after the experiments were performed, to determine the effect of the carbonated solution on the rock. The reactive transport model was developed in a geochemical code, PHREEQC, to simulate the experiments, and the simulation results were compared with experimental data.

2. Materials and Methods

2.1. Experimental Materials and Preparation

Carbonate rocks collected from the outcrops in Japan were used for this study. They are composed mainly

\textcopyright 2019 Jpn. Petrol. Inst.
of calcite and are under the digenesis phase similar to that of carbonate reservoirs in the Middle East. The diameter and length of carbonate core plugs are approximately 3.8 cm and 6 cm, respectively. Table 1 lists the properties of the rocks used in this study. The porosity and air permeability range from 12 to 18 % and from 1 to 100 md, respectively.

Carbonated water was made with distilled water and synthetic sea water, which is a representative composition of the target area, by bubbling CO₂ gas into water at 80 psig and 25 °C. Table 2 lists the ion concentrations in the sea water used herein. The measured pH of carbonated water ranged from 4 to 6.

Stock Tank Oil (STO) was obtained from the Middle East reservoir and was used as the oil sample in this work. The API gravity of STO was 30 API°.

2. 2. Experimental Setup and Procedure

Figure 1 shows the core flooding test apparatus. The distilled water, oil, and carbonated water were prepared in the accumulators. For the experiments, the temperature was set at 30 °C and the outlet pressure was maintained at 500 psig using the back pressure regulator (BPR).

Initially, the core sample was assembled into a core holder and saturated with distilled water. Then, we performed core flooding tests considering five cases: In Case 1, as the reference, the saturated core sample was injected with carbonated water. In Cases 2 to 5, the saturated core sample were assigned an irreducible water saturation (Swi) state by injecting the STO, in order to investigate the effects of the presence of oil on multi-phase flows. In Case 2, distilled water was injected into the core sample as secondary recovery, and then, carbonated water was injected as tertiary recovery. The core samples in Cases 3 and 4 were subjected to the ageing process for 7 days in order to achieve oil-wet conditions before secondary or tertiary recoveries. During ageing, pressure and temperature were maintained at 500 psig and 30 °C, respectively. In Case 3, the distilled water injection was followed by carbonated water injection, similar to the process in Case 2 after ageing. In Case 4, the core sample was injected with carbonated water without secondary recovery after ageing. The core flooding experiments were continued until 20 pore volume injected (PVI) flooded after differential pressure between the inlet and the outlet pressures in core sample was stable. In Case 5, the sea water and sea water-based carbonated water were used instead of distilled water-based carbonated water. The experimental procedure was identical to that followed for Case 2.

The effluent in secondary and tertiary recoveries was collected and analyzed in terms of the dissolved cations using inductively coupled plasma-mass spectrometer (ICP-MS). After the core flooding tests, the core samples were appropriately cleaned with solvents and dried. Then, the porosity and air permeability of core samples were measured again. Table 3 summarizes the experimental procedure.

2. 3. Modeling Approach

The interaction between carbonated water and rock during water injection into the carbonate rock sample was simulated using geochemical code PHREEQC. In this study, simulation of speciation, dissolution, and precipitation of minerals, and advective transport calculations were carried out in PHREEQC using the respective modules. The governing equations for each module are described in detail in ref. and are briefly explained in the following section.

Table 1 Rock Properties

| Sample ID | Diameter [cm] | Length [cm] | Dry weight [g] | Grain density [g/cm³] | Pore volume [cm³] | Porosity [%] | Air permeability [md] |
|-----------|---------------|-------------|----------------|-----------------------|------------------|--------------|----------------------|
| No. 1     | 3.798         | 6.072       | 156.4          | 2.72                  | 11.3             | 16.4         | 16.1                 |
| No. 2     | 3.801         | 6.079       | 161.8          | 2.69                  | 8.83             | 12.8         | 21.6                 |
| No. 3     | 3.797         | 5.895       | 152.0          | 2.70                  | 10.5             | 15.8         | 12.9                 |
| No. 4     | 3.797         | 5.869       | 146.6          | 2.70                  | 12.2             | 18.4         | 99.8                 |
| No. 5     | 3.796         | 6.036       | 151.6          | 2.69                  | 12.0             | 17.6         | 25.4                 |

Table 2 Ion Concentrations in Sea Water

| Na⁺ | Mg²⁺ | K⁺ | Ca²⁺ | Cl⁻ | SO₄²⁻ | HCO₃⁻ |
|-----|------|----|------|-----|-------|-------|
| 11300 | 1100 | 440 | 540  | 19000| 2700  | 120   |

All values are in mg/L.
The carbonate minerals can react with a solution to achieve thermodynamic equilibrium. The reactions are expressed by the mass-action equations as

\[
K_p = \prod_i (\gamma_i c_i)^{n_i,p} \tag{1}
\]

where \( K_p \) is the thermodynamic equilibrium constant for phase \( p \), \( \gamma_i \) is the activity coefficient of ion \( i \) [-], \( c_i \) is the concentration of ion \( i \) [mol/L], and \( n_i,p \) is the stoichiometric coefficient of ion \( i \) in phase \( p \) [-]. The activity coefficient, \( \gamma_i \), is calculated according to the extended Debye–Hückel rule \( \gamma = -A_i^2 \sqrt{I} + b_i I \tag{2} \)

where \( A \) [-] and \( B \) [-] are the temperature-dependent coefficients, whereas \( a_i \) [-] and \( b_i \) [-] are the ion-specific fitting parameters. The ionic strength \( I \) can be described as

\[
I = \frac{1}{2} \sum_{i=3}^{n} z_i^2 c_i^2 \tag{3}
\]

where \( z_i \) is the charge number of ionic species \( i \) in the solution and \( n \) is the total number of \( i \) in the aqueous solution.

Minerals are defined by the chemical reaction, an equilibrium constant, and enthalpy. The thermodynamic equilibrium constant \( K_p \) at a given temperature \( T \) [K] can be expressed as

\[
K_p = \exp \left( -\frac{\Delta_f G^0_{T}}{RT} \right) \tag{4}
\]

where \( \Delta_f G^0_{T} \) is the standard Gibbs energy of reaction at temperature \( T \) and \( R \) is the universal gas constant \( (8.31451 \text{ J/(mol K)}) \). The standard Gibbs energy of reaction is expressed as

\[
\Delta_f G^0_{T} = \sum \Delta_f G^0_{\text{products}} - \sum \Delta_f G^0_{\text{reactants}} \tag{5}
\]

where \( \Delta_f G^0_{T} \) is the Gibbs free energy of formation for a species at a given temperature \( T \). Table 4 lists, for the dissolution reactions of calcite used in the simulation, the equilibrium constant (log\( K_p \)) at standard condition and the standard heats of reaction (\( \Delta_f H^0 \)), which are used in the van’t Hoff equation \( 25\) to determine temperature dependence of the equilibrium constant. The input parameters for the phase-equilibrium module in PHREEQC (keyword “EQUILIBRIUM-PHASES”) were the type of phase (defined by dissolution reaction, log\( K_p \), and \( \Delta_f H^0 \)), as given in Table 4, the specified saturation index (which has a value of zero for equilibrium), and the amount of the mineral. The model is described in our previous works \( 26,27 \).

### 2.3.1. Phase-equilibrium

The flow of solution in a carbonate reservoir is modelled through the solution of the advection-reaction equation in PHREEQC. The governing equation is expressed as \( 25 \)

\[
\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + \frac{\partial q}{\partial t} \tag{6}
\]

where \( C \) is the ion concentration in water [mol/kgw], \( t \) is the time [s], \( v \) is the pore water flow velocity [m/s], \( x \) is the distance, and \( q \) is the concentration in solid phase (expressed as mol/kgw in the pores). The first term in the right-hand side of the equation represents advective transport and the second term represents the change in concentration in the solid phase due to reaction. The advective transport and chemical equilibrium reaction calculations were performed for each time step.

The advective transport calculation was carried out using the built-in model in PHREEQC (keyword “ADVECTION”). This simulation requires the number of cells and number of shifts. The shifts were calculated from the total time and time steps. The length of pore of carbonate rock was divided into a number of cells and each cell contained the same solution and minerals for thermodynamic equilibrium. One-dimensional advective transport takes place from injectant to pore water, which was in equilibrium with the minerals of calcite (Fig. 2). Thus, the advection model was applied with the phase-equilibrium model to simulate the flow of solution in carbonate rock.

### Table 4 Thermodynamic Properties of Minerals Used in the Simulation

| Phase | Reactions | log \( K_p \) at 25 °C | \( \Delta_f H^0 \) |
|-------|-----------|------------------------|---------------------|
| Calcite | \( CaCO_3 \leftrightarrow CO_2^{+} + Ca^{2+} \) | \(-8.48\) | \(-2.297\) |

**2.3.2. Advection**

The flow of solution in carbonate rock was divided into a number of cells and each cell contained the same solution and minerals for thermodynamic equilibrium. One-dimensional advective transport takes place from injectant to pore water, which was in equilibrium with the minerals of calcite (Fig. 2).
3. Results and Discussion

3.1. Case 1: Carbonated Water Injection in the Core Saturated with Water

The carbonated water with pH 4.0 was injected into the saturated core sample (No. 1 in Table 1) as a reference case. The measured water permeability as a function of injected pore volume is shown in Fig. 3(A). The permeability increased gradually up to 50 md for the injection of 50 PVI and a plateau was noted for the next 70-80 PVI. After that, the permeability reached approximately 80 md, and was then independent of pore volume injected. The measured pH of the effluent was approximately 5.5 and it did not change significantly throughout the injection of carbonated water. The calcite in the core sample was dissolved by the injected low-pH carbonated water; this increased the effluent pH and facilitated the release of calcium ions as well (Fig. 3(B)). The measured calcium concentration ranged from 100 to 250 mg/L after 150 PVI, which corresponds to stable permeability, although the concentration value was approximately 350 mg/L at the beginning of the experiment. The dissolution of calcite increased the porosity of the core sample, and thus increased the permeability.

The combined phase-equilibrium and advection transport simulation was carried out to predict the effluent concentration as a function of pore volume injected. The comparison is plotted in Fig. 3(B). The predicted pH of the effluent agrees fairly well with the measured values. Though the measured calcium concentration is scattered over the injected pore volume, the predicted values are constant with pore volume injected and reasonably reproduce the experimental Ca concentration.

Figure 4 shows the scanning electron microscope (SEM) images of a specific location of the core sample, obtained before and after performance of the core flooding experiment. Before the core flooding experiment,
the large grains could be clearly observed at the surface of the core sample. The pores that consisted of the large grains were also observed. After the core flooding experiment, however, small and obscure pores were observed. The large grains were not observed, and the texture of grains appeared smooth. This suggests that the surface of the core sample was dissolved with carbonated water, and this observation is consistent with the increase in calcium concentration detected in the effluent.

3.2. Case 2: Injection of Distilled Water Followed by Carbonated Water in the Core Saturated with STO

Both distilled and carbonated water were injected into the core sample (No. 2 in Table 1) saturated with STO. Initially, the distilled water was injected for 130 PVI, and then carbonated water was injected. The permeability changes during the injection are shown in Fig. 5(A). The permeability was very small (~3 md) during the injection of distilled water, and it gradually increased to 90 md during carbonated water injection. For distilled water, the calcite dissolution, which was examined through the measurements of calcium concentration and pH, was negligible as compared to that during the carbonated water injection (Fig. 5(B)). The pH was increased up to 5.5 and calcium concentration increased to 100-200 mg/L. The simulation was carried out in a similar manner to Case 1 to predict the calcium concentration and pH value. The predicted pH agreed well with experimental data for the injection of carbonated water. The model predicted well the calcium concentration for the injection of distilled water, but underprediction of the scattered calcium concentration was noted for the carbonated water injection. The final oil recovery for the injection of both solutions was 68%.

3.3. Case 3: Injection of Distilled Water Followed by Carbonated Water in the Aged Core Saturated with STO

The influence of ageing for Case 2 was investigated in this case. The conditions for the experiment were similar to those in Case 2, except that the core sample (No. 3 in Table 1) was aged for 7 days. Figure 6(A) shows the result of water permeability as a function of pore volume injected where the distilled water was injected till 100 PVI. The water permeability was approximately 3 md during the distilled water injection, whereas it increased to 10 md with injection of carbonated water. This value is much lower than the permeability reported for carbonated water injection without ageing. A significant change in water permeability, compared to in Cases 1 and 2, was not observed. It may be regarded that, in the case of without ageing, the pore surface of both small and large pores is water-wet, and the injected water penetrates through both pores and thus increases the permeability. However, the ageing turns the pore surface to oil-wet and retard the water penetration particularly in large pores. Although the ageing decreases the permeability, it does not remarkably affect the dissolution of calcite. The dis-
solution could be mainly in the small pores, which does not significantly contribute to flow. The final recovery of oil after injection was lower (≈55%) than that without ageing.

In the calculation model, it was assumed that the oil present in the pores due to ageing does not react with carbonated water and the residual oil was regarded as a part of the carbonate rock. It was defined by increasing the volume of the rock corresponding to the amount of oil present in the pores, that is, by decreasing the porosity of the rock. The predicted pH and calcium concentration were consistent with the measured data.

3.4. Case 4: Carbonated Water Injection in the Aged Core Saturated with STO

The experiment was conducted using only carbonated water as the injectant for the ageing sample (No. 4 in Table 1). The measured permeability was scattered, and the values were in the range of 5 to 30 md (Fig. 7(A)). As observed in Case 3, by the ageing effect, the water permeability was not improved. The measured pH of effluent was constant with the injected pore volume while the concentration of calcium gradually increased and reached a maximum value at 80 PVI; subsequently, this value gradually decreased, becoming constant at 100 mg/L after 200 PVI (Fig. 7(B)). The simulated calcium concentration and pH agreed with the experimental results; however, the predicted calcium concentration did not match at approximately 80 PVI. The recovery of oil with carbonated water injection was 41%, which was the lowest obtained compared to in other cases.

3.5. Case 5: Injection of Sea Water Followed by Carbonated Sea Water in the Core Saturated with STO

The effect of sea water injection was investigated in this case (sample No. 5 in Table 1). The measured permeability is shown in Fig. 8(A). The injection of sea water achieved very low permeability and the permeability increased gradually when sea water was replaced with carbonated sea water. The permeability changes were similar to those in Case 2; however, carbonated sea water caused the permeability to increase significantly, as compared to in other cases. The injection of carbonated sea water strongly altered the calcite and thus, permeability and the concentration of ions in effluent drastically changed. Figure 8(B) shows the measured pH and calcium concentration in the effluent, as predicted by the model as a function of pore volume injected. The model predicted well the measured pH and calcium concentration. The high concentration of calcium is due to its initial concentration in the sea water and the amount dissolved from calcite. The variation in calcium with pore volume injected is similar to that in Case 2, indicating that the effect of initial sea water injection on calcite dissolution is negligible. Carbonated sea water reduced the effluent pH to approximately 5. The final recovery of oil was 63%, which is close to the recovery value obtained in Case 2.

The core flooding of various injectants both with and without ageing changed the rock properties. Table 5

Fig. 7 (A) Measured Water Permeability; and (B) Comparison between Measured and Predicted Concentrations of Ca and pH Values for Case 4

Fig. 8 (A) Measured Water Permeability; and (B) Comparison between Measured and Predicted Concentrations of Ca and pH Values for Case 5
lists the ratio of rock properties after the core flooding to those before the core flooding. The weights of the core sample decreased and the porosity increased. This evidently resulted in the dissolution of the carbonate rocks. The porosity without the ageing process in Cases 1 and 2 increased by 7-9%, whereas the porosity with ageing in Cases 3 and 4 increased by around or less than 2%. The carbonate rocks without an ageing process were readily dissolved by carbonated water regardless of the presence of oil in the pore spaces. Owing to the ageing process, the rock surfaces were covered with oil, which prevented their reaction with carbonated water. The air permeabilities after the core flooding were much greater than those before the core flooding. High porosity after the core flooding becomes higher air permeability with an exception of Case 3. The increment in air permeability in Case 3 is the greatest among that in all cases, although the increment in porosity is the smallest in this case.

4. Conclusions

The interaction between carbonated water and carbonate rock in the core flooding was studied. The porosity and air permeability of the rock before and after the core flooding and the effluent calcium concentration and pH were analyzed to investigate the interaction. The carbonated water facilitated the dissolution of calcite mineral during the flooding, which increased the porosity of the rock, and thus, its permeability. A reactive transport model considering thermodynamic equilibrium between minerals and solution, and advection was developed in PHREEQC. Despite some discrepancies, the model well predicted the measured pH and calcium concentration in the effluent as a function of pore volume injected for different cases. This indicates that the proposed model could explain the ion exchange reaction in carbonate rocks during carbonated water injection. The presence of oil in the rock, occurrence of ageing, and the type of injectant significantly affect the porosity, air permeability, ion concentration of the effluent, and eventually, final recovery of the oil.

Acknowledgment

We would like to express our gratitude to Mr. Yasuyuki Akita, JOGMEC, for providing valuable assistance and advice regarding the core flood experiments, and Mr. Tatsuya Hattori and Ms. Emiko Shimbo for the SEM analysis.

Nomenclatures

EOR : enhanced oil recovery
PV : pore volume
PV1 : pore volume injected
STO : stock tank oil
\( k_r \) : thermodynamic equilibrium constant for phase p [-]
\( \gamma_i \) : activity coefficient of ion i [-]
\( c_i \) : concentration of ion i [mol/L]
\( n_{i,p} \) : stoichiometric coefficient of ion i in phase p [-]
\( I \) : ionic strength [mol/L]
\( z_i \) : charge number of ionic species i [-]
\( T \) : temperature [K]
\( R \) : universal gas constant [J/(mol K)]
\( \Delta G_i^p \) : standard Gibbs energy of reaction
\( \Delta G_i^p \) : Gibbs free energy of formation
\( \Delta H_i^p \) : standard heats of reaction

Unit Conversion Factors

\( 141.5/(131.5 + API^\circ) \) = specific gravity at 15.56°C
1 bbl = 1.589873E-01 m³
1 ft = 0.3048 m
1 psi = 6.894757 kPa
1 d = 1.0E-12 m²

References

1) Orr Jr., F. M., Taber, J. J., Science, 224, (4649), 563 (1984).
2) Haszeldine, R. S., Science, 325, (5948), 1647 (2009).
3) Stalkup, F. I., Journal of Petroleum Technology, 815 (1983).
4) Holm, L. M., Journal of Petroleum Technology, 817 (1986).
5) Mahaffley, J. L., Rutherford, W. M., Matthews, C. S., Society of Petroleum Engineers Journal, 6, (1), 73 (1966).
6) Lewis, E., Dao, E. K., Mohanty, R. K., SPE Journal, 13, (4), 432 (2008).
7) Christensen, J. R., Stenby, E. H., Skaug, A., SPE Reservoir Evaluation & Engineering, 4, (2), 97, (2001).
8) Lake, L. W., Pope, G. A., Carey, G. F., Sephehrnoori, K., In Situ, 8, 1 (1984).
9) Johnson, W. E., Producer Monthly, November, (1952).
10) Martin, J. W., Producer Monthly, July, (1951).
11) Holm, L. W., Producer Monthly, September, (1963).
12) Dong, Y., Dindoruk, B., Ishizuka, C., Lewis, E., Kubicek, T., SPE Annual Technical Conference and Exhibition, (2011), SPE-145380-MS.
13) Martin, J. W., Producer Monthly, May, (1951).
14) Hickok, C. W., Journal of Petroleum Technology, (1960), SPE-
1474G.
15) Christensen, R. J., the 7th Annual Meeting of Rocky Mountain Petroleum Sections of AIME, (1961).
16) Hickok, C. W., Ramsay, H. J., SPE Secondary Recovery Symposium, Wichita Falls, (1962), SPE-333-MS.
17) Scott, J. O., Forrester, C. E., Journal of Petroleum Recovery, December, 1379 (1965).
18) Nevers, N. D., Society of Petroleum Engineers Journal, 4, (1), 9 (1964).
19) Scott, J. O., Forrester, C. E., Journal of Petroleum Recovery, December, 1379 (1965).
20) Sohrabi, M., Emadi, A., Farzaneh, S. A., Ireland, S., SPE Annual Technical Conference and Exhibition, (2015), SPE-175159-MS.
21) Sayagh, S. G., Krause, F. F., Girard, M., DeBree, C., Annual Technical Meeting of Petroleum Society of CIM, (1987), PETSOC-87-38-78.
22) Krause, F. F., Sayegh, S. G., Girard, M., DeBree, C., Annual Technical Meeting of Petroleum Society of CIM, (1987), PETSOC-87-38-79.
23) Umezawa, R., Vaz, R. G., Koroishi, T., Vidal Vargas, J. A., Trevisa, O. V., the Abu Dhabi International Petroleum Exhibition and Conference, (2015).
24) Parkhust, D. L., Appelo, C. A. J., USGS Report, (1999).
25) Appelo, C. A. J., Postma, D., “Geochemistry, Groundwater and Pollution Second Edition,” CRC Press, London (2009).
26) Kari, O. P., Elakneswaran, Y., Iwasa, A., Nawa, T., Sato, T., Kurumisawa, K., Cement and Concrete Research, 40, 1756 (2010).

要 旨
原油増進効果に対する炭酸水と炭酸塩岩の相互作用の影響—実験と地化学モデリング—

下河原 麻衣†1,†2, Elakneswaran YOGARAJAH†2, 名和 豊春†3, 高橋 悟†1
†1) (株)石油自然ガス・金属鉱物資源機構 (JOGMEC) 石油開発技術本部技術部
†2) 北海道大学大学院工学研究院, 060-8628 札幌市北区北13条西8丁目
†3) 北海道大学, 060-0808 札幌市北区北13条西8丁目

炭酸水を用いる増進回収法 (EOR) は増進効果だけでなく、二酸化炭素の削減による地球温暖化への解決策の観点から注目されている。炭酸水圧入による EOR は実験室レベルの基礎的検討からフィールドでの適用まで報告されており、様々な増進メカニズムが提唱されているものの、岩石と炭酸水との相互作用やその増進効果への影響についてはいまだ不明な点がある。本研究の目的は、炭酸塩岩を用いたコアスキャン実験や移流反応平衡モデルを用いた数値計算を通じて、炭酸水と岩石の相互作用を評価することである。岩石コア実験では、岩石コアのエイジング、原油の存在の有無、圧入水の種類が与える原油回収への影響について調べた。その結果、排出水の pH およびカルシウムイオン濃度が増加するとともに浸透率が増加した。実験後の溶解析出量の測定から炭酸水は岩石を溶融したことが分かった。排出水のカルシウムイオン濃度や pH の変化を再現させるため、移流と平衡反応に基づく計算結果と比較したところ良い相関が確認されたことから、炭酸塩岩岩質層に炭酸水を圧入した際の岩石と炭酸水の相互作用を再現できる可能性が示唆された。