

A LABORATORY STUDY OF CLAY SWELLING PROBLEM IN CO₂ EOR BY CARBONIC ACID INJECTION IN CLAY SANDSTONE

KAJIAN LABORATORIUM PENGEMBANGAN MINERAL LEMPUNG DALAM PENINGKATAN PENGURASAN MINYAK METODA CO₂ MELALUI UJI INJEKSI ASAM KARBONAT PADA BATU PASIR LEMPUNGAN

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ABSTRAK

Selama proses peningkatan pengurusan menggunakan CO₂, sejumlah tertentu volume CO₂ terlarut dalam fluida air formasi reservoir membentuk lingkungan bersifat asam yang dapat merubah sifat interaksi batuan-fluida reservoir. Salah satu fenomena yang terjadi akibat interaksi ini adalah pengembangan mineral lempung (clay swelling) yang dapat mempengaruhi kinerja proses peningkatan pengurusan minyak. Beberapa percobaan telah dilakukan terhadap perconton batuan inti batu pasir, antara lain uji imbibisi, uji core flood, uji konduktivitas dan pengukuran pH. Uji imbibisi dilakukan untuk mengkaji kinerja air formasi tersaturasi CO₂ terhadap perolehan minyak (didekati dengan sifat asam karbonat) selama perlakuan lima hari dibandingkan dengan kinerja imbibisi air formasi (brine). Eksperimen injeksi batuan inti (core flooding) batu pasir juga dilakukan untuk menentukan efek CO₂ terlarut dalam air formasi, yaitu dengan melakukan simulasi injeksi larutan air garam (brine) diikuti dengan asam karbonat pada suhu di bawah 68,3°C. Pengukuran nilai konduktivitas dan pH dari fluida imbibisi dilakukan sebelum dan sesudah perlakuan uji untuk memastikan terjadinya pertukaran ion (kation). Hasil interpretasi uji imbibisi menunjukkan bahwa pada nilai pH 4 imbibisi asam karbonat menghasilkan perolehan minyak meningkat sebesar 15% dibandingkan imbibisi air formasi saja karena adanya pengembangan material lempung pada pori batuan pasir yang dapat mengakibatkan kerusakan formasi. Fenomena ini dikuatkan oleh adanya resistensi aliran fluida pada harga pH rendah dalam system batuan inti perconton yang nilainya lebih besar dari pada kondisi air formasi. Adanya penyumbatan (plugging) tersebut adalah akibat besarnya kejadian pengembangan material lumpur dalam pori. Fenomena tersebut juga dijelaskan oleh pengukuran pH dan konduktivitas yang menunjukkan besarnya kejadian pertukaran kation. Dapat diambil kesimpulan dari kajian ini bahwa interaksi fluida-batuan dalam reservoir akibat adanya penjejukan CO₂ dalam air formasi mengakibatkan perubahan nilai injektifitas serta kehilangan perolehan minyak. Temuan ini harus dapat dipertimbangkan dalam merencanakan operasi CO₂ EOR, khususnya ketika dilaksanakan pada reservoir minyak yang sudah mengalami water cut tinggi.

Kata kunci: air formasi terjenuhi CO₂, lingkungan asam, pengembangan mineral lempung, injektifitas.

ABSTRACT

Significant portion of CO₂ is dissolved in reservoir brine during CO₂-Enhanced Oil Recovery. Dissolved CO₂ forms an acidic environment which could modify rock-fluid interaction. One of the phenomena that could happen due to this interaction is clay swelling which may affect enhanced oil recovery performance. Several experiments were conducted in a number of sandstone core samples, i.e. Imbibition test, Core flood test, Conductivity test, and pH measurement. Imbibition test was conducted to evaluate CO₂-saturated brine (approached with carbonic acid) performance toward oil recovery during five days measurement compared with brine imbibition performance. Moreover, core flood experiment was run to determine the effect of dissolved CO₂ in brine on injection in sandstone. This is simulated by injecting brine (base case) followed by carbonic acid under 68.3°C. Thus, conductivity and pH of the imbibed fluids (before & after running imbibition test) were measured to justify occurrence of cation exchange. Interpretation of imbibition test indicated that imbibing carbonic acid, at pH value of about four, resulted in loss of oil recovery about 15% compared with brine due to formation damage, caused by clay swelling as sandstone contains clay. The existence of this phenomenon was confirmed by flow resistance at low pH in core sample which was higher than that in brine. This apparent plugging was expected due to severe clay swelling. Meanwhile, the existence of such phenomenon was also clarified with conductivity and pH measurement as there was a great amount of cation exchange. It can be inferred from this study that the rock-fluid interaction from CO₂-saturated brine can result in adverse effect, such as injectivity problem and loss of recovery. This finding must be considered in planning CO₂ EOR operations, especially when facing condition of watered out oil zone.

Keywords: CO₂-saturated brine, acidic environment, clay swelling, injectivity issue.

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I. INTRODUCTION

Carbon dioxide (CO₂) injection in the formations is one of several proposed methods for enhanced oil recovery. There are various typical operations of this injection in the oil industry, such as CCS (Carbon Capture and Storage), WAG (Water Alternating with Gas), CO₂-Foaming, Miscible Injection, Immiscible Injection, CWI (Carbonized Water Injection), and Huff & Puff. Through those processes, many physical and chemical processes are known to occur both during and after CO₂ injection, including diagenetic chemical reactions and associated permeability changes.

Variability in rock types responses suggests that CO₂ injection will induce changes in intrinsic rock properties such as porosity, permeability and wettability. This is due to coupled physical and chemical processes that occur during the interaction between CO₂ and rock minerals. Other potential phenomenon that may happen include severe formation damage due to clay reactivity that can be attributed to pH reduction from dissolved CO₂ in brine.

Moreover, this study mainly investigates clay problem phenomenon under supercritical CO₂

phase in CO₂ injection into sandstone reservoir. It is interesting to investigate this phenomenon since substantial amount of CO₂ is also dissolved in brine during injection. In spite of argued benefit, the swelling of clay can mechanically 'expulse' residual oil from the pore as also happens in low salinity water flood mechanism (Nasralla et al. 2011). On the other hand, the swelling of clay or migrated clay could also reduce the pore size and in turn permeability impairment which on severe case could lead to lack of CO₂ performance.

The focus of this study is to get better understanding of formation damage caused by clay swelling during CO₂ flooding that may affect EOR performance in typical CO₂ applications; such as such as CCS, injection in watered out oil reservoir, CWI, WAG, and Huff & Puff; through experimental observation. Those practices are conditions of clay reactivity occurrence as CO₂ mostly exposed to water/brine and is dissolved into water/brine, acidizing the water/brine environment. Furthermore, investigation of the phenomenon is mainly focused on clay type of kaolinite and montmorillonite as they tend to disperse and swell respectively due to aqueous solution and acidic environment. Also, their

structures (composition of octahedral and tetrahedral sheet in a packet) are different from each other and simpler than other clay type.

According to CO₂ phase envelope, CO₂ will behave as supercritical fluid above its critical temperature, 87.98 °F, and its critical pressure, 1071 psi. Hence, CO₂ will be formed as supercritical state at reservoir condition, in average. The injected CO₂ is partially miscible with brine (up to 1.6 – 2.6% mole of CO₂ can dissolve in brine with 0.01 to 0.03% NaCl (Bando 2003) and can be calculated with Duan & Sun equation (2003) as a function of pressure, temperature, and salinity (Duan et al. 2005). The solubility of CO₂ in water/brine will increase due to increase in pressure and decrease in high temperature and high salinity (due to salting out) (Bando 2003 & Green & Willhite 1998.

(Schaeff & McGrail 2004), and Sigfusson et al. 2015) reported that the created acidity can achieve significant level of pH value with range of 3 – 4 measured at reservoir condition. This change in acidity will occur as an increase in the amount of CO₂

being injected into a reservoir system that makes CO₂ being accumulated to dissolve (i.e. Carbon Capture & Storage and Huff & Puff activities).

As injection is initiated in sandstone reservoir, it is interesting to evaluate interaction between acidic solutions being formed and bearing formation, especially clay minerals. The severity of clay damage is not only caused by structure layer existing in the mineral (related to contact area), but also by the type and amount of exchangeable cation (Mungan, 1989). For instance, Na-montmorillonite swells more than Ca-montmorillonite because the Ca cation is strongly adsorbed compared with Na cation as the mineral is hydrated in aqueous media; according to Roger's work (1963) (Civan 2000). Based on preceding observation by Reed (1977), he stated that severity of clay swelling is a function of cation type. He mentioned that the most to least damage, causing permeability impairment, cation is H⁺ > Na⁺ > Ca⁺⁺ in a medium of mica with cation of K⁺ (illustrated in Figure 1) (Civan 2000). This is because ion K⁺ exchanges with a larger cation.

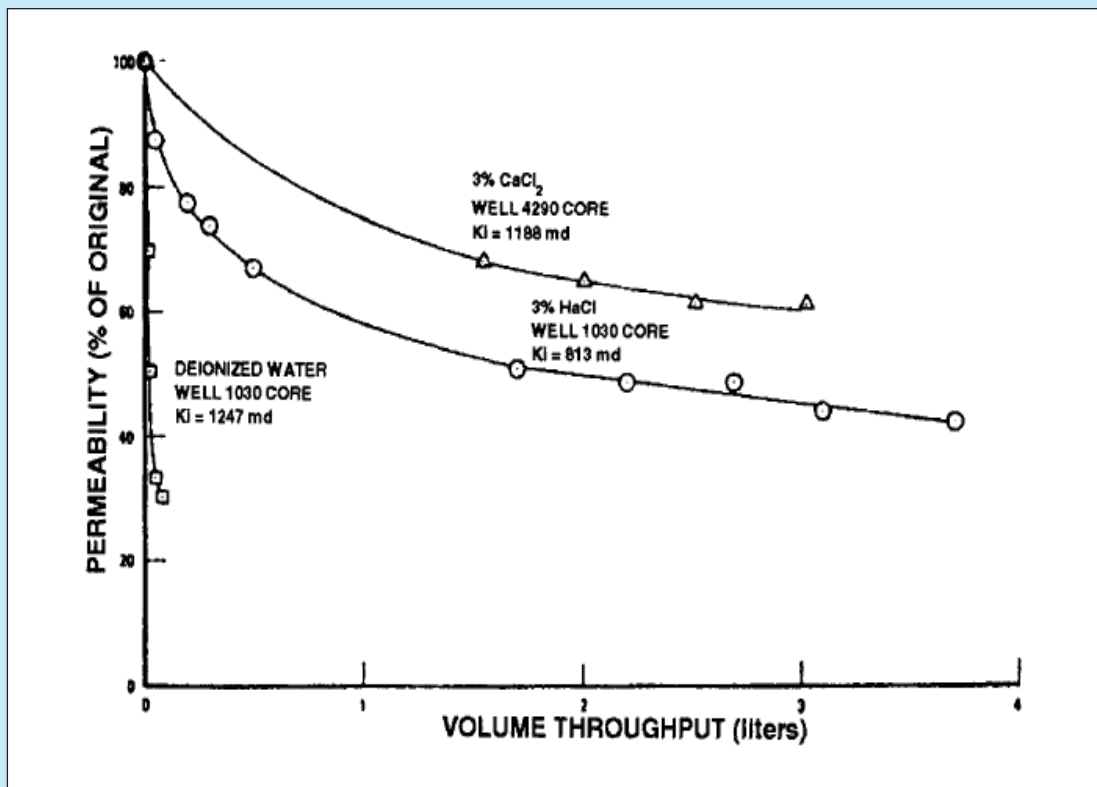
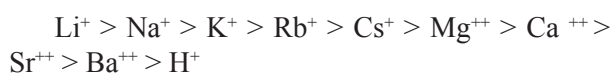


Figure 1
Reed study (1977) of comparison of the permeability damages (Civan 2000).

Meanwhile, Grim (1942) determined the order of replaceability of common cation in clay from most to least easy as follows (Civan 2000).



II. METHODOLOGY

The examination is conducted in several samples of artificial sandstone core. As CO_2 can be dissolved in water, the test was conducted by applying carbonic acid (H_2CO_3 , as a product of CO_2 solubility reaction) into all core samples. The solution of carbonic acid was made by titrating chloride acid (HCl, pH value of 1) with sodium carbonate (Na_2CO_3 , pH value of 12). The concentration of solution being formed has pH value of about 4. This pH was chosen to examine problem that was caused in condition of maximum concentration being achieved in typical practice. The details of ion composition of the solution being made are shown in Table 1.

Before conducting the tests, the tested core samples were prepared by saturating brine of sodium chloride (NaCl) with concentration of 500 ppm under nearly vacuum condition (during 4 hours). The use of 500 ppm NaCl was meant to make the same experimental condition to all experiments. That value was determined based on product in composing carbonic acid solution. Then, they were pressed forcibly to fill up oil sample to core samples using core flood apparatus at temperature of 68.3°C and confined pressure of 100 psi, until no brine is produced. After the cores had been filled with oil and brine, these cores were soaked for one day to ensure pore of the cores are fully saturated.

Composition and characteristics of each core samples are shown in Table 2 and Table 3.

Within this study, observation methods being exhibited were spontaneous imbibition and injectivity test using core flood apparatus (both were under

constant salinity) to investigate performance of carbonic acid (as a product of CO_2 solubility in water) in term of recovery and flow resistance. As to clay swelling evaluation due to cation exchange, conductivity and pH of imbibed fluid effluent were also observed. The details for those methods are explained further as follows.

A. Spontaneous Imbibition

This method compared oil recovery of core samples with different acidic environment and imbibed fluid in a static condition. The L-3 and L-7 samples were chosen to conduct this test according to the amount of initial oil saturation of each sample which was almost the same. L-3 core was imbibed with carbonic acid solution with pH value of 4. On the other hand, brine water (NaCl 500 ppm) was used to imbibe L-7 core as a control volume. After all samples were already prepared, the samples were

Table 1
Cation composition of acid solution

Cation Ion	Amount (ppm)
H^+	88
Na^+	500

Table 2
Core sample composition

Mineralogy	Weight Percentage (%)
Quartz	80.4
Kaolinite	2.8
Montmorillonite	2.8
K-Feldspar	14

Table 3
Core sample characteristic

Sample	D (cm)	H (cm)	K (mD)	Porosity (%)	S_{oi} (fraction)
L3	2.51	3.11	215.91	24.02	0.61
L7	2.52	3.24	151.97	23.40	0.69
L10	2.51	3.24	185.25	24.91	0.43

soaked in imbibition apparatus with temperature of 68.3°C (mimicking reservoir condition) during 5-days. Oil produced from both samples were examined regularly for 6 hours every day with measurement period of 30 minutes in the first day, every hour in the second day, and every two-hour for other days.

B. Core Flood Experiment

This method was applied for L-10 core sample by applying carbonate acid with pH value of 4 in flooding scenario for this sample. Constraints, used in performing the tests, were injection speed of 0.3 cc/minute (according to rule of thumb of 1 ft/day frontal velocity flooding), confining pressure of 100 psi and temperature of 68.3°C (mimicking the reservoir condition).

Implemented flooding scenario of this method was flooding sample with brine (until there is no more produced oil, indicated by constant pressure), then flooded it with carbonate acid with the same amount of injected PV as brine injection. This flooding series was meant to evaluate restriction flow whether injecting carbonic acid would give flow resistance change compared with injecting brine. Measurement of flow resistance, being indicated by pressure, was carried out every 5 minutes. The schematic of core-flood apparatus is shown in Figure 2.

C. Conductivity and pH Measurement

The conductivity of imbibed fluids, which consisted of pH-4 solution and brine, was measured using conductivity apparatus under different condition of imbibed fluids, before and after imbibition test. This test was meant to evaluate occurrence of ionic (cation) alteration fluid during imbibition test. The measurement was conducted by putting the measurement probe to be soaked into several imbibed fluids. The probe must be soaked until top mark and should be prevented from attaching chamber. This measurement was done ten times to ensure observation data consistency and conducted under room temperature.

Besides that, pH value of imbibed fluids (before and after imbibition test being held) was also measured. The measurement was performed at room temperature condition. This test also was conducted by soaking the probe of pH meter after the apparatus had been calibrated for measurement of each sample. This measurement was meant to convince that ionic change occurred.

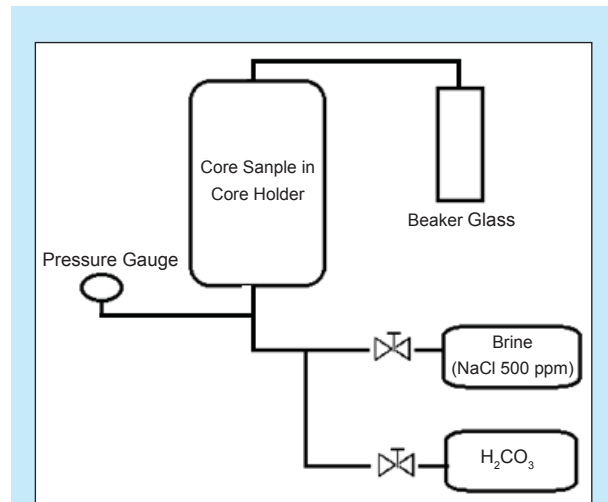


Figure 2
Scheme of core flood apparatus.

III. RESULTS AND DISCUSSION

A. Spontaneous Imbibition Test & Core flood Experiment

Figure 3 shows oil recovery of L-3 and L-7 core samples that resulted from spontaneous imbibition process under different acidic environment. From the figure, recoverable oil in imbibition process of brine water is higher (by difference of about 15 %) than that process of carbonic acid with pH value of 4. The cause of this phenomenon is expected to be induced by severe clay swelling at low pH environment. The increase of d-spacing of clay mineral, basically, occurs in both core samples, being clarified in conductivity test discussion, due to applied aqueous solution that is below critical salt solution according to Mohan & Fogler (1988) study. However, this severity occurred due to a great amount of cation being exchanged between solution and mineral. As explanation of Reed (1977) study, core sample applied with acid solution (L-3) will undergo severe swelling due to a huge amount of H⁺ ion. A lot of mineral's cations will diffuse out of the mineral (according to Fick's Law) and will be replaced by that ion until steady state, in terms of ionic balance, is achieved.

The occurrence of this term is also depicted in injectivity test (Figure 4). As carbonic acid solution injection is initiated, fluid flow tends to be more resistant than in injection of brine. It is clearly shown in the graph that there is a pressure increase after injecting acid solution, around 6 psi under steady condition. This flow resistance is mainly attributed to shrinking of pore throat in core sample due to

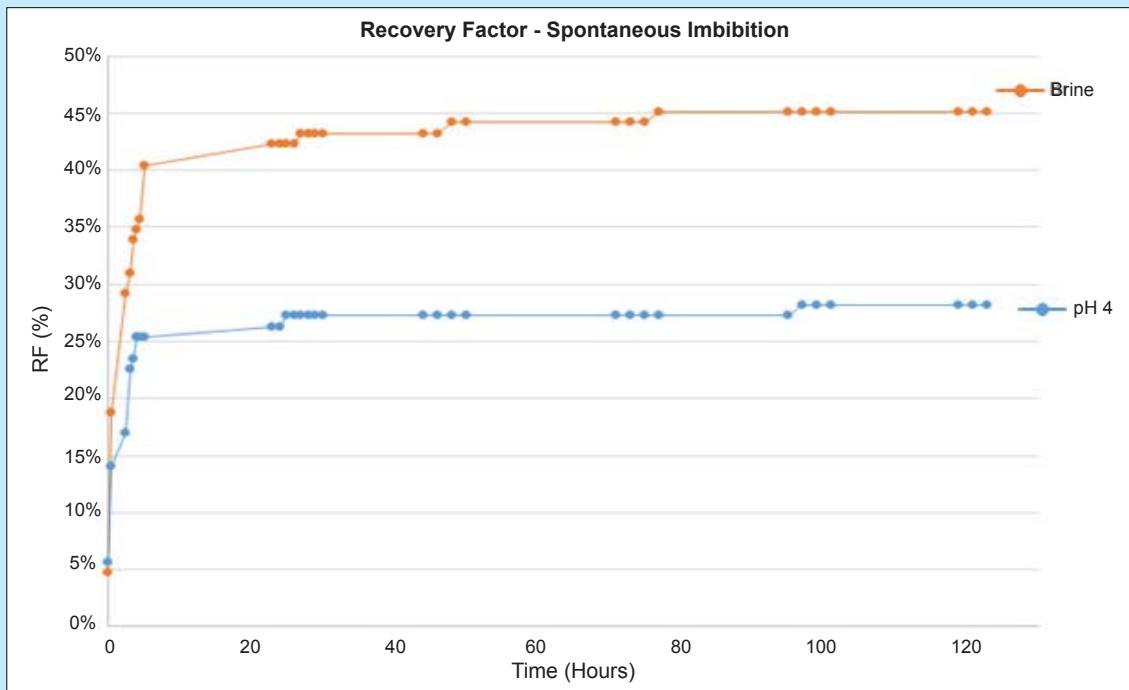


Figure 3
Recovery factor of imbibition test by imbibing brine and carbonic acid solution.

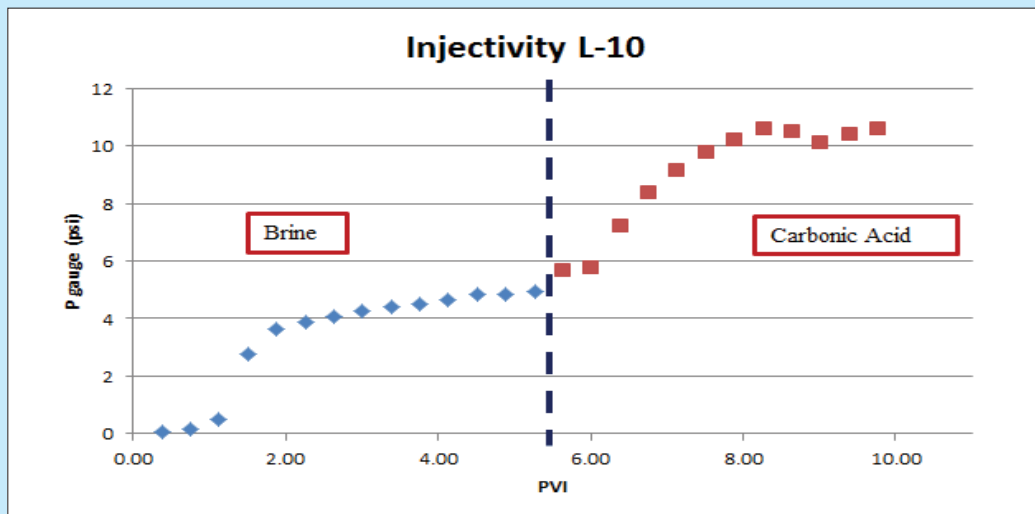


Figure 4
Result of injectivity test on L-10 by injecting brine, thus carbonic acid.

clay swelling. Swelled of migrated clay (Kaolinite type) also leads the flow resistance as it plugs the pore throat.

B. Conductivity & pH Evaluation

Measurement of conductivity of each imbibed fluid, being used for imbibition test, are shown in the following tables (Table 4 & 5).

From those evaluations, it could be inferred that cation exchange really happened. The great change of the value of conductivity, as expected, occurs in carbonic acid solution. Although parameter evaluation value of brine imbibition also changes, it is not significant compared with acid solution because the core samples have been saturated with fluid having the same characteristics as injected fluid.

Hence, there is only a little change to reach an ionic balance condition.

Whereas, alteration of pH for each imbibed fluid is shown below.

Table 4
Result of conductivity test of imbibed fluid of brine

Number of Measurement	Before Imbibition		After Imbibition	
	Conductivity (mSiemen)	Temperature (deg C)	Conductivity (mSiemen)	Temperature (deg C)
1	2.4	25.8	3.42	25.5
2	3.01	25.8	3.33	25.6
3	3.1	25.8	3.38	25.6
4	3.07	25.8	3.38	25.6
5	3.05	25.8	3.37	25.5
6	3.08	25.8	3.37	25.6
7	3.07	25.8	3.37	25.5
8	3.07	25.8	3.34	25.5
9	3.03	25.8	3.37	25.5
10	3.09	25.8	3.36	25.5
Average	3.00	25.80	3.37	25.54

Table 5
Result of conductivity test of imbibed fluid of carbonic acid solution

Number of test Measurement	Before Imbibition		After Imbibition	
	Conductivity (mSiemen)	Temperature (deg C)	Conductivity (mSiemen)	Temperature (deg C)
1	16.75	25.9	34.5	25.4
2	16.96	25.9	34.6	25.5
3	16.4	25.9	34.3	25.5
4	16.79	25.9	34.6	25.6
5	16.88	25.9	34.6	25.6
6	16.05	25.8	34.8	25.5
7	16.13	25.8	34.6	25.5
8	16.46	25.8	33	25.6
9	16.68	25.8	34.8	25.6
10	16.81	25.8	34.7	25.5
Average	16.59	25.85	34.45	25.53

Table 6
Result of pH measurement of imbibed fluid

Imbibed Fluid	pH Before Imbibition	pH After Imbibition
Brine (NaCl 500 ppm)	7.46	7.81
H ₂ CO ₃ (pH-4)	4.69	8.01

As ion H^+ replace a great number of cation in mineral, this cation (usually alkali or metal ion) will give a great change in fluid conductivity term. Besides that, the cation also will give an increase value of pH as it interacts with water to form a base solution, whether it is strong base solution, weak base solution, or both.

IV. CONCLUSIONS

In conclusion, performance of dissolved CO_2 in water during injection (approached by injecting carbonic acid with pH value of 4) leads to loss of performance. This is indicated by loss of oil recovery at static condition (using imbibition) and higher flow resistance than base case (injecting brine). This happens as a result of interaction between dissolved CO_2 in water and clay mineral. This interaction leads to severe clay swelling phenomenon as large amount of cation are being exchanged.

Furthermore, this investigation of this clay swelling phenomenon can be improved by conducting integrated SEM and NMR Analysis in capturing the evidence of clay swelling. Not only that, but further core flood test also should be conducted in investigating the phenomenon and evaluating recovery performance by varying pH in injection acid. Thus, pure CO_2 injection in watered oil core should be carried out in order to mimic field practice. The advance evaluation of effluent water in core flood test should be conducted in order to evaluate cation exchange level as a function of time, thus determining clay exchange capacity for each clay type and clay formation rate attributed to reactivity of clay type and cation diffusion rate.

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Nomenclature

D : Diameter of core sample [cm]

H : Height of core sample [cm]

K : Permeability [mD]

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