INVESTIGATIONS ON THE STORAGE EFFICIENCY OF CO_2 IN CARBONATE AQUIFERS

by
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I. INTRODUCTION

The production of associated and nonassociated gas increases due to additional new oil and gas fields. Consequently, there will be an increase of CO_2 released from associated gas, and especially, from nonassociated gas.

Actually, CO_2 may still be utilized in an attempt of increasing oil recovery through the methods of EOR (Enhanced Oil Recovery) or IOR (Improved Oil Recovery). In general, on the one hand, the CO_2 availability in the atmosphere is still be needed for the photosynthesis process. But, on the other hand, this gas can stimulate the greenhouse effect that influences the global warming and weather changes.

Prior being utilized, CO_2 can be stored first in the depleted oil reservoirs or in the aquifers. The feasibility of these reservoirs or aquifers as a CO_2 storage can be determined through the mechanisms of CO_2/water injection, or CO_2 solubility in the water. For the purpose of several experiments, specific characters of the cores and formation water were decided taken from a representative carbonate reef formation in West Java region to substitute the samples from Natuna Field. The experiments were then continued on studying the CO_2 solubility in the formation water not only at constant volume but also with varied volume, and also the CO_2 storage efficiency in the carbonate rocks saturated with water.

II. SOME ASPECTS ON CO_2 STORAGE

Prior determining a certain reservoir satisfied for CO_2 storage, an integrated assessment of the reservoir fluids and its geology are needed. This includes the characteristics of fluids at the reservoir conditions, the influence of increasing storage pressure to CO_2 solubility in the aquifers, the specific condition of the matrix rocks, and environment of the rock formation deposition. The storage capacity depends on the availability of wide area and enough pressure differentce between fracture pressure and reservoir pressure. Van der Meer (1993) suggested that both integrity and capacity include:

(1) The geology of its reservoir, the wider the area and the bigger the pores, the higher the CO_2 storage capacity. Permeability higher than 50 md gives a better convection-dispersion of fluids flow will be more freely distribute in the reservoirs. In general, the aquifer's depth, not less than 800 m, CO_2 itself is at the supercritical state. In this condition, at the same reservoir volume, hopefully, greater CO_2 volume can be stored. A cap layer should be exist at the top of the formation to prevent from CO_2 leakage that often needs more costs and materials. For this reason, structure traps are more suitable.

(2) Formation conditions, the lower both the injectivity and the conductivity, the lower the CO_2 injection and its sweeping.

(3) Storage pressure, the deeper the formation the higher the aquifer pressure that consists of overburden pressure and geostatic pressure.

(4) Transportation and injection system, the smaller the pipe's diameter the higher the flow rate, while the injection pressure is taken between 10 and 12 Mpa, for practical purposes. The water content higher than 500 ppm in the CO_2 flow along the pipe will cause a serious corossion.

(5) Environment aspects, care should be taken not to let the CO_2 leaks through surface installation, vertical injection pipe, or its geological reservoir.

III. MECHANISMS OF CO_2/WATER DISPLACEMENT

Very difficult to predict the real displacement process, because it is influenced by individual fluid mechanisms, fluids characteristics in the reservoirs, special conditions of rock matrix, and environment conditions of the reservoir formation. Closed model is made to repre-

sent the displacement model for CO_2 injection into the aquifers. In this model, carbonate rocks saturated with water (Sw =100%) at certain pressure was injected with CO_2 until reached a certain pressure. Not easy to predict the CO_2 distribution in this media, not only because of the dispersion and diffusion flow of the CO_2 itself, but also due the interreaction process between CO_2, water, and carbonate.

Pressure difference between reservoir pressure and fracture pressure is a reservoir's storage capacity to receive an amount of CO_2, besides its extention area and the reservoir thickness itself. The higher the pressure differences the bigger the space for CO_2 storage. This space can also be obtained from water compressibility, rock compressibility, also the reaction between CO_2, water and carbonate. Values of the compressibilities are around 10^{-6} vol/vol/psi, meaning that the space is very small for the storage. In the short time, the availability space cannot be expected from the reaction result between CO_2, water and carbonate. In the long run, this reaction plays the main role in creating large space for CO_2 storage. But, according to the researchers, the reaction results can be detected after 10 to 100 years.

In Figure 1 Van der Meer (1966) illustrated the basic concept displacement of the CO_2 into the aquifers. There are four types, i.e. A, B, C and D profiles can be identified during this displacement. Profile A is a shock front type as a result of CO_2 solubility in the water and absorbed as geochemical reactions. Profile B is a displacement front as a result of mixing process of two-phase fluids. Profile C is a maximum CO_2 saturation at S_{wir}, while profile D is a very high saturation of CO_2, and water will be absorbed it into dry CO_2.

Injection activity is usually followed by transition time, where the pressure is radially distributed, and the segregation influence will disappear. After CO_2 bubbles are formed, diffusion at the bubble edge occured, known as gas storage bubbles (Figure 2). The injected CO_2 will fill up the area around the wellbore to form much bigger CO_2 bubbles surrounded by several circles of two phase area, and the last circle is formation water. Next, gravitational effect reactive due to water saturated with CO_2 at the interface of CO_2/water lighter than water itself. This effect strongly depends on vertical permeability of the reservoir rocks.

Two things should be taken into account on the displacement process for the reservoir scale, i.e. mobility ratio and viscous fingering. As a certain fluid displacing another fluid, mobility ratio (M) can be defined as dis-

placing fluid mobility (CO_2) divided by displaced fluid mobility (water) and can be written as:

$$M = \frac{K_{r-CO2/\mu-CO2}}{K_{r-water/\mu-water}}$$

If M>1, means that below the pressure difference, CO_2 is able to push at the same water velocity, or faster than that. As CO_2 pushed the water, the gas tended by passing the water.

In general, CO_2 distribution in the aquifers is influenced by three basic mechanisms, i.e. displacement at microscopic, macroscopic, and megascopic scales.
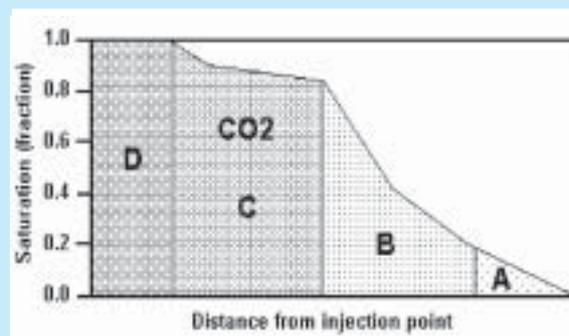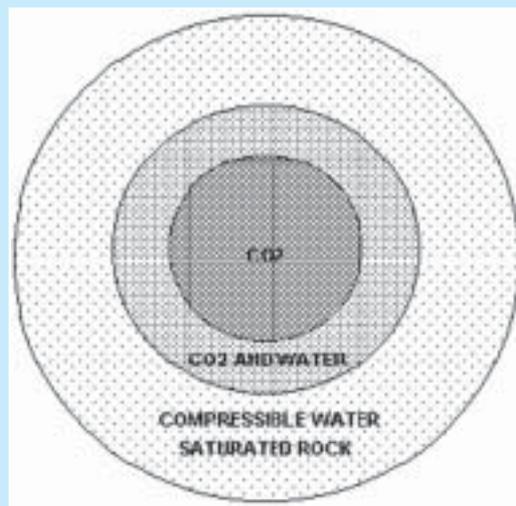

Figure 1
Displacement concept

Figure 2
Gas storage bubble around the wellbore

To assess whether an aquifer is potential to store CO$_2$, the effective volume should be determined first. But it is very difficult to estimate this volume, because of the variations under subsurface conditions. Even the estimation is obtained, but often misused the numbers. The storage efficiency of CO$_2$ is directly related to the pore volume itself, the higher the pore volume the bigger the potential storage.

IV. LABORATORY EXPERIMENTS

The experiments are conducted in order to evaluate CO$_2$ solubility in the water at various temperatures, and the storage efficiency of CO$_2$ in the water saturated carbonates. The most important variable to determine the storage efficiency of CO$_2$ is the pressure difference between the reservoir pressure and fracture pressure. This difference will determine the CO$_2$ solubility in water, the rocks compressibility, water compressibility, and the reaction between CO$_2$/water/carbonate that accelerates the form of new empty spaces. In the short term, the variable of CO$_2$ solubility in the water is the dominant factor. But in the long term, the space formed by this reaction also contributes upon the CO$_2$ storage.

A. Formation Water and Core Characterization

Based on the water analysis, the formation water content is around 18,000 ppm of dissolved solid. The water compressibility was measured at the temperatures of 200ºF and 250ºF, with the value of around 10^{-6} vol/vol/psi. The result of compressibility analysis indicated that formation water is a slight compressible, so that the volume changes were very small. The reservoir temperature of 200ºF and initial reservoir pressure of 1,000 psig that increased to 5,000 psig were only able to form the space of about 1.3%.

The properties of rock samples were obtained through SEM, X-ray diffraction and compressibility analysis. Based on the X-ray analysis, the rock content was almost 100% calcite, and a trace of dolomite mineral. Core plugs with the diameter of 3.82 cm and length of 6.9 cm were measured their porosity and permeability, the result is shown in the Table 1, while the compressibility were around 10^{-6} vol/vol/psi.

B. Experiment Equipments

Equipments for the experiment consist of three main parts, i.e. PVT cell, CO$_2$ displacement rig, and additional apparatus. The PVT cell, as shown in Figure 3, consists of cell with the volume of 635.021 cc at 60ºC. This cell is covered with a heating jacket, connected to a thermostat to maintain the experimental temperature. There is a valve in the lower part, connected to a displacing pump for increasing or decreasing the pressure. There is also a valve in the upper part, connected to two bottles, containing formation water and the CO$_2$, respectively; or a separator, if production or blow-down is conducted. Formation water bottle and CO$_2$ bottle are also equipped with pump to push each fluid to the PVT cell.

Schematic of the CO$_2$ displacement rig is shown in the Figure 4. It consists of core holder, with the length of

Table 1
Porosity and permeability core plugs data

No.	Lenghth (cm)	Diameter (cm)	Pore volume (cc)	Porosity (%)	Ka (mD)
1	1.81	3.82	2.22	10.69	0.36
2	5.07	3.82	7.80	13.45	5.96
3	6.83	3.82	21.38	27.38	51.40
4	6.98	3.82	12.15	15.21	1.97
5	6.83	3.82	11.99	15.35	1.51
6	6.97	3.81	14.74	18.54	2.75
7	6.97	3.81	14.87	18.70	2.75

6.90 cm and the diameter of 3.82 cm, is put into the circulating oven with a thermostat to control the temperature. Two bottles with piston, each containing formation water and CO_2 are also found inside the oven. *Quisix* pump is laid outside the oven connected to both bottles through tubing with inside diameter of 1/8 inch. A valve is also attached to both bottles to let them choose the connection with core holder much easier, if an injection is going to be conducted. The function of pressure trans-ducer at core holder's inlet and outlet is to observe their pressure changes. Meanwhile, a backpressure regulator set up at the core holder's outlet for adjusting the pressure inside the core. A separator is also available to separate CO_2 from the water during the production/ blow-down, if the experiment is finished.

C. *Experiment Modelling*

Two models used are applied to fulfil the purpose of the experiments. PVT cell is used for the first one, while CO_2 displacement rig for the second one.

The first model is solubility of CO_2 in the water at reservoir conditions. This model can be seen in the Figure 5. The PVT cell should be cleaned and vacuumed, before being injected with water of 80 cc psig. Then, it was heated up to 200 or 250°F and pressurized to 2,000 psig, shown as P1 at the initial condition. Next, CO_2 was injected into the cell with pressure of P2 until all the gas was soluble in the water. The P2 pressure was determined almost equal to mixed bubble pressure of CO_2/water. This injection was repeated several times until P3, P4 with pressure inside the cell was about 5,000 psig or estimated as reservoir fracture pressure. Finally, when the experiment concluded, a blow-down was conducted, where the fluids were pushed using a Quisix-pump and the volume obtained was noted for the following calculation.

The second model was an injection of CO_2 into the core plug saturated with water using the displacement rig apparatus as
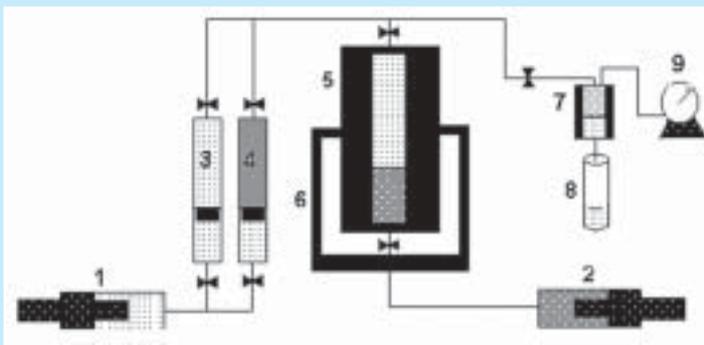
1. Injection pump
2. Displacement pump
3. Water bottle
4. CO_2 bottle
5. PVT cell
6. Shaker guard
7. Gasometer
8. Fraction collector
9. Gasometer

Figure 3
PVT cell
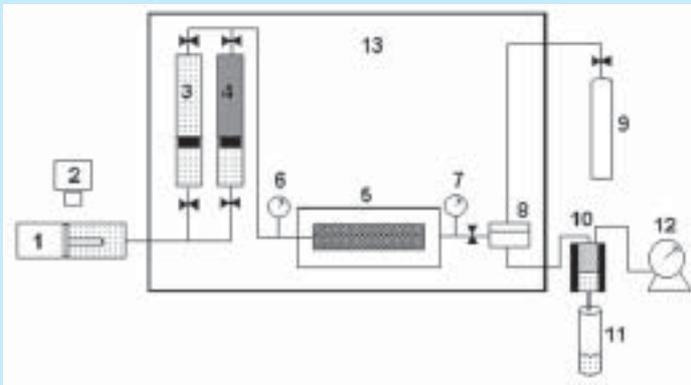
1. Injection pump
2. Controlling computer
3. Water bottle
4. CO_2 bottle
5. Core holder
6. Inlet pressure indicator
7. Outlet pressure indicator
8. Pressure regulator
9. Confining gas
10. Separator
11. Fraction collector
12. Gasometer
13. Oven

Figure 4
Displacement rig

P1<P2<P3<P4
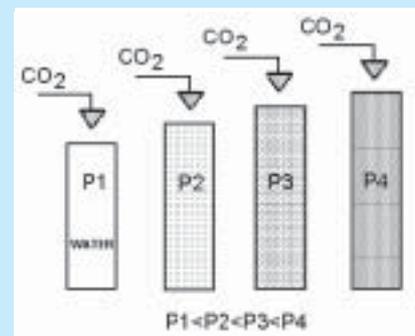
Figure 5
Model 1

shown in the Figure 6. Cleaned core plug with known porosity and permeability was laid in the core holder. Then, it was vacuumed for two days and heated until 200°F. Next, the screened formation water was injected into the core plug with the pressure of 1,600 or 2,000 psig (P1) assuming the same reservoir pressure. After that, CO$_2$ was injected into the core plug with the injection pressure (P2) higher than the water pressure in the core plug itself. This condition was remained for a few of time to let the occurring of dispersion and diffusion flows in the core plug and also the reaction CO$_2$/water/carbonate. After the pressure was stable, next injections are conducted with the pressure of P3, P4, or fracture pressure was reached. The blow-down was performed when the injection was done. A Brook-meter was used to measure the volume of CO$_2$, while the water in the tube would be analyzed its ions content.

D. CO$_2$ Solubility in the Water

This is influenced by temperature, pressure, and salt content. At high pressure and temperature, CO$_2$ becomes a supercritical (Figure 7), and this will be more soluble in water. In general, the higher the pressure the higher the CO$_2$ solubility will be in the water. At the constant pressure, the increase of temperature tends to decrease the solubility. The decreasing of solubility is also observed as salt content is increased.

The results are shown in Figure 8, which indicated that CO$_2$ solubility in water increased drastically as the pressure increased up to 3,000 psig. Beyond this, the solubility increased very small. At the pressure of 3,000 psig, the solubility was 147.46 SCF/STB at the temperature of 250°F, and it would be 157.54 SCF/STB at 200°F.

While at the pressure of 5,000 psig, the solubility was 177.69 SCF/STB at the temperature of 250°F, and it would be 189.09 SCF/STB at 200°F.

V. CO$_2$ STORAGE EFFICIENCY IN THE WATER SATURATED CARBONATE ROCK

This efficiency is evaluated through the experiment using the displacement rig. The experiments were performed four times with constant temperature of 200°F.

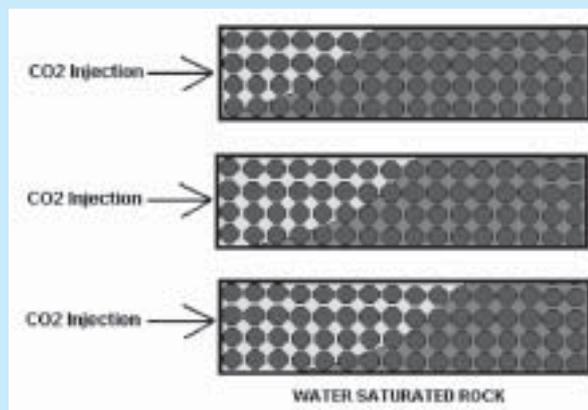First displacement was conducted to core plug No. 3 with its porosity of 27.38% and permeability
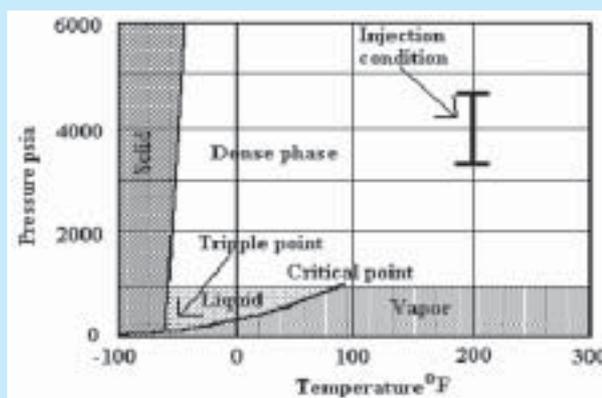
Figure 6
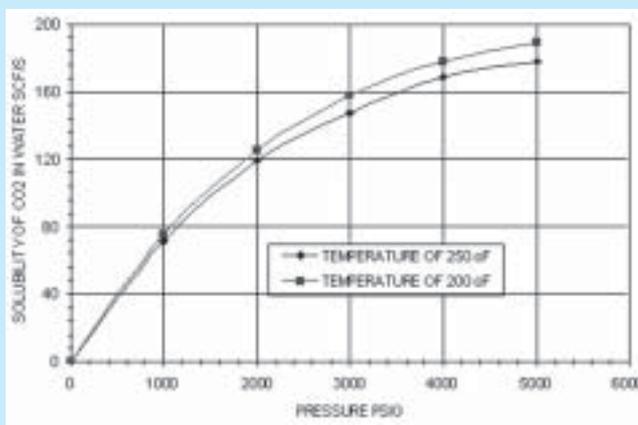**Model 2**

Figure 7
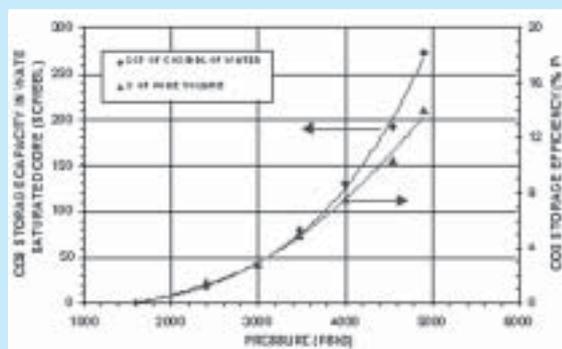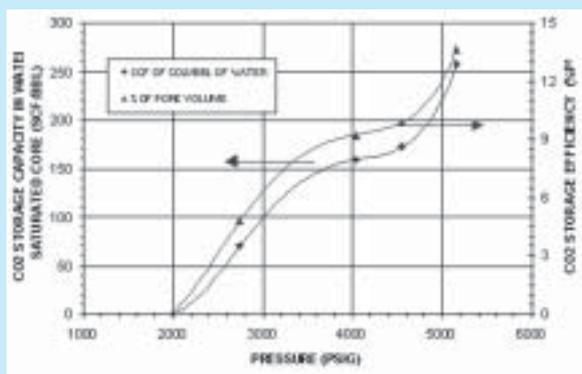**PT diagram for carbon dioxide**

Figure 8
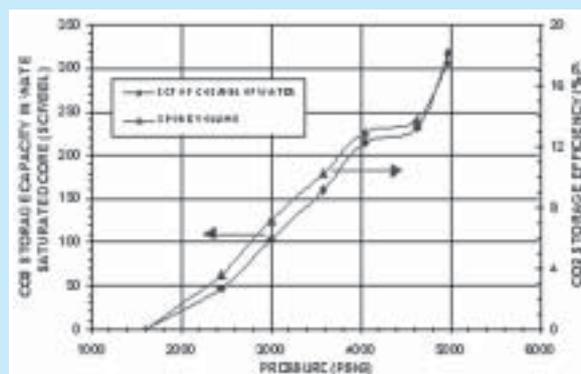**Solubility of CO$_2$ in water**
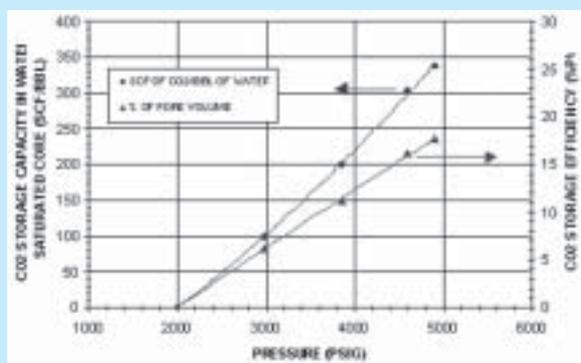
Figure 9
CO₂ storage efficiency in water saturated core no. 3

Figure 11
CO₂ storage efficiency in water saturated core no. 6

Figure 10
CO₂ storage efficiency in water saturated core no. 5

Figure 12
CO₂ storage efficiency in water saturated core no. 7

(Ka) of 51.40 md. The experiment results can be seen in the Figure 9, where with the initial pressure of 2,000 psig, the core plug was able to store CO_2 338.63 SCF/ BBL, or 17.72% pore volume at pressure of 4,912 psig.

Second displacement was conducted to core plug No. 5 with its porosity of 15.35% and permeability (Ka) of 1.51 md. The experiment result can be seen in the Figure 10, where with the initial pressure of 2,000 psig, the core plug was able to store CO_2 257.79 SCF/BBL, or 13.62% pore volume at pressure of 5,162 psig.

Third displacement is conducted to core plug No. 6 with its porosity of 18.54% and permeability (Ka) of 2.75 md. The experiment result can be seen in the Figure 11, where with the initial pressure of 1,600 psig and temperature of 200°F, the core plug was able to store CO_2

272.16 SCF/BBL, or 14.03% pore volume at pressure of 4,900 psig.

Fourth displacement is conducted to core plug No. 7 with its porosity of 18.70% and permeability (Ka) of 2.75 md. The experiment result can be seen in the Figure 12, where with the initial pressure of 2,000 psig, the core plug was able to store CO_2 318.11 SCF/BBL, or 17.62% pore volume at pressure of 4,967 psig.

VI. CHARACTER CHANGES OF FORMATION WATER AND CORE

After completing the experiment of CO_2 displacement into the water saturated core plugs, the fluids should be blown down, where the water and CO_2 were collected. Only Ca and Mg ions could be analyzed due to

limited volume obtained. Before and after the displacement, core plugs were evaluated through porosity and permeability measurements, XRD, SEM and Thin Section analysis. The purpose of this evaluation is to obtain the evidence changes, if any, on porosity, permeability, mineral content, and pores structure.

A. *Formation Water's Character Changes*

Table 2 shows the analysis result of Ca and Mg ions content, before and after the displacement. In general, the Ca ion content indicated a sharp increase. On the contrary, Mg ion content tended to decrease. Core plug No. 3, for instance, the Ca ion content before the injection was 2.45 ppm and became 28.19 ppm after the injection, or about 1050% higher. In general, the increase of Ca ion content was in the range of 442.86 to 1050%.

Meanwhile, the Mg ion content in the same core was 23.91 ppm that became 4.96 ppm, or a decrease of 79.26%. The average decrease of Mg ion was 12.68%

to 79.26%.

B. *Core Plugs' Character Changes*

The permeability to water decreased between 15.74% and 26.47% (Table 3). This is influenced by the reaction rate of the mixtures of CO_2/water/carbonate, since carbonate solubility produces loose grains that plug the rocks' pores. This kind of plugging could be detected when measuring the value of Kw after the displacement, where the inlet pressure and the outlet pressure showed instability. The stability could be obtained again after injected with high rate water, such as 3cc/min. After being dried, the core plugs were measured their porosity (Table 3). All core plugs indicated an increase of pore volume, between 0.74% and 1.80%. The value might be change depended on the reaction time.

C. *XRD and SEM Analysis*

Qualitatively, XRD analysis can't differentiate the minerals changes in the core plugs, before and after the

Table 2
Permeability and porosity of core plugs changes

| Core samples number	Ka (md)	Kw			Volume pori		
		Before injection (md)	After injection (md)	Changes (%)	Before injection (cc)	After injection (md)	Changes (%)
3	51.40	1.11	0.92	-17.415	21.51	21.71	0.93
5	1.51	0.29	0.22	-23.077	12.03	12.12	0.74
6	2.75	0.41	0.30	-26.471	14.81	14.93	0.80
7	2.75	0.45	0.38	-15.743	14.93	15.20	1.80

Kw: *Permeability to water*

Table 3
**Concentration of Ca and Mg ions in formation water changes**

| Core samples number	Concentration of Ca ion			Concentration of Mg ion		
	Before injection (ppm)	After injection (ppm)	Changes (%)	Before injection (ppm)	After injection (ppm)	Changes (%)
3	2.45	28.19	1049.99	23.91	4.96	-79.26
5	25.74	139.71	442.86	32.16	27.63	-14.08
6	25.74	149.51	480.95	32.16	28.08	-12.68
7	25.74	140.96	447.72	32.16	27.93	-13.16
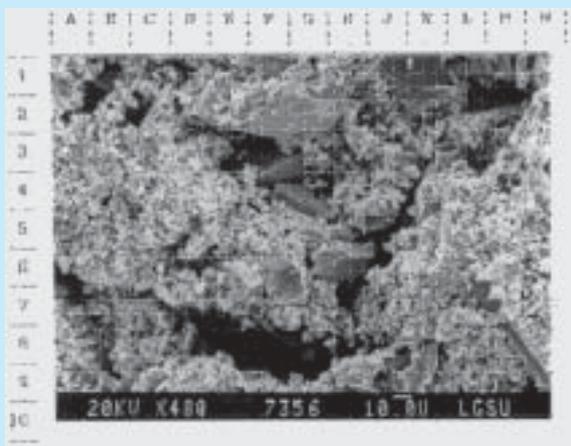
Figure 13
SEM analysis of core plug no. 5 before injection of CO$_2$
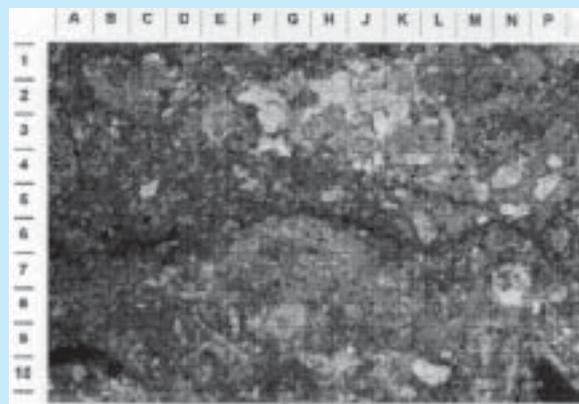
Figure 15
Thin section analysis of core plug no.5
before injection of CO$_2$
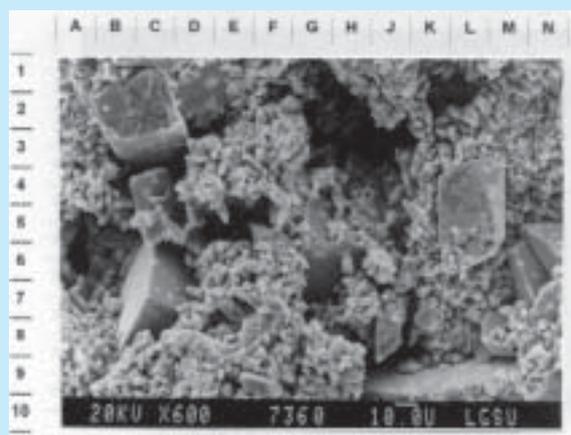
Figure 14
SEM analysis of core plug no. 5 after injection of CO$_2$
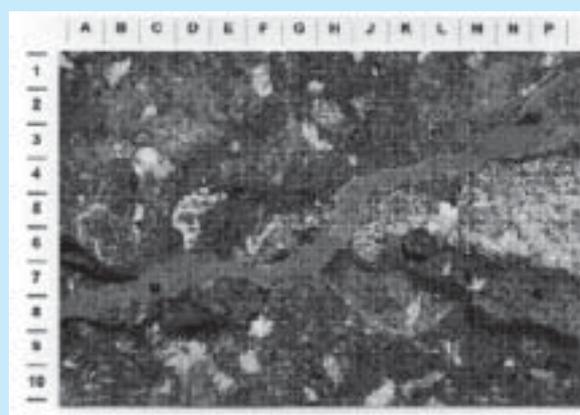
Figure 16
Thin section analysis of core plug no.5
after injection of CO$_2$

CO$_2$, due to short run on the chemical reaction between CO$_2$/water/carbonate.

Core plugs Nos. 3 and 5 were analyzed through SEM before and after injection. They are shown in Figure 13 for core plug No. 5 before injection with magnification 480 times, and Figure 14 for after injection. Figure 13 shows a good crystal of sparry calcite with black micro fracture, the spary calcite crystal growth in the rocks' pores (F-7) with rocks porosity distribution, and its matrix is still in the initial condition with good crystal shape (F-J, 3-6).

SEM after injection shown in the Figures 14 represents cleaning of soft materials from the surface of

micrite matrix and a big crystal of sparry calcite in the initial shape. This figure also indicates cleaner pore spaces with subrounded form of micro crystal.

D. *Thin Section Analysis*

Under the microscope, core plugs No. 3, 5 and 6 were photographed, before and after the injection. Photos for core plug No.5 after and before injection only, are also shown.

Figure 15 illustrates the core plugs No. 5 before injection with magnification 33 times. It indicates a coral boundstone of reef dolomite with closed suture stylolite, and a coral framework tightly cemented.

After the injection as shown in Figures 16 indicates that fracturing possibly due to the CO_2 injection pressure. Most of the fractures follow the suture stylolite but parts have crossed it.

VII. CONCLUSION

1. CO_2 solubility in the water is strongly influenced by pressure and temperature. This solubility increases drastically until the injection pressure is 4,000 psig. As the pressure higher than this, the solubility is insignificant. On the other hand, the increasing temperature tends to decrease the solubility. With the pressure of 5,000 psig, the solubility is 189.0 SCF/STB at temperature of 200°F, and to be 177.7 SCF/STB at 250°F.

2. The efficiency of CO_2 storage in the water saturated core plugs is influenced by the difference of initial pressure (reservoir pressure) and final pressure (fracture pressure), porosity, permeability and rocks damage. The higher the pressure difference the higher the storage efficiency. In general, the higher the porosity and permeability, tends followed by the higher its storage. In some cases, this storage is reduced by a decrease of permeability due to the reaction of CO_2/water/carbonate. With the initial pressure of 1.600-2.000 psig and the final pressure of 5.000 psig, the storage efficiency is around 13.6 to 17.7% of pore volume.

3. During the process of CO_2 displacement into the saturated water core plugs, a chemical reaction between CO_2/water/carbonate is occurred. This is indicated by an increase of Ca ion and a decrease of Mg ion the formation water. The average increase of Ca is 450%, while Mg decreases of 13%.

4. The chemical reaction decreases the permeability to water (Kw) of about 20% and increases the porosity of 1% in the core plugs.

5. Qualitatively, observation through SEM and Thin Section Analysis indicated that some carbonate mud is soluble in the water, micrite mineral changes into more subrounded form, and some fractures in the suture stylolite

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