CO_2 Sequestration in Deep Saline Aquifers: Investigation of pH Effects in Pressure and Temperature Representative Aquifers.

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***Abstract*—The purpose of this study is to study the sequestration of CO2 in deep saline aquifers. The means to sequestrate the CO2 in deep saline aquifers is a way to mitigate the emission of greenhouse gases that cause the nowadays global warming. The specific objectives of this study is to investigate the effect of the pH variations at various temperatures, to investigate the effect of brine salinity on pH of the solution at various reaction times and to study the carbonation process. The experiment is carried out in controlled lab in UiTM Shah Alam and using the specially designed rig setup that consists of equipment such as reactor and analytical devices. The maximum operating pressure and temperature for this experiment are 200 atm and 300°C respectively. The results of this study were then analyzed using X-Ray Fluorescent (XRF) to study for carbonation.**

***Keywords—Sequestration, deep saline aquifers, CO_2, pH, carbonation, mineral trapping, mineralization*.**

I. INTRODUCTION

Excessive increase of CO_2 has put burden on our earth and it is beyond earth's capacity to absorb all of this excessive gas naturally. The CO_2 contributed the highest amount, about 64% of the total greenhouse effects alongside with other greenhouse gases [1]. One of mitigation initiative is to store the CO_2 in a place isolated from our environment; which also termed as sequestration and deep saline aquifers are the best candidate for sequestration site; due to its largest potential in volume for CO2 storage in geological media [1]. It has been estimated that world aquifers could provide a storage capacity of up to 1 x 1113 tonnes of CO2 which is enough to store several hundred years of the world's CO2 emission [2]. Depleted oil and gas reservoirs always had been the best option among debaters when discussing the topic of potential sequestration sites. There are so many factors that favored the depleted oil and gas reservoirs to be the chosen site for unwanted CO2 sequestration. It is a good debate in general but further and meticulous judgment need to be done in assessing the suitability of using depleted oil and gas as sequestration site for long term action. Mathematically, the potential capacity offered by depleted oil and gas reservoirs is relatively small compared to other potential sites such as ocean and deep saline formation. By hook or by crook, in the future this disadvantage of capacity shortage will again rise again as possible problem for sequestration in depleted oil and gas reservoirs. Another vital consideration of depleted oil and gas reservoirs is that the readiness of the facility in place. This type of reservoir is considered as an option is mainly because of these several factors. First thing to note is that this type of reservoir or basin can provide all the proven characteristics due to the exploration and production that took place before that. Other than that, these reservoirs already extracted and leave us with some space that can be filled with CO2. To add, the depleted oil and gas reservoirs normally will having the abandonment phase as they were not economically or feasibly produce anymore. The most helping factor of all, this kind of reservoirs will aid sequestration in term of cost as for the facility they provide. The subsurface facility, the producing and injection wells and maybe the pipelines will lend a big hand to this sequestration project. Nevertheless, these already-in-place facilities will bring along the worries of the reliability of the facilities as if these facilities will create such potential leakage [4]. Thus, additional cost will be needed for ensuring the safety and reliability of these facilities although it will not cost as much as the initial startup. However, despite all the worries, the project at Weyburn, which consist of more than hundred wells, had successfully operated for more than four years without any reported leakage incident [5]. Deep saline aquifer is the underground formation that normally contained water and brines. Normally during the exploration phase, the oil and gas companies that intend to exploring the hydrocarbon-bearing formations facing a routine risk that they might found the unprofitable formations such as aquifer. The large capacity of this deep saline aquifer provides some assurance for future sequestration process. It is believed that the capacity offered by this type of site can afford the human to sequestrate the world's emission of CO2 for some decades [6]. The objective of this study is to investigate the effectiveness of CO_2 sequestration in deep saline aquifers by analyzing the pH variations at various temperatures and various brine salinity, also to analyze the chemical reaction during the reaction.

II. METHODOLOGY

The experiment utilized sand and shale taken from Malay Basin, and 2 brines with different concentration which were prepared as previous study done Qi Liu (2010) [3]. The reaction took place in a 1-L stainless steel reactor which can operate at temperature as high as 300 centigrade and at pressure not more than 3000 psi.

A. pH reaction in various temperatures

Sand and brine were mixed in the reactor followed by the injection of the CO_2 in the reactor. The reactor was then heated up to 70 ^{O}C and constant pressure of 1000 psi. The same procedure repeated with mixture of shale and brine. 1 hour reaction time allowed and the pH value of effluent was immediately measured using pH meter after recovered from the reactor. The experiment repeated using different temperatures which were 100 ^{O}C and 150 ^{O}C.

B. *pH variations in different brine salinity*

All of the procedures in A were repeated with some alterations on operating pressure and temperature. With constant pressure 1000 psi and constant temperature at 150 ^{O}C, the first set of experiment using 10000 ppm brine and followed by 15000 ppm brine in second set. The procedures repeated for both sand and shale samples.

C. *pH stability after carbonation reaction studies*

For this experiment, the pH of the effluents from experiment B was measured for every hour for the first 4 hours. These measurements after reaction were done for both sand and shale samples.

D. *Carbonation studies*

The mixture of sand and 15000 ppm brine was placed in the reactor followed by injection of CO_2 at 1300 psi. With the furnace set at 250 ^{O}C, the process was allowed for 1 hour. The effluent from the reactor recovered and filtered using Whatman filter paper. The solid part of the effluent was left in the dryer for 24 hours to remove all the moisture content. The dried solid was then analyzed using XRF for carbonation studies.

III. RESULTS AND DISCUSSION

A. *pH reaction in various temperatures*

Table 1: pH readings at various temperatures

Sample	Temperature (^{o}C)		
	70	100	150
Sand + 10000ppm brine	7.55	6.71	7.24
Sand + 15000ppm brine	6.42	6.84	7.07
Shale + 10000ppm brine	6.62	6.86	7.14
Shale + 15000ppm brine	6.52	6.64	7.25

The below graph was constructed using the data in Table 1. It shows the trend of the pH readings of the samples when reacted at different operating temperatures.

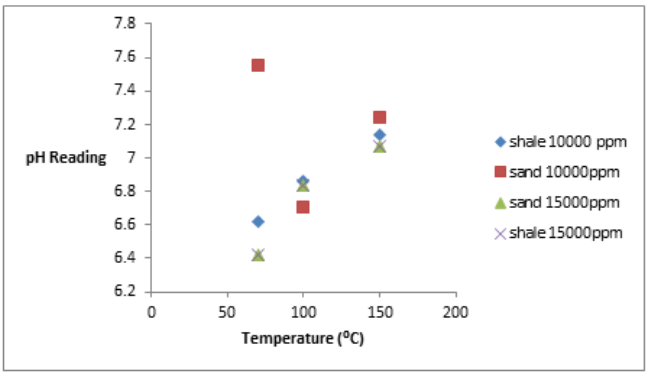


Fig. 1: Scattered chart for pH readings against various temperatures

From the analysis of the graph, it can be seen that pH readings will be stabilized or close to region of 7 when reacted at higher temperature. In their initial condition, the pH measurement for the mixture of sample indicated that they are basic with their pH readings were around the region of 9 – 10. After the reaction, most of the samples have significant decrease in their pH values. There is possibility that the samples have undergone carbonation during the reaction. The reaction of CO_2 with water will yield carbonic acid and this explains the decrease in their pH measurements.

B. *pH variations in different brine salinity*

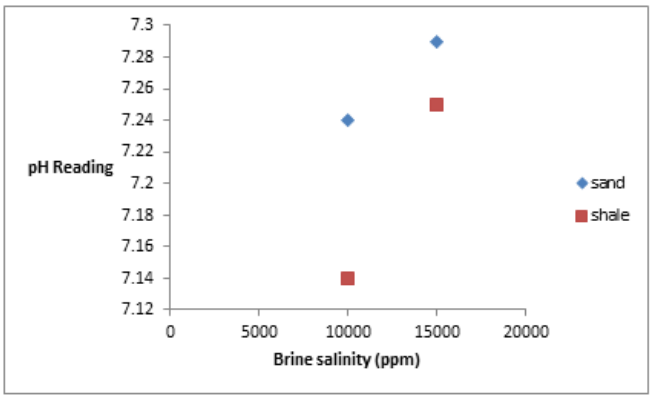


Fig. 2: Scattered graph of pH readings against different brine salinity

Through observations from the graph, it showed that values of pH varied significantly with brine salinity. The pH readings for shale sample were noticed more acidic than the sand. They indicated that, the higher the salinity of the brine, the higher the pH. This can be justified within the definition. Higher salinity means higher amount of dissolved contents. The higher salinity of the brine in turn has higher amount of dissolved metals in it.

C. *pH stability after carbonation reaction studies*

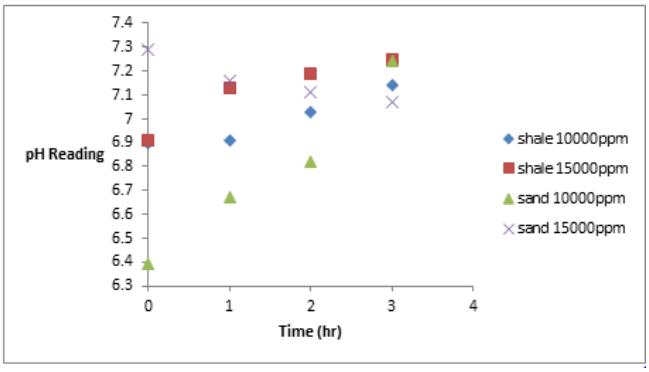


Fig. 3: pH readings after several hours

The above graph was plotted using the data in Table 4.4 where the measurements are taken for every 1 hour. There is an observable trend in the graph whereby, the values of pH increase accordingly with increasing of time after the reaction. To add, the sample's pH tend to stabilize around neutral zone after the reaction. This means that the reaction still occurred in the mixture after been discharged from the reactor. The bright side of this results is that we can be assure that their final pH were not acidic and not too basic which means it is an acceptable pH for aquatic living. Please note that actual seawater's pH is around 7 to 8.

D. *Carbonation studies*

Table 2: Weight comparison for sand sample

Sand Sample	Weight (g)
Before	5.00
After	5.11

The difference in weight of the sand sample suggested that there were some alterations on the sample that might occur during the reaction. There is high possibility that the extra mass after the reaction came from precipitation during carbonation process which took place in the reactor.

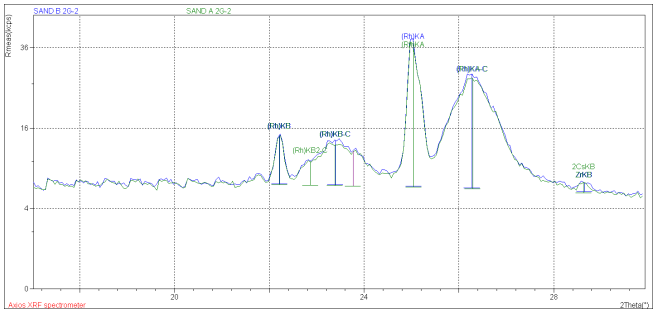


Fig. 4: XRF spectrum for sand samples

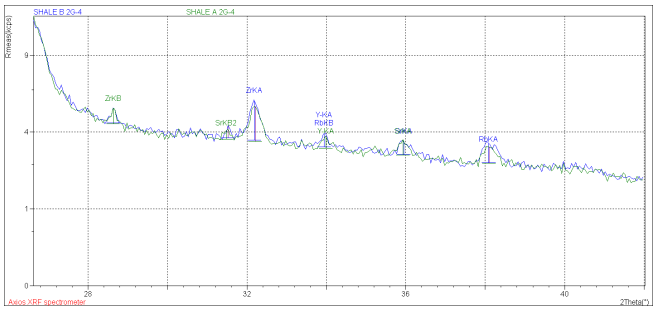


Fig. 5: XRF spectrum for shale samples

Based from the XRF results obtained, it can be observe that there are some slight changes on sample's composition after the reaction. By referring to the difference in sand's composition, some of major elements such as Mg, Al, Ti, Ca and Fe were reduced in their amount after the reaction. The other noticeable change is the existence of some new unknown elements with small quantities. These elements that have been discussed were undefined because of the limitation of the analytical device, in this case, x-ray fluorescent (XRF). The analysis using XRF was conducted by utilizing a special standard for sand detection and any other elements which uncommon in sand will be detected as unknown element. The loss of metal elements amount were believed had contributed in production of the new unknown elements, Y2O3 and ZrO2. It also observed that the amount of mercury elements in initial sample had been reduced after the reaction.

Meanwhile for the shale analysis, the observation from the results indicated that there were increments to the certain major elements such as Mg and Si. In contrast to the sand, the shale reaction is believed to enhance the oxidation of these elements. The amount of oxidized mercury in the shale sample found to be higher than in the sand but as the sand's reaction, the amount of oxidized mercury in shale also decreased after the reaction.

IV. Conclusion

The results indicated that various operating temperature will provide various outcomes. The higher temperature will contribute in higher pH readings towards the end of experiment. It also observed that the pH values of reacted samples will become closer to neutral as time flies by. The brine salinity also affects the sample's pH as higher salinity of brine will increase the initial pH readings. However, the pH after the reaction showed that the pH of reacted mixture will undergo significantly reduced pH. As for chemical reaction analysis, it is believed that mineralization process already occurred during the reaction. This is due to the gain of extra mass after the reaction in sand's sample. The detection of new elements through XRF analysis also supports the hypothesis that mineral trapping, or mineralization already occurred during the reaction. This carbonation experiments provided similar trends with previous study done by Qi Liu (2010). The carbonation process preferred to take place in pH higher than 9 which is in basic condition, and the values of pH have significantly reduced after the reaction. The temperature and pressure used for the reaction is considered as high temperature and high pressure as well as most deep saline aquifer's conditions. The highest dropped value of pH was observed to happen at the reaction with highest pressure and highest temperature which are 1300 psi and 250 ^{o}C thus justified that the carbonation could take place in actual deep saline aquifers. As for the solid analysis, a different trend observed for sand and shale reaction whereby the sand's composition happened to be reduced after the reaction added with new elements believed to be precipitated from carbonation reaction meanwhile the shale composition has a little increment after the reaction. The percentages of newly formed unknown elements are considered small but the research has met its objectives to find out the pH relationship with carbonation process and to investigate the carbonation of minerals during the experiment.

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