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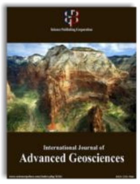

Investigation of PH effect in a mixture of basalt and iron on co_2 sequestration in synthetic brines

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Abstract

CO_2 sequestration in deep saline aquifers is a critical component of long-term storage options. It is suggested that the precipitation of mineral carbonates is mostly dependent on brine pH and is favoured above a basic pH of 9.0. However, brine pH will drop to acidic values once CO_2 is injected into the brine. Therefore, there is a need to raise brine pH and maintain it stable. Synthetic brines were used here instead of natural brines because of the difficulty in obtaining and storing natural brines. Therefore, experiments were conducted to prepare a series of synthetic brines and to compare their suitability to natural brines for carbon sequestration. A typical formation rock (basalt) and a buffer solution (0.3M Tris buffer solution) were selected to buffer brine pH. The results show that synthetic brines prepared can be used as analogues to natural brines for carbon sequestration studies in terms of chemical composition and pH response. This study investigates the effect of iron $(Fe^{2+}\ and\ Fe^{3+})$ in the pH of six synthetic brines prepared as analogue to oil-field brine by conducting a pH stability studies for CO_2-brine experiment and CO_2-basalt-brine experiment. In a subsequent step, studies were conducted to correlate how brine samples respond in the presence of basalt and the buffer solution. X-Ray powder Diffraction (XRD) analyses were also carried out to characterise the mineralogy of the synthetic brines. The result of the XRD confirmed that calcite was the major component that was dominated in the CO_2-brine–experiment while slight occurrence of calcite, iron oxyhydroxides and dolomite precipitated in the CO_2-rock-brine experiment. It was observed that ferric iron (Fe^{3+}) and its reaction with host rock (basalt) did not contribute to pH instability therefore making it suitable for precipitation of carbonate mineral while ferrous iron (Fe^{2+}) in the absence of host rock did not contribute to pH instability therefore making it also suitable for precipitation of carbonate mineral.

Keywords: *CO2 Sequestration; X-Ray Powder Diffraction; PH Stability; Basalt.*

1. Introduction

The capture and storage of CO_2 in geological formations can be seen as a significant method for preventing the effects caused by burning of fossil fuel on global climate change. Though some effort has been made to optimize the technologies needed for the sequestration of CO_2 to address or guide against potential dangers that is associated with increased atmospheric CO_2 concentration such as changes in the weather and sea level rise [1]. CO_2 geological storage along with conservation of energy and non-fossil fuel energy sources is described to be the only method of controlling the ongoing rapid increase of atmospheric CO_2 [2].

At a larger source of CO_2 emission such as biomass energy facilities or fossil fuel, CO_2 can therefore be captured directly, compressed and transported to a suitable storage location. [3]. Potential storage location for CO_2 includes saline aquifers in deep onshore and offshore sedimentary formations, the deep oceans and in basalts, ultramafic and granitic rock. Sequestration of CO_2 with the use of brine is an important technique necessary for controlling the effect of climate change. Brine solution is referred to as a saline-based solution which is produced during the production of oil and gas as a waste product. The production of brine in Pennsylvania is approximately 60 million gallons per year whereas the total production of brine in USA is estimated to be 19 billion gallons [4]. The occurrence of large amount of brine at the surface of the earth would supply potential feedstock for CO_2 conversion into carbonate minerals such as calcite, magnesite and siderite. Series of reaction are initiated as a result of dissolution of CO_2 in brine which causes the carbonate ion to be bonded together and eventually leading to the precipitation of carbonate. Druckenmiller et al. [5] emphasized on the significance of brine pH in the formation of carbonates. They identified the important parameters necessary for the precipitation of carbonate mineral. These include temperature, brine composition, pressure, rock composition and brine pH. They concluded that brine pH and composition is the most important parameter necessary for the carbonate formation. It is well known that oilfield brines are acidic in nature with the pH value ranging between 2-5.Injections of CO_2 into the brine would result in a more acidic pH and under these condition, the formation of mineral carbonate will not take place. It is therefore necessary for the brine pH to be increased to pH of close to 9.0 because of the presence of carbonate ion (CO_3^{2-}) in order to accelerate the formation of mineral carbonate. This can be achieved with the use of addictive or by using buffer solution. However, one factor that must be examined in order to accelerate the formation of mineral carbonate by adjusting pH in oil field brines is the effect of iron in the solution. The hydrolysis of this iron cation i.e both ferric iron (Fe^{3+}) and Ferrous iron (Fe^{2+}) in brine solution involves the adjustment of pH because of its ability to form series of partly oxidized divalent Fe^{2+} to oxidized insoluble Fe^{3+} complexes which might reduce the effectiveness of the oil field brine usage for CO_2 sequestration. Ferrous iron (Fe^{2+}) is highly soluble in brine solution while Ferric iron (Fe^{3+}) has low solubility with a pH of above 1.0. [6].Previous studies have shown that the presence of iron cation in brine might result in pH instability which then lowers the formation of mineral carbonates but it was not stated which of the iron cation (Fe^{2+}or Fe^{3+}) caused the pH instability[7]. In order to make the sequestration of CO_2 in brine through the formation of mineral carbonate a more promising option, the effect of iron cation in brine pH needs to be studied in order to predict a suitable range of pH for further mineral carbonate formation. Basaltic formations have been selected as the most favourable location for the precipitation of carbonate minerals when SO_2 - CO_2 gas mixtures are co-injected. Basalts are formed from volcanic eruption by the solidification of lava over a repeated occurrence leading to the accumulation of thick layer sequence .CO_2 injection into basaltic formation is considered very important because of the high reactivity of mafic rocks compared to its injection in a sandstone reservoir which converts the injected CO_2 into a solid phase. Basalt consists of minerals with high composition of magnesium, calcium and iron which reacts with CO_2 to form carbonate minerals. The Injection of CO_2 into a basaltic formation provides numerous benefits which includes potential storage via mineralisation and a greater storage volume capacity [8]. CO_2 are mostly injected as a separate buoyant phase and can be trapped underneath an impermeable cap rock layer into a very large sedimentary basins, this process requires a cap-rock with relatively high integrity for the long term storage of CO_2. The risk related with the buoyancy of CO_2 can be controlled when dissolved in water during injection process. Once the CO_2 is dissolved in water, it loses its buoyancy which makes its injection into fractured rocks e.g. basalts possible. A major advantage of storage within the basaltic formation is that some chemical component in basalts would react with CO_2 charged water to form stable carbonate minerals which increases the storage capacity

2. Problem definition

Brine pH and composition are identified as the most important parameter necessary for the precipitation of carbonate minerals during CO_2 sequestration in brine. Druckenmiller and Maroto-Valer [9] studied the effect of brine composition in sequestration of CO_2 in brine where barium and strontium were the main target ion investigated. They further concluded that barium and strontium does not affect the stability of brine pH. However, consideration should be given to studying other ions present in the brine which may have effect on the brine pH. Since the brine pH of close to 9 favours the precipitation of carbonate minerals, it is therefore necessary to adjust the initial pH of the brine to > 9 by using buffer solution and observe the stability of the pH when ferric and ferrous iron reacts with brine both in the presence and absence of a host rock (basalt). Basaltic formations have been selected as the most favourable location for the precipitation of carbonate minerals during CO_2 sequestration in brine but there are some questions that still need to be addressed relating to the effect of iron concentration in brine when reacting with basalt. These includes

1) Can the mixture of basalt and the buffer solution enhance the brine PH during the reaction?
2) What effect does ferric and ferrous iron have on the brine pH over time to promote mineral carbonate precipitation?
3) The effect of iron on the buffering ability of buffer solution to enhance brine pH to favour mineral trapping?

These questions can be answered by conducting a pH stability studies on this reaction. This would enable us to understand the relationship between brine composition and the ability of the brine to maintain an elevated pH that favours mineral trapping over time. The aim of this study is to conduct a pH stability studies to investigate the effect of iron concentration in brine when reacting with basalt to promote carbonate formation for CO_2 sequestration.

3. Methodology

The experimental work in this study will be divided into two groups. Firstly, three synthetic brine (brine 1, brine 2 and brine 3) were prepared with Fe^{2+}, Fe^{3+} and no iron respectively while the second stage is when this three synthetic brine reacts with a host rock (basalt). A total of 6 experiments were conducted (Table 1).pH stability studies were conducted to observe how this synthetic brines containing iron cation respond in the presence of this host rock. The experimental plan used in this study is in accordance with experimental methodology of Liu Q and Maroto-Valer [10] as described in the literature review

Table 1: Summary of the Experimental Studies

Experiment	Composition
1	Brine 1(containing Fe^{2+})
2	Brine 2 (containingFe^{3+})
3	Brine 3 (no iron)
4	Brine 1 with Fe^{2+} and basalt
5	Brine 2 with Fe^{3+} and basalt
6	Brine 3 containing basalt and no iron

3.1. Preparation of synthetic brine

In order to compare with previous studies and also to stimulate relationship that would show that the synthetic brines prepared can be used as analogues of natural brines for carbon sequestration studies, the average value of the target ion concentration of two natural brines PA and PBT which was used in a previous study (Micheal et al [11] and Liu Q and Maroto-Valer [12]) was chosen in this study for the preparation of the synthetic brine. The origin of brine (PA) came from natural gas well located in Pennsylvania, USA while Brine (PBT) was obtained from water treatment facility from which oil field brines are collected from different wells in Pennsylvania, USA. Due to the complex composition of oil field brine, the main ion chosen for the preparation of this synthetic brine includes Na^{+} Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, K^{+}, Cl^{-} Fe^{2+} and Fe^{3+}. These nine ion concentration was attained by the dissolution of the following salts KCL, NaCl, $MgCl_2.6H_2O$,$CaCl_2.2H_2O$,$SrCl_2.6H_2O$, $BaCl_2.2H_2O$, $FeCl_2$, $FeCl_3.6H_2O$ in deionized Millipore water. The reason for selecting these salts in this study is because they contain the nine main ions expected. The synthetic brine solution was mixed thoroughly in a beaker with magnetic stirrer until it was completely dissolved (fig.1). Accordingly, the selected target ion concentration for this study is representative of oil field brines for CO_2 sequestration. Tables 2, 3, and 4 show the target ion concentration and the amount of salt used for each brine. From the target ion concentration chosen, it can be seen that it is high salinity brine which was based on previous study [11]. The formular that was used to calculate the amount of salt used is given below:

$$\text{Mass of salt(g)} = \frac{\text{Molar mass of salt}}{\text{Molar mass of ion}} \times \text{Target ion concentration} \times \frac{1\ \text{litres}}{1000}$$

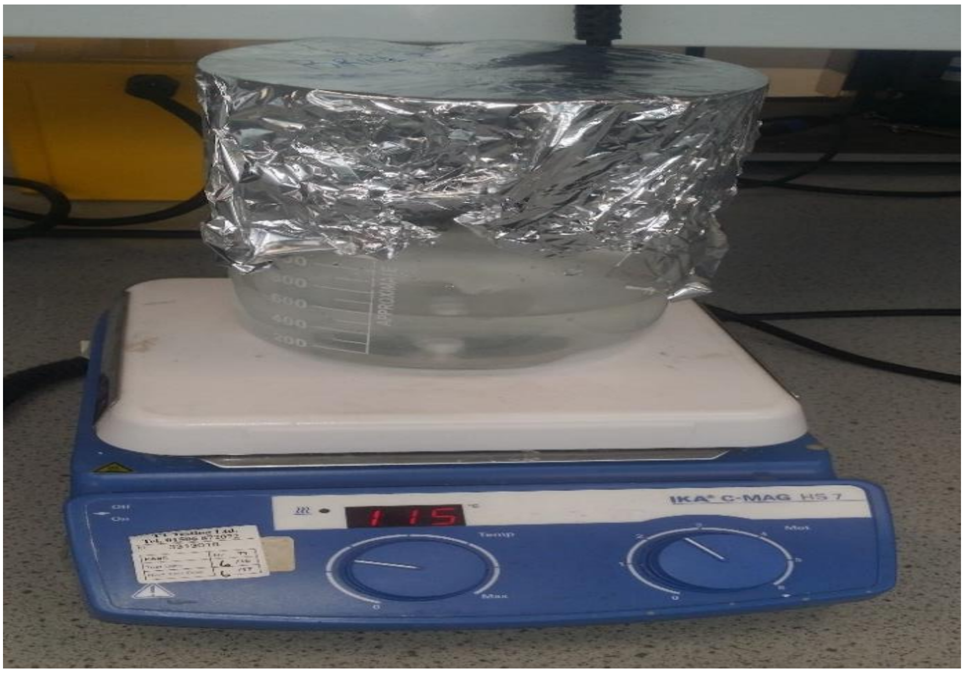

Fig. 1: Brine Solution Place on A Magnetic Stirrer.

Table 2: Target Concentration for Brine 1

ion	source	Target concentration (mg/l)	salt added (g)
Na^+	NaCl	57826	146.92
K^+	KCl	2898	5.53
Mg^{2+}	$MgCl_2.6H_2O$	2330	19.49
Ca^{2+}	$CaCl_2.2H_2O$	22500	82.69
Sr^{2+}	$SrCl_2.6H_2O$	1890	5.75
Ba^{2+}	$BaCl_2.2H_2O$	918	1.63
Fe^{2+}	$FeCl_2$	470	1.066
		TDS= 88832	

Table 3: Target Concentration for Brine 2

ion	source	Target concentration (mg/l)	salt added (g)
Na^+	NaCl	57826	146.92
K^+	KCl	2898	5.53
Mg^{2+}	$MgCl_2.6H_2O$	2330	19.49
Ca^{2+}	$CaCl_2.2H_2O$	22500	82.69
Sr^{2+}	$SrCl_2.6H_2O$	1890	5.75
Ba^{2+}	$BaCl_2.2H_2O$	918	1.63
Fe^{3+}	$FeCl_3.6H_2O$	470	2.275
		TDS= 88832	

Table 4: Target Concentration for Brine 3

ion	Source	Target concentration (mg/l)	salt added (g)
Na^+	NaCl	57826	146.92
K^+	KCl	2898	5.53
Mg^{2+}	$MgCl_2.6H_2O$	2330	19.49
Ca^{2+}	$CaCl_2.2H_2O$	22500	82.69
Sr^{2+}	$SrCl_2.6H_2O$	1890	5.75
Ba^{2+}	$BaCl_2.2H_2O$	918	1.63
		TDS=88362	

3.2. Criteria used in selecting buffer solution

The criteria used in selecting the buffer solution are as follows. Firstly, the buffer solution should have a pH greater than 9.0 because of the availability of carbonate ion (CO_3^{2-}) .There is high probability that metal cations such as calcium and magnesium ion when reacting with carbonate ion would form mineral carbonate at a basic pH of close to 9.0. Therefore, this factor was considered when choosing the buffer solution to adjust the brine pH. Secondly, it is necessary to ensure that the selected buffer solutions shouldn't contain any carbonate or bicarbonate ion in order to avoid any interference of mineral precipitation in the reaction. After careful examination of this factor, 0.3M Tris Buffer Solution with a chemical composition of $(HOCH_2)_3CNH_2$ was selected in this study to adjust the pH to 9.0. The selection of this buffer solution was based on studies from Liu Q and Maroto-Valer [12]

3.3. Characterization of the basaltic rock

The basaltic rock used in this study was grounded using hammer at the Engineering and Physical Science workshop and sieved to 160–100 µm in order to provide enough reaction surface. The rock samples were further grounded into a fine powder (75 µm) with the use of an agate mortar and pestle at the Centre for Innovation Carbon Capture and Storage (CICCS) Laboratory. The basaltic rock was analysed using XRD for the purpose of identifying the mineralogy. However, the initial mineralogical characterization of the basaltic rock was not considered in this research due to insufficient amount of rock sample available. The XRD analysis was conducted at the school of chemistry, Heriot-Watt University.

3.4. PH stability studies

The pH stability of the 6 experiment containing three different brine were studied with 0.3M Tris buffer solution as additive in both open and closed system for a period of 10days. In each of the experiment, 100 ml of synthetic brine was poured into a 250 ml conical flask. The synthetic bine solution was mixed thoroughly with magnetic stirrer until it was completely dissolved. The variation of pH with time was measured by a Thermo Orion 420A+ bench top pH meter. (Fig. 2). The open atmosphere system conducted in this studies were needed to provide an overview of how brine pH is influenced by atmospheric CO_2 while the closed atmospheric system were conducted in this study to identify the impact of buffer solution to accelerate the brine pH. For the CO_2 -rock–brine experiment, (experiment 4-6), the brine/rock ratio used was 10:1 which was based on previous study [13]. Since a pH of close to 9.0 would promote the precipitation of carbonate minerals, the initial pH of each experiment was adjusted to 9.0. The pH was measured every 10min for the first 1hour, then every 30mins for another 1.5 hour, and eventually every 24hours. After seven days of the experiment being closed, the beakers were opened to the atmosphere for another three days in order to correlate the response of rock and brine to atmospheric CO_2. pH measurements was stopped when pH became stable continuously at around ±0.3 for two days. The pH stability study was then completed. The brine solutions were then filtrated by using Whatman glass microfiber filters (90 mm diameter) and the solid product was then saved for XRD analysis. The error for pH measurement was ±0.02 due to the calibration of pH probe (every 24 hours before measurement is taken) and the variation in the room temperature of the laboratory. The pH stability studies on the six experiments were carried out at the Centre for Innovation Carbon Capture and Storage (CICCS) laboratory, Heriot Watt University.

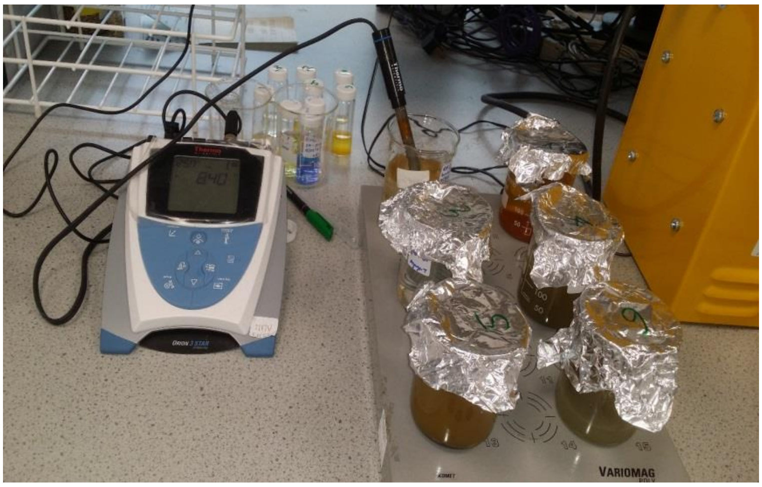

Fig. 2: Ph Measurement.

3.5. XRD Analysis of solid product

90mm Whatman microfiber glass filter paper together with vacuum filteration was used to separate the solids product from the brine solution. The brine samples were poured into a filtration apparatus which was then allowed to pass through a filter paper placed in the filteration apparatus. After filteration, the solid residue accumulated on the filter paper was then put in an oven operating at 50°C for the period of 24hours.The powdered samples were mounted in air and then Bruker D8 Advance powder diffractometer was used to collect the X-ray diffraction data. It operates with Ge-Monochromated Cu Kalpha 1 radiation with a wavelength of 1.5406Å and the lynx eye linear detector was in reflectance mode. The X-ray diffraction was collected over the angular range of between 5-85 degrees in two theta

4. Results and discussion

The result of the pH stability studies will be divided into two sections. The first section is the pH stability studies of $\boldsymbol{CO_2}$-brine experiment which includes experiment 1 (brine 1 containing Fe^{2+}), experiment 2 (brine 2 containing Fe^{3+}) and experiment 3 (brine 3 containing no iron).The role of iron as it affects the pH of brine 1, brine 2, its absence in brine 3 and also its buffering capacity will be discussed in this section while the other section will be pH stability studies of CO_2-basalt-brine experiment i.e the reaction between basalt and each of the brine in the first section, the buffering capacity and how the reaction affect the brine pH to favour precipitation of carbonate minerals will be discussed. Comparism was made on the metal concentration before and after the experiment and how it relates to mineral carbonate formation. Finally, XRD analyses were conducted to identify the carbonate minerals that have precipitated in the solid phase after the experiment.

4.1. $\boldsymbol{CO_2}$-brine experiment

The pH stability studies conducted in experiment 2 involving brines with Fe^{3+}shows an initial pH of 1.42. 40ml of tris buffer was required to adjust the brine pH to 9.0.The result shows decline in the pH from 9.0 to 8.93 in the first 10minutes of the experiment. The pH was also stable at a value of 8.97 for another 2hours. The pH gradually decreases from 8.87 to 8.82 after 144 hours and was stable at a pH of 8.82 in the closed system (fig. 3). After opening the samples to the atmosphere, the pH increased slightly to 8.85 and eventually became stable at a pH of 8.73.Drunkenmiller and Maroto-Valer [9] reported that brines with low concentration of iron (10ppm) showed a pH pattern relatively stable after the addition of a buffer solution but in contrast, the pH of brine with a very high concentration of iron between 120-476ppm declined rapidly and was levelled off afterwards. The reason for the drop in the pH was not explained in their study. The drop in the pH pattern of this brine with high concentration of Fe^{3+} (476ppm) was similar to the study conducted by these authors. The drop in the pH pattern in this experiment shows that brine pH is highly affected by Fe speciation.

The hydrolysis of ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron in aqueous brine solution usually entails changes in pH due to the existence and subsequent formation of partially oxidized aqueous complex of Fe^{2+} - Fe^{3+} thereby making oil field brines unsuitable for mineral carbonation. Ferrous iron (Fe^{2+}) is highly soluble in brine solution while Ferric iron (Fe^{3+}) has low solubility with a pH of above 1.0 [6]. Ferric (Fe^{3+}) iron is dominant in acidic solution as a hexaquo-complex of $Fe(H_2\,0)_6^{3+}$at a pH of less than 2.5. As a result of increased pH, the hexaquo-complex is transformed to mono and dyhidroxo complexes. In this study, the brine pH was adjusted to 9.0 above the pH limit where Fe$(OH)_2$ precipitates (between 7.0-9.0). In a recent study conducted by Cordoba et al [14], the pH was adjusted to 6.3 and 9.0 to avoid the precipitation of iron hydroxides which is induced by the KOH solution used to buffer the pH but the result of the XRD analysis still shows the precipitation of iron hydroxide. Therefore, at a pH of 9.0, it is possible to have iron precipitation. Before the addition of tris buffer commonly known as Tris (hydroxymethylaminomethane) with a composition of $(HOCH_2\,)_3CNH_2$ and a pH of between 10.1-11.The aqueous phase of experiment 2 containing Fe^{3+}would be oversaturated with iron compounds such as iron oxide or hydroxide and also free cation as Fe^{3+} can be oversaturated by $Fe_3(OH)_2^{4+}$, FeOH^{2+}, $Fe(OH)_2^{+}$, and Fe$(OH)_3$.

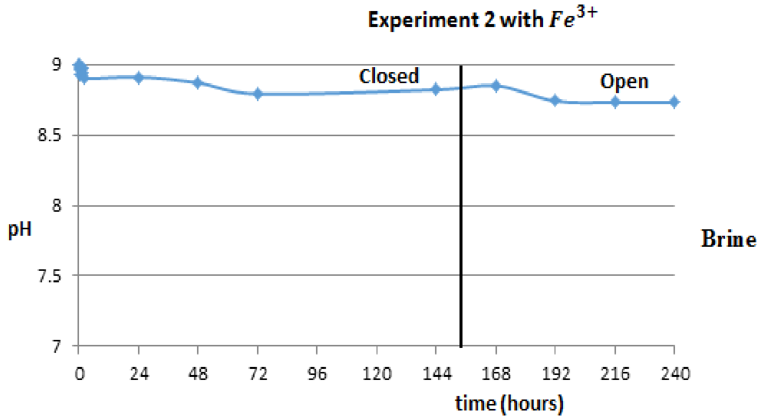

Fig. 3: Ph Stability Studies of Experiment 2 with Tris Buffer after 240 Hours.

The aqueous complex of Fe^{3+} starting from equation 6-10 would remain in the aqueous phase of experiment 2 which is said to be acidic. In this reaction, the 0.3M tris buffer (hydroxymethylaminomethane) will be represented as (HMA). The kinetic and mechanisms of redox reaction of Tris (hydroxymethylaminomethane) iron (ii, iii) i.e $Fe(HMA)_3^{3+}\ and\ Fe(HMA)_3^{2+}$ in aqueous brine solution have not yet been investigated but from thermodynamics aspect of view, It is possible that in a large excess of hydroxymethylaminomethane, $Fe(HMA)_3^{3+}$ is quantitatively reduced to $Fe(HMA)_3^{2+}$.This can be verified from modelling studies conducted by Cordoba et al, [14] where KOH (buffer used) reduced Fe^{3+} to Fe^{2+}since the translation of chemical potential in terms of redox potential would make the reduction of Fe^{3+} possible thermodynamically. The effect of this reduction reaction decreased the buffering ability of the tris buffer. It was observed that only 8ml of the 0.3M Tris buffer was required to raise the pH to 6.3 below the limit where iron hydroxide precipitates. An additional 30ml of 0.3M Tris buffer was required to raise the pH from 6.3 to 9.0 above the limit where iron hydroxide precipitates and also at the brine pH which favours precipitation of carbonate minerals Therefore, the fall in the pH trend of experiment 2 containing Fe^{3+} in both closed and open system could be as result of Fe^{3+} precipitation in the brine aqueous phase as Fe$(OH)_2$ and subsequent reduction of $Fe(HMA)_3^{3+}$ to $Fe(HMA)_3^{2+}$ which is induced by the tris buffer. The pH of experiment 2 was observed to be stable at 8.73.The result of these studies shows that the brine pH of experiment 2 containing Fe^{3+} became stable at the pH which still favours iron hydroxide precipitation and mineral carbonate precipitation. The purpose of the closed atmospheric system conducted in this study is to identify the impact of buffer solution to accelerate the brine pH. However, the result of experiment 2 shows that larger amount was required to raise the brine pH in the presence of reduction state of Fe^{3+}. Liu and Maroto- Valer [15] investigated the effect of 0.3M Tris buffer and fly ash to enhance brine pH, though the composition of their synthetic brine does not contain large amount of iron but the result shows that the 0.3M Tris buffer was 5 times more effective than any other buffer solution. This shows that the buffering ability of 0.3M tris buffer was affected as a result of Fe speciation in the reaction. The purpose of the open atmosphere system conducted in this study is to provide an overview of how brine pH is influenced by atmospheric CO_2. The result of experiment 2 shows that the brine pH was stable at a pH of 8.73 which favours the precipitation of calcite $(CaCO_3)$ as detected by the XRD. The result of this finding correlates with previous studies on mineral trapping of CO_2. Liu Q and Maroto-Valer, M.M [16] investigated the contribution of ferric and ferrous iron to pH stability and the result shows that ferric iron (Fe^{3+}) does not contribute to pH instability hence making it optimal for mineral carbonate precipitation.

pH stability studies were also conducted with brines without iron (experiment 3) in both open and closed system. 8ml of 0.3M Tris buffer was required to raise the pH from an initial value of 6.19 to 9.07. The pH decreases from 9.07 - 8.93 after 20minutes of the experiment. The pH value began to fluctuate afterwards between 8.93 to 9.07 and finally decrease to 8.48 in the closed system (fig 4.). After opening the system to the atmosphere, the pH became stable at 8.32. The trend in the brine pH when compared to experiment 1 and 2 shows that the absence of Fe affect the pH stability of brine. There is a clear difference between the amount of buffer needed to adjust the brine pH to 9.0 when the brine contains iron and when it does not contain iron. The amount of buffer needed to adjust the brine pH without iron was 42ml and 32ml lesser than when the concentration of brine solution contains Fe^{2+} and Fe^{3+}respectively.This shows that the precipitation of Fe recorded in previous experiments reduced the buffering ability of 0.3M Tris buffer solution to enhance brine pH to promote mineral carbonate precipitation. This result shows that the tris buffer was more effective to adjust the brine pH to 9.0 in the absence of Fe. The aqueous phase of experiment 3 was observed to have dissolved completely with no solid residue for XRD analysis. This shows that no precipitation occurred in experiment 3 with no iron

The result of the pH stability studies of experiment 1 involving Fe^{2+} shows an initial pH of 3.32. Since a pH of close to 9.0 favours precipitation of carbonate minerals, 50ml of the 0.3M Tris buffer solution was required to adjust the initial pH to 9.01 above the limit where Fe$(OH)_2$ precipitates. The pH evolution against time shows a fluctuation in the brine pH in the first 30minutes of the experiment with pH value ranging between 9.01-8.97. It was observed that the pH was stable at a value of 8.97 for approximately 1hour before declining to 8.83 after 2hours of the experiment. After 48hours, the pH decreased to 8.79 and finally 8.71 after 144hours for the closed system. (Fig5). After the sample was opened to the atmosphere, the pH decreased slightly to 8.58 after 24 hours and finally became stable at a pH of 8.42. The different fluctuation in the pH pattern in this experiment shows that brine pH is highly affected by Fe speciation. The fall in the pH of experiment 1 corresponds with the kinetic oxidation of $Fe(HMA)_3^{2+}$ to $Fe(HMA)_3^{3+}$ which would produces aqueous complex of Fe^{3+} resulting to a fall in the brine pH. Cordoba et al [14] reported a fall in the pH of the brine containing Fe^{2+} and this was attributed to the kinetic reaction following the oxidation of $Fe^{2+}$to Fe^{3+}which forms hydroxyl aqueous complex of Fe^{3+}. The effect of this kinetic oxidation reaction of Fe decreased the buffering ability of the 0.3M tris buffer. It was observed that only 10ml of the Tris buffer was required to raise the pH to 6.3 below the limit where iron hydroxide precipitates. An additional 40ml of tris buffer was required to raise the pH from 6.3 to 9.0 above the limit where iron hydroxide precipitates and also at the brine pH which favours precipitation of carbonate minerals. After the opening the system to the atmosphere, the pH was observed to be stable at 8.42.The result from the XRD analysis shows that this pH favours the precipitation of calcite.

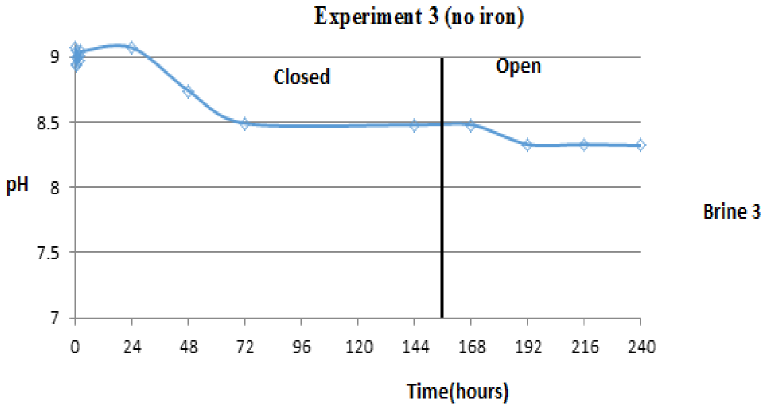

Fig. 4: Ph Stability Studies of Experiment 3 with Tris Buffer after 240 Hours.

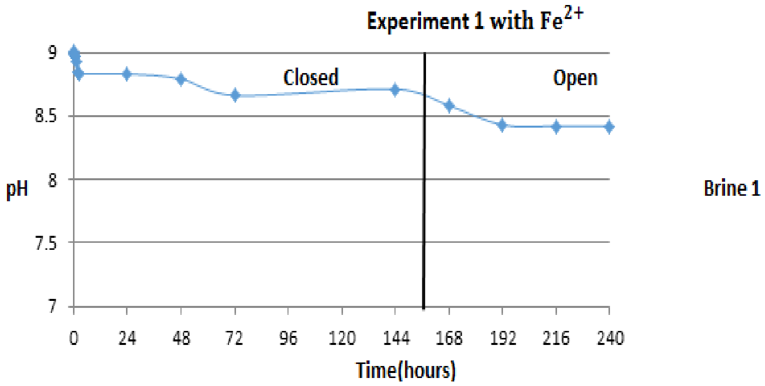

Fig. 5: Ph Stability Studies of Experiment 1 with Tris Buffer after 240 Hours.

4.1.1. XRD analysis for CO_2r -brine experiment

The XRD analysis of experiment 1 containing Fe^{2+} shows the presence of calcite (red colour band) observed at its peak which is indicated by the characteristic reflection at d spacing of 3.0314Å (29.5° 2θ). A clear evidence of calcite was also observed by the characteristic reflection at d spacing of 3.850Å (24° 2θ), 2.49311Å (36° 2θ), 2.83Å (39.8 2θ), 2.092Å (44° 2θ) and 1.873Å (48.5° 2θ).The result shows that the solid collected after the experiment is dominated with calcite which means that Ca^{2+} reacted with CO_3^{2-} during the experiment (fig 6). However, there is also evidence of the formation of halite(NaCl) represented with a blue colour band which is indicated by the characteristic reflection at d spacing of 2.822Å(33.5° 2θ) and 1.994Å(45° 2θ). This is as a result of high concentration of NaCl used in preparing the brine. Cordoba et al [14] also reported the precipitation of halite in a CO_2-brine experiment and the reason behind its formation was attributed to the large amount of NaCl salt used in preparing the brine solution. It was observed that the XRD pattern of experiment 2 was similar to experiment 1.The presence of calcite and halite was also observed in the XRD (fig 7). However, there was no evidence of iron hydroxide precipitation in the XRD for experiment 1 and 2 and this could be as a result of the small amount of solid presented for the XRD analysis. The aqueous phase of experiment 3 containing no iron was observed to have dissolved completely with no solid residue for XRD analysis. This shows that no precipitation occurred in experiment 3.

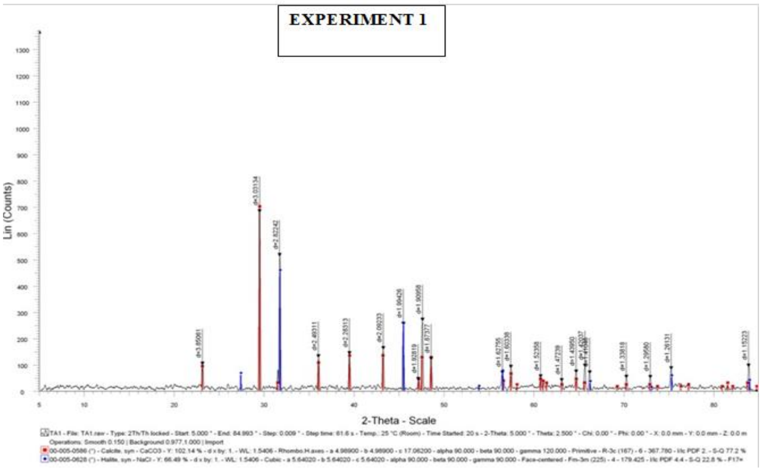

Fig. 6: XRD Analysis of Experiment 1 Containing Fe^{2+}.

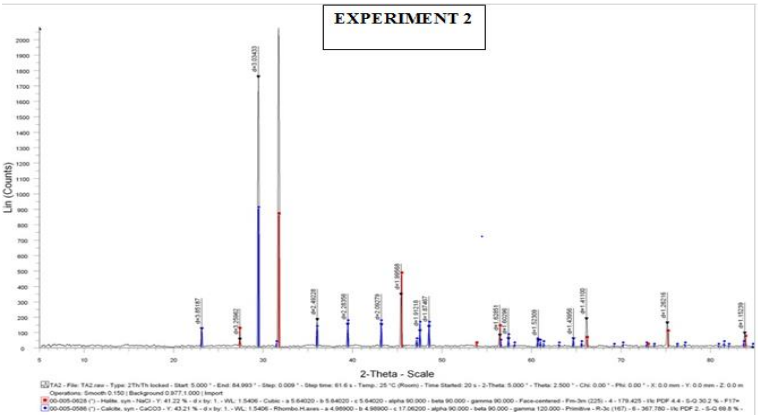

Fig. 7: XRD Analysis of Experiment 2 Containing Fe^{3+}.

4.1.2. Summary of CO_2- brine experiment

The pH stability studies of experiment 1-3 shows how brine pH relates in the presence and absence of Fe. 50ml of 0.3M Tris buffer required to raise the brine pH of the experiment was observed in experiment 1 containing Fe^{2+}, experiment 2 containing Fe^{3+} and a lesser amount in experiment 3 containing no iron. The reason for this large amount of buffer needed in experiment 1 and 2 can be attributed to the effect of the oxidation – reduction reaction taking place as a result of Fe speciation. There is a clear difference between the amount of buffer needed to adjust the brine pH to 9.0 when the brine contains iron and when it does not contain iron. The amount of buffer needed to adjust the brine pH without iron was 42ml and 32ml lesser than when the brine contains Fe^{2+} and Fe^{3+}respectively.This shows that the precipitation of Fe recorded in experiment 1 and 2 reduced the buffering ability of 0.3M Tris buffer solution to enhance brine pH to promote mineral carbonate precipitation. It can be concluded that the tris buffer was more effective to adjust the brine pH to 9.0 in the absence of Fe. The result also shows that at a final pH of 8.42 in experiment 1 and 8.73 in experiment 2, the precipitation of Calcite is favoured. Though the result of experiment 3 tends to contradicts that of experiment 1 and 2 as to the precipitation of calcite observed as a result of the decrease in the concentration of calcium at the end of the experiment. The presence of low concentration of Ca at the end of experiment 3 prevents a definitive linkage between the precipitation of calcite observed in experiment 1 and 2 and the absence of calcite in experiment 3.The non- existence of iron hydroxide in the XRD is surprising because its impact was felt in terms of buffering the brine pH above the limit where it precipitates. Its absence in the XRD could be as a res

4.2. CO_2-Rock-brine experiments

pH stability studies were conducted on experiment 5 containing $Fe^{3+}$and basalt in both open and closed system. 45ml of 0.3M Tris buffer was required to raise the pH from an initial value of 1.96 to 9.02.The pH decreases from 9.02 - 8.96 after 10minutes of the experiment and became stable at this pH value for additional 1hour of the experiment. The pH value began to fluctuate afterwards between 8.96 – 8.83 and finally decrease to 8.63 in the closed system (Fig 8). After opening the system to the atmosphere, the pH increases slightly from 8.63- 8.64 and became stable at a final pH of 8.59. The pH pattern of experiment 5 involving containing Fe^{3+} and basalt indicates high rate of chemical interaction between dissolved Fe in basalt, Fe [III] solution, 0.3M Tris buffer and subsequent effect of this interaction to brine pH. As a result of this interaction, the dissolution of basalt occurs which enhances the release of metal cation such as Fe^{2+}, $Fe^{3+}, Ca^{2+}\ and\ Mg^{2+}$into the solution. The pH pattern of experiment 5 was observed to have decreased from initial pH of 1.96 to final pH of 8.63 in the closed system and further became stable at a pH of 8.59 in the open system. The decrease in the pH could be as a result of loss of Fe via dissolution from basalt which in turn corresponds to an increase in Fe in the aqueous brine solution. The basaltic rock used in this study can be regarded as a base. The basaltic rock with a grain size of between 140-75µm was mixed with Millipore water and with a fluid – rock ratio of 10:1. The resulting pH of the water –rock system is 8.24. The presence of Fe [III] in solution reacting with basalt is greatly favoured over a very acidic pH. This can be confirmed from a study conducted by White et al, [17] to examine the fate of Fe [III] in a solution containing 10ppm of Fe [III]. The result shows that at an acidic pH of less than 4, Fe^{3+} became stable in the initial solution which indicates that Fe^{3+} was not reduced to $Fe^{2+}$and precipitation of oxyhydroxides was not observed as a result of this reaction. However, it was observed that the addition of basalt into the solution lowered the concentration of Fe [III] in the solution at a reaction rate that is proportional to the pH and the reacting surface area of the basalt. It was also observed in their study that Fe [II] concentration increased as a result of the reaction. This means that as a result of the reduction reaction, the pH of the basalt/water system became unstable under these conditions and fell to a very acidic solution when Fe [III] rich brine solution was added. This shows that the reaction between basalt and Fe^{3+} is favoured at a very acidic pH. This can be confirmed as the initial pH of the experiment 5 containing Fe^{3+} is 1.96. There is a clear difference when observing the pH of the basalt/water system and the pH of the reaction between basalt and Fe [III] rich brine solution. The pH was observed to have reduced from 8.24 to 1.96. It can be observed that in the presence of basaltic rock, Fe^{3+} is reduced to Fe^{2+}. However, it could be possible that all of the Fe^{2+} in the solution is contributed from the dissolved basalt and Fe [III] could be lost as a result of basalt-induced precipitation such as calcium carbonate as detected by XRD. In order to favour the precipitation of carbonate minerals, the pH of experiment 5 was adjusted to 9.0. As a result of this, the carbonate minerals which are expected to be precipitated includes calcite ($CaCO_3$), siderite ($FeCO_3$) and magnesite ($MgCO_3$) [18]. However, it should also be noted that at a pH of greater than 6.3, the precipitation of iron hydroxide is favoured [14]. This means that at a pH of greater than 6.3, the Fe^{3+} in the solution is depleted completely which could be as a result of lack of measurable Fe^{3+} from dissolution of basalt. Since the pH of experiment 5 containing Fe^{3+} became stable at a value of 8.59, then the concentration of Fe in this pH range might favour the precipitation of oxyhydroxides in the presence of 0.3M tris buffer. The absence of $Fe(OH)_2$ precipitation in the XRD of the experiment 5 solid phase could be as a result of insufficient concentration needed in order for it to be detected or formation of its amorphous phases. It was also observed that 8ml of the tris buffer as required to raise the initial pH of the brine from 1.9 to 6.0 below the limit where iron hydroxide precipitates; an additional 35ml of tris buffer was required to raise the brine pH from 6 to 9.02. This is as a result of the precipitation of iron hydroxide in the reaction. Since the pH stability studies was opened to the atmosphere to observe the effect of atmospheric CO_2 in the reaction, the precipitation of calcite ($CaCO_3$) was detected by XRD.

pH stability studies was conducted on experiment 4 containing Fe^{2+} and basalt in both open and closed system. 45ml of tris buffer was required to raise the pH from an initial value of 4.20 to 9.01.The pH decreases from 9.01 - 8.79 after 2hours of the experiment. The pH value began to fluctuate afterwards between 8.79 – 8.51 and finally increased to 8.53 in the closed system (Fig 9). After opening the system to the atmosphere, the pH increases slightly from 8.53- 8.56 and became stable at a final pH of 8.41

The reaction between Fe^{2+}brine rich solution, Fe^{3+} brine rich solution as a function of pH suggest that oxidation – reduction reaction takes place between Fe^{2+} and Fe^{3+} on basalt and also in the brine solution. White et al [17] reported that such oxidation- reduction reaction could be in the form below

$$(\mathrm{Fe(II)}\tfrac{1}{z}\mathrm{M}^{z})\mathrm{basalt} + \mathrm{Fe\ (III)\ solution} = \mathrm{Fe\ (iii)\ basalt} + \frac{1}{z}\mathrm{M}^{z}\ \mathrm{Solution} + \mathrm{Fe\ (II)\ solution}\ \text{(Equation 11)}$$

Where any form of reduction in Fe in the solution is directly charge-balanced as a result of the dissolution of charge Z (cation) emanating from the basalt. They further stated that the main driving chemical force influencing the above reaction is the oxidation of Fe [II] in the oxidized basaltic surface and the acceptance or release of electron into the solution. It was concluded by these authors that at a neutral to basic pH of between 7-8.8, Fe reduction in the solution as a result of the equation 11 is countered by the Fe oxidation which eventually leads to the precipitation of Ferric oxyhydroxides as stated in the equation 12

$$\mathrm{Fe}^{2+} + \frac{1}{4}\mathrm{O}_2 + 2\mathrm{OH}^- + \frac{1}{2}\mathrm{H}_2\mathrm{0} = \mathrm{Fe(OH)}_3\ \text{(Equation 12)}$$

Since the final pH of experiment 4 is 8.41, the reaction must favour ferric oxyhydroxides precipitation. This can be verified from the result of the XRD analysis the precipitation of Ferric oxyhydroxides. However, the precipitation of carbonate mineral is favoured over a basic pH of 9.0. In order for this to be achieved, the initial pH of the brine was adjusted to 9.02. It was observed that 10ml of 0.3M tris buffer was required to raise the pH of the brine to 6.3 below the limit where iron hydroxide precipitates. An additional 50ml was required to raise the brine pH from 6.3-9.02. This can be attributed to the precipitation of iron oxyhydroxides which reduces the buffering ability of the 0.3M tris buffer. Since the pH stability studies was opened to the atmosphere to observe the effect of atmospheric CO_2 in the reaction, precipitation of carbonate minerals was not detected in the XRD.

pH stability studies was conducted on experiment 6 (no iron) and basalt in both open and closed system. 5ml of tris buffer was required to raise the pH from an initial value of 6.46 to 9.09.The pH decreases from 9.09 - 8.40 after 2hours of the experiment. The pH value began to fluctuate afterwards between 8.40 – 8.16 and finally decreased to 7.97 in the closed system (Fig 10). After opening the system to the atmosphere, the pH decreases slightly from 7.97- 7.82 and became stable at a final pH of 7.79.The relatively small amount of tris buffer required to raise the brine pH to 9.0 shows that the buffering ability of 0.3M tris buffer is highly affected by Fe speciation. The result of the XRD shows that this reaction favours the precipitation of dolomite CaMg $(CO_3)_2$.

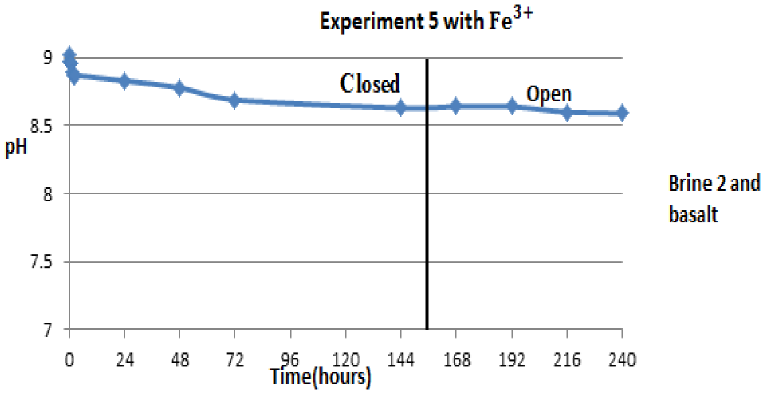

Fig. 8: Ph Stability Studies of Experiment 5 with Tris Buffer after 240 Hours.

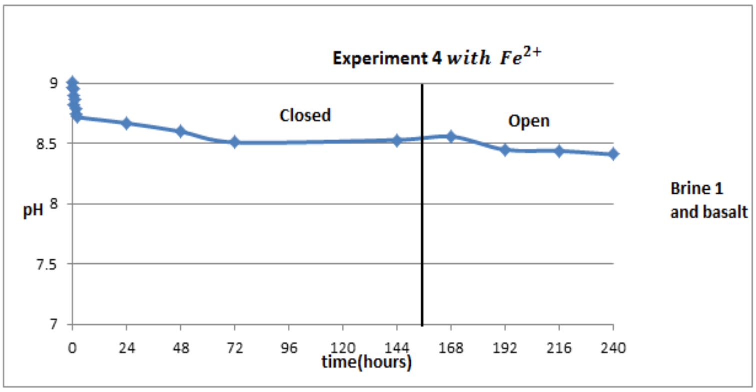

Fig. 9: Ph Stability Studies of Experiment 4 with Tris Buffer after 240 Hours (10days).

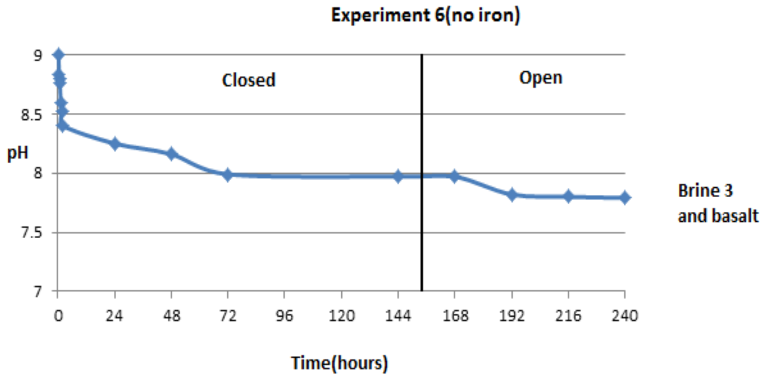

Fig. 10: Ph Stability Studies of Experiment 6 with Tris Buffer after 240 Hours (10days).

4.2.1. XRD analysis of solid products

The XRD analysis conducted on experiment 4 containing Fe^{2+} and basalt shows the detection of oxyhydroxides $Fe(OH)_3$ which is indicated with a red colour band (fig 11).It was observed at a reflection d spacing of 2.89Å (31°2θ) and 2.56Å (35° 2θ). The presence of Calcite was not observed in experiment 4 but was detected in experiment 5 containing Fe^{3+} and basalt (fig 12) and it's also indicated with a red colour band. This means that Ca^{2+} reacted with CO_3^{2-} during the experiment. The precipitation of dolomite was also observed in the XRD of experiment 6 containing basalt with no iron (fig 13).

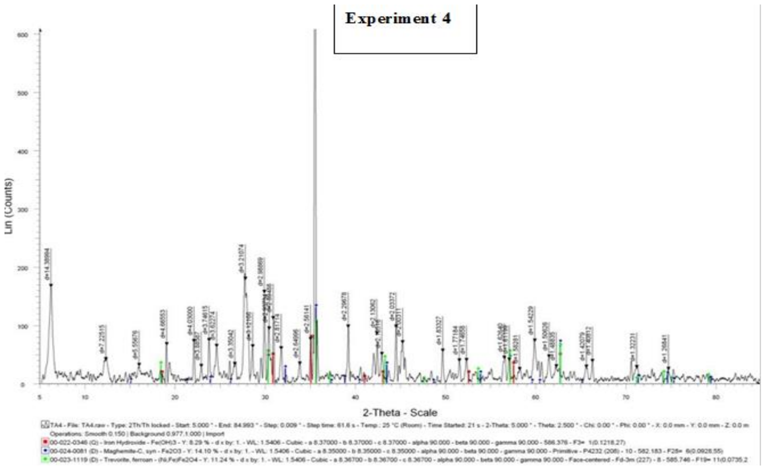

Fig. 11: XRD Analysis of Experiment 4 Containing Fe^{2+} and Basalt.

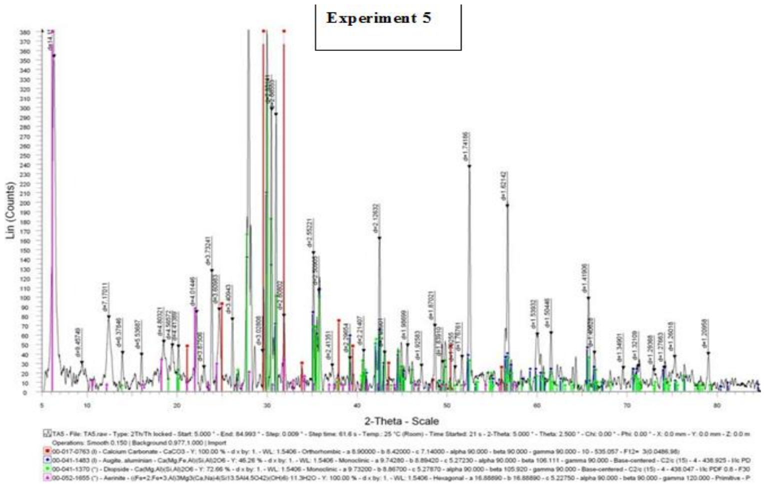

Fig. 12: XRD Analysis of Experiment 5 Containing Fe^{3+} and Basalt.

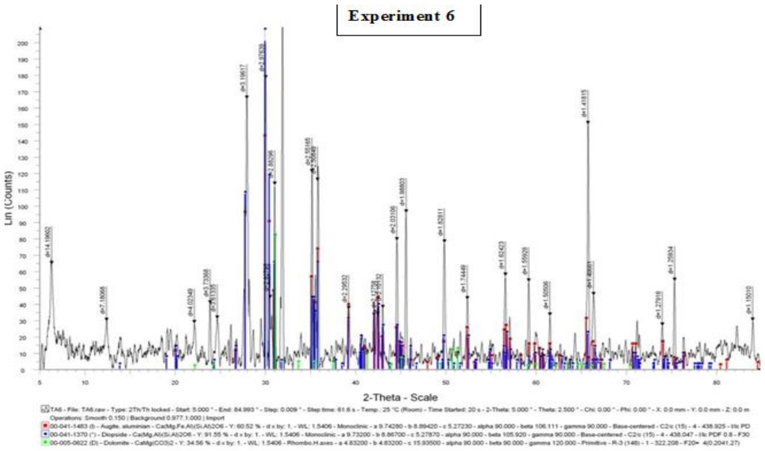

Fig. 13: XRD Analysis of Experiment 6 Containing Basalt with No Iron.

4.2.2. Summary of CO_2-rock-brine experiments

The result of the pH stability studies of experiment 4-6 shows how brine containing Fe^{2+} and Fe^{3+} relates in the presence of basalt. It was observed that the pH of experiment 4 contains Fe^{2+} and basalt, experiment 5 containing Fe^{3+} and basalt and experiment 6 containing basalt with no iron dropped and became stable at a final pH of 8.41, 8.59 and 7.79 respectively. The main driving chemical force influencing the drop in the pH was attributed to the oxidation- reduction of Fe in the basaltic surface and in the brine solution. The basalt used in this study can be regarded as a base with a pH of 8.24.However; it was observed that the mixture of basalt and 0.3M Tris buffer in experiment 4 containing Fe^{2+} and basalt was not effective to maintain the brine pH close to 9.0 to promote carbonate precipitation. This mean that at a final pH of 8.41 in experiment 4, the precipitation of carbonate mineral is not favoured as the XRD shows no presence of carbonate minerals. The effect of the iron oxyhydroxides precipitation reduced the buffering ability of the 0.3M tris buffer. 60ml of tris buffer was required to raise the pH to 9.01 and when compared with experiment 5 and 6, experiment 4 still has the highest amount of buffer used due to the precipitation of iron oxyhydroxides. The precipitation of calcite observed in experiment 5 containing Fe^{3+} and basalt is a clear indication that Ca^{2+} reacted with CO_3^{2-} during the experiment. However, the final pH of 8.59 and 7.79 to which calcite and dolomite was favoured in experiment 5 containing Fe^{3+} and basalt and experiment 6 containing basalt and no iron respectively contradicts studies from Soong etal [19] where they concluded that a pH of close to 9.0 favours the precipitation of carbonate mineral. Though the XRD for experiment 5 and 6 doesn't show that calcite and dolomite are the major component. Due to the complex mixture of materials in experiment 4-6, the XRD was dominated with basalt induced minerals such as Augite aluminium, Antigorite, Diopside and Silicon oxide

4.3. Comparative analysis

The overall aim of this research is to observe the stability of pH when ferric and ferrous ion reacts with brine both in the presence and absence of a host rock (basalt) to promote carbonate mineral precipitation. It is therefore necessary to make comparism between the CO_2-brine experiment which comprises of experiment 1 containing Fe^{2+}, experiment 2 containing Fe^{3+} and experiment 3 containing no iron and CO_2-rock-brine experiment which comprises of experiment 4 containing Fe^{2+} and basalt, experiment 5 containing Fe^{3+} and basalt and experiment 6 containing basalt and no iron. The comparative analysis will be divided into 3 sections which are the pH effect, buffering ability and XRD comparism.

4.3.1. PH effect

The pH pattern of experiment 1-6 varies in both the closed and open system. It should be noted that the purpose of the closed atmospheric system is to identify the impact of buffer solution to accelerate the brine pH which will be discussed in section 4.3.2 while the open atmospheric system is needed to provide an overview of how brine pH is influenced by atmospheric CO_2. After opening the experiment to the atmosphere, it was observed that the pH of both the CO_2-brine experiment and CO_2-rock-brine experiment decreased in a similar trend. Though it can be viewed that the pH of experiment 2 containing Fe^{3+} and experiment 3 containing no iron increased slightly before declining. After the addition of basalt into this experiment as recorded in experiment 5 containing Fe^{3+} and basalt and experiment 6 containing basalt and no iron for the CO_2-rock-brine experiment, the pH of experiment 5 was observed to be stable while that of experiment 6 decreased in a similar pattern with that of experiment 3 when it does not contain basalt. This means that experiment 5 was the fastest to become stable. It was recorded that experiment 5 became stable after 24hours of opening the experiment to the atmosphere. This result correlates with the finding of Liu and Maroto-Valer, [16] where they concluded that ferric iron does not contribute to any pH instability. It was also observed that experiment 4 containing Fe^{2+} and basalt took a longer time for the pH to be stable compared to when it does not contain basalt (experiment 1).It should be noted that after 10days when the pH stability experiment ended, it was only the pH of experiment 4 that did not become stable continuously. pH measurement still continued for only this experiment for additional 2days before XRD analysis and the result still shows wide decline as compared to other experiment where values were within ±0.3.This means that the pH of experiment 4 did not become stable throughout the duration of the experiment. This might be due to the different properties of the host rock and buffer solution used.

4.3.2. Buffering ability

The purpose of the closed atmospheric system is to identify the impact of buffer solution to accelerate the brine pH. The amount of buffer used to adjust the brine pH in experiment 4 containing Fe^{2+} and basalt was observed to be higher than when it does not contain basalt (experiment 1).60ml of the 0.3M tris buffer was required in experiment 4 while 50ml was required in experiment 1. This means that after the addition of basalt in experiment 4, an additional 10ml was required to raise the brine pH even despite the fact that the basalt was regarded as a base. This reaction could be as a result of the precipitation of Ferric oxyhydroxides in experiment 4. This shows that the mixture of basalt and 0.3M tris buffer was not effective to buffer the brine pH in experiment 4. The absence of carbonate minerals in the XRD of this experiment can also verify that. It was also recorded that the amount of buffer needed to adjust the brine pH without iron in experiment 3 was 42ml and 32ml lesser than when the brine contain Fe^{2+} in experiment 1 and Fe^{3+} in experiment 2 respectively. This shows that the precipitation of Fe as earlier discussed reduced the buffering ability of 0.3M Tris buffer to enhance brine pH to promote mineral carbonate precipitation. After careful comparism between the CO_2-brine experiment and CO_2-rock-brine experiment, it is worthwhile to say that the tris buffer was more effective to adjust the brine pH to 9.0 in the absence of Fe. This can be verified from the small amount of buffer used in experiment 3 and 6 which does not contain iron (fig 5).

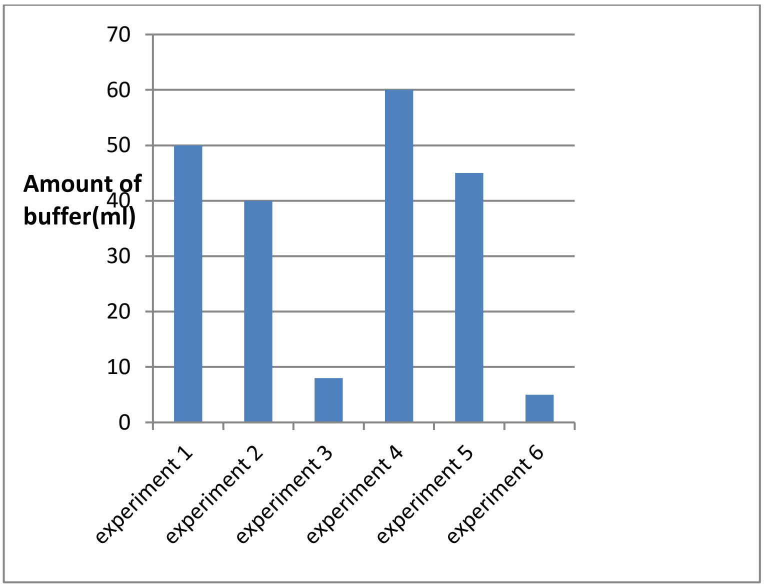

Fig. 5: Amount of Buffer Used in Experiment 1-6.

5. Conclusions

The overall aim of the study is to investigate the effect of iron concentration in brine when reacting with basalt to promote carbonate formation for CO_2 sequestration. In order to achieve the purpose of this study, pH stability studies and XRD analysis with brines containing Fe^{2+}, Fe^{3+} and without iron for CO_2-brine experiment and brines containing $Fe^{2+}$with basalt, Fe^{3+} with basalt and basalt with no iron for CO_2-rock brine experiment were conducted. For the pH adjustment studies for CO_2-brine experiment, the pH stability studies identified that brines containing Fe^{2+} and Fe^{3+} became stable at a final pH that was not close to 9.0 but still favours the precipitation of carbonate minerals. Though findings from previous studies shows that Fe^{2+}contribute to pH instability thereby making it unsuitable for mineral precipitation. The result from this CO_2-brine experiment stated contrary to this earlier claim because the presence of Fe^{2+} in the brine did not cause any pH instability which makes it optimal for carbonate precipitation. When brine containing Fe^{2+} and Fe^{3+} was reacted with the mixture of basalt and tris buffer to enhance the brine pH, it was observed that the mixture of basalt and tris buffer was not effective to buffer the brine pH close to 9.0 in all the CO_2-rock-brine experiment. However, the results of this study in terms of mineral carbonate precipitation do not illustrate any clear relationship between the formation of calcite observed in experiment 1, 2 for CO_2-brine experiment and experiment 5 for CO_2-rock-brine experiment at a final pH of 8.42, 8.73 and 8.59 respectively. This contradicts findings from previous studies that concluded that at a pH of close to 9.0, the precipitation of calcite is favoured. The result of the XRD confirmed that calcite was the major component that was dominated in the CO_2-brine–experiment while slight occurrence of calcite, iron oxyhydroxides and dolomite precipitated in the CO_2-rock-brine experiment. The precipitation of calcite in both CO_2-brine-experiment and CO_2-rock-brine experiment indicates that Ca^{2+} reacted with CO_3^{2-} during the experiment. Therefore, it can be concluded that ferric iron (Fe^{3+}) and its reaction with host rock (basalt) did not contribute to pH instability therefore making it suitable for precipitation of carbonate mineral while ferrous iron (Fe^{2+}) in the absence of host rock did not contribute to pH instability therefore making it also suitable for precipitation of carbonate mineral. It can be further concluded that the mixture of basalt and tris buffer was not suitable to buffer the brine pH to 9.0 and maintain for a long time.

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