GEOCHEMICAL CHARACTERIZATION OF OMANI SANDSTONE CORES-ANALYSIS OF CHANGE IN PH AND ROCK MINERAL CONSTITUENTS CONCENTRATIONS

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Abstract

pH sensitive polymers such as polyacrylic acid (PAA) hydrogel have recently been proposed for the oil industry as a conformance control agent. Previous studies showed that this type of microgel solutions will swell considerably as their pH increases above a critical value. Thus for an optimal condition for propagation through porous media, the micogel polymer should be in the unswelled state during injection. Therefore, understanding the geochemical properties of a reservoir is crucial to condition the reservoir before polymers can be applied for conformance control. In this paper, the geochemical behavior of Omani sandstone cores which were obtained from a reservoir candidate for conformance control were characterized by quantifying the change in the effluent pH after injecting 3wt% NaCl brine and 0.1 M HCl solution. The effect of shut-ins and injection rate on the pH of the effluent was investigated. The investigations were carried out in three 1.5 inch diameter by 2 inch long cores selected from the same formation. The measurements indicated a steady state pH value of around 2.8 between the injected acid and the rock minerals. Five pore volumes of 0.1 M HCl were required to achieve this steady state. This is because the fast reacting mineral which is the calcium was almost consumed as soon as the reaction started. The effluent pH was found to increase from the steady state value to about 3.5 (which is the equilibrium pH value) when shut-ins effect was applied for longer than one day while no change in the effluent pH was observed when shut-in period was less than one day. Large volume of acid injection decreased the increase in pH to values less than 3.5 even for very long shut-in periods. There was no effect of injection rate on the acid volume required to attain steady state. However, at steady state, the pH of the effluent was found to decrease as the injection rate decreased.

From the geochemical data, we concluded that the Omani field of interest from which the tested cores were collected can be considered as a good candidate for conformance control applications using the PAA polymers .

Keywords: Geochemical; pH sensitive polymer; Omani sandstone; fast and slow reacting minerals; equilibrium; pH value.

1. Introduction

Hydrogels or water-swollen crosslinked polymers have been a subject of extensive literature due to its significant applications in the biomedical (for reviews see Langer [12] and Roorda et al. [15]). Recent studies showed that watersoluble stimuli-response hydrogels are one of the most promising types of polymeric materials. They found to be sensitive to small change in their environment [6]. The water uptake of such hydrogels depends on pH, ionic strength, temperature, electric and magnetic field. A small change in these will cause a dramatic change in properties of the polymer.

pH sensitive polymers are materials that respond to change in pH of the surrounding medium by varying their dimensions. Polyelectrolytes are ideally suited for the preparation of pH-sensitive hydrogels. Katchalsky et al. [10] and Katchalsky [9] did much of the initial work on charged systems by examining the behavior of polyelectrolyte solutions and gels. They've expanded the gel equation of state by considering the system pressure and how it varies with the degree of polymer ionization and swelling. It is known that the response in these polymers is triggered due to the presence of ionisable functional groups such as COOH which interacts with counter ions in the solution. Muroga et al. [14] showed that the swelling behavior of the polyelectrolytes is strongly affected by the change in pH, ionic strength and polymer concentrations. Brondsted and Kopecek [3] summarized the

influence of these factors on the swelling of polyelectrolytes. The high ability of the polymer to swell is related to the efficient charge repulsion. In polar medium, like water, hydrogels containing groups (like COOH) which are ionisable at certain pH swell by increasing the charge density. This behavior increases the viscosity of the polymer chains upon ionization (see Kontturi et. al. [11]).

In the petroleum industry, it is only recent the recognition that pH triggered polymer can be utilized effectively. McTeir et al. [13] showed that Polyelectrolytes can be used as scale inhibitors near the wellbore. Al-Anazi and Sharma [2] examined a polyelectrolyte polymer called polyacrylic acid to be used as carrier fluid to transport sands for gravel packing operations. Also, Al-Anazi and Sharma [1] carried out the first experimental study to investigate the possibility of using PAA for conformance control to increase the productivity and injectivity of a well. They investigated the effect of pH, salts, temperature and polymer concentrations on the viscosity of the polymer solutions. The viscosity of PAA polymer solution was found to be very sensitive to pH. For example, the viscosity of some polymers varies from 5 cp at pH = 2.5 to 20,000 cp at pH above 6. It is believed that the rapid increase in viscosity at a certain pH value is due to mainly the ionization of the carboxyl groups in the PAA polymers.

Thus for the problem of improving injectivity discussed by Al-Anazi and Sharma [1], PAA solution exhibits a low viscosity at low pH, but at higher pH, the viscosity increases drastically and maintains more or less a plateau value with further increases in pH. This means a good injectivity can be achieved by injecting the PAA pH sensitive polymer at low pH. Once injected in the reservoir, the pH can increase due to geochemical reaction between the injected acid and the carbonate and other minerals in the reservoir rock. The increase in pH swells the polymer and forms gels deep in the high permeability zones which consequently will lower the mobility of water in these zones. So, the swelling of these polymers deep in the reservoir is controlled by the geochemical reactions between the acid and the mineral components in the rock.

Despite the importance in understanding the geochemical reactions between the acid and the reservoir rock minerals for conformance control, there are very limited amount of works that exploit the pH change of HCl acid and brine resulting from the geochemical reactions when injected through sandstone cores. Choi [4] investigated the change in pH of HCl solution and NaCl brine when injected through Barea sandstone cores as a function of time, injection rate and shut-in periods. They aimed to define the practical conditions at which in-situ conformance control method can be applied. The shut-in period is defined as the time or period at which no injection or flow is allowed through the core. Such investigation helps to locate the equilibrium pH of the examined Omani cores.

The present study focuses on evaluating thoroughly the geochemical reaction between the PAA hydrogels and Omani sandstone cores. Particularly, the change of pH in the effluent and the effect of injection rate and shut-in periods on the effluent pH are investigated. The objective is to study the applicability of using HCl acid as a preflush so the PAA polymer microgel can propagate through the Omani field of interest and start to swell once only it reaches the target location in the reservoir. The concentrations of ions in the effluent samples for five cations (silicon, aluminum, potassium, calcium and iron) were measured to examine the change in mineral composition in the cores as a function of time during acid injection. This was done using Perkin Elmer Atomic Absorption Spectro Photometer. Moreover, the results from the Omani sandstone cores are compared with those obtained by Choi [4] using Barea sandstone cores.

2. Experimental Set-up

The experimental studies on the geochemical characterization of pH change in real Omani sandstone cores were carried out by means of a core holder (see Fig. 1). A syringe pump was used to inject the fluid at a constant flow rate. Sodium chloride and Hydrochloric acid were used as injected fluids. The pressure drop across the core was measured by connecting a pressure tap at the inlet of the core while keeping the outlet at atmospheric pressure. The pH of the effluent was measured regularly as a function of time using pH meter. All experiments were conducted at room temperature (24°C).

Three Omani sandstone cores were used in the experiments. These cores consist of quartz, dolomite, clinochlore, Sanidine and Muscovite. The porosity and the permeability were measured using 3wt% NaCl. The dimensions and the properties of each core are given in Table 1. The displacement experiments were carried out at various injection conditions. Tables 2, 3 and 4 show the injection schedule followed in each experiment.

Fig. 1 Experimental setup used in studying geochemical characterization of pH change in core samples

Table 1 Dimensions and properties of the core samples used in the experiments

Cores	Length, cm	Diameter, cm	Porosity, %	Permeability, mD
Exp 1	5.03	3.77	29.0	1438
Exp 2	4.80	3.76	31.3	1863
Exp 3	4.85	3.77	31.4	1916

As in Choi [4], for the first injection experiment, two different injection rates (1 and 5 ml/min) were sequentially applied and a total of 5 shut-in periods were tested (see table 2). This allows a fair comparison with the geochemical results obtained by Choi using Barea sandstone cores.

Table 2 Injection schedule for Experiment #1

Exp 1: After saturating the core with 3wt% NaCl, the following are the next steps:	
Day No.	Task
Day 1	Inject 3% NaCl at 1 ml/min for 5 hrs
	Shut in for 6 hrs
	Inject 3% NaCl at 5 ml/min for 1 hr
	Shut in for 12 hrs
Day 2	Inject 3% NaCl at 5 ml/min for 40 min
	Inject 0.1 M HCl at 1 ml/min for 6 hrs
	Inject 0.1 M HCl at 5 ml/min for 1 hr and 12 min
	Shut in for 3 days & 16 hrs
Day 6	Inject 0.1 M HCl at 1 ml/min for 3 hrs
	Shut in for 1 day & 21 hrs
Day 8	Inject 0.1 M HCl at 1 ml/min for 3 hrs

The second core flood experiment was conducted to investigate the effect of shut-in on pH. It was done at a fixed injection rate of 2 ml/min. Initially 3wt% NaCl was pumped followed by HCl solution with five shut-in periods.

Table 3 Injection schedule for Experiment #2

Exp 2: After saturating the core with 3wt% NaCl, the following are the next steps:	
Day No.	Task
Day 1	Inject 3% NaCl at 2 ml/min for 1 hr
	Inject 0.1 M HCl at 2 ml/min for 2 hrs
	Shut in for 1 hr
	Inject 0.1 M HCl at 2 ml/min for 5 hrs
	Shut in for 2 days & 15 hrs
Day 4	Inject 0.1 M HCl at 2 ml/min for 1 hr
	Shut in for 2 hrs
	Inject 0.1 M HCl at 2 ml/min for 2 hrs
	Shut in for 4 hrs
	Inject 0.1 M HCl at 2 ml/min for 3 hrs
	Shut in for 12 hrs
Day 5	Inject 0.1 M HCl at 2 ml/min for 6 hrs
	Shut in for 5 days & 18 hrs
Day 11	Inject 0.1 M HCl at 2 ml/min for 1 hr

The third experiment was performed to examine the effect of injection rate using four different injection rates (1, 2, 4 and 8 ml/min) and one shut-in period (15 hours). Table 4 describes clearly the injection schedule used in this experiment.

Table 4 Injection schedule for Experiment #3

Exp 3: After saturating the core with 3wt% NaCl, the following are the next steps:	
Day No.	Task
Day 1	Inject 3% NaCl at 2 ml/min for 1 hr
	Inject 0.1 M HCl at 1 ml/min for 4 hrs
	Inject 0.1 M HCl at 2 ml/min for 2 hrs
	Inject 0.1 M HCl at 4 ml/min for 1 hr
	Inject 0.1 M HCl at 8 ml/min for 30 min
	Inject 0.1 M HCl at 2 ml/min for 2 hrs
	Shut in for 15 hrs & 30 min
Day 2	Inject 0.1 M HCl at 2 ml/min for 2 hrs

Finally, the effluent from the third coreflood experiment was carefully analyzed using Perkin Elmer Atomic Absorption SpectroPhotometer. This is to quantify the concentrations change of silicon, aluminum, potassium, calcium and iron in the effluent. Those elements represent the main minerals constituents that exist in the investigated Omani sandstone cores (quartz, dolomite, clinochlore, Sanidine and Muscovite). These results are compared with those obtained by Choi [4] using Barea sandstone.

3. Experimental Results

Well-characterized experiments have been carried out to investigate the geochemical characterization of pH change in Omani sandstone cores. The pH changes in the effluent were recorded with time while the effect of shut-ins and injection flow rate of both NaCl and HCl on the pH of the effluent were examined.

3.1. Effluent pH changes with time

The measured pH of collected effluent versus pore volume injected in the first, second and third experiments are presented in Figs. 2-4 respectively. One pore volume in principal should be equal to the total volume of pores in the core. It is clear that the equilibrated pH during 3wt% NaCl brine injection is about 9.5 for the three different cores. This reflects the need of a dilute acid preflush to facilitate polymer microgel propagation. After injection of 0.1M HCl solution, the pH of the effluent drops very sharply to around 2.8. The pH was found to stabilize at this value for all the three experiments.
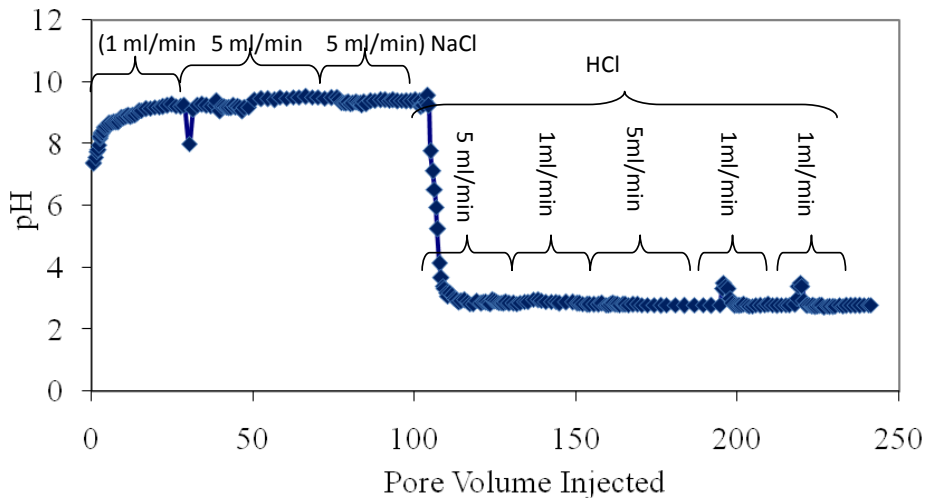
Fig. 2 pH versus pore volume injected for the first coreflood experiment
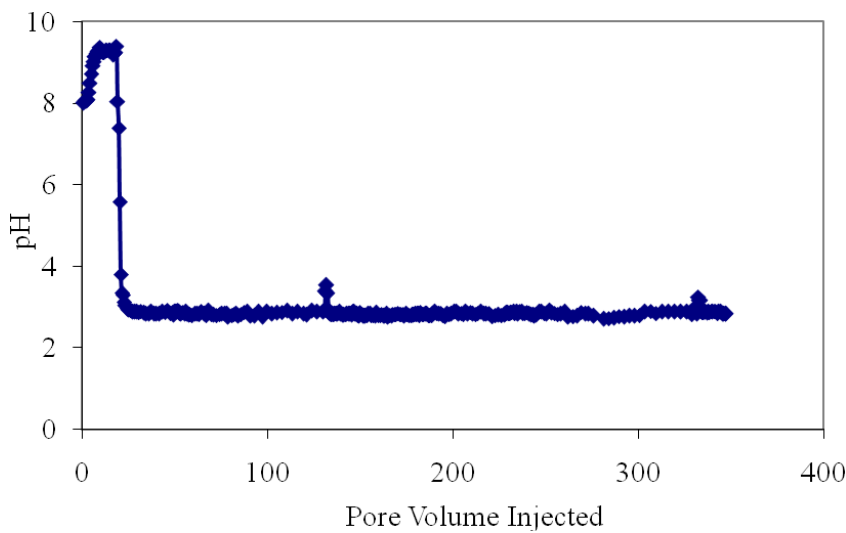

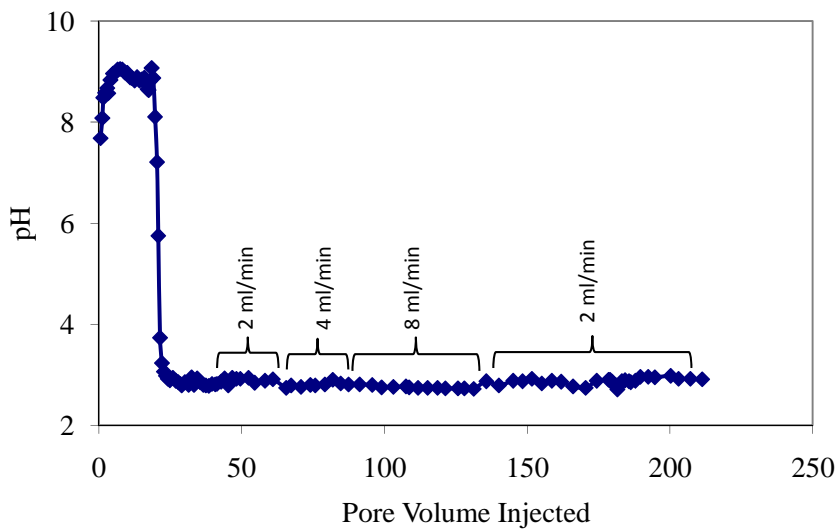Fig. 3 pH versus pore volume injected for the second coreflood experiment

Fig. 4 pH versus pore volume injected for the third coreflood experiment

3.2. Effect of shut-in

Fig. 3 shows the effect of shut-ins during 3wt% NaCl brine injection period in the first coreflood experiment. Two shut-in periods were examined. During the first shut-in period (6 hours) the pH decreases to 8 while in the second shut-in period (12 hours) no change in pH was observed which means that the NaCl brine is in equilibrium with the rock minerals.

After HCl injection, several shut-in effects were tested in the first, second and third experiments as shown in Figs. 2-4. In all experiments, when the shut-in periods were

allowed for more than a day, the pH of the effluent was found to increase slightly from 2.8 to around 3.3-3.5. On the other hand, no change in pH was observed when the injection was stopped for less than a day.

3.3. Effect of injection rate

The effect of injection rate on the pore volumes required to achieve steady state pH (the pH of the effluent stabilizes at around 2.8) between the injected acid and the rock minerals is insignificant. This is clearly seen from Figs. 2 and 3 where the pore volumes required in the first and second coreflood experiments are almost the same. In fact, the results showed that the effluent will attain a steady state pH value with the rock minerals as soon as 5 pore volume of 0.1 M HCl solution is injected.

Although the effect of injection rate on pH is not so clear from the first and second experiments, a better observation can be made from the third coreflood experiment as shown in Fig. 4. The lower the injection rate is, the higher the effluent pH becomes. The lower injection rate causes more protons to be consumed, resulting in a higher effluent pH. For example at injection rate of 1 ml/min, the average pH is found to be 2.9 while at injection rate of 8 ml/min, the average pH is equal to 2.73.

3.4. Minerals concentration of the examined Omani sandstone cores

The effluent from the third coreflood experiment was analyzed as a function of injected pore volume by Perkin Elmer Atomic Absorption SpectroPhotometer. Five cations (silicon, aluminum, potassium, calcium and iron) in effluent were selected for analysis. This helped in understanding the mineralogy of the experimented Omani sandstone cores reacting with HCl solution. The analysis of the results is presented in Figs. 5-9.

Fig. 5 shows the potassium concentration profile with pore volume injected. It is clear that the concentration of the potassium in the effluent is so small and almost negligible with a relatively constant value profile. It can be noted that this mineral constituent react very slowly with HCl acid. Small peak is observed at the end of the profile when relatively long time shut-in (15 hours) was made.
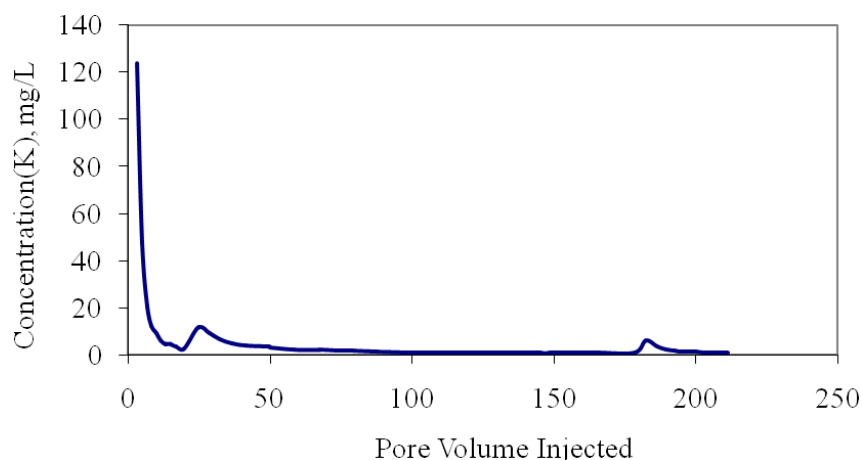

Fig. 5 Potassium (K) concentration profile from the third coreflood experiment

The concentration profiles of silicon, aluminum and iron are almost the same (see Figs. 6-8). Initially, a large peak was observed at the beginning of HCl injection. After that a constant profile was noted indicating that these minerals constituents are part of the slow reaction minerals.

Unlike silicon and iron, aluminum concentrations were found to be almost zero after injection of approximately 80 pore volume. This could be related to different reasons. One is that amount of aluminum exists in the examined core could be small. Second reason might be that 1 ml/min and 2 ml/min were used initially as injection flow rates while after that (after 80 pore volume) 4 ml/min and 8 ml/min were used as injection rates. Thus the residence time for the reaction to occur is small taking into consideration that Al is a part of the slow reaction mineral and it exists in small amounts. Finally, when the injection rate was stopped for long period (15 hours), large peak was observed for Fe and Si while a relatively smaller peak was observed for Al.
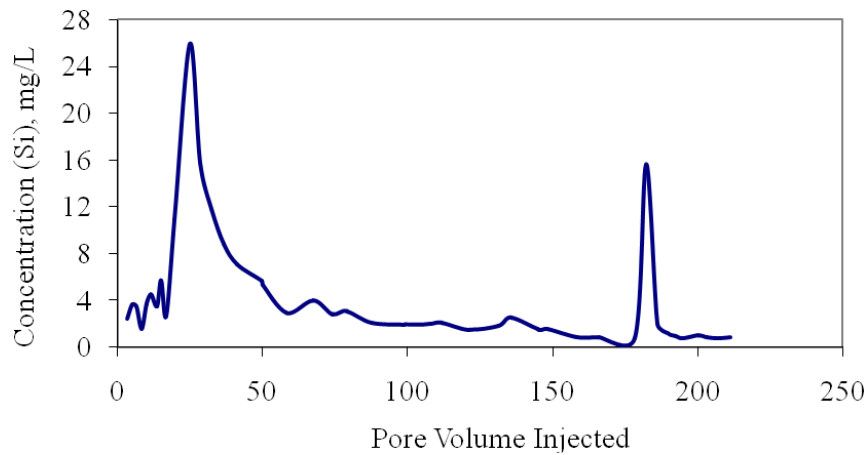
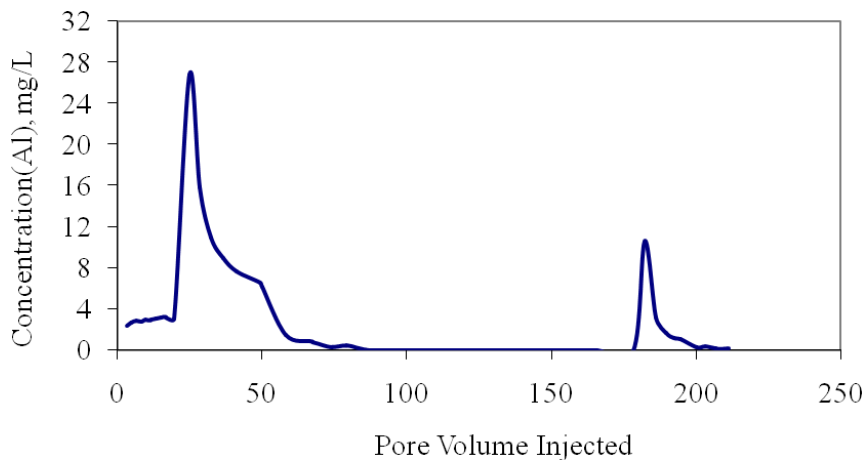Fig. 6 Silicon (Si) concentration profile from the third coreflood experiment

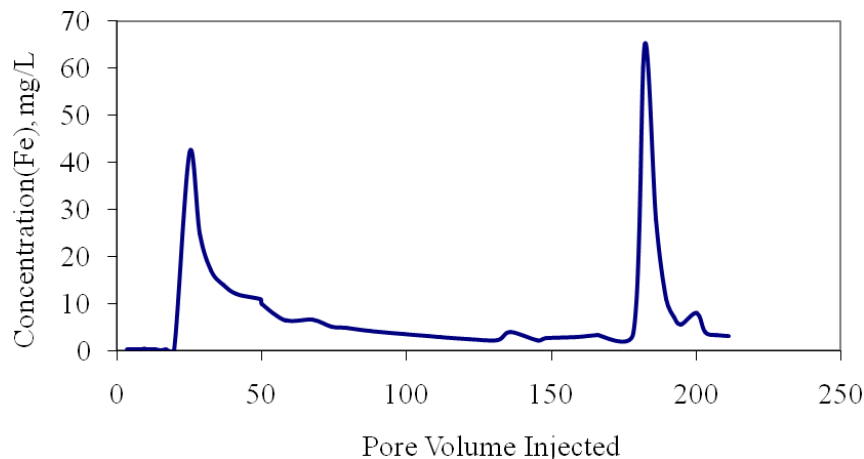Fig. 7 Aluminum (Al) concentration profile from the third coreflood experiment

Fig. 8 Iron (Fe) concentration profile from the third coreflood experiment

For the calcium (see Fig. 9), the concentration profile is found to decrease sharply initially with pore volume indicating that this mineral constituent is a part of the fast reaction mineral and it is almost consumed as soon as the reaction with HCl starts. Small peak was observed after the shut-in for 15 hours indicating that calcium was almost consumed.

4. Discussion

The pH profile of the effluent measured during the acid injection experiments was found to stabilize at around 2.8. This can be attributed to the consumption of minerals existing in the sandstone cores which obviously were not consumed completely. That's why the lowest pH stabilized at around 2.8 and does not reach the injected pH value (pH =1.0).

In other words, it is known that a number of mineral constituents exist in sandstone and its composition varies greatly due to different depositional environments and digenetic

processes. Therefore, when a 0.1M HCl solution with pH of 1.0 is injected, these minerals start to be consumed (quartz, dolomite, clinochlore, Sanidine and Muscovite), showing a stable balanced pH plateau of around 2.8.
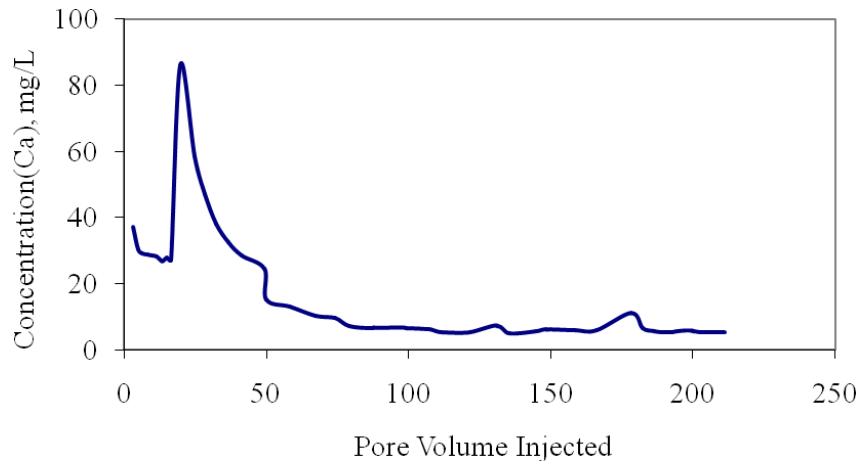

Fig. 9 Calcium (Ca) concentration profile from the third coreflood experiment

However, each mineral behaves or reacts differently in contact with acidizing fluids. Different behavior implies different reaction kinetics, physical and chemical characteristics, and many other parameters which as a whole create a very complex reaction process upon the interaction with treatment fluids. Thus for simplicity, the two-mineral model is used as an approximation to explain the pH history of the effluent after acid injection (see Hill et al. [7], Taha et al. [16]). This model requires a numerical technique to obtain a general solution which is beyond the scope of this work. Economides et al. [5] described the reservoir using the two-mineral model as having a fast reacting mineral, slow reacting mineral and a non-reacting matrix.

Comparing the concentrations profiles for the five elements analyzed in this study (Figs. 5-9), we can conclude that calcium is part of the fast reaction mineral whereas aluminum is part of the slow reaction mineral. Calcium concentration as shown in Fig. 9 drops sharply from 85 ppm to 15 ppm after about 30 pore volumes and stabilizes at approximately 6 ppm. It increases only to 11 ppm when a shut-in period of 15 hours was applied. On the other hand, the contribution of the aluminum towards increasing the pH is so small as depicted in Fig. 7. It is almost zero at flow rate higher than 4 ml/min (see the concentration from 80 to 170 pore volumes in Fig. 7).

In this work (see Figs. 2-4), only 5 pore volumes of 0.1 M HCl is required for the pH to drop from around 9.5 to about 2.8 at which it stabilizes. This stabilization reveals that almost all the fast reacting mineral (calcium as a part of the fast reacting mineral) was consumed as soon as acid injection started.

In this work, it is found that the effect of shut-in periods on the pH of the effluent as a result of HCl injection is significant only when the shut-in was made for more than one day. No change in pH was observed for shut-in period less than that (see Figs. 2 and 4). This indicates that all fast reacting minerals were immediately consumed (see the small peak for calcium concentration which is a part of the fast reaction mineral) and only very slow reaction minerals were left which needs longer time to have an effect on the pH of the effluent. This could be due to the very slow reaction on one hand and may be due to its present as small quantities in these Omani cores. Therefore, pH of around 2.8 represents the steady state pH between the 0.1 M HCl solution and the minerals.

For the effect of injection rate on the pH of the effluent during HCl injection, same number of pore volumes was required to achieve steady state pH in the three carried out experiments regardless of the injection flow rate used. This is attributed to the quick reaction of fast reacting minerals with the acid. It is believed that these minerals consumed as soon as the reaction started. The reaction of the slow reaction minerals seems to be very slow. That's why no pH change was observed when the injection was stopped for hours (see Figs. 2 and 4) and this could be the reason why there was no effect of injection rate on the pore volume required to attain steady state. It is believed also that the length of the core has no effect on these values since the injection was stopped for more than 5 days without any appreciable increase in the pH of the effluent.

The effect of injection rate on effluent pH was slightly observed from the results of the third experiment as shown in Fig. 4. Higher pH was recorded at lower injection rate. Lower injection rate means larger residence time which increases the possibility of the protons to be consumed during the propagation of the acid through the core.

From the effect of shut-in periods and injection rate, it is obvious that the minimum possible pH that can be achieved for these experimented cores is about 2.8. This pH increased to about 3.5 when the core was shut-in for more than one day. This pH value of around 3.5 represents the equilibrium pH between the 0.1 M HCl solution and the minerals indicating maximum possible proton consumption determined by equilibrium in the mineral-acid reactions. However, injecting large amount of HCl solution can reduce the pH to less than 3.5 even with long period of shut-in. This can be explained from the two peaks shown in Fig. 3 (Experiment #2) which represent an increase in the pH as a result of a shut-in for 2 days and 5 days respectively. The pH increase in the second peak (shut-in for 5 days) is lower than the first peak (shut-in for 2 days). This is because the amount of HCl injected through the core before it was shut for 2 days is much less than that injected before the 5 days shut-in period (see Fig. 3 and Table 3).

4.1. Comparison with Barea sandstone (Choi [4])

The work of Choi [4] is the only available study in the literature that carried out experimental work similar to the current study which characterizes an acid-matrix geochemical reaction in sandstone. He conducted an experimental acid floods in Barea sandstone cores and measured the effluent pH and cation concentrations as a result of the reaction between the injected acid (HCl) and the rock minerals. Therefore, a comparison between the results described in this work for real Omani sandstone cores and those obtained by Choi [4] using Barea sandstone cores can be made. The effluent pH and cation concentrations measurements by Choi [4] were obtained using 1.0 inch diameter by 9.0 inch long cores while in the current study all measurements were conducted using 1.5 inch diameter by 2.0 inch long cores. Similar conditions to those experimented by Choi [4] were investigated in this work for the first experiment. For comparison, the effluent pH data are plotted in terms of pore volumes injected for both studies as shown in Fig. 10.
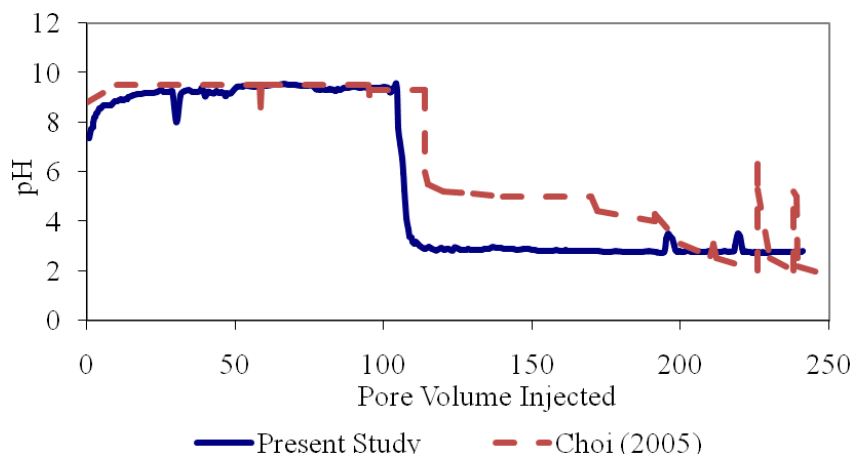

Fig. 10 Comparison of effluent pH history obtained from Choi (2005) (dashed line) and from the current work (solid line)

In agreement with the work of Choi [4], the pH starts to drop sharply as soon as the 0.1 M HCl solution started to flow out of the core. This qualitative effect can be seen in Fig. 10. However, unlike the current work at which the pH of the effluent during HCl injection stabilized at a value of 2.8, the pH of the effluent from Barea cores dropped initially to 5.2 and then to 4.2 after about 60 pore volumes of injected acid and finally stabilized at its lowest value of 1.5 approximately. It is believed that these two distinct behaviors of the pH profile are due to the presence of calcium (part of the fast reacting mineral). The calcium exists in the Omani cores was consumed almost completely as soon as the reaction started while in the Barea sandstone cores, the calcium was consumed after injecting 60 pore volumes of HCl solution.

For a fair comparison between the calcium concentrations in both studies, the concentrations results obtained by Choi [4] using the 9 inch core is multiplied by the volume of the core used in this study divided by the core volume used by Choi. The results are plotted as shown in Fig. 11. It is clear that the amount of calcium presents in the effluent coming

out of Barea sandstone is higher than that exists in the Omani sandstone cores. Also, it is obvious that calcium consumed faster in the Omani cores comparing to that in Barea cores. This illustrates why only 5 pore volumes of 0.1 M HCl solution were only required to reach stabilization (pH = 2.8) in the current work while not less than 100 pore volumes were needed to achieve stabilization in Choi [4] work (pH = 1.5).
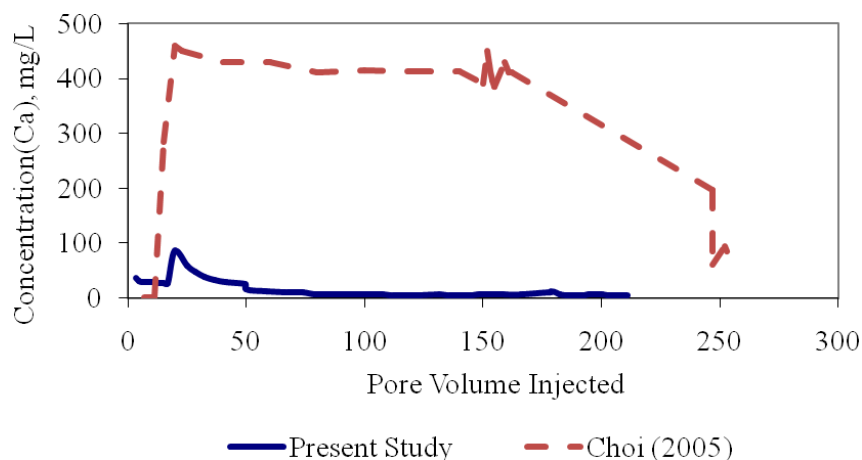

Fig. 11 Comparison of calcium concentrations profile obtained from Choi (2005) (dashed line) and from the current work (solid line)

In both studies, the pH of the effluent after acid injection was found to increase after long shut-in periods. This is due to the reaction with the slow reaction minerals. However, the pH of the effluent in the current study increased to about 3.5 while it increased to about 5.2 as reported by Choi [4]. Also, for shut-in periods less than one day, no pH change was observed in the effluent when Omani sandstone cores were used while an increase to pH around 5.2 was found when Barea sandstone cores were tested. This suggests that more reactive minerals exist in Barea sandstone.

Although it is more obvious in Barea sandstone since longer cores were used, both studies reveal that the pH of the effluent was found to increase as the injection rate increased due to the decrease in residence time. While the effect of injection rate on the acid pore volume required to achieve equilibrium in this work is insignificant, the total amount of pore volumes needed to attain steady state pH as reported by Choi [4] increased as the injection rate increased.

The examined sandstone reservoir (Omani and Barea cores) which is the candidate for conformance control contains brine of pH around 9. Thus, to inject the polymer solution into the reservoir for conformance control, a low pH reservoir environment should be established by flushing sufficient amount of mild HCl. This allows polymer to flow deep into the reservoir without swelling while its pH increases with propagation through the rock matrix as a result of the reaction with the minerals until it swells at its target location.

The pH of the effluent will reach a minimum value of 2.8. However, this pH value will increase during shut-ins which will raise the pH from 2.8 to 3.5. pH value equal to 3.5 is critical and injecting a low pH polymer microgel solution is likely to result in viscosity increase before reaching the target location. Therefore, to decrease the increase in pH during shut-ins, large amount of acid is desired to be flushed (see Fig. 3). Lower injection rate may be applied to allow longer residence time and as result prepared a relatively lower pH medium.

5. Conclusions

The effluent pH of the injected fluid and the concentrations of five elements in the effluent were measured along three 1.5 inch diameter by 2 inch long Omani sandstone cores with a pH meter and Perkin Elmer Atomic Absorption SpectroPhotometer respectively. All measurements were carried out using 3wt% NaCl brine and 0.1 M HCl solution. The following summarize the conclusions:

- pH of the effluent dropped from 9 to about 2.8 as soon as 0.1 M HCl was injected. This pH represents the steady state pH value between the injected acid and the rock minerals. Five pore volumes were needed to reach the steady state pH.
- Shut-ins effect was found to increase the pH of the effluent from 2.8 to 3.5. This will definitely affect the injectivity of the polymers as polymer microgel should be in

unswelled state during propagation. However, injecting large amount of acid was found to decrease the peak as a result of shut-in effect.

- No pH change in the effluent was observed when shut-in period was applied for less than one day.
- From the different experiments conducted, it was found that the acid injection rate did not really affect the acid pore volumes required to achieve steady state. However, the pH of the effluent at steady state was found to increase as the injection rate increased.
- The concentrations of calcium which represents part of the fast reacting minerals in the tested cores were found to consume as soon as the 0.1 M HCl solution was injected.
- The present data were found to agree partly with the experimental results by Choi [4]. Disagreement between the two studies arises from the fact the Choi [4] used different sandstone formation (Barea sandstone) which have different mineral concentrations.

Acknowledgment

References

[1]   Al-Anazi, H. A., Sharma, M. M., 2002a. Use of pH Sensitive Polymer for Conformance Control. SPE 73782 presented at SPE Intern. Symp. Formation Damage Control, Lafayette, LA, Feb. 20-21.

[2]   Al-Anazi, H. A., Sharma, M. M., 2002b. Evaluation of a pH-Sensitive Polymer for Gravel-Packing Operations. SPE Drilling & Completion, 28-36.

[3]   Brondsted, H., Kopecek, J., 1992. Polyelectrolyte Gels. Ed. By R. S. Harland, R. K. Prud'homme. ACS Symposium Series., Washington DC, Ch17.

[4]   Choi, S. K., Ermel, Y. M., Bryant, S. L., Huh, C., Sharma, M. M., 2006.Transport of pH-Sensitive Polymer in Porous Media for Novel Mobility Control Applications. SPE 99656 presented at SPE/DOE Enhanced Oil Recovery Symp., Tulsa, OK, Apr. 22-26.

[5]   Economides, M.J., Hill, A.D., Ehlig-Economides, C.A., 1994. Petroleum Production Systems. Prentice Hall, NY.

[6]   Galaev, I. Yu., Mattiasson, B, 1999. Smart polymers and what they could do in biotechnology and medicine. Trends Biotechnol, 17, 335–340.

[7]   Hill, A.D., Lindsay, D.M., Silberberg, I.H., Schechter, R.S., 1981. Theoretical and Experimental Studies of Sandstone. Acidizing. SPEJ, 21, 30-42.

[8]   Huh, C., Choi, S. K., Sharma, M. M., 2005. A Rheological Model for pH Sensitive Ionic Polymer Solutions for Optimal Mobility Control Applications. SPE 96914 presented at SPE Annual Tech. Conf., Dallas, TX, Oct. 9-12.

[9]   Katchalsky, A., 1971. Polelectrolyte. Pure Appl. Chem., 26, 327-372.

[10] Katchalsky, A., Lifson, S., Eisenberg, H, 1951. Equation of swelling for polyelectrolyte. J. Polym. Sci., 7, 571–574.

[11] Kontturi, K., Mafé, S., Manzanares, J. A., Svarfvar, B.L., Viinikka, P., 1996. Modeling of the salt and pH effects on the permeability of grafted porous membranes. Macromolecules, 29, 5740-5746.

[12] Langer, R, 1980. Polymeric delivery systems for controlled drug release. Chem. Eng. Commun., 6, 1-48.

[13] McTeir, M.D.K., Ravenscroft, P.D., Rudkin, C., 1993. Modified Methods for the Determination of Polyacrylic/Phosphinopolyacrylic Acid and Polyvinylsulphonic Acid Scale Inhibitors in Oilfield Brines. SPE 25260 presented at Oilfield Chemicals Symp., New Orleans, Mar 2-5.

[14] Muroga, Y., Noda, I., Nagasawa, M., 1985. Investigation of Local Conformations of Polyelectrolytes in Aqueous Solution by Small-Angle X-ray Scattering. 1. Local Conformations of. Poly(sodium acrylates). Macromolecules, 18, 1576-1579.

[15] Roorda, W.E., Bodde, H.E., De Boer, A.G. Junginger, H.E., 1986. Synthetic hydrogels as drug delivery systems. Pharmaceutisch Weekblad Scientific Edition, 8, 165-189.

[16] Taha, R., Hill, A.D., Sepohrnoori, K., 1989. Sandstone Acidizing Design With a Generalized Model. SPE Production Engineering, 4, 49-55.