CONTROL PH VALUE FOR SUPERABORBENT POLYMERS (SAPS) SOLUTIONS BY USING HYDROCHLORIDE ACID (HCL)

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ABSTRACT

In mature oil fields, the use of water injection is common, but is limited by reservoir heterogeneity. Differences in permeability can increase water production and subsequently increase operating cost. In many cases, superabsorbent polymers can be used to control reservoir flow, and therefore oil and water output. Understanding the fludic kinetics of these polymers, such as AT-O3S and 2G-110, is the key to their proper use during the treatments. The polymers used are both a crosslinked Sodium polyacrylic acid, which strongly depends on salinity, pH, and temperature. These three factors determine the extent to which the polymers will absorb water, which induces swelling. In this study, we investigated the influence of pH by using brines with different percent weight ratio of deionized water and Calcium Chloride. The polymer is destroyed and a white precipitate made of Calcium polyacrylate is formed, since Calcium Chloride is used for the salt. The salt solution added to the dry polymer inside the test tube. In order to decrease the effects of the reaction, the pH of the solution was modified. As pH drops, it is observed that the precipitation decreases substantially, especially in dilute solutions. It can be inferred that the precipitation effects can be mitigated through the appropriate use of acid washes, preflushes, and polymer concentration in many cases. However, high temperatures might cause further precipitation in brines containing divalent salts.

INTRODUCTION

In the past four decades, there has been a significant drive to increase extraction efficiency in oil reservoirs. Previously uneconomical reservoirs can become viable and productive assets to the petroleum companies. For the permeable reservoirs, water injection is very productive to artificially pressurize the formation and allow for continued production even with the low pressure gradient. It is a proven fact that water injection is limited by reservoir heterogeneity.
The variation of permeability and pore geometry in a reservoir can significantly affect the water injection recovery (Wu et al, 2012; Xu et al, 2014). As the water or brine is injected into the formation, the fluid will flow through the path of least resistance. Essentially, the fluid flows through the more permeable areas can sweep the oil from the high permeable formation which cause a leaving of remaining oil in the low permeability zones/areas (Chia and Bai, 2010; Cui et al, 2011). An example can be seen in figure 1a. After some time, oil production once again decreases as the high permeability zones are swept, although low permeability zones remain relatively untouched (Needham and Doe, 1987). The high permeability zones can be swept of around 60% of their oil while the low permeability zones only lose around a quarter of their oil during an untreated water injection according to the work done by Cui et al in 2011. This variation in permeability causes a substantial increase in water production (Chia and Bai, 2010). In fact, excess water production can reach up to 98% of a well's output (Veil et al, 2004). Greater water production can cause environmental and economic issues as the water tends to have a high salinity, especially after traveling through the reservoir. These high salinity brines must be processed, transported, and disposed of in a safe manner, all of which can be costly (Dalrymple, 1997). In fact, the worldwide cost of excess water production was estimated at $40 Billion dollars annually in 2000 (Bailey et al, 2000). Since then, this statistic has undoubtedly grown substantially alongside the oil industry.

In order to decrease excess water production and increase oil output in a permeable reservoir, the reservoir's heterogeneity must decrease (Needham and Doe, 1987). The best way to change the heterogeneity is to impede the access of the injected water to the high permeable zone. This can be done mechanically through the use of concrete or sand, or it can be done chemically through the use of gels and polymers. The focus of this work was on the use of a crosslinked Sodium polyacrylic acid, a super absorbent polymer (SAP), which absorbs water and swells. In heterogeneous and permeable reservoirs, SAPs can be inserted into the reservoir to decrease the permeability of the high permeability zone. Application of an SAP will drop the permeability of both the high and low zones. However, the treatment affects the high permeability zone much more than the low permeability zone when applied correctly (Elsharafi and Bai, 2016; Elsharafi and Bai, 2012). During injection, the pressure required to push an SAP particle through a passage goes up as passage diameter decreases (Bai et al, 2004-II). This allows for deeper SAP penetration in the high permeability zones and more effective blocking of these zones.

Understanding the fluidic kinetics of an SAP and planning a treatment based on reservoir conditions is crucial to its employment, as the kinetics determines the polymer's in-formation permeability (Elsharafi and Bai, 2015; Ekeigwe et al, 2004). Damage (or reduction in permeability) to the low permeability zone can cause serious issues, but an analytical method to prevent damage has been introduced (Elsharafi, 2013). Proper SAP treatment decreases the heterogeneity of the formation, resulting in a relatively even flow distribution. An example of a treated reservoir can be seen in figure 1b. The unswept low permeability zones can now be effectively waterflooded, allowing for increased production, a longer well life, and a higher reservoir utilization.

The above mentioned SAP swells to a specific amount when exposed to water. The swelling ratio strongly depends on the solution salinity, pH, and temperature (Bai et al, 2013). In a reservoir, the three most prevalent cations present are Sodium^{+}, Calcium^{+2}, and Magnesium^{+2} in descending order (McCain, 1990). The reaction between Sodium^{+} ions and SAPs is well documented, and the results show a drop in the swelling ratio as a brine's Sodium concentration increases (Elsharafi and Bai, 2015; Elsharafi and Bai, 2016; Chia and Bai, 2010; Zhang and Bai, 2011; Bai et al, 2004-II). The effects of divalent cations such as Calcium and Magnesium have not received the same attention, however. The presence of divalent cations in a brine, Calcium in the case of this work, is destructive to the swollen polymer. The Calcium present in a brine solution reacts with the Sodium salt present in the polymer chain. The result is Calcium polyacrylate, which precipitates out of the solution. This reaction destroys the polymer. Even dilute Calcium brines cause significant deswelling and precipitation, especially when introduced after the polymer has fully swollen. There is evidence that pH has a significant inhibiting effect on the precipitation reaction, which will be the focus of this work. The pH range of Calcium Chloride brines tends to be from about 9 pH to about 10 pH, while it has been stated that a pH range of approximately 3 pH to 4 pH will eliminate polymer destruction (Al-Anazi et al, 2002). Complicating matters, pH has a direct effect on the swelling of the SAP, increasing the swelling ratio as brine pH increases until reaching about 6 pH (Bai et al, 2004-II). Temperature can also affect the reaction. As temperature increases, the SAP becomes less stable in Calcium brines and precipitates out further. In the absence of divalent cations, an increase in temperature results in an increase in swelling ratio (Chia and Bai, 2010; Bai et al, 2004-II).

Mitigating the effects of divalent cations can be done through the use of preflushes, which can significantly dilute or remove undesirable salts. In many instances, reservoirs that have undergone prolonged waterflooding can be assumed to be preflushed (Sheng et al, 2015). Such treatments are not always successful, however (Sheng et al, 2015). Remnants of divalent cations may remain and prevention of the reaction between them and the polymer could increase the success rate of SAP treatments.

EXPERIMENTAL WORK

Equipment

In order to measure out the desired quantities for the brines and polymers, a Tree® HRB103 electronic precision balance was used. For agitation and mixing brines, a small VWR® Lab Dancer S41 test tube shaker was employed on either the 15mL or the 50mL graduated centrifuge tubes with screw on caps containing the material. The effects of temperature on the swollen polymer was investigated through the use of a Julabo® F25 MC bath circulator using water as the bath fluid. The temperature of the fluid and the samples was confirmed in Celsius using a glass thermometer. Disposable pipettes were used to introduce acid to the brine solutions and the pH of the solutions were measured with an Oakton® pH 11 series pH meter.

Materials

Brines were mixed using deionized (DI) water and Calcium Chloride. The concentration was measured by percent weight and was mixed in a clean centrifuge tube. If needed, the contents would be mixed using the test tube shaker for a short period of time. The Calcium Chloride concentration was either 1% (% wt.) or 0.5% (% wt.), with the latter being the main focus. Hydrochloric acid (HCl) at differing concentrations was used to control pH. The concentrations used were 0.1N and 6N. Two polymers were used, AT-O3S and 2G-110, which differ only in particle size. Both SAPs were crosslinked Sodium polyacrylic acids manufactured using inverse suspension polymerization, which results in spherical particles. The particle sizes ranged from 60-120 mesh for AT-O3S and 30-60 meshes for 2G-110. This particular polymer is sensitive to salinity, pH, and temperature. Both polymers were purchased from Emerging Technologies®.

Brine Preparation

In order to prepare the brines, the desired amount of DI water was weighed out on the electronic balance scale and added to a clean, dry centrifuge tube. Calcium Chloride was then weighed out and added to the water, creating a brine. The desired brine concentration determined the amounts of each component. Calcium Chloride concentrations varied from 1% (by wt.) to 0.5% (by wt.). The brine was agitated after addition of the salt to increase the dissolution speed. The pH of the brine solutions, which varied from 9 pH to 10 pH, was modified by using a disposable pipette to add hydrochloric acid, measured by drops, to the brine solution. The pH and temperature of the solution was then measured and recorded. The pH range achieved was mostly in the range of 0.5 pH to 4 pH.

Polymer Preparation

The polymer was weighed out by percent weight of the brine solution. Do note that the polymer was not included in the brine solution weight. For example, 1% polymer for 15 grams of brine would be 0.150 grams of polymer, and the test weight of the experiment would be 15.15 grams. After the correct amount of material had been weighed out, it was added to a separate, dry centrifuge tube.

Test Execution

After preparing the brine and polymer in 50mL centrifuge tubes, the next step was to add the brine to the polymer. The brine was poured on top of the polymer at time 0 and was immediately agitated on the test tube shaker. This lased for 40 seconds, after which the polymer was allowed to settle for 20 seconds and a volume reading was taken. The process was repeated, resulting in 1 minute time intervals. Readings were taken until changes in volume failed to occur for 4 to 5 minutes, at which point the solution was considered stable. The volume data was converted to swelling ratio by finding the change in volume from time 0 and dividing by the volume at time 0 as seen below in equation 1. Since the polymer was originally measured out by weight, density had to be used to find the original volume.

Equation 1.
$$S = \frac{v - v_O}{v_O}$$

In Equation 1, S is the swelling ratio, v is the recorded volume, and v_o is the preswelling volume.

Equation 2.
$$V_o = \frac{m_p}{\rho_p}$$

In Equation 2, V_o is the preswelling volume, m_p is the polymer's measured mass, and ρ_p is the polymer's density. The density used was 1.23 g/mL.

Temperature Effect

Temperature test samples composed of polymer and brine were collected from previously performed experiments and transferred to 15mL centrifuge tubes so they would fit in the circulator. The bath temperature was adjusted on the circulator, and after some time had passed, the temperatures of the samples were taken. If the samples were at the desired temperature, volume readings would be recorded for each sample. The temperatures tested were 24°C (room temperature), 40°C, 60°C, 80°C, and 90°C. The volume data was converted into swelling ratio by using the same density as above and the known room temperature final swelling ratio of the sample to find the original volume.

RESULTS AND DISCUSSION

Results for AT-O3S Polymer

The first tests were conducted using 1% AT-O3S in brines of 1% Calcium Chloride as seen in figure 2. The results show that the peak swelling ratio achieved decreases with pH, but the time it takes to reach solution stability increases. This is also displayed in the 0.5% Calcium Chloride results shown on the same figure. The results are unclear and inconclusive under these conditions, alluding to a decrease in reaction speed as pH decreases.

In response, Calcium Chloride concentrations were kept at 0.5%, and the amount of AT-O3S used increased to 1.25%. The results can be seen in figures 3a and 3b, each sample labeled by pH. As the pH decreased toward 6 pH to 7 pH, the peak swelling ratio increased, as did the final swelling ratio. After this range, the peak and final swelling ratios decreased in value once again.

Figures 3a and 3b are far from clear and are showing more than just the reaction between the SAP and Calcium ions. The direct effect of pH on the polymer is also a contributing factor. Since Calcium reacts with the polymer after it swells and the pH of the solutions remain constant, removal of the effects of pH can be done by finding the percent decrease in a sample from its maximum swelling ratio to its final swelling ratio. The results can be seen in figure 4. A clear trend can now be seen; the percent change in swelling ratio from maximum to final values declined as pH declined. This implies that pH has the capability to significantly decrease the ability of divalent cations to react with the polymer, reducing the change from maximum to final swelling ratios from -55% at 9 pH to a range of -2% to -5% in an area of 0.5 pH to 0.75 pH.

The ratio of polymer to Calcium also had an effect on the reaction. As the amount of SAP increased in the same Calcium brines, the change from peak to final swelling ratios decreased.

Modifications in sample temperature in almost all cases resulted in destabilization of the sample and further precipitation occurred, decreasing the swelling ratio by 15% to 30% at 90°C compared to the room temperature swelling ratio. In the range of 0 pH to 2 pH, temperature increases actually increased the swelling ratio of the polymer by almost 60% on average. Figures 5 through 7 show the effects of temperature on the test samples.

Results for 2G-110 Polymer

For the 2G-110 Polymer, the first tests were performed by varying pH levels for samples using 1.13% 2G-110 in 0.5% Calcium Chloride brines. Observing the results from the first tests, follow up trials were altered to use 1.25% 2G-110 while maintaining the 0.5% Calcium Chloride brine concentration.

The reactions of the 2G-110 polymer with the brine posed two problems, supposedly due to its particle size, in comparison to that of the AT-O3S. Due to the 2G-110's smaller particle size, the time interval of the reactions that took place between the brine and the polymer were much faster due to having more surface area per unit volume, and since the particles were comparably smaller, they became easily suspended in the solution for a significant portion of the reaction time as well. As such, after performing the same steps used as those used for the AT-O3S polymer trials, only the 2G-110's final swelling ratios were able to be accurately calculated after the solutions were allowed to settle for a significant time. The rest of the 2G-110's trials using the heat bath mirrored that of the AT-O3S.

Observing the results in Figure 8 and Figure 9, the effect of lowering the pH on the 2G-110 and brine solutions showed that, from the range of 2 pH and higher, the final swelling ratios appear to almost linearly decrease as pH was lowered across the trials, yet at a slight rate of decrease. However, at below 2 pH, the final swelling ratio significantly begins to drop.

Through heating the solutions at varying temperatures, the samples with pH values greater than 2 destabilized and further precipitated when the temperature was raised higher than room temperature, as shown in Figure 10 and in Figure 11 where the data was grouped by alike pH's. These samples experienced decreases in swelling ratios of around 5 to 20 percent, shown in Figure 12, when compared to the original swelling ratios of the samples. At pH levels of 2 and lower however, it was displayed that swelling ratios would range from relatively no change to significant increases of swelling ratios upwards of 140% as seen in figures 10 through 12.

CONCLUSIONS

- pH clearly has significant influence over the extent to which the polymer reacts with Calcium in solution; however, the ratio of polymer to Calcium also exhibits control over the reaction.
- As the pH of a solution decreases below 2 pH, precipitation effects become relatively insignificant at low salinities and higher SAP concentrations. Therefore, these effects can be neglected in many low pH situations. However, lowering the pH to these levels may create severe decreases in final swelling ratios in comparison to the swelling of higher pH concentrations.
- Temperature had mixed effects on the polymer. At pH ranges over 2 pH, an increase in temperature resulted in a significant decrease in the swelling ratio and increase in precipitation. This could cause greater formation damage. At lower pH values, swelling ratios actually increased far more significantly in the solutions. This is possibly due to the polymers not fully swelling at lower pH values, and that the introduction of heat catalyzed latent swelling reactions.
- It is recommended to industry that, when confronted with the possibility of high concentrations of divalent cations, preflushes and acid washes should be performed prior to SAP treatments. The amount of polymer used should also be increased depending upon expected reservoir conditions. These considerations become increasingly important as temperature increases.

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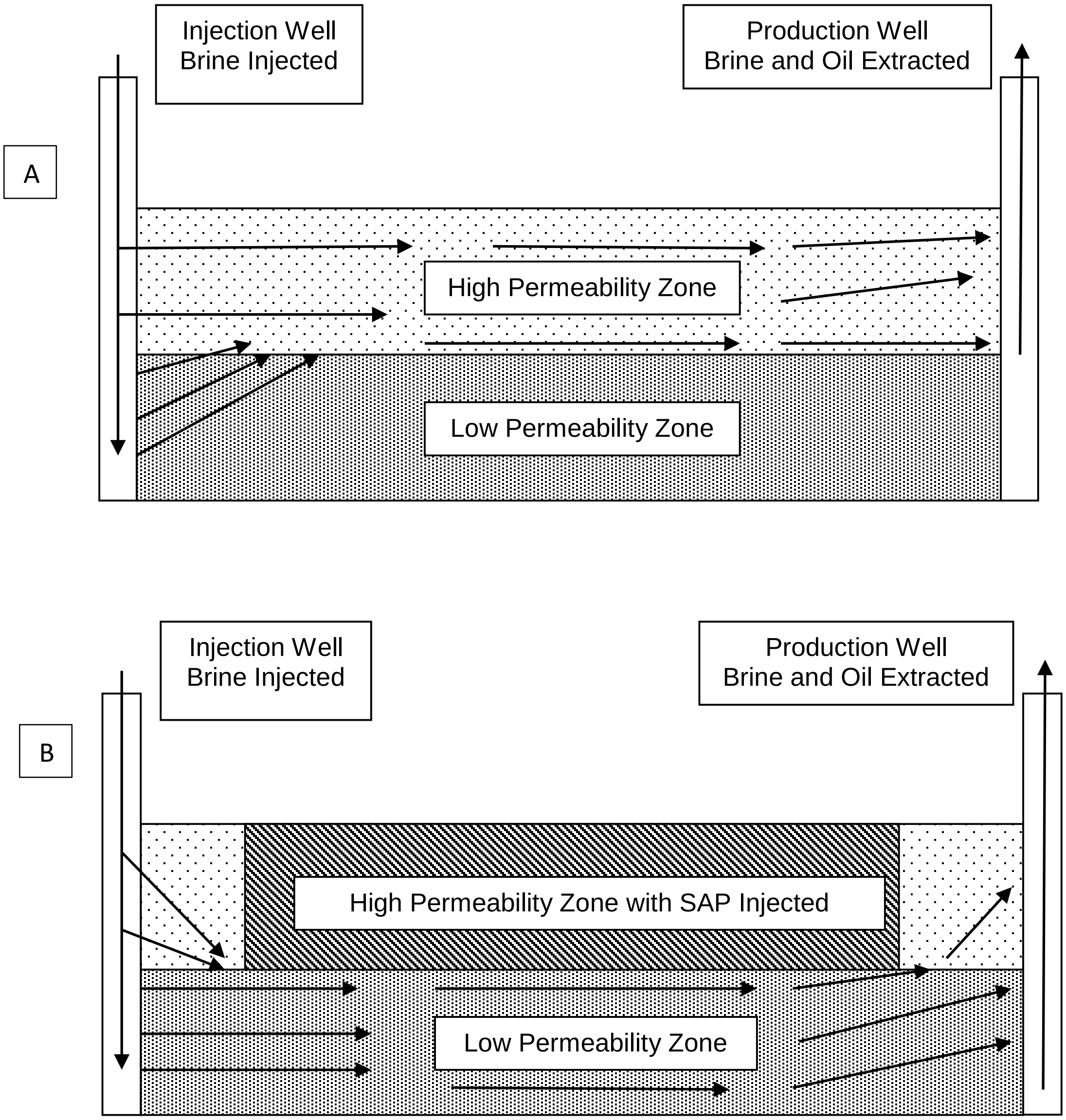

Figure 1. Heterogeneous Reservoir Flow during Water injection a) Before SAP Treatment and b) After SAP Treatment

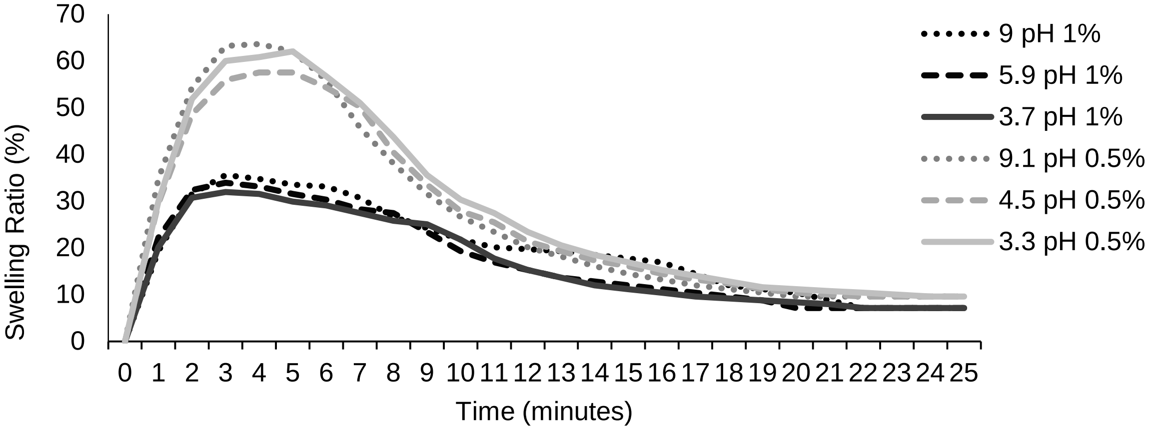

Figure 2. Swelling of AT-O3S in Calcium Chloride Brine (pH and concentration indicated in legend)

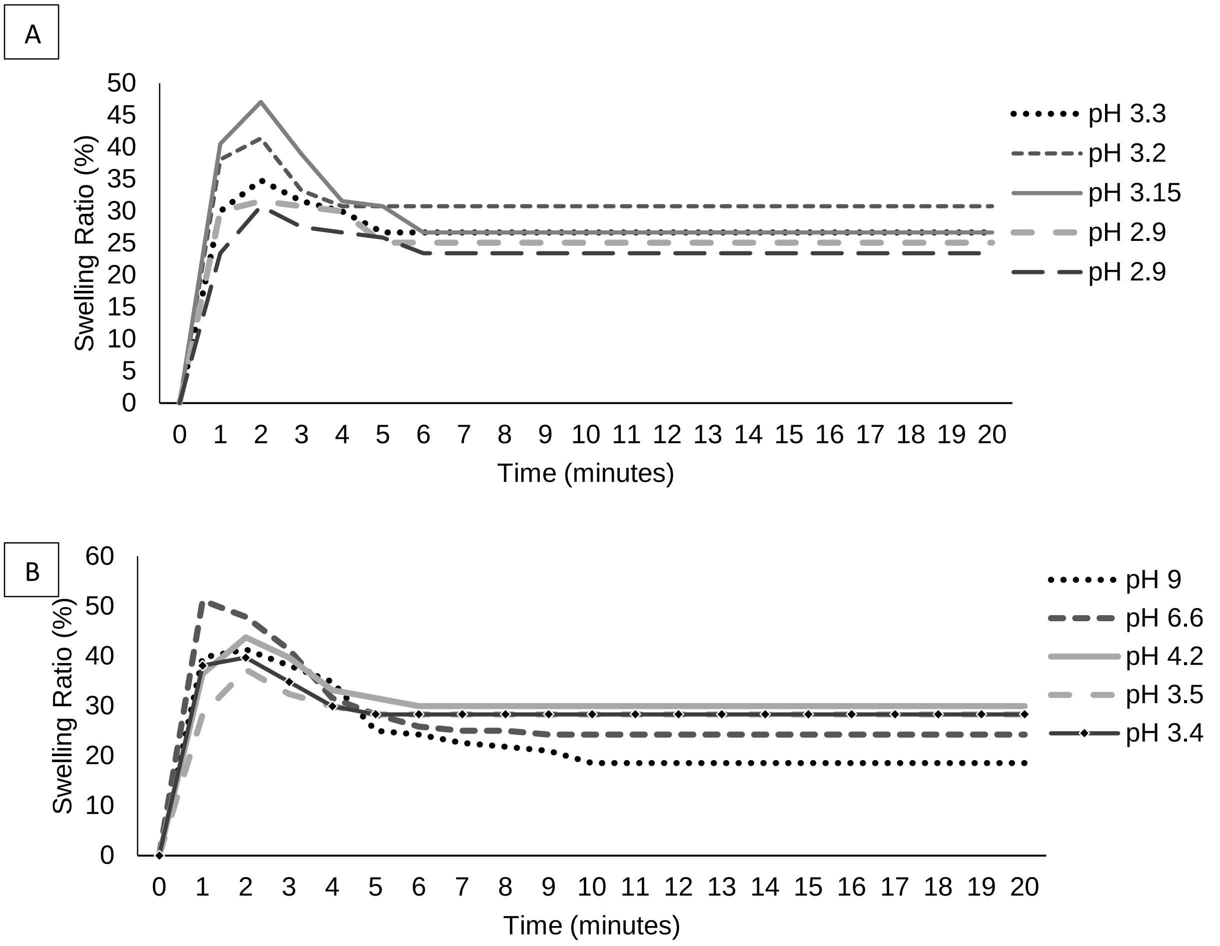

Figure 3. Swelling 1.25% AT-O3S in 0.5% Calcium Chloride at Varying Brine pH Values a) pH Value from 2.9 to 3.3 and b) pH Value from 3.4 to 9.

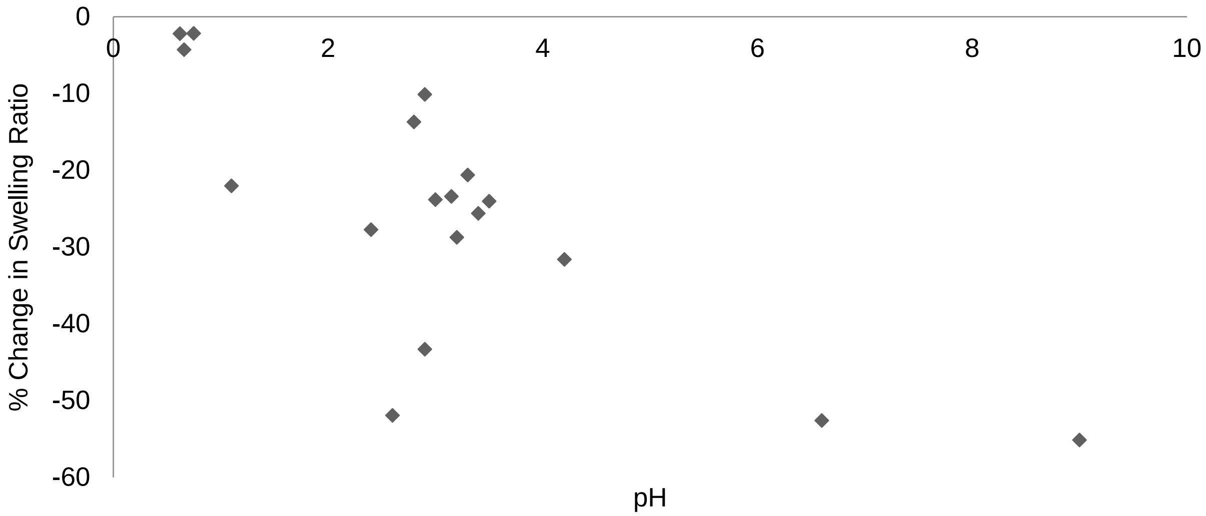

Figure 4. Percent Change in Swelling Ratio from Peak Value to Final Value by pH

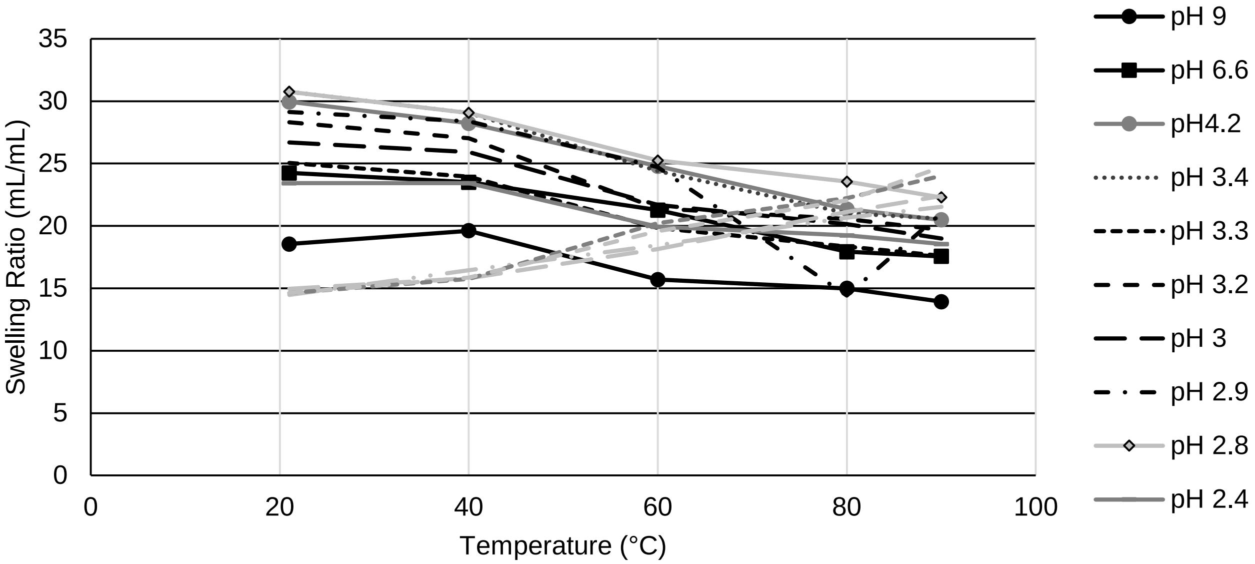

Figure 5. Swelling Ratio by Temperature 1.25% AT-O3S Polymer in 0.5% Calcium Chloride Brine

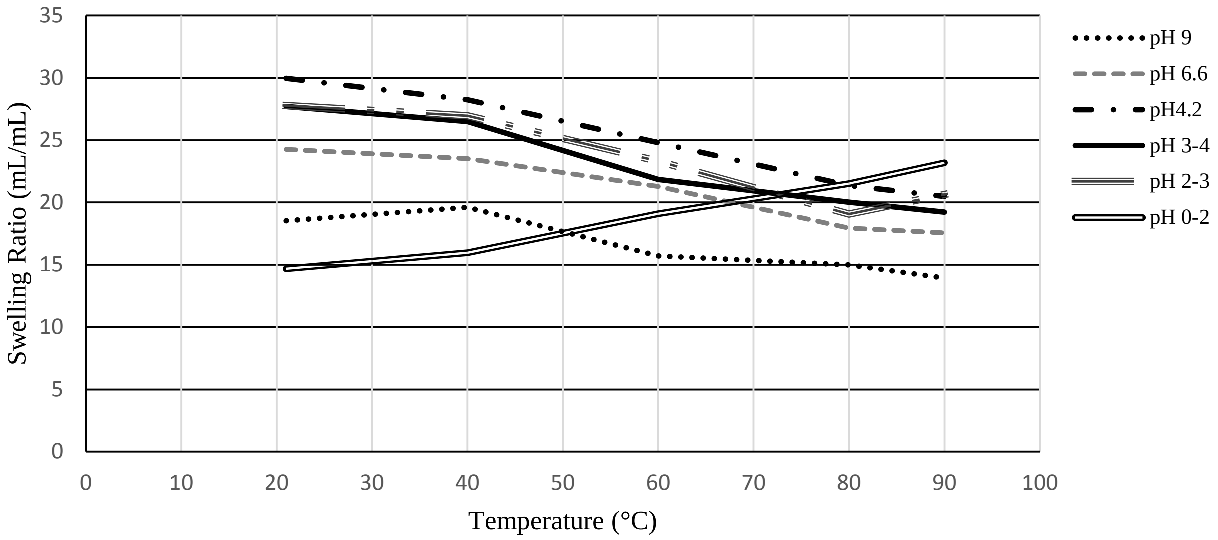

Figure 6. Swelling Ratio by Temperature 1.25% AT-O3S Polymer in 0.5% Calcium Chloride Brine

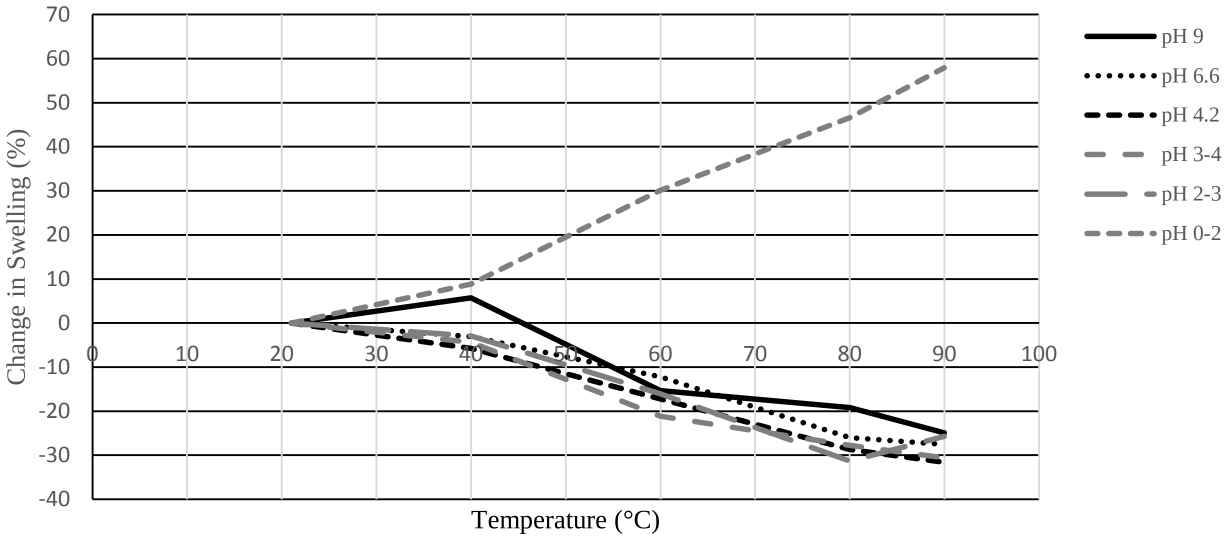

Figure 7. Percent Change in Swelling Ratio From Room Temperature 1.25% AT-O3S Polymer in 0.5% Calcium Chloride Brine

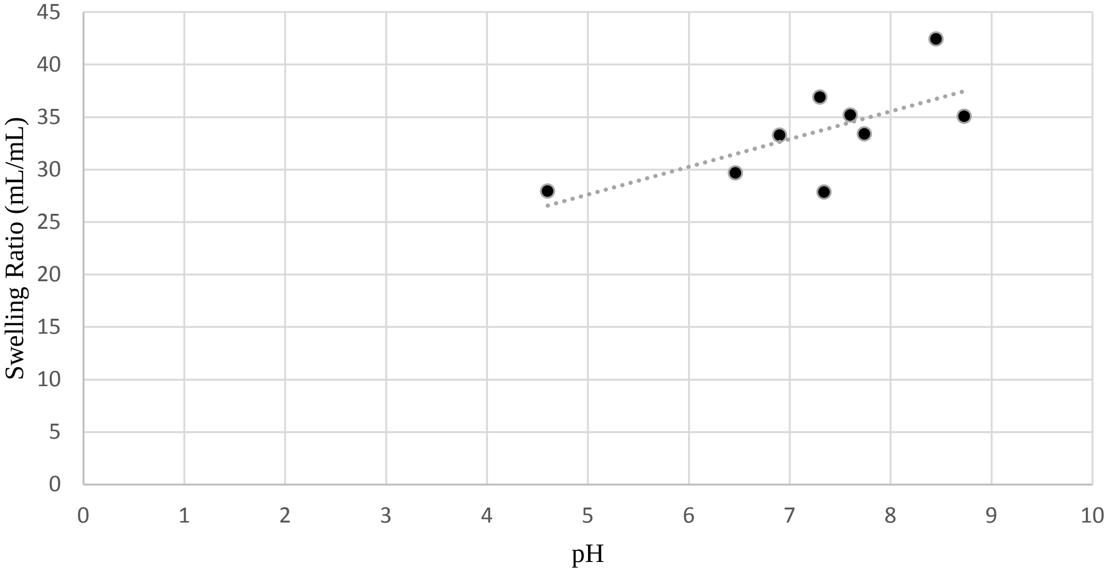

Figure 8. Final Swelling Ratio by pH for 1.13% 2G-110 Polymer in 0.5% Calcium Chloride Brine

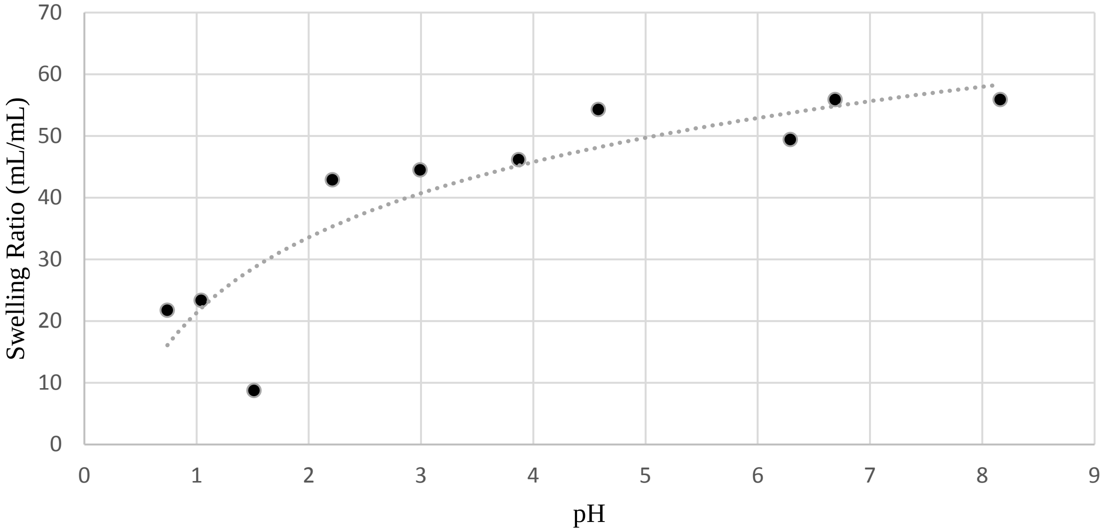

Figure 9. Final Swelling Ratio by pH for 1.25% 2G-110 Polymer in 0.5% Calcium Chloride Brine

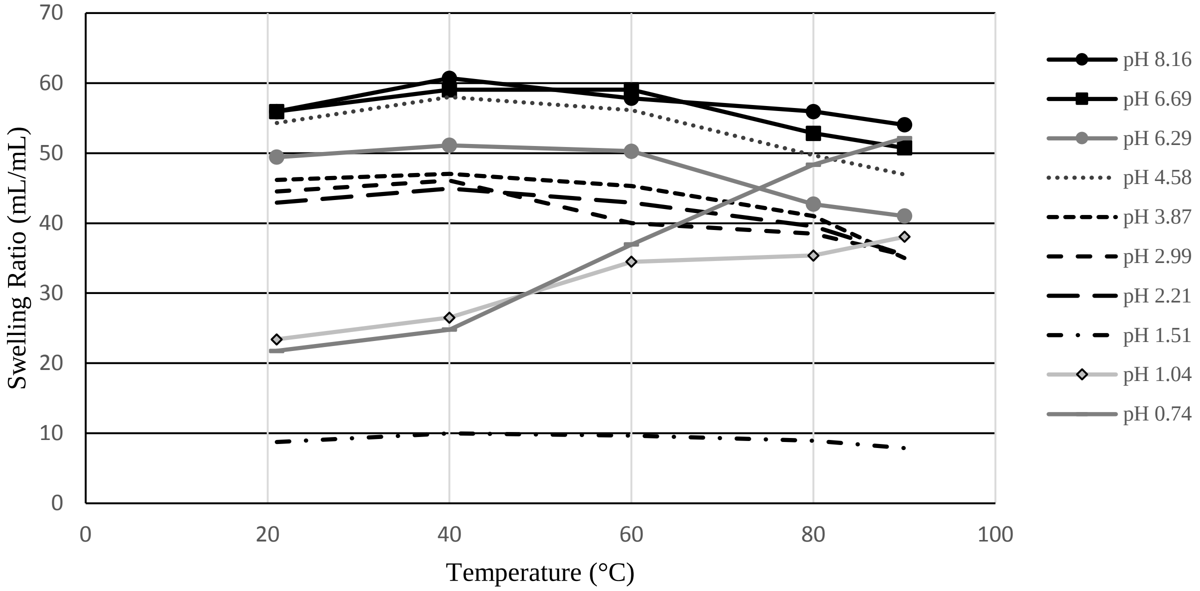

Figure 10. Swelling Ratio by Temperature 1.25% 2G-110 Polymer in 0.5% Calcium Chloride Brine

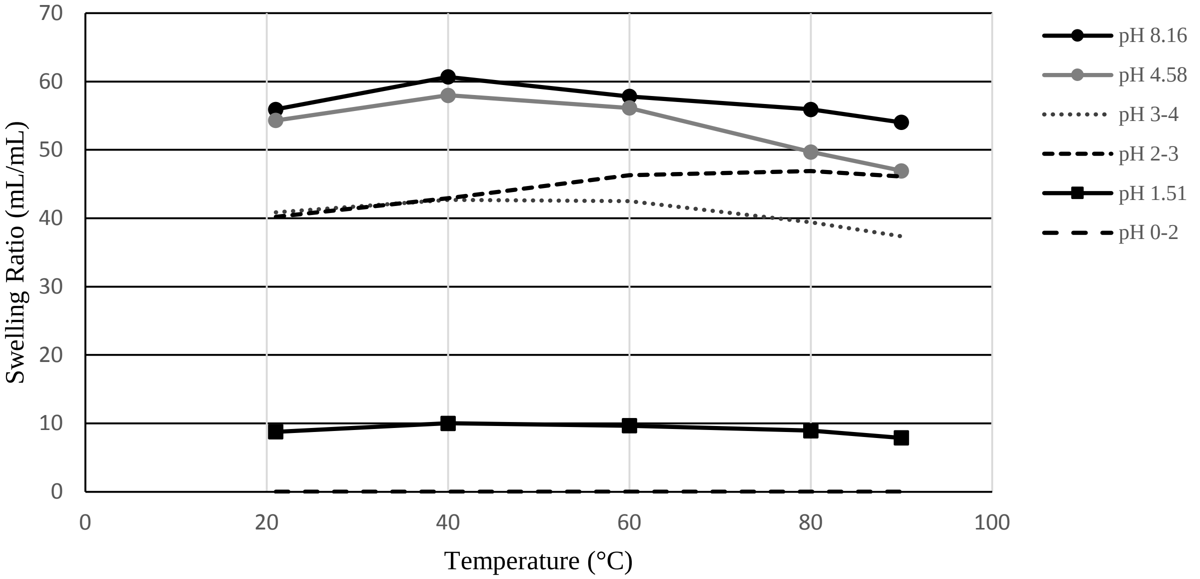

Figure 11. Swelling Ratio by Temperature 1.25% 2G-110 Polymer in 0.5% Calcium Chloride Brine

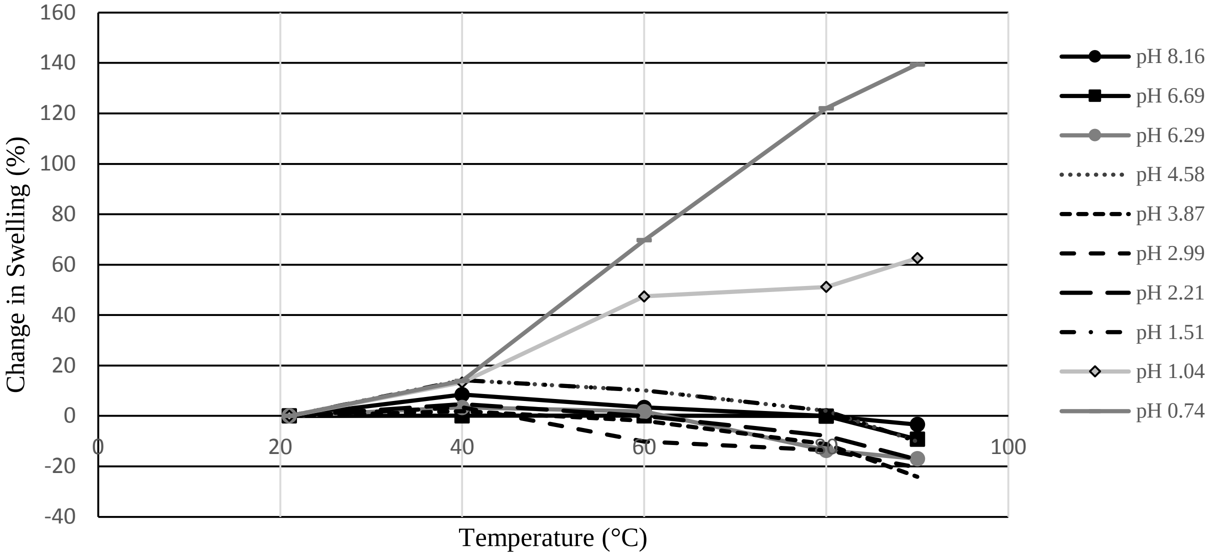

Figure 12. Percent Change in Swelling Ratio by Temperature 1.25% 2G-110 Polymer in 0.5% Calcium Chloride Brine