Swelling and deswelling kinetics of liquiblock 40F polymer

Abstract

In today’s oil industry, unwanted water production has become a serious issue. To increase oil production in a reservoir, a water injection method is commonly used. During water injection operations, water is injected into the oil reservoir in order to extract oil trapped in the formation. Due to the heterogeneity, in the reservoir formation, oil production will decline and water production will increase tremendously as injected water sweeps the high permeability zones. To flush out the remaining oil in tighter zones of the formation, several treatments can be used. One of the effective chemical treatments is the injection of a superabsorbent polymer (SAP) into the high permeability zones. The heterogeneity in reservoir permeability will be decreased by the swollen polymer, thus resulting in a greater sweep of the low permeability zones. The following work focuses on the use of Liquiblock 40F, a cross-linked acryl amide/potassium acrylate copolymer from Emerging Technologies®. The swelling and deswelling factors of such polymers are heavily influenced by salinity, temperature, and pH. To study the polymer’s kinetics, 1% wt polymer was allowed to swell and de-swell over time in brine solutions of deionized water, where 1% to 10%wt Sodium Chloride, 1% to 4%wt Calcium Chloride and, 1% to 10%wt mix brine range. The effects of temperature, ranging from 30°C to 80°C, on the swelling ratio of the gel was also investigated. Understanding the reaction of the SAP when exposed to different brines can help the oil industry utilize the technology in the most effective way.

Introduction

As oil reservoirs mature, methods to increase oil extraction efficiency become increasingly important to the economic longevity of reservoir production and utilization.1 Water injection is a common secondary method used to artificially pressurize a conventional oil reservoir, allowing for continued production after reservoir pressure drops due to extraction. Although a very useful technique, there are some drawbacks. Heterogeneity in reservoir permeability causes fingering and early breakthrough, leading to large increases in water production.2 This translates to greater production costs.3

As the percentage of water increases, the percentage of produced oil must decrease. In extreme cases, wells may be producing 98% water.4 In fact, the water saturation is of the biggest factors determining reservoir production.5 This formation water can have a relatively high concentration of metal ions from salts present in a formation or resulting from injection water, with the two most common reservoir cations being Sodium+ ions and Calcium2+ ions, followed by Magnesium2+ ions.6 As a result, scaling and corrosion of equipment becomes a major issue, as does the processing and disposal of the brine mix.7 The estimated cost of excess water production worldwide was reported around $40 Billion (USD) a year.7

Excess water production is often caused by differences in the permeability of a reservoir, which can affect fluid movement significantly.2,3,8 Since injected water can flow through the high permeability zones with less backpressure, the looser areas of the formation are cleared of oil first, and water production begins to increase dramatically after breakthrough.9 Although the reservoir may be producing small amounts of oil, a large reserve could remain in the unswept, low permeability zone.11 Figure 1 shows an example of the deviation of injected water into the high permeability zone in a heterogeneous reservoir.

The challenge is to decrease reservoir heterogeneity, namely by decreasing the permeability of the high permeability zone.11 Doing so allows for a far more efficient and effective sweep of the low permeability zone, and therefore greater oil production, greater extraction efficiency, and longer well lives. However, unwanted water could also originate from the reservoir itself, as natural ground water sources. The isolation of such sources and zones could also enhance oil recovery and production.

Chemical methods, used extensively in the past few decades, consist, specifically, of chemical products that are pumped into either production or injection wells.12,13 Chemical shut-off methods include: micro matrix cements, polymers, micro particle blends, foamed systems, and particulate chemical blend gels/gelant.

Most polymer solutions, with time, evolve from low viscosity liquids to either strong or weak gels, depending on the solution’s formulations. These gels can either partially or completely block the channels through which water is being produced. As a result, they are the basis of most water shut off (WSO) treatments. WSO treatments...
are frequently applied in fields with either water flooding or polymer flooding. They allow sweeping pattern to be redirected to those areas that have not yet been produced.

An important number of WSO chemical methods have been developed in the last twenty years. Among these gel systems using both polyacrylamides and different cross linkers have been the most extensively applied. These cross linkers can be classified as either inorganic or organic. The inorganic cross linking agents most widely used are based on Cr, Al, and Zr. These agents are used with partially hydrolyzed polyacrylamides (PHPA). These cross linkers generate ionic bonds with the carboxilate (negatively charged) groups in polymer. Organic cross linkers are more stable at high temperatures due to the covalent bonds generated with the polyacrylamides (PAM) amid groups.

Polyacrylamides can be used to control excess water production in heterogeneous, conventional reservoirs and such materials are considered superabsorbent polymers (SAP). SAPs swell into a gel in the presence of water, and the ratio to which they swell is typically dependent upon the solution conditions, in the case of a reservoir: the salinity, the pH, and the temperature. This polymer is inserted into a reservoir and allowed to swell, decreasing the permeability of the high permeability zone by entering and swelling in the pore throats, while having little effect on the low permeability zone. This causes a decrease in reservoir heterogeneity, which will increase the extraction efficiency and produce a better sweep pattern. Such an example can be seen in Figure 2.

![Figure 2 Example of water flow through an SAP treated reservoir.](image)

Such processes may also be used to completely isolate a zone. In order to best employ an SAP to a particular reservoir, it is important to understand the kinetics of the polymer so as to reduce formation damage and effectively target the high permeability zones. Although a problem, there exists an analytical method to predict and prevent such damage. It has been seen that the penetration depth of the polymer into the porous media is an indicator of permeability reduction, and since the pore throats tend to be smaller in the low permeability zones, the drop in permeability is considerably less in these areas. This causes a decrease in reservoir heterogeneity, which will increase the extraction efficiency and produce a better sweep pattern. Such an example can be seen in Figure 2.

The presence of divalent cations in a reservoir or a brine can cause serious issues when some types of SAP are introduced to it, especially in solutions with pH greater than 3 to 4. As the polymer absorbs water and becomes a gel, divalent cations react catastrophically with the cross linker in the gelled polymer. The ionization of the carboxyl group in the cross linker (polyacrylate salt) is the culprit, resulting in the replacement of the monovalent cations in the polymer chain by the divalent cations. The issues caused by Calcium and other divalent cations can be mitigated by the use of a preflush in a reservoir, although such action may not be successful. A similar effect can be observed in a reservoir that has been water flooded for an extended period of time. It has been seen that very low pH values can prevent precipitation through suppression of the carboxyl group’s ionization in the cross linker. Due to the possibility of unexpected divalent cations remaining in the solution, investigation of the polymer’s kinetics when exposed to such detrimental conditions is important to properly implementing a treatment.

### Experimental work

#### a. Equipment

An electronic precision balance, a Tree® HRB103, was used to weigh out all components used in this work Figure 3A. In order to measure pH values, an Oakton® pH 11 series pH meter, as seen in Figure 3B, was used.

![Figure 3 Lab equipment used A.) Electronic Precision Balance, Magnetic Mixer, and Agitator. B.) pH Meter. C.) Julabo Refrigerated Bath Circulator.](image)

In order to study the effect of temperature, a Julabo® F25 MC bath heater and circulator was employed Figure 3C. This device has the capability to both cool and heat samples inserted into the bath. To
measure the volume of the polymer during experiments, the work was
carried out in 15mL graduated centrifuge tubes Figure 4A, Figure 4B.
In order to ensure that uniform and correct results were acquired during
swelling and deswelling trials, a VWR® Lab Dancer S41 agitator was
used Figure 3A. The use of an agitator provided a repeatable way
to expose the lower SAP particles to the brine solution. An accurate
kinetic curve could then be recorded in a repeatable fashion.

Figure 4 Shows the A.) Unswollen Polymer in Graduated Centrifuge Tube. B.)
Partially Swollen Polymer Solution in Graduated Centrifuge Tube.

Materials

a. Brine

To manufacture the brine, deionized (DI) water from was used. Sodium Chloride, a popular salt in SAP kinetics studies, was mixed with the DI water by percent weight. Calcium Chloride was also used both alone in a brine and in conjunction with Sodium Chloride. The brines were mixed in a 15mL graduated centrifuge tube.

b. Polymer

The polymer used was Liquiblock 40F, which utilizes Potassium polycrylatefor the cross linker. The particle size of the polymer ranged from 35 to 60 mesh or 250 to 500 microns. The SAP used in this project was sensitive to brine salinity, temperature, and pH. This polymer has the ability to absorb large amounts of water.

c. Procedure

In order to study the kinetics of the polymer, it was allowed to
swell and deswell over time in brines comprised of DI water, Sodium Chloride, Calcium Chloride, or a mix of Sodium Chloride and Calcium Chloride. The effect of temperature on the final swelling ratio was then investigated by adjusting the temperature of preswollen samples. All components were weighed out on an electronic precision balance prior to being combined in the graduated centrifuge tubes. The brine solutions were mixed by percent weight and agitated until all visible evidence of salt had vanished. The Sodium Chloride concentration ranged from 1% to 10%, the Calcium Chloride concentration ranged from 1% to 4%, and the concentration of the combination of the two (mixed brine) ranged from 1% to 10% in a ratio of 9 parts Sodium Chloride to 1 part Calcium Chloride, measured by weight, as seen in Table 1 below. This ratio was chosen based on reported reservoir salinities from Montana and North Dakota in the United States.

Due to precipitation issues, the concentration ranges of brines containing Calcium Chloride had to be limited in order to prevent wasteful experiments. The pHs and temperatures were measured prior to brine introduction to the polymer, and the pH results can be seen in Table 2. After introducing the brine to the polymer, the tubes were immediately agitated on a test tube shaker. The readings were taken in mL by evaluating the volume of the polymer using the graduated on the centrifuge tubes.

Table 1 Salt Concentration by Brine Type

<table>
<thead>
<tr>
<th>Brine type</th>
<th>Concentration ranges (by % wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride</td>
<td>1%, 2%, 5%, 7.5%, 10%</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>1%, 2%, 3%, 4%</td>
</tr>
<tr>
<td>Sodium Chloride and Calcium Chloride</td>
<td>1%, 2%, 5%, 7.5%, 10%</td>
</tr>
<tr>
<td>(90% of salt wt. was Sodium Chloride, 10% was Calcium Chloride.)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 pH values by salinity and brine type for Liquiblock 40F

<table>
<thead>
<tr>
<th>Concentration (% wt.)</th>
<th>pH Sodium Chloride</th>
<th>pH Calcium Chloride</th>
<th>pH Mixed Brines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>6.62</td>
<td>6.41</td>
<td>6.27</td>
</tr>
<tr>
<td>2%</td>
<td>6.24</td>
<td>6.49</td>
<td>6.27</td>
</tr>
<tr>
<td>3%</td>
<td>-</td>
<td>7.18</td>
<td>-</td>
</tr>
<tr>
<td>4%</td>
<td>-</td>
<td>7.53</td>
<td>-</td>
</tr>
<tr>
<td>5%</td>
<td>-</td>
<td>-</td>
<td>6.54</td>
</tr>
<tr>
<td>7.5%</td>
<td>-</td>
<td>-</td>
<td>6.75</td>
</tr>
<tr>
<td>10%</td>
<td>-</td>
<td>-</td>
<td>7.03</td>
</tr>
</tbody>
</table>

d. Polymer swelling

i. The Liquiblock 40F was weighed out (1% by brine weight) and added to a separate, dry tube.

ii. The brine was mixed, then it was added to polymer in a dry tube, and agitated.

iii. Swelling was initially measured by the volume of the polymer. The following equation, where S is the swelling ratio, V is the volume of the polymer at the time of measurement, and \( V_o \) is the volume of the polymer in powder form (initial volume),

\[
S = \frac{V - V_o}{V_o}
\]

(1)

Provided the swelling ratio

In order to find the initial volume of the polymer, the density of the polymer had to be considered. Using the mass and density, the following equation was used to find \( V_o \).

\[
V_o = \frac{m_p}{\rho_p}
\]

(2)

Where \( m_p \) is the initial mass of the polymer and \( \rho_p \) is the density of the polymer. The original density used for the polymer was 0.54 g/mL and was acquired from the manufacturer’s data sheet.

c. Polymer deswelling

i. The SAP was weighed out at 0.1% by percent weight of the DI water and added to a dry centrifuge tube.
ii. 15g of DI water was then added to the polymer and it was agitated until fully swollen. Care was taken to allow a layer of water to remain free at the top of the tube to allow for quick dissolution of the salts, giving a more accurate curve.
iii. The salts were added to the solution by percent weight to provide the proper salinity.
iv. Deswelling was measured by the volume of the polymer then converted into swelling ratio using equations 1 and 2.
f. Polymer temperature sensitivity
i. Previously swollen SAP samples were placed in a heated and refrigerated circulator (Julabo® F25 MC) in order to control the temperature, which was varied from 30°C to 80°C.
ii. The tubes were allowed to reach the desired temperature, which was confirmed by the pH 11 meter.
iii. The volume of the polymer was then recorded and converted to swelling ratio using the same methods as above.
g. Polymer pH sensitivity
i. The procedure from polymer swelling was followed, with the difference that the pH of the brine was modified prior to exposing the SAP to it.

Results

a. Swelling kinetics
i. Sodium chloride brines: The results for the Sodium Chloride brines Figure 5 appeared to be relatively smooth. The polymer took approximately 30 minutes to reach stability, and experienced a decrease in swelling ratio as salinity increased. When brines of salinities of 5% NaCl (% wt) and over are compared to one another, the effects of a change in salinity on the final swelling ratio appears to decline. In the studied range, the final swelling ratio of the polymer appears to decrease exponentially as salinity increases.

Figure 5 PolyBlock 40F Swelling with Sodium Chloride

ii. Calcium chloride brines: When exposed to Calcium Chloride brines, the polymer experiences precipitation. This can be seen by the sporadic fluctuations in the swelling ratio prior to the 10 minute mark in Figure 6. Compared to polymer swollen in Sodium Chloride brines, polymer swollen in Calcium Chloride brines experiences less than half of the swelling. All four curves display a peak in swelling followed by a correction caused by precipitation. These curves can appear sporadic, as swelling and precipitation affect the gelling polymer simultaneously. The ionized carboxyl group in the copolymer’s cross linker (Potassium polyacrylate) results in the replacement of Potassium with the divalent salt. The formation of Calcium polyacrylate, which has very low solubility, is the product in this case.

Figure 6 PolyBlock 40F Swelling with Calcium Chloride

iii. Mixed brines (90% Sodium and 10% Calcium): Using mixed brines Figure 7, it was observed that at low concentrations, the swelling curves were relatively smooth. Equilibrium occurred much sooner than in the cases of just one or the other salt, with stability ensuing around the 10 minute mark. There were not observable peaks like the ones seen in CaCl₂ only brines. The swelling ratios were lower than the swelling ratios observed in NaCl only brines, although for 1% salinity the difference is small at about 3%. Unsurprisingly, as salinity increases, this difference increases. This difference grows to over 15% at 10% salinity as the amount of Calcium ions present increases.

Figure 7 PolyBlock 40F Swelling with 90%NaCl and 10%CaCl₂

b. Deswelling kinetics
i. Sodium chloride brines: Deswelling in Sodium Chloride brines, seen in Figure 8, occurred quickly and appeared to be quite smooth. It was seen that as salinity increased, the equilibrium position of the polymer decreased. Due to difficulties measuring the polymer, the salinities tested in the swelling experiments could not be examined in deswelling tests. This prevented comparison between the final swelling ratios of swelling and deswelling, which should approach the same equilibrium position.
ii. Calcium chloride brines: Calcium Chloride brines appeared to have a dramatic effect on the preswollen polymer’s swelling ratio Figure 9. Equilibrium took place within about 1 minute for all salinities and resulted in large amounts of precipitation. The swelling ratios appeared to approach the same value regardless of the solution salinity. This SAP appears to be very sensitive to divalent cations and is incompatible with solutions containing substantial concentrations of them during deswelling. This may be due to the smaller amount of polymer present in the solution (0.1% versus the 1% in the swelling solution).

iii. Mixed brines (Sodium and Calcium): Deswelling in mixed brines appeared to be quite stable in comparison with CaCl₂ only brines. The equilibrium position of the polymer varied with the salinity and looked quite similar to the deswelling curves of the Sodium Chloride only brines. The low concentrations of divalent cations in these brines appeared to further depress the final swelling ratios of the polymer samples in comparison with NaCl only brines without the dramatic polymer losses seen in the Calcium Chloride brines. The mixed brine results can be seen in Figure 10.

Figure 8 LiquiBlock 40F Deswelling in Sodium Chloride Brines.

Figure 9 LiquiBlock 40F Deswelling in Calcium Chloride Brines.

C. Temperature effects

Temperature caused polymer swollen in any brine to decrease in volume. Figures 11 through 13 show the swelling ratio of the polymer samples as temperature was adjusted. Sodium Chloride brines, seen in Figure 11, lost about 10% to 25% of their swelling ratio between room temperature and 80°C. This polymer deswells when exposed to higher temperatures, and salinity increases show a tendency to decrease the amount of volume lost to temperature increases.

The polymer samples swollen in CaCl₂ brines Figure 12 fared much worse, losing anywhere from 25% to 50% of their swelling ratio between room temperature and 80°C. Much of this change in volume can be attributed to a continuation of the reaction between Ca²⁺ and the ionized cross linkers due to the increase in the solution’s available energy. Further precipitate became visible as temperature increased.

In comparison, the samples swollen in the mixed brines Figure 13 decreased in swelling ratio at about the same rate as those in just NaCl brines, with an overall decrease between 15% and 25%. The swelling ratio losses in the mixed brines may include further precipitation losses, but the effects appear to be negligible at the tested salinities since the amount of Calcium present is relatively small.
The effects of pH on the swelling of the polymer is insignificant to slight for all three brines until reaching a pH value close to 1 pH. Near this value, the swelling experienced by the polymer decreases substantially. In fact, the swelling ratio of the Sodium Chloride brines Figure 14 decreased by about 85% as the pH approached 1pH. The swelling curve of the low pH polymer in Figure 14 is oddly shaped. This was caused by the formation of a gel pack on the surface of the polymer. More aggressive agitation was needed to properly expose the lower layers of the polymer to the brine solution.

The Mixed brine results Figure 15 showed quite similar final swelling ratios when compared to the Sodium Chloride brine curves. The Mixed brine with the pH of 0.9 showed some deswelling, most likely due to the same gel pack formation issue seen in the 1.1 pH Sodium Chloride brine. It was not quite as dramatic, however.

When examining the Calcium Chloride results in Figure 16, it is apparent that pH has some effect throughout the range. The 0.8 pH brine did not appear to suffer from gel pack formation issues to the same extent as the other low pH brines. It should be noted that precipitation could have influenced the amount of deswelling experienced by this brine. It was seen that deswelling was present over the entire pH range.

When viewing Figure 17, the relationship between the brine type and pH can be seen quite clearly. The difference between the Sodium Chloride and Mixed brines is not large throughout the pH range due to the low concentration of Calcium. When comparing these two to the swelling experienced by the Calcium Chloride brines, there is approximately a 60% decrease in swelling ratio above 1 pH. This could be attributed to precipitation. As pH declines and approaches 1 pH, the Calcium Chloride final swelling ratio approaches the same value as the Sodium Chloride swelling ratio. This implies that pH has successfully suppressed the ionization of the cross linker’s carboxyl group. This may also be the reason for the dramatic decrease in swelling ratio seen in the Sodium and Mixed brines as pH approaches 1pH.

**Conclusion**

The polymer reaction with Sodium Chloride resulted in smooth curves, and when the salinity increased, the polymer decreased exponentially in swelling ratio.

The polymer did not respond well to Calcium Chloride, as Calcium precipitated out of the solution with the cross linker due to the ionized carboxyl group in the cross linker.
Since the Potassium cross linker precipitates out in the presence of the divalent cation, this polymer is incompatible with such brine compositions at salinities above 1% to 2%.

Polymer deswelling in Calcium Chloride brines was extremely fast, and resulted in large amounts of precipitation. This could be due to the small amount of polymer exposed the brine, at 0.1% brine weight. There is not enough polymer to absorb the Calcium ions that are introduced to the solution.

As temperature increases, the polymer deswells. In addition, the Calcium Chloride brines appear to experience greater instability, and therefore further precipitation, as temperature increases.

It appears that at low brine concentrations, Calcium Chloride has little effect on swelling ratio changes in Mixed brines as temperature increases.

pH appeared to have little effect on the swelling ratios of the Sodium Chloride and Mixed brines until approaching the range of 1 pH. In this range, the polymer swelling ratio decreases quite dramatically.

Due to the suppression of carboxyl ionization in the cross linker, the Calcium Chloride, Sodium Chloride, and Mixed brines approach the same swelling ratio when the pH of the solution is near 1 pH.

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Conflict of interest

The author declares no conflict of interest.

References

