OIL EFFECT ON THE DEHYDRATION OF SUPERABSORBENT POLYMER

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ABSTRACT

As a reservoir matures the oil sweep efficiency decreases and water production increases significantly. This water can be from the formation, and/or water from an injection well. As the water production increases over the life of the reservoir, it can cause oil production to decrease and cost to rise. Water can reduce production even if a high volume of hydrocarbons exists in the reservoir. To alleviate these issues many companies in the oil industry are applying Superabsorbent Polymers (SAP). Superabsorbent preformed polymers can absorb one hundred times their weight in solution. This work was conducted to investigate SAP dehydration in oil field applications. LiquiBlock's AT-03S with a mesh of 35-60 (250-500 microns) and LiquiBlock's 2G-110 with a mesh of 60-120 (125-250 microns) were used. Both polymers were created using the inverse suspension polymerization process. This produces particles that are perfect spheres, increasing their surface to volume ratio and increasing absorption capacity and speed. Three different brines were created by mixing deionized (DI) water with Calcium Chloride, Sodium Chloride, and a mixture of both Sodium Chloride and Calcium Chloride to create a brine of particular salinity. Black oil, medium oil, and mineral oil were tested. After allowing the polymers to fully swell in brine, oil was added to the solution, which was then agitated and allowed to settle. The effects of temperature were then investigated. It was seen in this work that oil dehydration actually increased the swelling ratio of the polymer.

INTRODUCTION

The use of polymers in tertiary recovery has become more popular, as they provide an effective way to reduce both reservoir heterogeneity and phase viscosity differences (Slattery, 1971; Elsharafi and Bai, 2012; Elsharafi, 2015; Elsharafi and Bai, 2015). These two factors have a significant effect on sweep efficiency and sweep pattern during secondary recovery operations, primarily waterflooding or injection (Slattery, 1971; Xu et al, 2014). One active area of study is the swelling kinetics of superabsorbent polymers (SAPs) for water shut-off (WSO) applications.

The objective of water shut-off using SAPs is to decrease the permeability of high permeability zones while reducing damage to the low permeability zones. This effect is achieved by the increase in pressure gradient required for a polymer particle to enter a pore throat as the diameter of the throat decreases (Bai et al, 2013; Elsharafi and Bai, 2015; Elsharafi and Bai, 2016). This causes the formation of a gel pack within zones of high permeability while leaving the low permeability zones relatively unaffected. The result is a decrease in reservoir heterogeneity and thus an improvement in sweep efficiency (Needham and Doe, 1987; Xu et al, 2014). This in turn reduces water cut and extends the economic life of the well. Knowing the swelling kinetics of the SAP is crucial to understanding how it will react to in-reservoir conditions, which will determine the polymer pack's permeability (Elsharafi and Bai, 2015; Ekeigwe et al, 2004). In addition, there is an analytical method for estimating damage caused by the polymer to the formation (Elsharafi, 2013).

Typically, the swelling kinetics of the polymer is studied. It has been seen that the salinity, temperature, and pH of the solution that the polymer is exposed to has an effect on the amount of swelling experienced (Elsharafi et al, 2016-II). The type of cations present in the brine solution are also important considerations when evaluating a polymer application. For many polymers, specifically the polyacrylamides (PAMs) used in this work, divalent cations in-solution are detrimental to the integrity of the Sodium polyacrylate crosslinkers (Al-Anazi et al, 2002; Elsharafi et al, 2016-I). There is a reaction between the ionized carboxyl group in the crosslinker and the divalent cation, which results in the replacement of the Sodium ion with the divalent cation and the creation of an insoluble polymer. The presence of monovalent salts, typically a Sodium or Potassium salt, causes a decrease in swelling ratio and increase in polymer strength as salinity increases. Temperature effects are typically negligible for temperatures below 80C. However, extreme conditions such as high concentrations of divalent cations and very low pH values could have an effect (Al-Anazi et al, 2002; Elsharafi et al, 2016-I). The pH has been shown to have an effect on the swelling of the polymer, decreasing swelling as pH declines (Al-Anazi et al, 2002; Elsharafi et al, 2016-I).

It is clear that the conditions of a reservoir are incredibly important to the performance and chances of success of a polymer treatment. Brine type and concentration, temperature, and pH have been studied. In addition, the effects of polymer dehydration in fractures has been investigated. Results showed that this dehydration can cause lower than expected propagation rates, and this tends to occur in small fractures (Seright, 1999). Dehydration of the polymer results in a change in polymer swelling, which can cause greater than expected damage to the formation. In fact, the volume of polyacrylamide-Chromium acetate polymer can decrease by 50% to 70% (Krishnana et al, 2000). Spontaneous imbibition can cause polymer dehydration, which can lead to a shrinkage of gel pack volume and a decrease in gel pack back pressure (Brattekas et al, 2014). This water loss is caused by a large pressure gradient which forces water from the polymer. It was seen that both water and mineral oil can be dehydrating fluids for polyacrylamides when a pressure gradient is experienced (Krishnan et al, 2000). One field that has not been explicitly studied is the dehydration of polymer resulting from the presence of in-solution hydrocarbons, although Krishnan et al has shown that the dehydrating effect caused by a pressure gradient is increased by the presence of oil.

EXPERIMENTAL WORK

- Equipment and Materials

  1. Equipment

     An electronic precision balance, a Tree® HRB103, was used to weigh out all components used in this work. To mix solutions, a magnetic stirring machine was used. Agitation of the solutions was performed to ensure uniformity. A VWR® Lab Dancer S41 was utilized to perform this task. Studying the effects of temperature required a bath heater. The Julabo® F25 MC bath heater and circulator was used to perform this task. Figure 1 shows the equipment.

  2. Materials

     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. Different oils were employed. The types were mineral oil, heavy oil, and medium oil.

     Polymer solutions were also made. The two polymers used were Liquiblock AT-O3S and 2G-110, both Sodium salts of crosslinked polyacrylic acid. The particle sizes of the polymers ranged from 35 to 60 mesh or 250 to 500 microns, or 60-120 mesh or 125 to 250 microns respectively. Both polymers used in this work were incompatible with Calcium brines above extremely low salinities at standard pH values, limiting the polymer's applicability (Elsharafi et al, 2016). Figure 2 shows the materials used, including the polymer before and after swelling.

- Procedure
  1. Distilled water was measured out by using a graduated cylinder and then added to a beaker.
  2. Sodium Chloride and/or Calcium Chloride was measured s by using an electric precision balance and then added to the beaker.
  3. The 20% brine solution was constantly stirred using a magnetic stirrer.
  4. To acquire the various brine concentrations, the 20% brine solution was added to graduated centrifuge tubes and then diluted to the desired concentration.

5. Polymer was then measured out using an electronic precision balance and added to each of the tubes containing the various brine solutions.
6. The centrifuge tubes were shaken by hand and the polymer was allowed to settle 8 hours before the readings were taken.
7. 3 mL of mineral oil was added to each of the brine and polymer mixtures and shaken thoroughly for 20 seconds.
8. The tubes were placed in the water bath to heat to 100° C.
9. The tubes were removed and the effects of temperature were recorded.
10. The samples were allowed to cool fully and readings were recorded again.
11. We repeated steps 8-12 for each different oil sample.

RESULTS

When analyzing medium oil effects, Figure 3 A and B show that for almost every salinity the polymers increased in volume after oil exposure. All samples increased in volume after oil exposure and cooling, especially for the smaller particle size. The only polymer sample that did not increase, was the 35 to 60 mesh polymer in 20% salinity brine. The 2.5% solution fully gelled. In the 20% brine mixture you can see the phenomenon between particle sizes. In the large particle size you can see at the top where close to 3 ml of oil sits separated from the brine and the polymers are marked on the bottom (Figure 4). They are clear and heavy. They did not mix with the oil very much at all. In the smaller particle size it is impossible to tell where the oil stops and polymer starts. You can see the brine on bottom. This brine has no polymers in it. This same phenomenon happened in each oil sample. The larger particle size mixed with the brine and most polymers sunk to the bottom. The smaller polymers mixed with oil and floated. Almost all of the 3ml oil in the larger particle size was floating on top. In the small particle size about half had mixed with the polymers. In Figure 5 A and B, the effects of Calcium Chloride brines can be seen. Due to incompatibility of the polymer with such brines, the results show that the polymer essentially precipitates out. For mixed brines, (Figure 6 A and B) it was seen that as the amount of Calcium ions increased in the brine, the precipitation of polymer at high temperature more than offset the increase in volume given by the presence of oil. The 2.5% salinity sample broke even after cooling, and the gap between original and post cooling volume continued to grow with salinity.

When observing polymer exposed to light oil in NaCl brines, there is a relatively dramatic increase in polymer volume at the lower salinities. Overall, presence of light oil resulted in an increase in polymer volume except in two cases for the larger particle size (Figure 7 A and B). The Calcium Chloride results (Figure 8 A and B) looked quite similar to those obtained for the medium oil. Except for in two cases, both polymer sizes decreased in volume after oil and heat exposure. The smaller particle size was quite uniform in its performance over the salinity range. The light oil in the mixed brines caused lower volumes than the medium oil at low salinities, but polymer volume was effectively maintained throughout the range. The polymer could be oil wet, resulting in the low viscosity light oil forming a protective barrier around the polymer particles. This would prevent polymer exposure to divalent cations in the solution.

Mineral oil was ineffective at changing the large particle size polymer’s volume in Sodium Chloride. However, the small particle size saw a substantial increase over the entire salinity range. On average, there was an almost 20% increase in polymer volume, which is comparable to the medium oil (20%), but quite different from the change experienced in the light oil (6%). At high temperature, the presence of mineral oil actually increased the volume of the small particle size in low salinity brines containing divalent cations (Figure 11). After cooling, the volume decreased greatly. In mixed brines (Figure 12), mineral oil was not effective at preventing polymer precipitation, with average volume losses of 60 to 120 mesh polymer around 35%. In contrast, exposure to light oil actually led to the smaller particle increasing slightly in volume (7%).

CONCLUSION

- These results can help to identify which particle size and type of SAP to use according to the brine concentrations, temperatures, and specific gravity of reservoir fluids.
- When using polymers make note that oil may increase polymer absorption.

- In a multiphase environment, the wetting phase of the gel surface may require investigation. The results of this work may show influence of a change in wetting phase resulting in the drawdown of oil from the brine surface into the gel pack. As particle size changes, so too would the capillary pressures needed to enter the pack.
- Particle size selection should first depend on porosity of the formation.
- For reservoirs with high temperatures, polymer swelling is increased. Polymers may have lower density due to those high temperatures.
- The brine concentrations also affect the absorption of polymers. Lower swelling ratios will be experienced for higher brine concentrations in the oil well. If high concentrations of Calcium Chloride are present, polymers will originally swell, but quickly turn into precipitate. This makes the polymers useless in water absorption. Testing produced water for chemical composition is paramount.
- Using SAPs appropriately by following these guidelines can save substantial cost. Following these guidelines when applying SAPs will help produce oil that was once un-recoverable.

Literature

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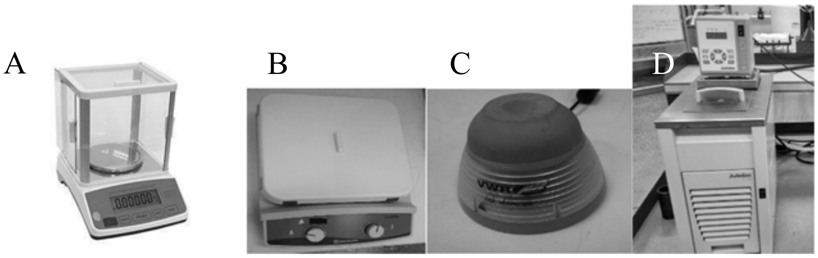


Figure 1 - Equipment Used in Work. A. Electronic Balance Scale. B. Magnetic Solution Mixer. C. Tube Agitator. D. Bath Heater.

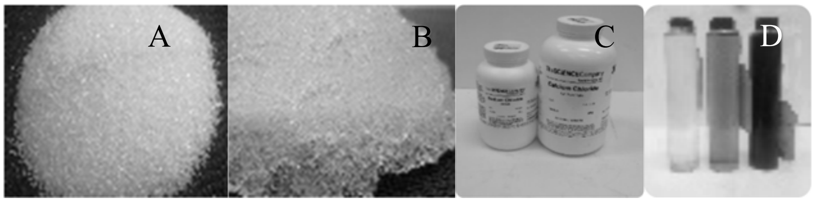


Figure 2 **-** A. Unswollen SAP. B. Swollen SAP. C. Salts used. D. Oils in Containers.

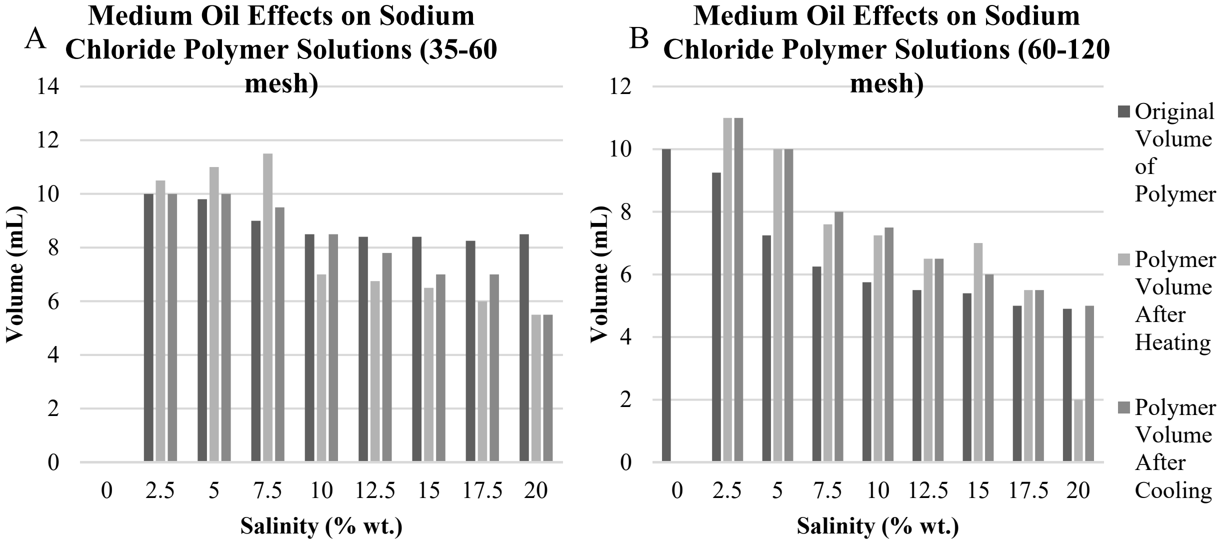


Figure 3 - Medium Oil Effects on Polymer in Sodium Chloride Brines. A. 30 to 60 mesh polymer B. 60 to 120 mesh Polymer.

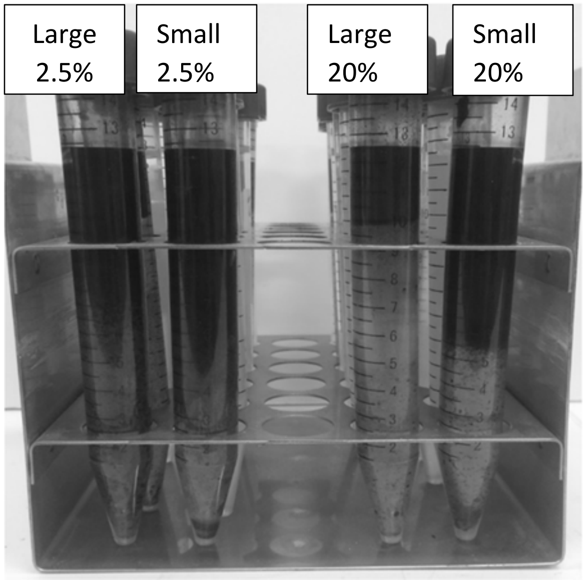
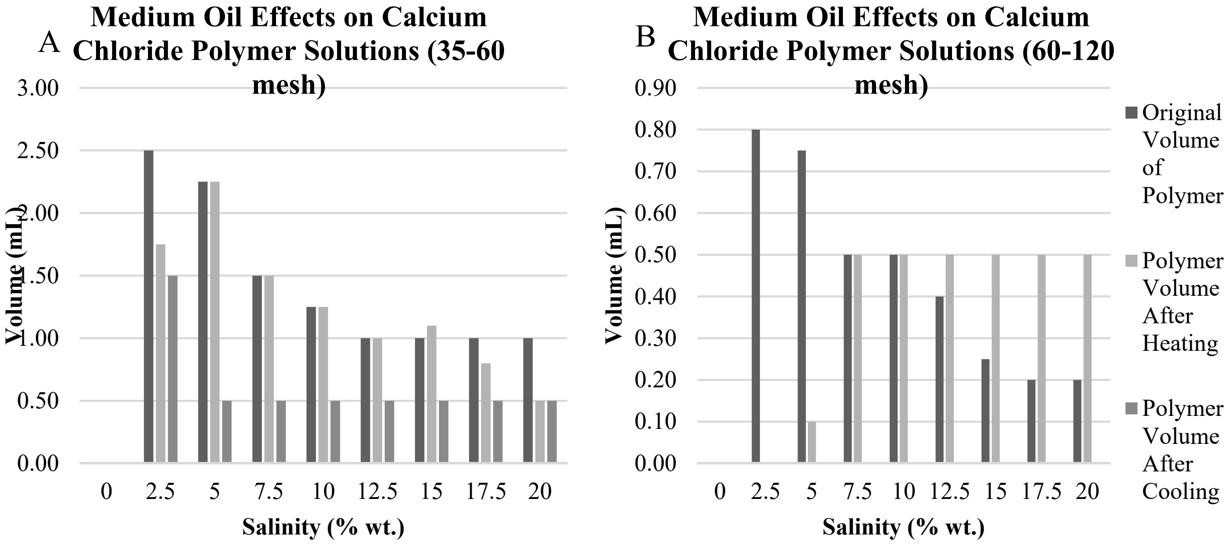


Figure 4 - Effects of Particle Size and Salinity on Oil Dispersion. Sodium Chloride Brine.


A Medium Oil Effects on Calcium Chloride Polymer Solutions (35-60 mesh)

B Medium Oil Effects on Calcium Chloride Polymer Solutions (60-120 mesh)

Figure 5 - Medium Oil Effects on Polymer in Calcium Chloride Brines. A. 35 to 60 mesh polymer. B. 60 to 120 mesh polymer.

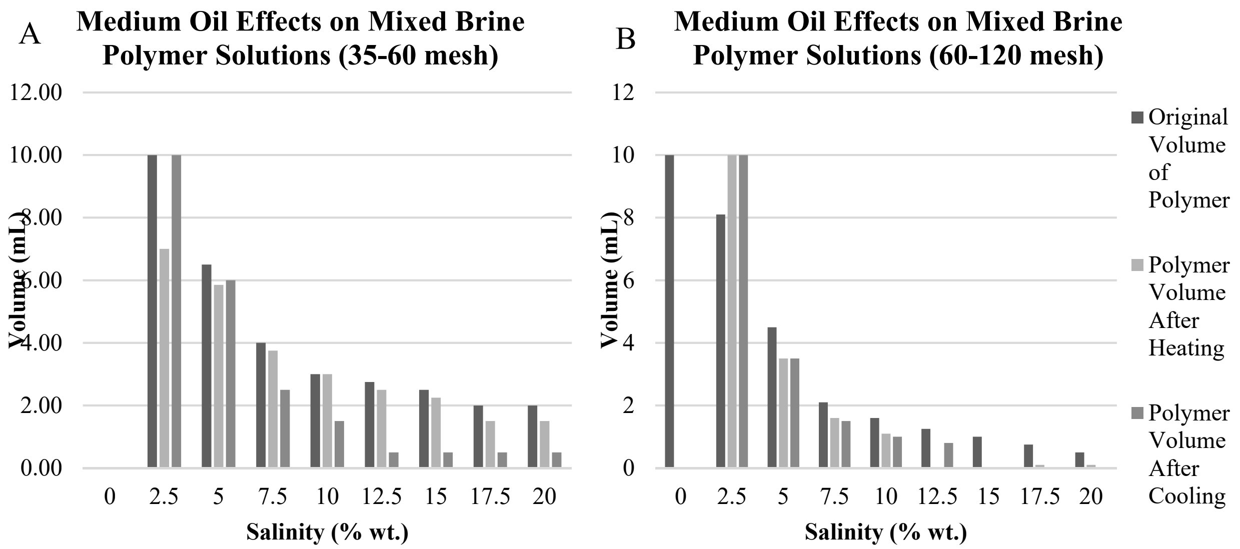


Figure 6 - Medium Oil Effects on Polymer in Mixed Brines. A. 35 to 60 mesh polymer. B. 60 to 120 mesh polymer.

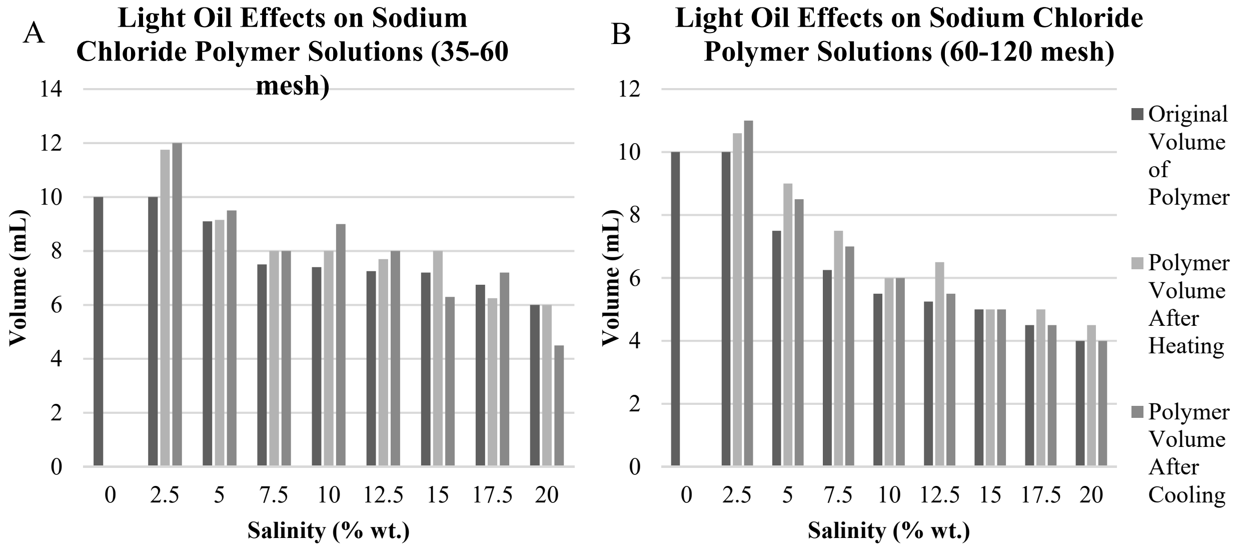


Figure 7 - Light Oil Effects on Polymer in Sodium Chloride Brines. A. 35 to 60 mesh polymer. B. 60 to 120 mesh polymer.

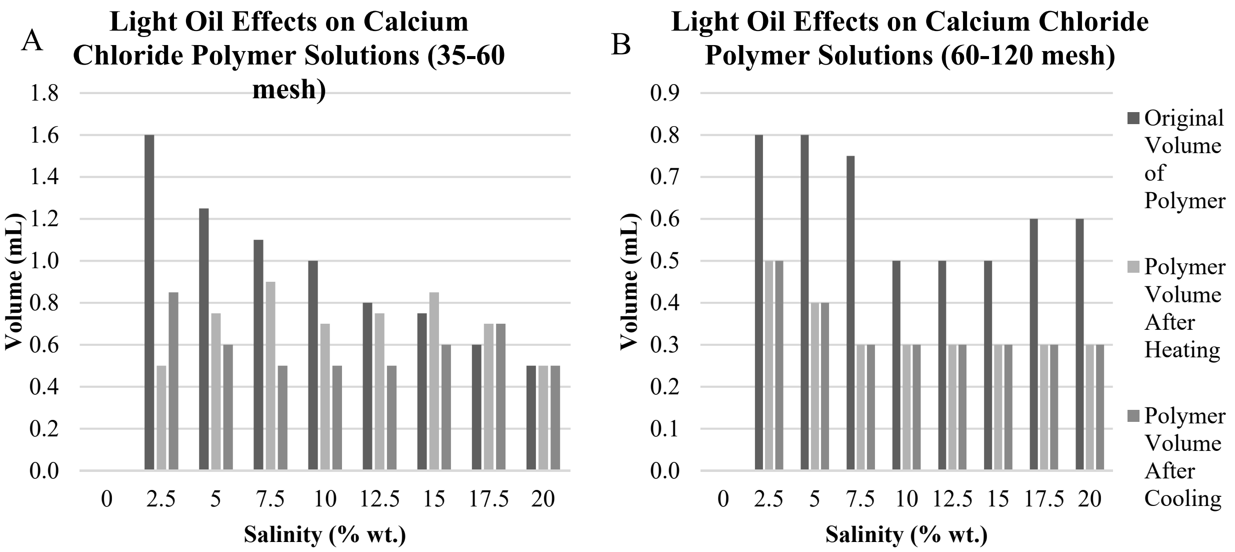


Figure 8 - Light Oil Effects on Polymer in Calcium Chloride Brines. A. 35 to 60 mesh polymer. B. 60 to 120 mesh polymer.

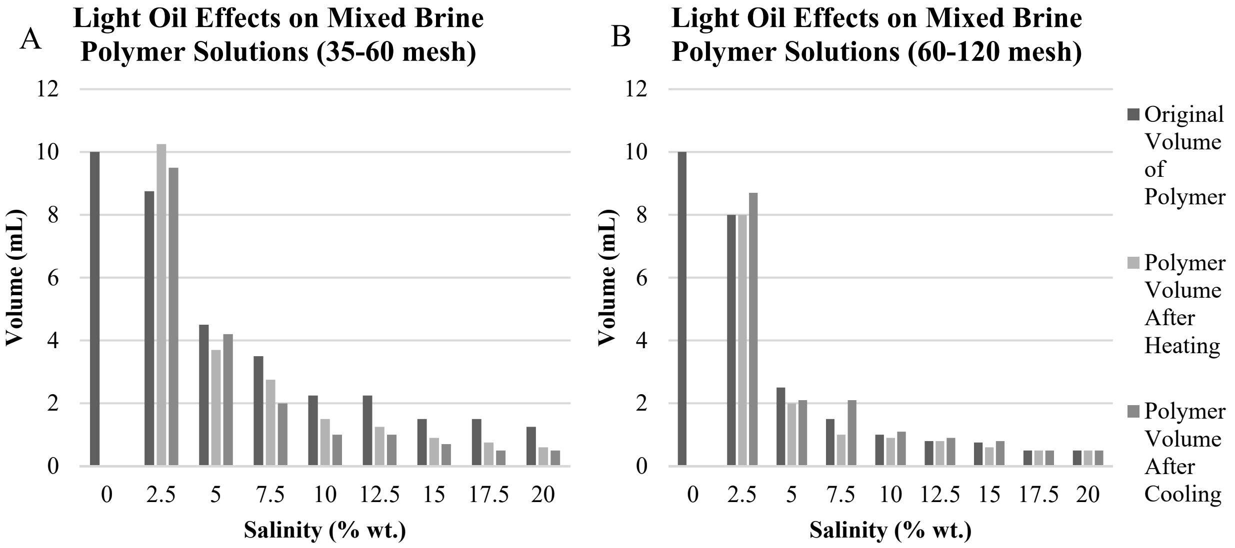


Figure 9 - Light Oil Effects on Polymer in Mixed Brines. A. 35 to 60 mesh polymer. B. 60 to 120 mesh polymer.

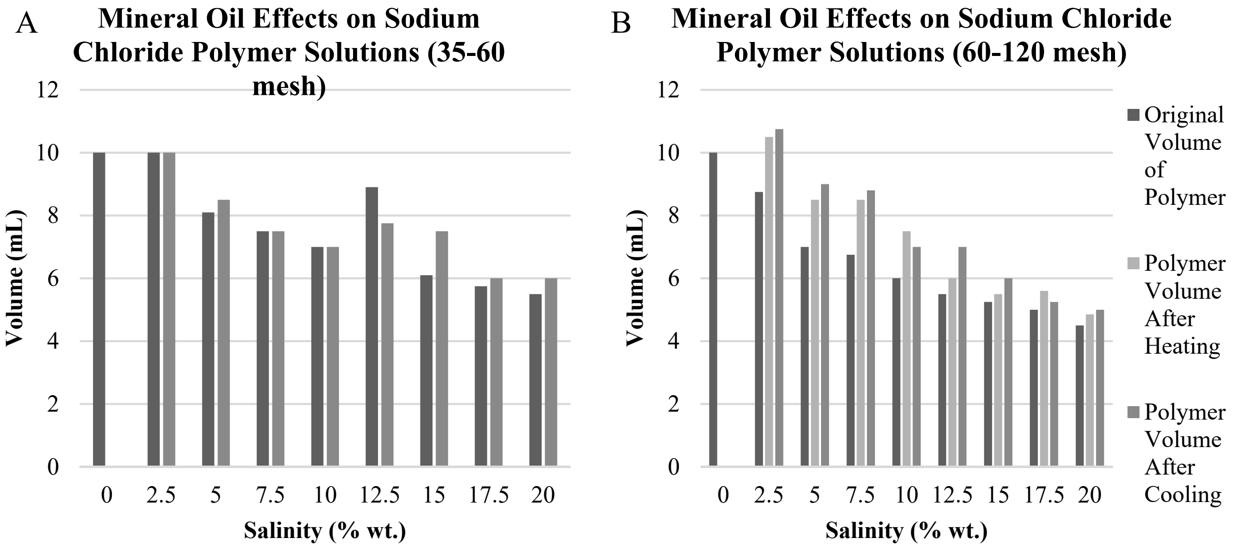


Figure 10 - Mineral Oil Effects on Sodium Chloride Brines. A. 35 to 60 mesh polymer. B. 60 to 120 mesh polymer.

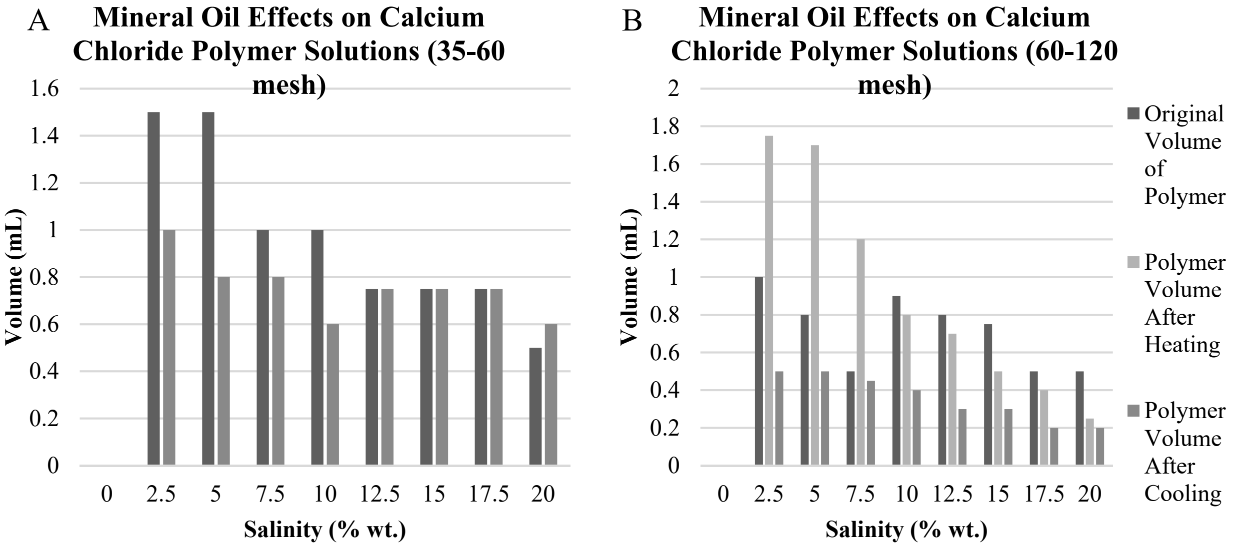


Figure 11 - Mineral Oil Effects on Polymer in Calcium Chloride Brines. A. 35 to 60 mesh polymer. B. 60 to 120 mesh polymer.

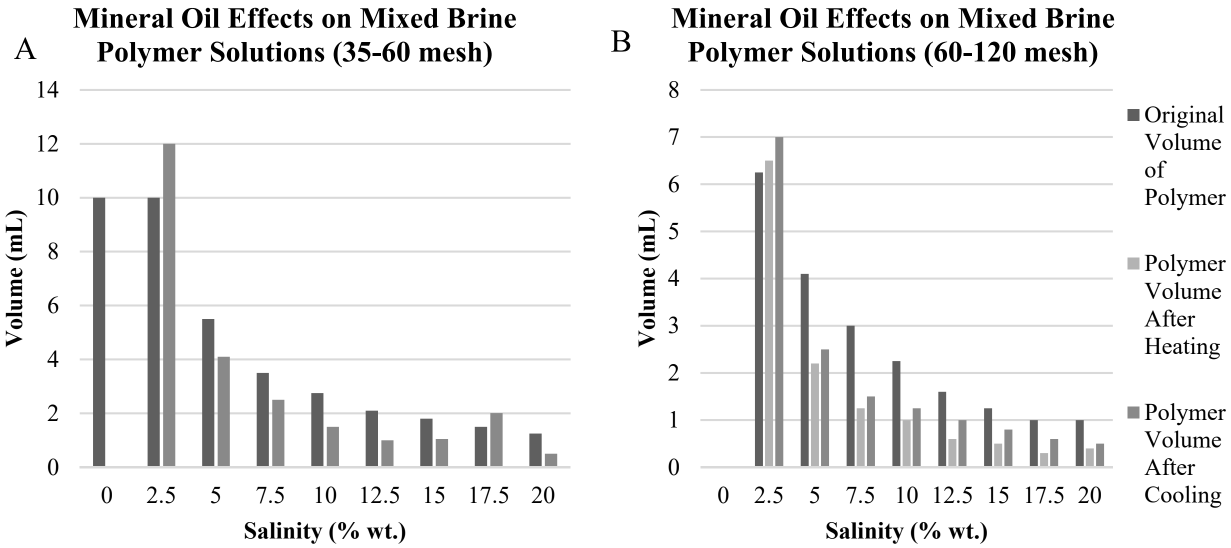


Figure 12 - Mineral Oil Effects on Polymer in Mixed Brines. A. 35 to 60 mesh polymer. B. 60 to 120 mesh polymer.