Permeability Modification Using a Reactive Alkaline Soluble Biopolymer

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Polymer injection has been used in reservoirs to alleviate contrasting permeability zones. Current technology relies on the use of cross-linking agents to initiate gelation. The use of biological polymers are advantageous in that they can block high permeability areas, are environmentally friendly, and have potential to form reversible gels without the use of hazardous cross-linkers. Recent efforts at the Idaho National Engineering and Environmental Laboratory (INEEL) have produced a reactive alkaline-soluble biopolymer from Agrobacterium sp. ATCC # 31749 that gels upon decreasing the pH of the polymeric solution. The focus of this study was to determine the impact an alkaline-soluble biopolymer can have on sandstone permeability. Permeability modification was investigated by injecting solubilized biopolymer into Berea sandstone cores and defining the contribution of pH, salt, temperature, and Schuricht crude oil on biopolymer gelation. The biopolymer was soluble in KOH at a pH greater than 11.4 and gelled when the pH dropped below 10.8. The Berea sandstone core buffered the biopolymer solution, decreasing the pH sufficiently to form a gel, which subsequently decreased the permeability. The effluent pH of the control cores injected with 0.01 M KOH (pH 12.0) and 0.10 M KOH (pH 13.0) decreased to 10.6 and 12.7, respectively. The permeability of the sandstone core injected with biopolymer was decreased to greater than 95% of the original permeability at 25°C in the presence of 2% NaCl, and Schuricht crude oil; however, the permeability increased when the temperature of the core was increased to 60°C. Residual resistance factors as high as 792 were seen in Berea cores treated with biopolymer. The buffering capacity of sandstone has been demonstrated to reduce the pH of a biopolymer solution sufficiently to cause the polymer to form a stable in-situ gel. This finding could potentially lead to alternate technology for permeability modification, thus extending the life of a reservoir and preventing premature abandonment.
ACKNOWLEDGMENTS

The authors acknowledge Jerry Casteel, Rhonda Lindsey, Suzanne M. Mehlhoff, Purna Halder, and Daniel Gurney of the U. S. Department of Energy, Office of Fossil Energy, National Petroleum Technology Office and Patricia St. Clair of the U. S. Department of Energy Idaho Field Office for their support.
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# ACRONYMS

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<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATCC</td>
<td>American Type Culture Collection</td>
</tr>
<tr>
<td>cP</td>
<td>centipoise</td>
</tr>
<tr>
<td>CSB</td>
<td>Coleville synthetic brine</td>
</tr>
<tr>
<td>EOR</td>
<td>enhanced oil recovery</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>INEEL</td>
<td>Idaho National Engineering and Environmental Laboratory</td>
</tr>
<tr>
<td>KOH</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>mD</td>
<td>millidarcy</td>
</tr>
<tr>
<td>NaCl</td>
<td>sodium chloride</td>
</tr>
<tr>
<td>RRF</td>
<td>residual resistance factor</td>
</tr>
<tr>
<td>RTD</td>
<td>resistance temperature detector</td>
</tr>
</tbody>
</table>
Permeability Modification Using a Reactive Alkaline-Soluble Biopolymer

1. INTRODUCTION

Polymers have been useful for enhanced oil recovery (EOR) for water shutoff technologies, and flow conformance. Microbial polymers are of interest due to their potential cost savings, compared to conventional use of synthetic chemical polymers. Numerous microorganisms are known to produce extracellular polysaccharides. However, most require an addition of divalent cations to increase the viscosity to a level useful for EOR technologies. One microbiological polymer of interest is curdlan, which has demonstrated gelling properties by a reduction in pH. Curdlan is a β-(1, 3) glucan polymer which is produced by Agrobacterium species and has a molecular weight of 74,000 Daltons. The ability of curdlan to gel upon a reduction in the pH was explored. Curdlan was soluble at pH 11.4 and becomes a gel when the pH is decreased below 10.8.
2. MATERIALS AND METHODS

2.1 Microorganism

*Agrobacterium sp.* # 31749 (formerly *Alcaligenes faecalis* subsp. *myxogenes*) was obtained from the American Type Culture Collection (ATCC). *Agrobacterium sp.* is an aerobe, gram-negative rod that produces an extracellular biopolymer called curdlan. Curdlan is an unbranched biopolymer composed of β−(1-3) glucose linkages. Curdlan is a water-insoluble, but alkaline-soluble biopolymer. Upon solubilizing curdlan at pH greater than 11.4 and subsequent reduction in pH to 10.8 an opalescent, firm gel is formed.

2.2 Maintenance and Growth Media

An ATCC lyophilized stock was cultured at 30°C in 5-mls of ATCC medium 3, Nutrient Broth. After 48 hours, the entire volume was transferred to 500-mls of fresh medium. Frozen stock cultures of log phase *Agrobacterium sp.* were prepared by resuspending the cell pellet in 1/20 the volume of medium 3 and adding an equal volume of 20% sterile glycerol. The stocks were stored at -80°C. A new freezer stock was thawed and used to initiate growth in seed culture medium. The seed culture was grown at 30°C, 150 rpm for 20 hours in 300-mls of medium. The seed inoculum contained $1.29 \times 10^8$ cells/ml and was used to initiate curdlan production in the basal fermentation medium. Seed culture and basal fermentation media have been previously described by Lee et. al., 1999. A 10% inoculum was transferred to basal fermentation medium and incubated aerobically at 30°C, 250 rpm for 5 days. All curdlan production experiments were conducted in 2 L Erlenmeyer flasks with 500-ml of broth. All media was pH adjusted to 7.2 prior to autoclaving. Phosphate stock solution was added after autoclaving. Sucrose and trace element solutions were filter sterilized using a 0.45 µm filter and aseptically added upon cooling. The culture pH was manually maintained at pH 7.0 for 24 hours using 5M KOH or 3M HCl.

2.3 Biopolymer Production

After 5 days, the culture was centrifuged using a Sorvall (Newton, CT) SLA-3000 rotor at 6,816 g for 20 minutes, and 20°C in tared 500-ml polypropylene centrifuge tubes. The supernatant was discarded and the tubes were weighed to determine the wet weight of the cells and curdlan. The pellet was treated overnight at 4°C with 5M KOH. The alkaline-treated pellet was centrifuged at 6,816 g for 20 minutes and 20°C. Curdlan was collected in the supernatant and pH adjusted to 7.0. The centrifuge tubes were weighed, and the differences in the weights were used to determine the dry weight of curdlan. Curdlan was transferred to tared 50-ml polypropylene centrifuge tubes. Curdlan was frozen, lyophilized to dryness, and weighed to determine the dry weight. All curdlan batches were homogenized using a mortar and pestle. The dry biopolymer was stored at room temperature.

2.4 Biopolymer Characterization

2.4.1 Solubility

Dry biopolymer was resuspended in 0.01 M KOH, 1 M KOH, and nano pure water in 10-ml glass test tubes and covered with parafilm. The solution was vortexed and set at room temperature for 30 minutes. A block heater was used to determine the effect of temperature on biopolymer solubility. An Accumet AB15 pH meter and pencil-thin pH probe were used to measure pH. The pH meter was calibrated prior to use with fresh pH 4, 7, and 10 buffers. Multiple biopolymer concentrations (1%, 4%, 10%) were tested to determine the solubility of the biopolymer at selected temperatures. Gelling
characteristics of the biopolymer were visually noted. The pH of the biopolymer solution was decreased using 3M HCl.

2.4.2 Viscosity

A Wells-Brookfield Cone/Plate Viscometer model LVTDV-IICP (Stoughton, MA) with spindle CP-40 or CP-51 was used to measure viscosity. The viscometer was calibrated with Brookfield silicone standards and the sample volume was 0.5-ml.

2.4.2.1 Salt Concentration. The amount of salt in the modified CSB was varied to determine if salt concentration alters biopolymer gelling. The concentrations of salt tested were 0.0%, 0.7%, 1.5%, 3% and 5% NaCl. Dry biopolymer (10% w/v) was added to 0.10M KOH or 0.01M KOH brine. The pH was adjusted using 3M HCl.

2.4.2.2 Temperature. A Cole Parmer Polystat heated circulating water bath was used to maintain temperature of the viscometer plate. The temperature range was 25, 50, 75, and 96°C. Initially, dry biopolymer (10% w/v) was solubilized in 0.01M KOH and viscosity measurements were measured at the selected temperature. Then, the biopolymer was gelled using 3M HCl and viscosity measurements were completed at the selected temperature.

2.4.3 Total Carbohydrate Analysis

Core effluent was monitored for total carbohydrate (Daniels, 1994) to verify that biopolymer was injected through the core. Additionally, the carbohydrate content of the dry biopolymer was measured using a total carbohydrate analysis for quality control. Pure curdlan, obtained from Carbomer (San Diego, CA) was used as the standard.

2.5 Core Preparation

2.5.1 Berea Sandstone Cores

Berea sandstone (Cleveland Quarries, Amherst, OH) was cut into cylindrical cores 1 inch in diameter by 6 inch in length, fitted with inlet and outlet endplates, and coated with Hysol epoxy (Dexter, Seabrook, NH). Pressure taps were prepared by drilling holes in the epoxy coating approximately 4-5 inches apart and fitted with stainless steel connectors. Each encapsulated core was evacuated and then saturated with Modified Coleville Synthetic Brine (CSB). Modified CSB consisted of 7g of NaCl, 0.14g CaCl₂ × 2 H₂O and 0.02g NH₄Cl per liter. Modified CSB was filtered and vacuum degassed prior to core saturation. Darcy’s law was used to determine the brine permeability of each core. Porosity and pore volume were determined using dry and wet core weights, brine density, and core dimensions. Potassium iodide was injected into the cores as a tracer and the effluent was measured using an Schimadzu UV160U spectrophotometer (Kyoto, Japan). The biopolymer solution was injected into the core after the tracer test. Schuricht crude oil was pumped through four (4) cores after the initial brine saturation and biopolymer solution was injected into an oil-saturated core.

2.5.2 Biopolymer Injection

Biopolymer powder (10% w/v) was dissolved in modified CSB with the addition of 0.10M KOH or 0.01M KOH and filtered with 20-25 µm cellulose papers. The viscosity, total carbohydrate, and pH of the polymer solution were measured prior to core injection. Biopolymer was injected using a stainless steel
accumulator (Temco, Tulsa, OK), an Isco syringe pump (Lincoln, NE) and controller at a constant flow of 1.0 ml/min for at least 5-pore volumes. Honeywell pressure transducers (Phoenix, AZ) recorded the pressure. Effluent was collected in 15-ml polypropylene tubes and monitored for pH and total carbohydrate. Cores were shut-in at the desired temperature (23°C or 60°C) for 6-11 days. Core temperature was controlled using a sand-packed heat block. Initially, a hand syringe filled with modified CSB was used to obtain effluent to measure the pH. Flow was established with an Isco pump using modified CSB after the pH decreased below 10.8. Post-injection permeability measurements were calculated for each core. The cores were then heated to 60°C and cooled for 48 hours. Flow was established at 60°C and when the core cooled. Post-injection permeability measurements were calculated at 60°C and again at ambient temperatures. When cores were heated to 60°C, the temperature of the injection brine was maintained using an Omega RTD controller, a variable autotransformer, a 1/8-inch RTD thermocouple, and Barnstead/Thermolyne heat tape. Table 1 shows the experimental set-up for the Berea sandstone cores. Permeability modification experiments were investigated by injecting the alkaline biopolymer into Berea sandstone cores and defining the contribution pH, salt, temperature, and Schuricht crude oil had on biopolymer gelation. Duplicate cores were conducted to measure the permeability modification, except single cores were used when the cores were saturated with Schuricht crude oil. Either 0.10 M KOH or 0.01 M KOH was injected into the control cores; biopolymer was not injected in the control cores. The buffering capacity of the control cores against 0.10M KOH or 0.01 M KOH determined the molarity of the solvent used for the remaining cores injected with biopolymer. The residual resistance factor (RRF) was calculated for each core according to equation (1):

\[ RRF = \frac{K_{\text{before treatment}}}{K_{\text{after treatment}}} \]  

Where K is the permeability, before treatment is the permeability prior to biopolymer injection, and after treatment is the permeability after biopolymer injection.

<table>
<thead>
<tr>
<th>Core</th>
<th>Injection</th>
<th>Brine Molarity</th>
<th>Temperature</th>
<th>Pre-Injection Saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>B12</td>
<td>Brine</td>
<td>0.01 M KOH</td>
<td>Ambient</td>
<td>Brine</td>
</tr>
<tr>
<td>B13</td>
<td>Brine</td>
<td>0.10 M KOH</td>
<td>Ambient</td>
<td>Brine</td>
</tr>
<tr>
<td>B14</td>
<td>Biopolymer</td>
<td>0.01 M KOH</td>
<td>Ambient</td>
<td>Brine</td>
</tr>
<tr>
<td>B15</td>
<td>Biopolymer</td>
<td>0.01 M KOH</td>
<td>Ambient</td>
<td>Brine</td>
</tr>
<tr>
<td>B16</td>
<td>Biopolymer</td>
<td>0.01 M KOH</td>
<td>60°C</td>
<td>Brine</td>
</tr>
<tr>
<td>B17</td>
<td>Biopolymer</td>
<td>0.01 M KOH</td>
<td>60°C</td>
<td>Brine</td>
</tr>
<tr>
<td>B18</td>
<td>Biopolymer</td>
<td>0.01 M KOH; 2% NaCl</td>
<td>Ambient</td>
<td>Brine</td>
</tr>
<tr>
<td>B19</td>
<td>Biopolymer</td>
<td>0.01 M KOH; 2% NaCl</td>
<td>Ambient</td>
<td>Brine</td>
</tr>
<tr>
<td>B7</td>
<td>Brine</td>
<td>0.01 M KOH</td>
<td>Ambient</td>
<td>Schuricht Crude Oil</td>
</tr>
<tr>
<td>B9</td>
<td>Biopolymer</td>
<td>0.01 M KOH</td>
<td>Ambient</td>
<td>Schuricht Crude Oil</td>
</tr>
<tr>
<td>B6</td>
<td>Biopolymer</td>
<td>0.01 M KOH</td>
<td>60°C</td>
<td>Schuricht Crude Oil</td>
</tr>
<tr>
<td>B11</td>
<td>Biopolymer</td>
<td>0.01 M KOH; 2% NaCl</td>
<td>Ambient</td>
<td>Schuricht Crude Oil</td>
</tr>
</tbody>
</table>
3. RESULTS

3.1 Biopolymer Characterization

3.1.1 Solubility

On average 50 g/L of dry biopolymer was produced from *Agrobacterium sp*. ATCC # 31749. The dry biopolymer was soluble when the pH was greater than 11.4, insoluble in nano pure water, and soluble when heated to 50°C. When the pH of the soluble biopolymer solution decreased to 10.8, a viscous free-flowing gel formed. If an insoluble biopolymer mixture was rendered soluble with heat, a semi-solid gel formed upon cooling.

3.1.2 Viscosity

3.1.2.1 Salt Concentration. Figure 1 shows the effect of pH and salt concentration on the viscosity of a biopolymer solution. The viscosity of the biopolymer is dependent on the pH, but not necessarily the salt concentration. Initially, all biopolymer solutions were below 50 centipoises (cP). The biopolymer solution became viscous when the pH dropped below 10.8, then any additional reduction in pH below 6.0 caused the viscosity of the biopolymer solution to decrease. The addition of salt did not affect the biopolymers ability to form a gel; however, a delay in gelling was observed when a 3% salt concentration was used. The biopolymer was not soluble when 5% NaCl was added to the 0.01M KOH brine.

After the pH was dropped below 10.8 a gel forms; any additional reduction in pH caused the viscosity to decrease. The biopolymer solution can then be increased to a pH above 11.4 and when the pH drops below 10.8 a gel reforms (data not shown).

![Figure 1. Viscosity of 0.01M KOH biopolymer as a function of pH and salt concentration.](image-url)
3.1.2.2 Temperature. Figures 2 and 3 show the reduction of viscosity as a function of temperature. Figure 2 displays the relationship of viscosity and temperature of a 10% biopolymer solution with an initial viscosity less than 20 cP and initial pH of 11.36. Figure 3 shows the correlation of viscosity and temperature of the gelled biopolymer with an initial pH of 8.08 and viscosity greater than 300 cP. The data demonstrates a reduction in viscosity as the temperature of the biopolymer increases, regardless of the initial viscosity of the biopolymer. The results also show that when 0.01M KOH is used as the solvent compared to 0.10M KOH, higher viscosities are obtained using 0.01M KOH. The results indicate that an elevated temperature is detrimental to biopolymer gelation.

![Figure 2](image2.png)

Figure 2. Viscosity of biopolymer solution as a function of temperature.

![Figure 3](image3.png)

Figure 3. Viscosity of gelled biopolymer as a function of temperature.
3.1.3 Carbohydrate Analysis

The total carbohydrate results from each pore volume of core effluent are shown in Figure 4. The results demonstrate that 2-5 pore volumes of biopolymer solution need to be injected for biopolymer breakthrough. Results of the total carbohydrate injected into the core are compiled in Table 2. The results show that 9,991 ppm to 13,986 ppm of carbohydrate was injected. Cores B14, B17, and B18 showed a higher effluent concentration of carbohydrate than what was injected. The carbohydrate analysis was completed to assure that the biopolymer solution was an acceptable concentration range for the core studies. No attempts were made to vary the concentration of the biopolymer solution injected.

Figure 4. Total carbohydrate analysis of core effluent.
3.2 Permeability Modification

3.2.1 Berea Sandstone Cores

Table 2 shows the physical parameters of the Berea sandstone cores used for experimentation.

Table 2. Core Characteristics.

<table>
<thead>
<tr>
<th>Core</th>
<th>Length (cm)</th>
<th>Diameter (cm)</th>
<th>Pore Volume (ml)</th>
<th>Porosity (%)</th>
<th>Total Carbohydrate Injected (ppm)</th>
<th>Viscosity of Injection Fluid (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B12</td>
<td>13.30</td>
<td>2.53</td>
<td>12.81</td>
<td>19.18</td>
<td>0</td>
<td>1.02</td>
</tr>
<tr>
<td>B13</td>
<td>13.30</td>
<td>2.53</td>
<td>12.90</td>
<td>19.31</td>
<td>0</td>
<td>1.13</td>
</tr>
<tr>
<td>B14</td>
<td>13.26</td>
<td>2.53</td>
<td>12.84</td>
<td>19.28</td>
<td>11,185</td>
<td>7.21</td>
</tr>
<tr>
<td>B15</td>
<td>13.34</td>
<td>2.53</td>
<td>12.99</td>
<td>19.39</td>
<td>13,386</td>
<td>11.70</td>
</tr>
<tr>
<td>B16</td>
<td>12.64</td>
<td>2.53</td>
<td>12.19</td>
<td>19.20</td>
<td>12,478</td>
<td>10.40</td>
</tr>
<tr>
<td>B17</td>
<td>13.40</td>
<td>2.53</td>
<td>13.10</td>
<td>19.47</td>
<td>9,991</td>
<td>2.92</td>
</tr>
<tr>
<td>B18</td>
<td>13.40</td>
<td>2.53</td>
<td>12.93</td>
<td>19.21</td>
<td>12,871</td>
<td>8.22</td>
</tr>
<tr>
<td>B19</td>
<td>13.30</td>
<td>2.53</td>
<td>12.73</td>
<td>19.06</td>
<td>12,871</td>
<td>8.22</td>
</tr>
<tr>
<td>B7</td>
<td>13.30</td>
<td>2.53</td>
<td>13.22</td>
<td>19.77</td>
<td>0</td>
<td>1.02</td>
</tr>
<tr>
<td>B9</td>
<td>13.30</td>
<td>2.53</td>
<td>13.37</td>
<td>20.00</td>
<td>12,725</td>
<td>5.96</td>
</tr>
<tr>
<td>B6</td>
<td>13.30</td>
<td>2.53</td>
<td>13.31</td>
<td>19.91</td>
<td>13,986</td>
<td>7.98</td>
</tr>
<tr>
<td>B11</td>
<td>13.34</td>
<td>2.53</td>
<td>12.84</td>
<td>19.15</td>
<td>12,627</td>
<td>3.62</td>
</tr>
</tbody>
</table>

The results of the Berea sandstone cores tested are shown in Table 3. The permeability increased in both control cores B12 and B13. The cause of the increased permeability in the control core is unknown. The pH of core B12 dropped from 11.93 to 10.68, whereas the pH of core B13 slightly decreased from 12.88 to 12.71. Even though the permeability increased in the control cores, the results indicate that Berea sandstone could sufficiently buffer 0.01 M KOH brine, but not 0.10 M KOH brine. Therefore, 0.01 M KOH brine was used for further core experiments. The remaining Berea sandstone cores injected with 0.01M KOH biopolymer solutions were effective at triggering gel formation and reducing the permeability. Previous reports (McCool, 1998) indicate that 0.10M KOH or 1M KOH was not sufficient to cause gelation. In contrast, our studies clearly indicate that 0.01 M KOH can be buffered by the internal core matrix and is adequate for gel formation. The specific mechanism of gelation within the core is unknown and no attempt was made to investigate the gelation mechanism. Test tube results showed that the biopolymer solution gelled when the pH dropped below 10.8. The Berea sandstone core buffers the alkaline brine causing a reduction in the pH and subsequent gel formation.
Table 3. Permeability Modifications.

<table>
<thead>
<tr>
<th>Core</th>
<th>Core Treatment</th>
<th>Pore volumes injected (ml)</th>
<th>Pre-injection Permeability (mD)</th>
<th>Post-injection Permeability (mD)</th>
<th>Permeability Reduction (%)</th>
<th>Residual Resistance Factor (RRF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B12</td>
<td>Control 0.01M KOH</td>
<td>10.00</td>
<td>122.69</td>
<td>186.80</td>
<td>-52.25</td>
<td>0.66</td>
</tr>
<tr>
<td>B13</td>
<td>Control 0.10M KOH</td>
<td>9.95</td>
<td>129.72</td>
<td>196.54</td>
<td>-51.51</td>
<td>0.66</td>
</tr>
<tr>
<td>B14</td>
<td>Biopolymer, ambient</td>
<td>10.03</td>
<td>112.00</td>
<td>0.32</td>
<td>99.71</td>
<td>350.00</td>
</tr>
<tr>
<td>B15</td>
<td>Biopolymer, ambient</td>
<td>9.48</td>
<td>134.65</td>
<td>0.17</td>
<td>99.87</td>
<td>792.06</td>
</tr>
<tr>
<td>B16</td>
<td>Biopolymer, 60°C</td>
<td>6.68</td>
<td>167.89</td>
<td>2267.46</td>
<td>-1250.56</td>
<td>0.07</td>
</tr>
<tr>
<td>B17</td>
<td>Biopolymer, 60°C</td>
<td>4.94</td>
<td>161.94</td>
<td>249.43</td>
<td>-54.03</td>
<td>0.65</td>
</tr>
<tr>
<td>B18</td>
<td>Biopolymer, 2% NaCl</td>
<td>9.23</td>
<td>152.93</td>
<td>64.97</td>
<td>57.52</td>
<td>2.35</td>
</tr>
<tr>
<td>B19</td>
<td>Biopolymer, 2% NaCl</td>
<td>8.84</td>
<td>146.70</td>
<td>5.13</td>
<td>96.50</td>
<td>28.60</td>
</tr>
<tr>
<td>B7</td>
<td>Control 0.01 M KOH; Schuricht oil</td>
<td>9.59</td>
<td>150.20</td>
<td>8.98</td>
<td>94.01</td>
<td>16.72</td>
</tr>
<tr>
<td>B9</td>
<td>Biopolymer, ambient; Schuricht oil</td>
<td>6.46</td>
<td>136.60</td>
<td>6.41</td>
<td>95.31</td>
<td>21.31</td>
</tr>
<tr>
<td>B6</td>
<td>Biopolymer 60°C; Schuricht oil</td>
<td>6.04</td>
<td>122.60</td>
<td>2.20</td>
<td>98.73</td>
<td>55.73</td>
</tr>
<tr>
<td>B11</td>
<td>Biopolymer, 2% NaCl; Schuricht oil</td>
<td>6.87</td>
<td>169.00</td>
<td>0.98</td>
<td>99.42</td>
<td>172.45</td>
</tr>
</tbody>
</table>

Figures 5-8 show the correlation of pH with permeability reduction. All cores injected with alkaline brine displayed a reduction in pH within 12 days. The effluent pH was measured prior to accumulating 1 pore volume so the injection brine did not alter the pH. The effluent was clear after shut-in. The pH of core B14 dropped from 11.45 to 10.21, and core B15 decreased from pH 11.28 to 10.04. The addition of heat catalyzed a sharper decrease in the pH. Core B16 initially had a pH of 11.73, and decreased to pH 9.35. The pH from core B17 decreased from 11.73 to 9.17. The pH of core B18 dropped from 12.04 to 10.67 and core B19 decreased from 12.04 to 10.46. A further decrease in pH was observed in all effluent, however this reduction can be attributed to brine introduction since the pH was measured after more than 1 pore volume was injected.

The post-injection permeability increased in the control cores, however the permeability decreased to greater than 95% when biopolymer was injected. For example, core B15, which had biopolymer injected and shut-in at ambient temperature decreased the permeability from 134.65 mD to 0.17 mD. Like the control cores (Figure 5), the post-injection permeability increased when the cores where heated (Figure 7). These results correlate with the data described previously in this document about a reduction in biopolymer viscosity at elevated temperatures.

The magnitude of residual resistance factor (RRF) varied from 0.03 to 792.06. A residual resistance factor of 792.06 was calculated for core B15 that was injected with biopolymer at ambient conditions. The control cores and cores heated to 60°C had low RRF’s; whereas, the cores injected with biopolymer had higher RRF’s. Lower RRF’s were observed when 2% sodium chloride was added to the brine.
Figure 5. Permeability modification and pH control of sandstone core.

Figure 6. Permeability modification and pH control of sandstone core at ambient temperature.
Figure 7. Permeability modification and pH control of sandstone core at 60°C.

Figure 8. Permeability modification and pH control of sandstone core with 2% NaCl brine.
Permeability results from the heat/cool treatments are shown in Figures 5-8. The post-injection permeability (60°C) represents the permeability calculated at temperature; whereas, the post-injection permeability (ambient) shown on the far right represents the permeability after the cores were heated and cooled to room temperature. A decrease in permeability was noted for the 0.01M KOH control core after the core was heated and then cooled; whereas, the permeability remained steady during the heat/cool treatment for the 0.10M KOH control (Figure 5). Cores B14 and B15, which were injected with biopolymer, maintained low permeability after the heat/cool treatment indicating that the heat/cool treatment did not alter biopolymer gelation. However, the remaining cores show mixed results. The variability is attributed to the fact that more that one pore volume of brine was injected to determine the permeability at 60°C. At elevated temperatures the biopolymer becomes less viscous, hence it is possible that the biopolymer washed-out from the core.

3.2.2 Schuricht Oil Cores

All cores saturated with Schuricht crude oil displayed a reduction in pH when 0.01 M KOH was injected. The results are shown in Figure 9. Control core B7 had an initial pH of 11.93 and dropped to 10.76. The pH of core B9, which had biopolymer injected, dropped from 11.62 to 10.59. The effluent pH of core B6, which was heated, decreased from 11.65 to 9.32. Core B11 initially had a pH of 10.62 and decreased to 9.85. These results are consistent with cores tested without Schuricht crude oil and confirm that the presence of Schuricht crude oil was not detrimental to the buffering capacity of Berea sandstone cores.

The post-injection permeability was reduced in all cores including the control core, which had no biopolymer injected. The permeability decreased 94% in the control core contrary to the increase in permeability observed in the control core without oil. This would indicate that Schuricht crude oil prevents the permeability from increasing. The post-injection permeability decreased from 122.60 mD to 2.20 mD when the cores were shut-in at 60°C. When comparing core B6 to core B16 and B17, which had biopolymer injected and were shut-in at 60°C, the permeability decreased in core B6 and yet increased in core B16 and B17. The only difference between the cores was the presence of Schuricht crude oil. The results indicate that the presence of Schuricht crude oil reversed the permeability increase in the cores that were heated to 60°C.

The residual resistance factors for cores with Schuricht crude oil are reported in Table 3. The RRF’s ranged from 16 to 172 in the cores with Schuricht crude oil. All cores injected with biopolymer showed an increase in the RRF compared to the control core. The highest RRF was 172.45 when 2% salt was injected with the biopolymer.
Figure 9. Permeability modification and pH control of sandstone core with Schuricht crude oil.
4. CONCLUSIONS

The results of the research described in the report can be summarized as follows:

- The dry biopolymer was soluble at pH greater than 11.4, insoluble in nano pure water, and soluble when heated to 50°C in KOH or water.

- A 0.01 M KOH and 0.10 M KOH solution dissolved the biopolymer.

- The addition of sodium chloride to the KOH brine did not affect the biopolymers ability to form a gel.

- The viscosity of the biopolymer solution increased when the pH dropped below 10.8.

- An increase in the temperature caused the biopolymer solution to become less viscous.

- Berea sandstone cores can effectively buffer a 0.01 M KOH solution, but not a 0.10 M KOH alkaline solution.

- The 0.01 M KOH biopolymer solution reacted with Berea sandstone cores with and without Schuricht crude oil causing a pH reduction, gel formation and reduction in permeability.

- Residual resistance factors as high as 792.06 after biopolymer treatment were calculated.
5. REFERENCES

