Formation and Performance Evaluation of Colloidal Dispersion Gels prepared using Sulfonated Polyacrylamides and Chromium (III) Acetate

Reza Rahimi a, Amir Hossein Saeedi Dehaghani a,1

a Department of Petroleum Engineering, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran.

Abstract
Using a sulfonated polyacrylamide (SPAM) and Cr³⁺, a new colloidal dispersion gel (CDG) was prepared. The viscosity of the CDG samples in different crosslinker concentrations and brine compositions was measured. The results showed that CDGs approach a Newtonian-like behavior in high crosslinker concentrations and salinities, signifying that they possess more rigid, less flexible particles that can be used to block some of the pore throats of the high-permeability layers. Therefore, three coreflood tests were performed and the retention of the polymers and the final RRF values (residual resistance factor) were determined. Although CDGs showed a lower tendency to be adsorbed onto the rocks, they caused drastically higher RRF values (caused higher permeability reductions). Thus, it can be concluded that CDGs are superior compared to normal polymer solutions in modifying the permeability. Moreover, changing the post-flood fluid from brine to distilled water caused the RRF to decrease, hence weaker effect on the permeability.

Key words: Permeability modification, CDG, Colloidal dispersion gel, Polyacrylamide, Chromium.

1. Corresponding author: Asaeedi@modares.ac.ir
1. Introduction

Mature reservoirs with a lot of unproduced oil need to receive more attention to be able to produce these unproduced reserves [1, 2]. Waterflooding is a common method to overcome the problems associated with these mature reservoirs and produce more oil. However, this method is associated with several limitations, such as low sweep efficiency, high water cut, early water breakthrough and viscous fingering. To overcome some of the limitations of regular waterflooding, the mobility ratio (Equation 1) must be improved.

\[
M = \frac{k_w/\mu_w}{k_o/\mu_o}
\]  

(1)

Where M is the mobility ratio, \(k_w\) and \(k_o\) are water and oil permeability and \(\mu_w\) and \(\mu_o\) are the water viscosity and oil viscosity, respectively [3-5]. One way to positively affect the mobility ratio is to increase the viscosity of the displacing fluid (water) or to decrease its permeability.

Polymers have been widely used as a method of enhancing the viscosity of water [6-11]. Among polymers, polyacrylamide family (Partially Hydrolyzed Polyacrylamide (PHPAM) and Sulfonated Polyacrylamides known as SPAM) have been frequently tested and used for this purpose [12-15]. These are polymers a portion of whose amide groups have been replaced by anionic groups.

A more novel approach to address the shortcomings of the regular waterflooding is to use colloidal dispersion gels (CDGs) [16, 17]. Colloidal dispersion gels are formed when the polymer and crosslinker concentrations are sufficiently low that no 3D structure is formed and most of the crosslinkings are intramolecular-the crosslinker (multivalent cation) links different anionic sites of the polymer to each other [18]. This causes the formerly straightly-aligned molecules of the polymer to form polymer coils that are more rigid and smaller than the normal polymers.

This property can be used to modify water flow in reservoirs by lowering the permeability of high-permeability streaks and thus diverting the flow towards layers with less permeability. As discussed by Wang et al., CDGs can alter the permeability of the rocks due to both adsorption onto the rock surface and blockage of the pore throats[19].

To the best of our knowledge, only a few researchers have studied the performance of colloidal dispersion gels in reducing the permeability of the high-permeability layers at the core scale. Wang et al. studied the permeability reduction caused by CDGs that were prepared using HPAM and Al\(^{3+}\). According to their results, the weak gels prepared using the aforementioned materials are highly more effective in reducing the permeability of the rock than normal HPAM solutions[19]. This can be attributed to the ability of the gel particles to block the pore throats. Spildo et al. studied the retention of CDGs prepared with HPAM and Al\(^{3+}\) in sandstone cores. They reported somewhat mixed results, as in some cases the polymer solutions showed higher retentions, while in others CDGs showed higher retention values. Moreover, they did not report any data on the permeability reductions caused by CDG or polymer solution[20]. Therefore, no direct conclusion can be drawn from their results to relate retention to the residual resistance factor or RRF (The permeability of the rock before the polymer/CDG flood to its permeability after the polymer/CDG flood).

Given that there are not enough quantitative studies on both the permeability reduction capacity and retention of a single CDG type, there is still controversy on the mechanism that CDGs reduce permeability. Furthermore, while there is a study on the CDG formation using Sulfonated polyacrylamides[18], no flow performance test has been conducted on the performance of CDGs that are formed using SPAM. Therefore, in this study, a sulfonated polyacrylamide was selected and used to prepare CDG samples. The viscosity of the samples in different shear rates, crosslinker to polymer ratios (CPR) and different brine compositions was measured. For the first time, a series of coreflood experiments was conducted to evaluate the SPAM-CDG retention and its capacity to lower the permeability.
2. Materials and methods
2.1. Materials
The polymer used in this study is a sulfonated polyacrylamide (AN 125) with a molecular weight of 8 million Daltons and a sulfonation degree equal to 25% [21] supplied by SNF Floerger. The crosslinker, Chromium (III) acetate hydroxide, was purchased from Sigma-Aldrich.
Four different salts, including NaCl, KCl, CaCl₂ and MgCl₂ were used to prepare the electrolytes in this research. All salts were of analytical grades and were purchased from Merck.
In order to study the retention and the permeability reduction capacity of the samples, three sandstone cores from the same formation with similar porosity and permeability values were used. The properties of the core samples are listed in Table 1.

Table 1: Properties of the cores used in this study

<table>
<thead>
<tr>
<th>Core</th>
<th>Length (cm)</th>
<th>Diameter (cm)</th>
<th>Porosity (%)</th>
<th>Permeability (md)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10</td>
<td>3.5</td>
<td>0.19</td>
<td>459</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>3.5</td>
<td>0.19</td>
<td>472</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>3.5</td>
<td>0.2</td>
<td>443</td>
</tr>
</tbody>
</table>

2.2. Methods
2.2.1. Sample preparation
First, a stock sample with a polymer concentration of 5000 ppm was prepared and stored for further use in preparing the polymer and CDG samples with the required concentrations (by diluting). The solution was stirred using a stirrer at 100 RPM for 48 hours. The 48-hour period was selected since after 48 hours, the polymer solutions seemed completely clear and homogenous.
Separately, a 1000-ppm cross linker (Cr³⁺) solution was prepared to be used in the CDG solutions. This was done because the chromium concentration in the CDG samples was extremely low (43 and 65 ppm) and using the powdered form of the crosslinker to prepare the final samples in a single step might cause significant experimental errors because of the errors in weighing the negligible amount of crosslinker.
Ultimately, the required amount of these stock solutions, crosslinker and polymer stock solutions, were mixed with the required amount of distilled water and salts to prepare the final CDG or polymer solutions with the required compositions. The samples were stirred at 100 RPM for two hours and then were placed in an oven at 60°C for four days to allow the crosslinking reactions to occur. Table 2 lists all the samples prepared and used in this study and their respective polymer, crosslinker and salt concentrations. The last column shows the values of the fitted power-law equation parameters for the samples.
Table 2: The polymer and CDG samples used in this study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer conc. (ppm)</th>
<th>CPR</th>
<th>Salt content</th>
<th>Power-law parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>k (Pa.s^n)</td>
</tr>
<tr>
<td>1</td>
<td>1300</td>
<td>0</td>
<td>0</td>
<td>0.452</td>
</tr>
<tr>
<td>2</td>
<td>1300</td>
<td>1/30</td>
<td>0</td>
<td>0.2527</td>
</tr>
<tr>
<td>3</td>
<td>1300</td>
<td>1/20</td>
<td>0</td>
<td>0.1457</td>
</tr>
<tr>
<td>4</td>
<td>1300</td>
<td>1/30</td>
<td>5000 ppm NaCl</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>1300</td>
<td>1/30</td>
<td>5000 ppm KCl</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>1300</td>
<td>1/30</td>
<td>5000 ppm CaCl_2</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>1300</td>
<td>1/30</td>
<td>5000 ppm MgCl_2</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2.2. Viscosity measurement
A rheometer (Anton Paar QC viscometer, Austria) was utilized in order to determine the apparent viscosity of the samples in different shear rates. The CC42 spindle, which is proper for low-viscosity polymer solutions, was used in this study. A circulator capable of maintaining the temperature was coupled with the rheometer to test the viscosities at 25 °C temperatures. All the viscosity measurements were conducted at 25 °C and atmospheric pressure.

2.2.3. Retention and permeability reduction
As mentioned in the materials section, three sandstone cores with almost similar permeability values were used in this study. The following steps were performed to determine the retention of polymers and the RRF caused by the polymer and CDG samples.
First, the cores were placed in a core holder and then two pore volumes of the 5000-ppm of NaCl solution was injected into the cores with a rate of 0.3 ml/min. At the end of this step, the differential pressure was recorded and known as \( dP_1 \). Second, two cylinders were filled with brine and the proper preformed polymer solution (either CDG or normal polymer solution). Then, the cores were flooded using two pore volumes of CDG or polymer solutions. Afterwards, in the third step, the cores were flooded by three pore volumes of the post-injection fluid (brine or distilled water). At the end of this step, the differential pressure is recorded and known as \( dP_2 \).

At the end of the process, the effluent solution’s polymer concentration was measured and the adsorbed amount of the polymer was calculated by subtracting the effluent polymer from the injected amount. For the purpose of determining RRF, Equation 2 can be used.

\[
RRF = \frac{dP_2}{dP_1}
\]  

\( dP_2 \) and \( dP_1 \) are described above.

3.2.4. Polymer concentration measurement
In this study, the UV-Vis method, a trusted method[22, 23], was used to measure the concentration of the polymer in the effluent solution[30,31]. Agilent Cary 60 Spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) is utilized in this research.

3. Results and discussion

3.1. CDG formation
In order to be certain of the formation of CDG, a thorough literature review was performed to understand whether CDGs are formed using AN 125 and chromium (III) acetate or not. Alvand et al. used AN 125 and chromium acetate (the same material used in this study) to prepare CDG solutions. The formation of CDG was confirmed in their study by means of DLS, SEM and viscosity measurements over time[18]. As Fig. 1 demonstrates, the viscosity of Sample 2 decreases with time, which is indicative of the formation of colloidal dispersion gel. This is also confirmed by other researchers, too, as they suggest that the reduction in viscosity after adding the crosslinker signifies the occurrence of intramolecular crosslinking reactions and thus the
formation of CDG\cite{10, 24}. One may argue that the reduction in the viscosity might be partly due to the thermal degradation of the polymer molecules (the samples were placed in an oven at 60 °C for four days). Nonetheless, as other researchers have mentioned, SPAM solutions are almost not affected by the thermal degradation up to 120 °C \cite{25}; therefore, the reduction in viscosity after adding the crosslinker is solely due to the formation of intramolecular bonds. It is also worth mentioning that the apparent viscosity of the CDG samples did not experience any significant reduction after four days, so all the samples were tested after being in a 60°C oven for four days.

Fig. 1. Apparent viscosity of Sample 3 Vs time

3.1. Viscosity

Different polymer and CDG samples with different polymer concentrations, CPR and salinities were prepared and their apparent viscosities were measured versus shear rate (see Table 2). These samples are used to study the effect of CPR and salinity on the apparent viscosity of CDG samples prepared using AN125 and chromium (III) acetate hydroxide. The viscosity data for the samples were fitted to the modified form of the power-law equation (Equation 5) and their respective $k$ and $n$ values are listed in Table 2. Equation 5 is derived by combining the power-law equation (Equation 3) and Equation 4.

\begin{align*}
\tau &= ky^n \quad (3) \\
\tau &= \eta \gamma \quad (4) \\
\eta &= ky^{n-1} \quad (5)
\end{align*}

Where $\tau$, $k$, $\gamma$ and $n$ are shear stress (Pa), flow consistency index (Pa.s$^n$), shear rate (s$^{-1}$) and the flow behavior index (dimensionless), respectively.
3.1.2. Effect of CPR
In this part of the study, the effect of CPR is discussed. Fig. 2 demonstrates the apparent viscosity of Sample 1, Sample 2 and Sample 3 which have different crosslinker:polymer ratios. As the graph suggests, the viscosity of CDG decreases when CPR increases. This is thought to be due to the intramolecular crosslinking reactions that occur in the solution. The more the crosslinking reactions occurring in the solution, the smaller the colloidal particles of CDG become and the lower the viscosity becomes[10, 18]. The power-law equation’s parameters for these three CDG and polymer samples are calculated and listed in Table 2. As the \( n \) values and the shape of the graphs in Fig. 2 suggest, adding crosslinkers to the polymer solutions causes the overall behavior of the solution to approach a Newtonian-like fluid behavior (the viscosity changes less with shear rate). This is thought to be due to the fact that the higher the rate of intramolecular reactions is, the more rigid the final formed particles are[26], and thus they are less prone to changing viscosity when the shear rate changes.

3.1.3. Effect of salt type
Wang et al. reported that the higher the concentration of the electrolytes in a CDG solution, the higher the tendency of the polymer clews to curl and thus the higher the probability of intra-molecular reactions [19], which are beneficial in lowering the permeability of the rock (will be discussed further in the paper). With this in mind, the effect of different salts on the crosslinking reactions was studied through viscometry. Four different salts, including NaCl, KCl, CaCl\(_2\) and MgCl\(_2\) were used to study the effect of salts on the stability of the CDG samples prepared using AN 125 and Chromium (III) acetate hydroxide. Two monovalent and two divalent cations were used to determine the relative effect of the cation type on the apparent viscosity and stability of CDG. All the samples in this part were prepared using 5000-ppm electrolytes. Fig. 3 demonstrates the apparent viscosity of the CDG samples prepared using different salts.
As shown in Fig. 3, adding salts to CDG samples decreases the viscosity (compare the viscosity values with those of Sample 3). As reported in the literature, increasing the salinity of a polymer solution leads to a decrease in its apparent viscosity[27]. The polymer macromolecules present in partially hydrolyzed polyacrylamide solutions start to change to polymer coils after a certain salinity (coiling equals to the shrinkage of the molecules) [28]. The aforementioned phenomenon can also occur in SPAM solutions. The lowest to highest reduction in the viscosity of the CDG samples are caused by NaCl, KCl, MgCl$_2$ and CaCl$_2$. Divalent ions show higher capacities in reducing the viscosity of the solution, as they produce a stronger electrolyte when dissolved in water with similar concentrations.

It is worth mentioning that in the salinity range of our experiments, the CDG samples have almost lost most of their viscosity, as their viscosities are closer to water (0.001 Pa.s) than they are to the pure polymer solution’s viscosity.

### 3.1.4. Permeability reduction

The first part of this study (CDG viscosity) suggests that CDG samples are inferior to the normal solutions because of their extremely lower viscosities. However, the viscosity of the displacing fluid is only one of the factors affecting the overall oil recovery factor in a flooding process. Although there has not been a comprehensive research on the ability of CDGs formed using SPAM and Cr$^{3+}$ in permeability modification, samples of CDG produced by HPAM and Al$^{3+}$ have been reported superior to polymer solutions in reducing the permeability of the porous media[19]. Causing this reduction, CDGs can modify the flow profile so that the injected water penetrates the streaks with lower permeability, too. Therefore, they can cause an increased overall oil recovery factor by lowering the permeability of high permeability streaks. In this part of the study, three different cores with nearly the same permeability and porosity were used to determine the polymer retention and the RRF. Table 3 lists the flood tests performed in this study with details about the type of the injected fluids.

![Fig. 3. Effect of salts on the viscosity of CDGs (1300/30/5000) at 25 ºC](attachment:fig3.png)
Three different samples were used as the flooding agents. Fig. 4 demonstrates the retention of the polymers (normal polymer particles or CDG particles) in the three experiments. In two of the experiments, CDG was the flooding agent in the second step (CDG and CDG-distilled in the graph). It must be noticed that in CDG, the post flooding fluid is the same electrolyte as the electrolyte with which the CDG sample was prepared, while in the case of CDG-distilled, the post-flooding fluid was distilled water. This was performed to study the effect of the electrolyte on the retention and permeability reduction of the samples. As Fig. 4 shows, there is not a noticeable difference between the retention of CDG and AN 125. However, AN 125 shows a slightly greater retention. This is also reported by Spildo et al., for CDGs prepared using HPAM and Al\(^{3+}\) [20]. This is thought to be partly due to the availability of more negative sites in the case of normal polymer solutions in comparison to CDG samples (in CDGs, some of the sites are crosslinked to Cr\(^{3+}\) cations). The negative sites of the polymers can enter interactions with the clay surfaces and adsorb onto them, while in CDGs, fewer available negative sites for these type of interactions exist, hence the lower retention of CDG [20].

![Fig. 4. Retention of the samples](image)

The calculated RRF values both samples are plotted in Fig. 5. According to Fig. 5, although the retention of the CDG sample is less than that of the polymer solution, the CDG is highly capable of reducing the permeability of the rock, while the RRF value for the polymer solution is only 2.12. This observation confirms the hypothesis that the rigidity of the particles play a major role in lowering the permeability of the rock. Although previous studies showed that the hydrodynamic diameter of CDG particles is lower than polymer solutions [10, 18], their more Newtonian-like behavior suggests that they are more rigid than normal polymer solutions. Therefore, these particles do not deform or stretch when exposed to high shear rates at pore throats, and can block some of the pores, while most of the retention of normal polymer solutions is caused by their adsorption onto the surface of the rock, not by blocking the pore throats. This causes the superiority of the CDG samples with respect to the normal polymer solutions in improving the flood.
Another observation made in this study was the fact that changing the post-flooding fluid can cause differences in the final RRF. As evidenced in Fig. 5, changing the post-flood fluid from the 5000-ppm NaCl solution to distilled water caused the overall retention to increase and the RRF to slightly decrease. This can be contributed to the desorption of some of the cations (Cr$^{3+}$ or Na$^+$) engaging with the negative sites of the CDG particles. As the distilled water is injected into the core, the overall ionic strength of the CDG solution in the rock decreases and the thermodynamic balance in the aqueous solution is disturbed. Therefore, some of the cations are desorbed into the solution and a new thermodynamic equilibrium is held. This desorption, causes the polymer coils to slightly expand and to have more available negative sites to enter interactions with the clay surfaces. Therefore, the adsorption of the polymer increases. However, this increased adsorption does not increase the overall RRF, as the newly expanded particles are less rigid and thus are able to pass through some of the pore throats.

### 4. Conclusions

A study was conducted on the formation and performance of colloidal dispersion gels prepared with sulfonated polyacrylamides and Cr$^{3+}$. The study is divided into two different parts: viscometry and flow performance tests. The results suggest that CDGs can be successfully prepared using the aforementioned materials. Moreover, the viscosity of the CDG decreases with increased concentrations of the crosslinker and salts. This increase in concentrations causes the CDG samples to approach a more Newtonian-like state, which can be indicative of the fact that their particles become more rigid and therefore less susceptible to shear rates. Therefore, although they lack the high efficiency of normal polymer solutions in mobility improvement, their more rigid particles can be used to block some of the pore throats in the rock, hence reducing the permeability of high-permeability streaks. Given this, three different core floods were performed. The results showed that although CDGs have less retention in rocks compared to normal polymer solutions, they exhibit a much better performance in lowering the permeability of the rocks by blocking some of the pore throats. Also, the composition of the post-food fluid is important. Changing the post-flood fluid from 5000-ppm NaCl solution to distilled water reduced the overall RRF of the CDG and slightly increased its retention.
5. References


