Effect of dissolved silica on stability of Hydrolyzed polyacrylamide in the Polymer injection

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Abstract. Polymer is one of the chemical used as mobility control agents in the enhanced oil recovery (EOR). There are several problems related to the polymer injection process such as loss of detectable polymer concentration and chemical reactions between the rock and the injection fluid. Loss of polymer concentration which leads the decreased viscosities makes the sweeping efficiency reduction. Selection of suitable polymers is undertaken as a preliminary screening step for the success of advanced oil recovery. Polymer synthesis is performed to obtain polymers that is appropriate to the objectives and research plan. Hence, the aim of the study is to acquire the appropriate upgraded polymer. The material used to gain upgraded polymer was polyacrylamide (PAM). It was then, hydrolysed to generate Hydrolysed polyacrylamide (HPAM) which had more resistance to temperature and salinity. Therefore, the variables of the study were temperature and salinity. Furthermore, Teos, the source of silica, was added to the HPAM, which was called HPAM-Si and showed that it could increase the durability to temperature and salinity. From the study, HPAM-Si still showed viscosity stability at temperature of 70 °C and salinity of 10.000 ppm.

Keywords: Polymer, Polyacrylamide, PAM, Hydrolysed Polyacrylamide, HPAM.

1. Introduction
Polymers are usually used in petroleum industry activities for water shut off, hydraulic fracturing, and chemical injection in the process of improving oil recovery (IOR). Commonly, the polymer types are synthetic polymer (polyacrylamide) and biopolymer (guar and xanthan gum). There are three potential ways in which a polymer flood can cause more efficient oil recovery process: (1) Though the effects of polymers on fractional flow, (2) by decreasing the water/oil mobility ratio, and (3) by diverting injected water from zones that have been swept [1].

In the polymer injection, there are several challenging to be encountered, those are: the suitability of polymer types in reservoir conditions, polymer injection methods and determining the amount of polymer required in the Enhanced oil recovery (EOR) process. The reservoir conditions consist of reservoir salinity, reservoir temperature, pH and polymer reactions with compounds contained in rock and water formation. While determining the amount of polymer needed more complex again. Determination of polymer concentrations associated with rheology needs to be assessed.
Volumetrically, the required injection volume of the polymer solution can be calculated by considering the pore volume injection design. However, the loss of polymers during the injection process also plays an important role in the success of the EOR process because technically, the urged solution loses its ability in urgency beyond the consideration of economic factors.

Loss of the polymer can be due to rock adsorption, mechanical trapping and hydrodynamic retention. The polymer adsorption process by rocks is considered an inevitable and reduced process [2,3]. It requires a large volume of water to release adsorption. Willhite suggest that polymer retention is largely due to large polymer molecules trapped within very small pore rocks [4].

The polymer required as an advanced oil recovery agent is a polymer which is capable to maintain its viscosity under reservoir conditions. Some of the polymer requirements that must meet as an Urge agent in the EOR are: soluble in water, high viscosity at low concentrations, good temperature resistance, resistance to salinity, and mechanical stability. To realize the concepts, the hydrolyzed polyacrylamide (HPAM) has been investigated in the laboratories study [5]. As one of method on enhanced oil recovery (EOR), the polymer injection using hydrolyze polyacrylamide has been secured to be effecting way to increasing oil production in the field [6,7].

In the laboratories scale, there are several researchers who have been published about modified HPAM. Iron and Oxygen dissolved to the HPAM can stabilize of viscosity on temperature until 90 °C [8]. On the other hand, HPAM solution under acidic condition can be much higher than at neutral condition. But the low pH condition will increase the absorption that indicated the polymer loses [9]. In the late-stage oil treatment (EOR), the use of water as an injection material will cause the phenomenon of water to flow first rather than oil, and oil out unevenly. Polymers can be used to increase the viscosity of water that plays a role in encouraging and urging oil to be maximally lifted.

Currently the availability of polymers as EOR agents is still heavily dependent on imported products. Actually, some research on polymer has been done and feasible, but the result is still not yet able to cheap and applicable in the field. Therefore, the study of polymers should still be done to obtain polymer products that are applicable, cheap and environmental friendly. This research is discussing about the modification of HPAM by addition of silica to stabilize of polymer viscosity in the formation water salinity and reservoir temperature.

2. Materials and Experimental Procedure

The materials consisted of acrylamide monomer, potassium persulfate, sodium hydroxide, methanol, pore water, TEOS (tetraethyl orthosilicate), and HCl. There were several steps in making polymer. The detail of material solutions can be explained briefly follow:

**Making PAM:** dissolve 7.5-gram of acrylamide monomers into the pure water of … ml. Then, the 120 ml of sodium hydroxide (missal 5N) was added to the three-neck flask in order to set the pH of the solution to a base condition (it is about 8). The solution was heated until approximately 55 °C and stirred at 200 rpm for 105 minutes. When the reaction temperature reached 55 °C, the 0.4 gram of persulfate potassium initiator was added. The result obtained was a gel-based PAM solution. Furthermore, methanol was added to the PAM solution with the volume ratio of PAM and methanol approximately 1: 2. As the result, the PAM solution turned into a white precipitate and then, it was filtered from the solution. The precipitation was heated in the oven to until the constant PAM weight obtained. Figure 1 shows the experiment equipment.

**Making HPAM:** the PAM solid was introduced into a three-neck flask containing 240 ml of 0.5 M NaOH solution and then, the heating and stirring were ignited at a fixed scale of 200 rpm. Once the PAM solids was completely dissolved, the temperature was kept constantly at 60 °C and the process run for 90 minutes. The result gained was HPAM solution. Afterwards, the methanol was appended to the HPAM solution with the volume ratio of HPAM and methanol about 1: 2 in order to precipitate the HPAM. The precipitation was then filtered, and latterly, the rest of methanol was removed by being heated in an oven until constant HPAM weight obtained.
Making HPAM-Si: the HPAM was dissolved in the pore water and TEOS was added about 50% by weight of HPAM in acidic atmosphere. Furthermore, the methanol was appended to the HPAM-Si solution with the volume ratio of HPAM-Si and methanol about 1: 2 in order to precipitate the HPAM-Si. The precipitation was then filtered, and finally, the rest of methanol was removed by being heated in an oven until constant HPAM-Si weight obtained.

3. Results and discussion
The HPAM product was tested for viscosity concentration of 5,000 and 10,000 ppm HPAM solution without salinity and HPAM concentration of 5,000 and 10,000 ppm with salinity of 5,000, 10,000 and 30,000 ppm. It appears in the picture that the solutions are clear and also indicating that the solution is homogeneous. The polymer is shown in the Figure 2. At a concentration of 10,000 ppm HPAM with salinity of 30,000 ppm also looks clear.
After several solutions were prepared with different concentrations of HPAM and salinity, the viscosities was measured by temperature variations, i.e., 30 °C, 40 °C and 80 °C. Measurement of viscosity was done by sensitivity test of polymer concentration, temperature and salinity with the measurement condition. Polymer viscosity measured using Brookfield Viscometer DV3TLV with Rheocalc software as shown on Figure 3.

3.1. HPAM synthesis

Figure 4a shows that the viscosity of polymer dropped from temperature 30 °C to 60 °C in the concentration HPAM free salinity. After that the temperature between 60 °C to 80 °C the viscosity of polymer gradually decreases. On the other hand, the salinity between 5000 ppm to 30,000 ppm shows that all of the viscosity slightly dropped compare with the free salinity. Even though the just little bit of salinity, effect of the presence of salinity in the polymer very influence on viscosity reduction. As can be seen on the salinity between 5,000 ppm to 30,000 ppm, the trend of viscosity reduction slightly decreases compared to the free salinity. In here, the addition of salinity will effect slightly on viscosity although the temperature increases.

Furthermore, in the Figure 4b displays that the viscosity performance in the HPAM concentration approximately 10,000 ppm. The trends of viscosity reductions are comparable with the HPAM concentration approximately 5,000 ppm. In the free salinity condition, the added of HPAM
concentration will increase the viscosity of polymer about 100% percent in the temperature 30 °C and HPAM concentration increase 5,000 ppm, respectively. Furthermore, in the HPAM concentration approximately 10,000 ppm, the viscosity increase about 120% in the free salinity compare to HPAM 5,000 ppm. In the next of temperature, the both of concentrations will comparable.

3.2. HPAM and HPAM-Si

Figure 5a shows the polymer viscosity in TEOS concentration approximately 5000 ppm. In here, adding Teos (source of silica) will effect on the viscosity maintenance. In the HPAM concentration of 10,000 ppm in the free salinity, the viscosity slightly higher compare to the HPAM concentration of 5000 ppm and the Si (silica) concentration of 5,000 ppm. In here, the effect of adding silica on the low concentration just little effect on polymer viscosity.

On the other hand, the Figure 5b displays that the viscosity almost constant in the free salinity on the various temperature. Furthermore, in the salinity added, the polymer viscosity dropped. But in here, the dropping of polymer viscosity can be slightly maintained if the silica adding approximately 10,000 ppm on the polymer solution. It is can be denied that adding salinity in the polymer solution makes the viscosity suddenly dropped. The salinity concentration of 5,000 ppm, the polymer viscosity slightly dropped in the increasing temperature. In here, the value of polymer viscosity still has applicable to inject to reservoir because in here, the polymer viscosity approximately 8 cp in the HPAM concentration and silica concentration of 5,000 ppm and 10,000 ppm, respectively. As result, The polymer solution in this research will applicable in the low salinity reservoir.

There is one reason that the silica can maintain the polymer viscosity. Figure 6 shows that the HPAM molecule and HPAM-Silica molecule. Adding silica on HPAM solution will change the cluster of molecule. The atom silica (Si) will move to inside of HPAM solution and remove the O, so the silica can bind the 3OH. In this case, adding group of the SiOH makes the HPAM-Silica more stable compare HPAM individually.

![Graphs showing viscosity versus temperature](image)

(a) Teos concentration 5000 ppm  
(b) Teos concentration 10,000 ppm

**Figure 5.** The comparison of viscosity versus temperature in HPAM concentration of 10,000 ppm, and the concentrations silica concentrations of 5000 ppm and 10,000 ppm
Figure 6. The molecular changing from HPAM to HPAM-Silica

4. Conclusions
The study results for HPAM and HPAM-Silica by varying the temperature and salinity showed that the temperature variation on HPAM in the salinity concentration of 5,000 to 10,000 ppm did not have significant effect on the polymer viscosity. It could be as a reference in the process of the polymer injection in the field. Adding silica on HPAM solution removed the O- and could blind the 3OH. Effect of this case, the HPAM-Si solution was more stable in the salinity approximately 10,000 ppm and the temperature until 70 °C. HPAM-Silica was more applicable in the reservoir condition for low salinity and temperature of reservoir lower than 80 °C.

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