EXPERIMENTAL INVESTIGATIONS ON THE GELATION BEHAVIOR OF PARTIALLY HYDROLYZED POLYACRYLAMIDE – HEXAMINE – PYROCATHECHOL GELS

UPENDRA SINGH YADAV & VIKAS MAHTO
Department of Petroleum Engineering, Indian School of Mines, Dhanbad, Jharkhand, India

ABSTRACT

This article presents an investigation on the effect of several parameters on the gelation behavior of partially hydrolyzed polyacrylamide – hexamine – pyrocatechol gel system which may be used as sealant to control excessive water production from hydrocarbon reservoirs. In this work, a polymer gel comprised of partially hydrolyzed polyacrylamide as a water-soluble polymer and hexamine and pyrocatechol as organic cross-linking agents of low toxicity was prepared in brine solution. The bottle testing method is used for the qualitative determination of the gelation behavior of the developed gel system and the time for the formation of stiff gel is reported. In this study, the temperature was varied from 80°C to 120°C and polymer and crosslinker concentration varied from 0.8 to 1.1 wt.% and 0.6 to 0.9 wt.% respectively. The experimental study investigates that the gelation time is mainly affected by temperature, polymer and crosslinker concentration and the developed gel is stable up to 120°C which shows its potential to control the excessive water production of high temperature reservoirs.

KEYWORDS: Polymer Gel, Gelation Time, Water Soluble Polymer, Cross Linker

INTRODUCTION

Excessive water production from hydrocarbon reservoirs is one of the most serious problems in the oil industry. It is always undesirable as it unfavorably results in scaling, emulsions, water blocks, corrosion or sand production¹,². This excess water production increases the produced fluid head in well bore and creates extra back pressure on the formation. This intern reduces a well’s flow capacity and it increases additional load in artificial lift techniques to lift the fluid up to the surface which increases the operating cost of the well³,⁴,⁵. The other operating costs include the expense to dispose, or re-inject this water, as well as the capital cost of surface facility construction, water treatment an efforts to ensure that environmental regulations are met⁶,⁷.

There are variety of commercially available techniques and materials for water control including mechanical and chemical methods, all of which perform differently and each has its unique limitations⁸. The mechanical method includes squeeze cementing and mechanical isolation with bridge or cement plugs have not been very successful in reducing the water production for a long period of time. The chemical methods include the use of organic and inorganic gels⁹. Organic gels have lower cost, ease of application, wider control over gelation time, compatibility with formation fluids and deeper penetration inside the treated formations. On the other hand, inorganic gels are usually silicon-based such as sodium silicate gels and it is difficult to control the gelation mechanism because of the short setting time.

Recently, organically crosslinked gels are used in the oil industries to control excessive water production from the hydrocarbon reservoirs as these gels have good stability at elevated temperature due to the covalent bonds between the polymer and the organic crosslinkers⁹,¹⁰,¹¹. Several eco-friendly crossliked gel systems are reported in literatures which are stable at higher temperature and applicable for high salinity reservoirs. These gel systems are usually developed by
partially hydrolyzed polyacrylamide polymer and organic crosslinkers like phenyl acetate, hexamethylenetetramine, glyoxal, hydroquinone, pyrogallol etc\textsuperscript{[13]-[15]}.

The present work involves the development of eco-friendly crosslinked polymer gel system using partially hydrolyzed polyacrylamide as base polymer and hexamine and pyrocatechol as crosslinking agent. The qualitative analysis of gelation behavior of this gel system were carried out using bottle testing method and different parameters affecting the gelation behavior of the gel system were thoroughly studied.

**EXPERIMENTAL WORK**

**Material Used**

The materials used for this work are Partially Hydrolyzed Polyacrylamide, Hexamine, Pyrocatechol, Sodium Chloride, Hydrochloric Acid and Sodium Hydroxide. Partially hydrolyzed polyacrylamide is procured from Oil and Natural Gas Corporation Limited, Mumbai, India. Hexamethylenetetramine is purchased from Otto Kemi Mumbai, India. Pyrocatechol and hydrochloric acid are purchased from Central Drug house (P) Ltd. New Delhi, India. Sodium chloride is purchased from Nice Chemical Pvt. Ltd. Cochin, India and sodium hydroxide is purchased from S. D. Fine-Chem Ltd. Mumbai, India.

**Experimental Procedure**

The bottle testing method is used for the determination of gelation time, as it is a suitable, faster and inexpensive method to study gelation kinetics. Initially stock solution of partially hydrolyzed polyacrylamide in brine solution was prepared and kept for aging at ambient temperature for 24 hrs and further fresh solution of crosslinkers (hexamine and pyrocatechol) were also prepared in brine. The appropriate solution of partially hydrolyzed polyacrylamide, crosslinkers solution and brine were thoroughly mixed at room temperature by magnetic stirrer. The pH of the gelant solution was measured by Century CP-901 digital pH meter and the pH of the gelant solution was maintained using 1N sodium hydroxide and 1N hydrochloric acid. Finally, the solution was transferred gelant solution into small glass bottle and kept at the desire temperature in the hot air oven (Temperature ranges from 80 °C to 120 °C). The quality of gel visually inspected at regular intervals and gelation time was noted. Finally, stiff gel was formed which was considered for the gelation time of our experimental work.

**RESULTS AND DISCUSSIONS**

**Effect of pH on the Gelation Time of PHPA-HMTA-Pyrocatechol Gel System**

The pH range of the developed gel system over which the experiments were carried out was from 8.0 to 9.5. Table 1 shows that pH has no significance effect on the gelation time. From the experiments carried out in the laboratory it was found that HMTA/pyrocatechol cross-linked partially hydrolyzed polyacrylamide is stable up to pH 9.5. Above pH 9.5, proper gelation did not take place and syneresis also occurred due to excess crosslinking. The results indicate that a suitable solution pH range for partially hydrolyzed polyacrylamide, hexamine and pyrocatechol crosslinking is between 8.0 to 9.5.

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<td>58</td>
<td>37.5</td>
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Table 1: Effect of pH on the Gelation Time at Temperature Ranges from 80°C to 120°C (1.0 Wt% PHPA, 0.5 Wt% HMTA and 0.3 Wt% Pyrocatechol)
Experimental Investigations on the Gelation Behavior of Partially Hydrolyzed Polyacrylamide – Hexamine – Pyrocatechol Gels

Effect of Salinity on the Gelation Time of PHPA-HMTA-Pyrocatechol Gel System

The gelation reaction between partially hydrolyzed polyacrylamide and hexamine-pyrocatechol gel system depends on solution salinity. The effect of salinity of polymer gelant on gelation rate at different gelation temperatures is given in Figure 1. Gelation occurs rapidly in presence of salt compared to distilled water. The polymer gel samples prepared with constant polymer and cross-linker concentration and varying brine salinity from 1.0 to 3.0 wt.% showed that the gelation time increases with the increase in concentration of brine.

![Figure 1: Effect of Salinity on the Gelation Time at Different Temperature and pH 8.5 (1.0 Wt% PHPA, 0.5 - 0.5 Wt. % HMTA-Pyrocatechol)](image)

The increase in brine concentration screens the cross-linking sites thus induction period increases due to which gelation takes longer time, moreover the gels formed are less elastic in nature. This is due to affecting sodium cations shield on the amide groups which resulted in shrinkage of the polymer chains or masked the crosslinking sites. Consequently, the number of active cross-linking sites decreased and thus the intensity of cross-links was lowered.

The gel formation takes much longer time. Further, the prepared gels in saline water were visually weaker than those prepared in distilled water. However, sodium ions can delay gelation more than potassium ions which are mainly because of the higher charge density of sodium ions compared to that of the potassium ions.

Effect of Temperature on the Gelation Time of PHPA-HMTA-Pyrocatechol Gel System

The gelling solutions were prepared with different concentrations of polymer and crosslinking agent at pH 8.5 and kept for gelation at different temperature. The reaction rate between amide group and methylol group was accelerated by increasing temperature and the gelation time decreased.

As increasing the gelation temperature result in a decrease in gelation time since at higher temperature gels are formed in lesser time due to rapid crosslinking as is depicted in Figure 2. A possible explanation for rapid cross-linking is either due to an increase in molecular mobility or formation of new cross-linking sites as a result of gelation reaction.

It is a known fact that degree of hydrolysis of the polymer increases at elevated temperatures which in turn increases the number of cross-linking sites that’s found increase the reaction rate and decreases the gelation time.
Figure 2: Effect of Temperature on the Gelation Time at Different Polymer and Cross-Linker Concentration and pH 8.5

Effect of Polymer Concentration on the Gelation Time of PHPA-HMTA-Pyrocatechol Gel System

The polymer concentration of the gelant varied from 0.8 to 1.1 wt% and constant concentration of crosslinker (0.5 wt% HMTA and 0.5 wt% pyrocatechol) was used at pH 8.5, which is depicted in Figure 3. As the polymer concentration increases, more crosslinking sites are available. Thus, the gel formation reaction increases, which leads to the decrease in gelation time. This trend is expected to be the same at all gelation temperatures under study. Thus, the required time to obtain a non-flowing polymer gel with a tolerable strength decreased when the polymer concentration was increased.

Figure 3: Effect of Polymer Concentration (PHPA) on the Gelation Time at Different Temperature and pH 8.5 (0.5 Wt% HMTA and 0.5 Wt% Pyrocatechol)

Effect of Cross-Linker Concentration on the Gelation Time of PHPA-HMTA-Pyrocatechol Gel System

The several samples were prepared to investigate the effect of crosslinker concentration on the network strength which is shown in Figure 4. Bottle testing results shown in Figure 4 indicate that when the concentration of both crosslinker was decreased the gelation rate and gel quality were decreased. In other words, when crosslinking agent concentration was increased, the stage of polymer gel changed from a state of flowing gel to one of deformable non-flowing gel, because crosslinking sites are increases for the formation of gel in lesser time intervals.
CONCLUSIONS

The several conclusions may be drawn from the present experimental study:

- The gelation time of partially hydrolyzed polyacrylamide-hexamine-pyrocatechol gel systems decreases with increasing the cross linker concentration and temperature.
- Gelation time is a controllable parameter from a few minutes to several days which depends on concentration of polymer and crosslinkers, pH and salinity.
- As concentration of polymer increased in the gelant solution, the gel strength increased and gelation time also decreased.
- As concentration of crosslinkers increased in the gelant solution, the gel strength increased and gelation time decreased.
- The developed polymer gel system is stable at pH up to 9.5.
- The increases in salinity concentration in the gelant, gelation time of the polymer gel system slightly increases.

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REFERENCES


