The effect of polymer type on the performance of gels

Tianci Zhang¹, Qingchen Zhao¹, Hongbin Guo¹ and Jijiang Ge¹*

¹School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong, 255680, China
*Corresponding author’s e-mail: gejj@upc.edu.cn

Abstract. Owing to the formation heterogeneity, the difference of mobility between sweeping phase and formation fluids, gravity segregation, the sweeping phase usually flows along the high permeability zone, which leads to the poor oil recovery. In general, gelling systems are used into the reservoir conformance improvement. The properties of gels are different for the different composition of gelling systems. In this paper, three polymers with different AMPS content were used to investigate the effect of polymer type on the performance of polymer gels. In addition, methenamine(MA) and hydroquinone(HQ) were employed as crosslinkers, thiourea(TH) was used as oxygen scavenger to improve the stability of polymers and gels. And the gelation time, strength and syneresis rate of gels were characterized respectively. The results showed that the stability of polymer and gel was enhanced with the increase of AMPS content, and the gelation time was increased with the increment of AMPS content. And an ultrastable thermal-resistance and salt-tolerance gel was developed with the AM/AMPS copolymer (AMPS content equals 70%), the syneresis rate was less 10% after heat treatment under the harsh conditions (temperature=130°C, salinity=223802.8mg/L) for 150 days.

1. Introduction
In the process of oilfield development, due to the unfavorable factors such as oil-water density difference, oil-water viscosity difference, gravity differentiation and formation heterogeneity, the phenomenon of early water breakthrough is generally existed, which is not conducive to water flooding effect, thus reducing the oil recovery. Accounting for these problems, profile control or water shut off agents were adopted to block the thief zone and enhance the waterflood efficiency, and eventually improved the oil recovery[1-3].

Gelling systems had been widely used as the blocking agent to improve the waterflood efficiency and oil recovery, owing to its special advantages, for example, low cost, low damage to formation, selective blockage. Recently, people attempt to improve the stability of polymers by the introduction of other functional monomers[4,5], for example, 2-acrylamido-2-methylpropanesulfonate(AMPS), N-vinylpyrrolidone (N-VP), and have achieved outstanding products. As to AMPS groups, there are two S-O coordination bonds that could enhance the ability of attracting electrons from the –OH-, which leads that AMPS is not sensitive to the ions. So the copolymer containing AMPS shows excellent capability bearing temperature and salt. Otherwise, the introduction of N-VP into copolymer is found to improve the performance under hostile environment conditions, this is because N-VP can inhibit the hydrolysis of amide(AM) in aqueous solutions and thus improve polymer thermal stability[6-8]. The above heat-resistant and salt-tolerance polymers have been adopted to develop gels and show great stability and strength under hostile conditions. On the one hand, copolymers containing functional monomers possess excellent thermal stability under high-temperature high-salt condition, which is favourable to obtain more stable gels. On the other hand, the presence of large side group(AMPS) may slow the crosslink...
rate between polymer and crosslinker molecules, and thus enhance the stability and strength of polymer gels[9].

According to the high temperature and high salt condition (130 ℃, 223802.8mg / L) of Tahe oilfield this paper plans to develop one gel formation that is suitable for the Tahe oilfield, thus achieving the purpose of plugging the high permeability water layer, improving the water drive effect and enhancing the oil recovery of Tahe oilfield.

2. Experimental section

2.1. Materials

Methenamine(MA) and hydroquinone(HQ) used in this paper are cross-linking agents. Thiourea(TH) is used as oxygen scavenger in following experiments. NaCl, KCl, CaCl2, MgCl2 and NaHCO3 are used to prepare synthetic Tahe water which is used in all the experiments below, and the ion composition is showed in Table 1. And the above agents are pursed from Sinopharm Chemical Reagent Company, and analytically pure.

| Ion type | Cl⁻ | HCO₃⁻ | Ca²⁺ | Mg²⁺ | Na⁺+K⁺ | Total |
|----------|-----|-------|------|------|--------|-------|
| Ion content(mg/L) | 137529.5 | 183.6 | 11272.5 | 1518.8 | 73298.4 | 223802.8.8 |

Three polymers are listed in Table 2, which are provided by Dongying Liuhe Chemicals Company. It should be noted that the material concentration in the following section is on a weight basis unless specified.

| Polymer name | AMPS[mol%] | Molecule weight |
|--------------|-------------|-----------------|
| AMPS-0       | 0           | 6-9×10⁶         |
| AMPS-25      | 25          | 6-9×10⁶         |
| AMPS-70      | 70          | 6-9×10⁶         |

2.2. Measurements of viscosity

The change of viscosity of polymer solutions with the aging time( at 130℃) was measured to evaluate the stability of polymers. The 0.6% polymer solutions were prepared and sealed in ampoules then put into an oven for different times, and 0.3%thiourea was added into polymer solutions to be as oxygen scavenger. The viscosity of these polymers solutions was measured by MCR 92 rheometer equipped with concentric cylinder (CC39).

2.3. Measurements of gel strength and gelation time

The gel strength is characterized by the gel strength code method[10].After the gelling solution was prepared, approximately 20 g solution was put into ampoules which were sealed by the alcohol blast burner. Thirdly, the sealed ampoules were kept in the oven which is set at the desired temperature (130℃ in the following experiemnts). Finally, the ampoules were removed from the oven at set intervals. The gel strength was observed by visual inspection according to the gel strength code method. And the time when the gel strength reaches “F” grade is defined as gelation time.

2.4. Measurements of syneresis rate

To evaluate the stability of the gelling systems, syneresis rate should be measured during the heat treatment (at 130℃) of gels. The definition of syneresis rate is adopt by the following expression.

\[ R = \frac{W_s}{W_g} \times 100\% \]
Where Rs is the syneresis rate of gels which are heat treated for a certain time interval. Ww is the weight of the water expelled from the gel aged for a specific time interval. Wg is the quality of gelling solution which is put into ampoules. Apparently, the less syneresis rate is, the more stable gel is.

3. Results and discussion

3.1. Effect of AMPS content on the stability of polymer

The viscosity of polymer solution was investigated to evaluate the effect of AMPS content on the stability of polymer. The change of viscosities of three polymer solution with aging time is shown in Fig1.

It can be seen that the viscosity of three different polymer solutions decreases in different degrees with the increasing of aging time. The phenomenon that viscosity is reduced has two reasons mainly: (1) the groups of the copolymer molecule, such as AM, AMPS are hydrolyzed into acrylic acid (AA) under the condition of high temperature, and the latter could interact with multivalent cations, consequently form precipitates. (2) At high temperature, polymer macromolecules breaks small molecules, which leads to the decrease of viscosity of polymer solution.

3.2. Effect of AMPS content on the gelation behavior

Gelation time is an important character of a gelling system, because gelation time is a crucial factor to the on-site construction safety. So the gelling solution with three polymers was prepared according the composition: 0.6%polymer+0.05/0.1/0.2%(MA+DB)+0.3%TH. The gel strength code at different aging time was listed in Table3.

Experimental results show that the gelation time decreases with the increasing of AMPS content, which is consistent with previous research. For example, when the concentrations of MA and DB are fixed at 0.2 wt%, the concentration of TH is 0.3 wt%, the gelation time (when the strength reaches “F”) of gelling systems containing AMPS-0, AMPS-25 and AMPS-70 are 2h, 3h and 9h, respectively. On the one hand, the amount of active groups (AM) that crosslink with crosslinker molecules is definitely reduced as AMPS content increases. And there is no doubt that the decreasing of active groups would reduce the crossliking rate and expand the gelation time. On the other hand, the existence of AMPS also hinders the crosslinking reaction owing to the steric effect of the large side group.

Table 3 Effect of AMPS content on the strength code of gels

| Gel Composition | Strength code of gels (hours or days) |
|-----------------|-------------------------------------|
| Polymer         | MA wt% | DB wt% | TH wt% | 1h | 2h | 3h | 6h | 9h | 12h | 18h | 24h | 48h | 7d | 30d |
| AMPS-0          | 0.05   | 0.05   | 0.3%   | A  | A  | B  | C  | D  | F   | G   | G   | --  | --  | --  |
3.3. Effect of AMPS content on the syneresis rate

As mentioned above, gels prepared with a high AMPS content (70%) copolymer still retain high strength after heat treatment of 30 days, so in this section the effect of AMPS content on the syneresis is investigated. The relation of syneresis rate versus aging time is plotted in Fig 2.

From the Fig 2 we can see, the syneresis rate of gel decreases with the increasing of AMPS content. When the AMPS content of copolymer reaches 70%, the gel has excellent stability under the harsh conditions (130°C, 22380 2.8mg/L), the syneresis rate is less than 10% after the heat treatment for 150days. However, the gel prepared with AMPS-0 showed very poor thermal stability and after the heat treatment for 2days, the syneresis rate was 88%. There is no doubt that the stability of gel is enhanced with the increase of the AMPS content of polymer. On the one hand, the existence of AMPS could improve the stability of polymers under hostile conditions, which eventually enhances the strength of 3D structures of gel. Water was trapped in the these strong structure, which leads a low syneresis rate. on the other hand the existence of AMPS could enhance the stability of gelling systems.

4. Conclusions

An ultrastable thermal-resistance and salt-tolerance gel was prepared with the AMPS-70 copolymer which has a high AMPS content (70%), the gel had excellent stability under the harsh conditions (130°C, 22380.8mg/L), the syneresis rate was less than 10% after the heat treatment for 150days. Otherwise, both the polymer properties and gel performance are effected by the AMPS content of AM/AMPS copolymers. As to the copolymers, it is clear that the increment of AMPS content could increase the stability of copolymers, i.e., the AMPS group can improve the stability of polymers under the conditions of high temperature and high salinity. As to polymer gels, owing to the steric effect of the large side group, AMPS could reduce the crosslinking rate and expand the gelation time. In addition, the AMPS could reduce the syneresis rate of gels, and the higher the AMPS content of copolymer is, the less the syneresis rate is. So the stability of copolymer gels is increased with the increment of AMPS content.

Acknowledgments

Financial support by the Major Scientific and Technological Projects of CNPC under Grant (ZD2019-183-007) is gratefully acknowledged.

References

[1] El-Karsani, K.S.M., Al-Muntasheri, G.A., Hussein, I.A. (2014) Polymer Systems for Water Shutoff and Profile Modification: A Review Over the Last Decade. J. SPE., 19: 135−149.
[2] Zargartalebi, M., Kharrat, R., Barati, N. (2015) Enhancement of surfactant flooding performance by the use of silica nanoparticles. J. Fuel., 143: 21−27.
[3] Wang, F.C., Wu, H.A. (2013) Enhanced oil droplet detachment from solid surfaces in charged nanoparticle suspensions. J. Soft Matter., 9: 7974−7980.
[4] Leena N., Kristian S., Sirkku H., Molesworth P. (2018) Sulfonated Polyacrylamides - Evaluation of Long Term Stability by Accelerated Aging at Elevated Temperature. In: SPE Improved Oil Recovery Conference. Tulsa. pp. 1-25.
[5] Vasquez, J.E., Eoff, L.S. (2010) Laboratory Development and Successful Field Application of a Conformance Polymer System for Low-, Medium-, and High-Temperature Applications. In: SPE Latin American and Caribbean Petroleum Engineering Conference. Lima. pp. 1-10.

[6] D.A.Z. Wever, F. Picchioni, A.A. Broekhuis. (2011) Polymers for enhanced oil recovery: A paradigm for structure-property relationship in aqueous solution, J. Progress in Polymer Science., 36: 1558-1628.

[7] Sabhapondit A., Borthakur A., and Haque I. (2003) Characterization of acrylamide polymers for enhanced oil recovery, J. Appl. Polym. Sci., 87: 1869–1878.

[8] Sabhapondit A., Borthakur A., and Haque I. (2003) Water soluble acrylamidomethyl propane sulfonate (AMPS) copolymer as an enhanced oil recovery chemical, J. Energy Fuels., 17: 683–688.

[9] Swathika Jayakumar., Robert H. Lane. Delayed Crosslink Polymer Gel System for Water Shutoff in Conventional and Unconventional Oil and Gas Reservoirs. In: SPE International Symposium on Oilfield Chemistry. Texas. pp. 1-9

[10] Sydansk R. D. (1990) A Newly Developed Chromium(III) Gel Technology. J. SPE., 5: 346-352.