

HPAM-Cr (III) Gel Syneresis in Bulk Volume

I. Gussenov^{1*}, S. Bakytzhan¹, S. Amangaliyev², Y. Abba²

¹Satbayev University, 22 Satbayev str., Almaty, Kazakhstan

²Kazakh-British Technical University, 59 Tole bi str., Almaty, Kazakhstan

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Abstract

This paper explores the crucial factors influencing the stability of polymer gels utilized in oil well treatments, with a focus on the effects of polymer mixing time and concentrations of polymer and crosslinker. Operating within a practical constraint of a 30-minute mixing time in surface facilities, our findings reveal that incomplete polymer dissolution leads to gel segregation and substantial water release over extended aging at 50 °C. Notably, a reduction in the crosslinker/polymer ratio, achieved by lowering crosslinker concentration or increasing polymer concentration, proves effective in mitigating water release to as low as 0–1% over 90–185 h of aging. Furthermore, gels prepared in sea and reservoir brines exhibit superior stability compared to those in distilled water, suggesting that ion presence in brines counteracts the repulsion between charged polymer chains observed in distilled water. This study provides valuable insights for optimizing polymer gel formulations under time constraints.

1. Introduction

Polymer gels have been extensively utilized for injection and production well treatment to enhance oil reservoir sweep efficiency and reduce water cuts. When placed inside a fracture, the polymer gel reduces water permeability, causing it to penetrate less permeable zones and displace upswept oil [1, 2].

Several field cases illustrate the effectiveness of this technology. For instance, in a study by Jia and et al., 2024 [3], 160 cubic meters of polymer gel were injected into the reservoir to improve sweep efficiency and decrease water production. The polymer gel treatment resulted in a significant increase in oil output and a reduction in water content.

In another study, the injection of 100 cubic meters of polymer gel into a well resulted in a 30% increase in oil production and a 50% reduction in water content [4]. The study concluded that polymer gels exhibit promising potential in enhancing the efficiency of oil recovery in oilfields.

At the Karabulak oilfield, the injection of 120 m³ of a 1% concentrated gellan solution led to a notable reduction in water cut from 80% to 40%. This highlights the efficacy of gellan gum in sealing specific high permeability channels and cracks. Similarly, at the Kumkol oilfield, the injection of 2 t of dry gellan powder resulted in an additional output of 5,890 t (equivalent to 43,108 barrels) of oil over 11 months, generating nearly \$2 million in net profit [5].

Besides that, since 2013, there has been active use of technology based on pre-crosslinked polyacrylamide particles. This technology has allowed reducing water cut by 3 to 15% and increasing oil production from 3 to 20 t per day under various reservoir conditions [6].

Besides technical and geological conditions, the success of the gel treatment strongly depends on the stability of the gel over time [7]. For example, HPAM-Cr (III) gel was shown to decompose after exposure to natural gas and release water in acidic conditions [8].

In this study, the stability of bulk gels was tested and determined by the ability of the gel to preserve its original volume and resist water release –

*Corresponding author.

E-mail address: iskander.gussenov@mail.ru

syneresis. Syneresis is the process of a reduction in the volume of a gel, accompanied by the expulsion of the solvent that was initially trapped within the self-assembled network [9]. Over-crosslinking has been accepted as a main mechanism of the syneresis of the HPAM-Cr (III) gel and takes place at a relatively high crosslinker/polymer ratio. Besides that, the presence of Ca^{2+} and/or Mg^{2+} also promotes the syneresis of the gel. For example, the presence of 0.1 M/L CaCl_2 can increase the syneresis rate of the gel from 0 to 90% within 7 days [10].

In matrix rocks with permeability around 500 mD syneresis has a low effect on gel performance even at high temperatures of 120 °C [11]. However, it may have a more pronounced effect on the stability of gels in fractures and channels, as these high permeability features are represented by continuous void space.

In this study, the gelation and syneresis of HPAM/ Cr^{+3} gels were investigated in a bulk volume at 50 °C. The dissolution time of the polymer, solvent salinity, as well as the concentrations of the polymer and crosslinker were varied to explore the impact of these factors. The results obtained hold significant importance for petroleum engineers engaged in the technological aspects of gelant preparation at surface facilities during field operations.

2. Materials and methods

2.1 Polymer and water

Hydrolyzed polyacrylamide (HPAM) with a hydrolysis degree of 5% and molecular weight of around 6–7 mln Da was used in all tests (Fig. 1). As illustrated in the formula (Fig. 1), the polymer comprises acrylamide and acrylate components. The presence of carboxylate groups ($-\text{COO}^-$) enhances the hydrophilicity and water solubility of the polymer. Additionally, the binding of multivalent ions to these carboxylate groups results in the crosslinking of polymer molecules, leading to gel formation.

Chromium acetate (CA) was added to the polymer solutions to obtain gels by crosslinking polymer molecules with Cr^{+3} . The selection of chromium ace-

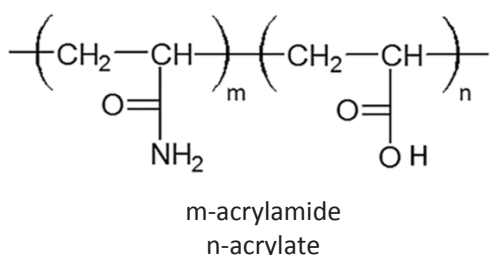


Fig. 1. Chemical formula of HPAM used in this study.

tate was based on its widespread application in polymer crosslinking, particularly in the Uzen oilfield in Kazakhstan, for which this experimental study was carried out. In most tests, the gelants were prepared by using sea brine. However, reservoir brine and distilled water were also used to study the effect of water composition.

The total dissolution time of the polymer in sea and reservoir brines was determined previously by Brookfield LVT viscosity measurements during polymer stirring at 6th speed by Velp F203A0161 MICROSTIRRER Magnetic Stirrer. The dissolution time of the polymer in reservoir brine is 60 min longer than that in sea brine [12]. This is explained by the higher salinity of reservoir brine that causes intensive charge shielding and prevents polymer molecules from extending their hydrodynamic radius in the solvent [13].

2.2 Gelants preparation

In this study, the gelants were prepared by impeller agitation at 330–380 rpm and 20–25 °C. In most experiments, chromium acetate was added along with the polymer. In all tests, the gelants and gels were aged at the target reservoir temperature (50 °C). The polymer and crosslinker concentrations ranged from 0.5 to 1.0 wt.% and 0.00625 to 0.1 wt.%, respectively, chosen to align with typical field operations for economic reasons and to avoid injectivity issues at higher polymer concentrations. Notably, in numerous studies, polymer concentration does not exceed 0.5–0.75 wt.% [14–18]. However, a formulation of 0.5 wt.% polymer and 0.05 wt.% chromium acetate was chosen for most experiments, as this specific formulation mirrors what is commonly utilized in field conditions for well treatment operations.

2.3 Gel stability determination

The stability of gels was determined by measuring the syneresis percentage of gels observed during fixed periods. The syneresis percentage was calculated by the following formula:

$$S = \frac{m_1 - m_2}{m_1} \times 100\%$$

where, m_1 – initial weight of the vial with fresh gel; m_2 – weight of the vial after taking out the released water by syringe.

The released water accumulated on the top of the residual gel was easily taken out by using a syringe.

3. Results and discussion

First, it should be stressed that the gels which were prepared according to the widely accepted procedure did not show any significant degradation due to the syneresis. This procedure includes the following steps and prerequisites:

1. Dispersing HPAM in stirred water by gradually adding the powder to the vortex.

2. Complete dissolution of HPAM at low shearing to avoid mechanical degradation of the polymer chains.

3. Gradual addition of CA after HPAM is completely dissolved. The CA should be introduced into the stirring HPAM solution in small portions to avoid local crosslinking.

4. For most formulations HPAM/CA weight ratio is equal to or less than 10. At a lower polymer/crosslinker weight ratio the number of intramolecular bonds may be higher relative to the number of intermolecular bonds, resulting in gel shrinkage and water release.

Figure 2 presents 0.5 wt.% HPAM/0.05 wt.% CA gels water release percentage versus aging time for various polymer mixing times. Of note is that in

samples that were mixed for 30–60 min chromium acetate was added along with the polymer, whereas 120 min sample was prepared according to the widely accepted procedure i.e., the crosslinker was added after complete dissolution of the polymer. As can be seen, the syneresis increases with the reduction of the polymer mixing time. The highest syneresis was observed for 30 min mixing time. Figure 3 presents photos of the gel samples.

As can be seen from Fig. 3, for 30, 45, and 60 min polymer dissolution time two types of gel were formed. The stronger gel adheres to the upper part of the vial upon the upside-down turn, while the less strong gel flows to the bottom. In the case with 120 min polymer dissolution time, the gel is formed having a homogeneous structure and does not separate. The formation of strong gel in case of incomplete polymer mixing (30–60 min) is explained by the settling of fish eyes, which are undissolved swollen polymer particles formed by water wetting of dry powder [19].

As demonstrated by other researchers, an elevation in the crosslinker/polymer ratio beyond a specific value has been shown to amplify the release of water from the gel structure [20]. Considering the

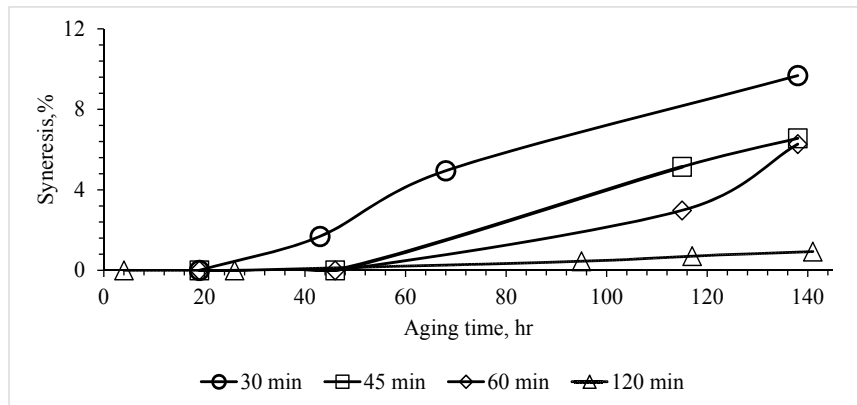


Fig. 2. Syneresis of 0.5 wt.% HPAM/0.05 wt.% CA gels versus polymer mixing and gel aging time. The gels were aged at 50 °C. Makeup brine – sea water.

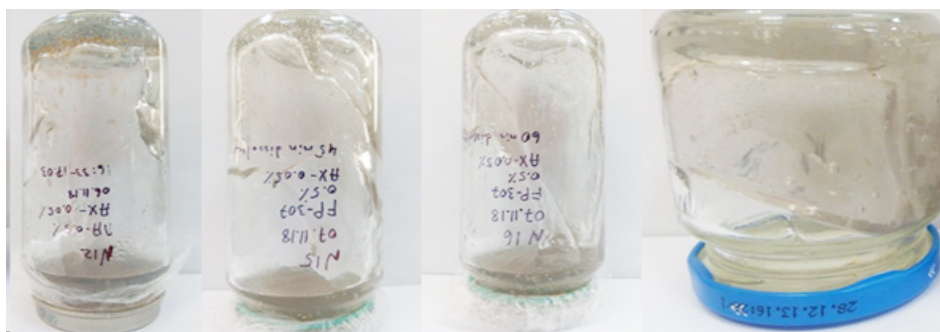


Fig. 3. Photos of 0.5 wt.% HPAM/0.05 wt.% CA gel samples prepared in seawater by varying polymer mixing time. Polymer mixing time from left to right: 30 min, 45 min, 60 min and 120 min.

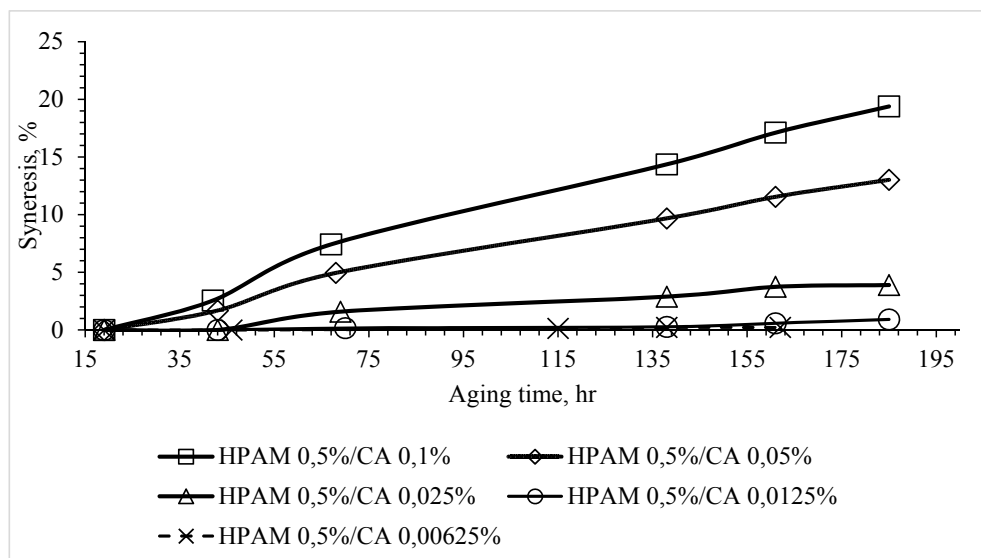


Fig. 4. Syneresis of 0.5 wt.% HPAM gels versus polymer/crosslinker concentration and gel aging time. In all samples, crosslinker was added along with the polymer and mixed for 30 min. The gels were aged at 50 °C. Makeup brine – seawater.

aforementioned information, it is reasonable to anticipate that, in gelling solutions with incompletely dissolved polymer, a reduction in the crosslinker/polymer ratio will lead to a decrease in water release from the gels. Figure 4 illustrates the relationship between water release and time for polymer and crosslinker mixing times of 30 min, highlighting various crosslinker/polymer ratios. Indeed, reducing the concentration of the crosslinker leads to a decrease in syneresis. For instance, decreasing the crosslinker concentration from 0.1 to 0.0125 wt.% resulted in a reduction of syneresis from 20 to 0.9%. Furthermore, further decreasing the crosslinker concentration from 0.0125 to 0.00625 wt.% resulted in minimal change in syneresis.

In general, and as can be seen from Figs. 4 and 5, the decrease of crosslinker concentration at constant polymer content results in less water release

and gel segregation. Thus, in cases where the complete dissolution of polymer is not possible due to the technical constrictions the decrease of crosslinker concentration may be employed to eliminate water release. Another way to decrease the crosslinker/polymer ratio is to use higher polymer concentrations.

Figure 6 shows the syneresis of 0.5–1% HPAM gels versus time. As can be seen, the increase of polymer concentration results in the reduction of syneresis, even though the mixing time was limited to 30 minutes. When the polymer concentration is increased under other equal conditions, even with incomplete dissolution (30 min), a greater number of polymer molecules enter the solution, which reduces the negative effect of over-crosslinking – the main cause of increased water release [10]. The photos of the samples are shown by Fig. 7.

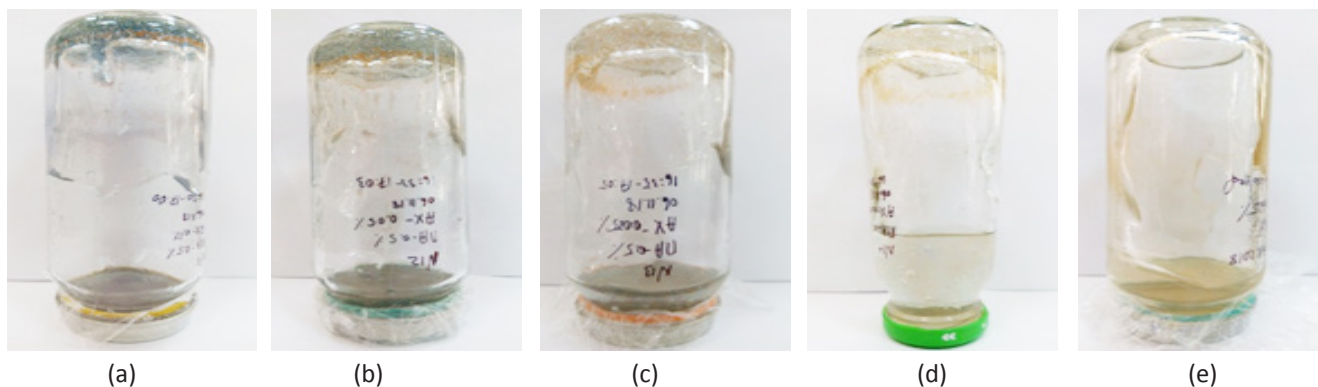


Fig. 5. Samples obtained through a combined 30-minute dissolution of HPAM and CA with a polymer concentration of 0.5% and crosslinker concentrations: a) 0.1%; b) 0.05%; c) 0.025%; d) 0.0125%; e) 0.00625%.

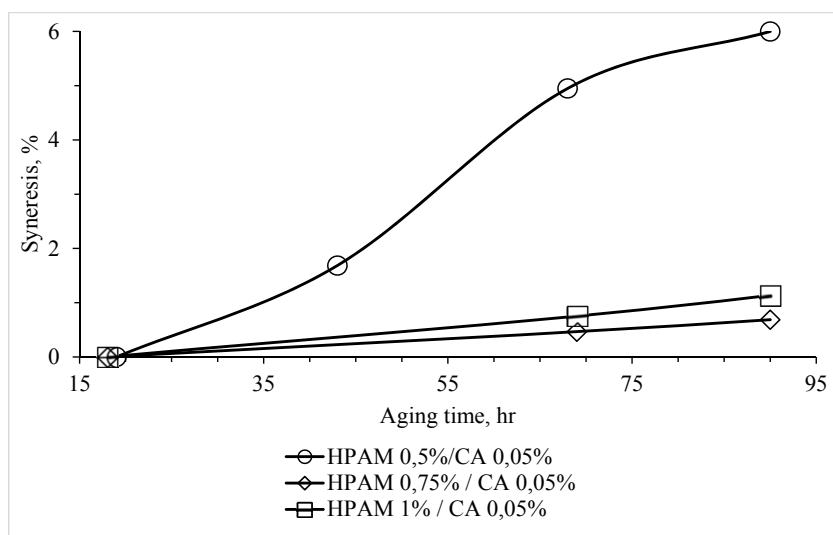


Fig. 6. Syneresis of 0.5–1 wt.% HPAM gels versus polymer/crosslinker concentration and gel aging time. In all samples, crosslinker was added along with the polymer and mixed for 30 min. The gels were aged at 50 °C. Makeup brine – sea water.

From Figs. 5 and 7 it can be seen that the decrease of crosslinker concentration relative to that of polymer provides weak gels. While the increase of polymer concentration relative to that of the crosslinker provides strong gels however water release is eliminated in both cases.

Another valuable observation made in this work is that the gels prepared by complete polymer dissolution in sea and reservoir brines showed very similar water release behavior. However, gels prepared by using distilled water release water a lot faster, see Fig. 8.

Probably, the repulsion between the charged carboxyl groups causes polymer chains to distance from one another. This results in the release of water from the gel structure. However, if ions are present the charges are shielded preventing the repelling be-

tween polymer chains. This may make the gel structure more dense and water release less pronounced.



Fig. 7. Formed gels obtained by combined mixing of polymer (HPAM) and crosslinker during 30 min. Crosslinker concentration 0.05 wt.%. Polymer concentration varies from left to right: 1 – 0.5 wt.%; 2 – 0.75 wt.%; 3 – 1 wt.%.

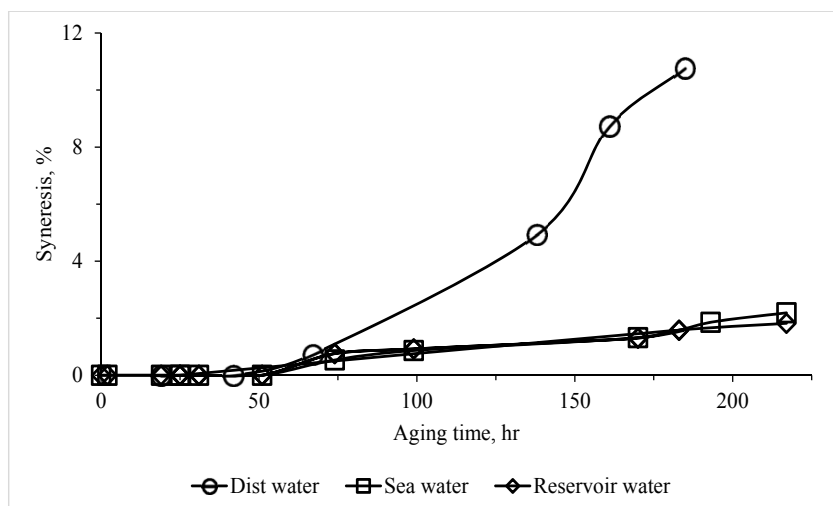


Fig. 8. Water release for different types of gel makeup water.

4. Conclusions

1. Incomplete dissolution of polymer results in gel segregation and significant water release at 50 °C over several days of aging.

2. The decrease of crosslinker/polymer ratio either by the decrease of crosslinker concentration or by the increase of polymer concentration can reduce water release from gels down to 0–1% over 90–185 h of aging at 50 °C.

3. Gels prepared by complete dissolution of polymer in distilled water showed much higher water release than those prepared in sea and reservoir brines. Probably this is due to the repelling between charged polymer chains in distilled water, which is absent if ions are present in water.

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