

# The Effect of Polymer Mixing Time on the Strength of HPAM-Cr(III) Gels

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## Abstract

The dissolution of hydrolyzed polyacrylamide, commonly used in gel treatments for enhanced oil recovery, takes between 2–3 to over 24 h at 20–25 °C. The duration is influenced by factors such as polymer molecular weight and brine salinity. In injection/production wells, gel treatments often involve injecting 50–150 m<sup>3</sup> of polymer solution within 1–2 days, resulting in the injection of partially dissolved polymer. This raises concerns about the stability and strength of gels containing partially dissolved polymer particles. This study demonstrates that when undissolved polymer particles are kept suspended during the gelation process, there is no significant visual distinction between gels obtained from 30 min or 12 h of polymer mixing. Additionally, viscometer measurements reveal that gels formed with shorter polymer mixing times exhibit higher resistance to shearing. This observation supports the concept that undissolved polymer particles act as a composite material, improving the gel strength. This paper does not advocate for the use of partially dissolved polymer gels. Undissolved polymer particles cannot effectively penetrate porous media. Gels containing such particles are primarily suited for addressing fracture conformance issues. Therefore, future research will focus on examining the impact of polymer mixing time on gel syneresis and resistance to washout from fractures.

## 1. Introduction

Polymer gels have found a wide range of applications [1, 2]. In oil industry gel treatments in injection and production wells are conducted with the aim to reduce water cuts and increase oil flow rates. There is a number of documented field cases in which gel treatments were proved to be effective [3].

The success of gel treatments mainly depends on several factors, including reservoir geology [4], oil viscosity [5], reservoir brine salinity, and temperature [6], as well as the salinity of the post-flush water [7], gelation time [8], volume of the injected gelling formulation [9], and the type of polymer and cross-

linker used [10], along with gel stability and strength [11, 12]. These factors have been extensively studied over the last 50–60 years by various researchers.

However, the success of the treatment is also determined by the quality of gelant preparation at the surface. In most cases, polyelectrolyte polymers are used to obtain gel plugs. These high molecular weight substances require a certain time to be fully dissolved in water, usually at least 1–2 h [13]. In fact, the complete dissolution of high molecular weight polymers may require even 12 h [14]. High solvent salinity also prolongs the dissolution time, as shown in the current study.

In surface facilities the polymer mixing time can be regulated by:

1) changing the injection flow rate and/or the volume of mixing vessels;

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2) changing polymer molecular weight and/or charge density;

3) switching to lower salinity water.

Unfortunately, these options are not always available due to the lack of space (offshore projects), technical limitations, and environmental protection concerns. Thus, in some field cases gels may be injected into the reservoir before polymer is fully dissolved in water. This raises up the question of whether the gels obtained from partially dissolved polymer solutions are less strong and stable than those obtained from fully dissolved polymer solutions.

The strength of the gels is critical for permeability reduction in fractures. In fact, many efforts have been dedicated to improve the strength of polymer gels by adding filling materials. For example, it was shown that the elastic modulus of polyacrylamide/polyethyleneimine gels substantially improved with the addition of coal fly ash [15]. In another work the increase of fiber concentration from 0.1 to 0.4 wt.% resulted in the increase of elastic modulus of polymer gel in 3 times [16]. Moreover, the use of polyvinyl alcohol fibers resulted in the reduction of gel syneresis from 30 to 3% during 120 days at 90 °C [17].

In this work the effect of polymer mixing time on the strength of HPAM/Cr(III)-acetate gels was studied.

## 2. Materials and methods

### 2.1. Chemicals and brines

Hydrolyzed polyacrylamides (HPAM) with properties shown in Table 1 were used in this study.

Cr(III)-acetate was added to the polymer solutions to obtain gels by crosslinking polymer molecules with  $\text{Cr}^{+3}$ .

In some tests the gelants were prepared by using Caspian Sea water. However, 1 g/L NaCl brine, 15 g/L brine, 61 g/L reservoir brine, and 70 g/L brine were also used. The chemical composition of sea water and 61 g/L brine can be found in Table 2. 15 g/L brine was prepared by diluting Ayrankol X, a 250 g/L reservoir brine, with distilled water. 70 g/L brine contained 60 g/L NaCl, 5 g/L  $\text{CaCl}_2$  and 5 g/L  $\text{MgCl}_2$ .

**Table 1.** Polymers used in this study.

#	Molecular weight, mln Da	Hydrolysis degree, %
1	6-7	5
2	8	5-10
3	17.2	30
4	18	30

**Table 2.** Chemical composition of sea water and reservoir brine.

Parameter/ Element	Sea water	Reservoir brine
pH	7.7	7.2
Density, g/cm <sup>3</sup>	1.011	1.043
Ca <sup>2+</sup> , mg/L	400.8	3,206.4
Mg <sup>2+</sup> , mg/L	730.6	1,094.4
Na <sup>+</sup> and K <sup>+</sup> , mg/L	4,473.5	18,816.3
Cl <sup>-</sup> , mg/L	7,231.8	37,605.4
SO <sub>4</sub> <sup>2-</sup> , mg/L	3,152.8	80.7
CO <sub>3</sub> <sup>2-</sup> , mg/L	Not detected	Not detected
HCO <sub>3</sub> <sup>-</sup> , mg/L	292.8	341.6
Total salinity, mg/L	16,281.3	61,144.8
Hardness, mg-eq/L	80	250

### 2.2. Preparation of gelants

In this study the gelants were prepared by impeller or magnetic bar agitation at 300–400 rpm and 20–25 °C. After polymer solution preparation Cr(III)-acetate was added and samples were aged at a target temperature. Aging time and temperature are specified in the text for each sample.

### 2.3. Determination of polymer dissolution time, gel strength and stability

The total dissolution time of the polymer in sea water and reservoir brine was determined by Brookfield LVT viscosity measurements during polymer mixing at 6th speed by Velp F203A0161 MICROSTIRRER Magnetic Stirrer. Polymer was thought to be fully dissolved after the viscosity of the solution stopped to increase with the dissolution time.

The experimental work to assess the strength of polymer gels was conducted through the following steps:

1. Determination of complete dissolution time of HPAM (6-7 mln Da, 5% hydrolysis degree) in sea water at the 6th speed of the magnetic stirrer. This involved stirring the polymer solution and measuring viscosity after every 10 min.

2. Preparation of three 0.5 wt.% HPAM (6-7 mln Da, 5% hydrolysis degree) solutions with different polymer mixing times, specifically ~0.4, 0.75, and 1.5 times the complete dissolution time (45, 90, and 180 min).

3. Addition of 0.05 wt.% of Cr(III)-acetate to each solution.

4. Aging of the solutions at 50 °C in an oven for a duration of 4 hr to allow gel formation.

5. Measurement of gel viscosity using an LV2 spindle at room temperature (30–33 °C in this step). The gel strength was evaluated by observing the movement of the Brookfield LVT viscometer indicator position over time during the stirring of the gel sample at the 6th speed using the LV2 spindle. Samples demonstrating faster movement of the viscometer indicator towards the highest limit were considered to exhibit higher strength. For each gel type three measurements were done.

Sydansk Gel Strength Code was used to access the strength of the gel samples [18]. The stability of the samples was determined through visual inspection for the presence of syneresis.

### 3. Results and discussion

Figure 1 demonstrates that the dissolution time required to fully dissolve 6–7 mln Da and 5% hydrolysis degree polymer at a concentration of 0.5 wt.% in sea water and reservoir brine was determined to be equal to 120 and 180 min, respectively. The longer dissolution time of the polymer in reservoir brine is explained by its higher salinity which causes intensive charge shielding and prevents polymer molecules from extending their hydrodynamic radius in the solvent.

In fact, in field conditions the dissolution time of polymer rarely exceeds 30–60 min. This is due to the relatively low volume of the mixing vessels (2 m<sup>3</sup>) and high injection rates (5–15 m<sup>3</sup>/h). Figure 2 shows the so-called fish eyes present in the polymer/

Cr(III)-acetate solution taken from a mixing vessel in field conditions. As can be seen a lot of fish eyes (swollen undissolved polymer particles) are present in the solution. This raises questions on the stability and strength of gels which contain undissolved polymer particles.

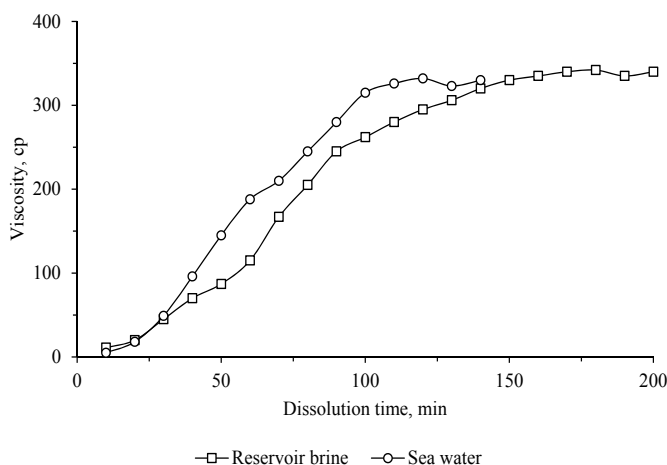
In order to demonstrate the effect of polymer dissolution time on the properties of gels, a number of bottle tests were conducted using polymers with different molecular weights and hydrolysis degrees.

The tests have demonstrated that for 18 mln Da HPAM with high degree of hydrolysis (30%), varying the polymer mixing time from 15 to 180 min in 1 g/L NaCl brine does not yield any significant effects on the strength of the gels after 24 h of aging at 40 °C (Table 3). These gels can be described as weak and flowing.

On the contrary, following just 30 min of mixing in low salinity brine (1 g/L NaCl) and subsequent aging for 24 h at 40 °C, the HPAM with relatively low molecular weight (8 mln Da) and hydrolysis degree (5–10%) produced a stronger gel (Table 3). This gel can be categorized as moderately flowing according to the Sydansk Gel Strength Code [18].

Thus, highly hydrolyzed polymers result in weak gels. This is due to excessive carboxyl groups that lead to intramolecular crosslinking, diminishing gel strength [19].

Surprisingly, when experimenting at a higher temperature (60 °C), it was observed that 30% hydrolysis degree polymer can provide a moderately flowing gel after complete dissolution of the polymer and one day of aging (Table 4). After three days of aging, the strength of the gel increased, resulting in a highly deformable non-flowing gel (Table 4).



**Fig. 1.** Viscosity versus dissolution time for 0.5 wt.% 6–7 mln Da and 5% hydrolysis degree polymer solution prepared by using sea water and reservoir brine at room temperature.



**Fig. 2.** Fish eyes (swollen polymer particles) in the sample taken from a mixing vessel in field conditions.

On the other hand, 5% hydrolysis degree polymer provided a moderately deformable non-flowing gel after complete dissolution and only one day of aging under the same conditions (Table 4).

These observations provide evidence that the gelation process of 30% hydrolysis degree HPAM takes significantly longer compared to that of a polymer with a lower hydrolysis degree. If gel samples are aged at higher temperatures and/or for longer periods, it is possible for 30% hydrolysis degree HPAM to achieve a gel strength close to that of a polymer with a lower hydrolysis degree.

Unfortunately, severe syneresis was observed in 30% hydrolysis degree HPAM gels after a few days of aging. On the other hand, 5% hydrolysis degree HPAM gel did not show any signs of gel syneresis during 7 days of aging at the same temperature (Table 4).

Based on these results, 6–7 mln Da and low hydrolysis degree polymers were selected for the subsequent experiments due to their higher gel strength and better stability over time. These properties are advantageous for permeability reduction in fractures. The potential concerns regarding the insufficient stability of polymer gels with relatively low molecular weight (6–7 mln Da) in core flooding can be alleviated based on the findings presented in reference [20]. In this study, the water permeability of a sand pack was remarkably reduced by a factor of 9,640–254,762 through the treatment of the model with a 7 mln Da HPAM gelant.

Various quantities of crosslinker were introduced into solutions of the polymer with molecular weight of 6–7 mln Da and hydrolysis degree of 5%, which had been mixed for 30 min or 12 h in 15 g/L brine. The samples mixed for 30 min contained a significant number of fish eyes. In order to prevent the settling of these fish eyes, some samples were periodically agitated during the initial 3–4 h of aging until the viscosity reached a level that impeded their separation.

**Table 3.** The strength of gels versus polymer type and mixing time.

Polymer type	Gel recipe	Polymer mixing time, min	Gel strength code
18 mln Da and 30% hydrolysis degree HPAM	0.5 wt.% Polymer / 0.05 wt.% Cr(III)-acetate	15	C
		30	B
		100	B
		180	B
8 mln Da and 5–10% hydrolysis degree HPAM	0.5 wt.% Polymer / 0.05 wt.% Cr(III)-acetate	30	D

**Table 4.** The strength of different HPAM gels prepared in 70 g/L brine and aged at 60 °C.

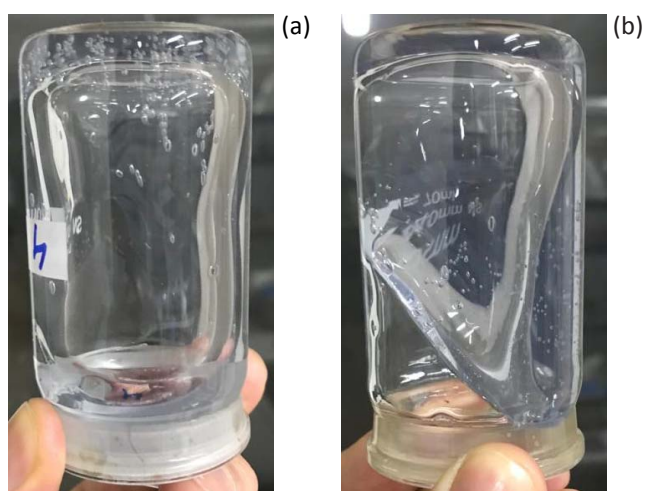
Polymer type	Gel recipe	Aging time at 60 °C, days			
		1	3	4	7
17.2 mln Da, 30% hydrolysis degree	0.5 wt.% Polymer / 0.05 wt.% Cr(III)-acetate gel	D	F	~ 10% syneresis	> 10% syneresis
6–7 mln Da, 5% hydrolysis degree	0.5 wt.% Polymer / 0.05 wt.% Cr(III)-acetate	G	G	G	G

**Table 5.** The strength of gels prepared by partial and complete dissolution of the polymer.

Polymer type	Gel recipe	Partial dissolution – 30 min mixing	Complete dissolution – 12 h mixing
HPAM – 6-7 mln Da, 5% hydrolysis degree	0.5 wt.% HPAM / 0.025 wt.% Cr(III)-acetate	D	D
	0.5 wt.% HPAM / 0.05 wt.% Cr(III)-acetate	D	D

Table 5 illustrates a comparison between gel samples resulting from polymer mixing for 30 min and 12 h, followed by 24 h aging process at 50 °C. Through visual assessment, it became apparent that in cases where the polymer particles were uniformly suspended within the solution, no noteworthy distinction was discernible between the gel samples obtained from 30 min or 12 h of polymer mixing. Furthermore, decreasing the concentration of Cr(III)-acetate from 0.05 to 0.025 wt.% did not exhibit a significant impact on the strength of the gels (Table 5).

An important observation is that if the polymer is not fully dissolved in brine, different results can be obtained depending on whether the samples are periodically agitated to keep the polymer particles suspended or just aged under static conditions. As shown in Fig. 3, the sample (a) exhibits a distinct separation, where a portion forms a weak gel that flows to the beaker cap upon inversion, while another portion forms a strong, non-flowing gel. This separation is attributed to the settling of undissolved polymer particles (fish eyes). Conversely, the sample (b) results in a more homogeneous gel.



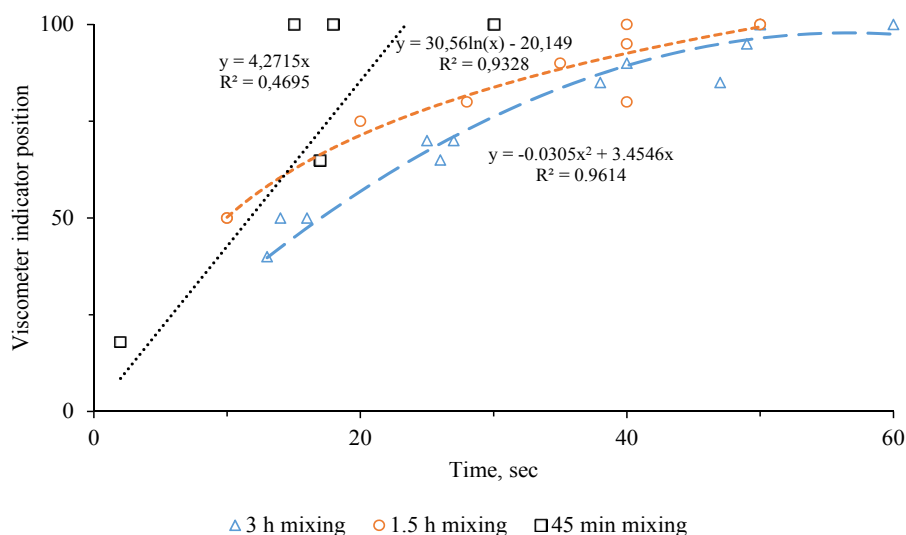
**Fig. 3.** 0.5 wt.% HPAM/0.05 wt.% Cr(III)-acetate polymer gels in 15 g/L brine aged at static (a) or dynamic (b) conditions for 24 h at 50 °C. Polymer mixing time – 30 min. HPAM – 6-7 mln Da, 5% hydrolysis degree. Brine – Ayrankol X brine diluted to 15 g/L.

Even though the gels presented in Table 5 appear to possess similar strength, it is worth noting that the presence of undissolved polymer gel particles could potentially exhibit composite material behavior and enhance the overall strength of the gel.

To validate this assumption, the resistance of 0.5 wt.% HPAM/0.05 wt.% Cr(III)-acetate gels against stirring was assessed using Brookfield LVT viscometer equipped with LV2 spindle, as previously described. As depicted in Fig. 4, the most rapid increase in the position of the viscometer indicator was observed during the stirring of the gel sample, which resulted from a polymer mixing duration of only 45 min (approximately 0.4 times the complete dissolution time). Consequently, this particular gel exhibited the highest strength in comparison to those derived from longer polymer mixing periods. Remarkably, the strength of the gel achieved through 90-min polymer mixing duration (equivalent to 0.75 times the complete dissolution time) surpassed that of the gel obtained by mixing the polymer for 180 min (1.5 times the complete dissolution time). This observation supports the idea that undissolved polymer gel particles behave like composite materials and enhance the strength of the gel.

On average, 200 m<sup>3</sup> of polymer gelant is injected into a well. If the mixing vessels are composed of three sections, each with a volume of 2 m<sup>3</sup> (for a total volume of 6 m<sup>3</sup>), the injection flow rate of 2 m<sup>3</sup>/h will roughly correspond to a dissolution time of 3 h. Reducing the dissolution time from 3 h to 45 min will allow for a fourfold increase in the injection flow rate (up to 8 m<sup>3</sup>/h). Taking into account the well shut-in time of 24 h, the total treatment time can be reduced from 124 h to 49 h (a 2.5-fold reduction).

It should be noted that undissolved polymer particles cannot effectively penetrate porous media. Gelants containing such particles can only be applied to address fracture conformance issues. As part of future research, core flooding experiments should be conducted to investigate the impact of polymer mixing time on the resistance of gels against wash-out from fractures.



**Fig. 4.** Brookfield LVT viscometer indicator position change over time during the stirring of 0.5 wt.% HPAM/0.05 wt.% Cr(III)-acetate gels, prepared by mixing polymer for different periods of time, with LV2 spindle at 6<sup>th</sup> speed and 30-33 °C. HPAM – 6-7 mln Da, 5% hydrolysis degree. Brine – sea water. Gels were aged for 4 h at 50 °C.

#### 4. Conclusions

High hydrolysis degree (30%) and molecular weight (18 mln Da) polyacrylamide gels are not recommended for gel treatments in injection and production wells.

Gels composed of polyacrylamide with a lower hydrolysis degree (5%) and molecular weight (6-7 mln Da) are more favorable due to their quicker gelation process, higher gel strength and stability.

Incomplete dissolution of the polymer has no noticeable negative effect on gel strength, provided that the fish eyes are kept suspended throughout the gelation process.

Viscosity measurements support the idea that partially dissolved polymer particles behave like a composite material and improve the gel strength.

Reducing the dissolution time from 3 h to 45 min will result in a 2.5-fold reduction in treatment time.

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Samples shown in Table 4 were prepared by students Abeldinova Zh. and Arstanova K., who assisted me in the laboratory work.

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