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RESEARCH PAPER

The Comparison of Three Metallic, Organic, and Polymeric Crosslinked HPAM Gels for Water Conformance Applications

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Abstract

Unwanted production of water in oil and gas reservoirs due to water coning is one of the headaches of the petroleum industry. Despite mechanical methods, some chemicals are also developed to delay or prevent this problem. Polymer gels have been proved to be a reliable and economical solution for water production. In this paper, we present a summary of tests for three different gel systems for a pre-determined reservoir condition. A metallic crosslinker (Chromium(III) Acetate), a polymeric crosslinker (Polyethylenimine), and an organic crosslinker mixture (Hexamethyleneteramine + Hydroquinone) are used for crosslinking HPAM polymer. The tests are performed for different concentrations of polymer and cross-linker. Gel strength and stability of these polymer gels are recorded over six weeks. The apparent viscosity of these gels is recoded and compared. The impact of salinity on gel strength and stability is also investigated. The results show that for the determined reservoir conditions HPAM-Chromium(III) Acetate and HPAM-Hexamethyleneteramine-Hydroquinone gels could form a stable and rigid barrier against water.

Keywords:
Coning,
Cross Linker,
HPAM,
Polymer,
Water Shutoff

Introduction

In the petroleum industry, “produced water” is referred to as the water that may accompany extracted hydrocarbons from the wellbore. Water production is an undesirable phenomenon that imposes extra costs of water separation, treatment, and disposal on oil companies. According to Bailey et al., on a worldwide average, for each barrel of produced oil, three barrels of water are produced [1]. This number could be as high as 20 barrels of water per one barrel of oil [2]. It is estimated that 21.2 billion barrels of water in the US alone were produced in oil and gas fields in 2012. In this year, the US national average water-to-oil ratio and the water-to-gas ratio has been 10 barrels of water for every barrel of oil, and 100-200 barrels of water for every million cubic feet of natural gas [3]. Depending on the location of the field and the method of disposal, handling of produced water could cost between 5 cents to 20 dollars per barrel of water [1, 4].

Water production occurs in both conventional and unconventional reservoirs. It usually intensifies as the reservoir reaches the latter stages of depletion. In general, there are several

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causes for water production from wells [1]. These causes are listed below and are illustrated in Fig. 1.

1) Leakage from casing, tubing and/or packer (Fig. 1a)
2) Poor cement job (Fig. 1b)
3) Rising of water-oil contact in formations with very low vertical permeability (Fig. 1c)
4) Water coning in formations with moderately high vertical permeability (Fig. 1d)
5) Faults and fractures between water layer and perforations in vertical wells (Fig. 1e) or horizontal wells (Fig. 1f)
6) [in water flooding] Water bypassing from injector wells to producer wells through faults and fractures (Fig. 1g)
7) [in water flooding] Non-uniform sweeping due to permeability anisotropy (Fig. 1h)
8) [in water flooding] Water under-run due to gravity segregation in thick reservoirs with high vertical permeability (Fig. 1i)

Water cross-flow in highly permeable layers without flow barriers (Fig. 1j)

The application of polymer gels to prevent water production has become globally widespread in recent decades. In some instances, the polymer gel is injected through water flooding injection wells either for “profile modification” or for “in-depth fluid diversion”. These two techniques, despite some similarities, are quite different. In profile modification, the main objective is to cover the zones of high permeability in a maximum radius of a few hundred feet from the wellbore. The purpose of in-depth fluid diversion, however, is to reduce unswept areas that are located well-deep in the reservoir by injecting massive amounts of polymer gel.

The main focus of this research would be on how to prevent or delay water coning near production wells, by applying polymer gels. Water coning usually takes place in reservoirs with moderately high vertical permeability. In horizontal wells, this phenomenon is sometimes called cusping. If the distance of water-oil contact and perforations is short, this phenomenon could happen in a matter of months or even weeks. One obvious solution for preventing coning in these reservoirs is to reduce the production rate beneath its critical coning rate. However, this solution is not applicable in many cases since the critical coning rate is usually too small to be economically justified. Other solutions include cement injection or re-locating perforations. Another method for mitigating water production problems is to inject polymers, hydrogels, and gel polymers in near-well areas. This method has been applied since a few decades ago but in recent years it has been vastly modified.

In 1967, Sandyford patented the idea of using water-soluble polyacrylamide for water control in oil and gas wells [5]. Until 1973, polymer injection was performed in more than 200 wells, most of which experienced a 60% – 90% reduction in the water-oil ratio [6]. In 1974, Thachuk and Tharkur [7] used numerical simulation to depict the effectiveness of polymer injection in reducing water production in wellbores with coning problems. The injected polymer was usually either polyacrylamide (PAM) or hydrolyzed polyacrylamide (HPAM). During the hydrolysis process, some amide groups of polyacrylamide are replaced with carboxyl groups (Fig. 2). Since both amide and carboxyl groups are polar they are highly soluble in water. They also easily adhere to sandstone and carbonate surfaces [6].

Polymer gels are comprised of two main components; a polymer with high molecular weight, and a crosslinker. Besides PAM, other synthetic polymers such as polyvinyl alcohol (PVA), polyvinyl amine (PVAm), polyacrylonitrile (PAN), and biopolymers like starch, xanthan gum, guar gum, lignin, and cellulose are employed in the oil and gas industry.

The crosslinker bridges the polymer chains together via covalent or ionic bonds. By crosslinking, the gel system attains a 3-dimensional structure that acts rigid-like at the macroscopic level while retains its liquid-like behavior at the microscopic level. As a result, the mechanical properties of the gel are modified. De Aguiar et al. (2020) reviewed several types of research performed on the application of in-situ polymer hydrogels for water shutoff in oil reservoirs [8]. In another review paper, Zhu et al. summarized polymer water conformance gel applications for high-temperature reservoirs [9]. Recently, different crosslinkers were investigated in various reservoir conditions [10-13].

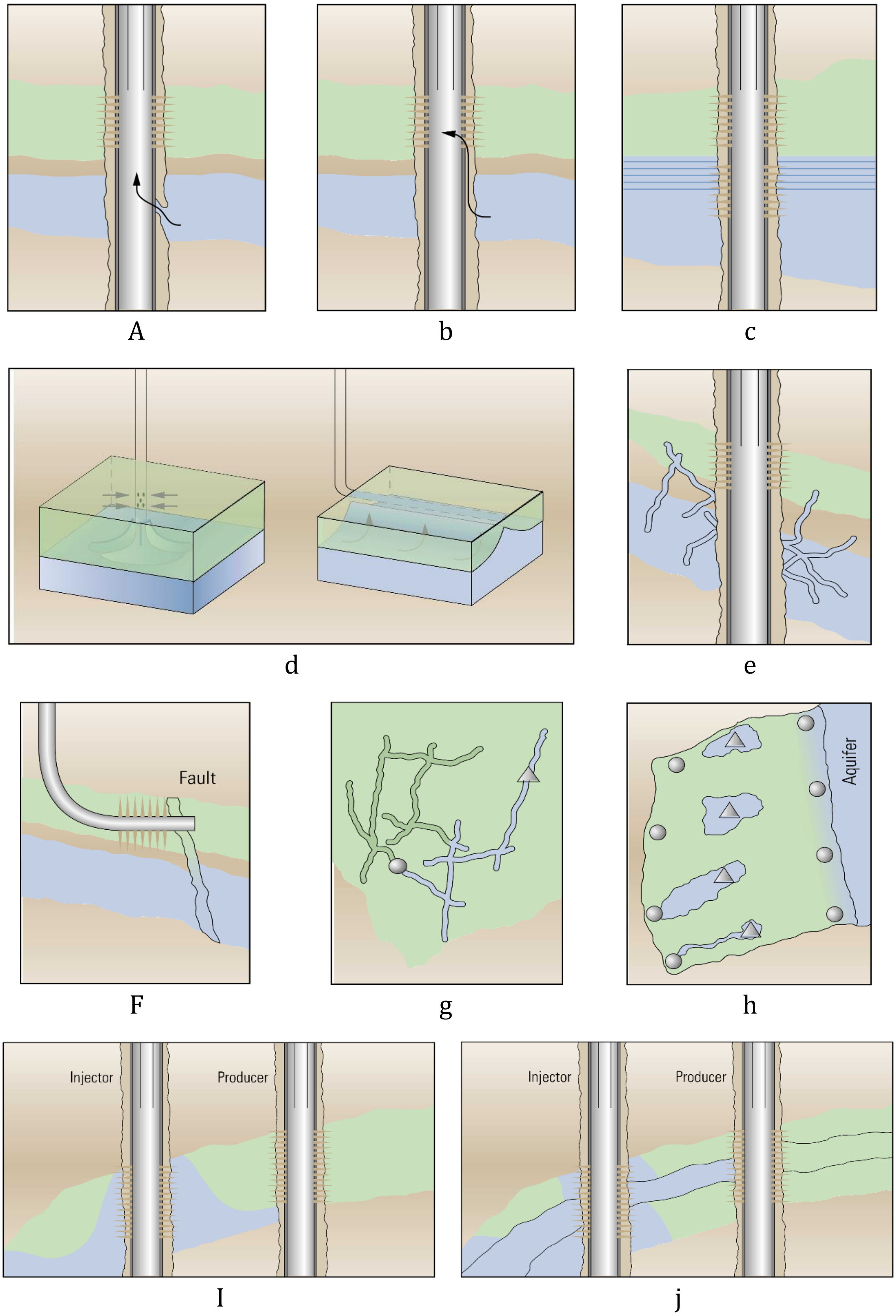
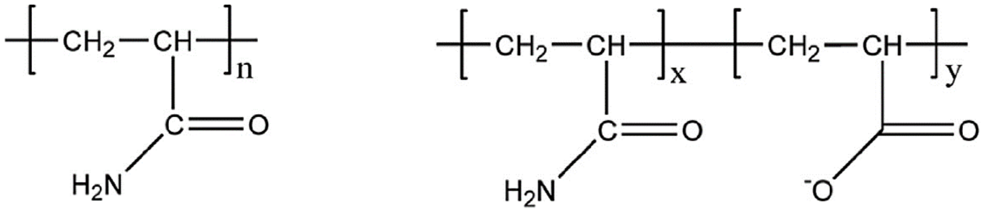


Fig. 1. Causes of water production in wells [1]



Polyacrylamide (PAM) Partially Hydrolyzed Polyacrylamide (HPAM)

Fig. 2. Molecular structure of PAM and HPAM

Metallic Cross-linked HPAM

Unlike electrically neutral polyacrylamide, hydrolyzed polyacrylamide has a negative charge. Therefore HPAM tends to form an ionic bond with multivalent cations [14]. Aluminum sulfate was one of the first cross linkers to be employed for conformance control by the oil industry. However, this gel system was proved to be highly sensitive to pH and therefore, hard to control. Another gel system is based on using Cr (VI) as the crosslinking agent. This system has an extended gelation time in low-temperature reservoirs but a relatively short gelation time in high-temperature reservoirs. Being classified as a carcinogenic agent and also susceptibility to H_2S are two major downsides of this crosslinker. In 1987, Sydansk & Argabright patented a new polymer gel based on HPAM as base polymer and Chromium (III) Acetate as crosslinker [15-18]. They studied the gelation of polyacrylamide (PA) and HPAM with varying amounts of the polymer-cross linker ratios. They used a bottle qualitative test to rank gel strength with time. In addition to Cr(III), other multivalent ions, such as Al(III), Zr(III), Ti(III), and Fe(III) are used as metallic crosslinkers. Dai et al. investigated the effectiveness of Zirconium Acetate crosslinkers with a high molecular weight HPAM (MW=1.0×106 g/mol) in low-temperature shut-off conditions.

Organic Cross-linked HPAM

To better control the gelation time of polymer gels, especially in high temperature/high salinity/high pH conditions or in sour environments, several organically cross-linked polymers are designed and tested in the field. These crosslinkers may also have fewer adverse environmental impacts compared to metallic crosslinkers. Two main groups of organic crosslinkers are aldehydes (formaldehyde, paraformaldehyde, hexamethylenetetramine, …) and phenols (phenol, hydroquinone, resorcinol, …). Jia et al. reported successful use of resorcinol/phenol-formaldehyde as a crosslinker for polymer gels in high temperature and high TDS conditions [19].

In this paper, for the first time, the performance of three polymer gels for a certain reservoir condition is compared. For this, a metallic crosslinker (Chromium (III) Acetate), an organic crosslinker (Hexamethylenetetramine + Hydroquinone), and a polymeric crosslinker (Polyethylenimine) are used. The effect of polymer and crosslinker concentrations as well as total dissolved solids on gel strength and stability is investigated

Gel Strength Measurement

To measure gel strength at different stages of the investigation, two methods were used. In the quantitative method, the apparent viscosity of gel was measured using a FANN35-type viscometer. In the qualitative method, the gel strength code proposed by Sydnak and Argabright (Marathon Oil Company) was used [17]. In Table 1 the description of each code is presented. Fig. 3 demonstrates the visual guide for this code.

Table 1. Qualitative code system for gel strength [17]

Code	Description
A	No detectable gel formed: the gel appears to have the same viscosity as the original polymer solution.
B	Highly flowing gel: the gel appears to be only slightly more viscous than the initial polymer solution.
C	Flowing gel: most of the gel flows to the bottle cap by gravity upon inversion.
D	Moderately flowing gel: only a small portion (5-10%) of the gel does not readily flow to the bottle cap by gravity upon inversion (usually characterized as a tonguing gel).
E	Barely flowing gel: the gel can barely flow to the bottle cap and/or a significant portion (>15%) of the gel does not flow by gravity upon inversion.
F	Highly deformable non-flowing gel: the gel does not flow to the bottle cap by gravity upon inversion.
G	Moderately deformable non-flowing gel: the gel deforms about halfway down the bottle by gravity upon inversion.
H	Slightly deformable non-flowing gel: only the gel surface slightly deforms by gravity upon inversion.
I	Rigid gel: there is no gel surface deformation by gravity upon inversion.
J	Ringing rigid gel: a tuning fork-like mechanical vibration can be felt upon tapping the bottle.

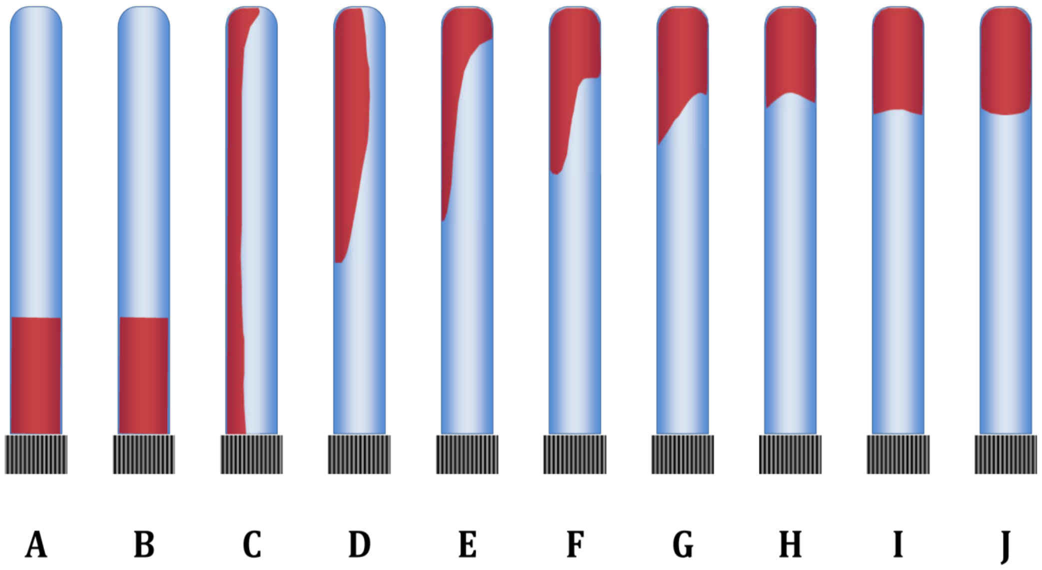


Fig. 3. Gel strength code

Materials

Partially hydrolyzed polyacrylamide (HPAM) with an average molecular weight of 5.0×10^6 and a hydrolysis degree of 18% was supplied by BDH, UK. Branched Polyethylenimine (PEI) solution with an average molecular weight of 2.5×10^4 was obtained from Sigma-Aldrich. Chromium (III) Acetate powder was purchased from Carla Erba, Spain. Resorcinol, Hexamethylenetetramine, and salts were provided by Sigma-Aldrich.

Methods

Three different polymer gels were prepared as follows:

1) HPAM + Chromium (III) Acetate

The pre-determined concentration of HPAM powder was diluted in water under constant stirring by a mechanical stirrer. After 30 minutes Chromium (III) Acetate was added and the solution was mixed for another 30 minutes at a high RPM of about 1000. The solution was heated at reservoir temperature (55 °C/131 °F). The concentration of polymer was 0.5%, 1%, and 1.5%. The concentration of crosslinker was 0.05%, 0.1%, and 0.2%.

2) HPAM + Polyethylenimine

HPAM powder was diluted in water under constant stirring by a mechanical stirrer for 30 minutes. The same procedure was repeated for PEI in another container. HPAM and PEI solutions were mixed for another 30 minutes under high RPM (>1000). The solution was heated at reservoir temperature (55 °C/131 °F). The concentration of HPAM was 0.5%, 1%, and 1.5%. The concentration of PEI was 0.1%, 0.25%, and 0.5%.

3) HPAM + Hexamethylenetetramine + Hydroquinone

HPAM powder was diluted in water under constant stirring by a mechanical stirrer for 30 minutes. The specific amount of Hydroquinone and HMTA was added to the solution and were mixed for another 60 minutes under high RPM (>1000). The solution was heated at reservoir temperature (55 °C or 131 °F). The concentration of HPAM was 0.5%, 1%, and 1.5%. Two different sets of concentration of HMTA and Hydroquinone were tried: {0.1% HMTA and 0.1% Hydroquinone}, and (0.5% HMTA and 0.25% Hydroquinone).

To test the effect of salinity on the performance of gel, synthetic brines with the total dissolved solids (TDS) of 10,000, 20,000, and 30,000 mg/L were prepared. The TDS of all brines were consisted of 85% NaCl, 10% $CaCl_2$, and 5% $MgCl_2$. In all other tests, the TDS of 10,000 mg/L was used.

Using a FANN35-type viscometer the viscosity of gels was initially measured. Then, for evaluating the strength and stability of gels, the gel code system was employed (Table 1 and Fig. 3).

Results and discussion

Nine different HPAM-Chromium(III) Acetate gels (Fig. 4) were prepared with three concentrations of polymer and three concentrations of crosslinker. The qualitative measurement of gel strength reveals that in general increasing the weight percentage of both polyacrylamide and chromium (III) acetate results in gelling rate and also more final rigid gels (Table 2). However, there seems to be an optimum range for the ratio of polymer to crosslinker. In our tests, this ratio varied between 1:30 to 1:2.5. The results show that for the ratio of 1:15 to 1:5 the best results are archived. Fewer ratios of crosslinker to polymer resulted in very weak gels. That could be interpreted that not enough bonds were made to form a 3-dimensional polymer network. Also, too much crosslinker in the gel system appears to only slightly improve the results. The best results in these tests were achieved with 1.5% HPAM and 0.1% and 0.2% chromium (III) acetate. Both mixtures showed the final gel strength of code I (rigid gel). However, the gel with more crosslinker is not necessarily a better choice since its gelation time may not be sufficient for injection in field.

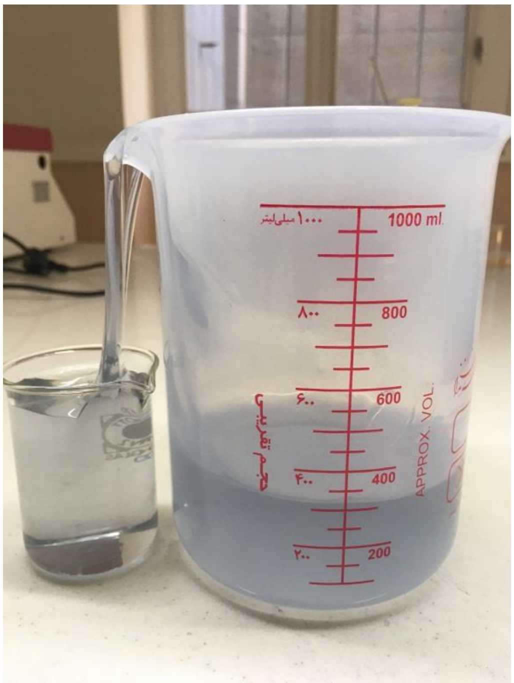


Fig. 4. HPAM-Chromium(III) Acetate gel

Table 2. Gel strength variation concerning time for HPAM-Chromium(III) Acetate gels

Concentration		**Gel Age (days)**																			
HPAM	CL*	0	½	1	2	3	4	5	6	7	8	9	10	11	12	13	14	21	28	35	42
0.5%	0.05%	A	A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	-**	-	-	-
	0.1%	A	A	A	B	B	B	B	B	B	B	B	C	C	C	C	C	C	C	B	-
	0.2%	A	A	B	B	B	B	B	B	C	C	C	C	C	C	C	C	C	C	-	-
1%	0.05%	A	A	A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	-	-	-
	0.1%	A	A	B	B	B	B	B	C	C	C	C	D	D	D	E	E	F	G	G	H
	0.2%	A	B	B	B	B	B	C	C	C	D	D	D	D	D	E	F	G	G	G	G
1.5%	0.05%	A	B	B	B	B	B	B	B	B	B	C	C	C	B	-	-	-	-	-	-
	0.1%	A	B	B	C	C	C	D	D	D	D	E	E	E	F	G	G	H	I	I	I
	0.2%	A	C	C	C	D	D	D	D	E	E	F	G	G	G	H	I	I	I	I	I

* Chromium(III) Acetate

** The cells without numbers denote gels that became two-phase, dehydrated or deformed

In Table 3 the qualitative measurements of nine different HPAM-Polyethylenimine gels (three concentrations of polymer and three concentrations of crosslinker) are presented. The results show that similar to HPAM-chromium (III) acetate gels, increasing the weight percentage of both polyacrylamide and Polyethylenimine increases the gelation rate and stability of gels. The most adequate gels are obtained with the ratio of polymer to crosslinker between 1:6 to 1:2. . In our tests the final gel strength of HPAM-PEI gels after six weeks was code G which is correspondent to “moderately deformable non-flowing gel”. This slow gelation rate may be desirable for profile modification and in-depth fluid diversion in waterflooding operations. However, for water shutoff purposes this may be translated to insufficient stability and slow-acting barrier-forming against water coning. Though it should be noted that under different circumstances (reservoir temperature, TDS, pH, …) the HPAM-PEI might be a good selection, especially considering its less environmental footprint.

Fig. 5. Qualitative measurement of gel strength

Table 3. Gel strength variation concerning time for HPAM-Polyethylenimine gels

Concentration		**Gel Age (days)**																			
HPAM	CL*	0	½	1	2	3	4	5	6	7	8	9	10	11	12	13	14	21	28	35	42
0.5%	0.1%	A	A	A	A	A	A	A	A	A	A	-**	-	-	-	-	-	-	-	-	-
	0.25%	A	A	A	A	B	B	B	B	B	B	B	B	C	C	C	B	-	-	-	-
	0.5%	A	A	B	B	B	B	B	B	C	C	C	C	C	D	D	D	D	-	-	-
1%	0.1%	A	A	A	A	A	A	A	B	B	B	B	B	B	B	B	B	B	B	-	-
	0.25%	A	B	B	B	C	C	C	C	D	D	D	E	E	E	E	E	F	F	F	F
	0.5%	A	B	B	C	C	D	D	D	D	E	E	E	E	E	F	F	G	G	G	G
1.5%	0.1%	A	A	A	A	A	A	A	B	B	B	B	B	B	A	A	-	-	-	-	-
	0.25%	A	B	B	C	C	C	D	D	D	D	E	E	E	F	F	F	G	G	G	G
	0.5%	A	B	C	C	D	D	D	D	E	E	F	F	F	G	G	G	G	G	G	G

* Polyethylenimine

** The cells without numbers denote gels that became two-phase, dehydrated or deformed

Table 4 summarizes the results of gel strength codes for six different HPAM-Hexamethylenetetramine-Hydroquinone gels (three concentrations of polymer and two sets of concentrations of crosslinkers). It could be inferred from the results that increasing polymer concentration from 0.5% to 1% drastically improves the gel behavior but further increasing it to 1.5% does not greatly change the results. Also, it could be seen that gels with low concentrations of HMTA and Hydroquinone are very weak and unstable. The weight ratio of water: HPAM:HTMA: Hydroquinone equal to 100:1:0.5:0.25 presents a gel with good gelation rate and stability.

Table 4. Gel strength variation with respect to time for HPAM-Hexamethylenetetramine-Hydroquinone gels

Concentration		**Gel Age (days)**																			
HPAM	(CL1,CL2)*	0	½	1	2	3	4	5	6	7	8	9	10	11	12	13	14	21	28	35	42
0.5%	(0.1,0.1)%	A	A	A	A	-**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	(0.5,0.25)%	A	A	B	B	B	C	B	C	C	C	C	C	D	D	D	D	-	-	-	-
1%	(0.1,0.1)%	A	A	A	A	A	B	B	B	B	B	B	-	-	-	-	-	-	-	-	-
	(0.5,0.25)%	A	B	C	C	C	D	D	E	E	E	E	F	F	F	F	F	G	H	H	I
1.5%	(0.1,0.1)%	A	A	A	B	B	B	B	B	B	-	-	-	-	-	-	-	-	-	-	-
	(0.5,0.25)%	A	C	C	D	D	D	E	E	F	F	G	G	G	G	G	G	H	H	I	I

* (Hexamethylenetetramine, Hydroquinone)

** The cells without numbers denote gels that became two-phase, dehydrated or deformed

The comparison between the three examined gel systems shows that for the pre-described conditions of these experiments, the HPAM-Cr(III) Acetate gel and HPAM-HTMA-Hydroquinone reached the rigid gel state. The gel containing 0.2% Cr(III) acetate and 1.5% HPAM attained rigid state after 14 days while the gel containing 0.5% HMTA, 0.25% Hydroquinone and 1.5% HPAM attained rigid state after 35 days. The selection among these two gels may well depend on reservoir/well conditions.

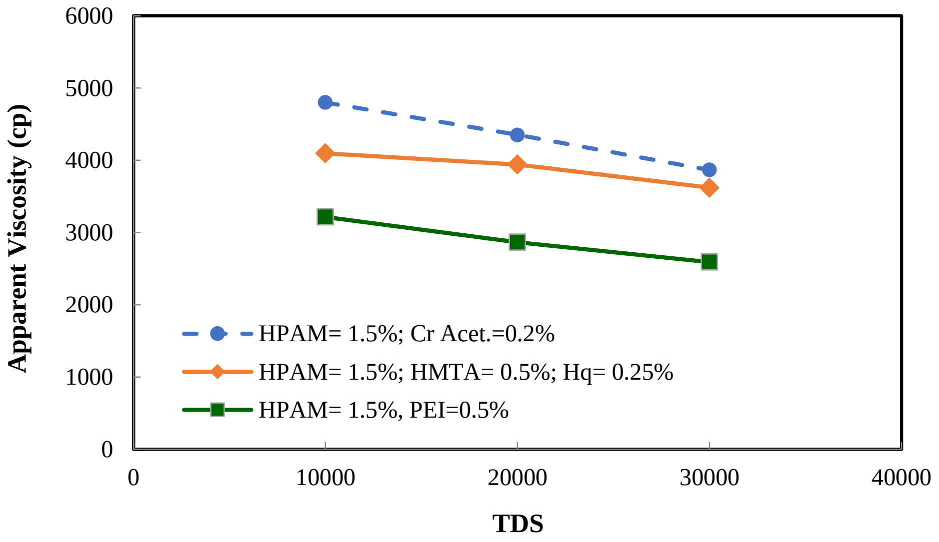


Fig. 6. Qualitative measurement of gel strength

The effect of salinity on the apparent viscosity of gels is also tested and presented in Fig. 6. For this purpose, of each gel system one composition is selected. Using the viscometer, the apparent viscosity of gels at different salinities is measured. It could be observed that the viscosity highly depends on TDS. The more the salinity, the less the viscosity of the polymer gel would be. The main reason for this is the shielding of amide groups by sodium hence the masking of the cross-linking sites and shrinkage of the polymer chains. Because of their lower charge density, potassium ions could also delay the gelation, but to a less degree compared to sodium ions [20].

Conclusion

In this paper (to the best of our knowledge, for the first time in available literature) one metallic polymer gel and two organic polymer gels are compared for certain reservoir conditions. Different concentrations of polyacrylamide and crosslinkers are investigated.

- The strength of gel increase with increasing polymer and crosslinker concentrations. But there seems to be a limit over which increasing the concentrations may adversely affect the gelation behavior.
- There is an optimum ratio of polymer to crosslinker concentration. Below this ratio, the three-dimensional structure of gel is not completely formed. Above this ratio, not much change in strength and stability of gel could be detected.
- HPAM-Chromium(III) Acetate and HPAM-HMTA-Hydroquinone gels showed suitable stability and rigid state during the test period for reservoir conditions.
- The rate of gelation for HPAM-Polyethylenimine gel was too slow for water shut-off purposes. However, this prolonged gel formation could be quite useful in profile modification and in-depth fluid diversion in water flooding.

Salinity delays gel formation for all three gel systems. As a result, it could be a parameter by which the gelation time could be controlled.

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