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A rheological investigation of a high temperature organic gel used for water shut-off treatments

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Abstract

Polyacrylamide-based gels are used in many water shut-off treatments. In this study, a copolymer of polyacrylamide/*tert*-butyl acrylate is cross-linked with polyethyleneimine. The kinetics parameters of the gelation reactions were determined using steady shear viscometry at temperatures of 80 to 130 °C.

The addition of salts to the mixing water was found to increase the gelation time. On the other hand, higher polymer and cross-linker concentrations reduced the gelation time. The activation energy was found to be 118 kJ/mol in distilled water and decreased to 93 kJ/mol in seawater. The reaction orders were found to be first order with respect to both PATBA and PEI. The effects of initial pH and contamination with iron(III) on the gelation time were also examined in detail. Recommendations for field application of this gelling system are given.

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Keywords: Polyacrylamide-based gels; Organic cross-linkers; Gelation kinetics

1. Introduction

As oil and gas reservoirs mature, water production increases. The cost of lifting, separating, treating and disposing produced water is high. Moreover, problems such as scale, corrosion, emulsion, bacteria, and sand production can arise as a result of excessive water production. It is estimated that for each barrel of oil produced worldwide, an average of three barrels of water are produced. Disposing off the produced water costs \$40 billion

every year (Bailey et al., 2000) and, therefore, it is essential to minimize water production.

Several techniques are available for water shut-off including mechanical and chemical means. The choice of a specific method to reduce water production depends on the candidate well. Chemical means, including gelling polymers are cost effective as they do not necessarily require a workover rig and they control water production for a longer period of time. In addition, the gelling solution can be placed deep into the reservoir by controlling the gelation time (Hutchins et al., 1996).

Water-soluble polymers such as polyacrylamides and polysaccharides have been used as means for improved oil recovery since the 1950s (Prud'homme et al., 1983). These polymers are cross-linked to form three dimensional structures. For polyacrylamide-based gels, the

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46 cross-linker can be either metallic or organic. In metallic
47 cross-linking, the carboxylate groups of the polymer chain
48 react with multivalent cations forming ionic bonds.
49 Chromium is the most commonly used metallic cross-
50 linker. The chromium cross-linkers, especially those
51 based on Cr^{+6} (Lockhart, 1991), are toxic and do not
52 meet the current environmental regulations. Moreover, the
53 ionic bonds are unstable at temperatures greater than
54 70 °C (Moradi-Araghi, 2000). Another concern with in-
55 organic cross-linkers is their short gelation times at
56 temperatures greater than 60 °C (Albonico et al., 1994;
57 Lockhart, 1994). At temperatures greater than 100 °C,
58 polyacrylamide-based polymers exhibit hydrolysis and
59 oxidative degradation of the polymer chains (Moradi-
60 Araghi and Doe, 1987). Also, at temperatures greater than
61 75 °C, and in the presence of multivalent cations, over
62 cross-linking occurs, which results in expulsion of water
63 out of the gel structure, known as syneresis (Moradi-
64 Araghi and Doe, 1984).

65 Organically cross-linked gels (OCP) are known to
66 have good stability at elevated temperatures. This is at-
67 tributed to the covalent bonds between the polymer and
68 the organic cross-linker (Moradi-Araghi, 2000). There are
69 several organically cross-linked gels reported in the liter-
70 ature such as phenol and formaldehyde (Moradi-Araghi,
71 1994). These gels were reported to be stable at temper-
72 atures up to 150 °C (Moradi-Araghi et al., 1993). How-
73 ever, phenol and formaldehyde are not environmentally
74 friendly (Moradi-Araghi, 1994). One way to overcome
75 this problem is to use precursors of phenol and formal-
76 dehyde such as phenyl acetate and hexamethylenetetra-
77 mine (HMTA) that thermally hydrolyze in-situ forming
78 phenol and formaldehyde, respectively.

79 A copolymer of acrylamide and *tert*-butyl acrylate
80 (PAtBA) cross-linked with polyethyleneimine (PEI) was
81 reported to be stable at high temperatures (Hardy et al.,
82 1998, 1999). Due to the high temperatures encountered in
83 some local oil and gas reservoirs, the PAtBA/PEI system
84 was investigated in this study. The PEI cross-linker has a
85 low toxicity and was approved for food contact in the
86 USA (Reddy et al., 2003).

87 Several researchers examined the propagation and
88 ability of this gel system to reduce permeability of reser-
89 voir cores (Hardy et al., 1998; Hoek et al., 2001; Alqam
90 et al., 2001; Okasha et al., 2001; Zitha et al., 2002;
91 Vasquez et al., 2003). The gel strength of this system in
92 bulk was also reported (Al-Muntasheri et al., 2007a).
93 Hardy et al. (1999) and Polo et al. (2004) reported field
94 applications of this gelling system in the North Sea and
95 south of Mexico, respectively.

96 A successful water shut-off treatment requires careful
97 examination of key factors that affect the gelation time

and a thorough examination of compatibility between
the gelling solution and reservoir fluids. Temperature is
a key parameter that determines the gelation time. The
gelation time at reservoir temperature is needed to find-
out how deep the gel can be placed in the formation and
how long the shut-in time should be. At room temper-
ature, the viscosity of the gelling solution increased over
a period of several days, but no strong gel was noted. It
is clear from this result that the gelling solution should
be pumped within a few hours following mixing on the
surface. It will be difficult to pump a gelling solution
that has been sitting in the mixing tank for several days.
In addition to temperature, it is important to examine the
effect of polymer and cross-linker concentrations on the
gelation time.

Therefore, the objectives of this study were to:
(1) determine the effects of the following parameters on
the gelation time: type of mixing water, type and con-
centration of simple inorganic salts, initial pH, temper-
ature, polymer concentration, cross-linker concentration,
and contamination with ferric iron, (2) explain variations
in the gelation time in terms of published gelation mech-
anisms, (3) examine compatibility of gelling solution
with reservoir fluids, and (4) give recommendations for
field application.

2. Experimental studies

2.1. Materials

The gelling system consisted of the PAtBA copoly-
mer cross-linked with an organic cross-linker, PEI. Both
chemicals were received in liquid form and were used
without further purification. The active contents of the
polymer and the cross-linker were determined by ther-
mogravimetric analysis (TGA) and were found to be 20
and 30 wt.%, respectively. The activity of PAtBA was
further confirmed by precipitation in pure ACS grade
isopropanol following the procedure described by Tay-
lor and Nasr-El-Din (1994). The activities of PAtBA and
PEI agree with those reported by Zitha et al. (2002).

All gel compositions are reported in terms of the con-
centration of the active chemical present in the sample
received. Most of the gelation tests were conducted with a
polymer concentration of 7 wt.% and a cross-linker con-
centration of 0.3 wt.%. The pH value of gelling solution at
these concentrations was found to be 8.3. No attempts
were made to adjust the pH of the gelling solution, unless
otherwise indicated.

The polymer has an initial degree of hydrolysis less
than 0.1 mol%. The weight average molecular weight of
the polymer is 250,000–500,000 g/mol (Hardy et al.,

147 1999; Reddy et al., 2003). The ester groups of the
 148 copolymer represent 5 mol% (Reddy et al., 2003). The
 149 degree of hydrolysis and ester content of the polymer
 150 were experimentally confirmed by running ^{13}C Nuclear
 151 Magnetic Resonance (^{13}C NMR) on the polymer using
 152 equipment and procedures given elsewhere (Al-Munta-
 153 sheri et al., 2006). The pH of neat polymer solution is
 154 4.2. The molecular weight of PEI is nearly 70,000 g/mol
 155 and has a pH of 11.6.

156 Mixing waters with three salinity levels were used to
 157 prepare the gelling solutions. These were distilled water,
 158 seawater and field mixing waters. Seawater and field
 159 mixing waters were filtered to 0.45 μm to remove sus-
 160 pended solids. Chemical analyses of the field mixing
 161 water (typical mixing water used in Southern fields pres-
 162 ent in Saudi Arabia) and seawater from the Arabian Gulf
 163 are given in Table 1.

164 The effect of various inorganic salts on the gelation
 165 time was examined in detail. Salts examined included:
 166 NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. All salts
 167 were ACS grade.

168 3. Gelation mechanism

169 A detailed investigation on the gelation mechanisms
 170 of this system is reported by Al-Muntasheri et al. (2006).
 171 Hence, a brief summary will be presented in this section.
 172 The ester groups ($\text{R}-\text{COO}-\text{R}'$) on the PATBA polymer
 173 provide masked cross-linking sites. These groups either
 174 hydrolyze or thermolyze according to pH and temper-
 175 ature. At low pH values and temperature, PATBA hy-
 176 drolyzes and forms partially hydrolyzed polyacrylamide
 177 (PHPA) and *tert*-butyl alcohol as confirmed through ^{13}C
 178 NMR by Al-Muntasheri et al. (2006). On the other hand,
 179 PATBA thermolyses at high temperatures and pH
 180 producing PHPA and isobutene gas. More information
 181 on the gas products of this system can be found else-
 182 where (Al-Muntasheri et al., 2007b). Hardy et al. (1999)

183 reported the chemical reactions of this system. After the
 184 breakage of the ester groups, carboxylate groups are
 185 formed. Hardy et al. (1999) reported the cross-linking
 186 mechanism of this system as a nucleophilic substitution
 187 by an imine nitrogen from the PEI on the carbonyl
 188 carbon attached to the ester groups. This should result in
 189 a covalent bond between the PEI nitrogen and the ester
 190 carbonyl carbon. A second mechanism for the gelation
 191 process was reported by several authors (Reddy et al.,
 192 2003; Vasquez et al., 2005) where the PEI nitrogen
 193 forms a covalent bond with the acrylamide carbonyl
 194 carbon on the PATBA. In fact, both mechanisms are
 195 nucleophilic substitution where the leaving group is
 196 substituted by an imine nitrogen (nucleophile) of the
 197 PEI. The leaving groups are either the tertiary butyl ester
 198 ($-\text{CO}-\text{OC}(\text{CH}_3)_3$) as in the first mechanism or the
 199 amide ($-\text{CO}-\text{NH}_2$) as in the second mechanism.

200 4. Measurement of the gelation time

201 A thorough literature review revealed that the gela-
 202 tion time is measured using various techniques and is
 203 defined in several ways. The gelation time is defined as
 204 the time needed to reach a certain viscosity (Terry et al.,
 205 1981; Jordan et al., 1982).

206 A second definition for the gelation time is the time
 207 needed to reach a specific gel strength (Sydansk, 1993; te
 208 Nijenhuis et al., 2003). An oscillatory viscometer is used
 209 to measure gel strength evolution as a function of time,
 210 hence determine the gelation time. The point that cor-
 211 responds to the maximum slope in the elastic modulus-
 212 time curve has been defined as the gelation point (Prud'-
 213 homme and Uhl, 1984).

214 A third definition of the gelation time is the time
 215 needed for the elastic and viscous moduli to intersect
 216 (Mortimer et al., 2001). A more precise definition is the
 217 time at which the moduli ratio becomes independent of
 218 frequency (Ponton et al., 2002).

219 In the present study, the gelation time is defined as
 220 the time needed to reach the inflection point on the
 221 viscosity-time curve (Fig. 1). The inflection point cor-
 222 responds to the onset of the gel formation (Hardy et al.,
 223 1998) and has been used by several authors to determine
 224 the gelation time (Jurinak et al., 1991; Broseta et al.,
 225 2000; Reddy et al., 2003; Vasquez et al., 2005).

226 Steady shear measurements were performed using a
 227 Brookfield viscometer (Model PVS) with Couette geom-
 228 etry. The outer and inner radii of the cup and bob were 3.8
 229 and 3.4 cm, respectively. Sample volume was 30 ml.
 230 Viscosity measurements during gelation were made at
 231 various temperatures up to 150 $^\circ\text{C}$. The shear rate was
 232 kept constant at 8.52 s^{-1} . In order to prevent sample

t1.1 Table 1
 t1.2 Chemical analysis of mixing waters

t1.3 Variable	Field water	Seawater
t1.4 Ca	126	592
t1.5 Mg	53	2304
t1.6 Na	228	19,325
t1.7 K	14	730
t1.8 Cl	361	31,106
t1.9 SO_4	233	4108
t1.10 HCO_3	171	183
t1.11 TDS ^a	1186	58,348
t1.12 pH	7.8	7.9

t1.13 All concentrations are in mg/l.

t1.14 ^a Total dissolved solids (TDS) were determined by addition.

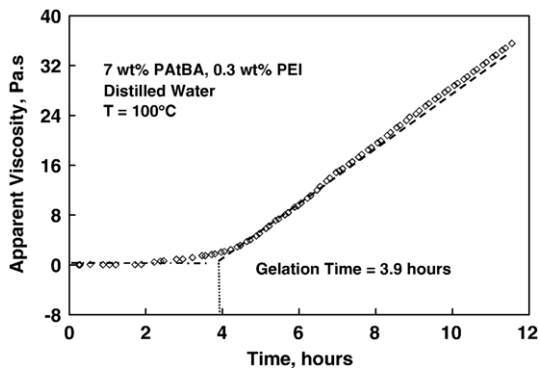


Fig. 1. Determination of the gelation time.

233 evaporation, nitrogen gas was used to pressurize the
 234 system up to 2.07 MPa (300 psi). The elastic modulus was
 235 measured using an ARES rheometer at room temperature
 236 with a cone and plate geometry. The angle of the cone was
 237 1° and the plate diameter was 25 mm.

238 Samples of the gelling solutions were prepared at
 239 room temperature and loaded immediately into the vis-
 240 cometer, which was set at the desired test temperature. It
 241 should be noted that zero time was taken as the time the
 242 gelling solution was placed in the viscometer. Table 2
 243 lists the parameters investigated in the present work and
 244 their ranges.

245 5. Results and discussion

246 5.1. Effect of mixing water on the gelation time

247 Gels can be prepared in the field using fresh water,
 248 aquifer water or seawater. These waters contain various
 249 ions that can impact the gelation process. Therefore, it is
 250 of interest to measure the gelation time for gels prepared
 251 in various waters (Table 1). Fig. 2 shows the viscosity
 252 evolution for two gelling solutions that contained 7/
 253 0.3 wt.% PAI/BA/PEI. The first solution was prepared in
 254 distilled water (initial pH of 8.3); whereas the second
 255 solution was prepared in seawater (initial pH of 8.7).
 256 Viscosity measurements were conducted at 120 °C. The
 257 gelation time for the gel prepared in distilled water was

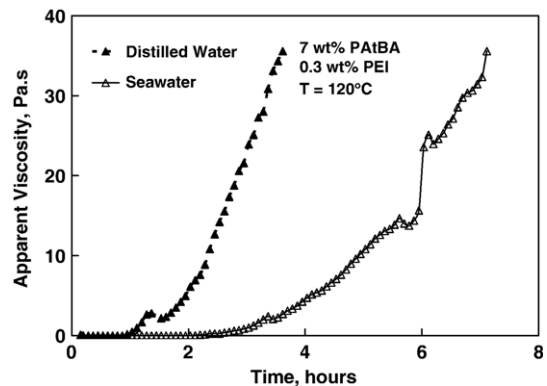


Fig. 2. Viscosity evolution for gels prepared using distilled water and seawater.

1.5 h. However, the gelation time was doubled for the
 gel that was prepared using seawater.

It is clear from the data shown in Fig. 2 that increasing
 the salt content of the mixing water increased the gela-
 tion time. These results can be explained as follows.
 The initial degree of hydrolysis of the polymer is less
 than 0.1 mol% and its ester content is nearly 5 mol%. At
 high temperatures, the ester groups will thermolyze/
 hydrolyze into carboxylate groups, which carry negative
 charges. Carboxylate groups can also form upon the
 hydrolysis of the amide groups of the polymer in alkaline
 conditions (Kurenkov et al., 2001). The repulsive forces
 between the negative charges will increase the hydro-
 dynamic volume of the polymer chains. As a result, the
 cross-linking sites become more accessible to the cross-
 linker molecules. This explains the short gelation time
 that was noted when distilled water was used to prepare
 the gel.

On the other hand, the concentrations of mono- and
 divalent cations in seawater are high (Table 1). These
 cations shield the negative charges available on the car-
 boxylate groups and, as a result, the polymer chains
 collapse (Ward and Martin, 1981; Nasr-El-Din et al.,
 1991). Consequently, potential cross-linking sites on the
 polymer chain are not as accessible to the cross-linker
 molecules. The gelation induction period will be longer
 in this case and hence the gel will take a longer period of
 time to form. The effect of simple inorganic salts on the
 gelation time was noted with other polyacrylamide-
 based gelling systems (Kakadjian et al., 1999; Broseta
 et al., 2000; Romero-Zeron et al., 2004).

The most important aspect of the results shown in
 Fig. 2 is that the gelation time is strongly dependent on
 the salt content (ionic strength) of the mixing water. The
 viscosity deeps and humps noted in Fig. 2 will be
 discussed in the gelation kinetics section. Therefore, the

Parameter	Range
Temperature	25–150 °C
Polymer concentration	4.3–7 wt. %
Cross-linker concentration	0.3–0.9 wt. %
TDS of mixing water	0–58,348 mg/l
Initial pH	3–12
Iron(III)	100 and 1000 mg/l

294 gelation time should be measured for gels that are pre-
 295 pared using either the field water or a mixing water
 296 representative of that used in the field. Using a different
 297 type of water can cause large differences between the
 298 measured and the actual gelation time in the field. This
 299 can lead to inadequate shut-in time or premature gelling
 300 during pumping the solution, which can cause opera-
 301 tional problems.

302 5.2. Effect of monovalent cations on the gelation time

303 The effect of the salt content (ionic strength) of the
 304 mixing water on the gelation time was significant. It was
 305 decided to examine the effects of mono- and divalent
 306 cations on the gelation time separately. Gelling solutions
 307 were prepared and various amounts of sodium chloride
 308 were added such that the final polymer and cross-linker
 309 concentrations were 7 and 0.3 wt.%, respectively. The
 310 gelation time was measured at a temperature of 120 °C.
 311 Fig. 3 shows the effect of sodium ion concentration on
 312 the gelation time. The gelation time increased when
 313 5000 mg/l of sodium ions was added to the gelling
 314 solution. The gelation time further increased with in-
 315 creasing sodium ion concentration and reached 14 h at
 316 50,000 mg/l of sodium ions. Fig. 3 also shows that the
 317 effect of potassium ion on the gelation time was similar
 318 to that of the sodium ions. However, sodium ions de-
 319 layed gelation more than potassium ions. This is mainly
 320 because of the higher charge density (ionic charge/size)
 321 of sodium ions compared to that of the potassium ions
 322 (Uddin et al., 2002).

323 5.3. Effect of divalent cations on the gelation time

324 The effect of divalent cations on the gelation time
 325 was also examined. Fig. 4 shows that Ca^{+2} delayed the
 326 cross-linking reaction more than K^{+} . Calcium ions are
 327 divalent, whereas potassium ions are monovalent. The
 328 charge/size ratio for calcium ions is twice that of po-

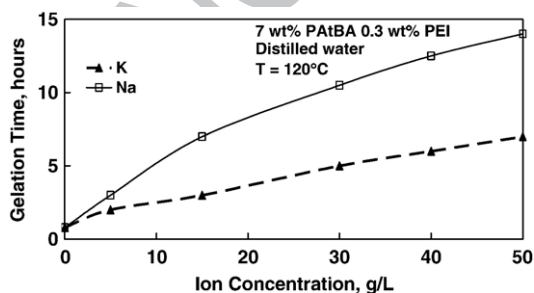


Fig. 3. Effect of monovalent cations on the gelation time.

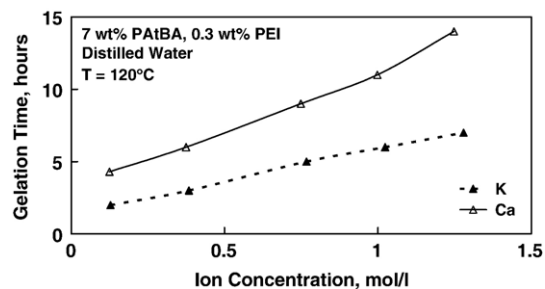


Fig. 4. Effect of cation type on the gelation time.

tassium ions. This result suggests that the gelation time
 is a function of the charge/size ratio of the cation that is
 present in the mixing water.

From the previous discussion, it is clear that mono-
 and divalent cations increase the gelation time. If only
 saline water is available on site, then the gelation time
 can be reduced by either increasing the concentration of
 the polymer or the cross-linker.

Shorter gelation times at higher salinity levels can be
 obtained by adding more polymer, Fig. 5, or cross-
 linker, Fig. 6. However, adding too much cross-linker
 may cause over cross-linking and loss of gel volume
 with time, which is known as gel syneresis (Eggert et al.,
 1992). It should be noted that syneresis is not desirable,
 especially when the gel is placed in naturally fractured
 reservoirs. This is because the reduction in gel volume
 will generate new flow paths, which will reduce the
 effectiveness of the gel treatment (Bryant et al., 1996).

It was visually observed that gels prepared in saline
 water were physically weaker than those prepared in
 distilled water. To further investigate the effect of salts
 on gel strength, the elastic modulus, G' , for various gels
 was measured in the linear viscoelastic region at a fre-
 quency of 0.3 rad/s. The procedure described by Al-
 Muntasheri et al. (2007a) was followed. Table 3 sum-
 marizes G' values for gel samples prepared in different
 salinity brines. The elastic modulus or gel strength was
 highest for gels prepared in distilled water. The elastic
 modulus decreased by nearly 45% when the gel was
 prepared in the field mixing water. The elastic modulus
 decreased as the concentration of sodium ion was in-
 creased. Potassium ions at 5000 mg/l also decreased the
 elastic modulus of the gel.

5.4. Effect of the initial pH value on the gelation time

To examine the effect of the initial pH value on the
 gelation time, the initial pH value of the gelling solution
 was adjusted by adding a few drops of either 1 N NaOH
 or 15 wt.% HCl. The viscosity was measured as a

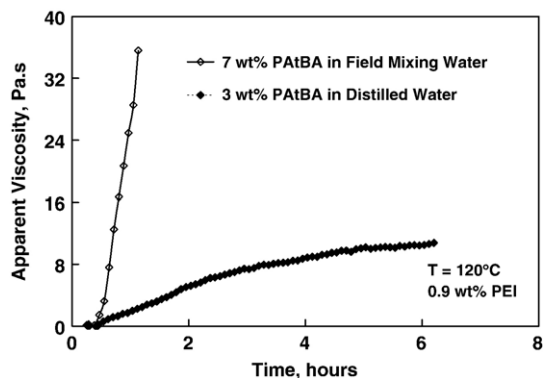


Fig. 5. Compensation for the TDS effects by adding more polymer.

367 function of time at a constant shear rate and a temper-
368 ature of 120 °C (Fig. 7).

369 A rapid increase in the viscosity of the gelling
370 solution was noted at initial acidic pH conditions. The
371 apparent viscosity reached the maximum viscosity that
372 can be measured with the viscometer (35.6 Pa s); how-
373 ever, it gradually decreased to 7000 mPa s after a few
374 hours (Fig. 7). The gel formed under acidic conditions
375 did not last for a long period of time. According to Hardy
376 et al. (1999) and Meszaros et al. (2004) the free-pair of
377 electrons on the imine nitrogen of PEI becomes more
378 protonated at low pH value. As a result, PEI nucleophi-
379 lity decreases making it less effective in cross-linking the
380 PATBA. This may lead to gel breakage that was noted in
381 the results shown in Fig. 7.

382 At pH=8.3, Fig. 8, the gelation time was nearly
383 1.6 h. The viscosity started to increase after 1.5 h and
384 monotonically increased with time. A similar trend was
385 noted at pH=11.9, however, the gelation time increased
386 to nearly 2.7 h. This delay in the cross-linking reaction
387 is most likely due to sodium ions that were introduced

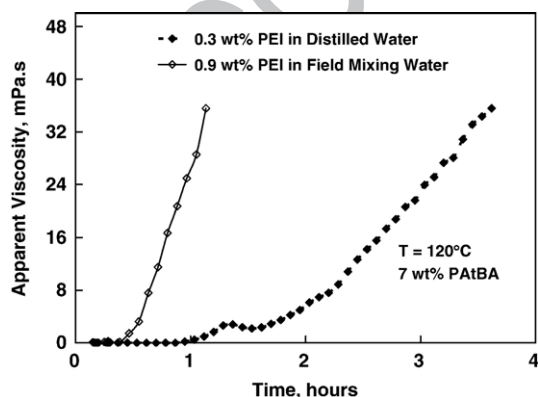


Fig. 6. Compensation for the TDS effects by adding more cross-linker.

Table 3		t3.1
Effect of salinity of mixing water on the elastic modulus		t3.2
Salinity of mixing water (mg/l)	Elastic modulus G' (Pa)	t3.3
~20	1025	t3.4
1186 (field mixing water)	562	t3.5
5000 of Na in distilled water	414	t3.6
50,000 of Na in distilled water	356	t3.7
5000 of K in distilled water	360	t3.8

All gels contained 7 and 0.3 wt.% of PATBA/PEI heated for 12 h and 150 °C.
 G' was measured at 0.3 rad/s.

to the gelling solution with the addition of sodium
hydroxide.

The most important conclusion that can be inferred
from these results is that the gelation time depends on
the initial pH value of the solution. Low pH values can
adversely affect the gelation process. A pH value of at
least 8 is needed to produce a stable gel under the
conditions given in Fig. 8.

5.5. Gelation kinetics

5.5.1. Effect of temperature on the gelation time

Fig. 9 shows the viscosity evolution obtained at
various temperatures (80 to 135 °C), and a pressure of
2.07 MPa (300 psi). Measurements were conducted on
gelling solutions that contained 7 wt.% PATBA and
0.3 wt.% PEI prepared in distilled water. At 80 °C, the
initial apparent viscosity was nearly 10 mPa s and
sharply increased after 17 h, indicating the onset of gel
formation. At 100 °C, the gelation time decreased to
4.3 h. The gelation time further decreased to 1.9 h at
a temperature of 110 °C. Viscosity evolution was similar
at all temperatures examined, but the gelation time de-
creased with increasing temperature. This reflects the
endothermic nature of the gelation reactions.

At temperatures of 110 and 120 °C, a gel break
point can be seen in Fig. 9 as the apparent viscosity
dropped and then resumed its build-up. This trend was
noted in the results reported by Vasquez et al. (2005)
who examined this system at higher PEI concentra-
tions. It was noted also in the data reported by Broseta
et al. (2000) for polyacrylamide cross-linked with
chromium acetate. It should be mentioned that this
break in viscosity evolution was not considered in the
determination of the gelation time, and most probably
occurred due to the shear applied while measuring the
gelation time.

The gelation time of this system was very short at
high temperatures (less than 1 h at 135 °C). Therefore, in
high temperature reservoirs, a suitable preflush should

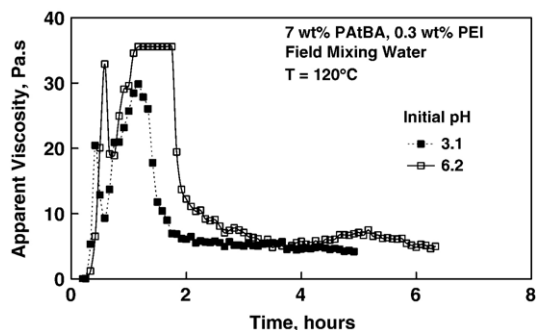


Fig. 7. Viscosity evolution at acidic initial pH conditions.

426 be used to cool-down the formation and extend the
427 gelation time as needed.

428 The effect of temperature on the gelation time can be
429 predicted using Arrhenius-type relationship (Hurd and
430 Letteron, 1932; Jordan et al., 1982):

$$431 \quad GT = M \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

432 where E_a is the activation energy in kJ/mol, GT is the
433 gelation time in hours, R is the universal gas constant in
434 kJ/mol K, T is the absolute temperature in K and M is
435 the frequency factor in hours.

436 From Eq. (1), a plot of the natural log of GT vs. $1/T$
437 should give a straight line with a slope of E_a/R and an
438 intercept of $\ln M$.

439 Eq. (1) was used to fit the gelation time for gels
440 prepared in the three mixing waters as shown in Fig. 10.
441 It should be mentioned that these data were obtained at
442 temperatures greater than 100 °C. It is clear that gel
443 prepared in seawater had the longest gelation times at all
444 temperatures examined.

445 The activation energy, calculated using Eq. (1),
446 decreased with increasing water salinity as shown in
447 Table 4. The variation of E_a with salt content is similar

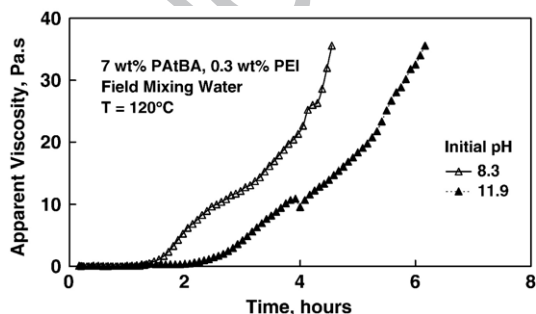


Fig. 8. Viscosity evolution at basic initial pH conditions.

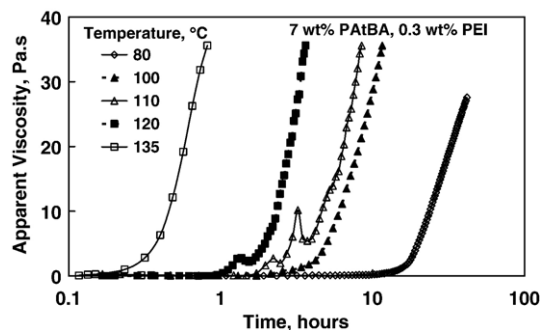


Fig. 9. Viscosity evolution at various temperatures in distilled water.

to that noted with polyacrylamide-based gels (Jordan
448 et al., 1982).

449 Table 5 gives the literature values reported for the
450 activation energy of various acrylamide-based polymers
451 cross-linked with various organic cross-linkers, includ-
452 ing the results obtained in the present study. The data
453 obtained for the gelling system examined are within the
454 same order of magnitude as those reported in the liter-
455 ature. It is important to note that the activation energy
456 extracted from the data reported by Hardy et al. (1999) is
457 slightly lower than those reported in the present study.
458 This is mainly due to preparing the gel using water with
459 different salinities and measuring the gelation time at a
460 different temperature range. Hardy et al. (1999)
461 measured the gelation time at temperatures less than
462 100 °C; whereas we measured the gelation time at tem-
463 peratures greater than 100 °C. They also prepared their
464 gel in 2 wt.% KCl brine.
465

5.5.2. Effect of polymer concentration on the gelation time

466 The effect of polymer concentration was examined
467 by measuring the viscosity of gelling solutions that
468
469

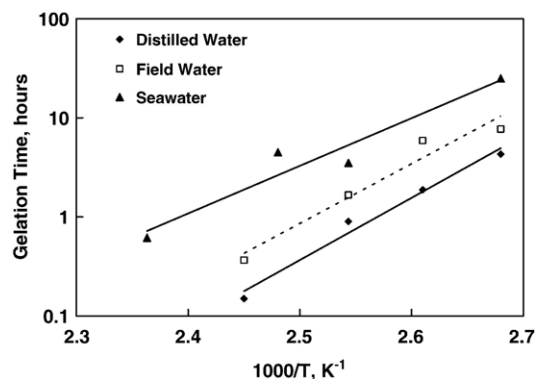


Fig. 10. Arrhenius-type fit for 7 wt.% PATBA, 0.3 wt.% PEI in various mixing waters.

t4.1	Table 4			
t4.2	Kinetic parameters of PATBA/PEI gel using various mixing waters			
t4.3	TDS (mg/l)	Activation energy (kJ/mol)	Frequency factor (h)	R^2
t4.4	~20	120	7 E-17	0.9563
t4.5	1186	115	7 E-16	0.9517
t4.6	58,348	92	3 E-12	0.9593
t4.7	All gels contained 7 wt.% polymer and 0.3 wt.% cross-linker.			

470 contained 0.3 wt.% PEI and various polymer concentra-
 471 tions from 4.33 to 7 wt.%. In order to simulate field
 472 conditions, field mixing water was used to prepare these
 473 solutions and viscosity measurements were conducted at
 474 a temperature of 120 °C. It can be seen in Fig. 11 that as
 475 the polymer concentration was increased, the gelation
 476 time decreased. As the polymer concentration or the
 477 number of cross-linking sites increases, the rate of gel
 478 formation increases and hence, the gelation time
 479 decreases. The effect of polymer concentration on the
 480 gelation time at 0.3 wt.% of PEI and 120 °C can be
 481 presented using Eq. (2):

$$482 \quad GT = 9.8C_p^{-n} \quad (2)$$

483 where C_p is the polymer concentration in wt.% and n is
 484 the reaction order with respect to the polymer. The reac-
 485 tion order was found to be 1.0, which is in good agree-
 486 ment with the data obtained by Hardy et al. (1999) for
 487 this system at polymer concentrations of 3 to 10 wt.%
 488 and a cross-linker concentration of 2 wt.% of PEI. Their
 489 data were collected at 96 °C using 2 wt.% KCl brine.

490 5.5.3. Effect of cross-linker concentration on the 491 gelation time

492 Fig. 12 shows the apparent viscosity of gelling solu-
 493 tions that contained 7 wt.% PATBA and various cross-
 494 linker concentrations as a function of time. Increasing
 495 the cross-linker concentration reduced the gelation time.

t5.1	Table 5	
t5.2	Activation energies of acrylamide-based polymers reacted with different organic cross-linkers	
t5.3	Gelling system	Activation energy (kJ/mol)
t5.4	Acrylamide-based/phenol and hexamethylenetetramine (Eriksen et al., 1997)	33–58
t5.5	Acrylamide-based/phenol and formaldehyde (Eriksen et al., 1997)	26–50
t5.6	Polyacrylamide/glyoxal (Han et al., 1997)	70
t5.7	PATBA/PEI (Hardy et al., 1999)	55–83
t5.8	PATBA/PEI (present study)	92–120

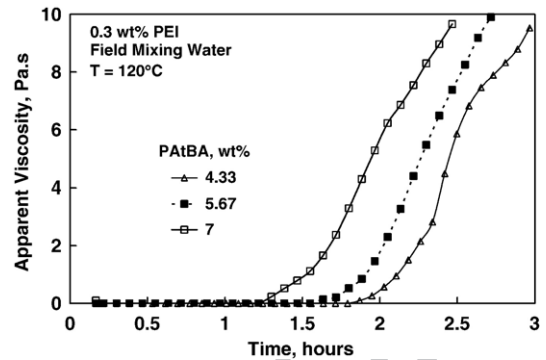


Fig. 11. Viscosity evolution at different polymer concentrations.

Similar to the effect of polymer concentration, the gel-
 496 ation time was found to vary exponentially with the
 497 initial cross-linker concentration according to Eq. (3):
 498

$$499 \quad GT = 0.39C_x^{-m} \quad (3)$$

500 where C_x is the cross-linker concentration in wt.% and
 501 m is the reaction order with respect to the cross-linker.
 502 The reaction order with respect to PEI is calculated as
 503 1.0 which is in agreement with literature values for this
 504 system (Hardy et al., 1999) reported at 96 °C with 8 to
 505 10 wt.% of PATBA and PEI concentration from 0.5 to
 506 2 wt.%.

507 5.6. Effect of iron contamination on the gelation time

508 In a typical field application, the polymer and cross-
 509 linker are mixed with water in large tanks that may contain
 510 corrosion products. There is a possibility of contamination
 511 with Fe(III), especially if the tank contains residual acid
 512 (tank bottoms). Similar to Cr(III), Fe(III) is a trivalent
 513 cation and can interact with the polymer molecules and
 514 affect the gelation time. In order to investigate the effect of

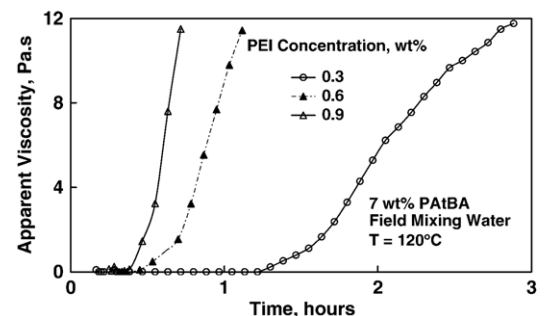


Fig. 12. Effect of cross-linker concentration on viscosity evolution.

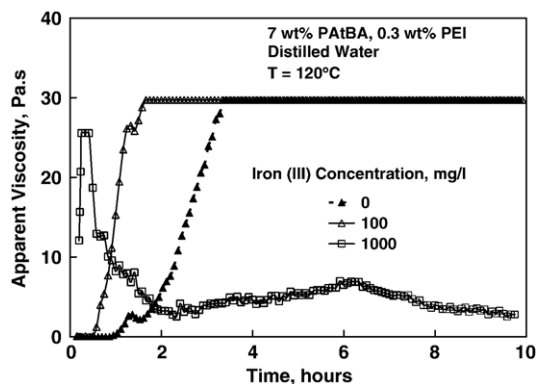


Fig. 13. Effect of iron content on viscosity evolution.

515 Fe(III) on the gelation time, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to
 516 gelling solutions that contained 7 wt.% PAtBA and
 517 0.3 wt.% PEI in distilled water such that the final so-
 518 lutions contained 100 and 1000 mg/l of Fe(III). Then, the
 519 apparent viscosity of each solution was measured as a
 520 function of time at 120 °C.

521 Fig. 13 shows a fast build-up in the apparent viscosity of
 522 the gelling solution that contained 100 mg/l Fe(III). A gel
 523 was formed that did not break by shear for 10 h. Increasing
 524 the concentration of Fe(III) to 1000 mg/l reduced the time
 525 needed to build-up the viscosity. The high viscosity did not
 526 last more than 25 min, and significantly decreased to
 527 3200 mPa s.

528 The results shown in Fig. 13 indicate that Fe(III) did
 529 reduce the gelation time at 120 °C. This result indicates
 530 that some of the iron(III) ions did cross-link the polymer
 531 (via the carboxylate groups). The gel formed at
 532 1000 mg/l iron did not last, indicating the iron conta-
 533 mination can adversely affect the quality of the gel.

534 5.7. Implication on field application

535 The viscosity of the gelling solution increased with
 536 time at ambient conditions. It will be very difficult to
 537 pump the gelling solution if it is left for several days
 538 after mixing. Therefore, it is recommended to add the
 539 cross-linker just before pumping.

540 The results obtained in the present study highlighted
 541 the importance of the salinity of mixing water. It is
 542 strongly recommended to prepare the gelling solution
 543 using the field mixing water.

544 It is also important to use clean tanks for mixing the
 545 gel in the field. Residual acids can adversely affect the
 546 gelation time.

547 Iron(III) can react with the polymer and accelerate
 548 the gelation process and produce a gel that breaks in a

short period of time. Therefore, every effort should be
 made to use clean tanks or better internally coated tanks.

It is advisable not to apply this gel right after acid
 treatments, especially in sandstone reservoirs. In this
 case, the concentration of iron in the wellbore area is
 high. This iron can cause premature setting of the gel. If
 there is a need to apply gel treatment following an acid
 treatment, then the well should be allowed to flow back
 until iron concentration is reasonably low. This proce-
 dure will also ensure that there is no residual acid
 downhole.

The pH of this gel system is greater than 8. The
 formation brine contains a high concentration of
 divalent cations (ranges from 10,000 to 15,000 mg/l).
 There is a potential of divalent cations precipitation once
 the gelling solution enters the formation. This can cause
 injectivity problems during gel placement. This problem
 can be addressed by injection of a low-salinity preflush.
 The main objective of this preflush is to reduce the
 concentrations of divalent cations around the critical
 wellbore area. A second objective is to cool-down the
 formation. This will give adequate time for gel place-
 ment, which is needed in high temperature wells.

There is also a good chance that the gelling solution
 will be mixed with the native crude oil. The gelling
 solution has a high pH value and some crude oils con-
 tain acidic components (Nasr-El-Din, 1996). Mixing of
 the two fluids can result in the generation of in-situ
 surface active species, which can cause emulsion forma-
 tion. To address this issue, compatibility tests should
 be conducted using reservoir fluids (oil and produced
 water).

The gelling system exhibited syneresis at a cross-
 linker concentration of 1.2 wt.% for gels prepared in the
 field mixing water or seawater. Therefore, it is very
 important to use the right cross-linker concentration.

6. Conclusions

The gelation time of the PAtBA/PEI system was
 measured as a function of various key parameters. The
 following conclusions were obtained:

1. Salts of mono- and divalent cations were found to
 increase the gelation time and this effect was found to
 be a function of the charge/size ratio of the cation
 present.
2. The gelation time decreased with temperatures fol-
 lowing Arrhenius-type of relationship.
3. The activation energy of PAtBA/PEI gelling system
 was found to be 118 kJ/mol in distilled water and
 93 kJ/mol in seawater.

- 598 4. The reaction orders with respect to both PATBA and
599 PEI agree with those reported in literature at temper-
600 atures less than 100 °C.
- 601 5. Initial pH value showed a strong influence on the
602 viscosity of the gel. Higher viscosities were obtained
603 at high initial pH values. At acidic conditions, the
604 gelation time was short and the gel did not last for a
605 long period of time.
- 606 6. The presence of high iron concentration (1000 mg/
607 l Fe(III)) resulted in short gelation times and the gel
608 did not last for more than a few hours.

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