Advances in Geo-Energy Research

Vol. 6, No. 3, p. 230-240, 2022

Original article

Sensitivity analysis of parameters affecting nano-polymer solution for water shutoff in carbonate rocks

Sakar Soka[1], Hiwa Sidiq[2]*

[1]*Department of Petroleum and Energy, Sulaimani Polytechnic University, Kurdistan Region, Iraq*

[2]*Department of Petroleum Engineering, Komar University of Science and Technology, Kurdistan Region, Iraq*

Keywords:
Nano-polymer solution
polyacrylamide/polyethylene
cross-linker
water shut-off
polymer

Cited as:
Soka, S., Sidiq, H. Sensitivity analysis of parameters affecting nano-polymer solution for water shutoff in carbonate rocks. Advances in Geo-Energy Research, 2022, 6(3): 230-240.
https://doi.org/10.46690/ager.2022.03.06

Abstract:
Excessive water production impacts the economics of petroleum reservoir and often leads to their premature shut-in. Production of high saline water represents a major corrosion for casing, tubing, flow lines, and production facilities. Polymer solution has been used to control water production and to plug in high-temperature reservoirs. Most of these polymer solutions consist of polyacrylamide-based polymer and an organic or inorganic cross linker. Polyethylene mine has been used as an organic cross-linked for polyacrylamide. Literature reported that polyethylene mine can also form ringing gels with polyacrylamide copolymers in addition to polyacrylamide concentration. In this study, nano-chemical solutions has been prepared and studied in detail for their efficacy at reservoir condition. The compositions of the nano-chemicals mainly consisted of polyacrylamide mixed with nano particles, cement, coated-clay and polyethylene mine as cross-linker. The aim of using nano particles and coated-clay was to control gel performance and strength under the reservoir condition. Moreover, the effect of nano-chemical composition at higher temperature have been studied extensively on the gelation properties, elastic modulus, viscosity, and swelling ratio. Results showed that the elastic modulus and viscosity improve significantly with the increasing nano particle concentration. Coated-clay can control the gelation time as clay swallows and absorbs more formation water in the target zone, when its thin coated film breaks down, lesser water production can be predicted.

1. Introduction

For reducing excessive water production in oil fields, water shut-off techniques are used. Low oil recovery and early water breakthrough in reservoirs are caused by permeability heterogeneity, induced fractures high permeability channels, thief zones, or streaks. These are quite common phenomena in mature fields as they are subjected to extensive water flooding. Consequently, large amounts of movable oil and gas remains trapped in low permeability zones (Al-Dhafeeri et al., 2005)

In many cases, water cuts rise above 90% and challenges the profit of the field (Seright et al., 2003). Therefore, this problem has promoted the development of different methods to reduce excessive water production. Water shut-off system can be classified into two types: mechanical (Seright et al., 2003; Qin and Krzysztof, 2009; Vega et al., 2010) and chemical method. The mechanical method is easy to implement provided the down-hole devices are already installed on the well. Whereas the chemical method, however it is time consuming, can remediate excessive water production in situ the reservoir and plug the fractures where water floods the wells because polymer solution has the characteristics of water swelling, which expand rapidly in the process of its injection into the high water-cut layer (Sydansk and Southwell, 2000; Seright et al., 2003).

Polymer is one of the best and most effective techniques used for water shut-off and improved oil recovery because of its insoluble, not fusible, infinite molecule build up and ability to swell reversibly. Furthermore, it is also used for plugging fractures and high permeable zones, achieving a successful conformance control and decreasing water content usually observed after the polymer injection (Mousavifar et al., 2012).

*Corresponding author.
E-mail address: sakar.soka@gmail.com (S. Soka); hiwa.sidiq@komar.edu.iq (H. Sidiq).

Yandy Scientific Press

Received February 25, 2022; revised March 20, 2022; accepted April 2, 2022; available online April 10, 2022.

Polymers can interact with both types of cross-linkers: organic and inorganic. Partially hydrolyzed polyacrylamide (PHPA) is the most widely used polymer with inorganically cross-linker chemicals (Cr^{3+}, Al^{3+}, Zr^{4+}) (Al-Muntasheri et al., 2010).

The aim of this study was to perform a sensitivity analysis on the parameters affecting the nano-chemical solution that is planned to be used in carbonate rock for excessive water control and fracture plugging. Several nano-chemical solutions have been studied for their conformance control and investigated against the screening criteria of Taq Taq oil field (Soka and Sidiq, 2021). The best nano-chemical solution has been brought forward for extensive experimental study in order to define the optimum gel strength, gelation time and microstructure of nano-chemical solution for the use in field application.

2. Review of current trends in polymer solution researches

This section provides an extensive literature review of the current trends in polymer solution researches including nano-composite polymer studies. Furthermore, the factors affecting gel strength as well as the parameters needed for successful field trial are studied and evaluated.

2.1 Factors affecting polymer solution at lab scale

One of the main problems with polymer injection is the stability of polymer and polymers degradation under reservoir condition. This starts with breaking down the polymer molecules and reducing its molecular weight as the solution gets degraded thus loses much of its viscosity (Sidiq et al., 2008). Factors such as chemical, mechanical and biological degrading causes the instability of the polymers in the solution. Reducing the amount of oxygen in the solution decreases the chemical degradation caused by oxidation and ferric ions. Mechanical degradation can be optimized through controlling the injection speed. To control biological degradation; however, some additives can be added in the polymer solution (Sheng et al., 2015). The viscosity of the solution will be reduced at high temperatures as the polymer's molecular chains turns to monomers chains.

Researchers studied the effects of temperature and pressure on the stability a polymer gels. They found that, for instance, polyacrylamide-based copolymers cross-linked with phenol/ formaldehyde and PHPA cross-linked with Cr^{3+} to improve the polymer solution stability at reservoir condition (Moradi-Araghi et al., 1993; Sydansk and Southwell, 2000). This stability is achieved by covalent bonding between the polymer and the cross-linker (Moradi-Araghi, 2000). The organic cross-linker polyethylene mine (PEI) has been used to form gels with PAtBA (Hardy et al., 1999) thus improved stability. Whereas Allison and Purkaple (1988) have reported that at room temperature PEI can form gels with PHPA.

In a study Jiang et al. (2016) investigated different types of hydrophilic silica's that were synthesized by in situ polymerization. They found that for both the cross-linked and uncross-linked systems any additional silica improves the mechanical properties of the hydrogel. They concluded that with increasing silica content, secondary networks will be formed more completely. However, adding excessive silica causes the crosslink reaction to be incomplete and resulting in a poor gel network structure. On the other hand (Xin et al., 2015) reported that polymers with nano silica structure display enhanced resistance to degradation, viscosity properties, and tolerance to high salt concentration.

Polymers that were used for water shut-off have a large molecule build-up by the repetition of small units. It is divided into two groups of *biopolymers* and *synthetic*. Although the synthetic polymers have acceptable adsorption ability on the rock surface, it degrades due to shear stress and salinity. Whereas, the biopolymers cannot adsorb on the rock surface, however it has better performance under high injection rate and salinity. Moreover, they are sensitive to bacterial degradation (Buchgraber, 2008; Sheng, 2013; Sheng et al., 2015).

For instance, Sidiq et al. (2008) as well as Sidiq et al. (2019) investigated the effect of rock heterogeneity on the success of polymer treatment. They found that successive injections of different polymers (low to high molecular weights) result in an improved conformance control.

Amiri (2019) studied that nano clay-Based (Na-MMT and Bentonite) prepared by crosslinking of aqueous solutions of synthesized nano composite copolymer with Chromium (III) acetate showed acceptable gel strengths, gelation time and gel stability. Recently (Soka and Sidiq, 2021) studied the effect of nano and coated-clay particles on the gel performance at reservoir condition, they found the coated-clay delays gelation time when compared to the non-coated-clay because coating prevents the clay particle to interact with water and swell. Higher concentration of salt ions in the Nano-solution delays gelation time and decreases viscosity (Xin et al., 2015). At low concentration, nano-solution do not show any significant effects on viscosity and gel strength of the polymer (Soka and Sidiq, 2021).

2.2 Effect of nano particles on gel performance

Nano technology is a particle as a minute object that performs as a complete unit with respect to its transport and properties. The size of the nanoparticles is usually between 10-100 nanometers. Several researchers used nano polymer for conformance control by using nano clay-based (Na-MMT and Bentonite). Their results showed that an increase in elastic modulus of hydrogels can be observed when nano particles were added. This is because polymer chains can be diffused between the clay layers, and increased loss modulus induced by the reversible interaction between clay and acrylamide chains (Amiri, 2019); however, many studies in the literature showed that the addition of nanoparticles in polymer-solution increased the elastic property more significantly than the viscous property, because the dynamic adsorption/desorption equilibrium with the polymer chains show a greater elasticity in the material (Okay and Oppermann, 2007; Aalaie et al., 2008).

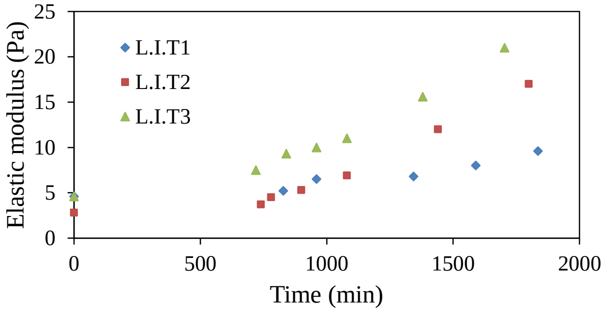


Fig. 1. Elastic modulus vs. time for different PAM concentration obtained from earlier study.

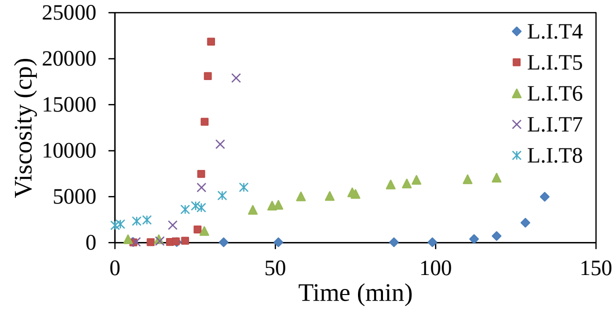


Fig. 2. Viscosity vs. time for different polymer mixtures at different test conditions obtained from literature. See Table A1 in appendix for their compositions.

2.3 Factors affecting the success of nano-chemical injection at field scale

Several factors need to be considered for the field trial: nano chemical composition; temperature; and polymer degradation, chemical, mechanical, and biological degradation (Standnes and Skjevrak, 2014). Polymers are mainly affected by molecular weights and permeability heterogeneity of the targeted formation (Aifen et al., 2016).

Other factors are rheological properties, type of the reservoir fluids (Cai et al., 2015), presence of fractures in the formation, wettability and mineral compositions of the reservoir rocks. These factors control the rate of absorption to the surface of the rocks while adsorption rates are affected by temperature and polymer concentration (Zhao et al., 2015).

The type of the cross-linker is the main factor affecting nano-chemical polymer. (Zhao et al., 2015) have experimentally investigated (polyacrylamide (PAM)/PEI and PAM/Cr^{3+}) solution at 130 °C. Their results showed that the initial value of the elastic modulus for the PAM/PEI was higher than elastic modulus for PAM/Cr^{3+}, because the viscosity of the PEI was higher than the Cr^{3+}. When the temperature increased beyond 130 °C, no more differences were observed between the types of cross-linkers. Polymers would not be successful, or suitable candidates if it did not meet the selection criteria for the well. Since rock properties vary widely from a location to another, details study requires selecting candidate nano-chemicals for water shut-off treatment.

2.4 Viscosity and gelation time

Several studies have studied the effect of PAM concentration on polymer's viscosity and gelation time. Fig. 1 shows elastic modulus of different polymer solutions studied in literature, the composition of polymer solutions "L.I.T1 to L.I.T3" can be found in Table A1 in appendix. PAM concentration increases from L.I.T1 to L.I.T3 polymer solution which proportionally increased their elastic modulus, because the cross-linking between PEI and PAM was believe to be through a nucleophile substitution in which the amide group at the carbonyl carbon of PAM will replace the imine nitrogen in PEI and amide group which may increase the elastic modulus in the presence of PEI. This observation was in agreement with the data reported for organically cross-linked solution (Al-Muntasheri et al., 2009). Whereas, with increasing polymer concentration in "L.I.T4 and L.I.T8" solution their gelation time was decreases drastically as shown in Fig. 2.

3. Experimental procedures

The experimental sequence in this work was designed based on our earlier study (Soka and Sidiq, 2021) in which three nano-chemicals were studied for their rheological properties. One of the chemicals (N-B) was selected for sensitivity analysis and presented in this research work.

3.1 Nano chemical selection

The N-B nano-chemical is selected based on meeting the following criteria. It is then subjected to a series of tests in order to determine its suitability as a candidate nano-chemical for conformance control in Taq Taq oil field. Details of the research work and test sequences are presented in Fig. 3.

Nano-Chemical Selection Criteria;

1-Initial viscosity of the nano-polymer solution; 10-20 cp.

2-Gel strength; 0.06-0.08 MPa.

3-Gelation time of the polymer; 600-1200 min.

4-Temperature resistance (Reservoir temperature); 60-70 °C.

A research workflow is also designed for this study, see Fig. 3.

3.2 Core sample computed tomography scanning

A cylindrical core sample was taken from the carbonate reservoir rock samples in Taq Taq oil field located in Kurdistan region; it measuring about 3.7×5.6 cm^2 (60.2 cc) and consisting of dolomitic limestone with calcite. The core sample underwent computed tomography (CT) scanning for investigating rock internal networks. Accordingly, three-dimensional CT images constructed and studied using radiant viewer. This software allows to analyzes the CT data in the steps of image segmentation and skeletonization. In general, the CT images of saturated pores with air appear in grayscale images while the rest of the signal are from the grain space. The image segmentation process was performed by the edge-finding in house developed algorithm. Kriging was used to estimate the two-point correlation function of the image using voxel principle.

CT image showed that the core sample was cross-cut by axial plane and axial fractures. The dimensions of the

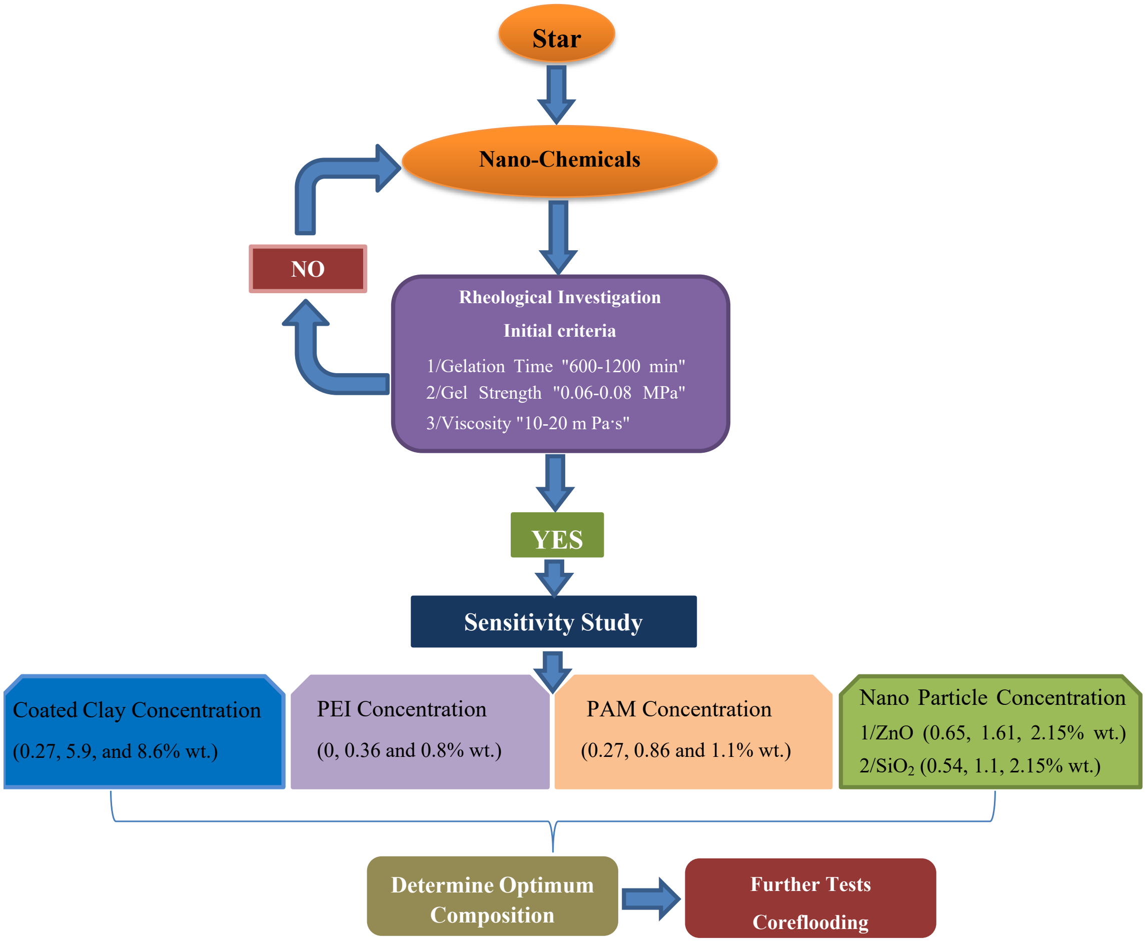


Fig. 3. Experimental design for nano-polymer solution.

Table 1. Petro physical Properties of the core sample scanned.

Core	Diameter (cm)	Length (cm)	Total volume (cm^3)	Matrix PV (cm^3)	Fracture PV (cm^3)	Absolute porosity (%)
CS	3.7	5.6	60.22	1.95	0.00195	3.24

fractures roughly measure (W×L×H) (1.2×6.2×2.6) mm and approximately a volume of "0.017 cc", see Table 1. Thus, the average secondary porosity measures 0.0317.

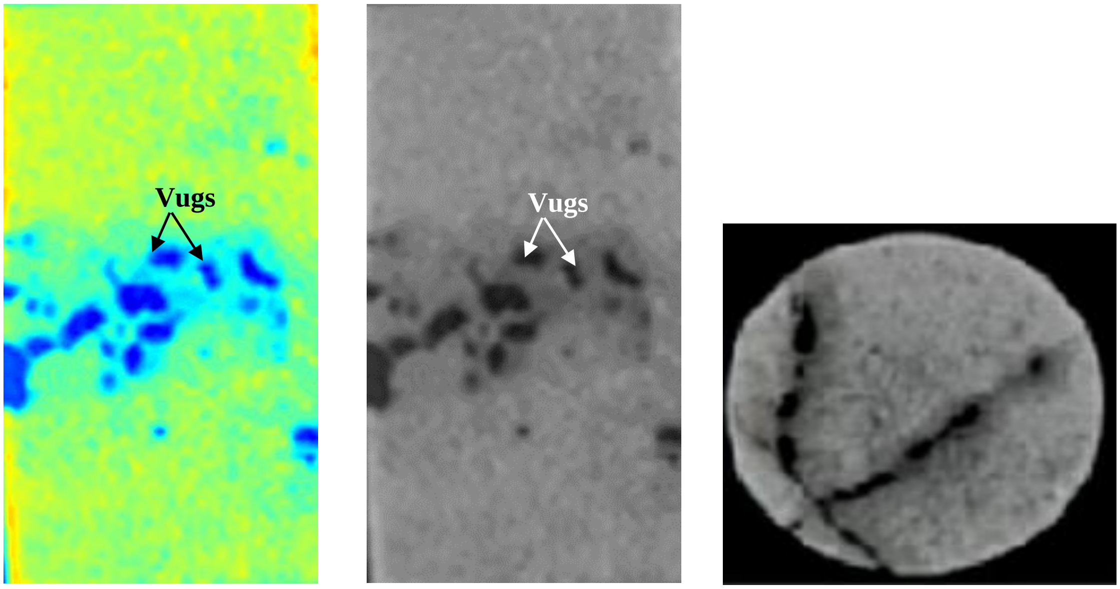
The measurement of secondary porosity was performed using the in house developed algorithm. Any pore diameter was less than 65 μm has been excluded from the quantitative measurement as it is considered the matrix pore diameter.

Fig. 4(a) shows gas filling vugs and pores with diameter greater than 65 μm. Whereas, the matrix porosity showed around 4%. The Hounsfield unit method was used to determine the porosity. The CT-Scan shows the sample having dead-end and isolate pore system, which they do not contribute to the conductivity of the core sample; refer to Fig. 4.

3.3 Nano-chemical composition

The source, detail, and composition of chemicals, cross linkers and Nano-particles used in the preparation of N-B are explained below and presented in Table 2. This nano-chemical (N-B) has met the field selection criteria and subjected to further experimental studies in order to investigate the magnitude of its parameters such as the concentration of coating, Nano particles, Nano-composition, and PAM and PEI on its rheological properties; the parameters range were studied and highlighted in Table 2. The aim was to tune N-B composition and improve its mechanical and chemical stability under reservoir conditions.

- Polyethylene imine as a cross-linker, CAS 25987-06-8; Average Mw = 750000.
- PAM, CAS No = 9003-05-8.
- Nano chemicals (ZnO) and (SiO_2) white powder CAS: 1314-13-2, Mw = 81.38 g/mol, particle size = 50-100 nm
- Cement and Starch.
- Coated-clay (bentonite-montmorillonite), CAS Number 1302-78-9.
- NaCl and $CaCl_2$ were used in powder.
- Brine water was used in the preparation of all the hydrogel samples; Table A2 in appendix shows its composition.



(a) (b) (c)

Fig. 4. CT scan for carbonate reservoir rock sample (CS-1), (a) gas accumulate in pores, (b) shows end-dead and isolate vugs, (c) cross-sectional view of the fractures.

Table 2. Chemical composition nano-chemical N-B solution.

Test symbol	Coated-clay % wt.	Swelling Ratio %	PAM % wt.	PEI % wt.	NaCl % wt.	$CaCl_2$ % wt.	Starch % wt.	Cement % wt.	ZnO % wt.	SiO_2 % wt.	Non-coated clay % wt.
N-B1	0.27	6.3	0.86	0.35	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B2	5.9	6.3	0.86	0.35	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B3	8.6	6.3	0.86	0.35	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B4	0.27	11.4	0.86	0.35	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B5	0.27	34.2	0.86	0.35	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B6	0.27	42.9	0.86	0.35	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B7	0.27	6.3	0.27	0.35	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B8	0.27	6.3	0.86	0.35	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B9	0.27	6.3	1.1	0.35	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B10	0.27	6.3	0.86	0	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B11	0.27	6.3	0.86	0.36	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B12	0.27	6.3	0.86	0.8	0.14	0.64	5	5.4	0.65	0.54	5.9
N-B13	0.27	6.3	0.86	0.35	0.14	0.64	5	5.4	2.15	0.54	5.9
N-B14	0.27	6.3	0.86	0.35	0.14	0.64	5	5.4	0.65	2.15	5.9
N-B15	0.27	6.3	0.86	0.35	0.14	0.64	5	5.4	0	0	5.9

3.4 Experimental apparatus

Six-speed rotary viscometer. This viscometer used for measured the rheological properties of nano-polymer solution such as gelation time, elastic modulus, gel strength and viscosity changes with time.

Balance sensitive. It is a very sensitive balance with a reading scale of 0.0001 g.

Laboratory hot plate. Hot plate is a flat surface with heating element is used in laboratory to heat sample and act chemical reactions or for numerous other actions.

Hamilton Beach mixer. It is used to prepare the mixture of the nano-chemical solution.

Scanning electron microscopy (SEM) measurements. SEM used for the observation particles and size of the coated-clay in the nano-polymer solution.

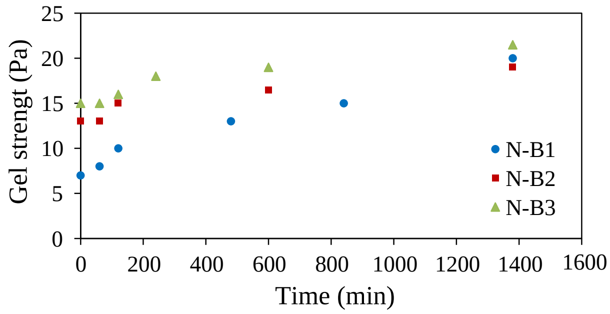


Fig. 5. Gel strength for different coated-clay concentration vs. Time. N-B1 = 0.27%; N-B2 = 5.9% and N-B3 = 8.6% of coated-clay concentration.

4. Result and discussion

Factors affecting the rheological properties of nano-chemical solution are presented in below sections. Effect of each parameter such as coated-clay, PAM and PEI concentration as well as nano-composition were investigated in detail on the gel strength of N-B nano-chemical. The optimum composition of nano solution then determined.

4.1 Effect of coated-clay

The reasons for using coated-clay in this research work were to achieve a longer gelation time and to improve conformance control when the Nano-polymer was injected into the reservoir formation. The clay will absorb more formation water in the reservoir when coat will breakdown, thus lesser water production can be observed. The results showed that the presence of coated-clay in the solution improved the mechanical and conformance control of the chemicals designed for water shutoff in carbonate rocks (Soka and Sidiq, 2021).

To determine the optimum weight percent of coated-clay in the solution, three weight percentages were investigated (0.27%, 5.9% and 8.6%). By increasing the coated-clay concentration, elastic modulus and viscosity of the nano-chemical solution increased, see Fig. 5. This occurred due to the direct interaction of clay particles and water; resulting in the increase of the solutions viscosity and rigidity. It appears that the best nano-chemical solution with higher coated-clay concentration (8.6% wt.) shows an improved mechanical property.

4.2 Effect of swelling ratio

Swelling was one of the most important and fundamental features of hydrogels. Many research studies have shown to produce gel PEI react with variety of polymers containing acrylamide pendant groups via a transamination reaction pathway (Jia et al., 2012). The swelling ratio of nano-chemical N-B has been measured at additional brine weigh percentage (5%, 15%, 30% wt.) at 3, 6, and 9 hrs., see Fig. 6. At each additional brine to the mixture, a sample of N-B is taken and measured for its rheological properties at reservoir conditions, see Fig. 7. The gel strength of N-B at both additional 5% and 15% of brine displayed a plateau around 0.426-0.498 MPa; this means N-B has the ability to absorb more water into its structure while maintaining its stability. Whereas the 30% of

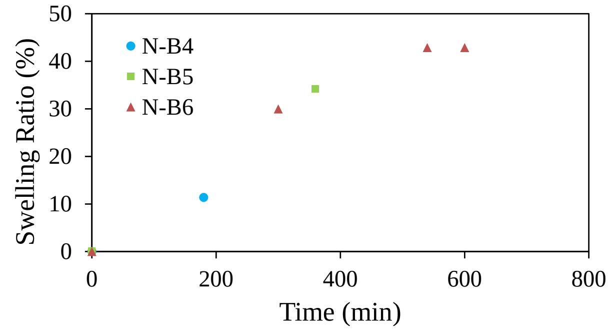


Fig. 6. Swelling ratio % as a function of time (min) for nano-chemical N-B at different times. N-B4 = 81.1%, for N-B5 = 83.4% and for N-B6 = 86.4% of brine water concentration.

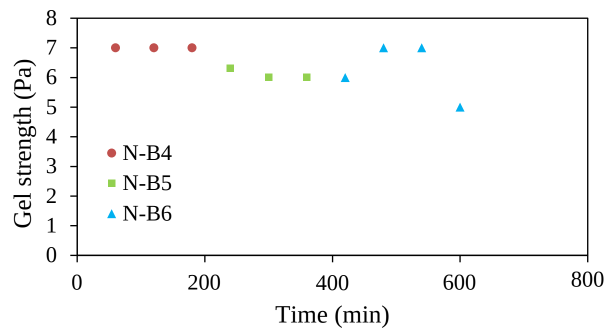


Fig. 7. Gel strength for Nano-polymer solution at different time. N-B4 = 81.1%, for N-B5 = 83.4% and for N-B6 = 86.4% of brine water concentration.

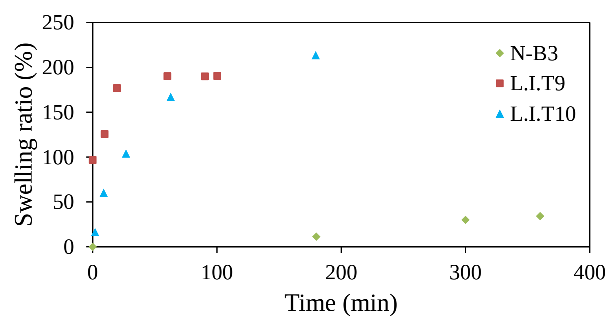


Fig. 8. Swelling ratio for nano-chemical N-B and different polymer at different time. N-B3 = 8.6% of coated-clay concentration.

brine added to N-B initially showed an improvement of its strength; however, at around 500 minutes the nano-chemical N-B start to degrade. Coated-clay swells absorbed a certain amount of brine, but after (10 hrs.) it did not swell any further and started to degrade.

The result of this paper has been compared with literature (Helvacıoğlu et al., 2011; Adewunmi et al., 2018), displayed in Fig. 8. They studied the effect of Neat PAAm and coal fly ash on swelling ratio. Adding 30% of brine N-B swells 50% more than its initial volume. This ratio is reasonable, as an increase of more than 50% will clog the formation pores and leads to permeability impairment. The effects of coated-clay clear as the swelling ratio increases more steadily if compared

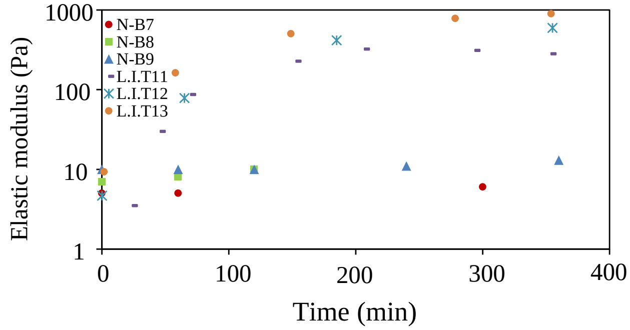


Fig. 9. Elastic modulus of polymer increase with increasing PAM concentration. PAM concentration in N-B nano-chemical solution are (N-B7 = 0.27% wt. of PAM, N-B8 = 0.86% wt. of PAM, N-B9 = 1.1% wt. of PAM). But PAM concentration in literature were (L.I.T11 = 3% wt. of PAM, L.I.T12 = 5% wt. of PAM, L.I.T13 = 7% wt. of PAM.

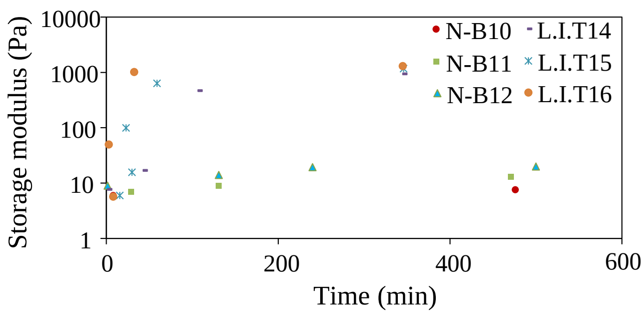


Fig. 10. Storage modulus of polymer increase with increase PEI concentration. N-B10 = 0%; N-B11 = 0.35% and N-B12 = 0.8% of PEI concentration.

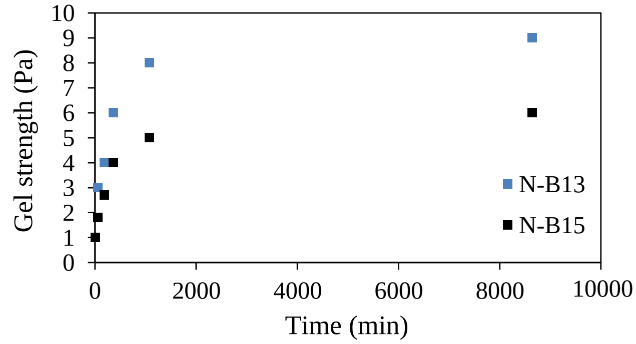


Fig. 11. Effect of nano concentration on gel strength as a function of time. N-B13 = '2.15% wt. of ZnO'; N-B15 = '0% wt. of SiO_2' concentration.

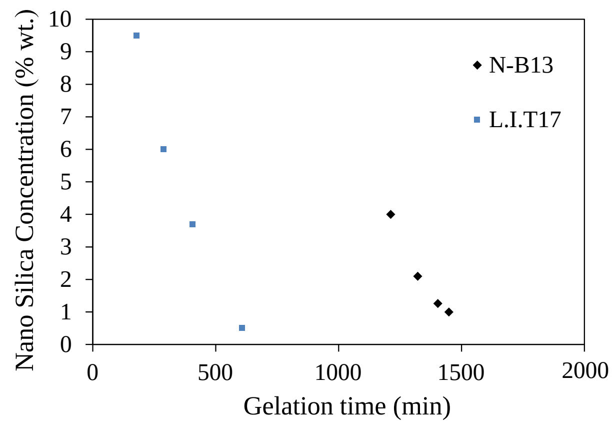


Fig. 12. Different nano silica concentration at different gelation time. N-B13 = 2.15% wt. of ZnO.

to the result of literature (Helvacıoğlu et al., 2011; Adewunmi et al., 2018). For more detail refer to Table A1 in appendix.

4.3 Effect of PAM and PEI concentration

The concentrations of cross linker and polymer were critical for the structure and properties of nano-polymer solution. With increasing PAM concentration in the solution, the viscosity of the solution increases gradually. The optimum ratio of PEI and PAM concentration would be around 0.8 and 1.1% respectively, at this range nano-chemical N-B solution displayed a higher elastic modulus. This modulus depends on cross-linker and polymer concentration from both organically or inorganically cross-linker (Omari, 1995; Grattoni et al., 2001). Whilst others (Zhao et al., 2015) have made similar observations; by increasing polymer and cross-linker concentrations, both elastic and viscous modulus increase, see Fig. 9. On the other hand, an increase of PAM concentration in the nano-chemical solution leads to shorter gelation time therefor inorganic salts can also be used to retard the gelation reaction, see Fig. 10. Table A1 in appendix provides the compositions of literature data displayed in Figs. 9 and 10.

4.4 Effect nano particles

Nano silica is widely used in the oil industry design for conformance control and water shut-off. It has a small size and large specific surface area. The Nano silica particles are stabilized in an alkaline pH solution and carry negative charge in which there is repulsion forces preventing them from colliding with each other; the zeta potential is lowered, so that the gelation is triggered by adding the counter ions (Lakatos et al., 2015). The gelation time is an important parameter of water shutoff, which is closely related to the time required for conformance control in the field. The effect of nano particles on the gelation time was investigated, and the result showed in Fig. 11.

In this study, two types of nano particles were used at different concentrations. Nano particle ZnO and SiO_2 have molecular weight of around 81.38 gm/mol and particle size ranges between 50-100 nm. The objective of using nano particle as discussed in literature was to increase viscosity and gel strength of the polymer solution. The elastic modulus of N-B solution increased when 2.15% wt. of ZnO added to the solution. The improvement of gel strength was by a ratio of 1.52.

The gelation time is mainly controlled by of cross-linkers. Since the cross-linker PEI concentration was kept constant, the change of gelation time for N-B solution can be inferred to the presence of nano silica. This has reduced the gelation time and acted as cross-linker role because nano silica may have interacted with water and helped the solution with thickening and solidifying quickly.

When the concentration of nano silica increased, the gelation time was reduced, see Fig. 12. This might have happened because The Nano silica acted as the thickening additive in the solution. (Zeyghami et al., 2014) reported similar observation the increase of viscosity when nano silica/AM-AMPS added to the solution (acrylamide copolymer of 2-acrylamido-2-methyl-propanesulfonate).

The adsorption mechanism for negatively charged polycarboxylate ether was considered to be hydrogen bonding of the side chains with the silica particles. The increase of nano silica concentration leads to increase in viscosity of the polymer solution and decrease in gelation time (Zhu et al., 2014; Lashari et al., 2018; Fadil et al., 2020; Pereira et al., 2020).

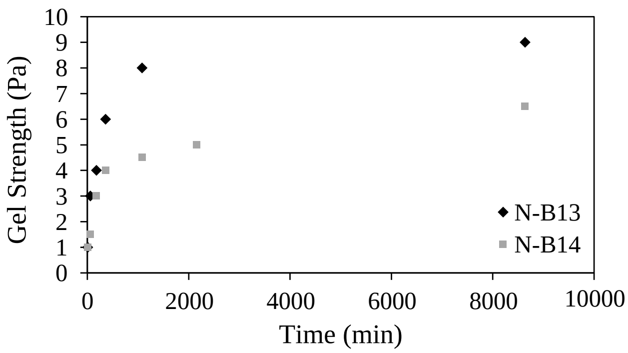


Fig. 13. Gel strength for different Nano-polymer solution at different time. N-B13 = '2.15% wt. of ZnO'; N-B14 = '2.15% wt. of SiO_2'.

However, the types of the nano-chemical have significant impact on rheology of the polymer solution. Fig. 13 shows the effect of ZnO and SiO_2 on gel strength of the nano-polymer solution. Three concentrations (0.65%, 1.1%, 2.15% wt) for each nano particles (ZnO and SiO_2) were investigated on N-B rheology. For each nano-chemical, the concentration were studied. When nano (ZnO) particles were added, the nano-chemical solution became more viscous and showed an improved elastic property if compared with the same concentration of the (SiO_2); therefore, this nano-chemical (ZnO) it's in it, higher rheological properties and gel strength. Moreover, ZnO has high electrical stability. The nano ZnO could improve the fabricated nano composites, mechanical and barrier properties, and could change the thermal and optical properties of the composite. ZnO is owing to the improvement of yield point (Wang, 2004; Youssef et al., 2015).

The summary of these sensitivity tests determining which composition would perform optimally at reservoir condition is explained in Table 3. The optimum concentration for the field application is determined and the next phase of the project will be assessing N-B at porous media. Fig. 14 illustrate the effect of each parameter on gel strength at 600 minutes. Obliviously PAM, PEI and coated-clay concentrations were the main parameters affecting the quality of nano-chemical solution. SiO_2 nano particles showed the least effect on the gel strength.

5. Conclusions

The following points are the main key takeaways from this research work:

Table 3. The best (polymer, cross-linker and nano-chemicals) concentration used for conformance control.

No	PAM Con	PEI Con	Coated-Clay Con	Nano (ZnO) Con	Nano (SiO_2) Con
1	1.1% wt.	0.36% wt.	8.6% wt.	0.65% wt.	0.54% wt.

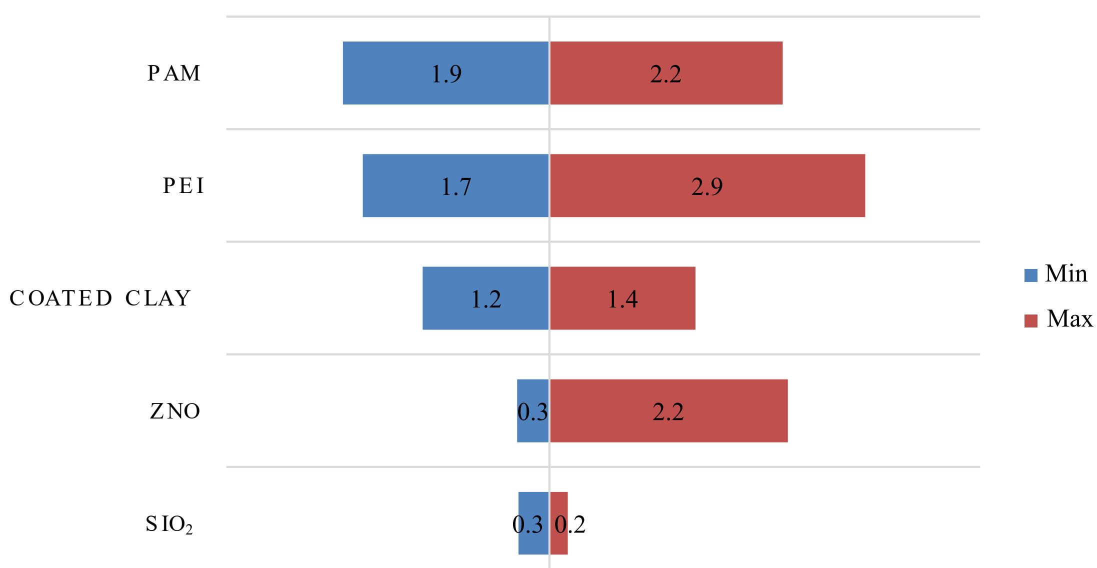


Fig. 14. Shows the magnitude of each parameter on gel strength at 600 minutes.

- The coated-clay delays gelation time if compared to the non-coated-clay. The reason of this observation is that the coatings preventing the clay particle to react with water.
- When an amount of Nano-particles added to the solution, the mechanical properties of nano-chemical polymer improved significantly.
- The swelling ratios of the nano-chemical solution increased to a certain time, but it has been degraded and decreased its gel strength after 10 hrs.
- Elastic modulus of the polymer solution with Nano-particles had a higher viscosity than the polymer without it.
- The PAM and PEI cross linked gel with and without nano silica show favorable elastic property but different in gelation time.

Acknowledgement

Authors would like extend our appreciation to University Sulaimani Polytechnic for providing the labs and necessary equipment to conduct the experimental work. Furthermore, we thank Dr. Kosar Kamal for conducting the CT-scan of the core samples used by this work.

Conflict of interest

The authors declare no competing interest.

References

Aalaie, J., Vasheghani-Farahani, E., Rahmatpour, A., et al. Effect of montmorillonite on gelation and swelling behavior of sulfonated polyacrylamide nanocomposite hydrogels in electrolyte solutions. European Polymer Journal, 2008, 44(7): 2024-2031.

Adewunmi, A. A., Ismail, S., Sultan, A. S. Crosslinked polyacrylamide composite hydrogels impregnated with fly ash: Synthesis, characterization and their application as fractures sealant for high water producing zones in oil and gas wells. Journal of Polymers and the Environment, 2018, 26(8): 3294–3306.

Aifen, L., Haopeng, S., Haojun, X. Influence of inaccessible pore volume on seepage law of polymer flooding. Petroleum Geology and Recovery Efficiency, 2016, 2: 70-75.

Al-Dhafeeri, A., Nasr-El-Din, H. A., Seright, R., et al. High-permeability carbonate zones (super-K) in Ghawar Field (Saudi Arabia): Identified, characterized, and evaluated for Gel treatments. Paper SPE 97542 Presented at International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, Malaysia, 5-6 December, 2005.

Allison, J. D., Purkaple, J. D. Reducing permeability of highly permeable zones in underground formations, United States Patent, 1988.

Al-Muntasheri, G. A. Conformance control with polymer gels: What it takes to be successful. Arabian Journal for Science and Engineering, 2012, 37(4): 1131-1141.

Al-Muntasheri, G. A., Nasr-El-Din, H. A., Al-Noaimi, K. R., et al. A study of polyacrylamide-based gels crosslinked with polyethyleneimine. SPE Journal, 2009, 14(2): 245-251.

Al-Muntasheri, G. A., Sierra, L., Garzon, F., et al. Water shut-off with polymer gels in a high temperature horizontal gas well: a success story. Paper SPE 129848 Presented at Improved Oil Recovery Symposium, Tulsa, Oklahoma, 24-28 April, 2010.

Amiri, S. Preparation and characterization of nanoclay-based (Na-MMT and bentonite) polyacrylamide hydrogels as water shut-Off agent for enhanced oil recovery. Silicon, 2019, 11(3): 1193-1203.

Buchgraber, M. An enhanced oil recovery micromodel study with associative and conventional polymers. Leoben, University of Leoben, 2008.

Cai, S., He, X., Kun, L., et al. Interaction between HPAM and urea in aqueous solution and rheological properties. Iranian Polymer Journal, 2015, 24(8): 663-670.

El-Karsani, K. S. M., Al-Muntasheri, G. A., Sultan, A. S., et al. Gelation of a water-shutoff gel at high pressure and high temperature: rheological investigation. SPE Journal, 2015, 20(5): 1103-1112.

Fadil, N. A., Sonny, I., Isa, N. A. M., et al. Gelation behavior of polyacrylamide reinforced with nano-silica for water shutoff treatment in oil field. Solid State Phenomena, 2020, 307: 252-257.

Grattoni, C. A., Al-Sharji, H. H., Yang, C., et al. Rheology and permeability of crosslinked polyacrylamide gel. Journal of Colloid and Interface Science, 2001, 240(2): 601-607.

Hardy, M., Botermancs, W., Hamouda, A., et al. The first carbonate field application of a new organically crosslinked water shutoff polymer system. Paper SPE 50738 Presented at International Symposium on Oilfield Chemistry, Houston, Texas, 13-16 February, 1999.

Helvacıoğlu, E., Aydin, V., Nugay, T., et al. High strength poly (acrylamide)-clay hydrogels. Journal of Polymer Research, 2011, 18(6): 2341-2350.

Jia, H., Zhao, J-Z., Jin, F-Y., et al. New insights into the gelation behavior of polyethyleneimine cross-linking partially hydrolyzed polyacrylamide gels. Industrial & Engineering Chemistry Research, 2012, 51(38): 12155-12166.

Jiang, Z., Cao, X., Li, Z., et al. Rheological behaviors and secondary networks of polyacrylamide hydrogel filled with silica. Journal of Petroleum Exploration and Production Technology, 2016, 6(1): 93-99.

Lakatos, I. J., Lakatos-Szabo, J., Szentes, G., et al. New alternatives in conformance control: Nanosilica and liquid polymer aided silicate technology. Paper SPE 174225 Presented at European Formation Damage Conference and Exhibition, Budapest, Hungary, 3-5 June, 2015.

Lashari, Z. A., Yang, H., Zhu, Z., et al. Experimental research of high strength thermally stable organic composite polymer gel. Journal of Molecular Liquids, 2018, 263: 118-124.

Moradi-Araghi, A. A review of thermally stable gels for fluid diversion in petroleum production. Journal of Petroleum Science and Engineering, 2000, 26(1-4): 1-10.

Moradi-Araghi, A., Bjornson, G., Doe, P. H. Thermally stable gels for near-wellbore permeability contrast corrections. SPE Advanced Technology Series, 1993, 1(1): 140-145.

Mousavifar, M. A., Kharrat, R., Parchizedeh, A., et al. Comparison between EOR methods (gas Injection, water injection and WAG processes) in one of Iranian Fractured oil reservoirs. International Journal of Engineering Science, 2012, 3(4): 503-507.

Okay, O., Oppermann, W. Polyacrylamide-clay nanocomposite hydrogels: Rheological and light scattering characterization. Macromolecules, 2007, 40(9): 3378-3387.

Omari, A. Rheological study of the gelation kinetics of the scleroglucan—zirconium system. Polymer, 1995, 36(4): 815-819.

Pereira, K. A. B., Aguiar, K. L. N., Oliveira, P. F., et al. Synthesis of hydrogel nanocomposites based on partially hydrolyzed polyacrylamide, polyethyleneimine, and modified clay. ACS Omega, 2020, 5(10): 4759-4769.

Qin, W., Krzysztof, W. A. Water problems and control techniques in heavy oils with bottom Aquifers. Paper SPE 125414 Presented at Americas E&P Environmental and Safety Conference, San Antonio, Texas, 23-25 March, 2009.

Seright, R. S., Lane, R. H., Sydansk, R. D. A strategy for attacking excess water production. SPE Production & Facilities, 2003, 18(3): 158-169.

Sheng, J. J. Polymer flooding—fundamentals and field cases, in Enhanced Oil Recovery Field Case Studies, edited by J. Sheng, Elsiver, Houston, pp. 63-82, 2013.

Sheng, J. J., Leonhardt, B., Azari, N. Status of polymer-flooding technology. Journal of Canadian Petroleum Technology, 2015, 54(2): 116-126.

Sidiq, H., Abdulsalam, V., Nabaz, Z. Reservoir simulation study of enhanced oil recovery by sequential polymer flooding method. Advances in Geo-Energy Research, 2019, 3(2): 115-121.

Sidiq, H. H., Amen, R., Kennaird, T. A laboratory investigation of water abatement chemicals for potential use in the wanaea oil field. Paper SPE 117142 Presented at Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, UAE, 3-6 November, 2008.

Soka, S., Sidiq, H. Nano chemical design for excessive water production control in Taq Taq oil field. Paper SPE 208546 Presented at Eastern Europe Subsurface Conference, Kyiv, Ukraine, 23-24 November, 2021.

Standnes, D. C., Skjevrak, I. Literature review of implemented polymer field projects. Journal of Petroleum Science and Engineering, 2014, 122: 761-775.

Sydansk, R. D., Southwell, G. P. More than 12 years' experience with a successful conformance-control polymer-gel technology. SPE Production & Facilities, 2000, 15(4): 270-278.

Vega, I., Morris, W., Robles, J., et al. Water shut-off polymer systems: Design and efficiency evaluation based on experimental studies. Paper SPE 129940 Presented at Improved Oil Recovery Symposium, Tulsa, Oklahoma, 24-28 April, 2010.

Wang, Z. L. Zinc oxide nanostructures: Growth, properties and applications. Journal of Physics: Condensed Matter, 2004, 16(25): R829-R858.

Xin, H., Ao, D., Wang, X., et al. Synthesis, characterization, and properties of copolymers of acrylamide with sodium 2-acrylamido-2-methylpropane sulfonate with nano silica structure. Colloid and Polymer Science, 2015, 293(5): 1307-1316.

Youssef, A. M., Yousef, H. A., El-Sayd, S. M., et al. Mechanical and antibacterial properties of novel high performance chitosan/nanocomposite films. International Journal of Biological Macromolecules, 2015, 76: 25-32.

Zeyghami, M., Kharrat, R., Ghazanfari, M. H. Investigation of the applicability of nano silica particles as a thickening additive for polymer solutions applied in EOR processes. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2014, 36(12): 1315-1324.

Zhao, G., Dai, C., Zhao, M., et al. Investigation of preparation and mechanisms of a dispersed particle gel formed from a polymer gel at room temperature. PLoS One, 2013, 8(12): e82651.

Zhao, G., Fang, J., Gao, B., et al. Study and application of the adsorption of anionic and cationic polymer. Oilfield Chemistry, 2015, 32: 62-66.

Zhu, D., Han, Y., Zhang, J., et al. Enhancing rheological properties of hydrophobically associative polyacrylamide aqueous solutions by hybriding with silica nanoparticles. Journal of Applied Polymer Science, 2014, 131(19): 40876.

Appendix A

Table A1. Effect the amount of polymer and composition on gelation Time.

Test symbol	Polymer composition	PAM Conc. % wt.	PEI Conc. % wt.	References
L.I.T1	PAM/PEI/KCl/Cross-linker	0.5		Vega et al. (2010)
L.I.T2	PAM/PEI/KCl/Cross-linker	0.7		Vega et al. (2010)
L.I.T3	PAM)/PEI/KCl/Cross-linker	1		Vega et al. (2010)
L.I.T4	PAM, Partially hydrolized PAM ammonia (NH_3) and cromium3, PEI, Zirconium			Al-Muntasheri (2012)
L.I.T5	PAtBA, PEI, NaCl, Crosslinker			Al-Muntasheri et al. (2010)
L.I.T.6	Acrylamid, acrylic acid, methyl methacrylate			Zhao et al. (2013)
L.I.T7	PAtBA 7% wt./PEI		1	Al-Muntasheri et al. (2009)
L.I.T8	PAM/Clay, nanocomposed copolyme, materials = cromium3, NaCl			Amiri (2019)
L.I.T9	PAM/PEI/Coal fly ash (2% wt.)			Adewunmi et al. (2018)
L.I.T10	Neat PAAm with ethylene glycol dimeth acrylate			Helvacıoğlu et al. (2011)
L.I.T11	PAM/PEI	3		El-Karsani et al. (2015)
L.I.T12	PAM/PEI	5		El-Karsani et al. (2015)
L.I.T13	PAM/PEI	7		El-Karsani et al. (2015)
L.I.T14	PAM/PEI		0.3	El-Karsani et al. (2015)
L.I.T15	PAM/PEI		0.6	El-Karsani et al. (2015)
L.I.T16	PAM/PEI		0.9	El-Karsani et al. (2015)
L.I.T17				Fadil et al. (2020)

Table A2. Chemical analysis of the brine water.

NO.	Ion	Concentration (mg/L)
1	Cl^-	70
2	Ca	32
3	MG	14.57
4	SO_4	97.5
5	Ph	8.7
6	TDS	305.28
7	Total hardness	140
8	Electrical Conductivity	477 ms/cm