

Effect of Inorganic Polymer Gel Systems on Residual Resistance Factor in Fractured Core Model

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ABSTRACT: Excessive water production through fractures become an important problem in oil exploration of fractured reservoirs. For this purpose, polymer gels were prepared by crosslinking of aqueous solutions of polymer and crosslinker for the purpose of water management in high water cut fractured reservoirs. A copolymer of sulfonated polyacrylamide was used as polymer and chromium triacetate ($\text{Cr}(\text{OAc})_3$) and aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were used as inorganic crosslinkers at 90°C . Two quadratic models were presented for the two inorganic polymer gel systems to predict the gelation time by using a central composite design which showed highly significant results. The results also showed that polymer concentration was the main effect on gelation time. Increasing polymer concentration leads to accelerate the gelation process and then decrease of gelation time. Based on the gelation time and strength of three dimensional structure of polymer gel, the selected polymer gels of $\text{Cr}(\text{OAc})_3$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were applied to study the performance of polymer gel system in fractured core with the same polymer concentration of 37071 ppm and the crosslinker concentration of 13096 ppm and 2707 ppm, respectively. Also, the gelation time of these polymer gels was determined 12 h and 34 h, respectively. For this purpose, the coreflooding test was carried out to measure the output flow rate before and after polymer gel treatment in order to calculate the Residual Resistance Factor (RRF). As a result, after polymer gel treatment, the output flow rate decreased intensively and by increasing injection pressure, the RRF decreased gradually. The polymer gels of $\text{Cr}(\text{OAc})_3$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in the fracture were renitent up to 70 and 60 bar against the water pressure drop, while these polymer gels were renitent up to 60 and 40 bar against the oil pressure drop, respectively. The polymer gel of $\text{Cr}(\text{OAc})_3$ demonstrated a higher residual resistance factor than the polymer gel of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

KEYWORDS: Polymer gel treatment, Inorganic crosslinker, Gelation time, Fracture core, Residual resistance factor.

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INTRODUCTION

Some parts of hydrocarbon reservoirs are fractured consist of hydraulic or natural fractures which can produce an enormous volume of water among the process of hydrocarbon production [1, 2]. Excess water produced from fractured reservoirs is a serious issue in oil production. Water cut production not only limits the life of production wells but also causes several problems including corrosion, sand production and facilities cost to separate excessive water [3-5]. Several chemical and mechanical water shutoff methods such as polymer gels, preformed particle gels, resins and elastomers, expandable packers, bridge plug, and so on, have been used in the oil reservoir [6-8]. Among all, polymer gel is relatively low-cost and has shown its effectiveness for water management in fractured reservoirs by sealing fractures near wellbore [9-10]. Polymer gel systems generally contain a mixture of polymer and crosslinker which called gelant. The common polymers used for water shutoff treatments are usually synthetic polymers such as polyacrylamides and a natural polymer such as polysaccharides [11]. Crosslinkers are also categorized into metallic or organic. In metallic polymer gel systems, the reaction took place between the carboxylate groups of the polymer chain and the multi-valent cations forming ionic bonds. Chromium is the most widely used as a metallic crosslinker in order to curb the high water production rate in fracture reservoirs [7, 12]. The crosslinking metal ion Cr^{+3} can be placed in a solution in the form of chromium acetate, chromium malonate and chromium propionate [9, 13]. Other metallic crosslinkers used include aluminum added to polyacrylamides in form of aluminum citrate, titanium and zirconium that have lower toxicity than chromium metal ions are also frequently used in near wellbore applications [14, 15]. Acrylamide-based polymers with an organic crosslinker such as phenol and formaldehyde proposed by *Albonico* and *Lockhart* [16]. The phenol-formaldehyde polymer gel system can be survived over several months at temperatures up to 150 °C [17]. Phenol and formaldehyde are toxic and not environmentally friendly, so researchers proposed other alternatives such as hexamethylenetetramine (HMTA) and hydroquinone that are suitable for high temperature reservoirs [17-18]. Polyethyleneimine (PEI) has been also used as an organic crosslinker for different acrylamide-based polymers that can be used at a wide range of

temperatures [15, 19-20]. Among acrylamide-based polymers, the polyacrylamide and t-butyl acrylate (PAtBA)/PEI system is a favorite polymer gel, which has been performed in several reservoirs around the world to deal with water shutoff treatment. The drawback of these polymer gel system for water shutoff treatment is the high cost because the required polymer concentration is too high (as much as 7 wt %) [20].

The objective of this research is the comparison study of the two inorganic crosslinkers (chromium acetate as a common polymer gel system used for water cut reduction in fractured reservoirs and aluminum nitrate nonahydrate as a new inorganic crosslinker) on the gelation time and their performance in water shutoff treatment at temperature of 90 °C. It must be mentioned that gelation time is an important parameter in water shutoff operation. To have a successful gelant operation in natural fractured reservoirs, the gelant must be placed deep into the fracture of the reservoir to divert water path or water stream. Therefore, if the gelation time is too short, the gelant would form rapidly, block the fracture and high permeable zones near wellbore regions and gel can no longer disperse through formation rock. In other words, if the gelation time is too long, gel forming would take some time while the production operation must be suspended which is not acceptable economically [12].

For this purpose, by using Central Composite Design (CCD) as the most popular form of Response Surface Methodology (RSM) experiments designed to predict the gelation time of these polymer gels. By using CCD, not only the effect of each factor was studied on the gelation time of the polymer gel, but also two quadratic mathematical models were presented for the two inorganic polymer gels systems with high significance. The performance of polymer gel in water shutoff treatment was evaluated with Residual Resistance Factor (RRF) which defined as the resistance to the flow of injected water or oil after polymer gel treatment. Water and oil RRF was investigated by the coreflooding test which conducted to confirm that polymer gel application in the fracture can be an effective method for water shutoff treatment. For this end, two fractured core models were applied in the coreflooding test and RRF of water and oil were obtained for each polymer gel system. Therewith, the resistance of the polymer gels to water and oil flow in the fracture was evaluated by the coreflooding test at high injection pressures.

Table 1: Chemical composition of formation water.

Composition	Concentration (ppm)
Na ⁺ /K ⁺	63024
Ca ²⁺	13600
Mg ²⁺	2673
Cl ⁻	127436
HCO ₃ ⁻	2440
SO ₄ ²⁻	500
Total	209673

EXPERIMENTAL SECTION

Materials

The polymer gels were conducted by using an acrylamide-based polymer which is a copolymer of 2-acrylamido-2-methyl-propanesulfonic-acid sodium salt (AMPS) and acrylamide (AcA), with an average molecular weight of 2000 kDaltons. This copolymer was supplied by SNF Floerger Co. (France) and also called sulfonated polyacrylamide (PAMPS), under the trade name of AN125 VLM, in white powder form. In addition, two inorganic crosslinkers used in this research were chromium triacetate and aluminum nitrate nonahydrate, purchased from Carlo Erba Co. (Italy) and Sigma-Aldrich Co. (Germany), respectively. The Chemical composition of formation water used in this paper is reported in Table 1 and purchased from Sigma-Aldrich Co. (Germany).

Preparation of Polymer Gels

Gelant solutions were prepared by mixing the polymer solution of required concentration and a certain amount of crosslinkers at room temperature according to the following steps. Firstly, in order to prepare the PAMPS solutions, at the concentration of 5%, the solutions were obtained by mixing the copolymer powder and distilled water for the period of 24 h and then held, without stirring, for 2 days to obtain a homogeneous solution. Shortly before the experiment, the PAMPS solutions were diluted to the required concentrations and the mixtures were stirred in 200 rpm for 5 min by a magnetic stirrer (Stuart CB162). The spinning rate is equal for all the samples. Then, crosslinker was also mixed with distilled water at room temperature for 5 min, as a second solution. Finally, the PAMPS and second solutions were mixed for 10 min to obtain the

homogeneous gelant solution. Since most of the south Iranian reservoirs have a high temperature, around 90°C, this temperature was selected for experiments and the samples were kept in the glass tube at the 90°C oven.

Gelation Time Determination

Gelation time is defined as the time required for the gelant to form a gel. The gelation time will determine the injection period and how deep the gel solution can be placed into the formation. The process of gelation starts very slowly with no apparent increase in viscosity for a period of time, followed by a period of the rapid increase in viscosity. Therefore, gelation time may be defined as the time at which the rapid increase in viscosity is observed, or the time at which the viscosity reaches a certain value [21]. In this work, the bottle test method was used to study the effect of polymer and crosslinker concentrations on the gelation time of polymer gel. Generally, the bottle test method, as an experimental technique, provides semi-quantitative measurement of gelation rate and gel strength. Also, it can be considered as a faster and inexpensive method to study gelation kinetic. In this method, which was defined by Sydansk [22], gel strength during the development of gelation kinetic was expressed as an alphabetic code of A through I. According to this method, the gel strength codes were ranged from high flowing gels with barely any gel structure visibly detectable to rigid rubbery gels as alphabetical codes of A, B, C, D, E (fluid hydrogel), F, G, H (non-fluid hydrogel), I, and J (gel) [22]. Therefore, the gelation time was considered as the period of time which change is no longer observed in the gel strength code. In the present work for each test, the gelant solution was formulated and placed in the bottle at 90°C. The bottle was inverted during each reading time at different intervals and the gel flow behavior was recorded under the influence of gravity. Finally, a gel strength code was allocated with its related code.

Coreflooding Setup

For the coreflooding experiment, two cylindrical core samples with a diameter of 36 mm and a length of 72 mm were used to fabricate the fractured core model. As shown in Fig. 1, each cylindrical core sample was cut in half from the center, and then inserted two rectangular stainless-steel sheets (width of 15 mm and a length of 72 mm)



Fig. 1: Schematic of the fractured core model used in the coreflooding test.

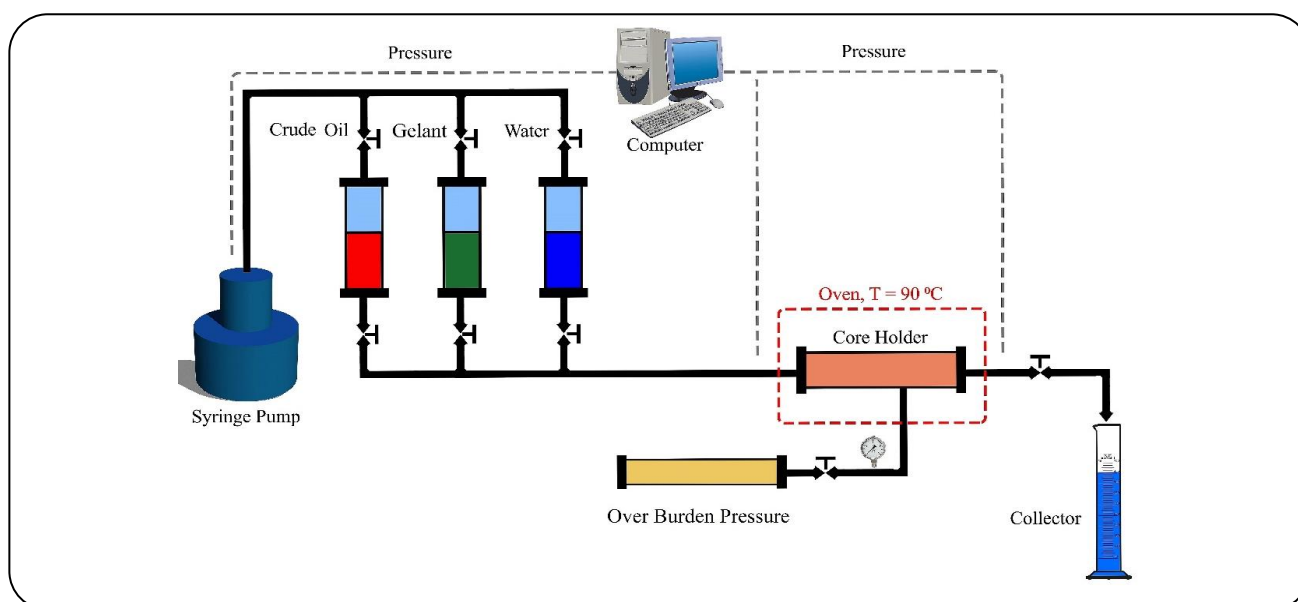


Fig. 2. Schematic diagram of the coreflooding setup.

as a spacer between two halves of the cylindrical core to obtain a fractured core model. The fracture width and length were 0.1 mm and 5 mm, respectively.

The coreflooding experiment was conducted to evaluate the performance of the polymer gel on Disproportionate Permeability Reduction (DPR) to water and oil in the fractured core model. The schematic diagram of the coreflooding setup is shown in Fig. 2. The experimental setup consisted of a syringe pump, a transfer vessel, a hand pump, a core holder, and a pressure transducer connected to a desktop computer for the recording of the pressures. The experimental procedure of coreflooding is presented as follows:

1) Formation water was injected in several flow rates and the absolute permeability of the fractured core model was calculated.

2) Crude oil was injected to displace water until there is no evidence of water in output and ensure to reach residual water saturation condition.

3) Formation water was injected in several injection pressure and the output flow rate of water was recorded.

4) Gelant was injected into fractured core and the experimental system was kept intact for 48 h at 90°C to ensure gelant forms a three dimensional network structure.

5) Formation water was injected again in several injection pressures (all injection pressures were the same as step 3) output flow rate of water after polymer gel treatment was recorded, and then RRF for water (F_{nw}) was calculated.

6) The polymer gel that absorbed the surface of the fracture was cleaned and the fractured core model was employed again in the core holder.

7) Crude oil injected to fractured core model to reach the oil saturation condition.

8) Formation water was injected to displace crude oil there is no evidence of crude oil in output and ensure to reach residual oil saturation condition.

9) Step 3 to Step 5 was repeated by a difference that instead of formation water used crude oil to calculate RRF for oil (F_{ro}).

CCD Approach

In other to investigate the interaction effect of two factors (polymer and crosslinker concentration) towards response (gelation time), Central Composite Design (CCD) was used as the most popular form of response surface methodology [23, 24].

According to the central composite design, the total number of experimental combinations is $N=2^K+3K+C_p$, where K is the number of independent variables and C_p is the number of repetitions of the experiments at the center point. For statistical calculation, the experimental variables X_i have been coded as x_i according to the following transformation equation:

$$x_i = \frac{x_i - x_o}{\Delta x} \quad (1)$$

Where x_i is the dimensionless coded value of the variable X_i , x_o is the value of X_i at the center point, and Δx is the step change. The value of star points can be obtained as well; $\alpha=2^{K/4}$. Since 2 factors were used in this study, the value of α was 1.41. Enough information could be generated to fit a second-order polynomial called "quadratic", using these many levels. Standard statistical software can compute the actual fitting of the model. Coded factors can be presented in five levels ($-\alpha, -1, 0, +1, +\alpha$). The optimum gelation time condition having satisfactory performance can be achieved with a minimum number of experiments without any need of studying all possible combinations experimentally. In order to evaluate the random error, three central points were designed in the table to evaluate each factor in the average value of its minimum and maximum. So, the random error and the amount of model significance would be determined by using the analysis of variance (ANOVA) [21].

Residual Resistance Factor (RRF)

The RRF of water or oil related to permeability reduction caused by the polymer gel treatment. According

to Darcy's law, Newtonian fluid flow can be expressed as [24-25]:

$$Q = \frac{kA}{\mu L} (P_{in} - P_{out}) \quad (2)$$

Where Q is the flow rate; k is the absolute permeability; μ is the viscosity of fluid; A is the sectional area of the fractured core; L is the fracture core length, and $P_{in} - P_{out}$ refer to the pressure drop across the fractured core. The RRF was calculated by dividing the permeability before the polymer gel treatment by the permeability of after the polymer gel treatment. According to Eq. (2), the RRF can be computed by dividing the injection flow rate before the polymer gel treatment by the injection flow rate after the polymer gel treatment at the same pressure drop, as follows:

$$F_{rrw} = \frac{k_b}{k_a} = \frac{Q_b}{Q_a \Delta P} \quad (3)$$

Where F_{rrw} is water residual resistance factor; k_b is permeability before the polymer gel treatment; k_a is permeability after the polymer gel treatment; Q_b is the injection flow rate before the polymer gel treatment; and Q_a is the injection flow rate after the polymer gel treatment. According to the coreflooding procedures the residual resistance factor for water and oil can be calculated by Eq. (3).

RESULTS AND DISCUSSION

The selected control factors, polymer concentration (A) and crosslinker concentration (B) are illustrated in Table 2. A range of 20000-40000 ppm of polymer concentration and the suitable ranges crosslinker concentration for two kinds of inorganic crosslinker were selected to determine their effect on the gelation time.

Modeling Process Remarks

Twelve bottle test experiments were designed to determine the interaction effect of polymer concentration and crosslinker concentration on gelation time by CCD method. The results of the strength code (H) of polymer gels were presented at different recording times (Table 3). According to the results, the syneresis phenomenon was occurred for sample 3 of $Cr(OAc)_3$ polymer gel and sample 5 of $Al(NO_3)_3 \cdot 9H_2O$ polymer gel after 140 and 110 days, respectively. The syneresis phenomenon refers to shrinkage and reduces the volume of polymer gel because

Table 2: Experimental factors and levels in central composite design.

Variable		$-\alpha = -1.41$	(-1)	(0)	(+1)	$+\alpha = +1.41$
A: Polymer concentration (ppm)	AN125VLM	20000	22929	30000	37071	40000
B: Crosslinker concentration (ppm)	Cr(OAc) ₃	2000	3904	8500	13096	15000
	Al(NO ₃) ₃ .9H ₂ O	1000	1293	2000	2707	3000

Table 3: The variation of polymer gel strength codes at different times.

Time (h)	Chromium acetate												Aluminum nitrate nonahydrate											
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12
2	A	A	A	A	A	A	A	A	A	B	A	A	A	A	A	A	A	A	A	A	A	A	A	A
4	B	E	F	B	C	A	B	C	B	F	B	B	A	A	A	A	A	A	A	A	A	B	A	A
8	B	F	G	D	E	B	D	D	D	H	D	D	A	B	B	A	B	B	A	A	A	C	A	A
12	C	G	H	E	G	B	E	F	E	I	E	E	A	D	E	B	B	D	B	B	B	D	B	B
16	C	I	I	G	H	C	G	E	G	I	F	G	B	F	F	B	F	D	B	B	B	F	D	B
24	E	I	I	H	I	E	H	G	H	I	G	H	C	F	G	D	G	E	D	D	D	E	E	D
36	F	I	I	I	I	F	I	I	I	I	I	I	E	H	I	F	H	F	F	E	F	H	E	F
48	G	I	I	I	I	G	I	I	I	I	I	I	F	I	I	H	I	G	H	F	H	I	E	H
72	I	I	I	I	I	I	I	I	I	I	I	I	F	I	I	I	I	I	I	G	I	I	F	I
96	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	H	I
120 (10 days)	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
360 (15 days)	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
720 (30 days)	I	I	I	I	I	I	I	I	I	I	I	I	I	S	I	I	I	I	I	I	I	I	I	I
1080 (45 days)	I	I	I	I	I	I	I	I	I	I	I	I	I	-	I	I	I	S	I	I	I	I	I	I
1440 (60 days)	I	I	I	I	I	I	I	I	I	I	I	I	I	-	I	I	I	-	I	I	I	I	I	I
2160 (90 days)	S	I	I	I	I	S	I	I	I	I	I	I	I	-	S	S	I	-	S	I	S	I	I	S
2640 (110 days)	-	I	I	S	I	-	S	S	S	I	I	S	S	-	-	-	I	-	-	S	-	S	I	-
2880 (120 days)	-	I	I	-	I	-	-	-	-	I	S	-	-	-	-	-	S	-	-	-	-	-	S	-
3360 (140 days)	-	S	I	-	S	-	-	-	-	I	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3840 (160 days)	-	-	S	-	-	-	-	-	-	S	-	-	-	-	-	-	-	-	-	-	-	-	-	-

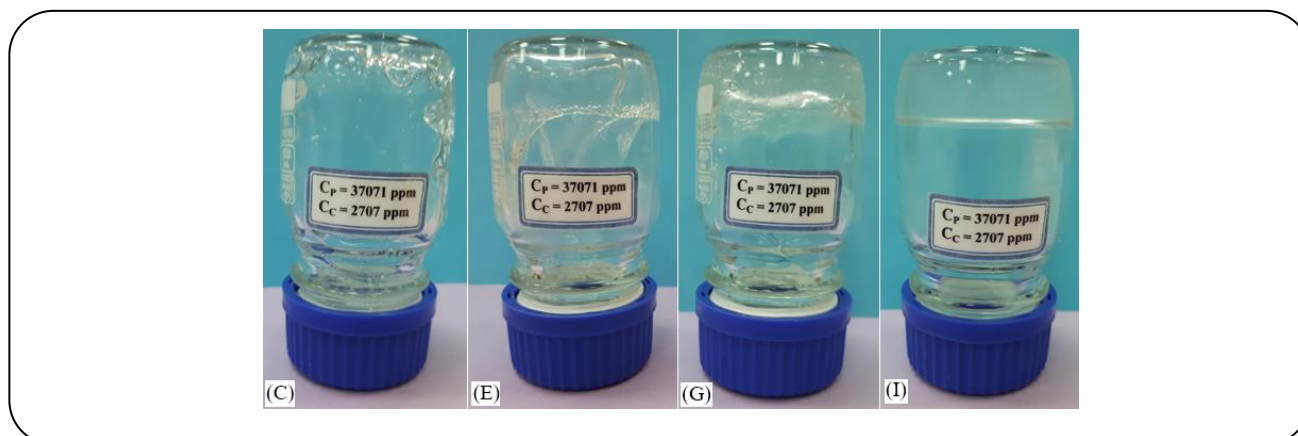
of extraction of water phase from the polymer network structure [12]. When the syneresis phenomenon occurs the water phase of hydrogel extracts and polymer structure shrinkages, whereby the performance of the hydrogel system reduces in hydrocarbon reservoirs. Fig. 3 shows the situation of polymer gel at four different times which describe with gel strength code. As it is illustrated by increasing time at the temperature of 90°C, 3D structure

of polymer gel formed when polymer gel surface showed no deformation under the gravity effect (code I).

Table 4 shows the experimental plan of the polymer gels and the gelation time as a response at the temperature at 90°C. In order to find the mathematical model, the responses (gelation time) were inserted in "Design Expert (DX7)" software (State-Ease, version 7.1.3, USA).

Table 4: The experimental plan of the gelation times and their responses.

Run	Polymer concentration (ppm) (A)	Crosslinker concentration (ppm) (B)		Hydrogel gelation time (h)	
		Cr(OAc) ₃	Al(NO ₃) ₃ .9H ₂ O	Cr(OAc) ₃	Al(NO ₃) ₃ .9H ₂ O
1	20000	8500	2000	52	92
2	30000	15000	1000	14	37
3	37071	13096	1293	12	32
4	30000	8500	2000	24	51
5	37071	3904	2707	15	34
6	22929	3904	1293	57	59
7	30000	8500	2000	24	52
8	30000	2000	3000	31	78
9	30000	8500	2000	25	50
10	40000	8500	2000	8	35
11	22929	13096	2707	27	98
12	30000	8500	2000	24	51

Fig. 3: The appearance of Al(NO₃)₃.9H₂O polymer gel at different strength code.c

Among several possible models, two quadratic models were found to be adequate for the prediction of the gelation time which was given by the following equations:

Gelation Time (h):Polymer gel of Cr(OAc)₃

$$\text{Gelation Time} = 24.25 - 14.9A - 7.13B + 6.75AB + 3.35A^2 \quad (4)$$

Polymer gel of Al(NO₃)₃.9H₂O

$$\text{Gelation Time} = 51 - 21.45A + 12.37B - 9.25AB + 4.65A^2 \quad (5)$$

In these models, all variables are indicated through the coded values, where A is polymer concentration and B is crosslinker concentration and hence AB is considered as the interaction of the main factors. As can be seen in presented equations the interaction between variables had significant effects on the responses; so here the results are preferably presented and discussed in terms of interactions. The statistical significance of Eqs. (4) and (5) is shown in Table 5, where the mean square, the sum of squares and model Degree of Freedom (DOF) terms are, respectively, defined as the estimation of the model variance, a total of the sum of squares for the terms in the model and the number of model terms. DOF shows

Table 5: The ANOVA results of the developed model.

			Sum of square	DOF	Mean square	F-value	P-value	R ²
Gelation time (h)	Polymer gel of Cr(OAc) ₃	Model	2442.22	4	610.16	210.45	<0.0001	0.99
		Residual	20.29	7	2.9	-	-	
		A	1776.84	1	1776.84	612.86	<0.0001	
		B	406.72	1	406.72	140.28	<0.0001	
		AB	182.25	1	182.25	62.86	<0.0001	
		A2	74.82	1	74.82	25.81	0.0014	
	Polymer gel of Al(NO ₃) ₃ .9H ₂ O	Model	5392.35	4	1348.09	67.28	<0.0001	0.98
		Residual	123.90	7	17.70	-	-	
		A	3681.26	1	3681.26	207.99	<0.0001	
		B	1224.7	1	1224.7	69.19	<0.0001	
		AB	342.25	1	342.25	19.34	0.0032	
		A2	144.15	1	144.15	8.14	0.0246	

the total number of model terms, including intercept minus one while meaning square estimates the model variance, calculated by the sum of squares divided by degrees of freedom.

It is evident that the models as suggested by the model F-value and low probability value (P-value) are highly significant. The high value of R-square, for the developed quadratic models, indicated that the quadratic polynomial was capable of representing the system for the given experimental domain [21]. In Fig. 4, the residuals vs. predicted plot were shown for both systems. It must be mentioned that these plots are random scatters representing the validity of laboratory data and the presented model.

As presented in Eq. (4), the coefficient of factor A (polymer concentration) was higher than the coefficient of factor B (Cr(OAc)₃ concentration), so that factor A was selected as the main effect in contrast with factor B and their interaction AB which had the same effect on the gelation time. In addition, the perturbation plot is shown in Fig. 5. The perturbation plot compares the effect of all factors at a particular point in the design space. The response is plotted by changing only one factor over its range while holding the other factors were constant. In Fig. 5, the reference point is set at the midpoint (coded 0) of all the factors. A steep slope or curvature in a factor shows that the response is sensitive to that factor. As can be seen, in both crosslinker, the polymer concentration has

a steeper slope, as a result, the gelation time is more sensitive to the concentration of the polymer.

Fig. 6 indicated the 3D surface of the effect of two factors of the polymer gels on the gelation time.

As can be seen in Fig. 6, the maximum gelation time of the polymer gel of Cr(OAc)₃ happened in the minimum concentration of polymer and crosslinker. The gelation time was also increased by increasing of Cr(OAc)₃ and polymer concentration. In Cr(OAc)₃ polymer gel system, triacetate groups of Cr(OAc)₃ are replaced by nucleophilic sites (carboxylate group) of the polymer chain and so that 3D structure of polymer gel can form. By increasing of the polymer and crosslinker concentration, more sites are available to form complexes with Cr³⁺ and also more concentration of Cr(OAc)₃ increase the amount of crosslinking through the replacement of acetate group by nucleophilic sites of polymer that leads to accelerating the gelation process and thereby gelation time decreases. As shown in Fig. 6 the gelation time in polymer gel of Al(NO₃)₃.9H₂O was higher than the polymer gel of Cr(OAc)₃. According to Eq. (5) in polymer gel of Al(NO₃)₃.9H₂O the polymer concentration was the main effect on the gelation time. By increasing the polymer concentration, carboxylate groups as a crosslinking site increased, as a result, the crosslinking reaction accelerated and gelation time decreased. In contrast with the polymer gel of Cr(OAc)₃, the crosslinker concentration in polymer gel of

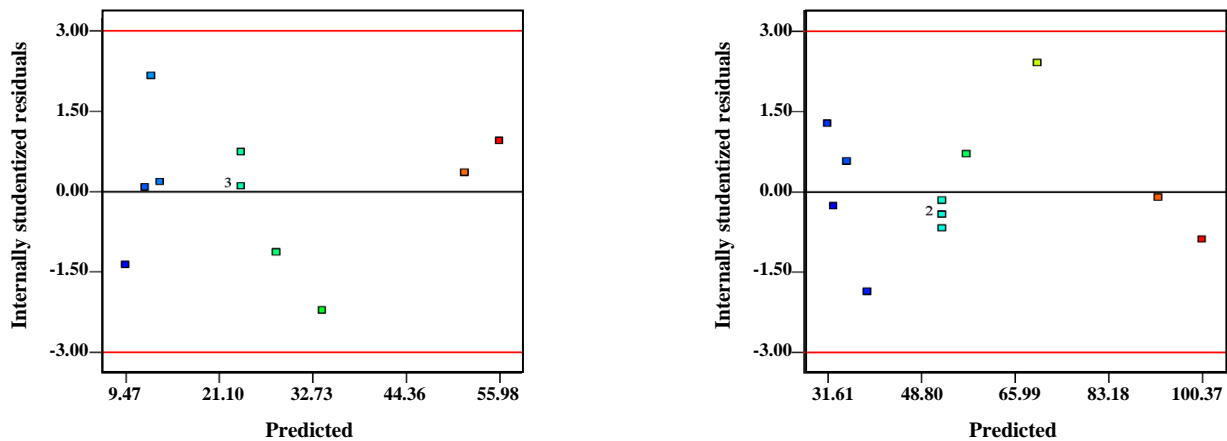


Fig. 4: Residuals vs. predicted gelation time.

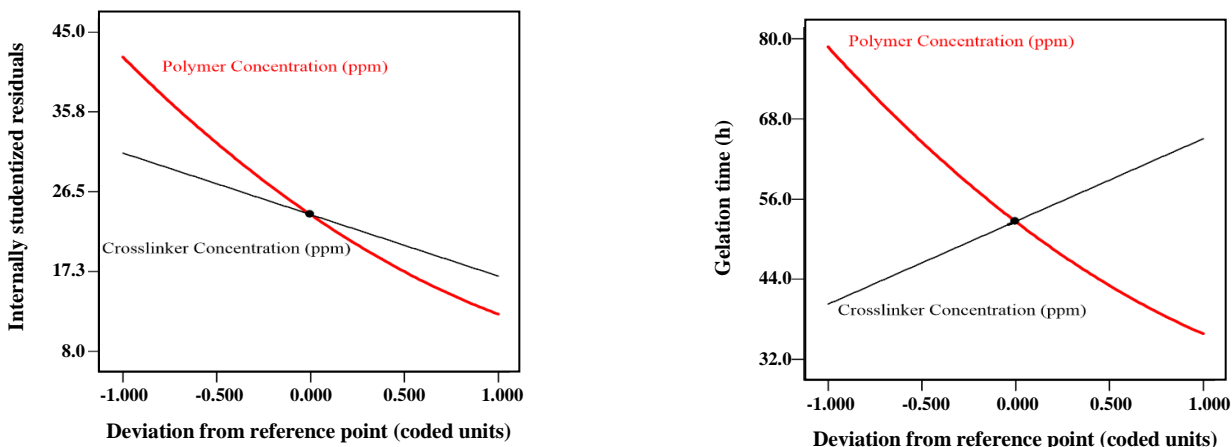


Fig. 5: The Perturbation plot.

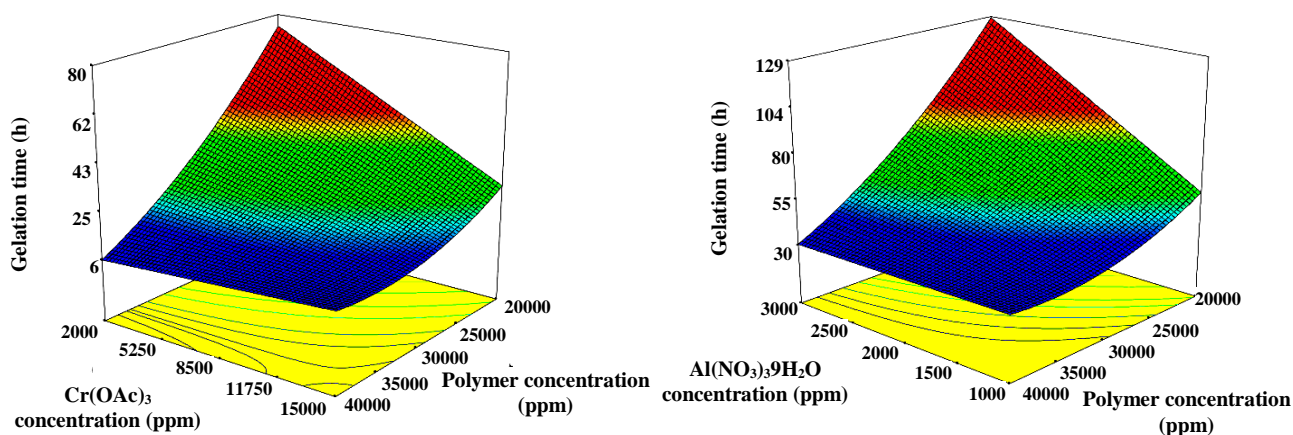


Fig. 6: Effect of polymer and crosslinker concentration on gelation time.

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ played a reverse role on the gelation time. In other words, the increasing amount of crosslinker concentration leads to an increase in the gelation time. This behavior could be attributed to the hindrance of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ due to infrastructure of 9 water molecules presence due to the presence of 9 infrastructure water molecules in the chemical structure of the crosslinker which prevents the coordination of polymer chain with Al^{3+} . Therefore, by increasing the concentration of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, the crosslinking reaction was reduced, the gel formation rate was decreased, and consequently the gelation time was increased [12]. Accordingly, based on the syneresis time and gelation time, two samples of the polymer gel of $\text{Cr}(\text{OAc})_3$ with copolymer concentration of 37071 ppm and crosslinker concentration of 13096 ppm (Sample 3), and also the polymer gel of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with copolymer concentration of 37071 ppm and crosslinker concentration of 2707 ppm (sample 5) were selected as the optimum compositions among the other designed polymer gels samples to study the performance of polymer gel system in the fractured core model. Although similar to sample 3 of $\text{Cr}(\text{OAc})_3$ polymer gel the syneresis phenomenon occurred for sample 10 after 140 days. However, the gelation time in this sample was very short that leads to the formation of gelant rapidly. Thus, it couldn't propagate through the fracture and deep zones.

Coreflooding Experiments

The blocking capacity of polymer gel in the fractured core model was investigated via a coreflooding test. Absolute permeabilities of fractured core model applying for coreflooding test were 297 and 314 mD for polymer gel of $\text{Cr}(\text{OAc})_3$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, respectively. In order to calculate F_{rw} and F_{ro} in fractured core model, based on Eq. (3), the output flow rates of water and oil before and after the polymer gel treatment was measured at the same pressure drop up to 2 bar. Tables 6 and 7 illustrated the output flow rates of water and oil obtained in coreflooding test for polymer gel of $\text{Cr}(\text{OAc})_3$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at temperature of 90 °C. The results indicated that these polymer gel systems have suitable performance for water shutoff treatment in fractured reservoirs. During polymer gel treatment, the fracture was completely filled by polymer gel therefore the

mainstream pass of flow was block and water production reduced. Recording output flow rate of water demonstrated that after polymer gel treatment, the output flow rate of water reduced ten times in comparison with before polymer gel treatment. So, these polymer gel systems can almost act as a barrier to water flow in fractured reservoirs and treat excessive water problems.

F_{rw} and F_{ro} for polymer gels of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cr}(\text{OAc})_3$ are depicted in Fig. 5. By increasing of pressure drop, RRF decreased, where after polymer gel treatment, the flow could pass primarily through the matrix at the very beginning and increasing of pressure drop lead to an increase of output flow rate across the matrix and then RRF gradually decreased [26]. In continue no new pass would form and hence, the RRF tends to stabilize at higher pressure drop. As shown in Fig. 5, the residual resistance factor of water for two polymer gel systems is higher than the residual resistance factor of oil. The reason for this result can be attributed that the polymer gel of $\text{Cr}(\text{OAc})_3$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are hydrophilic hydrogels which can absorb water in their 3D structures. Therefore, these can swell adjacent water in fracture and then show more resistance in contact with the water flow rate. However, in oil injection step the polymer coating the fracture surfaces was squeezed in adjacent oil and a narrow passage could be found to pass oil in the fractured core. Therefore, by increasing the pressure drop, the output flow rate of oil increased and finally, the F_{ro} decreased. As illustrated in Fig. 5, RRF for polymer gel of $\text{Cr}(\text{OAc})_3$ is higher than polymer gels of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ due to the strength of 3D structure of polymer gel. As recorded in Table 3, the syneresis time for Sample 3 of $\text{Cr}(\text{OAc})_3$ polymer gel and Sample 5 of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ polymer gel is 140 and 110 days, respectively. For as long as syneresis time, the strength of 3D structure for polymer gel of $\text{Cr}(\text{OAc})_3$ is more than polymer gel of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ [12]. Therefore, the polymer gel of $\text{Cr}(\text{OAc})_3$ exhibits a higher resistance to flow with a higher residual resistance factor.

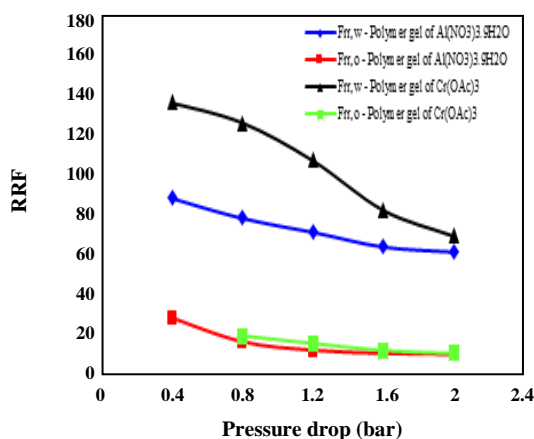
In order to investigate the resistance of polymer gel to flow, after polymer gel injection, pressure drop continued up to 90 bar. Table 8 presents the output flow rates of water and oil after polymer gel treatment. As listed, by increasing pressure drop, output flow rates of water after 60 and 70 bar increased intensively for polymer gel of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cr}(\text{OAc})_3$, respectively. Where output flow rates of oil took place after 40 and 60 bar

Table 6: Water residual resistance factor based on the pressure drop in the coreflooding test.

Pressure drop (bar)	Polymer gel of Cr(OAc) ₃			Polymer gel of Al(NO ₃) ₃ .9H ₂ O		
	The output flow rate of water (mL/min)		F _{rrw}	The output flow rate of water (mL/min)		F _{rrw}
	Before polymer gel treatment	After polymer gel treatment		Before polymer gel treatment	After polymer gel treatment	
0.1	1.8	0	–	2.4	0	–
0.4	6.8	0.05	136	8.8	0.1	88
0.8	12.6	0.1	126	15.6	0.2	78
1.2	21.4	0.2	107	28.4	0.4	71
1.6	32.8	0.4	82	31.8	0.5	63.6
2	41.4	0.6	69	48.8	0.8	61

Table 7: Oil residual resistance factor based on the pressure drop in the coreflooding test.

Pressure drop (bar)	Polymer gel of Cr(OAc) ₃			Polymer gel of Al(NO ₃) ₃ .9H ₂ O		
	The output flow rate of oil (ml/min)		F _{rrw}	The output flow rate of oil (ml/min)		F _{rrw}
	Before polymer gel treatment	After polymer gel treatment		Before polymer gel treatment	After polymer gel treatment	
0.1	0.6	0	–	0.7	0	–
0.4	2.4	0	–	2.8	0.1	28
0.8	3.8	0.2	19	4.8	0.3	16
1.2	7.6	0.5	15.2	8.2	0.7	11.7
1.6	10.4	0.9	11.5	11.2	1.1	10.2
2	14.2	1.4	10.1	16.4	1.7	9.6

**Fig. 5: Comparison of residual resistance factor for two inorganics of polymer gel systems.**

in the polymer gel of Al(NO₃)₃.9H₂O and Cr(OAc)₃. This intensive increase in output flow rates was because of high injection pressure that makes the piece of polymer gel to be flushed out gradually of the fracture and the resistance of

remaining polymer to flow reduced [24]. Hence, a new channel formed through fracture and flow without any resistance can be easily transported through the fracture.

CONCLUSIONS

A comparison study for two inorganic crosslinkers (chromium triacetate and aluminum nitrate nonahydrate) on the gelation time of the polymer gels was carried out by using CCD method under the temperature of 90°C. Two quadratic polynomial models were presented for each polymer gel systems to predict the gelation time with high values of predicted R² and acceptable accuracy. By adjusting the polymer and crosslinker concentration, the gelation time of Cr(OAc)₃ polymer gel and Al(NO₃)₃.9H₂O polymer gel could be controlled within the range of 8 h to 52 h and 32 h to 98 h, respectively. The polymer concentration in both polymer gel systems was the main effect on the gelation time. By increasing the polymer concentration, the crosslinking reaction was accelerated

Table 8: Output flow rates of water and oil after polymer gel treatment.

Pressure drop (bar)	Polymer gel of Cr(OAc) ₃		Polymer gel of Al(NO ₃) ₃ .9H ₂ O	
	Output flow rate (mL/min)		Output flow rate (mL/min)	
	Water	Oil	Water	Oil
5	1.8	2	2.1	2.8
10	2.6	3.6	3.6	4.2
20	4.2	5.2	5.8	6.8
30	7.8	8.4	9.8	10.1
40	9.6	14.6	12.6	14.6
50	12.2	16.8	14.4	62.8
60	14.9	24.4	11.2	85.4
70	18.2	72.4	72.4	106.8
80	66.8	106	92.8	178
90	162	–	188	–

and gelation time was decreased. The crosslinker concentration plays a different role in the gelation time of these polymer gel systems. Increasing the crosslinker concentration led to a decrease the gelation time in the polymer gel of Cr(OAc)₃, where in polymer gel of Al(NO₃)₃.9H₂O by an increase of crosslinker concentration the gelation time increased. Finally, considering the gelation time and strength of 3D structure of polymer gel, the polymer gels of Cr(OAc)₃ and Al(NO₃)₃.9H₂O with the same polymer concentration of 37071 ppm and the crosslinker with a concentration of 13096 ppm and 2707 ppm were selected as the optimum composition to be studied for the performance of the polymer gel system in the fractured core model. The results of the coreflooding test indicated that polymer gel filled fracture and blocked flow path. The output flow rate of water after polymer gel treatment reduced 10 times more than before polymer gel treatment in the fractured core. In both polymer gel systems water, residual resistance factor is higher than the oil residual resistance factor in the same condition. The residual resistance factor for polymer gel of Cr(OAc)₃ is higher than the polymer gel of Al(NO₃)₃.9H₂O due to the greater strength of 3D structure. Also, the polymer gel of Cr(OAc)₃ exhibited higher resistance to water and oil flow within the fracture at high injection pressure.

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