Preparation an Optimal Hydrogel of Water Shutoff for Iranian Oil Field

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Abstract

Presenting a suitable hydrogel for water shutoff in Iranian oil field is based on gelation time and gel strength. Rheological behavior of gel was the main purpose of this research. To determine the gelation time, thermal stability and gel strength a plan of bottle tests were conducted by using the central composite design method with two factors. The hydrogels composed of AN125VLM and chromium triacetate as copolymer and crosslinker, respectively were recorded for 8 weeks. Furthermore, the consistency modulus of the gels was measured by amplitude sweep tests using the Paar-Physica universal spectrometer, model MCR501. A hydrogel with 26,339 ppm concentration of copolymer and 0.12 ratio of crosslinker/copolymer and also gelation time of 2 days was selected as the optimal one. Also, it showed the maximum value of consistency modulus of 31,900 Pa among the other samples, tremendously, which showed the highest resistance against external stress. To ensure the gel strength among different effective parameters on the gel in porous media, a plan of rheological experiments were carried out. A 12 Run Plackett-Burman design was used for screening the eight parameters of NaCl, $CaCl_2$, KCl and $MgCl_2$ concentrations, temperature, pH, sodium lactate and nanoclay while keeping the optimal hydrogel component constant. Finally, it was found that temperature was the most effective parameter to

control gelation time and also pH had negligible effect on the gelation time of this optimal gel.

Keywords: Hydrogel, Bottle test, Rheological tests, Consistency modulus, Central Composite Design, Plackett-Burman Design

Introduction

Since high water production in oil producing wells happened, conformance challenges have always been an issue for petroleum engineers. For several decades, engineers have applied various improved methods to overcome high water production problems to increase oil recovery [1]. Water shut-off methods can be classified in two different types: mechanical and chemical methods. The mechanical methods are limited to the application of specific completion tools as dual systems to avoid water conning or the use of hydro-cyclones to separate water while it is being produced [2]. On the other hand, the chemical methods, extensively used in the last decade [3, 4], consist namely of chemical products that are pumped into producer or injector wells. A more recent development is the use of an internally crosslinked polymer that expands to form a blocking phase far from the injection well. These gels which are the basis of the most water shut-off treatments can partially or completely block the channels through which water is being produced. Several authors have reported the characteristics of gel polymers (hydrogels) utilized for other purposes in detail [5]. Selection of a polymer gel system for a given well treatment strongly depends on reservoir conditions such as temperature, salinity, hardness and the pH of the water used for preparation of the gelant. Salinity of the formation water, permeability of the target zone, and the lithology of the formation, are the other parameters that could be considered for the proper selection of a given polymer gel system [6, 7]. Studying the effect of different parameters (polymer concentration, crosslinker concentration, salinity and pH) on the gelation time of the polyacrylamide/polyethyleneimine (PEI) gel [8] was showed that initial pH value had a strong influence on gel viscosity. Higher viscosities were obtained at higher initial pH values. Under acidic conditions, the gelation time was short and the gel did not last for a long time. Other researchers [9] analyzed the gelation process and effect of clay (montmorillonite) content and ionic strength on the swelling behavior of sulfonated polyacrylamide (PAMPS)/chromium (III) acetate using dynamic rheometery. They showed that the swelling ratio of nanocomposite gels in tap water decreased as the concentration of the clay increased. Among the different techniques that measure the consistency of gelling systems (such as bottle tests and rheological tests), rheology is considered as the most complete technique of characterization of polymer systems [10].

To present an optimal hydrogel used in water shutoff systems, a series of experiments was conducted using bottle tests planned with central composite design (CCD) measuring gelation time. In continue the candidate hydrogels were compared by rheological tests, using the Paar-Physica universal spectrometer, model MCR501, in part of their consistency modulus and crosslinking density versus time. Then the sensitivity of the optimal hydrogel was screened with eight effective factors to show the main effective one on the gelation time. For this purpose, a 12-run Plackett-Burman (PB) design was conducted by rheological tests using Rheolab QC for viscosity measurements.

Experimental

Materials

The hydrogels were prepared by a copolymer of 2-acrylamido-2-methyl-propanesulfonic-acid sodium salt (AMPS) and acrylamide (AcA), with an average molecular weight of 2 million Dalton and sulfonation degree of 25%, provided by SNF Co. (France). It is also called sulfonated polyacrylamide (PAMPS), under the trade name of AN125VLM, in powder form. Furthermore, chromium triacetate, as an ionic crosslinker, purchased from Carlo Erba Co. (Italy), was used in powder form. NaCl, $CaCl_2$, $MgCl_2$ and KCl of analytical grade, HCl and NaOH solutions were purchased from Merck Co. (Germany). Nanoclay used in this study was Na-montmorillonite with d_{001} interplanar spacing of 12, supplied from Advanced Technology (China). Sodium lactate was also used as retarder, and was provided by Merck Co. (Germany) in the form of a colorless liquid.

Samples Preparation

First of all, in order to prepare the PAMPS solution at a concentration of 3%, the co-polymer powder and distilled water were mixed for a period of 24 hour. The mixture was 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 for 5 min. Then the crosslinker was also mixed with distilled water at room temperature (according to the experimental design composition), using a magnetic stirrer (Stuart CB162, UK) for 5 min. Finally, the PAMPS and crosslinker solutions were mixed for 10 min to obtain the gelant solution. Since most of the south Iranian reservoirs have a high temperature, around 60 to 90^{o}C, this range of temperature was selected for the experiments.

Bottle Test

Bottle test method, as an experimental technique, provides a semi quantitative measurement of gelation time and gel strength. As a simple and basic method to study the gel performance, bottle test results can be used to determine the gelation time, stiffness and final gel consistency of the gel by visual examination. In this method, the gel strength during its formation is expressed as an alphabetic code of A through I, which was defined by Sydansk [7]. To select the optimal component of the hydrogel, central composite design method, the most popular method of response surface methodology was used for experiments [11, 12]. For this purpose, gelant solution, were prepared according to CCD plan at 90^{o}C and then were transferred into high thermal resistance glass tubes (Screwthread GL32). The glass tubes were inverted at various time intervals (during the first week, each 10 hours, and after that each day) and the corresponding gel property was recorded under the influence of gravity. The samples were kept for 8 weeks in oven (90^{o}C) to study the thermal stability of the gels.

Rheological Test

To investigate the crosslinking density and consistency modulus [13] of the hydrogels and select of optimal hydrogel, the dynamic rheological measurements of gel samples were performed. For this purpose, a Paar-Physica universal spectrometer, model MCR501 (Austria), with smooth plate-plate surfaces of 50 mm diameter and 3 mm gap was used. During the hydrogel operation, gelation time is more important than the other operating factors. Therefore, the effect of process variables during gel formation must be investigated to have the sensitivity of the hydrogel to the gelation time. In order to conduct the least number of experiments, a 12-run Plackett-Burman design [12] was used to screen eight factors influencing the gelation time. Therefore, to screen the effective factors on gelation time, the rheological tests were carried out with a Rheolab QC (US200, Anton Paar, and Austria) for viscosity measurements.

Results and Discussion

The bottle tests were carried out using central composite design with two factors in five levels and the gelation time as response. A wide range of copolymer concentration (5,000-30,000 ppm) and crosslinker/copolymer ratio (0.05-0.5) were selected to determine their effect on gelation time.

The final results can be observed in table (1).

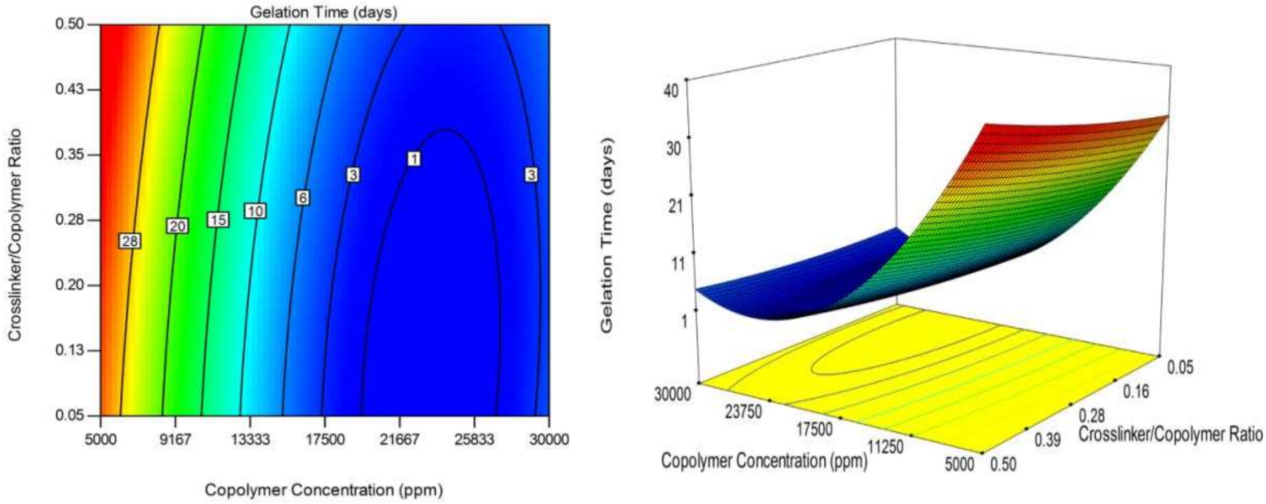
Table (1) Bottle test results for designed gel

Sample No.	1 day	7 days	14 days	21 days	56 days
1	A	F	F	G	syneresis
2	G	I	I	I	I
3	A	F	F	G	syneresis
4	F	H	H	H	H
5	A	A	C	F	F
6	G	H	I	I	I
7	G	H	H	H	syneresis
8	B	G	H	H	H
9 (center point)	D	G	H	syneresis	syneresis

To determine the effect of copolymer concentration and crosslinker/copolymer ratio on the gelation time, the samples with an alphabetic code of G were considered and corresponding in terms of day and gelant composition were inserted in "Design Expert (DX)" software (State-Ease, version 7.1.3, USA). Among several possible models, the following quadratic polynomial was found as the best correlation to fit the experimental data.

$$\text{Gelation Time} = 3.7 - 11.02 \times A + 1.56 \times B - 0.8 \times AB \qquad (1)$$

In this quadratic polynomial all variables are indicated through the coded values, where A is copolymer concentration, B is crosslinker/copolymer ratio and AB is the interaction of the two factors on the gelation time as a response. The coefficient of each factor and its sign indicate the importance and type of parameters effect on the response. As can be seen, the copolymer concentration with the greatest coefficient identified as the main effect on the gelation time. The interaction effect of two factors on gelation time can be observed in figure (1-a) As shown in this figure, at constant values of crosslinker/copolymer ratio, the gelation time decreased with increase of copolymer concentration. Figure (1-b) shows the response surface plot. It illustrated the different variety of the surface slop with the copolymer changes and with the crosslinker/copolymer ratio changes which is greater with copolymer changes.



a B

Fig. (1) Effect of copolymer concentration and crosslinker/copolymer ratio on the gelation time (a: Contour, b: response surface plot)

As the results indicated, samples 3 and 9 for repulsion of water out of the gel structure due to shrinkage in gel volume (syneresis), sample 5 for the weak strength of the gel network, sample 7 for short life time and syneresis, and sample 1 for the long time of gelation and non economical for field operation [13] were not appropriate in field operating. As the results indicated, samples 3 and 9 for repulsion of water out of the gel structure due to shrinkage in gel volume (syneresis), sample 5 for the weak strength of the gel network, sample 7 for short life time and syneresis, and sample 1 for the long time of gelation and non economical for field operation [14] were not appropriate in field operating. Finally, the rheological experiments would be necessary to determine the suitable

components for the gel for strength gel network. Samples 2, 4, 6 and 8 were the candidate in the next step to be studied rheological for selecting the optimal gel.
So, as the results of experimental design indicated, the highest strength would be found in high concentration of copolymer and low ratio of crosslinker/copolymer. Therefore, the sample 4 compared with sample 2 (with the same concentration of copolymer) had lower strength due to the higher ratio of crosslinker/copolymer. According to the rheology experiments among the hydrogel candidates, sample 2 had the maximum value of crosslinking density of about 2,790 and the maximum consistency modulus of about 31,900 Pa figures (2, 3) which was not unexpected.

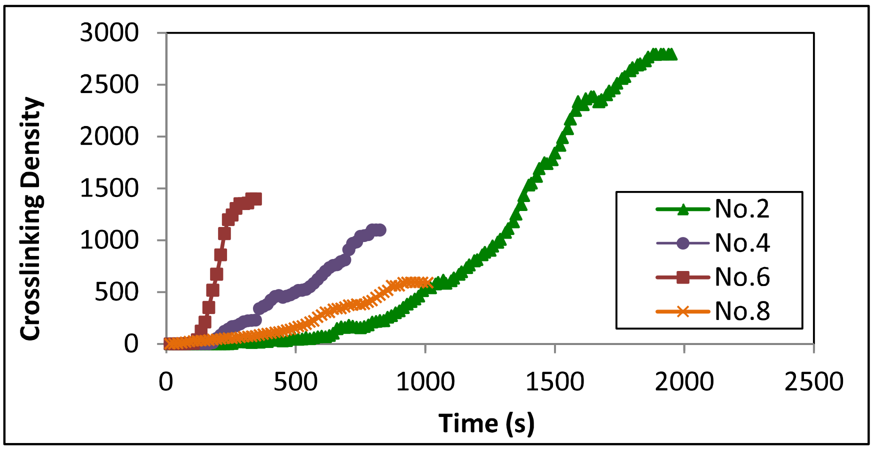


Fig. (2) Comparison of the crosslinking density between the gelant samples

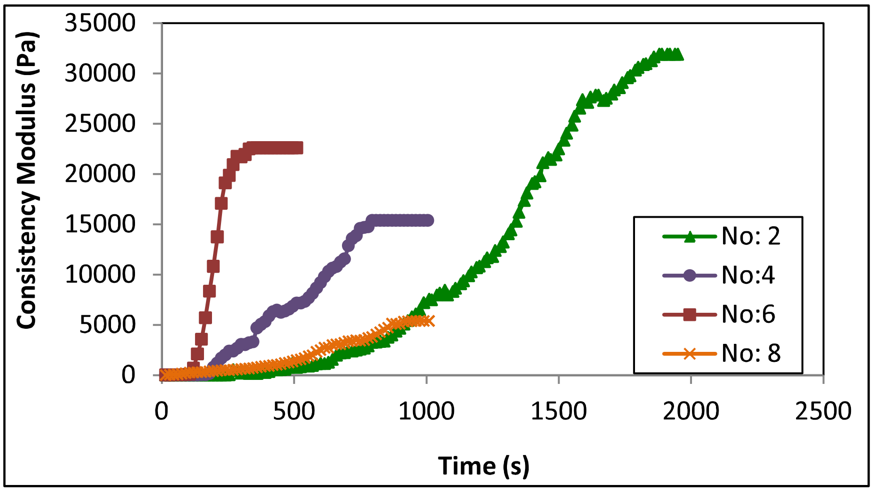


Fig. (3) Comparison of the consistency modulus between the gelant samples

The eight factors (NaCl, CaCl2, $MgCl_2$ and KCl concentrations, temperature, pH, sodium lactate and nanoclay) with the wide selected range for each of them were conducted.

Table (2) shows the experimental plan of PB design and corresponding responses from which the main effects of variables were evaluated, using DX7 software as follow:

Table (2) Experimental plan of the PB design with eight factors and their responses

No.	A	B	C	D	E	F	G	H	Gelation Time (sec)
1	+1	+1	-1	+1	+1	+1	-1	-1	250
2	-1	+1	+1	-1	+1	+1	+1	-1	15
3	+1	-1	+1	+1	-1	+1	+1	+1	3300
4	-1	+1	-1	+1	+1	-1	+1	+1	420
5	-1	-1	+1	-1	+1	+1	-1	+1	15
6	-1	-1	-1	+1	-1	+1	+1	-1	2000
7	+1	-1	-1	-1	+1	-1	+1	+1	275
8	+1	+1	-1	-1	-1	+1	-1	+1	2300
9	+1	+1	+1	-1	-1	-1	+1	-1	3670
10	-1	+1	+1	+1	-1	-1	-1	+1	4020
11	+1	-1	+1	+1	+1	-1	-1	-1	15
12	-1	-1	-1	-1	-1	-1	-1	-1	1520

The gels were prepared with constant component of copolymer concentration and crosslinker/copolymer ratio of sample 2 and the designed additives according to the plan. According to the PB results and Eq. 2 (shown for instance for the factor A where R is the response), the effect of each parameter were measured and illustrated among other parameters in figure (4).

$$mA = -R_1 - R_2 - R_3 - R_4 + R_5 + R_6 + R_7 + R_8 - R_9 + R_{10} - R_{11} + R_{12} \quad (2)$$

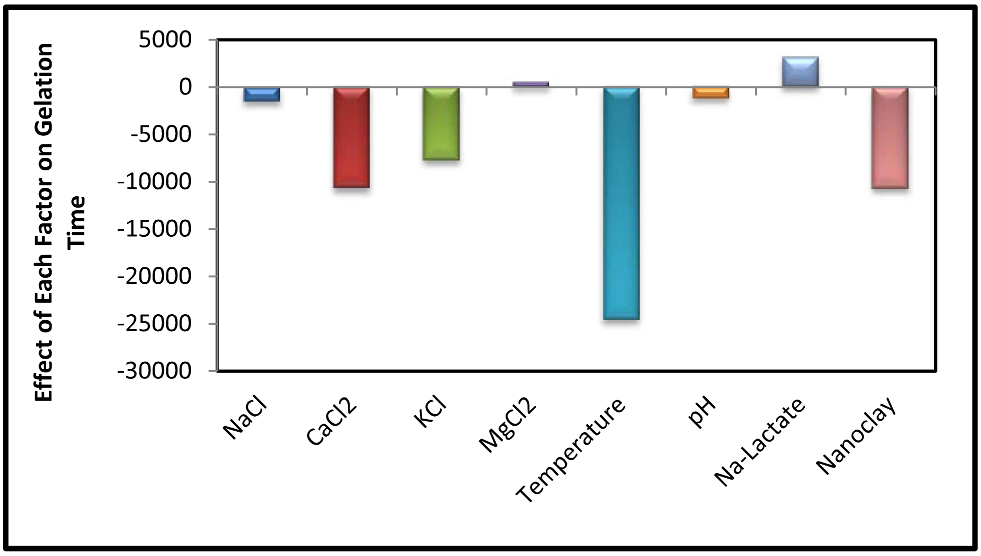


Fig. (4) Effect of each factor on the gelation time

In fact, the effect of each parameter on gelation time of the hydrogel can be studied through it. As can be seen, the gelation time decreased by increase of temperature and pH where it increased by increase of other factors.

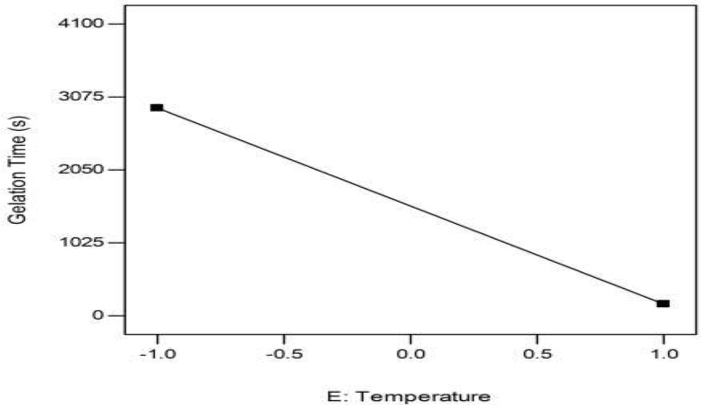


Fig. (5) Effect of temperature on the gelation time of optimal hydrogel with PB design

As can be seen, figure (5) also illustrated that temperature had the most effect on gelation time in comparison with other factors, so it was mentioned as the main effect on gelation time.

Conclusions

1. The copolymer was obtained as main effect through bottle tests and rheological tests.
2. A quadratic polynomial equation was represented for each response of experimental design based on two factors of copolymer concentration and crosslinker/copolymer ratio.
3. During the bottle tests, the gelation time decreased with increase of copolymer concentration.
4. As the results of bottle tests indicated, samples 3 and 9 for repulsion of water out of the gel structure due to shrinkage in gel volume (syneresis), sample 5 for the weak strength of the gel network, sample 7 for short life time and syneresis, and sample 1 for the long time of gelation and were not appropriate in field operating.
5. Among all results of the tests of outside porous media, the gel of samples 2 composed of 26340 ppm concentration of copolymer and 0.12 ratio of crosslinker/copolymer with gelation time of 2 days, the maximum value of consistency modulus of 31900 Pa and the maximum value of crosslinking density of 2,790 was selected as the optimal hydrogel.
6. Screening of the eight effective factors on the gelation time of the optimal hydrogel was carried out by the plan of PB design, using DX7 software. The results showed that the gelation time decreased by increase of temperature and pH where it increased by increase of other factors.

7. Temperature had the most effect on gelation time in comparison with other factors, so it was mentioned as the main effect on gelation time of the optimal hydrogel.

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