THE EFFECT OF SALINITY AND PH ON GELATION TIME OF POLYMER GELS USING CENTRAL COMPOSITE DESIGN METHOD

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ABSTRACT
Among the methods available to reduce water production, injecting a gelling system composed of a polymer and a crosslinker has been widely used. In this work, a hydrogel was prepared by crosslinking of an aqueous solution containing chromium acetate (III) and the co-polymer of 2-acrylamido-2methyl-propanesulfonic-acid sodium salt (AMPS) and acrylamide (PAMPS). The effects of pH, salinity and their interactions, on the gelation time were investigated. In order to determine the significant factors that affect the gelation time and also to develop the quadratic mathematical models for optimizing the process, central composite design (CCD), the most popular form of Response Surface Methodology (RSM), was applied. Therefore, the main purpose was to establish functional relationship between the two variables (sodium concentration and pH) and the gelation time by using a statistical technique. The results of analysis of variance (ANOVA) of the developed model illustrated that the fitted model was significant in 99% confidence limit. The results were also shown that the gelation time depended more on pH than sodium concentration and in higher pH; gelation time was increased with increasing of sodium concentration to an optimum level.

INTRODUCTION
Water production in oil-producing wells becomes a more serious problem as the wells mature [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 on chemical products that are pumped into producer or injector wells. Most of these systems are based on polymer solutions that after a given time turn from low viscosity liquids to strong or weak gels depending on their formulations. Several authors have reported the characteristics of gel polymers (hydrogels) utilized for other purposes in detail [5-7]. 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 [8, 9]. Broseta et al. [10] used rheological measurements to study polyacrylamide/Cr (III) gelation as a function of temperature, crosslinker concentration, polymer concentration and polymer molecular weight. They showed that the gelation time was a weak function of crosslinker concentration for acrylate/chromium (III) (with the molar ratio of 2 to 10) and a much stronger function of polymer concentration. Al-Muntasheri et al.

[11] studied the effect of different parameters (polymer concentration, crosslinker concentration, salinity and pH) on the gelation time of polyacrylamide and polyethyleneimine (PEI). They found that initial pH value had a strong influence on gel viscosity. Consequently, in this research, the parameters influencing the gelation time were investigated with the central idea of conducting the least number of experiments. In order to present the general result, for the range of both of the experimental variables of the studied factors, response surface methodology (RSM) was used to obtain the interactions of salinity and pH. Central composite design (CCD), as the most popular form of RSM, is used extensively in building the second order response surface models [12].

Finally, the main purpose of this research was to establish a functional relationship of gelation time in terms of pH and salinity factors via the experimental design matrix proposed by the CCD approach. The significant factors that affect the gelation time are presented with the development of a quadratic mathematical model. The optimized model with respect to the selected factors well predicted the maximum gelation time for a particular salinity and pH condition.

EXPERIMENTAL

MATERIALS

In this section, a general description of experimental measurements are presented. The tests were conducted by the use of a co-polymer of 2-acrylamido-2-methyl-propanesulfonic-acid sodium salt (AMPS) and acrylamide (AcA), with an average molecular weight of 8,000,000, sulfonation degree of 25% and water content of less than 10 wt%, provided by SNF Co. (France). It is also called sulfonated polyacrylamide (PAMPS), under the trade name of AN125, in powder form. Chromium triacetate, as a metallic crosslinker, purchased from Carlo Erba Co. (Italy), was used in powder (pure) form. NaCl of analytical grade, HCl (0.01 M) and NaOH (0.01 M) were used for preparation of acidic or basic water, respectively.

SAMPLES PREPARATION AND GELATION TIME MEASUREMENT

The polymer gels were prepared according to the following three steps. At first, PAMPS solutions, at the concentration of 2%, were obtained by mixing the co-polymer powder and distilled water for the period of 2 hour. The mixture was then held, without stirring, for 2 days to obtain a homogeneous solution. Shortly before the commencement of the experiment, the PAMPS solutions were diluted to the required concentrations and the mixtures were stirred for 5 min. Then Cr (III)-acetate (as crosslinker) and NaCl were also mixed with acidic or basic water at room temperature, using a heater magnetic stirrer (Stuart CB162, UK) for 5 min, as a "second solution". Finally the PAMPS and second solutions were mixed for 5 min to obtain a gelant solution. Since most of the south Iranian reservoirs have a high temperature, around 90^{o}C, this temperature was selected for experiments in the present work.

In the present study, gelation time is presented as the time needed to reach the inflection point on the viscosity versus time curve. The inflection point corresponds to the starting point of gel formation [13]. All tests were carried out on a Rheolab QC (US200, Anton Paar, Austria) used for viscosity measurements, with a thin layer of silicone oil was added to the outer circular surface of the samples to prevent water loss.

CENTRAL COMPOSITE DESIGN APPROACH

The most popular response surface method is the central composite design which is used in experimental design [12]. According to the central composite design, the total number of experimental combinations is $2^k + 2k + n_0$, where k is the number of independent variables and n_0 is the number of repetitions of the experiments at the centre point. For statistical calculation, the experimental variables X_i have been coded as x_i according to the following transformation equation:

$$x_i = \frac{X_i - X_0}{\delta X} \quad (1)$$

where x_i is the dimensionless coded value of the variable X_i, X_0 is the value of X_i at the center point, and δX is the step change. This design consists of the following parts: (1) a full factorial or fractional factorial design; (2) an additional design, often a star design in which experimental points are at the distance from its center (±α); The value of star points can be obtained as well; $\alpha = 2^{k/4}$, As can be seen, the value of α depends on the number of factors. Since we used 2 factors, the value of α was 1.41. It should be noted that the codification of factors is important, because it enables the investigation of factors of different orders of significance without the greater influencing the evaluation of the lesser. (3) a central point. 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 minimum number of experiments without any need of studying all possible combinations experimentally, utilizing design of experiments based on RSM. Furthermore, the input levels of the different variables for a particular level of response can also be determined. In order to determine a critical point (maximum, minimum, or saddle), it is necessary for the polynomial function to contain quadratic terms according to the following equation.

$$y = \beta_0 + \sum_{i=1}^{k} \beta x_i + \sum_{i,j=1}^{k} \beta_{ii} x_i^2 + \sum_{i,j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

Where $k, \beta_0, \beta_i, x_i, \beta_{ii}, \beta_{ij}$ and ε represent the number of variables, constant term, coefficients of the linear parameters, variables, coefficients of the quadratic parameters, coefficients of the interaction parameters and residual associated to the experiments, respectively [14].

RESULTS AND DISCUSSION

The selected control factors, NaCl concentration and pH, are illustrated in Table 1. Each factor was varied in five levels, while the other operational parameters affecting the gelation time, were kept constant.

Table 1. The level of variables in the CCD.

Variable	Low axial $-\alpha = -1.41$	Low factorial (-1)	Center (0)	High factorial (+1)	High axial $+\alpha = +1.41$
A: Na concentration (ppm)	0	4393	15000	25607	30000
B: pH	2	3	6	8	9

MODELING PROCESS REMARKS

Thirteen viscometric experiments were designed applying the CCD method. Table 2 shows the experimental conditions and their responses. The results were inserted in "Design Expert (DX)" software, with, from among several possible models, a quadratic model, and fitted to the results. The quadratic models were found to be adequate for the prediction of the gelation time which was given by the following equation:

$$\text{Gelation Time} = 281.6 - 11.34\,A - 15.3\,B - 30\,AB + 7.95\,A^2 + 12.95\,B^2 \quad (3)$$

Table 2. The experimental plan of the gelation times and their responses.

Std	Run	A		B		Gelation time (sec)
		Coded	Actual (ppm)	Coded	Actual	
3	1	-1	4393	+1	8	300
13	2	0	15000	0	6	340
6	3	+1.41	30000	0	6	290
5	4	-1.41	0	0	6	360
11	5	0	15000	0	6	340
4	6	+1	25607	+1	8	280
10	7	0	15000	0	6	350
8	8	0	15000	+1.41	9	240
12	9	0	15000	0	6	360
1	10	-1	4393	-1	3	260
7	11	0	15000	-1.41	2	270
2	12	+1	25607	-1	3	280
9	13	0	15000	0	6	340

In this model all variables are indicated through the coded values, where A is NaCl concentration and B is pH and hence AB is considered as the interaction of the main factors. As can be seen in Eq. (3), 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 Eq. (3) is shown in Table 3. It is evident that the model is highly significant, as suggested by the model F value and a low probability value (P-value = 0.0047). Figure 1 presents the predicted values of the obtained model versus actual values of the experiment's results of the gelation time.

Table 3. The ANOVA results of the developed model.

		Sum of square	DOF	Mean square	F-value	P-value
Gelation time	Model	17974.97	5	3594.99	9.7	0.0047
	Residual	2594.26	7	370.61		

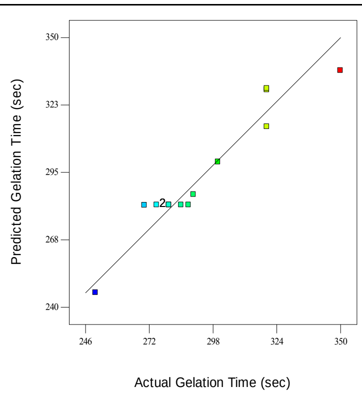

Figure 1. Predicted based on the model in Eq.3 vs. actual values of the gelation time. (label 2 shows the number of replication of one point.).

The value of R-square for the developed quadratic model was 0.9245. The high value of R-square indicates that the quadratic polynomial was capable of representing the system for the given experimental domain. As presented in Eq. 3, the coefficient of pH was higher than the salinity coefficient, so that the effect of pH was greater than salinity. Figure 2 shows the effect of each factor alone on the gelation time.

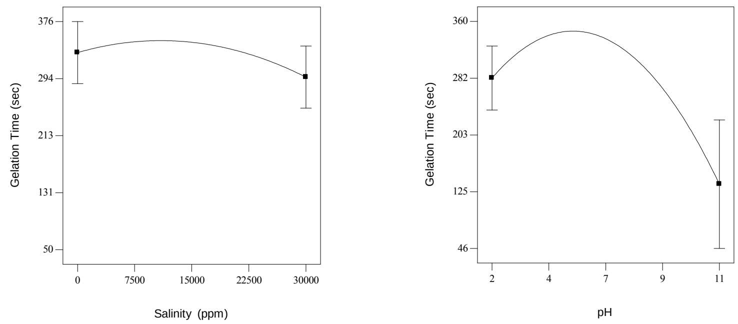

Figure 2. Effect of salinity and pH separately as main effects on gelation time.

In order to describe this fact, the simultaneous effect of both two factors must be investigated. Figure 3 shows a contour plot of pH and NaCl concentration; at low pH (2-4) the gelation time increased with increasing of NaCl concentration, whereas at pH greater than 4 the gelation time decreased with increasing of NaCl concentration.

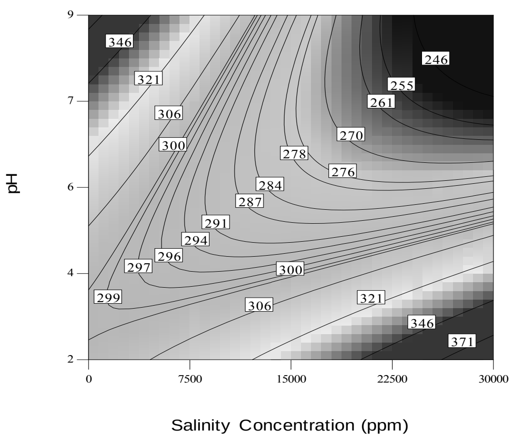

Figure 3. Effect of pH and salinity on gelation time (contour).

OPTIMIZATION

The purpose of optimizing the response surface is to find a desirable location in the design space. This could be maximum, minimum, or an area where the response is stable over a range of factors. In this research, a simultaneous optimization technique was used (using the DX7 software) for the response optimization. The surfaces generated by linear models can be used to indicate the direction in which the original design must be displaced in order to obtain the optimal conditions. However, if the experimental region could not be displaced due to physical or instrumental reasons, the researcher must find the best operational condition inside the studied experimental condition by visual inspection. Table 4 shows the optimum conditions obtained by solving the three equations simultaneously for the purpose of maximizing gelation time.

Table 4. Optimum process condition and its result.

Gelation time (sec)	pH	Concentration Na (ppm)	Target
384.055	2	29050	Maximize
377.793	9	0	Maximize

CONCLUSIONS

The gelation time of the PAMPS/Cr (III)-acetate hydrogels was measured as a function of pH and NaCl concentration, and their interaction, using the CCD method. The results shown that the addition of NaCl and increasing of pH, individually, caused a reduction in the gelation time, and pH is the most significant factor affecting the gelation time in comparison with NaCl concentration. For low pH (2-4) the gelation time increased with increasing of NaCl concentration, whereas for high pH>4 the gelation time decreased with increasing of NaCl concentration. Finally by using the CCD method of experimental design, the response optimization was evaluated and based on the maximum values of gelation time, and then two optimized points were presented for the gelation time.

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