Gelation Time of Hexamethylenetetramine Polymer Gels Used in Water Shutoff Treatment

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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 hexamethylenetetramine (HMTA) as crosslinker, hydrochloric acid (HCl) as an activator, and the co-polymer of 2-acrylamido-2methyl-propanesulfonic-acid sodium salt (AMPS) and acrylamide (PAMPS). In order to indicate the effective factors on the gelation time and also to develop the quadratic mathematical models, central composite design (CCD) was applied. Therefore, the main purpose was to establish functional relationship between the three factors (polymer concentration, HMTA, and hydrochloric acid) and a response (gelation time) by using a statistical technique. In order to determine the optimum value of these factors for maximum gelation time, a simultaneous optimization was also applied. The results of the analysis of variance (ANOVA) of the developed model illustrated that the fitted model was significant in a 99% confidence limit. The results showed that hydrochloric acid was identified as the main factor effecting the gelation time and there was also an interaction between HMTA and hydrochloric acid. Finally, a mechanism for the reaction between PAMPS and HMTA were presented.

Keywords: Polymer Gel, Gelation Time, Hexamethylenetetramine, Central Composite Design

Introduction

Unwanted water production in association with crude oil is one of the major production difficulties for the petroleum industry, as more reservoirs become mature. It is a real problem that leads to the processing of large volumes of water in the downstream facilities [1]. Many different methods and materials can be used as water shut-off to remedy unwanted water production. The use of gelling systems as water shut-off is widely practiced today to improve production of oil and gas. These materials are based on a polymer and a crosslinker mixed at the surface. Then, the mixture (gelant) injected into the reservoirs where it should form a three dimensional (3D) structure, acting as a barrier to water flow [2]. The polymer may be natural such as xanthan biopolymer or synthetic such as polyacrylamide; cross-linkers are generally classified as metallic or organic. There are several manuscripts dealing with gelation of acrylamide-based polymers with metallic and organic cross-linking systems. Chromium is the most widely used metallic crosslinker. The cross-linking metal ion Cr^{+3} can be placed in solution in the form of chromium acetate, chromium

malonate and chromium propionate [3]. Other metallic cross-linkers used include aluminum added to polyacrylamides in the form of aluminum citrate [4]; titanium and zirconium that have lower toxicity than Cr metal ions are also frequently used in near well-bore applications [5]. Albonico and Lockhart [1] proposed phenol and formaldehyde as an organic crosslinker for acrylamide-based polymers with organic cross-linking systems. This polymer is thermally stable under harsh environmental conditions. Unlike the metallic cross-linking that occurs between the carboxylate groups of the polymer and the multivalent cations, these gels are the result of cross-linking between the acrylamide groups and phenol-formaldehyde reaction product. A major problem associated with the use of phenol and formaldehyde cross-linking system is the toxicity of phenol and particularly the carcinogenic character of formaldehyde [6]. Because of environmental concerns as well as the safety of workers performing these treatments, other alternatives were developed like hexamethylenetetramine (HMTA) [7]. Hutchins et al. [8] described the application of a new high-temperature organic cross-linking system suitable for high temperature gel treatments. They found out that

gels can be mixed in a wide range of brine salinities, can be used over a wide range of temperatures and can have a wide range of gel strengths. This cross-linking system believed to be a combination of HMTA as primary cross-linker and hydroquinone (HQ) as secondary crosslinker. The primary crosslinkers can be effective by themselves at high temperatures but the gels are often unstable. The secondary crosslinkers have little or no gelation properties by themselves, but they effectively stabilize the gels containing the primary crosslinkers at high temperatures. At low and medium temperatures, the secondary cross-linkers can form gels with some polymers [9]. Polyethyleneimine (PEI) has been used as an organic crosslinker for different acrylamide-based polymers that can be used at a wide range of temperature. This crosslinker has low toxicity and has been widely applied in several oil fields for water shut-off treatment [10].

In this research, the effects of HMTA as crosslinker, hydrochloric acid (HCl) as an activator, and polymer concentration on the gelation time were investigated with considering the minimization of the number of experiments. In order to present the general result in the range of both of the experimental variables of the studied factors, response surface methodology (RSM) was used to obtain the interactions of the factors. Central composite design (CCD), as the most popular form of RSM, is used extensively in building the second order response surface models. To sum up, the main purpose of this research was to establish a functional relationship between gelation time and HMTA%, HCl%, and polymer concentration 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.

Experimental
Materials

The tests were conducted by the use of sulfonated poly-acrylamide (PAMPS), under the trade name of AN125, in powder form. It is a co-polymer of 2-acrylamido-2-methyl-propanesulfonic-acid sodium salt (AMPS) and acrylamide (AcA) with an average molecular weight of 8,000 kDaltons, sulfonation degree of 25%, and water content of less than 10 wt% supplied by SNF Co. (France). HMTA as crosslinker and HCl as activator were purchased from Merck Company (Germany).

Samples Preparation and Characterization

The polymer gels were prepared according to the following three steps:

A) PAMPS solutions, at the concentration of 3%, were obtained by mixing the co-polymer powder and distilled water for a period of 24 hours. 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.

B) HMTA and HCl were also mixed with distilled water at room temperature (according to the experimental design composition), using a heater magnetic stirrer (Stuart CB162, UK) for 5 min, as a "second solution".

C) The PAMPS and second solutions were mixed for 10 min to obtain a gelant solution.

Since most of the south Iranian reservoirs have a high temperature, around 90 °C, this temperature was selected for the experiments in the present work.

Gelation Time Determination

Gelation time is a fundamental parameter in oil field applications. The gelation time will determine the injection period and how deep into the formation the gel solution can be placed. The process of gelation starts very slowly with no apparent increase in viscosity for a period of time, followed by a period of 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. Among the several methods available for the determination of polymer gel properties such as bottle test method, sealed tube method, dynamic shear method (rheometer), and static shear method (viscometer) [11], in this work the bottle test method was used to study the effect of various parameters on the gelation time of polymer gel. Generally, the bottle test method, as an experimental technique, provides a semi-quantitative measurement of gelation rate and gel strength. Also, it can be considered as a faster and inexpensive method to study gelation kinetics. In this method, which was defined by Sydansk [12], gel strength during the development of gelation kinetics was expressed as an alphabetic code of A to I, which is shown in Table 1. 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 [13]. Therefore, the gelation time was considered in this work as the period of time in which no change is observed in the gel strength code. In the present work, gelant solution was formulated and placed in the bottle at a 90°C for each test. The bottle was inverted during each reading time at different intervals and the gel property was recorded under the influence of gravity. Finally, a gel strength code was allocated as defined in Table 1.

Table 1: Gel strength code

Gel Strength Code	Gel Description
A	No detectable gel formed
B	Highly flowing gel
C	Flowing gel
D	Moderately flowing gel
E	Barely flowing gel
F	Highly deformable non flowing gel
G	Moderately deformable non flowing gel
H	Slightly deformable non flowing gel
I	Rigid gel

Central Composite Design Approach

The most popular response surface method is the central composite design which is used in experimental design. 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:

$$x_i = \frac{X_i - X_0}{\delta X} \tag{1}$$

where, x_i is the dimensionless coded value of the variable; X_i is the value of X_0 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 ($\pm \alpha$); The value of star points can be obtained as well;. As can be seen, the value of $\alpha = 2^{k/4}$ 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" by using these many levels. Standard statistical software can compute the actual fitting of the model. Coded factors can be presented in five levels, namely $-\alpha$, -1, 0, $+1$, α. 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 by using the 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.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta x_i + \sum_{i,j=1}^{k} \beta_i x_i^2 + \sum_{i,j=1}^{k} \beta_j x_i x_j + \varepsilon \tag{2}$$

where, k, β_0, β_i, x_i, β_{ii}, β_{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

Twenty bottle test experiments were designed byapplying 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 which was 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:

$$(GT)^{1/2} = 3.36 - 0.77A + 0.44B - 2.19C + 0.079AB + 0.25AC - 0.88BC \tag{3}$$

According to the coefficients of the above equation, the higher the coefficient of the factor is, the higher the effect on gelation time becomes. So factor C (HCl) is the most effective factor in contrast with the other two factors and the BC interaction is more effective than the other interactions between these three factors. It is also indicated that factors A and C cause gelation time to decrease where factor C increases it. The statistical significance of Equation (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 < 0.0001).

In order to increase the efficiency of model in overlapping with the experimental data, a second curve is presented by using DX7 software depicted for Ln(Residual). The λ is suggested 0.5 for the exponent of the gelation time (Figure 1).

Figure 2 presents the predicted values of the obtained model versus actual values of the experimental results of the ESR. The value of R-square for the developed quadratic model was 0.9905. The high value of R-square indicates that the quadratic polynomial was capable of representing the system for the given experimental domain.

Figure 3 shows the effect of each factor on gelation time separately. As it is shown, an increase in factor A leads to a decrease in gelation time while the decreasing trend of the response has not changed. The gelation time also has not changed a lot by increasing crosslinker concentration up to 0.3%; but, at higher concentrations, it increases. The dual behavior of the response of hydrochloric acid concentration can be seen in Figure 4, which indicates the response sensitivity to this factor. Therefore, selecting the optimum value of this factor has a high impact on the gelation time.

As Figure 4 indicates, at the constant concentration of polymer, increasing HMTA causes a decrease in gelation time initially and then results in an increase; in fact, gelation time decreases up to concentrations lower than 0.23% and then starts increasing intensively at concentrations higher than 0.23%,which expresses the interaction between these two factors.

At a constant concentration of polymer, increasing HCl caused a decrease in gelation time initially (HCl concentration lower than 1%), but gelation time increased at HCl concentrations higher than 1%), which showed the interaction between these two factors (Figure 5). That is because in acidic media the nucleophilicity of the polymer functional groups decreases as the amount of acid increases. So, the tendency of functional groups for adding the nucleophilics to iminium ion resulted from HMTA will be reduced. Therefore, the gelation rate decreased and consequently the gelation time increased.

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

Run	Polymer Concentration (ppm) (A)	HMTA % (B)	HCl %(C)	Gelation Time (hr)
1	16000	0.3	0.85	12
2	16000	0.3	1.2	14
3	16000	0.1	0.85	22
4	16000	0.3	0.85	11
5	13621	0.18	0.64	60
6	13621	0.18	1.06	18
7	18378	0.42	0.64	72
8	16000	0.3	0.85	12
9	16000	0.3	0.85	13
10	12000	0.3	0.85	32
11	18378	0.42	1.06	6
12	13621	0.42	0.64	108
13	16000	0.3	0.85	10
14	18378	0.18	1.06	9
15	18378	0.18	0.64	28
16	20000	0.3	0.85	12
17	16000	0.5	0.85	30
18	13621	0.42	1.06	13
19	16000	0.3	0.5	110
20	16000	0.3	0.85	10

Table 3: The ANOVA results of the model obtained by CCD design

		Sum of square	DOF	Mean square	F-value	P-value
Gelation Time	Model	111.81	9	12.42	116.05	0.0001 >
	Residual	1.07	10	0.11		
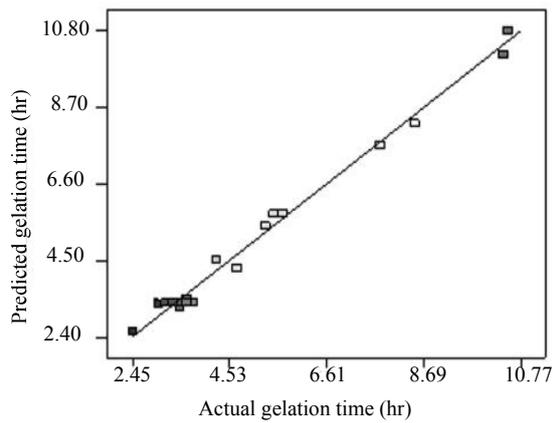
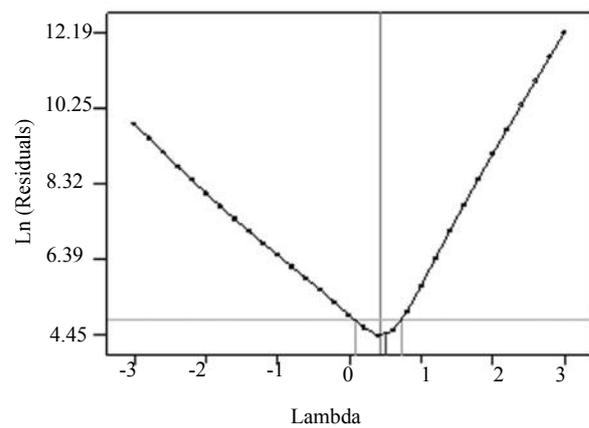**Figure 1:** Box-Cox plot for power transforms

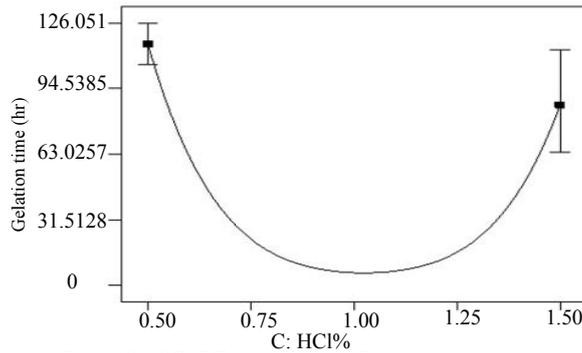**Figure 2:** Predicted based on the model in Equation 3 vs. actual values of the gelation time
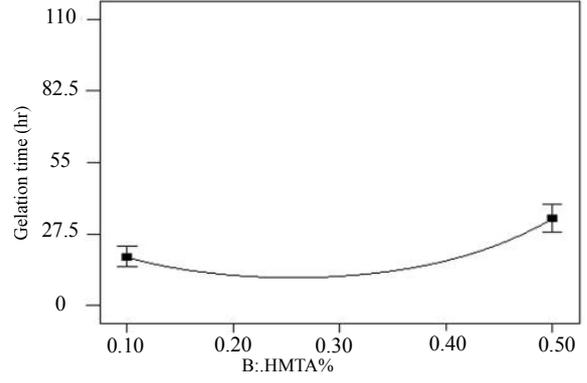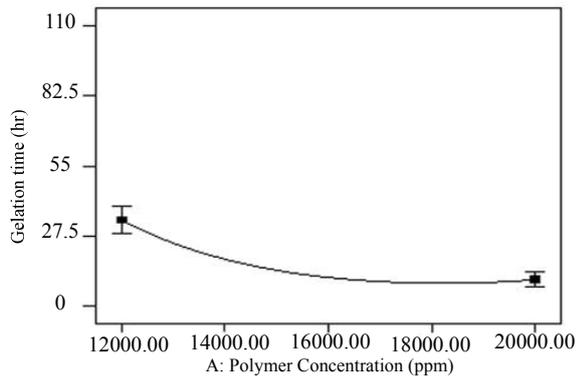
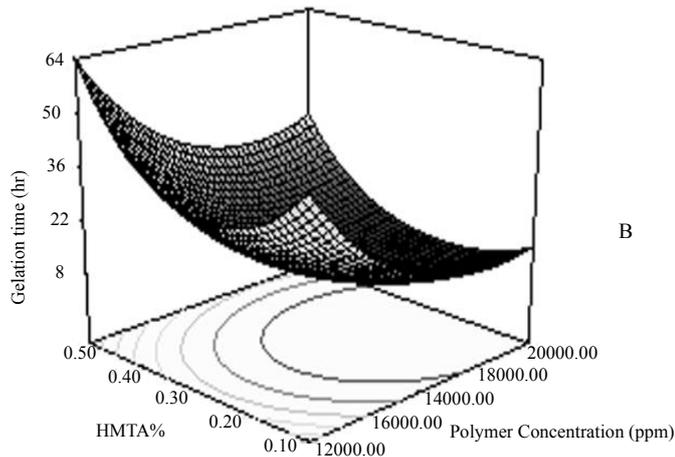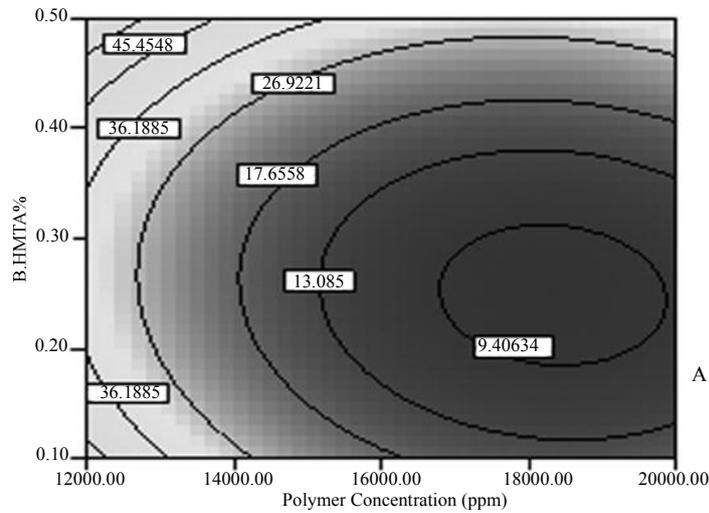**Figure 3A-3C:** Effect of different factors on gelation time

Figure 4: Effect of polymer concentration and HMTA% on the gelation time (A: contour; B: response surface plot)
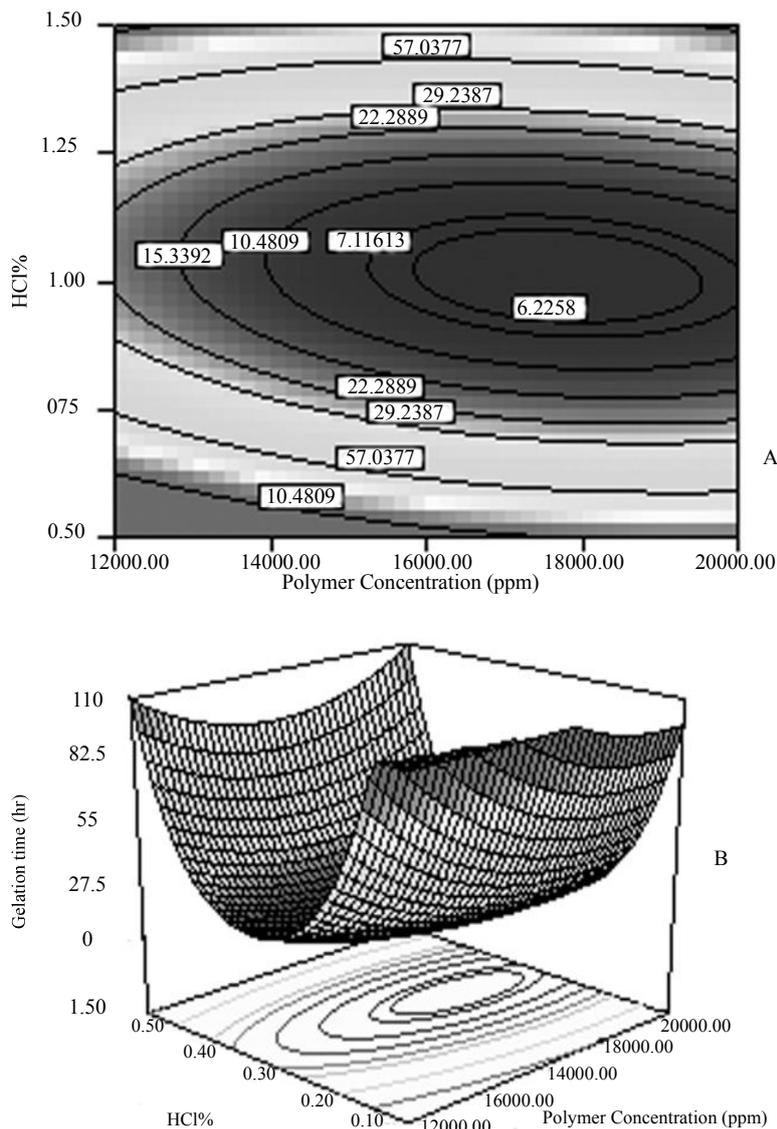
Figure 5: Effect of polymer concentration and HCl% on the gelation time (A: contour, B: response surface plot)

According to Figure 6, at a constant concentration of HMTA, increasing the amount of HCl leaded to a decrease and then an increase in gelation time respectively. Generally, the reaction of a secondary amine and a carbonyl compound lead to the formation of an iminium ion. The mechanism of this process for HMTA in an acid medium is shown in Figure 7a. The propored intermediate is a highly reactive carbonyl group. The reaction of in-situ prepared iminium ion with nucleophilic functional groups can explain the gelation of a co-polymer of AMPS and acrylamide (AcA) with HMTA in the presence of HCl (Figure 7b).

In order to reform the gel network, the reformation of the iminium ion is required. In this step, the iminium ion is reformed the same as previous step and exposed to the attack of the nucleophilic groups of the other polymer chain; so, two polymeric chains are connected together. Therefore, the three dimensional network of the gel is formed by the connection of these polymeric chains (Figure 7c).
According to the above description and the fact that im-

inium ion is a rarely strong electrophile, the attack of the nucleophilic groups of polymer is expected. For the attack of the nucleophilic groups of polymer to the iminium ion, highly acidic media is not suitable. In other words, the acid concentration should not be more than its critical value (1 wt%); in highly acidic media, the nucleophilic groups of polymer are protonated with acid and thus their nucleophilicity are decreased while the gelation time is increased. Besides, if acid concentration is less than its critical value (1% wt), the concentration of prepared iminium ion is not adequate for gel formation and thus gelation time is increased.

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 The surfaces generated by linear models can be used software) for the response optimization.
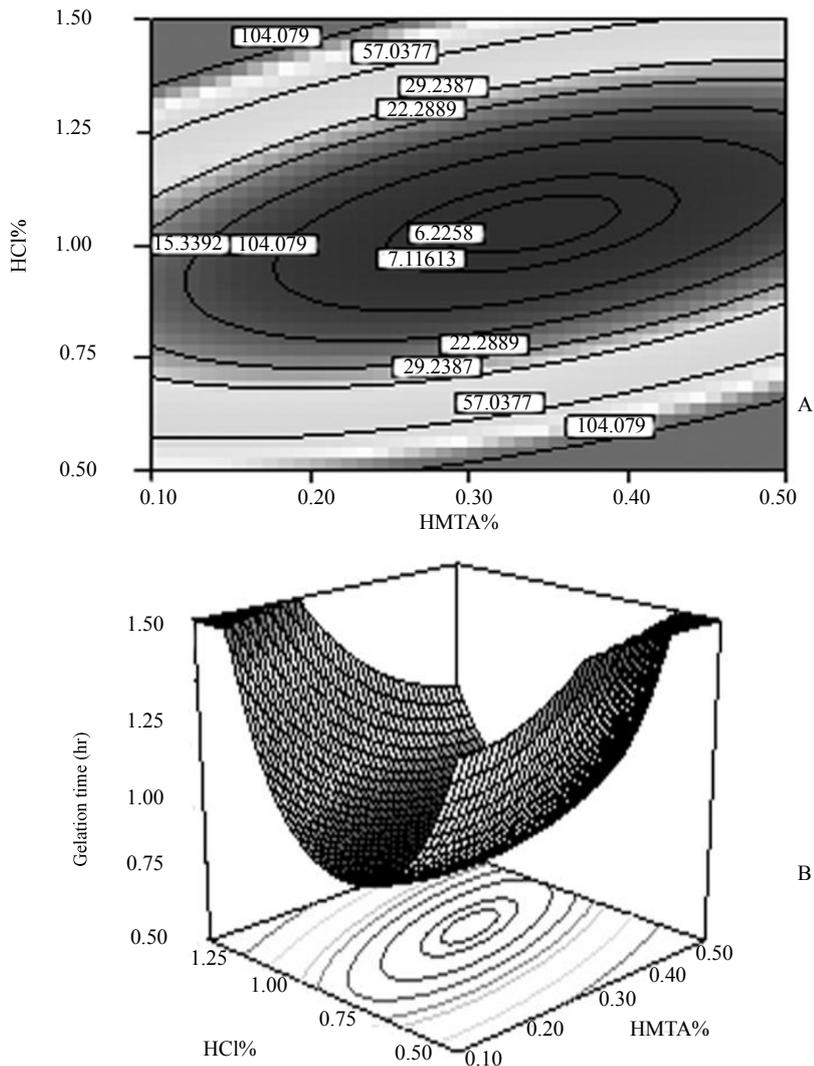
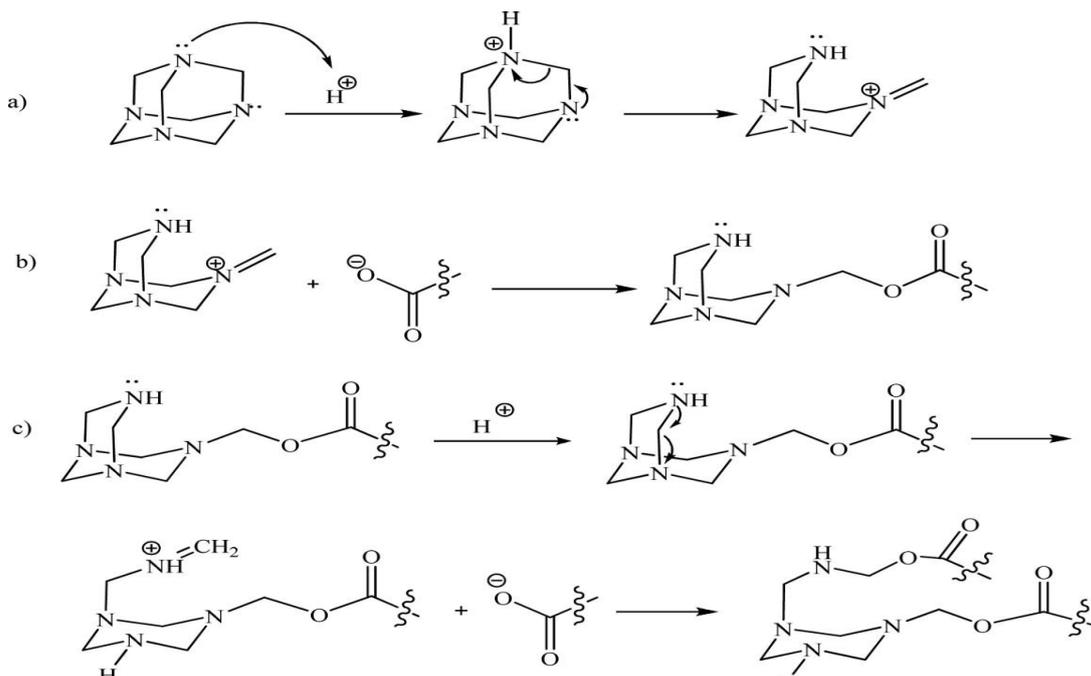**Figure 6:** Effect of HMTA% and HCl% on the gelation time (A: contour, B: response surface plot)

Figure 7: Suggested mechanism of the reaction between PAMPS and HMT

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 conditions inside the studied experimental conditions by visual inspection. For quadratic models, the critical point can be characterized as a maximum, minimum, or saddle. It is possible to calculate the coordinates of the critical point through the first derivative of the mathematical function which describes the response surface and equate it to zero [15]. The quadratic function obtained for two variables (x_1 and x_2), as described below, is used to illustrate the example:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2$$

$$\frac{\partial y}{\partial x_1} = \beta_1 + 2\beta_{11} x_1 + \beta_{12} x_2 = 0 \qquad (7)$$

$$\frac{\partial y}{\partial x_2} = \beta_2 + 2\beta_{22} x_1 + \beta_{12} x_1 = 0$$

Table 4 shows the optimum conditions obtained by solving the three equations simultaneously for the purpose of maximizing gelation time.

Conclusion

An exponent equation is presented in order to predict the gelation time based on three parameters which are 99% significant and the following conclusions were obtained:
1. HCl had the most significant effect on gelation time in contrast with HMTA and polymer concentration; the response sensibility is also the highest.
2. At a constant concentration of polymer, increasing HMTA caused a decrease in gelation time initially and then increased it, which expressed the interaction between these two factors.
3. At a constant concentration of polymer, increasing HCl caused a decrease in gelation time initially (at HCl concentrations lower than 1%) and then increased it (at HCl concentrations higher than 1%), which showed the interaction between these two factors.
4. At a constant concentration of HMTA, increasing HCl first leaded to a decrease in gelation time, but then increased it.
5. Although the optimum values need to be evaluated, acids were generally shown that they were suitable accelerators up to an optimum value.

Table 4: Optimum process conditions and its corresponding results

Gelation time (hr)	HMTA%	HCl%	Polymer Concentration (ppm)	Taraget	Case
170.087	0.11	1.41	12238.96	Maximize	Gelation time
16478.2	0.43	0.52	16533.33	Maximize	Gelation time
153.096	0.13	1.46	15963.06	Maximize	Gelation time
143.156	0.27	0.51	13266.03	Maximize	Gelation time

References

[1]. Albonico P., and Lockhart T., "*Divalent Ion-resistant Polymer Gels for High Temperature Applications: Syneresis Inhibiting Additives*", Presented at the International Symposium on Oilfield Chemistry. New Orleans. March 1993; Paper SPE 25220.

[2]. Al-Muntasheri Gh., and Zitha P., "*Gel under Dynamic Stress in Porous Media: New Insight Using Computed Tomography*", Presented at the Saudi Arabia Section Technical Symposium and Exhibition held in AlKhobar. Saudi Arabia. May 2009; Paper SPE 126068.

[3]. Hardy M., Botermans W., Hamouda A., Valdal J., and Warren J., "*The First Carbonate Field Application of a New Organically Crosslinked Water Shutoff Polymer System*", Presented at the International Symposium on Oilfield Chemistry held in Houston. Texas.February 1999; Paper SPE 50738.

[4]. Needham R., Threlkeld C., and Gall J. "*Control of Water Mobility Using Polymers and Multivalent Cations*", Presented at the 1974 SPE-AIME Improved Oil Recovery Symposium, Tulsa. April 1974; Paper SPE 4747.

[5]. Moffit P., Moradi-Araghi A., Janway V., and Young

G., "*Development and Field Testing of a New Low Toxicity Polymer Crosslinking System*", Presented at the Permain Basin Oil & Gas Recovery Conference held in Midland. Texas. March 1996; Paper SPE 35173.

[6]. Moradi-Araghi A. "*A Review of Thermally Stable Gels for Fluid Diversion in Petroleum Production*", Journal of Petroleum Science and Engineering, 26: pp. 1–10, 2000.

[7]. Moradi-Araghi A. *Application of Low Toxicity Crosslinking Systems in Production of Thermally Stable Gels*, Presented at the SPE/DOE Ninth Symposiumon Improved Oil Recovery, Tulsa, Paper SPE/DOE 27826, April 1994.

[8]. Hutchins R., Dovan H., and Sandiford B. "*Field Applications of High Temperature Organic Gels for Water Control*", Presented at the 10th SPE/DOE Improved Oil Recovery Symposium. Tulsa, Paper SPE/DOE 35444, April 1996.

[9]. Dovan H., Hutchins R., and Sandiford B. "*Delaying Gelation of Aqueous Polymers at Elevated Temperatures Using Novel Organic Crosslinkers*", Presented at the International Symposium on Oilfield Chemistry. Texas.; Paper SPE 37246, February 1997.

[10] Al-Muntasheri Gh., Zitha P., Nasr-El-Din H. *A New Organic Gel System for Water Control: A Computed Tomography Study*, Presented at International petroleum technology conference, Dubai, Paper SPE 129659, December 2007.

[11]. Simjoo M., Vafaie Sefti M., Dadvand Koohi A., and Hasheminasab R., "*Polyacrylamide gel polymer as water shutoff system: preparation and investigation of physical and chemical properties in one of the iranian oil reservoirs conditions*", Iran. J. Chem. & Chem. Eng., 26, 2007.

[12]. Sydansk R. *Conformance Improvement in a Subterranean Hydrocarbon-bearing Formation Using a Polymer Gel*, US Patent: 4683949, 1987.

[13]. Sydansk R.D., Smith T.B., "*Field Testing of a New Conformance-Improvement-Treatment Chromium (III) Gel Technology*", Presented in the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa., paper SPE. 17383, April 1988.

[14]. Bezera M., Santelli R., Oliveira E., Villar L., and Escaleira L., *Review Response Surface Methodology (RSM) as a Tool for Optimization in Analytical Chemistry*, Talanta, 76: 965, 2008.

[15]. Myers R., and Montgomery D., *Response Surface Methodology: Process and Product Optimization Using Designed Experiments,*. New York: John Wiley & Sons. 1995.