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Optimization of Swelling Percentage of Poly(AAm-*co*-AA) in $BaCl_2$ Salt Solution Using Response Surface Methodology (RSM)

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Unwanted water production from oil and gas reservoirs is a crucial problem for producers. Preformed particle gel (PPG) treatment is a benefit approach to control excess water production. Swelling percentage of PPG samples in saline water is a key factor affecting the efficiency of water conformance process. In this study, an efficient set of PPGs was synthesized and their swelling behavior was assessed. The design of experiments (DOE) software was used to design a minimum number of synthesis experiments with the aim of optimum swelling percentage of PPGs in $BaCl_2$ salt solution. The optimum ranges of acrylamide (AAm) to acrylic acid (AA) mole ratio, mole percentage of N,N'-methylenebisacrylamide (MBA) and swelling time were found to be 6.8 to 7.4, 4.2 to 4.5% and 179.8 to 180 min, respectively; this leads to obtain the swelling percentage of the synthesized PPGs in $BaCl_2$ salt solution up to 529%. Finally, an empirical correlation was proposed to predict the swelling percentage of the PPGs in $BaCl_2$ salt solution.

Keywords: Response surface methodology (RSM), Optimization, Synthesis, Copolymerization

INTRODUCTION

Unwanted water production is a great challenge for oil and gas producers. Water/oil ratio (WOR) is an essential factor in the economy of oil and gas production. WOR is a critical ratio when the water treatment costs are equal to oil and gas production benefits [1,2]. Most producers try to work below WOR economic limit. The control of excess water is a vital part of reservoir management [3]. As about fifty percent of world oil reserves are naturally fractured carbonate reservoirs [4], one reason for producing excess water can be fractures existing in a water zone [5]. Previous researchers have examined several types of fractured reservoirs as well as the properties of rocks and fluids existing in them [6-9]. One approach to treat unwanted water production is gel placement in the fractures. There are two gel treatment approaches: *in situ* gel [10-14] and preformed particle gel (PPG) [15-18]. The main mechanism of *in situ* gel to control excess water production is to reduce water-oil-interfacial tension (IFT) and to alter rock wettability of reservoirs from oil wet to water wet [19-21], while the principal role of PPGs is to block water production from fractures [22-24]. Hitherto, several researchers indicated that PPGs were more successful than *in situ* gels in water conformance processes [25-27]. PPGs usually have acrylamide in their structures and swell when they contact with water [28]. The swelling percentage of PPG in the formation brine is a key factor that can affect PPG success to control unwanted water production from oil and gas reservoirs. The properties of hydrogels and salt solutions in which hydrogels were placed can affect the swelling capacity of PPGs; the properties of hydrogels include mole ratio of monomers [29,17], type and mole percentage of crosslinking agent [30], type of additive [31,16] and type and concentration of initiator [32]; salt solution properties include salt type [33], concentration [34]

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and pH value [35,30]. Superabsorbent hydrogels are mainly composed of AAm, AA and their derivatives. The monomers are commonly polymerized by solution and suspension polymerization approach. Although both approaches are important in their own place, solution polymerization (such as free radical approach) is economically more famous [36-38]. The presence of crosslinking agents in the structure of hydrogels causes to swell hydrogel in a three-dimensional network and forms a gel [39]. MBA is a popular industrial crosslinking agent used in polymerization reactions. Usually, thermal or redox initiator, or a combination of them, is applied to start the polymerization reaction. Potassium persulfate (PPS) and ammonium persulfate (APS) are two initiators largely used for polymerization [40-42].

Researchers usually try to optimize the process response by changing input parameters. So far, many authors have attempted to optimize the key factors affecting the synthesis reaction of hydrogels [15,43,16]. One of the optimization tools used to determine key factors affecting the synthesis reaction of PPG samples is design of experiments (DOE) software [44-46]. DOE designs experiments with minimum possible tests while numerous factors affect the response of experiments. In addition, DOE reveals how to carry out the experiments without eliminating vital factors.

The aim of this work is to synthesize an efficient set of PPGs so that they can be largely swollen in the formation water and economically utilized in water conformance process. To do so, AAm and AA were used as the monomer, MBA was used as a crosslinking agent and KPS was used to start the free radical polymerization reaction. Since there is plenty of barium ion in oil reservoirs which can affect the swelling percentage of PPGs, the swelling percentage of the synthesized samples was examined in $BaCl_2$ salt solution at a concentration of 200000 ppm and pH 5. To the best of our knowledge, this is the first study that proposes an empirical correlation to optimize the swelling percentage of hydrogels in $BaCl_2$ salt solution with the use of Design-®V7 software package.

CENTRAL COMPOSITE DESIGN (CCD)

Response surface methodology (RSM) is one of the optimization techniques used in DOE. Optimization is performed with a collection of numerical or mathematical methods. Generally, the optimum, is a minimum or a maximum of output variables. There are several experimental designs in response surface methodology. CCD is one of the most common design methods with center points and a set of supplementary axial points. It suggests a mathematical model and represents results in two-dimensional or three-dimensional diagrams with designing suitable tests and finding optimum conditions of vital factors.

In this study, the amount of mole ratio of AAm/AA and mole percentage of MBA were considered as key factors in the synthesis reaction of PPG samples; time was considered as a vital factor in swelling study. Experiments were designed with three central points. Table 1 shows the mixing range of AAm/AA, MBA and swelling time, respectively. The swelling percentage of PPG samples in $BaCl_2$ salt solution was considered as the response of the software. In this study, CCD approach suggested 17 experiments; three of them were replicated as the central point. Table 2 reveals the proffered experiments.

EXPERIMENTAL

Synthesis

Based on the proposed runs by CCD, the experiments were randomly performed to avoid a statistical error in the study. In each run, 0.50 g of AAm as a monomer (Sigma-Aldrich, >99%) together with 1.0 ml of distilled water were added to a straw. A certain amount of AA as a monomer (Sigma-Aldrich, >99%), proposed by CCD, was then added to the straw. Based on the proposed mole percentage of MBA by CCD, a certain amount of MBA as a crosslinking agent (Sigma-Aldrich, >99%) was mixed with l.0 ml of distilled water and 0.2 ml of this prepared solution was then taken and added to the straw. To begin the copolymerization reaction, 0.1 ml of the potassium persulfate solution as an initiator (0.1 g $K_2S_2O_8$/ml water, Sigma-Aldrich, >98%) was added to the reaction medium. The straw was then kept in the oil bath (80 °C) for 5 h. In the end, the synthesized hydrogels were removed from the straw, cut into small pieces and dried in an oven (for 2 h) and followed by more drying in a vacuum oven (for 24 h).

Table 1. The Coded Level of Affected Variables

Process Variables	Designation	Units	-1 Level	+1 Level
Acrylamide/acrylic acid	AAm/AA	-	2.40	9.65
N,N`-methylenebisacrylamide	MBA	Mole%	4	20
Time	Time	min	3.00	180.00

Table 2. Central Composite Design

Run	AAm/AA (mole ratio)	MBA (mole%)	Time (min)
1	4.82	16	90
2	4.82	16	3
3	4.82	4	3
4	4.82	16	90
5	4.82	16	180
6	2.41	20	180
7	2.41	16	90
8	4.82	20	90
9	2.41	20	3
10	9.65	4	3
11	4.82	4	90
12	4.82	16	90
13	9.65	4	180
14	9.65	18	90
15	2.41	4	180
16	9.65	20	180
17	9.65	20	3

Swelling

After preparation of PPG samples, 0.1 g of each PPG sample swelled in 20 ml of $BaCl_2$ salt solution (at a concentration of 200000-ppm and pH 5) at ambient temperature and pressure. At a certain time, which was specified by CCD, the swollen PPGs were firstly removed

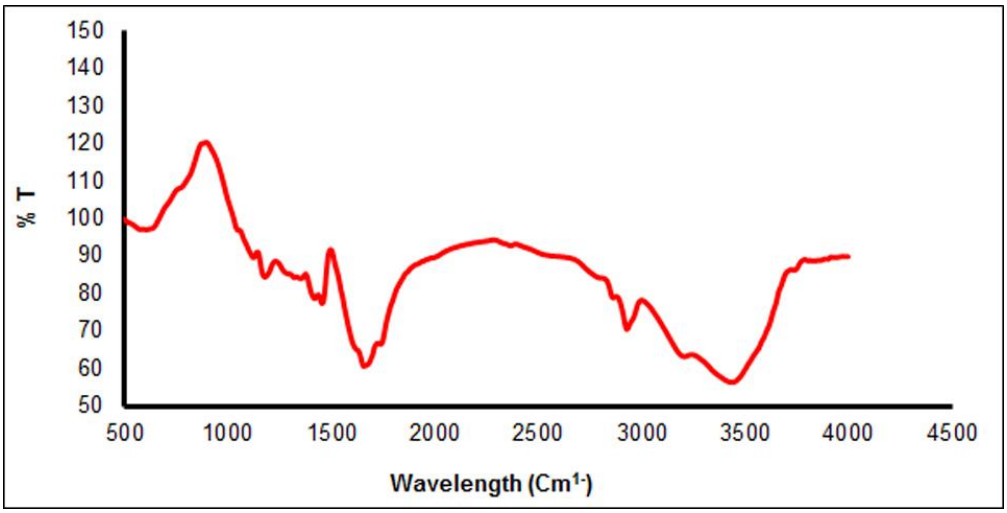

Fig. 1. Fourier transform infrared spectroscopy of sample 1.

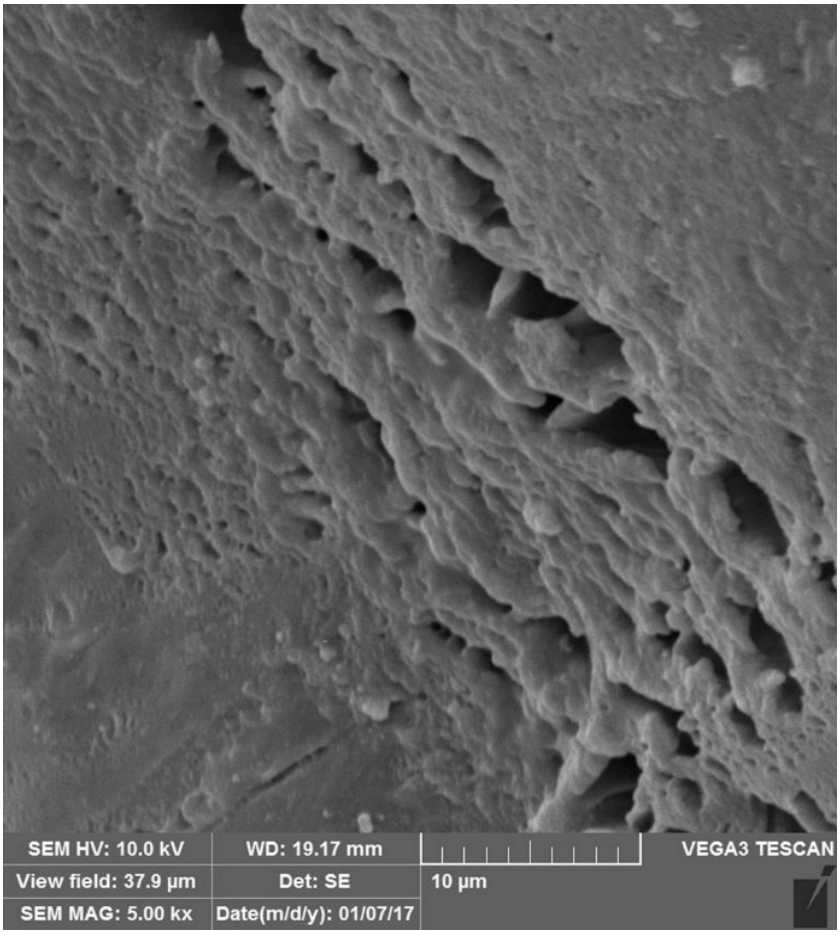

Fig. 2. Scanning electron microscopy (SEM) image of sample 1.

Table 3. Central Composite Design Matrix

Run	AAm/AA (mole ratio)	MBA (mole%)	Time (min)	Swelling (%)
1	4.82	16	90	172.186
2	4.82	16	3	43.1956
3	4.82	4	3	54.3091
4	4.82	16	90	169.546
5	4.82	16	180	340.295
6	2.41	20	180	244.795
7	2.41	16	90	158.697
8	4.82	20	90	145
9	2.41	20	3	31.2209
10	9.65	4	3	62.489
11	4.82	4	90	263
12	4.82	16	90	173.89
13	9.65	4	180	507.489
14	9.65	18	90	152.93
15	2.41	4	180	471.898
16	9.65	20	180	266.818
17	9.65	20	3	35.568

Table 4. ANOVA Analysis (Partial Sum of Squares) for Response Surface Quadratic Model (Response: Swelling%)

Source	Sum of Squares	df	Mean Square	F-Value	p-value
Model	327203.9	7	46743.41	1383.724	< 0.0001
A-AAm/AA	999.8269	1	999.8269	29.59742	0.0004
B-MBA	39621.66	1	39621.66	1172.902	< 0.0001
C-Time	260270.5	1	260270.5	7704.668	< 0.0001
AB	251.738	1	251.738	7.452086	0.0232
BC	23048.89	1	23048.89	682.3057	< 0.0001
A^2	709.1876	1	709.1876	20.99376	0.0013
C^2	491.5497	1	491.5497	14.55112	0.0041
Residual	304.0279	9	33.78088		

from the brine container, then dried (by a Whatman filter paper, grade 40:8 μm) and finally weighed (by a Sartorius balance, BP 210 S, German). The swelling percentage of PPG samples (%S) was calculated by the following equation:

$$\%S = \frac{\text{Wet weight of the PPG sample - Dry weight of the PPG sample}}{\text{Dry weight of the PPG sample}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

In this study, based on the suggested tests by CCD, 17 PPG samples were synthesized by the free radical approach. The mole ratio of AAm/AA, mole percentage of MBA and swelling time were considered as key factors in CCD. Swelling behavior of PPGs was investigated in $BaCl_2$ salt solution. The occurred reaction in the synthesis medium was shown in Scheme 1. Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) indicated the desired structure and morphology of the prepared PPG samples. Figure 1 exemplifies the FT-IR of PPG sample 1. According to Fig. 1, the formation of poly(AAm-*co*-AA) was confirmed by appeared bands in the range of 3100-3500 cm^{-1} (O-H and N-H stretching). Two absorption peaks around 3394 and 3163 cm^{-1} can be undoubtedly attributed to the asymmetric and symmetric NH_2 stretching vibrations of acrylamide. In addition, the -OH bands related to carboxylic groups were in the wide absorption bands from 3400 cm^{-1} to 2975 cm^{-1}. The occurred picks at 2916 and 1846 cm^{-1} were related to CH_2 and CH stretching vibrations, respectively. The values at 1643 and 1720 cm^{-1} were attributed to C-O stretching vibrations of carbonyl groups of acrylamide and acrylic acid, respectively. The appeared band at 1436 cm^{-1} confirmed C-N stretching vibrations. The peak observed at 1118 cm^{-1} was pertained to C-C stretching. Figure 2 exemplifies SEM image of PPG sample 1. The holes, which are visible in the structure of the sample, confirm the formation of network structure in the synthesized sample.

After the preparation of PPG samples, they were swelled in $BaCl_2$ salt solution as previously described. The measured swelling percentages of PPG samples are presented in Table 3. The obtained results from swelling experiments were inserted into CCD as the input data for further analysis. The fit summary analysis of the software suggested a quadratic model as a statistically significant model for the response.

Analysis of Variance (ANOVA)

ANOVA is a statistical appraisement used to assess the validity of the proposed model. Additionally, ANOVA can determine the importance of each factor and offer the acceptable level of each significant parameter. The details of the ANOVA tab are summarized in Table 4. Since the P-value of the model was less than 0.0001 and the F-value was equal to 1383.72, the proposed quadratic model was significant with the statistical confidence level of 95%. In the proposed model, A, B, C, AB, BC, A^2 and C^2 terms were significant factors with P-values less than 0.0500. Hence, the swelling percentage of PPG samples was influenced by all dominant factors (AAm/AA mole ratio, MBA mole percentage and swelling time).

No transformation model was used to adapt the process parameters and response surface. According to Table 5, the value of R square is almost one, and therefore the experimental results are in good agreement with the predicted values. In addition, the difference between R^2 and adjusted R^2 was less than 0.2 and there was a good accordance between Pred R^2 and adjusted R^2 indicating the accuracy of the proposed model.

Equation (2) presents the regression equation proposed for the model parameters by CCD.

$$Swelling\% = -24.86 + 21.84 \times A + 0.64 \times B + 2.54 \times C - 0.2 \times A \times B - 0.08 \times B \times C - 1.35 \times A^2 + 0.00157 \times C^2 \quad (2)$$

where, *A*, *B*, and *C* are the parameters defined in Table 4.

Model Validation

The validation of the model can be examined with the diagnostic tab in the design software. The normal plot of the residuals is shown in Fig. 3. Most residuals were on the straight line, and therefore there was a normal distribution of errors in the experiments. In addition, there was no abnormal pattern or structure in the residuals plot (Fig. 4).

CCD changes one of the effective factors over its entire range and keeps constant the other factors. The perturbation plot is a benefit approach to report the effect of process

Table 5. Different Statistical Values from ANOVA Analysis

Std. Dev.	5.81	R-Squared	0.9991
Mean	193.73	Adj R-Squared	0.9983
C.V. (%)	3	Pred R-Squared	0.9961
PRESS	1280.83	Adeq Precision	121.015

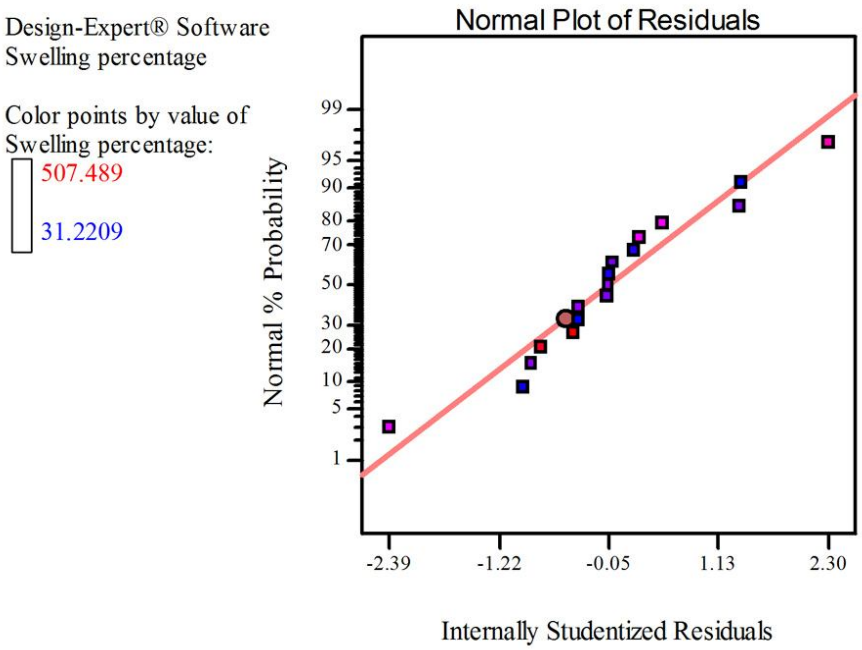

Fig. 3. Normal probability plot of residuals.

parameters on the response surface. Figure 5 shows the perturbation plot. This plot reports the effect of dominate parameters on the swelling percentage. As can be seen, the swelling time parameter has a higher deviation from the reference point, defined by the design software, than the amount of the other effective parameters (AAm/AA mole ratio and MBA mole percentage).

The difference between predicted and actual values of the response was shown in Fig. 6. A 45º-line almost covered all the points, and therefore there were negligible errors between the predicted and actual responses. Thereupon, the proposed mathematical regression was authentic.

Increasing the swelling percentage of PPG samples over time is reasonable. However, the swelling behavior of PPG samples needs more study due to the variations of AAm/AA mole ratio and MBA mole percentage.

Figure 7 shows a three-dimensional plot of the response against the mole ratio of AAm/AA and mole percentage of MBA. The rising trend of the swelling percentage curve with decreasing the mole percentage of MBA is obvious from Fig. 7. This was chiefly because of increasing the density of crosslinking agent, which lead to decreasing the spaces among the copolymer chains. Additionally, the response curve had a maximum point against the amount of AAm/AA mole ratio. The rising section of the curve was due to decreasing carboxylate groups existing in the AA

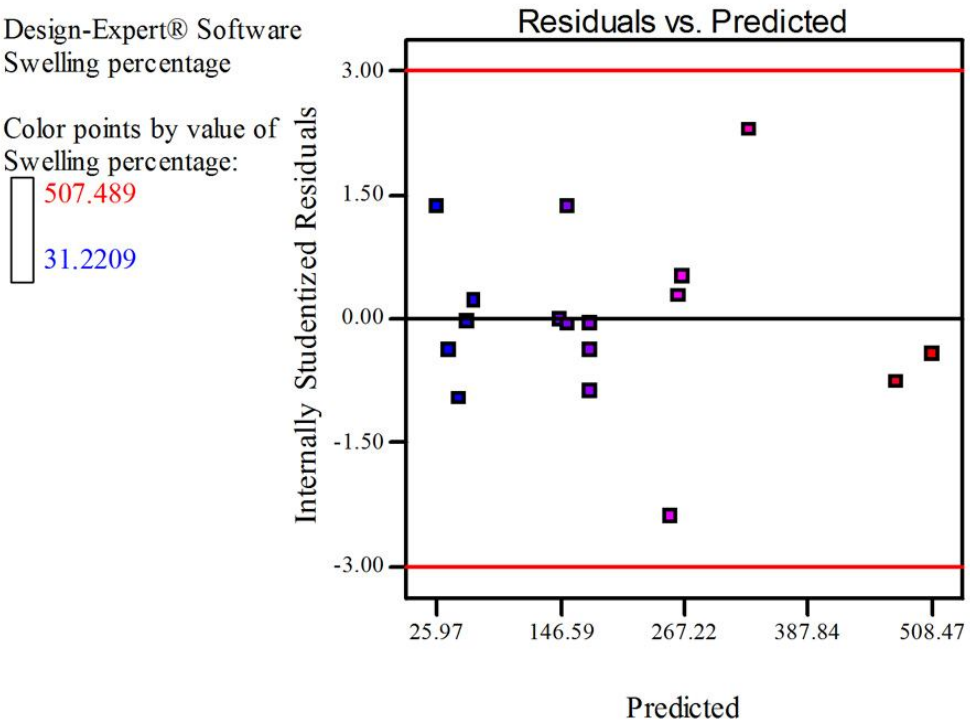

Fig. 4. Residuals *versus* predicted values.

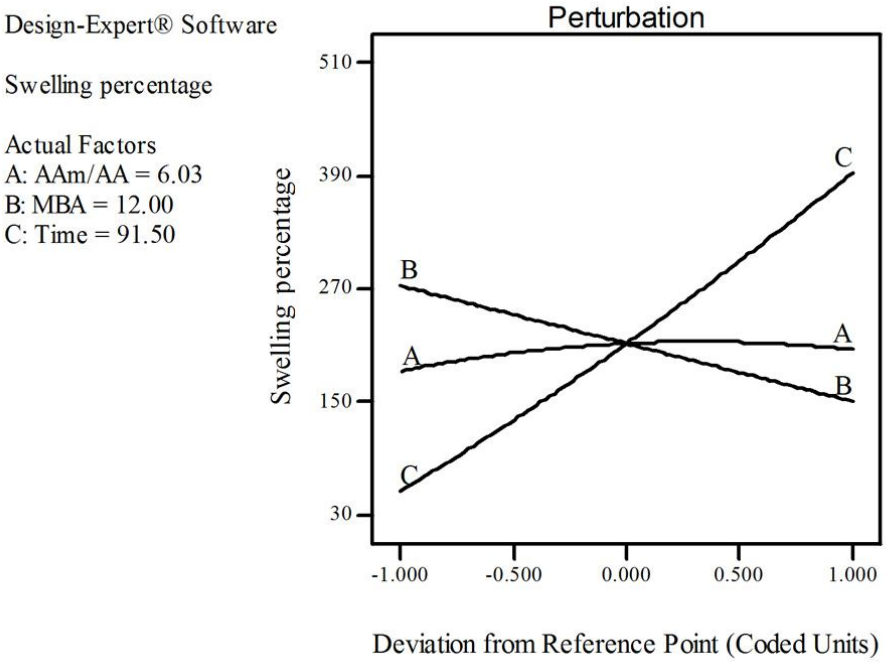

Fig. 5. Perturbation plot.

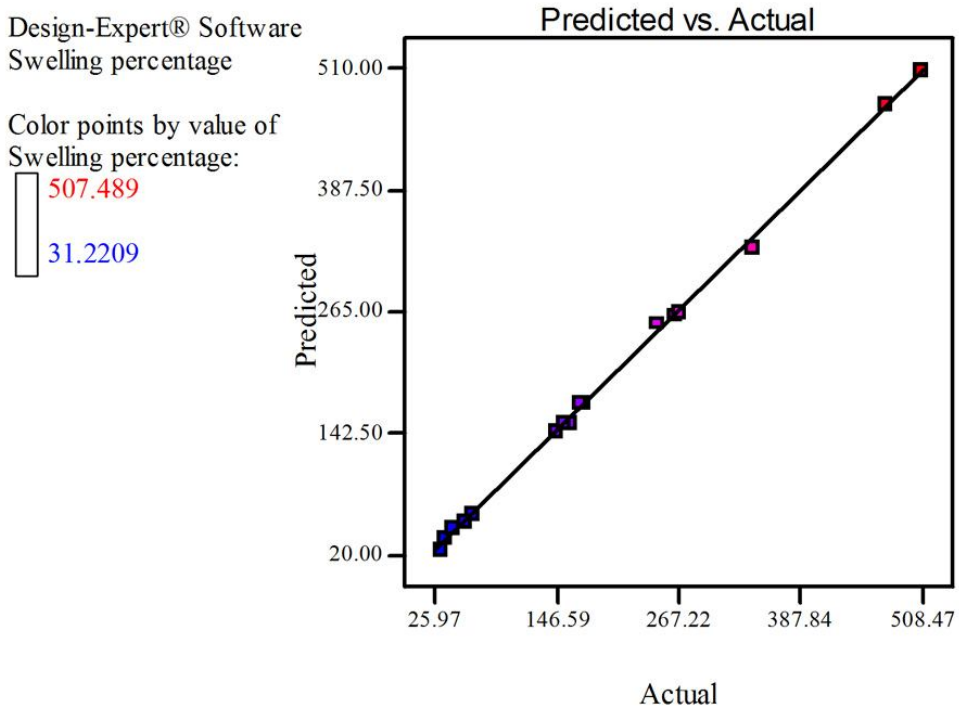

Fig. 6. Predicted against actual responses.

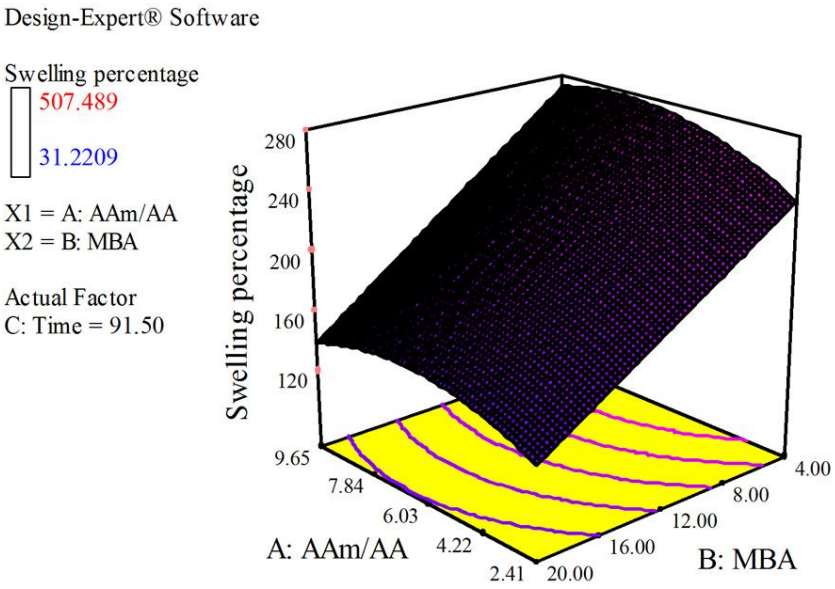

Fig. 7. 3D surface graph of swelling percentage against the mole ratio of AAm/AA and mole percentage of MBA.

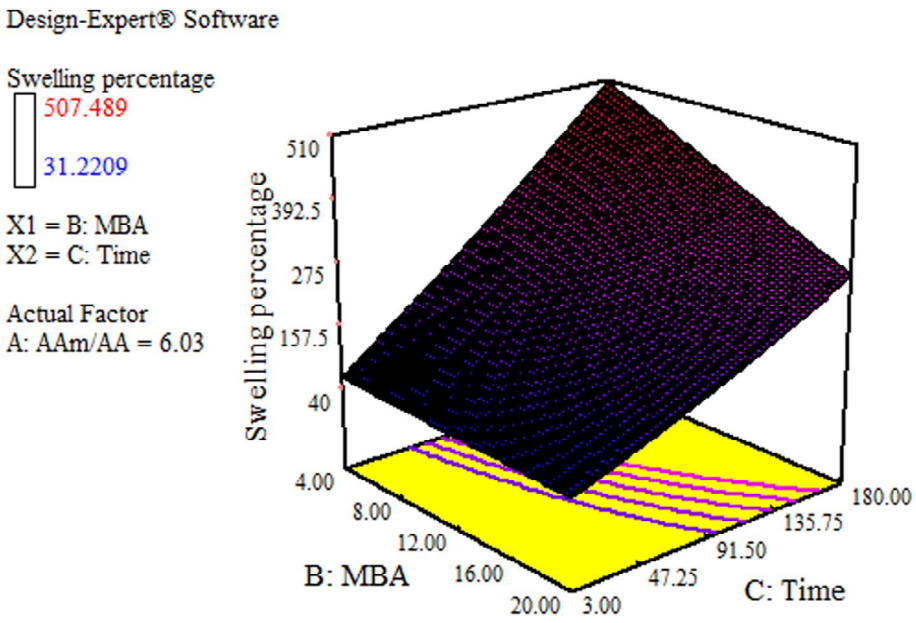

Fig. 8. 3D surface graph of swelling percentage against the mole percentage of MBA and swelling time.

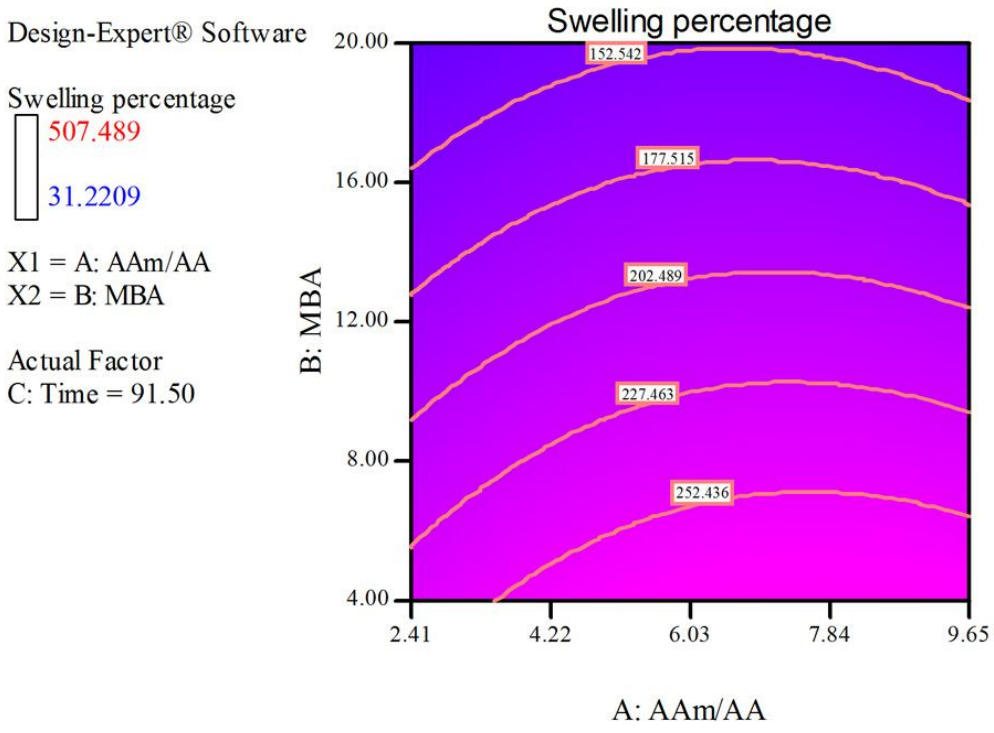

Fig. 9. Contour plot of swelling percentage against the mole ratio of AAm/AA and mole percentage of MBA.

Table 6. Optimal Conditions Obtained by Numerical Optimization

Solutions	AAm/AA (mole ratio)	MBA (mole%)	Time (min)	Desirability
1	6.79	4.2	179.97	1
2	7.43	4.32	179.78	1
3	6.69	4.48	180	0.993

Table 7. Comparison of Existing and Experimented Data

Run	AAm/AA (mole ratio)	MBA (mole%)	Time (min)	Predicted swelling (%)	Obtained swelling (%)
1	6.79	4.2	179.97	508.7498	508.17
2	7.43	4.32	179.78	507.568	505. 96
3	6.69	4.48	180	504.3541	505.87

structure and therefore decreasing repulsive forces among them with increasing the AAm/AA mole ratio. The falling trend of the curve was because of both decreasing the movement of reactants with increasing viscosity and decreasing the osmotic pressure with decreasing carboxylate groups existing in the AA monomer [47,48]. Figure 8 clarifies the rising trend of swelling percentage over time and falling trend of it against MBA mole percentage.

The results of Figs. 7 and 8 can be confirmed by the contour plot shown in Fig. 9. It is clear that high swelling capacity of PPG samples results from the average values of AAm/AA mole ratio and small amounts of MBA mole percentage.

Numerical Optimization

Since our goal was to optimize the swelling percentage of PPG samples in $BaCl_2$ salt water, numerical optimization created by StatEase Inc [49] was used to achieve this goal. To do so, the process parameters including mole ratio of AAm/AA, mole percentage of MBA and swelling time have to change in their ranges so that the response factor would be able to reach to its maximum value. As it is obvious from Table 6, there were 3 possible solutions to maximize the response factor.

The subsidiary experiments have to be performed to examine the optimum conditions suggested by the design software. Hence, these proposed possible solutions were performed in the laboratory. Results of the performed experiments affirmed the accuracy of the mentioned optimum conditions. Table 7 shows the difference between the predicted and actual results in the optimum conditions.

CONCLUSIONS

The aim of this study was to achieve an efficient set of PPG samples to control unwanted water production from oil and gas fields. To this end, several experiments were designed by CCD and were performed in the laboratory. Based on our laboratory results, an empirical correlation was proposed. The correlation precisely predicts the best conditions for the preparation of PPG samples with the aim of optimum swelling percentage in $BaCl_2$ salt water; these conditions include the mole ratio of AAm/AA, mole percentage of MBA and swelling time. Since PPG treatment

is an economically cost-effective approach to control unwanted water, the proposed model is benefit for oil and gas producers.

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