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Response Surface Methodology and Optimized Synthesis of Partially-Hydrolyzed Polyacrylamide Based Hydrogels for Water Shut-Off

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Abstract-**In this research article, a hydrogel was prepared out of the crosslinking of a partially-hydrolyzed polyacrylamide (PHPA) polymer and zirconium triacetate on the purpose of performing a water shut-off process in an oil reservoir. The tests were conducted to evaluate the effect of the composition of the hydrogel on its gelation time. Then, Central Composite Design (CCD) and Microsoft Excel were used to determine the parameters of a quadratic mathematical model for the gelation time, as function of the polymer concentration and the crosslinker/polymer ratio. Furthermore, regression analysis was used to evaluate the agreement of the model with the experimental data. The regression analysis results showed that the model fitted well to the experimental data and provides the optimum gel formulation. The obtained model shows that the crosslinker/polymer ratio has a slightly higher effect on the reduction of gelation time of the hydrogel system. Hence, optimum gel formulation may be suitable in water shut-off job for the oil fields.**

Keywords- Hydrogel; PHPA polymer; water shut-off; gelation time; oilfield

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I. INTRODUCTION

During the oil production, the primary energy of the reservoir tends to deplete and it makes necessary to act on the maintenance of the pressure inside the reservoir to continue the recovery. Water flooding is a commonly used process of displacement of oil by the injection of water [1]-[3]. The primary objective of water flooding is to fill the void spaces created by the produced oil fractions with water, thus avoiding the reservoir pressure to deplete with the increased oil production. This leads to a higher water/oil ratio (WOR) during the production but allows an increased recovery ratio from the reservoir. The efficiency of the water flooding tends to go down with the increased time as water starts to channel its way from the injection well to the production well and produce large amounts of produced water. Different methods might occur and leading to different problems solution such as mechanical and chemical methods [4]-[6].

Among the mechanical and chemical methods, the polymer gel treatment is one of the most efficient methods to control excessive produce water production. By crosslinking of polymer with transition metal ions results into a hydrogel system that is more stable on harsh environments. The aqueous solution of PHPA (Partially hydrolyzed polyacrylamide) as polymer and Cr (III) acetate as crosslinker based gel system most widely used for water shut-off in oil and gas wells [7]-[9]. That gel system firstly reduced the water permeability and consequently increasing the oil recovery. The gelation time and the gel strength of a polymer gel system are main parameters for effective well treatment. Those two parameters strongly depend on the concentration of polymer and crosslinker and reservoir conditions such as temperature, hardness, salinity etc. The gelation time will determine the injection period and how deep in to the formation the gel solution can be placed. Various researchers studied on the gelation behaviour of the polyacrylamide/Cr(III) based gel system to provide useful design data. There are several methods for the study of gelation behaviour like dynamic shear method (rheometer), sealed tube method, bottle testing method, and steady shear method (viscometer) are reported in the literatures [10]-[13].

Several researchers did extensive studies for the determination of gelation time and the effect of different parameters on gelation time by bottle testing method. But, it requires many experiments to get the effect of different parameters on the gelation time. Several researchers used the fractional factorial design to develop a functional relationship between the gelation time and the effect of different parameters on the gelation time by conducting least experiments. They also developed the quadratic model to predict the optimum gelation time and the analysis of variance (ANOVA) was used to evaluate the quality of the quadratic model [14]-[16].

In this research, partially-hydrolyzed polyacrylamide (PHPA) polymer and zirconium triacetate based hydrogel was prepared by cross-linking of polyacrylamide chains with zirconium triacetate. Then the effects of two factors (crosslinker/polymer ratio and polymer concentration) and their interactions on the gelation time were determined by using central composite design (CCD). The optimum gel formation was determined by using response surface methodology (RSM) and regression analysis was used to evaluate the agreement of the model with the experimental data. Hence, partially-hydrolyzed polyacrylamide (PHPA) polymer and zirconium triacetate based hydrogel system may be suitable in water shut-off job for oil and gas fields.

II. EXPERIMENTAL STUDIES

II.I. Materials

Partially-hydrolyzed polyacrylamide (PHPA) was obtained from Oil and Natural Gas Corporation Limited, Mumbai, India. Sodium chloride salt was procured from the Merck Pvt. Ltd., Mumbai, India and Zirconium acetate was purchased from Sigma-Aldrich, USA.

II.II. Preparation of the hydrogel system

Firstly, partially-hydrolyzed polyacrylamide aqueous stock solution was prepared in brine by using constantly stirred on a magnetic stirrer until uniform viscous solution was obtained. For the proper dissolution of the polymer in brine, the polymer aqueous stock solution aged for almost 24 hours at normal temperature. After 24 hours, the fresh solution of zirconium acetate crosslinker was prepared in a different beaker in desired concentrations and mixed it with the polymer solution at specific ratio which is called as gelant. Gelants were taken in glass tubes and kept in hot air oven at 90 ^{o}C for gelation and inspected visually the gel formation at regular intervals.

II.III. Preparation and gelation study of hydrogel

The gelation time for gel system can be determined by the two methods as bottle testing method and viscosity analysis method. Among the two methods, the bottle testing method is inexpensive, fast and semi-quantitative measurement method for the determination of gelation kinetics of different concentration formulations. For the preparation of hydrogel, firstly the gelant solution was prepared according to the CCD plan at 90 ^{o}C and then transferred into the 30 ml capacity bottles with 15-20 ml of gelant. Bottles filled with gelant kept into the oven and investigated at frequent intervals by the tilting of bottles to observe gel formation. The gelation time was noted after gel formed and expressed in alphabetic code of A through J according to Syndansk's method [8]-[9] as shown in table 1.

Table 1: Syndansk's code method and gel description

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

III. EXPERIMENTAL DESIGN METHOD

III.I. Regression Analysis

In statistics, regression analysis is basically a process of determining the relationship among variables. It helps on the understanding of how the value of a dependent variable changes with variation on the independent variable values and on the forecasting of the dependent variable value with the independent values.

A linear regression model might be expressed as

.
$$Y = \mathrm{X} \cdot \mathrm{Q} + \mathrm{C} \qquad \textbf{(1)}$$

Where, the unknown parameters vector are denoted by Q, the independent variables vector, or Design Matrix, denoted by$\mathrm{X}$, the dependent variables vector, denoted by$Y$ and the residual vector, denoted by C.

The Design-Expert shows that the model that best fit to the relationship between the gelation time and composition of hydrogel system is a quadratic model.

The quadratic model might be expressed as

$$T = \mathrm{Q}_1 + \mathrm{Q}_2 A + \mathrm{Q}_3 B + \mathrm{Q}_4 AB + \mathrm{Q}_5 A^2 + \mathrm{Q}_6 B^2 \qquad (2)$$

Where, the PHPA concentration, in ppm, denoted by A, the Crosslinker/PHPA ratio, denoted by B and the gelation time is denoted by T.

III.II. Leverage and Cook's Distance

Leverage is defined as the measure of how far away the independent variable values are from the others. In regression analysis, the leverage of the i-th run is the i-th diagonal element of the Projection Matrix as given by Equation 3:

$$H = \mathrm{X}(\mathrm{X}^t\mathrm{X})^{-1}\mathrm{X}^t. \qquad (3)$$

Cook's Distance relates both the residual and the leverage of each data point in an observation. It is a measure of the estimated influence of a data point on the model fitted when performing the least-squares regression analysis. It is defined as

$$D_\mathrm{i} = \frac{{}_\mathrm{i}^2}{MS_{Res} \cdot (\mathrm{k}+1)}\left[\frac{h_\mathrm{i}}{(1-h_\mathrm{i})^2}\right] \qquad \textbf{(4)}$$

where k is the number of independent variables and MS_{Res} is the mean square residual. The MS_{Res} is given by

$$MS_{Res} = \frac{\sum_{\mathrm{i}=1}^{n}(y_\mathrm{i} - \hat{y}_\mathrm{i})^2}{n - \mathrm{k} - 1} \qquad (5)$$

Design Expert software version 7.0.0 (STATE-EASE Inc., Minneapolis, USA) was used for regression analysis and analysis of variance (ANOVA). The ANOVA consists of calculations that provide information about levels of variability within a regression model and form a basis for tests of significance. The total variance of the data is partitioned into the variance of the model and the variance of the residual. The probability density function for the F-value was calculated using the FDist function from Excel®. For a significance level of 5% ($\alpha = 0.05$), if the probability is lesser than 10%, it means that the source of variance is significant. Hence if it's greater than 10%, the source of variance is not significant [14]-[16].

As described earlier, the main goal of the present work is to determine a mathematical model that enables the prediction of the gelation time. Also, it is possible to determine the optimum points (i.e. hydrogel system composition) that will result in a specified gelation time. This is possible by solving the Equation 2 for a specified T.

IV. RESULTS AND DISCUSSION

IV.I. Response Surface Methodology (RSM)

A central composite design (CCD) was used to develop a model for determination correlation between the polymer concentration (A) and crosslinker/polymer ratio (B) variables to the gelation time. Through initial experiments, it was found that minimum polymer concentration is 4000 ppm and 0.12 crosslinker/polymer ratio required for the development of hydrogel system. Therefore, polymer concentration and crosslinker/polymer ratio were selected in range of 4000–10701 ppm and range of 0.12-0.49 respectively as shown in Table 2.

Table 2: Factors and limits for the regression analysis.

Variable	Low axial - = -1.41	Low factorial (-1)	Center (0)	High factorial (+1)	High axial + =+1.41
A: Polymer concentration (ppm)	4000	4981	7351	9720	10701
B: Crosslinker/polymer ratio	0.12	0.17	0.31	0.44	0.49

Twenty four bottle test experiments were designed for applying the CCD method. Table 3 shows the experimental results obtained for the gelation time as function of the polymer concentration (A) and the crosslinker/polymer ratio (B).

Table 3: Experimental runs and results

	Experimental Variables		
Run	**A: Polymer Concentration (ppm)**	**B: Crosslinker/Polymer ratio**	**Gelation Time (Hrs.) / Actual**
1	7097	0.27	2.85
2	7097	0.27	2.70
3	7097	0.27	2.80
4	7097	0.27	2.80
5	7097	0.27	2.42
6	7097	0.27	2.45
7	7097	0.27	2.66
8	7097	0.27	2.83
9	7097	0.27	2.44
10	7097	0.27	2.64
11	7097	0.49	0.47
12	7097	0.49	0.45
13	7097	0.49	0.45
14	10701	0.27	0.40
15	10701	0.27	0.38
16	10701	0.27	0.42
17	9200	0.12	2.37
18	9200	0.12	2.62
19	9200	0.43	0.42
20	9200	0.43	0.42
21	4000	0.27	2.95
22	4000	0.27	2.85

23	4900	0.43	1.00
24	4900	0.43	1.05

IV.II. Regression Analysis

The ANOVA analysis was performed by testing the model and the lack of fit (Table 4). The results of the statistical analysis are shown in Table 4.

Table 4: ANOVA for response surface quadratic model

Source	**SS**	**d.f.**	**MS**	**F-value**	**Prob> F**	**Result**
Model	26.25	5	5.25	195.70	0.0000	Significant
Residual	0.48	18	0.03			
Lack of Fit	0.00	3	0.00	0.01	0.9985	Not Significant
Pure Error	0.48	15	0.03			

The results shown on

Table indicate that the model has a significant fitting. The statistical analysis of the experimental runs was shown in Figure 1. A figure shows R^2 near 1 which indicates that the model is adequate to describe the evaluated relationship.

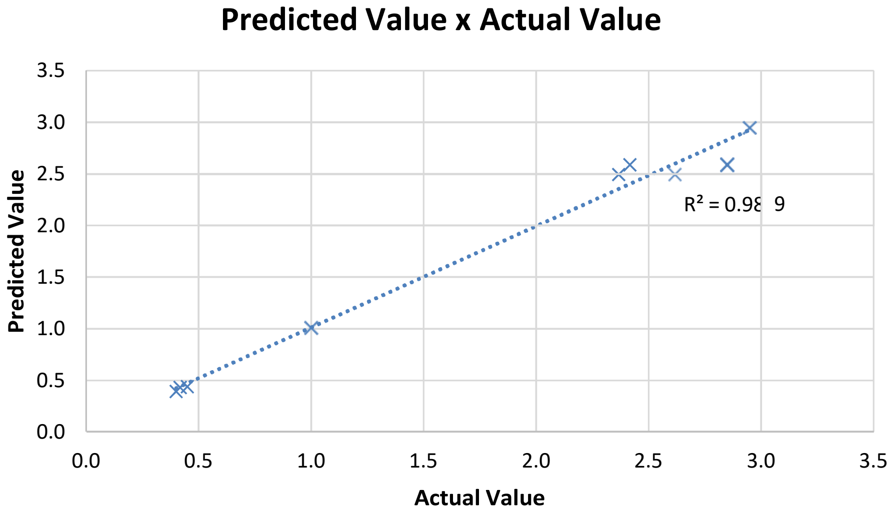

Figure 1: Scatter plot of the predicted versus the actual value.

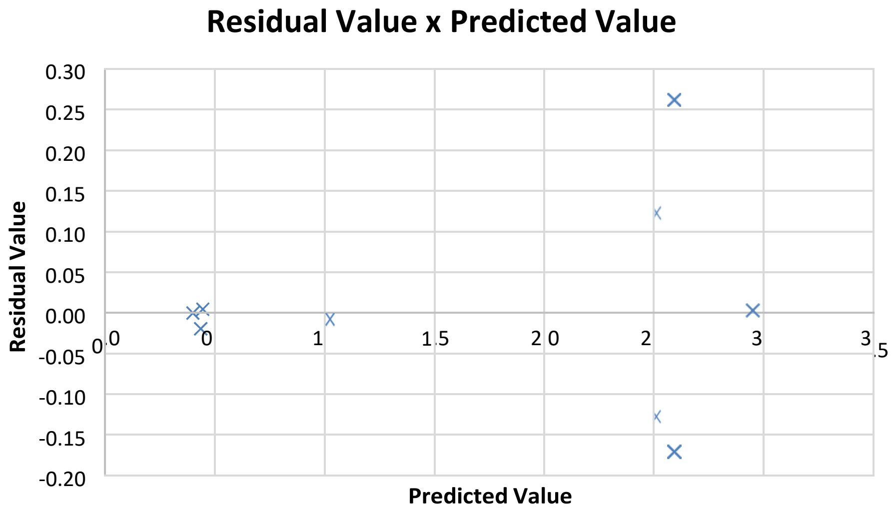

Figure 2: Scatter plot of the residual versus the predicted value.

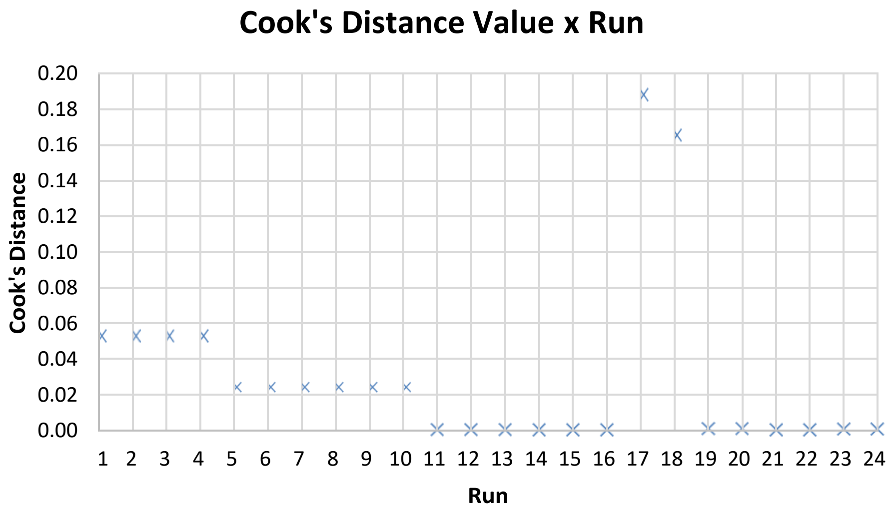

Figure 3: Cook's Distance plotted versus experimental run

The Figure 2 shows the random points with no trendline which indicates that the experimental runs were performed with minimum influence. As shown in Figure 1 and Figure 2, the model fitted well to the experimental runs with a minimum influence on the performing of these. The data point can be considered influential if the Cook's Distance is higher than$4/k$, where k is the number of experimental runs, in this case 0.17. Therefore, model was well fitted with minimum influence. The ANOVA analysis gives the quadratic model was fitted to the experimental runs and predict the outcome of gelation time by the following equation:

$$T = 2.19 - 0.8A - 1.2B + 0.4AB - 0.41A^2 - 0.04B^2 \qquad (6)$$

From the coefficients, we can see that the crosslinker/polymer ratio (B) has a slightly higher effect on the decreasing of the gelation time than the polymer concentration (A). The contour and response surface plot are shown in Figure 4 and Figure 5.

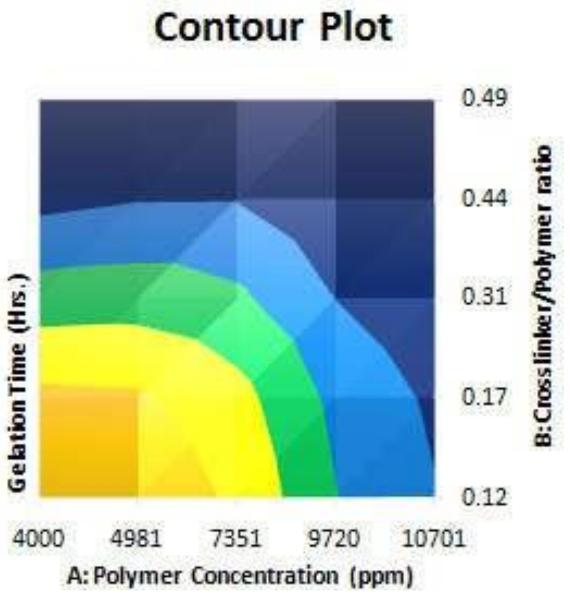

Figure 4: Contour plot for the fitted model.

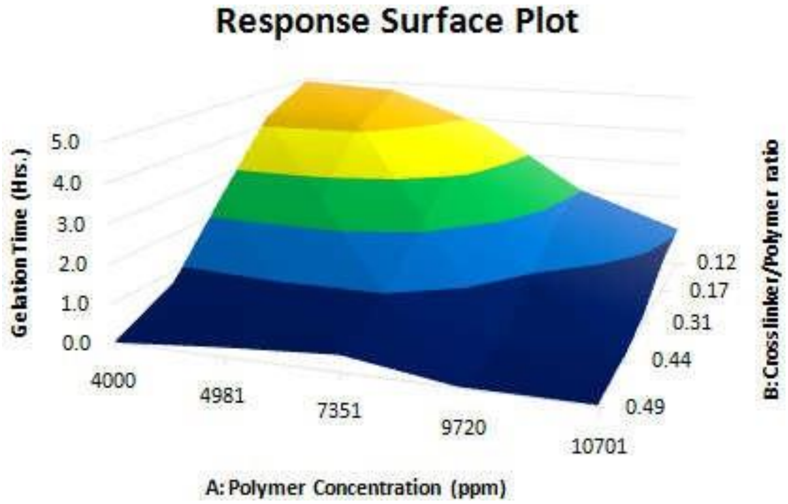

Figure 5: Response surface plot for the fitted model.

IV. III. Optimization of Gelation Time:

In most of the cases, longer gelation time is favourable but few researchers suggest that short gelation time is also favourable. They suggested that in the range of about 2 hours to about 4 hours are sufficient for a well treatment. In this study, the optimization of the gelation time was performed to seek for an optimum gel formation at which the optimum gelation time is achieved. The software predicted that optimized conditions for gelation time were obtained when the polymer concentration and crosslinker/polymer ratio were at 4749 ppm and 0.27 respectively, with predicted gelation time of 3.0 hours. By the experimental analysis, the gelation time was found 3.4 hours. So, it shows that the model is very close to the experimental vale and the model fitted well to the experimental run.

V. CONCLUSION

The regression analysis results showed that the model fitted well to the experimental data. The obtained model shows that the crosslinker/polymer ratio has a slightly higher effect on the reduction of gelation time of the hydrogel system. The model predicted an optimum gel formation with optimum gelation time which also verified with experimental analysis. Therefore, this hydrogel system may be used on water shut-off processes for enhanced oil recovery.

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REFERENCES

[1] Y. Bai, C. Xiong, F. Wei, J. Li, Y. Shu, and D. Liu, "Gelation study on a hydrophobically associating polymer/polyethylenimine gel system for water shut-off treatment", Energy & Fuels, vol. 29(2), pp.447-458, 2015.

[2] C. Dai, G. Zhao, Q. You, and M. Zhao, "A study on environment-friendly polymer gel for water shut-off treatments in low-temperature reservoirs", Journal of Applied Polymer Science, vol. 131(8), 40154 (1-7), 2014.

[3] U.S. Yadav, and V. Mahto, "Rheological study of partially hydrolyzed polyacrylamide-hexamine-pyrocatechol gel system", International Journal of Industrial Chemistry, vol. 4(1), pp.1-6, 2013.

[4] R. Singh, and V. Mahto, "Preparation, characterization and core flood investigation of polyacrylamide/clay nanocomposite hydrogel system for enhanced oil recovery", Journal of Macromolecular Science, Part B, vol. 55(11), pp.1051-1067, 2016.

[5] U.S. Yadav, and V. Mahto, "Investigating the effect of several parameters on the gelation behavior of partially hydrolyzed polyacrylamide–hexamine–hydroquinone gels", Industrial & Engineering Chemistry Research, vol. 52(28), pp. 9532-9537, 2013.

[6] R. Singh, K. Kant, and V. Mahto, "Study of the gelation and rheological behavior of carboxymethyl cellulose-polyacrylamide graft copolymer hydrogel", Journal of Dispersion Science and Technology, vol. 36(6), pp.877-884, 2015.

[7] G.P. Karmakar, and C. Chakraborty, "Improved Oil recovery using polymeric gelants: a review", Indian Journal of Chemical Technology, vol. 13 (2), pp.162-167, 2006.

[8] R.D. Sydansk, "A newly developed chromium (III) gel technology", SPE Reservoir Engineering, vol. 5(03), pp.346-352, 1990.

[9] R.D. Sydansk, and G.P. Southwell, "More than 12 years of experience with a successful conformance-control polymer gel technology", SPE Production & Facilities, vol. 15 (4), pp. 270-278, 2000.

[10] S.L. Bryant, M. Bartosek, T.P. Lockhart, and D. Giacca, "Polymer gelants for high temperature water shutoff applications", SPE Journal, vol. 2(04), pp.447-454, 1997.

[11] W. Cai, and R. Huang, "Study on gelation of partially hydrolyzed polyacrylamide with titanium (IV)", European polymer journal, vol. 37(8), pp.1553-1559, 2001.

[12] R. Banerjee, B. Ghosh, K. Khilar, F. Boukadi, and A. Bemani, "Field application of phenol formaldehyde gel in oil reservoir matrix for water shut-off purposes", Energy Sources, Part A, vol. 30(19), pp.1779-1787, 2008.

[13] H. Jia, W.F. Pu, J.Z. Zhao, and F.Y. Jin, "Research on the gelation performance of low toxic PEI cross-linking PHPAM gel systems as water shutoff agents in low temperature reservoirs", Industrial & Engineering Chemistry Research, vol. 49(20), pp.9618-9624, 2010.

[14] U.S. Yadav, and V. Mahto, "Experimental studies, modeling and numerical simulation of gelation behavior of a partially hydrolyzed polyacrylamide-hexamine-pyrocatechol polymer gel system for profile modification jobs", International Journal of Advanced Petroleum Engineering and Technology, vol. 1(1), pp. 1−16, 2012.

[15] R. Singh, and V. Mahto, "Study of the polymer concentration and polymer/crosslinker ratio effect on gelation time of a novel grafted polymer gel for water shutoff using a central composite design method", Polymers for Advanced Technologies, vol. 27(2), pp.204-212, 2016.

[16] U.S. Yadav, and V. Mahto, "Modeling of partially hydrolyzed polyacrylamide-hexamine-hydroquinone gel system used for profile modification jobs in the oil field", Journal of Petroleum Engineering, vol. , pp.1-11, 2013.