

# EFFECTIVENESS OF PARTIALLY HYDROLYZED POLYACRYLAMIDE – HEXAMINE – PYROCATECHOL GEL FOR PROFILE MODIFICATION JOBS

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## ABSTRACT

A major problem in maximizing oil production potential is the maintenance of adequate mobility control and favorable permeability profiles within the reservoir. Currently, polymer gel systems are receiving a great deal of attention in this application. A laboratory investigation of a partially hydrolyzed polyacrylamide-hexamine-pyrocatechol gel system was conducted to determine whether the system develops In-depth permeability modification in unconsolidated sand packs. Flow experiments were conducted in 35cm long, 2.85cm internal diameter unconsolidated sand packs in which the gel solution was mixed before injection. Injection rates were designed to provide adequate residence time for the gel solution to develop in-situ flow resistance during displacements based on bulk gel characterization tests. Sand pack core flooding experiments show that the mentioned gel has good plugging ability and may be used for profile modification jobs in the oilfields.

KEYWORDS: Profile Modification, Cross, Linked Polymer Gel, Gelation Time, In-Situ Gelation, Plugging Ability

#### **INTRODUCTION**

The effectiveness of polyacrylamide and polysaccharides gel systems in reservoirs with temperatures above about  $160^{\circ}F(71^{\circ}C)$  is questionable because of thermal instability of the gels[1]-[2]. Due to this reason, the crosslinked polymer gel systems are now used in profile modification of petroleum reservoirs as they have high temperature stability and capability to provide rigid gel having high mechanical strength [3]-[8]. The base polymers are cross linked with eithers inorganic or organic cross linkers. Inorganic cross linkers include Cr (III), Al (III) and Zr<sup>+4</sup> and have been mostly utilized to crosslink partially hydrolyzed polyacrylamide. Inorganically crosslinked gels result from the ionic bonding between the negatively charged carboxylate groups and the multivalent cation. The gelation mechanism of organic crosslinkers is done by covalent bonding, which is much more stable than the ionic bonds. Organic crosslinkers were introduced to obtained gels that can remain stable over a wide temperature range. For high temperature (>90°C) reservoirs, acrylamide based copolymers with organic crosslinking agents, such phenol-formaldehyde and its derivatives, can be used to form a gel with thermal stability, and the gelation time is adjustable [9]-[11]

Effectiveness of polymer gel system is generally evaluated by In-situ gelation experiments. The resistance to water flow, which is defined by residual resistance factor, persists after the polymer gel has been plugged of water in the porous media. If there is reduction in permeability by the In-Situ gelation studies in porous media, the value of the residual resistance factor will always be greater than unity [12].

In this work, the partially hydrolyzed polyacrylamide polymer is crosslinked with hexamine-hydroquinone and hexamine-pyrocatechol crosslinkers to form the polymer gel. The plugging ability of these polymer gel systems were thoroughly investigated at several temperatures ranges from 80°C to 120°C and also determine the effect of temperature, polymer and crosslinkers concentration on effectiveness of polymer gels in In-Situ condition for its suitability in the profile modification jobs.

## **EXPERIMENTAL WORK**

#### Material Used

The materials used for this work are partially hydrolyzed polyacrylamide, hexamine, hydroquinone, pyrocatechol, sodium chloride, hydrochloric acid and sodium hydroxide. Partially hydrolyzed polyacrylamide is procured from Oil and Natural Gas Corporation Limited, Mumbai, India. Hexamine is purchased from Otto Kemi Mumbai, India and Hydroquinone is procured from Ranbaxy Fine Chemicals Ltd., New Delhi, India. Pyrocatechol and hydrochloric acid are purchased from Central Drug house (P) Ltd. New Delhi, India. Sodium chloride is purchased from Nice Chemical Pvt. Ltd. Cochin, India and sodium hydroxide is purchased from S. D. Fine–Chem Ltd. Mumbai, India.

#### **Experimental Procedure**

Initially, porous media was prepared in the core holder using IS 60/70 mesh size sand particles which was connected to injecting fluid container and high pressure syringe pump (as shown in Figure 1). This core holder was kept in the hot air oven for the study of plugging ability of polymer gel in the porous media under insitu conditions.

The brine was taken in the injecting fluid container and injected into the core holder by high pressure syringe pump. The injection rate was adjusted by controller provided with pump. Brine was injected at 10 psi and 2-3 pore volume was passed through porous media (sand pack). It was assumed that the sand pack was totally saturated with brine. Effluent brine sample was collected in measuring cylinder with time and the initial absolute permeability of the sand pack was calculated. After brine injection, prepared gelant solution was injected in sand pack at same condition and 2-3 pore volume of gelant was collected. When the core was saturated with gelant and effluent sample of gelant was collected in small glass bottle. The core holder and effluent gelantwere kept in hot air oven for certain period to insure the gel formation. When the gel was formed in the small glass bottle contained effluent gelant sample and the time was noted. The core holder was kept in hot air oven (shown in Figure 1) for more than 3 times of noted gelation time of the effluent gelant solution. Then again brine was injected through it at the same condition to find out the post gelation permeability, percentage permeability reduction and residual resistance factor.

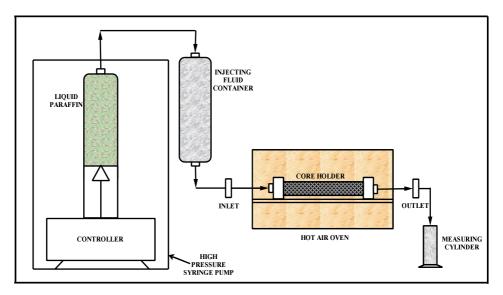


Figure 1: Flow Diagram of In-Situ Gelation Setup

# **RESULTS AND DISCUSSIONS**

The brine solution was injected into five sand pack samples namely A, B, C, D and E and the flow rate of the whole process was recorded and a summary of the injecting conditions is shown in Table 1. Further, gelant solutions were

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injected at the same pressure. It was observed that injection of gelant solution occurs at 10 psi differential pressure which shows that the developed solution have good injectivity.

Sl.	Sample	Porosity	Flow Rate	Pre-Gelation
No.	No.	(%)	(ml/sec)	Permeability (Darcy)
1	А	36.7254	0.2041	1.6460
2	В	36.7254	0.2128	1.7162
3	С	36.7254	0.2083	1.6799
4	D	36.7254	0.2083	1.6799
5	Е	36.7254	0.2041	1.6460

Table 1: Before In-Situ Gelation Study of Flow Rate and Pre-Gelation Permeability at 10 Psi

The sand pack flooded with polymer gel solutions containing different concentrations of partially hydrolyzed polyacrylamide polymer, hexamine and hydroquinone crosslinkers were kept in the hot air oven at reservoir temperature ranges from 80 to 120°C.

After the complete gelation in the sand packs, the brine solution was again injected at different pressure drop (shown in Figure 2). The behavior of flow rates at various pressure drops are shown in Table 2. As increasing in pressure drop, the brine flow rate increases.



Figure 2: Sand Pack after In-Situ Gelation of PHPA-HMTA-Pyrocatechol Gel System Table 2: In-Situ Gelation Studies at Different Temperature (1.0 wt% PHPA, 0.5 wt% HMTA, 0.5 wt% Pyrocatechol)

	Pressure	Flow Rate (ml/sec)						
Sl.	Drop		°C)					
No.	$\Delta \mathbf{P} (\mathbf{atm})$	80	90	100	110	120		
		Sample A	Sample B	Sample C	Sample D	Sample E		
1	197.28	2.00	1.00	0.71	0.63	0.05		
2	204.08	2.43	1.43	0.83	0.70	0.09		
3	210.88	2.67	1.67	0.98	0.85	0.10		
4	217.69	3.00	2.00	1.40	1.08	0.12		
5	224.49	3.50	2.50	1.67	1.30	0.18		
6	231.29	3.83	3.33	1.93	1.50	0.21		
7	238.10	5.60	3.80	2.32	1.70	0.25		
8	244.90	7.00	4.67	2.68	1.91	0.30		

The post gelation permeability increases with increase in the pressure drop in the sand pack at temperature ranges from 80 to 120°C was shown in Tables 3. The large difference between pre and post gelation permeability leads to plugging ability of polymer gel system.

	Pressure	Post Gelation Permeabilities (X 10 <sup>-3</sup> ) (Darcy)					
Sl.	Drop						
No.	$\Delta \mathbf{P}$ (atm)	80	90	100	110	120	
		Sample A	Sample B	Sample C	Sample D	Sample E	
1.	197.28	55.62	27.81	19.75	17.52	1.33	
2.	204.08	65.30	38.41	22.31	18.82	2.33	
3.	210.88	69.39	43.36	25.50	22.11	2.60	
4.	217.69	75.61	50.41	35.28	27.09	2.90	
5.	224.49	85.54	61.10	40.81	31.77	4.40	
6.	231.29	90.92	79.07	45.78	35.58	5.06	
7.	238.10	102.08	87.56	53.46	39.17	5.85	
8.	244.90	156.82	104.62	60.04	42.79	6.74	

Table 3: Effect of Temperatures on Post Gelation Permeabilities (1.0 wt% PHPA,0.5 wt% HMTA, 0.5 wt% Pyrocatechol) at pH 8.5

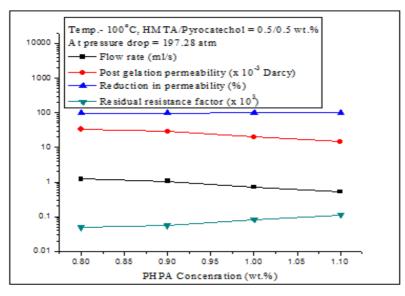
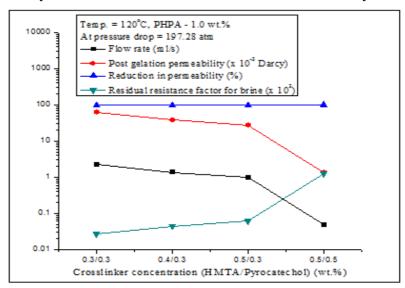


Figure 3: Effect of Polymer Concentration on Effectiveness of PHPA-HMTA-Pyrocatechol Gel System





The effect of polymer and crosslinker concentration on post gelation permeability is shown in Figure 3 and Figure 4 respectively. The increase in polymer and crosslinker concentration decreases the post gelation permeability because of the strength of the gel is strongly depends on polymer and crosslinker concentration.

	Pressure	<b>Reduction in Permeabilities (%)</b>						
Sl.	Drop	Temperature (°C)						
No.	$\Delta \mathbf{P} (\mathbf{atm})$	80	90	100	110	120		
		Sample A	Sample B	Sample C	Sample D	Sample E		
1	197.28	96.62	98.38	98.82	98.96	99.92		
2	204.08	96.03	97.76	98.67	98.88	99.86		
3	210.88	95.78	97.47	98.48	98.68	99.84		
4	217.69	95.41	97.06	97.90	98.39	99.82		
5	224.49	94.80	96.44	97.57	98.11	99.73		
6	231.29	94.48	95.39	97.27	97.88	99.69		
7	238.10	92.16	94.90	96.82	97.67	99.64		
8	244.90	90.47	93.90	96.43	97.45	99.59		

Table 4: Effect of Temperatures on Reduction in Permeabilities (1.0 wt% PHPA, 0.5 wt%HMTA, 0.5 wt% Pyrocatechol) at pH 8.5

The reduction in permeability decreases with increase in the pressure drop in the sand pack at temperature ranges from 80 to 120°C was shown in Table 4. The effect of polymer and crosslinker concentration on permeability reduction was also shown in Figure 3 and Figure 4 respectively. With increase in polymer and crosslinker concentration, the permeability reduction increases because of the strength of the gel is strongly depends on polymer and crosslinker concentration. At 120°C, the polymer gel system shows very good result at 197.2789 atm and 244.8980 atm where permeability reduction were 99.92% and 99.59% respectively.

Table 5: Effect of Temperatures on Residual Resistance Factor (1.0 wt% PHPA, 0.5 wt%HMTA, 0.5 wt% Pyrocatechol) at pH 8.5

	Pressure	<b>Residual Resistance Factor (X 10<sup>3</sup>)</b>							
Sl.	Drop	Temperature (°C)							
No.	$\Delta \mathbf{P}$	80	80 90 100 110 120						
	(atm)	Sample A	Sample B	Sample C	Sample D	Sample E			
1	197.28	0.030	0.062	0.085	0.096	1.233			
2	204.08	0.025	0.045	0.075	0.089	0.706			
3	210.88	0.024	0.040	0.066	0.076	0.633			
4	217.69	0.022	0.034	0.048	0.062	0.568			
5	224.49	0.019	0.028	0.041	0.053	0.374			
6	231.29	0.018	0.022	0.037	0.047	0.325			
7	238.10	0.013	0.020	0.031	0.043	0.281			
8	244.90	0.011	0.016	0.028	0.039	0.244			

Residual resistance factor is the ratio of before and after gel treatment permeabilities. The residual resistance factor was decreases with increasing the pressure drop in the sand pack at temperature ranges from 80 to  $120^{\circ}$ C was shown in Tables 5. The effect of polymer and crosslinker concentration on residual resistance factor was also shown in Figure 3 and Figure 4 respectively. With increase in polymer and cross linker concentration the residual resistance factor increases as the strength of the gel is strongly depends on polymer and crosslinker concentration. At  $120^{\circ}$ C, the polymer gel system is a show the very good result at 197.2789 atm is  $1.233 \times 10^3$  and 244.8980 atm is  $0.244 \times 10^3$ .

#### CONCLUSIONS

The experimental study shows that the plugging ability of polymer gel systems in the porous media is the function of temperature, polymer and crosslinker concentration. With increase in temperature, polymer and crosslinker concentrations the value of permeability reduction and residual resistance factor increases. From these studies, it was experimentally found that the developed gel systems are effective up to 120°C. Hence, these gel systems shows good plugging ability and may be used for profile modification jobs in high temperature and high pressure wells.

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