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Gel Formula Optimization by Ascertaining Polymer Concentration, Crosslinker Concentration and Delaying Agent-Crosslinker Ratio

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Abstract: *In this study, we used a polyacrylamide polymer crosslinked by Chromium III cross linking agent. The used simulated formation water has a salinity of 40000mg/L. To synthesize an appropriate gel that will respond to reservoir conditions and requirements, we tried to optimize the crosslinker concentration, the polymer concentration and the delaying agent concentration by taking into account the given reservoir condition. We used the cross linking with different concentrations which are 25mg/L, 50mg/L, 75mg/L, 100mg/L, 125mg/L, 150mg/L, 25mg/L and 200mg/L. After the cross linker concentration was ascertained, we try to optimize the polymer concentration by changing its value into the following values 3000mg/L, 3500mg/L, 4000mg/L and 4500 mg/L with the ascertained value of cross linker. After ascertaining the crosslinker and polymer concentration, the delaying agent has been ascertained. To ascertain the delaying agent concentration, we used the delaying agent (thiourea) – cross linker ratio in the following values 0.2:1, 0.4:1, 0.4:1, 0.6:1, 0.8:1, 1:1. During these experiments, the used materials for viscosity measurement is a rotational viscometer.*

Keywords: *Crosslinker, Gelation time, Gel formula optimization, Polymer concentration, Viscosity*

1. Introduction

The gel method is mainly used to solve the water channelling problem caused by the high heterogeneity of some reservoirs. Many reservoirs are produced by water flooding.Waterflooding is a successfully and broadly used technology to advance oil recovery[1][2]. Previous studies showed the gel method is a successful method to solve the water channelling and increase the oil recovery by increasing the displacement efficiency. Using polymer gel to solve water channelling is proved to be a successful method [3]. Polymer gels have great interests for their applications in petroleum production, these interests include water-cut treatments on production wells and the modification of the fluid or miscible gas injection profile of injection wells [4]. Polymer gels have been successfully applied to extend the productive life of mature oilfields by decreasing water production and increasing the recovery of oil[5]. Polyacrylamide has been widely used in making polymeric gels[6]. Moreover, to use this technology successfully the gel formula has to be optimized by ascertaining some critical parameters of the gel formula such as the appropriate polymer concentration, the cross linker concentration, the gelation time of the gel. Crosslinking environment can greatly affect the gelation time and the strength of the gel [7]. It is very important to determine the optimum concentration of polymer and crosslinker, at which a good gel can be formed based on specific oilfield conditions and parameters. When HPAM is mixed to a crosslinker according to the concentration of the two chemicals, a gel system can be made [2]. Therefore, to achieve this goal we conducted some experiments. We made experiments on polymer concentrations, cross linker concentrations, and the delaying agent-cross linker concentration ration.

2. Methods And Materials

In this study, the main used materials and chemical can be described as followings: The polymer source, a polyacrylamide (with a molecular weight of about 14 million, solid form) was used as the main polymer. The used crosslinking agent is cr^{3+}, and to prevent a quick gelation, thiourea (CH_4N_2S)

was used as a delaying agent. We used a rotary viscometer for viscosity measurement during this study. The simulated formation water has a salinity of 40000mg/L.

Organically cross-linked gels have been widely used to control water-cut in some reservoirs. Most of these gels involve a polyacrylamide-based polymer and an organic cross-linker[8].

2.1. Synthesis of the Gel

First, a gel with the following characteristics has been made. Polymer concentration 3000mg/L, Crosslinker concentration 50 mg/L, the PH and Temperature of the crosslinking environment are PH=7 and T= 20^{o} C, the concentration of simulated formation water is 40000 mg/L. The gel sample preparation procedures played a significant role (Willhite et al. 1988).

2.2. Gel formula optimization

According to the GGY (Ordos basin, China) reservoir formation properties, the gel is optimized by optimizing the main parameters which can have on the gel strength, gelling time and stability. These parameters are crosslinking concentration, polymer concentration, the delaying crosslinking agent concentration.

2.2.1. Crosslinking Agent Concentration Optimization

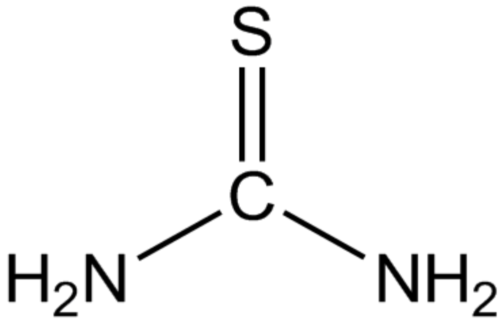
To determine the suitable crosslinker concentration, the crosslinker concentration has been changed to many values while the other parameters were kept to a constant value. For these experiments, many gel samples have been used in which the concentration of the Crosslinking agent (main elements of Crosslinking agent Cr^{3+} Concentration meter) has been set to the following values the 25 mg/L, 50 mg/ L, 75 mg/L, 100 mg/L, 125 mg/L, 150 mg/L, 200 mg/L. Meanwhile, in the whole samples, the polymer concentration was kept at 3000 mg/L, the PH of Crosslinking system with a value of PH 7, Crosslinking reaction temperature was 20 ℃. The simulated formation water salinity was 40000 mg/L.

2.2.2. Polymer Concentration Optimization

The optimization of the concentration of the crosslinking agent was conducted according to the above experiments, the optimum concentration of the crosslinking agent (major role in crosslinking agent concentration of elements) is 50mg / L. So, to determine the suitable concentration of the polymer, many samples have been made in which the, pH of the crosslinking system was 7, the polymer concentration was adjusted to the following six values 2000mg / L, 2500 mg / L, 3000mg / L, 3500mg / L, 4000mg / L, 4500mg / L. The crosslinking reaction temperature was at 20 ℃, simulated formation water salinity was 40000mg / L and the crosslinker concentration was fixed at its suitable value, found in the first experiment series (crosslinker concentration evaluation). The results have been recorded and are shown in a graph.

2.2.3. Effect of Delaying Agent Concentration on Gel Properties

There are some conditions in which it is very important to delay or postpone the gelation time of the gellant when it is flowing from the wellbore to the target formation. In fact, when the temperature increases, the gelatin time tends to become shorter. This phenomenon not only happens when the temperature increases but also it can result from the crosslinking reaction condition and concentrations (crosslinking agent concentration and polymer concentration). When the gelation time is shorter, the gel may not reach the targeted area in the reservoir that will result in gel treatment operation failure. There two times in the process of gelling of the gel, the first is the initial onset time of the gel (time at which the first gel particles are formed) and the second time is the required time for the gel to reach the maximum of its strength. To treat the formation matrix the gel should be injected at the first time (gel onset time). There are some methods to determine this gel onset time such as bottle testing, core flooding injectivity experiments, the filtration testing, dynamic oscillatory viscosity techniques. If a delaying agent is not used in case of crosslinked polymer gels, the gel full strength can be achieved rapidly after the first gel onset time. Therefore, it is crucial to synthesis a gel with the appropriate properties of gelation time relatively long to reach the targeted zones in the porous medium. For CC/AP many chemical products as used as delaying agents such as strong carboxylate ligands, thiourea, sodium malate, carboxylate salt, sodium lactate, lactic, acid, thiourea, etc. In this research work the used chemical as delaying agent or retarding agent is thiourea (a chemical compound with a similar structure than urea, it is structure the oxygen atom is substituted by the sulfur atom, its formula is CH_4N_2S, with a molecular weight of 76,12 g/mole, and temperature of fusion of about 182 degrees Celsius). Thiourea can be synthesized by using the ammonium thiocyanate (NH_4SCN), but generally, it is made by using hydrogen sulfide (H_2S and calcium cyanamide($CaCN_2$) in the existence of carbon dioxide CO_2.



Thiourea molecule from Wikipedia).

The gelation time governs injection penetration depth at which certain agent can be driven (Dai et al. 2012), [9]. To optimize the gelation time of the gel , other parameters were kept constant during the experimental time at the following values: Crosslinker concentration of 50mg / L (in a concentration of major elements of a crosslinking agent), polymer at a concentration of 3000mg / L. Simulated formation water salinity was 40000mg / L, the pH was adjusted profile 7, the reaction temperatures were 30 ℃, rotary viscometer was used for viscosity measurement, then thiourea is used as a delaying in different concentrations in the systems to investigate gelation properties, the ratio of crosslinking agent and the delaying agent was adjusted to the following values 1:0.2 : 1:0.4; 1:0.6; 1:0.8; 1:1.0 to achieve the best performance of the gelation time.

3. Results And Discussion

3.1. Cross linking Agent Concentration Optimization for Gel Formulation

The following table shows the gel viscosity change when the cross linker concentration was changed. The following results were recorded for 8 days. During the 8 days the temperature was 20^{o} C, the PH was 7, the polymer concentration was 3000mg/L.

Table1. *Viscosity change with the change of cross linker concentration*

	Cross linker concentrations						
Time (days)	**25mg/L**	**50mg/L**	**75mg/L**	**100mg/L**	**125mg/L**	**150mg/L**	**200mg/L**
	Viscosity (mPa.s)						
0.0	465.1	466.1	232.6	233.5	99.0	465.1	466.1
0.5	37.1	501.2	501.2	2129.2	10501.7	12361.3	43294.0
1.0	290.1	756.2	2150.7	2848.4	34479.8	18661.1	30989.3
1.5	558.8	1258.4	39400.8	29165.8	47306.2	16841.5	29397.4
2.0	114.1	1511.5	39188.7	40350.6	51279.4	29883.0	34301.8
2.5	838.1	2931.3	38282.8	47819.1	55259.4	24326.7	48044.9
3.0	406.1	4593.4	37850.8	43897.6	15059.0	4825.9	407.1
3.5	684.5	23941.5	30686.0	44871.8			
4.0	464.7	26744.0	29536.8	37209.7			
4.5	739.2	34460.8	31903.5	15157.5			
5.5	795.7	35680.2					
6.5	855.2	35740.6					
8.0	232.6						

It can be seen while the polymer concentration is constant, when the Crosslinking agent concentrations increased, the gelling speed system increased greatly. When the concentration of the crosslinking agent is increased to a certain degree, the stability gel formation deteriorates, the reason may be due to the concentration of the crosslinking agent is too large, the ratio between the polymer and the crosslinking agent causes excessive crosslinking of the gel dehydration shrinkage. With the polymer concentration of 3000mg/L, the suitable gel is reached with a crosslinker concentration of about 50-70mg/L.

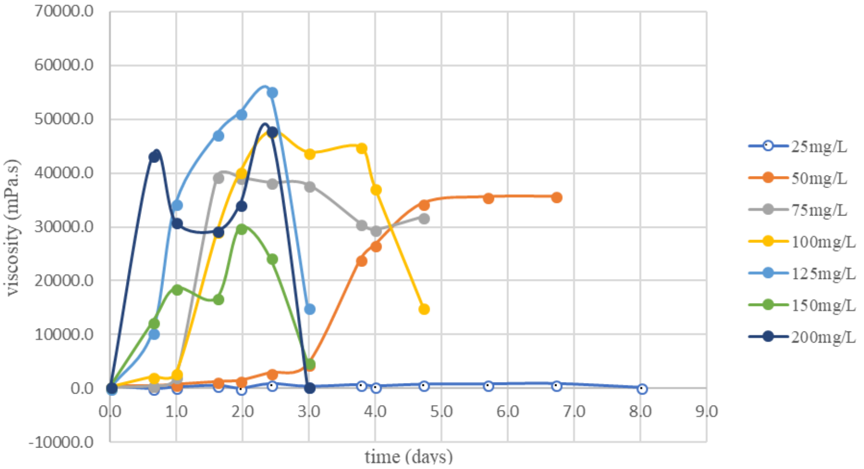


Fig1. *Viscosity change with cross linker concentrations*

The amount of crosslinking agent directly affects the macroscopic and microstructure of the gel and the gel properties. When the amount of the crosslinking agent is too small, the crosslinking reaction may be small with PM-1 molecule with a centre ion concentration, the gel strength of the formation is small. When the amount of the crosslinking agent is 50 mg / L, the degree of reaction with an amount of intermolecular crosslinking PM-1 has reached the maximum. When the amount is more than 75mg / L, due to the high concentration of the crosslinking agent, it is too easy to produce a crosslinked partially syneresis system, destroy the continuity of the gel network structure, thus increasing the strength of the gel system as crosslinker concentration, Large and worse, gel strength also decreased

3.2. Effect of Polymer Concentration on the Gel Properties

After the experiments, the collected data are shown in the table below

Table2. *Viscosity change based on the polymer concentration*

	Polymer concentration change					
Time (days)	**2000mg/L**	**2500mg/L**	**3000mg/L**	**3500mg/L**	**4000mg/L**	**4500mg/L**
0.0	234.0	466.9	466.9	233.5	233.5	234.0
0.5	244.7	10.7	233.5	233.5	233.5	244.7
1.0	250.8	250.8	466.9	233.5	233.5	250.2
2.0	267.5	501.0	466.9	466.9	466.9	500.0
3.0	750.7	515.8	466.9	466.9	466.9	983.7
4.0	768.0	767.5	933.9	1400.8	1867.7	7770.9
5.0	83.9	1717.7	1867.7	4902.7	13073.9	13624.3
6.0	100.7	1501.0	3268.5	10972.8	16575.9	19244.2
7.0	117.5	2451.6	9105.1	14708.2	33852.1	33268.7
9.5	158.2	3893.6	23112.8	48326.8	32918.3	48252.1
10.5	408.9	4144.4	38988.3	47859.9	41089.5	49436.2
12.5	676.0	5111.8	35019.5	50194.6	41089.5	49002.8

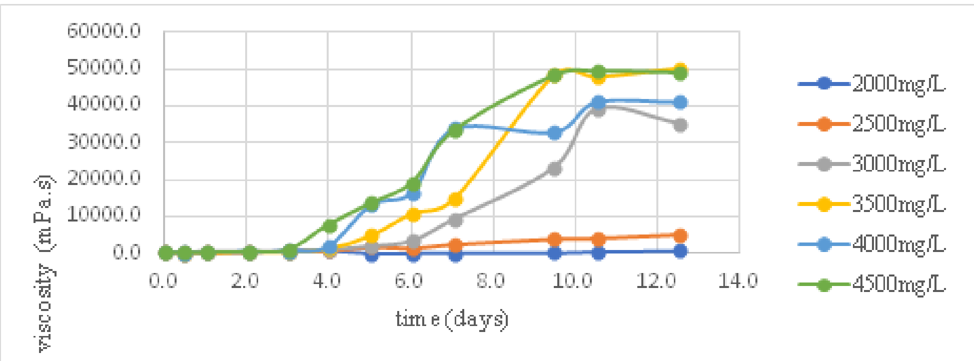


Fig2. *Viscosity change with the polymer concentration*

As it can be seen from the figure, with the increase of the polymer concentration, the gelation time is shortened, the strength is increased, the system increases the reactive group -COO PM-1 concentration $^{-}$ concentration increases, the reaction rate of the crosslinking agent with the polymer in the polymer -COO $^{-}$ proportional to the concentration, thus increasing the polymer concentration Will inevitably lead to the rate of cross-linking reaction to speed up the system into a shorter gel time. When the polymer has a concentration of 2000mg / L to 2500mg / L, gel strength is weak, although the system crosslinker concentration is sufficiently high. It constitutes the nodes in the network structure, but constitute a linear macromolecular network structure, a low concentration, it cannot form a good gel network structure.

When the polymer concentration is greater than the amount of 2500mg / L, the greater strength capable of forming a gel, the gel strength increases with the amount polymer concentration increases, but with the use of excessive PM-1, the initial viscosity of greater cross-sectional adjustment system increases, then the operation becomes more difficult, and also the production cost is improved. Suitable cross-linking system profile is reached when PM-1 is at a concentration of 3000 ~ 4000mg / L. Polymer gel process is based on the diffusion of aggregates as the control reaction diffusion reaction, the edge of the aggregate easily cross-linked with the main elements of the crosslinking agent. Within a certain concentration range, the higher the concentration of the polymer, the higher the concentration of cross-linker, the faster the plasticizing, and the larger the viscosity after the plasticizing. This is because of the increase of the concentration and the increase of the carboxylate content in the solution, which increases the probability of effective collisions with the main elements released from the crosslinking agent, then accelerates the complexation reaction and shortens the gelling time. The greater the amount of polymer, the denser the gel network, the greater the gel polymer strength.

3.3. Effect of Delaying Agent Concentration on Gel Properties Results

After the experiments, the collected data are shown in the table below

Table3. *The viscosity changes according to the delaying agent concentration*

TIME	ratio 1:0.2	ratio 1:0.4	ratio 1:0.6	ratio 1:0.8	ratio 1:1
0.00	0.00	53.23	106.46	0.00	53.23
0.50	106.46	106.46	206.00	56.00	53.23
1.00	159.70	200.00	353.23	100.55	53.23
1.50	1490.49	798.48	585.55	106.46	53.23
2.00	3939.16	2874.52	2448.67	1224.33	106.46
2.50	6920.15	7878.33	3566.54	2608.37	585.55
3.00	12669.20	11391.63	6174.90	4045.63	1703.42
4.00	11338.40	12030.42	10646.39	6174.90	2768.06
5.00	11870.72	11444.87	11817.49	6973.38	2182.51

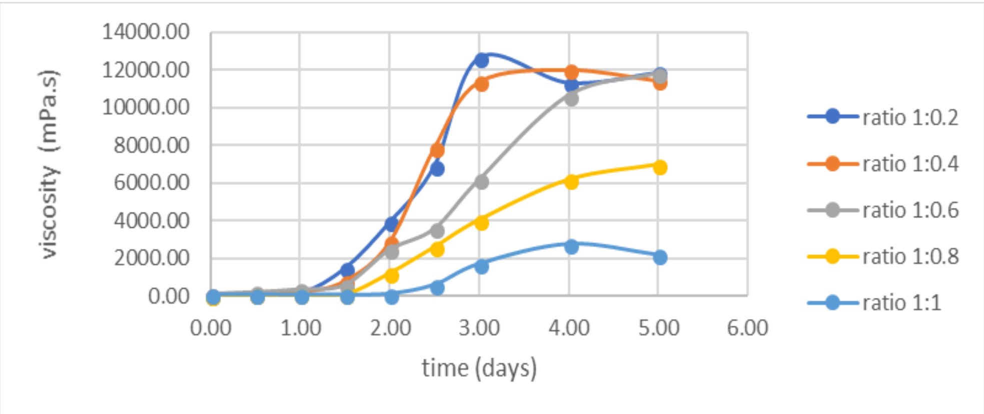


Fig. 3 The impact of delaying agent concentration

4. Conclusion

- The higher the polymer concentration, the shorter is the gelation time;
- When the cross linking agent concentration increases, the gelation time decreases;
- The optimum gel gelation time and strength were reached with a polymer concentration of 3000 to 4000 mg/ L, a cross linker concentration of 50 mg/L and a delaying agent-cross linker ratio of 0.6.

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