

## Effect of pH on Gelling Performance and stability of HPAM/Cr<sup>3+</sup> Weak Gel

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**Abstract:** The article studied the influence of pH to the gelling properties and stability of HPAM/Cr<sup>3+</sup>, the results shows that the alkaline environment could promote the gelation rate and strength. The gelation rate can be lifted properly by increasing the pH value. The HPAM/Cr<sup>3+</sup> which exist in the alkaline has shorter stable stage and worse stability. When existing in the environment of pH=8, the gel get the largest viscosity. Considering both strength and stability, the best range of pH value is 7~8.

### Introduction

At present, many oil fields in China have come into the middle or late period of exploitation. With the raising of moisture content, the heterogeneity of layer became more and more serious and the profile control water plugging became much more important <sup>[1]</sup>. The HPAM/Cr<sup>3+</sup> weak gel profile control system is the commonly used system, and its performance affected by many factors such as polymer concentration, crosslinking agent concentration, salinity, pH and temperature. The performance of weak gel include gelling performance and stability performance. Most of the present research focus on the gel system itself <sup>[2,3]</sup>. The study about the rule of influence of pH, especially how does pH change the stability of weak gel, is relatively less <sup>[4]</sup>. The gelling and stability performance relate directly to the efficiency and result of profile control. Through large amount of lab experiments, the relation of gelling speed, strength and stability with pH has been discussed in this article.

### Experiments

**Reagents and Equipment.** The experimental temperature is 25°C. The HPAM produced by World chemical company in China. The molecular weight of HPAM is 14 million, and its degree of hydrolysis is 15%. The cross-linking agent is organic chromium ion solution and it was produced by our lab. The concentration of chromium ion is 50mg/L. The NaCl used in experiment is analytically pure and was produced by Shandong Baomo chemical company. Hydrochloric acid is analytically pure and was produced by Shanxi Xilong chemical company. The testing range of precise pH test paper used in the experiments is 0~14. The model of viscometer we used is brookfield DV-III.

**Experiment method.** The salinity of water used in all tests is 8000mg/L. The experiments control the pH of the system by adding various amounts of hydrochloric acid and determine the pH value by precision pH test paper. The pH values of six groups of water were 4, 5, 6, 7, 8, 9. Then we prepared corresponding six groups HPAM/Cr<sup>3+</sup> system. Every group keep same concentration of HPAM and Cr<sup>3+</sup> and fixed HPAM concentration of each group was 3000mg/L, Cr<sup>3+</sup> concentration of 50mg/L. The parameters of evaluating the gelling strength in the tests is viscosity. Test the

viscosity every day and get the gelling strength–time curve in different pH values. Keep recording the viscosity of each group after each group reach peak viscosity. Finally we drew out the viscosity loss curve of each group which started with the respective peak viscosity.

## Results and discussion

**Influence of pH on the Gelling Strength.** The results of the change of gelling strength of HPAM/Cr<sup>3+</sup> with time under different pH value are shown in the figure 1.

From figure 1, it can be observed that there is a close relationship between the pH value and gelation. When the pH value is 4, the viscosity of the system has no significant difference with the pure polymer solution which crosslinking agent is not added. The viscosity has been maintained at 30mPa·s for a long time and there were barely crosslinking reaction in the HPAM/Cr<sup>3+</sup>. Meanwhile the curve in figure 1 also shows that the gelation reaction may occur in the pH range of 5~9. This is because that the smaller pH value means more H<sup>+</sup> and that the larger number of H<sup>+</sup> curb the process Hydrogen ions dissociating from the carboxyl group of polymer macromolecular chains. Less COO<sup>-</sup> groups on the molecular chain resulting in a smaller repulsion between groups [5]. Finally the polymer chains can't be fully extended, further crosslinking severely suppressed. In addition, the figure 1 shows that in the pH range can gelation, gelling speed and a gel strength significantly affected by pH value. The gelling rate of pH are 8 and 9 are faster than the others. It is noteworthy that when the pH is 9, the gelling speed is the fastest in all groups and the viscosity curve begins to rise rapidly when crosslinking time is only 2 days. The gel has reached a peak intensity in 6 days, peak intensity of 10754mPa · s. When pH value is 8, the gelling rate is second only to the group which pH is 9. However, the group pH is 8 get the maximum gelling strength that peak viscosity reach 13767mPa·s. The gelling rate and strength of pH value is 5 and 6 are lower than the other three groups. Moreover, when the pH value is 5, the sample get the minimum gelling speed and strength.

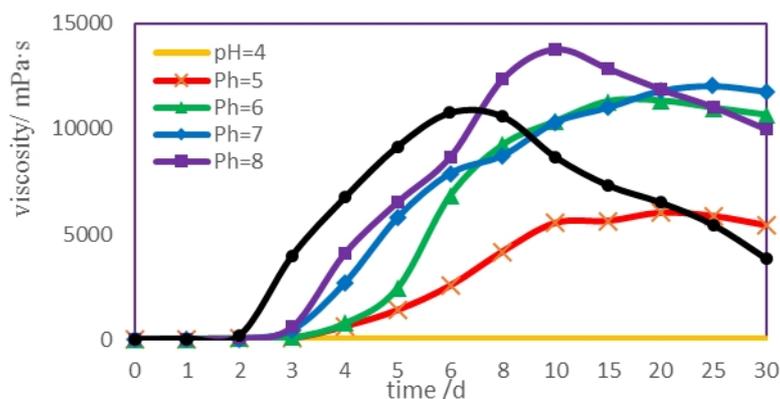


Figure 1 Changes of viscosity of HPAM/Cr<sup>3+</sup> with time under different pH

From the description of figure 1, we can summarize the influence of pH on the crosslinking reaction. First of all, when the pH in proper range (5~9), the bigger pH value could accelerate the gelling rate. Moreover to a gel strength is concerned, when the pH is alkaline, the viscosity is bigger than the sample under acidic conditions. This is because that the HPAM is partially hydrolyzed and the amide hydrolysis on the molecular chain produce carboxyl [6]. So there are lots of amide and a number of carboxyl on the chain. At the same time the solution contains a large amount of hydroxyl under alkaline conditions. On the one hand the presence of carboxyl hydroxyl will promote the dissociation rate, so that the number COO<sup>-</sup> on HPAM macromolecular chains increased rapidly. The repulsive force between each group increases, the molecular chain quickly spread, eventually leading to gel faster. On the other hand, hydroxyl promote the hydrolysis process of amide to

generate carboxyl and amino, the increase of carboxyl group is directly led to the increase of the total number of  $\text{COO}^-$  group in the molecular chain. And studies have proved that  $\text{Cr}^{3+}$  only complex with hydrolyzed polyacrylamide which means  $\text{COO}^-$  is crosslinking points for  $\text{Cr}^{3+}$ . More  $\text{COO}^-$  means more cross-linking points, so the final gelling strength significantly increased under alkaline conditions. In addition, higher pH values are also conducive to the release of cross-linking agent metal ion  $\text{Cr}^{3+}$  in the System. Under acidic conditions, dissociation of carboxyl and hydrolysis of the amide group are inhibited. This results in relatively that HPAM molecular chain easy to bend into a slug, while crosslinking points  $\text{COO}^-$  less, leading to the final gelling strength and speed are less than a gel strength and speed under alkaline conditions. Secondly, but not the bigger pH the better, pH value is too large or too small will affect to some extent into a gel strength. Therefore, gel strength of pH is 8 is greater than that pH is 9. The reason is that when the pH value is too large,  $\text{OH}^-$  concentration is too high and the dissociation rate of carboxyl is too fast. A large number of  $\text{COO}^-$  and  $\text{Cr}^{3+}$  rapidly complex in a short time so that macromolecular chains too late to extend itself over the crosslinking reaction occurred. From the analysis above, 8 is the ideal pH value to get higher gel strength. Furthermore, we could get the faster gelation rate by appropriately increasing the pH value, if it's needed.

**Influence of pH on the Gel Stability.** In this section we only analyze five groups which the crosslinking reaction could happen. From figure 2 we see that the viscosity of HPAM/ $\text{Cr}^{3+}$  gel will slowly creases after reach the peak. Viscosity decreases until the gel complete dehydration is its inherent properties. Because the internal crosslinking happens all the time, cross-linked macromolecular network structure continued contraction until the final all the packaged water inside is squeezed out. From peak to fail completely dehydrated, gel viscosity decrease curve can be divided into three intervals: stable zone, burst dewatering zone and continued contraction zone. After gel system reached peak viscosity, through a period of relatively stable period, the viscosity slowly declining, known as the stabilization period. With the increase of time, until a certain point in time to produce pure phase, part of the water can be observed to separate from the polymer colloid. The period which gel viscosity decreased rapidly dehydration can be called a burst dewatering period. Then the viscosity of the gel is slow and there are regular decline, and this phase is called continued contraction period [7]. The length of the stationary phase can be used as a measure of gel stability.

As can be seen from Figure 2, the slope of curves of the two groups which pH is 8 and 9 is significantly greater than the other three groups, they entering the burst dewatering zone within 20 days. This shows that the relative stability of the gel under alkaline environment worse than that under acidic conditions. With a pH of 9, for example, the colloid enter the burst dewatering zone soon after the gel reaches peak intensity. In the fifth day, gel had a viscosity loss of 20%, then the curve slowed into a continued contraction period. When pH value is 8, the gel enter the burst dewatering zone within 15th days and its stability is better than which pH is 9. The pH of the three groups 5, 6 and 7, no significant decrease in viscosity within 20 days, are in stable. This shows that the difference of stability between HPAM/ $\text{Cr}^{3+}$  gel under acidic conditions and neutral conditions is not large, but the stability under acidic conditions and neutral conditions was better than the stability of the gel under alkaline conditions. The viscosity of two tests pH is 5 and 6 decreased value respectively of 22% and 14% in about 20 days, significantly better than the stability of the gel under alkaline conditions. The stability of gel PH is 7 is the best of all and its stability period could last 20 days. In the first 15 days after reaching peak intensity, viscosity decreased only 5%, 20 days is only reduced by 13%.

From Figure 2 it can be concluded, the stability of the gel under alkaline condition is the worst,

and better stability in neutral environment and a bit acidic environment.

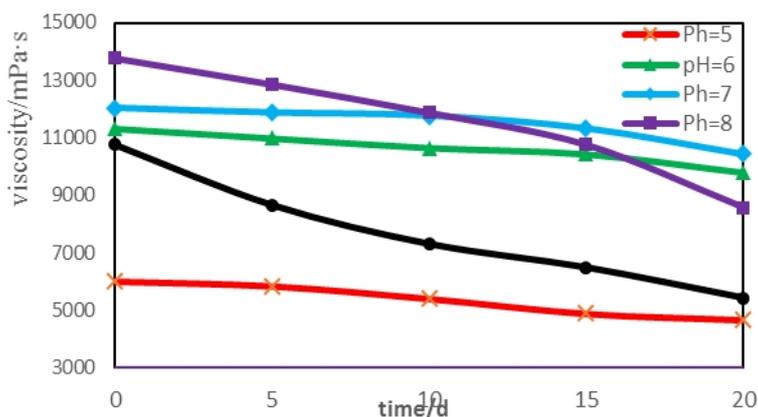


Figure 2 Gel viscosity decreases curve with time of HPAM/Cr<sup>3+</sup> under different pH

### Conclusions

- (1) A bit more alkaline environment can promote the gelling speed and strength of HPAM/Cr<sup>3+</sup> Gel. In the range of pH can gelation (5~9), the bigger pH value, the faster gelling rate. The faster gelation rate can be achieved by increasing the system's pH value in proper range.
- (2) The HPAM/Cr<sup>3+</sup> gel is relatively stable under neutral and acidic environment compared with the gel under alkaline environment. The gel under alkaline environment get a shorter stable period and rapid dehydration.
- (3) The HPAM/Cr<sup>3+</sup> gel get maximum strength when pH value is 8. To obtain high strength while taking into account the stability of gel, pH preferably in the range of 7 to 8.

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