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The Effect of Hydrogen Sulfide Concentration on Gel as Water Shutoff Agent

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Résumé — Effet de la concentration en sulfure d'hydrogène sur un gel utilisé en tant qu'agent de traitement des venues d'eaux — Pour le forage et le traitement des venues d'eau dans des réservoirs d'huile et de gaz contenant du sulfure d'hydrogène (H_2S), les effets de l'H_2S sur les gels couramment utilisés pour le traitement des venues d'eau sont étudiés. Les gels incluent un gel de $Na_2Cr_2O_7/Na_2SO_3$/HPAM, un gel de $Na_2Cr_2O_7/(NH_2)_2CS$/HPAM, un gel d'acétate de Cr(III) & lactate de Cr(III)/HPAM et un gel à base de résine de phénol formaldéhyde/HPAM. Les résultats montrent que :

– pour un gel de $Na_2Cr_2O_7/Na_2SO_3$/HPAM et un gel de $Na_2Cr_2O_7/(NH_2)_2CS$/HPAM, l'H_2S en tant qu'agent réducteur (la réductibilité est plus efficace que celle du Na_2SO_3 et du $(NH_2)_2CS$) peut réduire le Cr(VI) en Cr(III) et accélérer la réaction de réticulation avec le HPAM en présence d'une faible concentration en H_2S, tandis qu'il peut réagir avec le Cr(III) en produisant un précipité de Cr_2S_3 en présence d'une concentration élevée en H_2S, ce pour quoi le gel en masse ne peut se former sans Cr(III) ;

– pour un gel d'acétate de Cr(III) & lactate de Cr(III)/HPAM, H_2S peut prolonger le temps de gélification et réduire la résistance du gel par diminution de la valeur du pH ;

– pour un gel à base de résine de phénol formaldéhyde/HPAM, H_2S peut prolonger légèrement le temps de gélification et réduire légèrement la résistance du gel par diminution de la valeur du pH. De ce fait, selon les études complètes des effets de l'H_2S sur des gels utilisés en tant qu'agent pour le traitement des venues d'eau, le gel de résine de phénol formaldéhyde/HPAM est recommandé dans les réservoirs d'huile and gaz contenant de l'H_2S.

Abstract — The Effect of Hydrogen Sulfide Concentration on Gel as Water Shutoff Agent — *For drilling and water shutoff of oil and gas reservoirs containing hydrogen sulfide (H_2S), the effects of H_2S on widely used gel as water shutoff agents are studied. The gels include $Na_2Cr_2O_7/Na_2SO_3$/HPAM gel, $Na_2Cr_2O_7/(NH_2)_2CS$/HPAM gel, Cr(III)-acetate & Cr(III)-lactate/HPAM gel and phenol formaldehyde resin/HPAM gel. The results show that:*

– *for $Na_2Cr_2O_7/Na_2SO_3$/HPAM gel and $Na_2Cr_2O_7/(NH_2)_2CS$/HPAM gel, the H_2S as reducing agent (the reducibility is more efficient than that of Na_2SO_3 and $(NH_2)_2CS$) can reduce Cr(VI) into Cr(III) and accelerate crosslinking reaction with HPAM in low concentration of H_2S, while it can react with Cr(III) generating Cr_2S_3 precipitation in high concentration of H_2S, for which the bulk gel can not form without Cr(III);*

– *for Cr(III)-acetate & Cr(III)-lactate/HPAM gel, H_2S can prolong the gelation time and reduce the gel strength by decreasing pH value;*

– *for phenol formaldehyde resin/HPAM gel, H_2S can slightly prolong the gelation time and slightly reduce the gel strength by decreasing pH value. Therefore, according to the comprehensive investigations of the effects of H_2S on gel as water shutoff agents, the phenol formaldehyde resin/HPAM gel is recommended as the water shutoff agents suitable for oil and gas reservoir containing H_2S.*

INTRODUCTION

H_2S frequently appeared in oil and gas reservoir which can lead to problems usually met in drilling, workover, oil and gas production. For example, in the Northeast Sichuan of China, the leak, kick and blowout of gas well containing H_2S were solved using gel materials in in the process of drilling and workover (Xunyong Nie, 2006; Jianjun Wang, 2005). Some gasfields containing H_2S are seriously affected by an excessive water production. At the present time, gas recovery by discharging water is used to solve the problem all over the world (Jiyong Zhou, 2005). If the gas wells with producing water can be directly solved by water shutoff technology, it will not only reduce costs and increase the economic efficiency, but it will also avoid the problems of the treatment of large amount of produced water, of production of sands and of the corrosion of pipeline. Some oilfields also encounter some H_2S related problems, such as Zhanarol (Russian name) oilfield in caspian offshore basin of Kazakhstan. For this huge and complex fractured carbonate reservoir, it is extremely urgent to carry out water shutoff for the well which has a high water cut. However, from 2002 to 2006, the effectiveness of chemical water plugging treatment was very low. In addition to the water shutoff troubles, there exists other problems related to the high concentration of H_2S, which is about 600~1 000 mg/L. Gels as water shutoff agents are widely used due to their low price, easy preparation and injection, good applicability. At the present time, there are no studies on how H_2S affects gel used as water shutoff agents: it was necessary to study this aspect based on the reservoir conditions of Zhanarol oilfield.

1 DESCRIPTION AND APPLICATION OF EQUIPMENT AND PROCESSES

1.1 Drugs and Reagents

HPAM: HPAM is purchased from Yuguang Company: its viscosity-average molecular weight is 1.6×10^7, degree of hydrolysis is 24.4%, and solid content is 90.9%.

Crosslinker: two inorganic chromium crosslinkers from Yuguang company, one is a complex of $Na_2Cr_2O_7/Na_2SO_3$, another one is a complex of $Na_2Cr_2O_7/(NH_2)_2CS$ are used. YG107 from Yuguang company is an organic chromium crosslinker, it is a complex of Cr(III)-acetate and Cr(III)-lactate. YG103 also from Yuguang Company is a phenol formaldehyde resin crosslinker.

Chemical reagents: H_2S (analytical reagent) from Beijing Multi Technology Company is used. Hydrochloric acid (analytical reagent), dimethylamino aniline hydrochloride (analytical reagent), iron trichloride (analytical reagent), ammonium dihydrogen phosphate (analytical reagent) and zinc acetate (analytical reagent) come from Beijing chemical reagents company.

TABLE 1

The composition of simulation produced water (mg/L)

Components	$Na^+ + K^+$	Ca^{2+}	Mg^{2+}	HCO_3^-	CO_3^{2-}	SO_4^{2-}	Cl^-
Concentration (mg/L)	8 272.7	1 120.0	192.0	784.5	44.1	762.2	14 146.3

Brine: the simulation produced water is prepared according to the Zhanarol oilfield composition, its total salinity is 25 321.8 mg/L and pH value is 6.53. The water composition is shown in Table 1.

1.2 Test Equipment

A pHS-25 digital pH meter is used to measure the pH value of the solution. SX721 digital spectrophotometer is used to determine the concentration of H_2S in the simulation produced water. BS423S balance is used to weigh materials. ICP (Inductively Coupled Plasma emission spectrometer) permits to measure the concentration of chromium and sulfur in the solution. An electric centrifuge is used to centrifugate the solution in order to separate the supernatants and the precipitates from the solution.

1.3 Test Method

1.3.1 Preparation Method of Simulation Produced Water Containing H_2S

H_2S is a very toxic gas, its solubility is not easy to detect directly. The following method is used to prepare simulation produced water containing H_2S: in the fumed cupboard, connect the conical beaker filling simulation produced water with H_2S containing gas cylinders, open the valve of H_2S gas cylinders, pump H_2S into conical beaker for a time, then close the valve and make H_2S dissolve in equilibrium, using the methylene blue method (SY/T 5329-94, 1995, this is one of Chinese oil and gas industry standards) to determine the concentration of H_2S in the simulation produced water. The concentrations of H_2S range from 0 mg/L to 3 700 mg/L.

1.3.2 Preparation Method of Gelants Containing H_2S

Simulated produced water without containing H_2S was used to prepare a 0.6% HPAM solution, the gelants were prepared by adding crosslinker and simulated produced water containing H_2S used to dilute 0.6% HPAM into 0.5% HPAM. At the same time, the concentration of H_2S in gelants is calculated. Then put HPAM solution and crosslinker into sealed glass bottle and mixed them, then put them into oven at the temperature of 60°C until the gel is fully formed (according to Sydansk's method (Sydansk, 1988)).

1.3.3 The Testing Method of Gelation Time

The gelants composed of HPAM and different crosslinker are put into an oven at the temperature of 60°C until the gel is fully formed. Gelation time is when the gelants change from code A into code G according to the Sydansk's method (Sydansk, 1988). Code A refers to the state that continuous gel can not be detected and the viscosity of gelants is the same than the polymer solution. Code G refers to the state that continuous gel can be detected and gel will become deformed and increase about half of its height when the sealed glass bottle is turned upside down.

1.3.4 The testing Method of Gel Strength

Breakthrough vacuum method (Caili Dai, 2001) is used to determine the gel strength. The measurement device is shown in Figure 1. Its principle is that the gel strength is measured by using the pressure difference between atmospheric pressure and the pressure of safety bottle. It has to be corrected in order to separately determine water-based and oil-based water shutoff agent by water and glycerol before using it. The breakthrough vacuum values of water and glycerol are 0.007 MPa and 0.028 MPa separately.

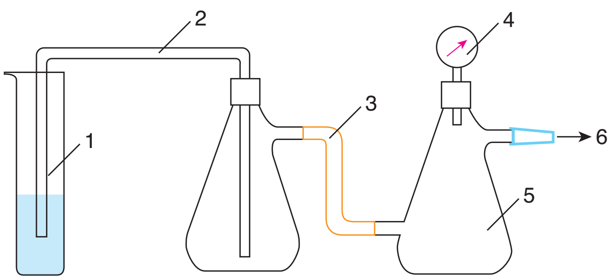


Figure 1

The determination installation of breakthrough vacuum method (Caili Dai, 2001).

1: Colorcomparison tube; 2: U-tube; 3: rubber tube; 4: pressure gauge; 5: safety bottle; 6: vacuum pump.

2 RESULTS AND DISCUSSION

2.1 The effect of H_2S on Inorganic Chromium Crosslinking Gelants

The composition of two inorganic chromium crosslinking gelants named 1# and 2# are shown in Table 2. Figures 2-5 show that the results of H_2S effect on two inorganic chromium crosslinking gel. The *X* axis is H_2S concentration and the *Y* is gelation time/gel strength. It can be seen that the effect of H_2S on inorganic chromium crosslinking gel was significant. When the concentration of H_2S was smaller than 100 mg/L, the gelation time decreased rapidly with the concentration of H_2S, and the gel strength increases. But when the concentration of H_2S was higher (1# was higher

TABLE 2

Composition of the gelants

No.	Composition of the gelants
1#	0.5% HPAM + 0.2% $Na_2Cr_2O_7$ + 0.4% Na_2SO_3
2#	0.5% HPAM + 0.2% $Na_2Cr_2O_7$ + 0.4% $(NH_2)_2CS$
3#	0.2% $Na_2Cr_2O_7$ + 0.4% Na_2SO_3
4#	0.2% $Na_2Cr_2O_7$ + 0.4% $(NH_2)_2CS$
5#	0.5% HPAM + 0.4% YG107
6#	0.5% HPAM + 1.2% YG103

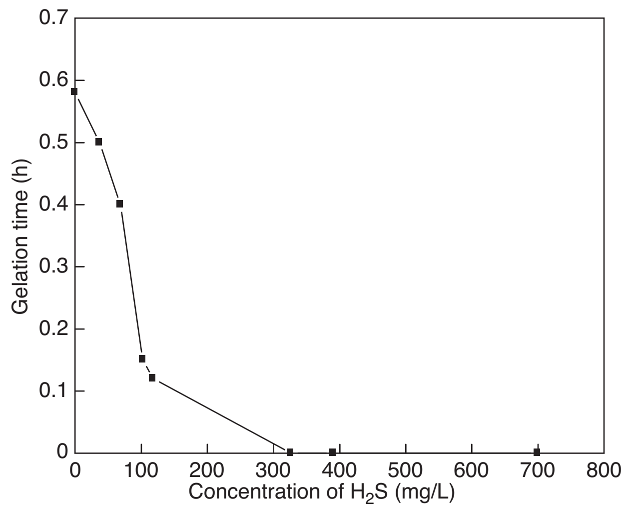


Figure 2

The effect of H_2S on the gelation time of $Na_2Cr_2O_7$/ Na_2SO_3/HPAM gel.

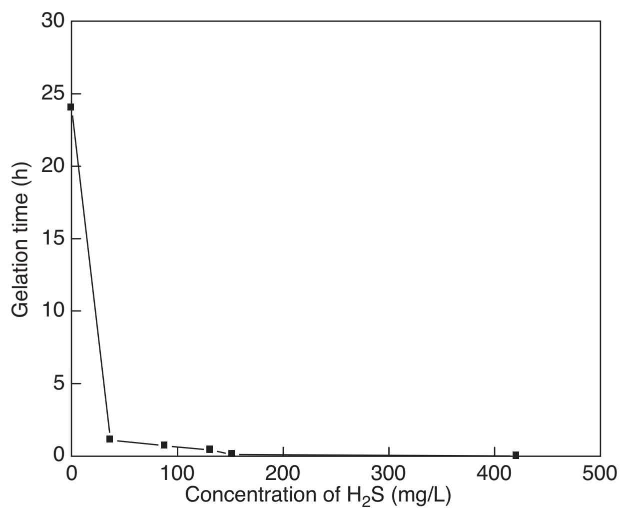


Figure 3

The effect of H_2S on the gelation time of $Na_2Cr_2O_7$/ $(NH_2)_2CS$/HPAM gel.

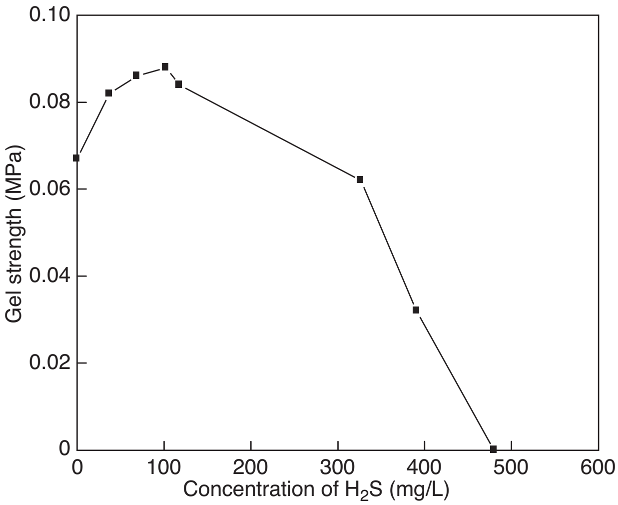


Figure 4

The effect of H_2S on the gel strength of $Na_2Cr_2O_7$/ Na_2SO_3/HPAM gel.

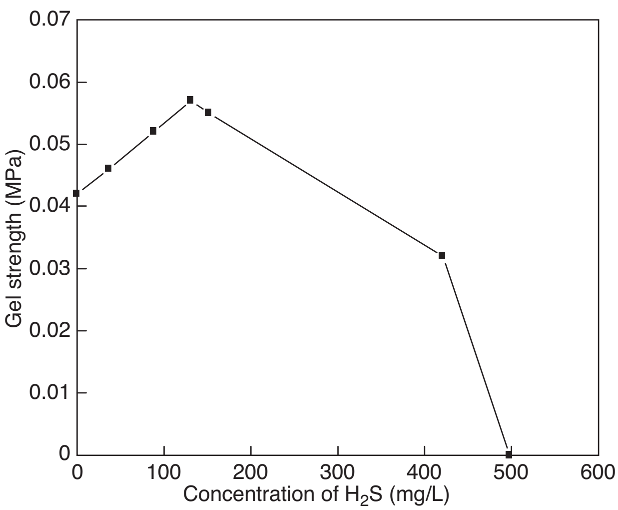


Figure 5

The effect of H_2S on the gel strength of $Na_2Cr_2O_7$/ $(NH_2)_2CS$/HPAM gel.

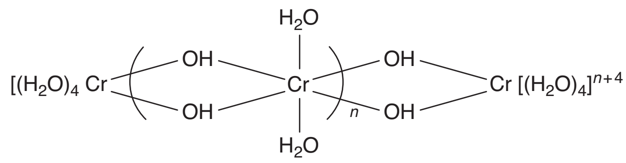
than 390 mg/L, $2^\#$ was higher than 420 mg/L), the gelants only formed a blue small mass jelly and didn't form bulk gel.

In two inorganic chromium crosslinking gelants, both Na_2SO_3 and $(NH_2)_2CS$ are reducing agents (Zhao, 2003; Maxcy, 1998), they can reduce Cr(VI) of $Na_2Cr_2O_7$ to Cr(III), that is:

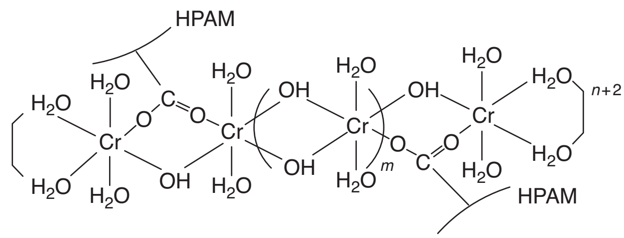
$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

$$Cr_2O_7^{2-} + 6(NH_2)_2CS + 8H^+ \rightarrow 3(NH_2)(NH)CSSC(NH)(NH_2) + 2C_r^{3+} + 7H_2O$$

Then the multi-core hydroxyl bridge ligand of Cr(III) was generated through hydrolysis action and hydroxyl bridge action, further hydrolysis action and hydroxyl bridge action:



Then, the multi-core hydroxyl bridge ligand of Cr(III) crosslinked with carboxyl of HPAM to form bulk gel:



S is the most active part of the molecule of $(NH_2)_2CS$, which is a kind of organic matter. The reaction of $(NH_2)_2CS$ depends on the activity of S. The carbon-sulfur double bond is a covalent one, and this covalent bond has to be destroyed during the reaction process. The reducibility of Na_2SO_3 is stronger than $(NH_2)_2CS$. Also, Na_2SO_3 can have a stabilizing effect on $(NH_2)_2CS$ (Liyuan Chai, 2002), and without H_2S, the gelation time of $1^\#$ gelant is much shorter than that of $2^\#$ gelant.

H_2S is also a kind of reducing agent, and its reducibility is stronger than Na_2SO_3 and $(NH_2)_2CS$. When the concentration of H_2S is small in $1^\#$ and $2^\#$ gelants, H_2S will react with $Na_2Cr_2O_7$ first, and the reaction velocity is faster than Na_2SO_3 and $(NH_2)_2CS$. Thus, the presence of H_2S decreases the gelation time of the two inorganic chromium crosslinking gelants. Further, because the reducing effect of H_2S is much stronger than $(NH_2)_2CS$, the gelation time of $2^\#$ gelant decreases more obviously. The shorter the gelation time is, the stronger the gel strength is (Caili Dai, 2001). So the gel strength increases when the concentration of H_2S increases, which is shown in Figure 4.

But when the concentration of H_2S reaches a certain value, the reduction reaction happens quickly. Redundant Cr(III) reacts with excessive H_2S and generates Cr_2S_3 precipitation, and ultimately it can't form bulk gel.

The composition of the other systems named $3^\#$ and $4^\#$ is shown in Table 2. The following experiments where HPAM solution is replaced by the simulation water without this compound reconfirm the existence of the above precipitation reaction. The injection of 964 mg/L and 1 083 mg/L concentrations of H_2S in $3^\#$ and $4^\#$ systems generates blue precipitation. The concentration of chromium and sulfur in the solution is measured before and after generation of the precipitate by ICP and the experimental result are shown in

Table 3. We can see that the concentration of chromium and sulfur in the solution decrease obviously, so it confirms that most of chromium and sulfur have already formed the Cr_2S_3 blue precipitation.

TABLE 3

Comparison of Cr concentration and S concentration before and after reaction

Type of the gelants	$3^{\#}$ gelant		$4^{\#}$ gelant	
Elements	Cr	S	Cr	S
Theoretical value (mg/L)	793.9	1 923.2	739.9	2 703.5
Measured value (mg/L)	5.75	1 279.0	2.37	2 164.0

2.2 The effect of H_2S on Organic Chromium Crosslinking Gelant

The composition of the organic chromium crosslinking gelant for system $5^{\#}$ is reported in Table 2. Figure 6 and Figure 7 show the effect of H_2S on organic chromium crosslinking gel. The *X* axis is H_2S concentration and the *Y* is gelation time/gel strength. It can be seen that the gelation time prolonged and the gel strength slightly decreased.

The simulation produced water without HPAM is used in the test instead of HPAM solution. When adding H_2S, there is no precipitation in $5^{\#}$ gelant. After a period of time, there is no change; during the opening of the bottle of $5^{\#}$ gelant, there is a strong smell of H_2S. It is found that the concentration of sulfur in H_2S falls from 538 mg/L to 457 mg/L. There is only a slight decrease (because of H_2S from the bottle to atmosphere as opening for examination the concentration of sulfur in H_2S) which demonstrates that H_2S does not react with the organic chromium crosslinker.

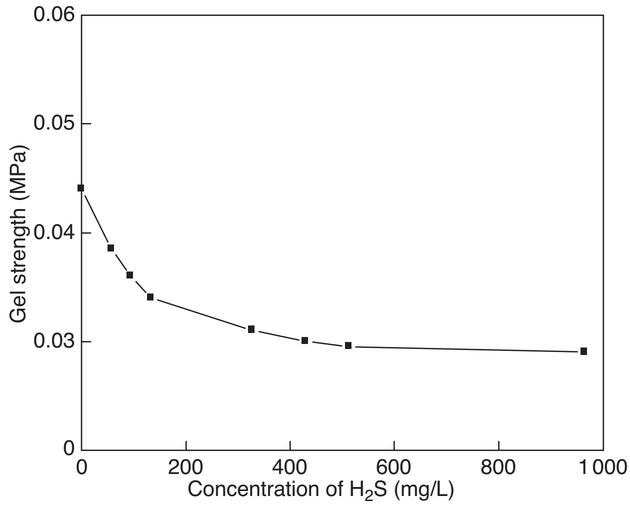


Figure 7

The effects of H_2S on the gel strength of Cr(III)-acetate & Cr(III)-lactate/HPAM gel.

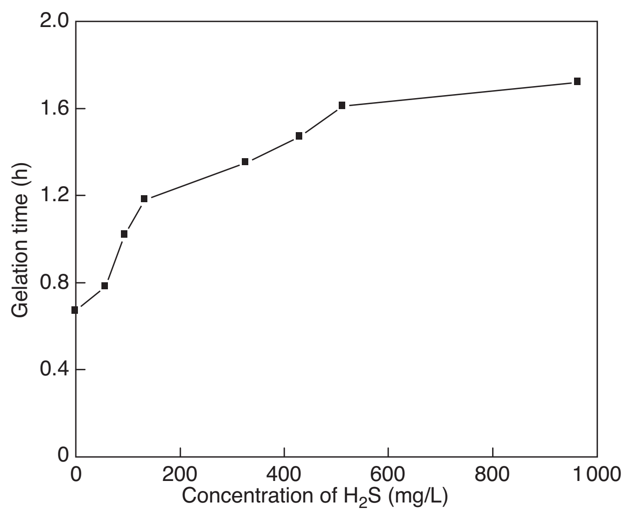


Figure 6

The effect of H_2S on the gelation time of Cr(III)-acetate & Cr(III)-lactate/HPAM gel.

H_2S is replaced by hydrochloric acid to comparatively study the influence of pH for $5^{\#}$ gelant. After adding hydrochloric acid instead of H_2S, the gelation time is also prolonged and the gel strength is slightly decreased. It shows that the mechanism of H_2S affecting the organic chromium crosslinking gelant is different from that of the inorganic chromium crosslinking gelant. H_2S affects the organic chromium crosslinking gelant by changing pH value of the gelant. Figure 8 shows the influence of H_2S on the pH value of the produced water.

As shown in Figure 8, the pH value of the system becomes lower with the increase of the concentration of H_2S; the influence of H_2S on pH value becomes also smaller with the increase of the concentration of H_2S. Therefore, a low H_2S concentration has a large influence on the gelation time and the gel strength of the organic chromium crosslinking gelant. When the concentration of H_2S reaches a certain level, the influence becomes smaller.

YG107 crosslinker is a complex of Cr(III)-acetate and Cr(III)-lactate. Lactic acid root and actate acid root reacts with Cr(III) by chelation which delay the crosslinking reaction of Cr(III) and polyacrylamide. The released Cr(III) should first be hydrolyzed into $Cr(H_2O)_6$(III), then through hydroxyl bridge action. Further hydrolysis action and hydroxyl bridge action, comes into a complexion of chromium which crosslinks with carboxyl of HPAM.

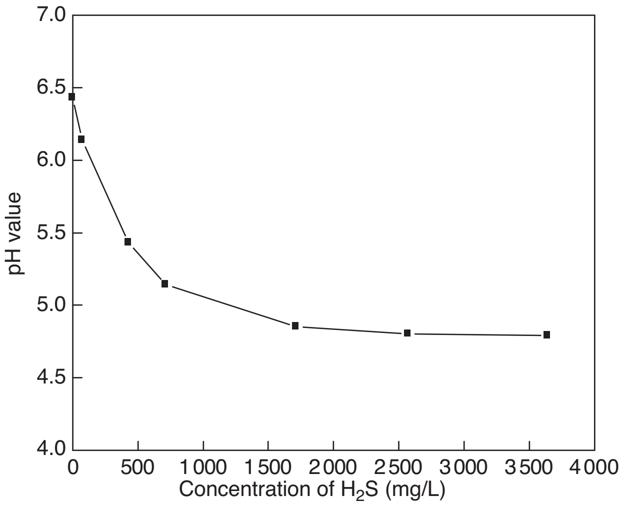


Figure 8

The pH value of the simulation produced water containing H_2S.

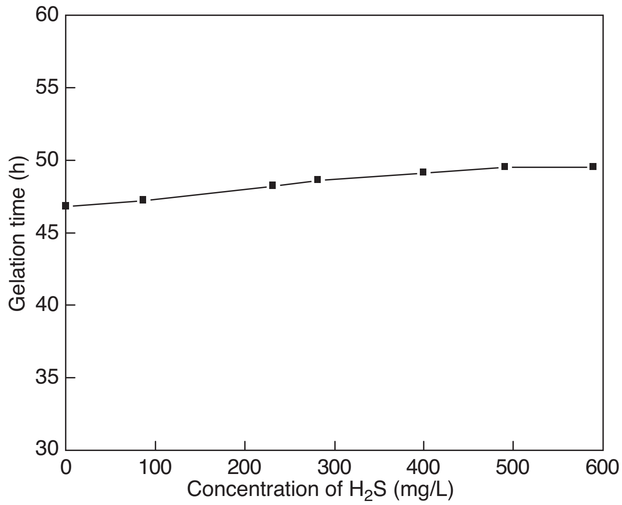


Figure 9

The effects of H_2S on the gelation time of phenol formaldehyde resin/HPAM gel.

The higher the pH is, the more easily HPAM gel forms and the better its stability is. The main reasons are:

- a high pH value is favorable for the hydrolysis of Cr(III). It helps to form gel;
- a high pH value is also favorable for the hydrolysis of amide and increasing charged groups of molecules. The increase of charged groups is beneficial to stretch the molecular chain, and then cross linking reaction is easy to happen. On the other hand, crosslinked junctions trend to increase, which increases the gel strength. Therefore, the injection of H_2S prolongs the gelation time and decreases the gel strength.

2.3 The Effect of H_2S on Phenol Formaldehyde Resin/HPAM Crosslinking Gelant

The composition of the phenol formaldehyde resin crosslinking gelant of system 6# is given in Table 2. Figure 9 and Figure 10 show that the results of H_2S on phenol formaldehyde resin crosslinking gel, the *X* axis is H_2S concentration and the *Y* is gelation time/gel strength. It can be seen that the gelation time is slightly prolonged and the gel strength slightly decreases, due to the effect of H_2S.

YG103 is a phenol formaldehyde resin crosslinker, which is a water soluble resin and that is formed as the prepolymer of phenol and formaldehyde under catalyst with sodium hydroxide. It is also known as resol. Sodium hydroxide can not only have a strong catalysis effect on addition reaction between phenol and formaldehyde, but also improves the resol solubility in reaction medium.

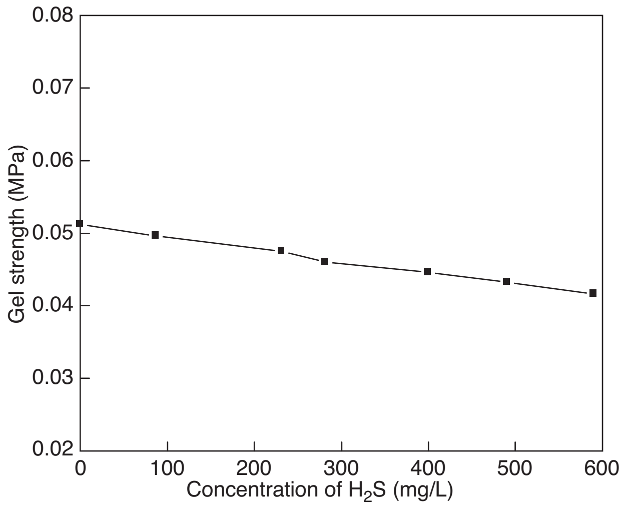
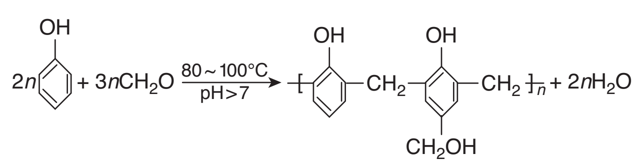


Figure 10

The effects of H_2S on the gel strength of phenol formaldehyde resin/HPAM gel.



The crosslinking reaction between phenol formaldehyde resin and HPAM happens between hydroxymethyl of phenol formaldehyde resin and amide of HPAM. The more the numbers of hydroxymethyl functional groups are, the faster the crosslinking reaction is and the stronger the gel is.

The addition of H_2S can reduce the rate of the crosslinking reaction by affecting the pH value of the gelant, but YG103 itself is a weak alkaline compound, and the phenolic hydroxyl group of YG103 can have certain buffering effects on the pH changes of the gelant. The effects of H_2S on the gelant of phenol formaldehyde resin/HPAM are relatively slight.

CONCLUSIONS

The effects of H_2S on the gels including $Na_2Cr_2O_7$/Na_2SO_3/HPAM gel, $Na_2Cr_2O_7$/$(NH_2)_2CS$/HPAM gel, Cr(III)-acetate & Cr(III)-lactate/HPAM gel and phenol formaldehyde resin/HPAM gel are studied in this paper. The effects of H_2S on $Na_2Cr_2O_7$/Na_2SO_3/HPAM gel and $Na_2Cr_2O_7$/$(NH_2)_2CS$/HPAM gels are dramatic. When the concentration of H_2S is less than 100 mg/L, the gelation time decreases obviously with the increase of the concentration of H_2S. The gel strength increases significantly; but, when the concentration of H_2S reaches a certain value, the gelants can not form bulk gel. With the increase of the concentration of H_2S, for Cr(III)-acetate & Cr(III)-lactate/HPAM gel, H_2S can prolong the gelation time and reduce the gel strength. For phenol formaldehyde resin/HPAM gel, H_2S can just slightly increase gelation time and decrease gel strength.

The mechanisms of actions of H_2S on the gels have also been studied. For $Na_2Cr_2O_7$/Na_2SO_3/HPAM gel and $Na_2Cr_2O_7$/$(NH_2)_2CS$/HPAM gel, as the reducer, H_2S can reduce Cr(VI) into Cr(III) and accelerate the reaction for low concentration of H_2S, while it can react with Cr(III) and generate Cr_2S_3 precipitation in high concentration of H_2S, for which the bulk gel can not form without Cr(III). For Cr(III)-acetate & Cr(III)-lactate/HPAM gel and phenol formaldehyde resin/HPAM gel, H_2S can prolong the gelation time and reduce the gel strength by decreasing the pH value.

If the gelation time is too short, it is hard to control its application in oil and gas field. When the gel strength is too weak, the stability of gel is poor and a good water shutoff effect can not be achieved. Therefore, according to the comprehensive investigations of the effects of H_2S on gel as water shutoff agents, the phenol formaldehyde resin/HPAM gel is recommended as a water shutoff agent suitable for oil and gas reservoir containing H_2S.

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