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# Development and Performance Evaluation of a Selective Plugging System for High-Temperature and High-Salinity Water-Bearing Gas Reservoir

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**Abstract:** In the development of natural gas reservoirs, the water produced in wells will cause a decline in gas well productivity. In this study, a selective frozen gel plugging agent system suitable for water plugging in gas reservoirs under conditions of high temperature and high salinity. The plugging capacity of the gel system was evaluated. The experimental results showed that: (1) the optimal experimental scheme of the frozen gelling system was as follows: 107 °C with 1.0% AM-AMPS +0.6% p-benzenediol +0.6% hexamethylenetetramine +0.2% thiourea. (2) The optimal injection volume of the system for water phase plugging was 0.5 PV, and the system has an excellent plugging effect at a permeability of 356–3118 mD. (3) The system could also effectively improve the degree of heterogeneity, and the smaller the degree of heterogeneity, the better the improvement effect. (4) The gel system had a good effect on different plugging methods, and the gas medium did not affect the plugging performance. This study provides a sufficient theoretical basis for the exploitation of high-temperature and high-salinity water-bearing gas reservoirs through experimental research, which is of great significance for improving production capacity.

**Keywords:** high temperature and high salinity; water-bearing gas reservoir; selective water shutoff agent; permeability; plugging property



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## 1. Introduction

With the continuous growth in global energy demand, gas reservoir development has become one of the main sources of oil and gas supply. Studies have found that in the process of deepening the exploration and development of gas reservoirs with edge and bottom water, the productivity of gas wells decreases gradually, and water production is the key factor affecting productivity. The water production problem of gas wells can be effectively suppressed by injecting chemical agents by chemical water plugging in gas wells, but water plugging in gas wells is more risky and more difficult than water plugging in oil wells. White et al., Zaitoun et al. and Ranibar et al. believed that the main reasons are as follows. First, capillary force is the driving force for water displacement in oil reservoirs, but in gas reservoirs, because the gas–water capillary force is greater than the oil–water capillary force, it will be more difficult to develop or cause water lock damage and other phenomena in the gas reservoir. Second, the technology for finding the water level in gas reservoirs is immature, and it is difficult to achieve fixed-point water plugging. Third, in selective water plugging of gas wells, the water plugging agent may enter the gas layer, and the water in the water plugging agent may cause gas reservoir pollution or even a water lock near the wellbore area [1–3]. Therefore, it is necessary to research and screen effective chemical systems for gas well water plugging to improve gas wells' productivity and benefits.

Research into water shutoff agents for gas wells is relatively sparse. At present, Nie et al., Chunsheng et al., Kewen et al., Chaabouni et al., Xiong et al., Lakatos et al., Lakatos et al., Yu et al. and Guo et al. believed that the main types of water shutoff agents commonly used include polymer colloids, microemulsions, cement, nanomaterials and so on [4–12]. According to the crosslinking form, polymer shutoff agents can be divided into polymer crosslinking technologies and polymer bridge bond adsorption technologies. Dovan et al. optimized a partially hydrolyzed polyacrylamide/chromium frozen gel as a water shutoff agent to reduce daily water production to 50 barrels per day through physical simulation experiments [13]. Wassmuth et al. also proposed that a partially hydrolyzed polyacrylamide/chromium frozen gel could effectively inhibit the water produced by gas wells, but the frozen gel must be replaced with natural gas or foam [14]. Al-Muntasheri et al. developed a low-molecular-weight polymer, PAtBA, and used an organic crosslinking agent (PEI) to plug horizontal wells in high-temperature gas reservoirs [15]. However, Zaltoun et al. indicated that there are some problems in the application of polymer crosslinking technology in gas wells. Polymer selectivity is not obvious in gas wells, and may lead to an inability to produce natural gas, and the risk is large. The polymer bridge bond adsorption technology without crosslinking agent can reduce the influence of the crosslinking reaction on gas well productivity, and the good stretching performance of the polymer adsorption layer can be used to improve the water plugging effect [16]. Zaitoun et al. of the French Petroleum Research Institute achieved the purpose of selective water blocking but not gas blocking through the adsorption of polymer bridge bonds in the formation pore throat [2]. Ranjbar et al. used an ethylene sulfonate-vinylamide-acrylamide terpolymer with a molecular weight of 500,000 as a water plugging agent, and reduced the water produced by gas wells from 90 $m^3$/day to 2 $m^3$/day [17]. Tielong et al. studied a frozen gel water plugging agent, and the natural gas production of each well was increased by at least 10% after construction [18].

At present, when a frozen gel is used as a plugging agent in gas wells, the main method used to solve the decrease in gas well productivity is to establish a gas phase seepage channel in the frozen gel or to replace the frozen gel with a certain fluid that enters the reservoir to reduce the damage by the frozen gel on the gas well's productivity. Dovan et al. first summarized the generation mode of a gas seepage channel, and compared the water plugging effects of several frozen gel solutions injected alternately with nitrogen with the results of Hutchins et al. [12]. Wawro et al. stated that the injection volume of frozen gel can be designed according to the water production capacity of the gas well, and the water production capacity can represent the frozen gel acceptance capacity of the gas well to some extent [19]. Wassmuth et al. of the Alberta Research Society found through physical and numerical simulation studies that foam is an effective replacement fluid [20]. In order to reduce the water produced by gas wells, this study screened a water plugging system that is suitable for high-temperature and high-salinity conditions through experiments and evaluated its plugging performance, so as to provide effective theoretical guidance for oil and gas production.

## 2. Experiment

### *2.1. Experimental Material and Equipment*

The experimental frozen gel materials include AM-AMPS (sulfonic acid content: 30%) (Shandong Chemical Technology Co., Ltd., Heze, China), p-benzenediol (analytical purity; Aladdin Chemical Reagent Co., Ltd., Los Angeles, CA, USA), hexamethylenetetramine (analytical purity; Chemical Reagent Co., Ltd., Los Angeles, CA, USA), thiourea (99.0% high purity; Aladdin Chemical Reagent Co., Ltd., Los Angeles, CA, USA), and nitrogen. The salinity of the homemade ion solution (salinity $22.38 \times 10^4$ mg/L) is shown in Table 1.

**Table 1.** Salinity table of the formed water solution.

| Ionic Types | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | Cl | $HCO^{3-}$ | Salinity |
|---|---|---|---|---|---|---|
| Mass concentration, mg/L | 73,298.4 | 11,272.5 | 1518.8 | 137,529.5 | 183.6 | 223,802.8 |

The main instruments used in the experiment mainly included an electronic balance (Model: BSM-32002) (Shanghai Zhuojing Electronic Technology Co., Ltd., Minhang, China), an electronic stirrer (Model: 78-1 magnetic heating stirrer) (Changzhou Tongchuang Experimental Instrument Factory, Tianning, China), an electric blast drying oven with a constant heating temperature (Model: 101-00) (Shaoxing Supo Instrument Co., Ltd., China), a high-temperature curing tank (Jiangsu Lianyou Research Instrument Co., Ltd., Nantong, China), a core flow device (Jiangsu Lianyou Research Instrument Co., Ltd., Nantong, China), etc.

### *2.2. Experimental Method*

#### 2.2.1. Preparation of the Frozen Gel System

Preparation of the frozen gel system involved several experimental steps. First, according to the proportions of the polymer solution, the appropriate amount of frozen gel was placed in an ampoule bottle for complete sealing, and then the ampoule bottle was placed in a high-temperature curing tank in a blast drying oven at a constant temperature of 130 °C in to investigate the stability of the frozen gel. Next, the frozen gelation time was determined by the frozen gel strength codes of Sydansk as shown in Table 2 and Figure 1; the time corresponded to frozen gel code F [21]. Third, the amount of dehydration was determined by the ratio of frozen gel dehydration quality to the total frozen gel weight.

**Table 2.** Frozen gel strength codes [21].

| Frozen Gel Strength Code | Frozen Gel Description |
|---|---|
| A | No detectable frozen gel formed: The frozen gel appears to have the same viscosity as the original polymer solution |
| B | Highly flowing frozen gel: The frozen gel appears to be only slightly more viscous than the initial polymer solution |
| C | Flowing frozen gel: Most of the frozen gel flows to the bottle cap by gravity upon inversion |
| D | Moderately flowing frozen gel: Only a small portion (5–10%) of the frozen gel does not readily flow to the bottle cap by gravity upon inversion (usually characterized as a tonguing frozen gel) |
| E | Barely flowing frozen gel: The frozen gel can barely flow to the bottle cap and/or a significant portion (>15%) of the frozen gel does not flow by gravity upon inversion |
| F | Highly deformable nonflowing frozen gel: The frozen gel does not flow to the bottle cap by gravity upon inversion |
| G | Moderately deformable nonflowing frozen gel: The frozen gel deforms about halfway down the bottle by gravity upon inversion |
| H | Slightly deformable nonflowing frozen gel: only the frozen gel's surface slightly deforms by gravity upon inversion |
| I | Rigid frozen gel: There is no frozen gel surface deformation by gravity upon inversion |

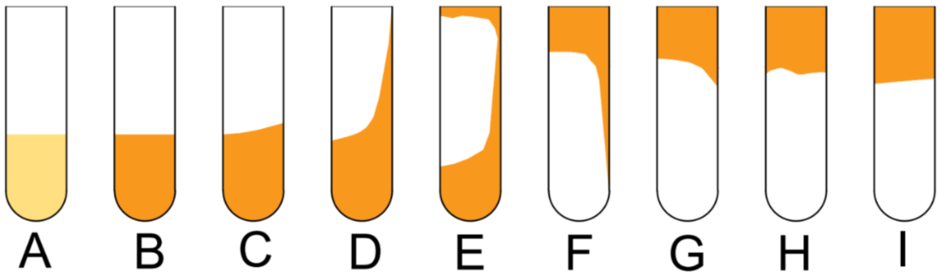



**Figure 1.** Morphology of the frozen gel strength codes [21].

### 2.2.2. Frozen Gelling Performance Test of the Frozen Gel System

The effects of the polymer mass fraction, the crosslinking agent mass fraction, the oxygen scavenger mass fraction and temperature on the formation of the frozen gel were investigated by the control variable method. The polymer, crosslinking agent, oxygen scavenger mass fraction and temperature were determined by the formation time and dehydration rate of the frozen gel. The experimental scheme is as shown in Tables 3–6.

**Table 3.** Scheme of the polymer mass fraction optimization experiment.

| AM-AMPS Mass Fraction | p-Benzenediol/Hexamethylenetetramine Agent Mass Fraction | Oxygen Scavenger Mass Fraction | Temperature |
|---|---|---|---|
| 0.5% | 0.1% | 0.2% | 107 °C |
| 0.6% | | | |
| 0.8% | | | |
| 1.0% | | | |
| 1.2% | | | |

**Table 4.** Scheme of the crosslinking agent mass fraction optimization experiment.

| AM-AMPS Mass Fraction | p-Benzenediol/Hexamethylenetetramine Agent Mass Fraction | Oxygen Scavenger Mass Fraction | Temperature |
|---|---|---|---|
| 1.0% | 0.1% | 0.2% | 107 °C |
| | 0.2% | | |
| | 0.4% | | |
| | 0.6% | | |
| | 0.8% | | |
| | 1.0% | | |

**Table 5.** Scheme of the oxygen scavenger mass fraction optimization experiment.

| AM-AMPS Mass Fraction | p-Benzenediol/Hexamethylenetetramine Agent Mass Fraction | Oxygen Scavenger Mass Fraction | Temperature |
|---|---|---|---|
| 1.0% | 0.6% | 0.005% | 107 °C |
| | | 0.075% | |
| | | 0.1% | |
| | | 0.2% | |
| | | 0.3% | |

**Table 6.** Scheme of the temperature optimization experiment.

| AM-AMPS Mass Fraction | p-Benzenediol/Hexamethylenetetramine Agent Mass Fraction | Oxygen Scavenger Mass Fraction | Temperature |
|---|---|---|---|
| 1.0% | 0.6% | 0.02% | 107 °C |
| | | | 120 °C |
| | | | 130 °C |

### 2.2.3. Test of the Plugging Performance in a Homogeneous Model

The experimental steps of the water phase plugging performance were as follows. First, we prepared a certain amount of sand, and cleaned and dried it for later use. Next, the dried sand was placed in the sand filling pipe, and the water phase permeability was measured with lab-made ionized water at room temperature. Next, the mass of the instrument after the addition of water to saturation and the mass difference of the instrument and sand before saturation was calculated, that is the pore volume (PV) of sand in the instrument was calculated. The drum dryer was set to a constant temperature of 107 °C. Next, the plugging agent was reverse injected into the instrument at a flow rate of 0.5 mL/min, close the valve, and we waited for the frozen gel to form. After that, lab-prepared ionized water was reverse injected into the instrument at a flow rate of 0.5 mL/min. After the gel became frozen, lab-prepared ionized water was injected into the instrument at a water injection rate of 0.5 mL/min. At the end, we measured and recorded the pressure difference between the two ends of the instrument. The experimental flow chart is shown in Figure 2.

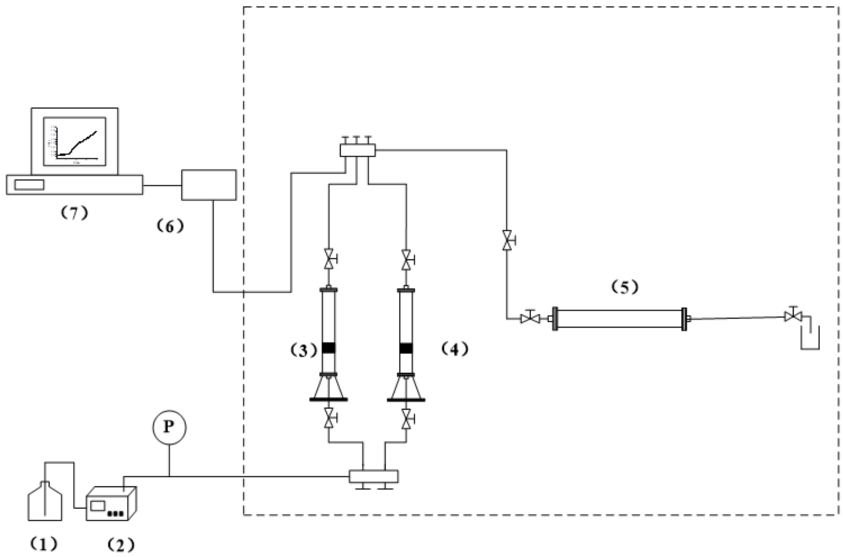



**Figure 2.** Flow chart of the water plugging experiment. (1) Distilled water tank; (2) horizontal flow pump; (3) brine water tank; (4) plugging agent material tank; (5) sand filling pipe; (6) pressure sensor; (7) computer.

### 2.2.4. Plugging Performance Test in a Heterogeneous Model

The steps of the heterogeneous plugging experiment were as follows. First, we prepared a certain amount of sand, and cleaned and dried it for later use. Next, the dried sand was placed in the sand filling pipe, and we measured the water phase permeability with lab-prepared ionized water at room temperature. After that, the characteristics of the sand filling pipe after saturation was determined, and the pore volume (PV) of the sand filling pipe was calculated. Next, the drum dryer was set at a constant temperature of 107 °C, then the parallel tube was injected with lab-made ionized water at a flow rate of 0.5 mL/min and the shunt rate was measured after the parallel tube had discharged. After that, the plugging agent was injected into the reverse tube at a flow rate of 0.5 mL/min, close the valve, and we waited for the frozen gel form. Next, lab-made ionized water was injected back into the parallel tube at a flow rate of 0.5 mL/min. After the gel had frozen, lab-prepared ionized water was injected into the sand-filling pipe, the pressure difference at both ends of the sand-filling pipe was measured, the water flow of the two pipes was recorded and the water separation rate was calculated. After the system became stable, the water phase permeability of a single pipe was measured, and the selective plugging of formations of plugging agents with different levels of permeability was investigated. The experimental flow chart is shown in Figure 3.

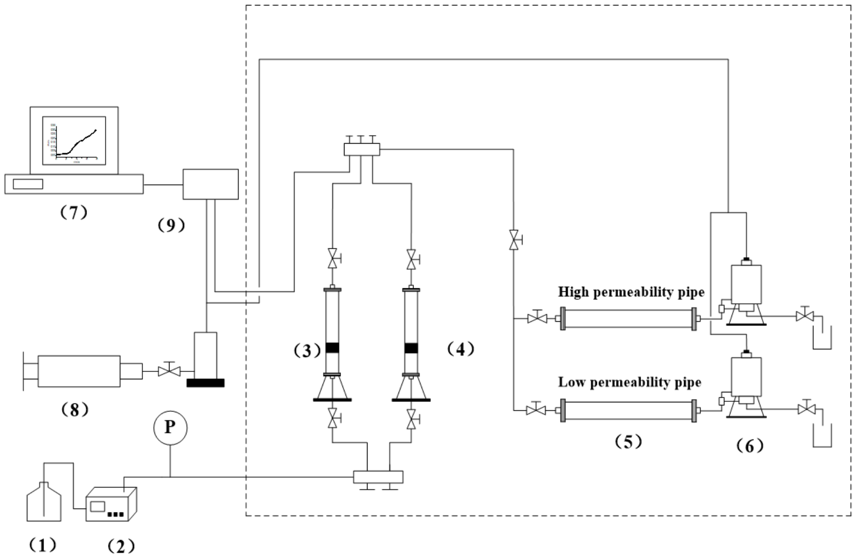



**Figure 3.** Flow chart of the plugging experiment for different heterogeneous formations of the plugging agent. (1) Distilled water tank; (2) horizontal flow pump; (3) strata water tank; (4) plugging agent material tank; (5) sand filling pipe; (6) back-pressure valve; (7) computer; (8) back pressure pump; (9) pressure sensor.

2.2.5. Performance Test of Plugging and Dredging Integration

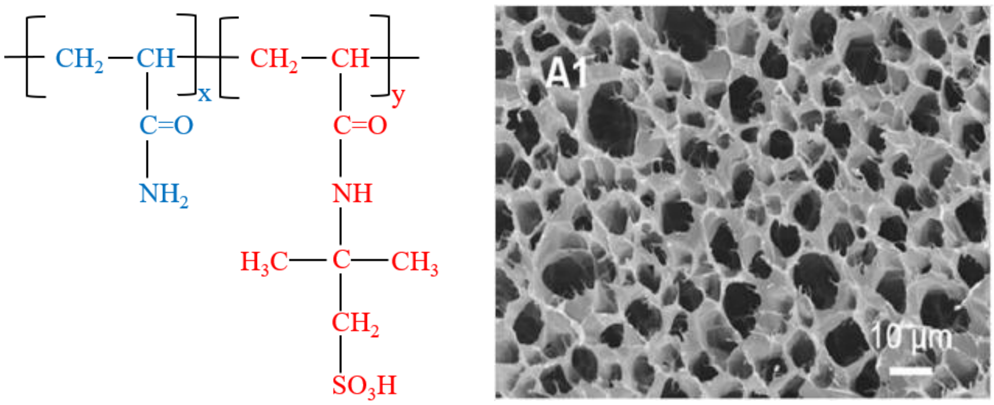
The experimental steps of gas–liquid injection were as follows. First, we prepared a certain amount of sand, and cleaned and dried it for later use, then the dried sand was placed in the sand filling pipe and the water phase permeability with lab-prepared ionized water was measured at room temperature. Next, the mass of the instrument after saturation with water and the mass difference of the instrument and sand before saturation were calculated, that is, the pore volume PV of sand in the instrument was calculated. Next, the drum dryer was set at a constant temperature of 107 °C and a certain volume of formation water was injected into the instrument at a flow rate of 0.5 mL/min. At the same time, a certain volume of frozen gel solution was reverse injected at a flow rate of 0.5 mL/min and $CH_4$ was reverse injected at different rates close the valve. After waiting for freezing, when the glue became glue, one group was injected with water at a rate of 0.5 mL/min and the other group was injected with air ($CH_4$) at a certain rate. The experimental flow chart is shown in Figure 2.

The experimental procedure of liquid injection before gas injection only needed to be changed the final step; that is, after reverse injection of a certain volume of the frozen gel solution at a flow rate of 0.5 mL/min, different volumes of $CH_4$ were injected to complete the experiment.

## 3. Results and Discussion

### *3.1. Research and Development of the Experimental Frozen Gel System*

The methyl propane sulfonic acid group existing in the molecular structure of AM-AMPS (Figure 4a) increased the resistance of the molecule when the spatial position changed, and inhibited the hydrolysis of the polymer and other reactions. The S-O bond contained in the sulfonic acid group of 2-acrylamide-2-methyl propane sulfonic acid (AMPS) monomers in the molecular structure weakened the ability of S to attract electrons from −OH and reduced the absorption capacity of salt ions. The sulfonic acid group contained in the AMPS could be infinitely dissolved in water, which improved the tolerance of polymers to calcium and magnesium ions, and had higher stability under conditions of high temperature and high salinity. At the same time, the amino group in the AM-AMPS polymer is hydrophilic, which can realize the plugging effect of the water phase. AM-AMPS achieved the following two processes by reacting with p-benzenediol/hexamethylenetetramine: (1) hydroxymethylation of the nitrogen atoms on the amide group; (2) forming multiple alkylation crosslinking with phenol rings. A frozen AM-AMPS gel with a honeycomb network structure, as shown in Figure 4b, was formed, so the gas could pass through the network structure to achieve the effect of ventilation. Therefore, it can be applied to water plugging operations in gas wells. Through the experimental study on the stability of the polymers, the crosslinking agents, the oxygen scavenger mass fraction and the temperature on the frozen gel's stability, the optimal system could be selected for field operations to improve oil and gas production.




(**a**) (**b**)

**Figure 4.** (**a**). Molecular structure of the AM-AMPS copolymer. (**b**). Microstructure of the AM-AMPS polymer.

Figure 5 shows the experimental diagram of the influence of the AM-AMPS mass fraction on the frozen gel. The experimental results showed that increasing the mass fraction of AM-AMPS could greatly reduce the gelation time and the dehydration rate of the frozen gel. When the mass fraction of AM-AMPS was 1.0 and 1.2%, the gelation time of the frozen gel was 21 h and 18 h, respectively. When the mass fraction of polymer was 1.0%, the dehydration rate of the frozen gel began to flatten, and the dehydration rates at 1.0% and 1.2% on Day 180 were 12.9% and 10.3%, respectively, indicating that increasing the mass fraction of the polymer appropriately was beneficial for improving the overall stability of the frozen gel. A frozen gel with high stability could be obtained when the mass fraction of AM-AMPS was 1.0%, and costs were saved.

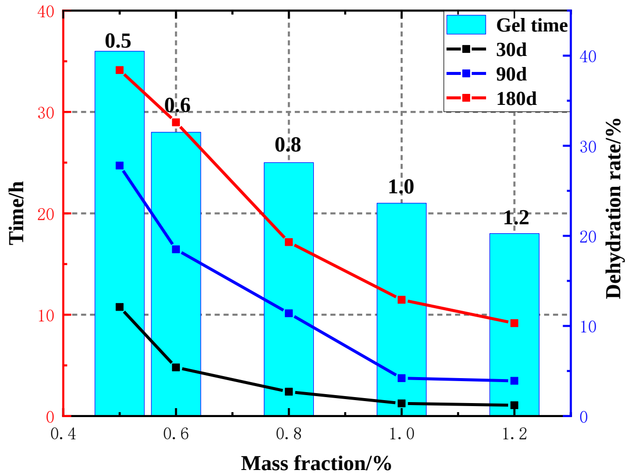



**Figure 5.** Effect of the polymer mass fraction on the stability of frozen gel. Note that the left y-axis values in Figure 5 is used for histograms, and the right y-axis values are used for the line charts; 30 d/90 d/180 d represent 30 days, 90 days, 180 days of dehydration, respectively.

Figure 6 is the experimental diagram showing the influence of the crosslinking agent mass fraction on the stability of the frozen gel. According to the results, the gelation time of 0.1% p-benzenediol/hexamethylenetetramine was 21 h, and the dehydration rate was 12.9% after 180 d. When the mass fraction of the crosslinking agent was increased, the gelation time was shortened. The dehydration rate reached the lowest value when the mass fraction of the crosslinking agent was 0.6%, and the dehydration rate was only 2.6% after 180 d and the frozen gelation time was 12 h. When the mass fraction of the crosslinking agent continued to increase, the dehydration rate began to increase again. When the mass fraction of the crosslinking agent increased to 1.0%, the gelation time was only 8 h but the dehydration rate was as high as 23.2%, indicating that a 0.6% mass fraction of p-benzenediol/hexamethylenetetramine obtained a frozen gel with good stability. However, with a high concentration of the crosslinking agent, the increase in the frozen gel dehydration rate was due to the fact that AM-AMPS accelerates the crosslinking speed of AM-AMPS under the action of excessive crosslinking agent molecules, resulting in the formation of frozen gel network pores that were too narrow and the structure that was too close to play the role of bounding water molecules, which made the water molecules flow out from the frozen gel structure and increased the dehydration rate of the frozen gel.

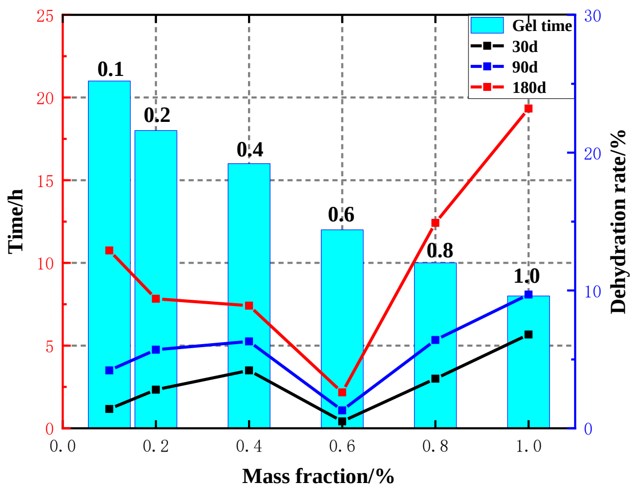



**Figure 6.** Effect of the crosslinking agent mass fraction on the stability of the frozen gel. Note that the left y-axis values in Figure 6 is used for histograms, and the right y-axis values are used for the line charts; 30 d/90 d/180 d represent 30 days, 90 days, 180 days of dehydration, respectively.

Figure 7 is the experimental diagram of the effect of the thiourea mass fraction on the stability of the frozen gel. It can be seen from the experimental results that the dehydration rate of the oxygen scavenger increased from 0.005% to 0.2%, the dehydration rate decreased significantly, the dehydration rate for 180 days was 2.6%, and the gelation time was 12 h. With an increase in the amount of oxygen scavenger, the gelling time was shortened, but the effect was not obvious; when the oxygen scavenger dosage reached 0.3%, the dehydration rate increased significantly compared with that at 0.2%, indicating that 0.2% oxygen scavenger could help stabilize the frozen gel structure.

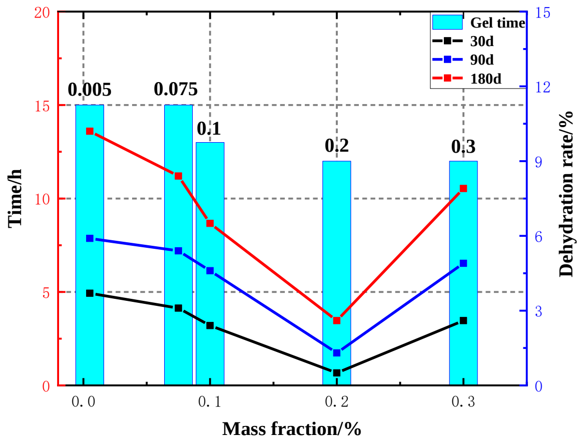



**Figure 7.** Effect of the mass fraction of the deaerator on the stability of frozen gel. Note that the left y-axis values in Figure 7 is used for histograms, and the right y-axis values are used for the line charts; 30 d/90 d/180 d represent 30 days, 90 days, 180 days of dehydration, respectively.

Figure 8 shows the experimental diagram of the effect of temperature on the stability of the frozen gel. The results show that increasing the system temperature reduced the gelation time of the frozen gel slightly, but the dehydration rate of the frozen gel increased significantly. At 107 °C, the dehydration rate at 180 d was 2.6%, but when the system temperature rose to 120 °C, the dehydration rate at 180 d was 5.8%, an increase of more than double. The main reasons for the dehydration of the frozen gel at high temperatures are as follows: (1) at high temperatures, the crosslinking speed of the system is too fast, resulting in a tight spatial structure of the frozen gel, which cannot bound water molecules, thus leading to dehydration; (2) under sustained high-temperature conditions, the original intact spatial network structure of the frozen gel system was destroyed, resulting in the outflow of water molecules from the pore and dehydration. Therefore, the frozen gel system is suitable for application in a reservoir environment of 107 °C.

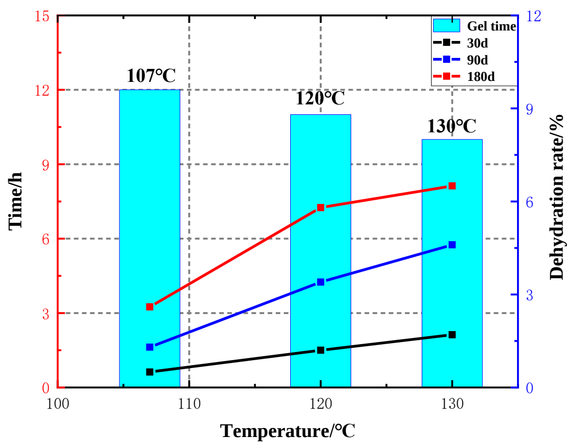



**Figure 8.** Effect of temperature on the stability of frozen gel. Note that the left y-axis values in Figure 8 is used for histograms, and the right y-axis values are used for the line charts; 30 d/90 d/180 d represent 30 days, 90 days, 180 days of dehydration, respectively.

### 3.2. Test of Water-Phase Plugging Performance in Homogeneous Model

The optimal experimental scheme of the AM-AMPS frozen gel system was obtained through the experiments described above. The plugging performance of the frozen gel system was investigated in combination with the injection amount and permeability of the frozen gel. The following are the specific results of the experiment.

In the experiment on the frozen gel injection volume, in order to evaluate the water plugging ability of different frozen gel injection volumes, frozen gel solutions of 0.1 PV, 0.2 PV, 0.3 PV, 0.4 PV, 0.5 PV and 0.6 PV were injected. An analysis of the experimental results in Table 7 and Figure 9 shows that the greater the amount of frozen gel injected, the more obvious the water plugging effect. When the amount of frozen gel injected was increased to 0.2 PV, the water phase permeability decreased by 90.9%. At 0.5 PV and 0.6 PV, the displacement pressure difference could reach more than 1.5 MPa and the plugging effect was remarkable. The displacement pressure of the final system was stable at 0.097 MPa, 0.23 MPa, 0.75 MPa, 1.13 MPa, 1.77 MPa, and 2.15 MPa. When the displacement pressure difference of 0.5 PV was 0.4 PV, it was 1.5 times more than that of 0.5 PV, and the difference in the breakthrough pressure gradient was 0.7 MPa. When the amount frozen gel injected was 0.6 PV, the increase was less than that at 0.5 PV. Through the above analysis, it can be seen that 0.5 PV of the equivalent frozen gel solution is suitable for field operations, with obvious effects and cost savings.

**Table 7.** Effect of the amount of frozen gel injected on the water plugging rate and the residual resistance coefficient.

| Volume of Frozen Gel Injected (PV) | Water Phase Permeability Reduction Rate (%) | Residual Resistance Coefficient | Breakthrough Pressure Gradient (Mpa/m) |
|---|---|---|---|
| 0.1 PV | 75 | 4 | 0.7 |
| 0.2 PV | 90.9 | 11 | 1.46 |
| 0.3 PV | 97.1 | 35 | 2.5 |
| 0.4 PV | 98.3 | 57.5 | 3.7 |
| 0.5 PV | 98.9 | 87.5 | 4.4 |
| 0.6 PV | 99.1 | 107 | 5.0 |

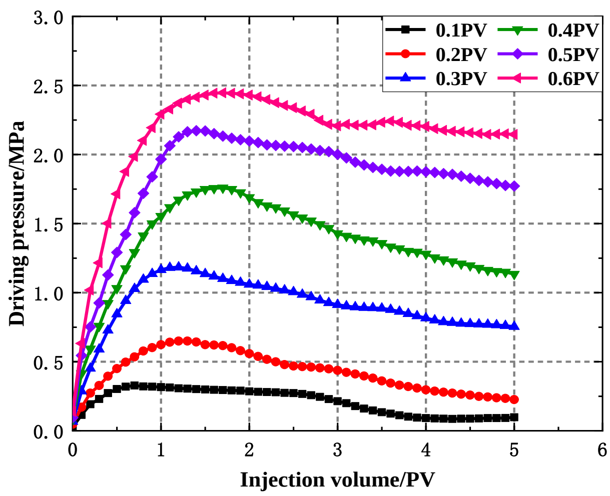



**Figure 9.** Effect of the frozen gel injection rate on plugging performance.

The effects of permeability on the sealing performance were as follows. Without changing the other conditions, the effects of permeability of 356 mD, 523 mD, 964 mD, 1874 mD and 3118 mD on the sealing performance were explored. The experimental results are shown in Table 8 and Figure 10. The results show that the frozen gel had better sealing ability at low permeability. After the frozen gel had formed, the water injection volume continued to increase, possibly due to the partial migration of the frozen gel, resulting in a small drop in the displacement pressure; with a rapid increase in the displacement pressure, the maximum displacement pressure of the system reached 3.26 MPa, 2.68 MPa, 1.71 MPa, 1.22 MPa and 1.01 MPa, respectively, for 356 mD, 523 mD, 964 mD, 1874 mD and 3118 mD. With continuous water flooding, the displacement pressure decreased and finally stabilized at 2.14 MPa, 1.25 MPa, 1.09 MPa, 0.62 MPa and 0.52 MPa, respectively. When the permeability was lower than 964 mD, the displacement pressure difference could be maintained at more than 1.5 MPa, and the residual drag coefficient and breakthrough pressure gradient at 356 mD were 2.9 times and 1.23 times that at 621 mD, respectively, indicating that the lower the permeability, the better the plugging effect of the system.

**Table 8.** Effects of permeability on the water plugging rate and the residual friction coefficient.

| Permeability (mD) | Water Plugging Rate (%) | Residual Resistance Coefficient | Breakthrough Pressure Gradient (MPa/m) |
|---|---|---|---|
| 356 | 99.8 | 593 | 6.64 |
| 621 | 99.5 | 203 | 5.4 |
| 936 | 99.1 | 114 | 3.6 |
| 1874 | 97.0 | 32.5 | 2.8 |
| 3118 | 93.7 | 16 | 2.4 |

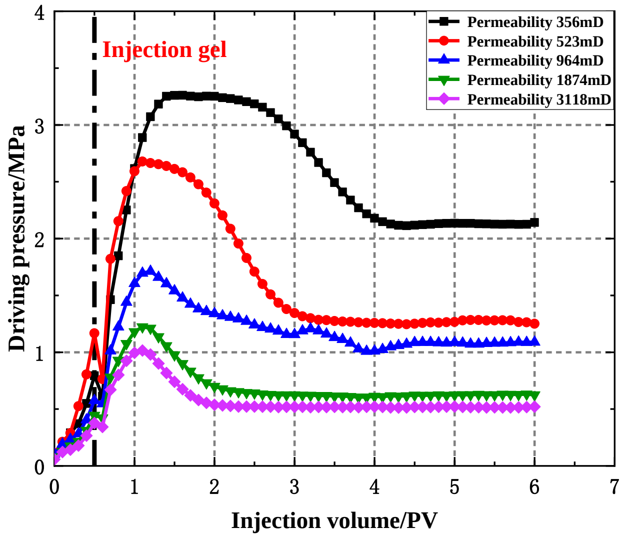



**Figure 10.** Experimental diagram of the influence of permeability on plugging performance.

### *3.3. Test of Water-Phase Plugging Performance in the Heterogeneous Model*

For the plugging experiment of heterogenous formations, the results are as follows. Combined with the influence of permeability on water phase plugging in the above experiments, the frozen gel system had a good effect when plugging low-permeability reservoirs. However, due to the differences in the geological properties of the strata where the reservoirs are located, the frozen gel system will inevitably preferentially enter high-permeability reservoirs, which will affect the plugging effect. In this experiment, the AM-AMPS frozen gel system selected for heterogeneous formation was studied under extreme differences of 4, 8 and 20, indicating that the AM-AMPS frozen gel system still had an effect on improving the formations with high heterogeneity, and the effect was the best for low-heterogeneity formations.

Figure 11a–c shows the relationship between the pipes with high and low permeability and the injection volume when the permeability ranges were 4, 8 and 20, respectively. It can be seen from the figure that the shunt rates of the high- and low-permeability pipes were about 85% and 15%, respectively, indicating that most of the fluid produced before the injection of frozen gel came from the high-permeability pipe. After the injection of frozen gel, the diversion rate of the high-permeability pipe decreased rapidly because the flow limitation of the frozen gel in the core with high permeability was small, and the frozen gel first entered the high-permeability pipe; when the frozen gel has formed, it inhibited the flow of the water phase and reduced the flow volume of the high-permeability pipe. When the liquid was injected again, the liquid flow volume of the low-permeability pipe increased. On the contrary, in the presence of frozen gel, the liquid flow volume of the high-permeability pipe decreased. The smaller the permeability ratio, the better the frozen gel system could improve the heterogeneity of the formation. When the range was 4, the heterogeneity was effectively improved.

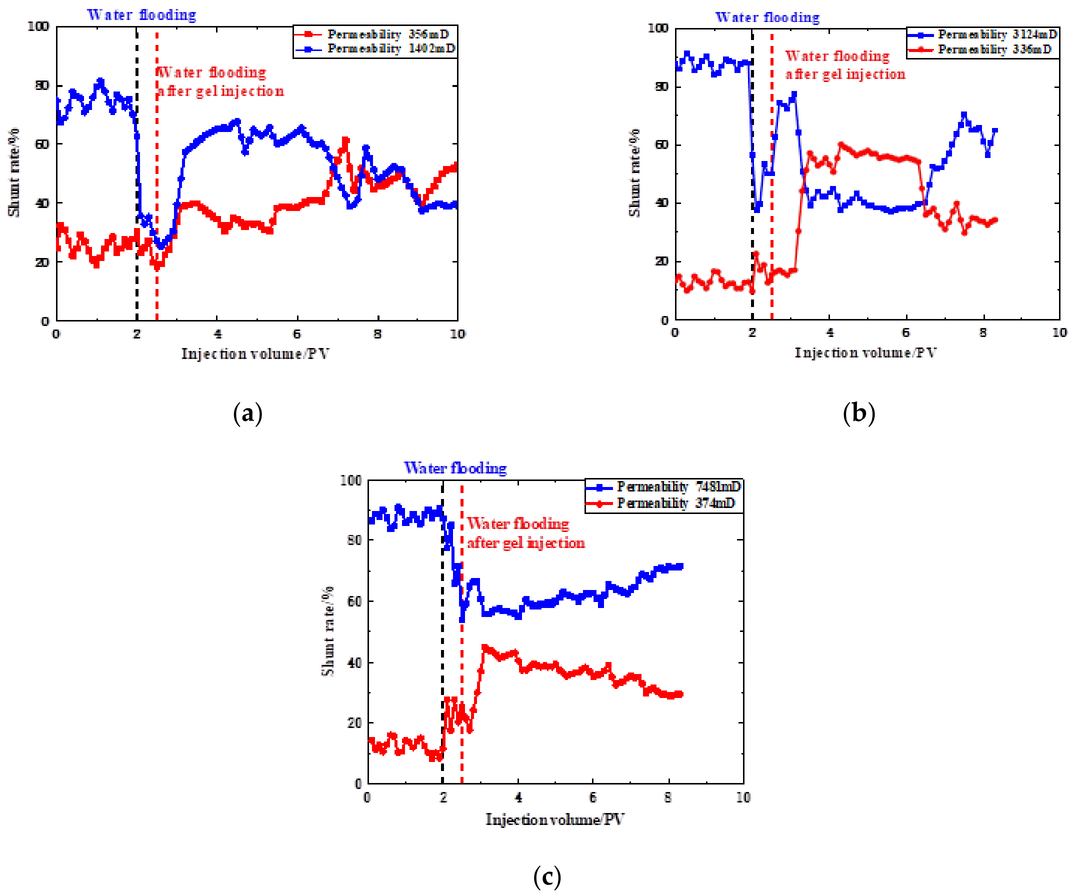



**Figure 11.** (**a**). Shunt rate of high- and low-permeability pipes with an extreme difference of 4. (**b**). Shunt rate of high- and low-permeability pipes with an extreme difference of 8. (**c**) Shunt rate of high- and low-permeability pipes with an extreme difference of 20.

### *3.4. Plugging and Dredging Integration (also Known as the Selective Plugging Experiment of Water Plugging but Not Gas Plugging)*

When the frozen gel system was used to block the water in a gas field, the frozen gel liquid was injected directly into the formation. The frozen gel had a strong plugging effect on the water phase and a strong effect on the gas phase. However, due to the high fluidity of the gas, the plug formed by the frozen gel system could be broken through to ensure that the gas production was only slightly or not affected. Therefore, in this experiment, the gas–liquid two-phase selective plugging of the AM-AMPS frozen gel system was investigated through water injection and gas injection, so as to ensure that the system could produce gas phase channels while plugging water, and realize the integration of gas–liquid plugging and dredging.

Simultaneous injection of gas and frozen gel-forming liquid was carried out. In this experiment, 2 mL/min, 4 mL/min, 10 mL/min and 20 mL/min flow rates were used to reverse inject $CH_4$. From the experimental results, as shown in Figures 12 and 13, it can be seen that when the displacement pressure increased rapidly to the peak, the frozen gel structure was destroyed, and the pressure began to decrease when the injection volume continued to increase. When the injection rate was 2 mL/min, 4 mL/min, 10 mL/min and 20 mL/min, the maximum water displacement pressure of the system was 3.94 MPa, 3.01 MPa, 2.83 MPa and 1.29 MPa, and the maximum gas displacement pressure was 2.58 MPa, 2.06 MPa, 1.68 MPa and 0.65 MPa, respectively, indicating that the blocking effect of the frozen gel on the water phase was better than that on the gas phase. However, when the injection rate increased, the plugging effect became worse, which manifested as a gradual decrease in the displacement pressure, indicating that this method had little effect on gas production. When the gas injection rate was 20 mL/min, the displacement pressure of water flooding and gas flooding was very small. This is because when the gas injection rate was too high, the frozen gel network structure was destroyed as a whole, and the water plugging effect was greatly reduced. Therefore, the system is not suitable for operations at a high flow rate. When the gas injection rate was 10 mL/min, the water flooding pressure was relatively high, while the gas flooding pressure was low, indicating that 10 mL/min is the optimal gas injection rate which can reduce the impact on gas flow capacity while blocking water.

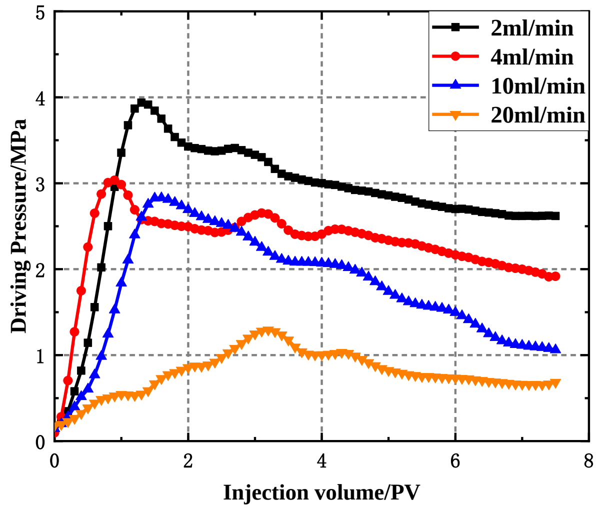



**Figure 12.** Relationship between the gas injection rate and injection amount during water injection.

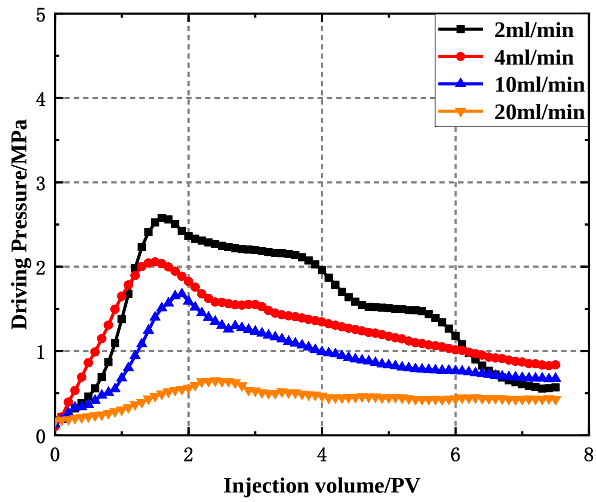



**Figure 13.** Relationship between the gas injection rate and injection amount during gas injection.

We also injected the glue first and then the gas. Under the constant conditions of the experiments described above, the amount of reverse injected $CH_4$ was changed from 2 PV to 4 PV, 6 PV and 8 PV to explore the selective plugging effect of the water–gas dual phase with different amounts of injected gas after the injection of glue first. Figures 14 and 15 show the relationship between the gas injection amount and the water injection amount during water injection, and the relationship between the gas injection speed and the water injection amount during gas injection, respectively. The experimental results show that when the gas injection volume was 2 PV, 4 PV, 6 PV and 8 PV $CH_4$, the maximum water flooding displacement pressure of the system was 3.63 MPa, 3.06 MPa, 2.86 MPa and 1.48 MPa, respectively, and the maximum gas flooding displacement pressure was 2.05 MPa, 1.67 MPa, 0.97 MPa and 0.53 MPa. When the gas injection volume was 8 PV, the displacement pressure of water flooding and gas flooding was small, and the effect of water plugging and gas drainage was poor. When the gas injection volume was 6 PV, the water flooding pressure was relatively high, while the gas flooding pressure was low, indicating that the gas injection equivalent of 6 PV is the optimal gas injection volume, which is suitable for field plugging operations.

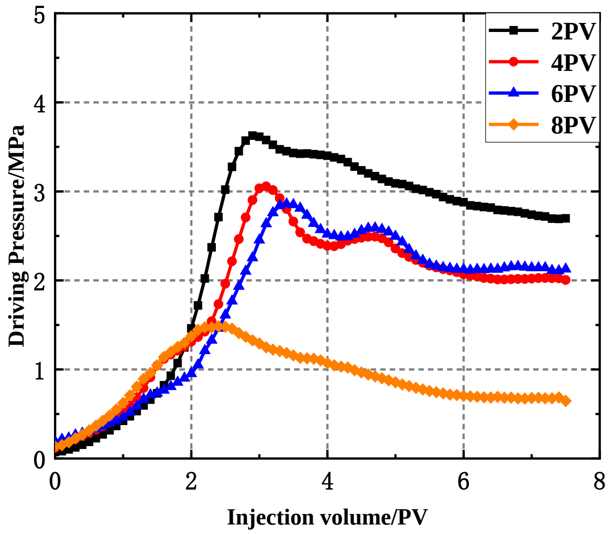



**Figure 14.** Relationship between the gas injection rate and the water injection rate during water injection.

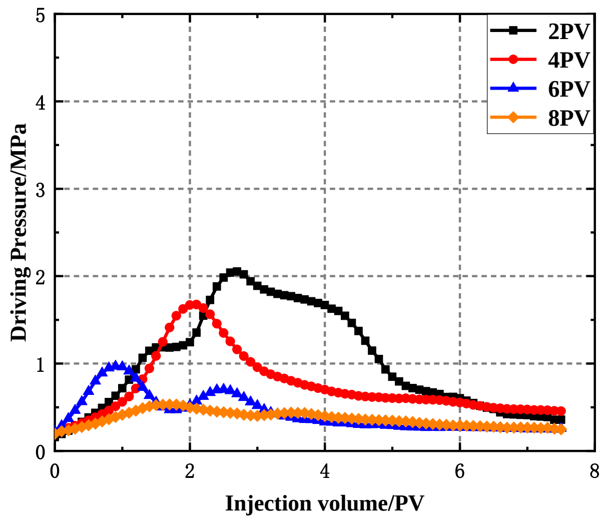



**Figure 15.** Relationship between the gas injection volume and the water injection volume during gas injection.

The gas medium test experiment applied the two different injection methods used in the test of the plugging effect, without changing the other conditions for the $CH_4$, to determine the plugging effect of $CO_2$ gas. Figure 16 shows the experimental results of the injecting gas media at a rate of 10 mL/min in the opposite direction when the gas and liquid were injected together. The results show that the maximum water flooding pressure of $CH_4$ and $CO_2$ was 2.83 MPa and 3.05 MPa, respectively, and the maximum gas flooding pressure was 1.68 MPa and 1.71 MPa, respectively. Figure 17 presents the experimental results of reverse injection of the gas media at 6 PV when the gelled liquid was injected first and then the gas was injected. The results show that the maximum water displacement pressure of water flooding for $CH_4$ and $CO_2$ gas was 2.86 MPa and 2.79 MPa, respectively, and the maximum water displacement pressure of gas flooding was 0.97 MPa and 0.93 MPa, respectively. It can be seen from the experimental results that there was no significant change in the displacement pressure, indicating that the gas medium hardly affected the plugging performance of the frozen gel.

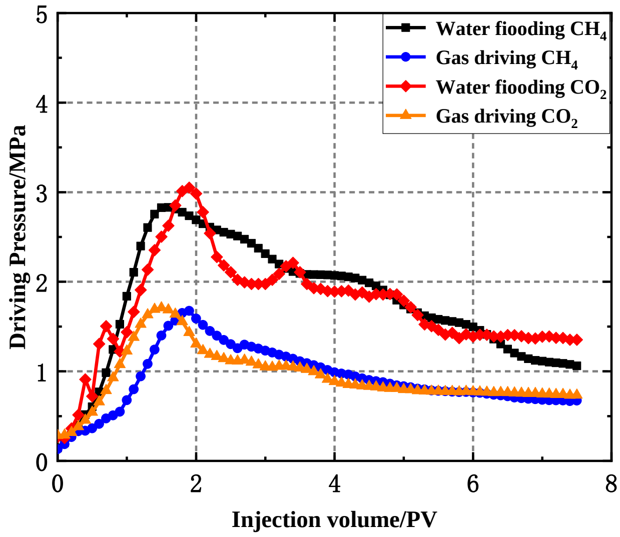



**Figure 16.** Test results of plugging with different gases under gas–liquid co-injection.

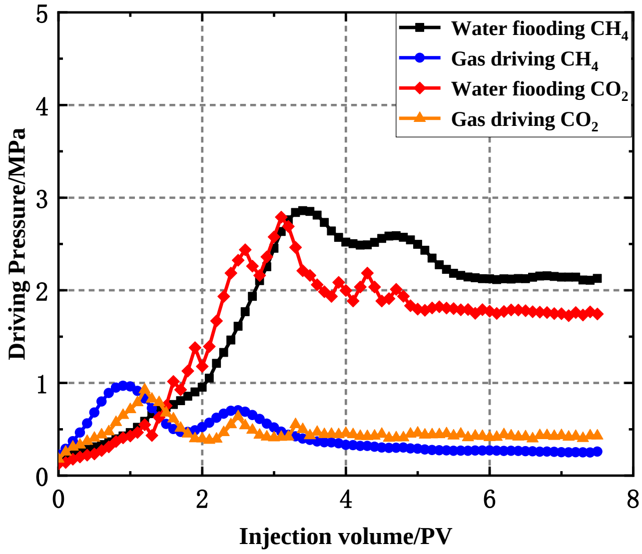



**Figure 17.** Experimental results of plugging with different gases when injecting glue first and then the gas.

## 4. Conclusions and Recommendations

In this study, a plugging agent system suitable for plugging water in gas wells under conditions of high temperature and high salinity was developed from the existing polymers, crosslinking agents and deoxidant materials. The physical experimental models of a sand filling pipe and parallel pipes were used to evaluate the water plugging and gas drainage ability of the prepared plugging agent system, and the optimal conditions for the application of the plugging agent system were selected, which can provide guidance for the application of the plugging agent system in gas fields. The main conclusions and suggestions are given below.

1. Through the investigation of the effects of the polymer mass fraction, the crosslinking agent mass fraction, the deoxidant mass fraction and the temperature on the stability of the frozen gel system, the best experimental scheme of AM-AMPS was selected: 1.0% AM-AMPS +0.6% p-benzenediol +0.6% hexamethylenetetramine +0.2% deoxidant thiourea at 107 °C. Under the experimental conditions, the gelling time of the frozen gel system was 12 h, the 180 d dehydration rate was 2.6% and the stability was relatively good.
2. In the water phase plugging experiment, the optimal injection volume of the frozen gel system was 0.5 PV, and the water plugging effect reached more than 90% when the permeability was between 356 and 3118 mD. The plugging performance tests at formation heterogeneity ranges of 4, 8 and 20 showed that the system could improve the heterogeneity of formation. When the degree of heterogeneity is low, the improvement effect was the best; that is, when the range was 4, the frozen gel system could effectively improve the degree of heterogeneity formation. Therefore, in the field, a stratum with low heterogeneity should be selected for using the frozen gel system.
3. According to the experimental results of gas–liquid two-phase plugging by simultaneous injection of gas and the frozen gel solution, when the injection rate was 2 mL/min, 4 mL/min, 10 mL/min and 20 mL/min $CH_4$, the maximum water displacement pressure of the system was 3.94 MPa, 3.01 MPa, 2.83 MPa and 1.29 MPa, respectively, and the maximum gas displacement pressure was 2.58 MPa, 2.06 MPa, 1.68 MPa and 0.65 MPa, respectively. The optimal gas injection rate was 10 mL/min. When the injection rate was 20 mL/min, the frozen gel structure was destroyed and the displacement pressure was very small, so it is not recommended to use the frozen gel system at high speeds.
4. According to the experimental results of gas–liquid two-phase plugging by injecting the glue before the gas, the maximum water flooding displacement pressure of the system was 3.63 MPa, 3.06 MPa, 2.86 MPa and 1.48 MPa when the gas injection volume was 2 PV, 4 PV, 6 PV and 8 PV $CH_4$, respectively, and the maximum gas flooding displacement pressure was 2.05 MPa, 1.67 MPa, 0.97 MPa and 0.53 MPa. The optimal gas injection volume is 6 PV of gas, and the effect on water plugging and gas drainage was better. When the gas injection volume was 8 PV, the sealing ability of the system could not be seen.
5. When gas–liquid co-injection was used, the maximum pressure of water flooding for $CH_4$ and $CO_2$ was 2.83 MPa and 3.05 MPa, respectively, and the maximum pressure of gas flooding was 1.68 MPa and 1.71 MPa, respectively. When the gelling fluid was injected first and then the gas was injected, the maximum water flooding pressure of $CH_4$ and $CO_2$ gas was 2.86 MPa and 2.79 MPa, respectively, and the maximum pressure of gas flooding was 0.97 MPa and 0.93 MPa, respectively, indicating that no matter which injection method is used, the gas medium will not affect the gel's plugging performance.

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