Research on adsorption and damage characteristics of slick water in coalbed methane development

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Abstract. In the process of coalbed fracturing, the drag reducers absorbed on the surface of the coalbed causes water lock damage and decreases gas production efficiency of coalbed methane. Thus, research on low-damage coalbed drag reducers is of great significance. Aiming at four drag reducers with different molecular weights, the law of drag reducers adsorption was investigated through static adsorption test and contact angle tests. Afterwards, a core displacement experiment was carried out to study the damage rate of slick water to the coalbed, and the nanoemulsion CND was used for competitive adsorption to relieve the influence of fracturing fluid adsorption on the core damage. Finally, through the static adsorption test results, combined with core SEM images before and after displacement, the internal relationship between adsorption and damage was revealed, and the optimal principles and control methods for reducing the damage of drag reducers to the coalbed were proposed. The results show that: the drag reducers with larger molecular weight are more likely to adsorb in the coalbed, which caused more severe damage to the coalbed reservoir. In contrast, drag reducers with lower molecular weight show a lower damage rate (less than 20%) to the reservoir, which is suitable for the preparation of low-damage slick water. Mechanistic studies have shown that the drag reducers is adsorbed on the surface of the organic matter in the coalbed, leading to the exposure of the hydrophilic end. Therefore, the hydrophilic area on the surface of the coal powder was enlarged, which forms the water film adhesion in the pore throat, causing the water lock to block the gas and liquid seepage channel, resulting in reduced permeability; Nanoemulsion and coal powder are more closely adsorbed, which can reduce the adsorption of drag reducers through competition with the adsorption matrix, reduce water lock damage, facilitating the subsequent drainage and gas collection process.

1. Introduction

As an efficient and green energy source, Coalbed methane has abundant geological reserves in China. Coalbed methane reservoirs generally have the characteristics of complex geological structure, strong
adsorption capacity, high organic matter content and ultra-low permeability, etc. Reflecting the great heterogeneity and anisotropy, it is often more susceptible to suffer irreversible damage during the hydraulic fracturing process [1-4]. The slick water fracturing fluid has been used on a large scale in shale gas development due to its good drag reduction effect and low formation damage [5], but in the development and application of coalbed methane, the practical development effect is far lower than the expected output. Currently, there are few reports on the adsorption and damage characteristics of slick water on coalbed.

The damage of fracturing fluid to coal reservoirs is mainly concentrated in the reduction of permeability caused by the adsorption and retention of fracturing fluid itself in the coal bed matrix, thereby affecting the permeability of gas and liquid [6,7]. Cong et al. applied GC/MS technology to evaluate the adsorption capacity of coal-adsorbed guar gum fracturing fluid. The results showed that coal has stronger adsorption of organic matter, but this test can only detect a small part of the organic components when it comes to the complex composition. It is difficult to completely analyze the adsorption mechanism of fracturing fluid [8]. Therefore, targeted reservoir damage analysis will help optimize coalbed methane fracturing operations and improve economic benefits. In this paper, the coal sample was taken from Linfen 5# coal, and four commercial drag reducers were used to configure fracturing fluid respectively. Through static adsorption experiment, contact angle test, spontaneous imbibition experiment and core damage experiment, the damage mechanism of slick water to the coalbed was studied. Besides, the feasibility of using nanoemulsion CND to relieve coalbed damage was also unraveled. Finally, the core SEM images before and after the flooding were combined to further verify the pulverized coal adsorption and CND's ability to reduce drag reducers adsorption, the static adsorption test results are used to uncover the internal relationship between adsorption and damage. At the same time, control measures were also proposed to reduce the damage of slick water to coalbed methane.

2. Experimental

2.1. Materials

The four drag reducers were purchased from Beijing Kemaishi Oil & Gas Technology Co., Ltd. The indexes of the drag reducers are shown in Table 1.

| Drag reducers model | Appearance | Ion species | Slick water configuration concentration / % | Molecular weight |
|---------------------|------------|-------------|---------------------------------------------|------------------|
| RY246               | Yellow emulsion | Anion     | 0.1                                        | 6-8 million      |
| NT06                | Yellow emulsion | Anion     | 0.1                                        | 10-12 million    |
| RY70                | White emulsion  | Anion     | 0.1                                        | 12-15 million    |
| 5330W               | White emulsion  | Anion     | 0.1                                        | 16-18 million    |

The stock solution of nanoemulsion CND consists of about 10 wt% alkanes and/or alkenes as the oil core of the micelles, 30 - 50 wt% non-ionic surfactants (such as ethanol ethoxylates) to stabilize the micelles, and 20 - 40 wt% alcohol is used as a co-solvent.

2.2. Static adsorption experiments

Configure 0.1% fracturing fluids with different concentrations under room temperature and measure the optimal wavelength with UV-vis spectrophotometry, then the concentration-absorbance standard curve was obtained, and draw a linear regression equation for the curve. Put the sieved coal particles into a Soxhlet extractor to wash oil and salt, and dry them in an oven at 65 °C for 24 h until the weight is constant, so that the coal powder and fracturing fluid are mixed in a ratio of 1:15. After stirring evenly, keep them undisturbed for 0-480 min, and detect in sections. Pour the fully adsorbed coal
powder and fracturing fluid mixture into a centrifuge tube, measure the spectrophotometry sequentially, analyze the changes in the concentration before and after adsorption in each solution according to the concentration-absorbance standard curve, and calculate the adsorption capacity based on the discrepancy of the concentration.

The static adsorption capacity is calculated according to the following formula:

\[ \Gamma_i = \frac{(C_0 - C_i)V}{m} \]

Where \( \Gamma_i \) is surface active agent apparent adsorption capacity, \( C_0 \) is the mass concentration of surfactant in the solution before adsorption, \( C_i \) is the mass concentration of surfactant in the solution after adsorption, \( V \) is liquid volume in the adsorption system, \( m \) is the quality of the rock sample.

2.3. Contact angle test
Use a JY-PHB contact angle tester to measure the contact angle of coal rock before the drag reducer is adsorbed. Then, the contact angle of coal rock after soaking in 4 different kinds of slick water will be measured. Finally, the contact angle of coal rock, CND, and slick water is measured after being soaked together.

2.4. Spontaneous imbibition test
The ring method and the weighing method are used to measure the self-absorption amount of the core after being damaged by the slick water (RY246), and the CND reduces the absorption of the drag reducers. First, the core was placed into the treatment solution and saturated under vacuum for 24 h. After the entire saturation, use a core displacement device to continue to saturate the core for 2~4 PV, and then age it at 80 °C for 12 h; then dry the core, and re-adopt the ring method and weighing method. Measure the self-priming of the core over time. Compare the slick water (RY246) damage and the core self-absorption volume before and after CND treatment to judge the wettability change.

2.5. Core damage test
The size of the coal core is 2.5*2 cm, the confining pressure applied in the experiment is 2-3 MPa, after checking the pipeline connection, carry out constant flow displacement at a flow rate of 0.3 mL/min. The core damage experiment includes: (1) Forward displacement of formation water (2% KCl solution), and record the stable permeability; (2) Reverse displacement of slick water simulates the damage process, then forward displacement of formation water, and record the permeability after the pressure difference stabilizes; (3) The reverse displacement CND simulates the process of reducing the adsorption of drag reducers, and then forward displacement of formation water, and the permeability is recorded after the pressure difference is stabilized.

Among them, 2% KCl solution with mass fraction is selected to simulate the formation water, which can restrain the influence of water absorption and expansion of clay minerals in pulverized coal on the experimental results [9, 10]. Taking core matrix permeability as an evaluation index, the calculation formula of damage rate is as follows:

\[ \beta_d = \left(\frac{k_a - k_b}{k_a}\right) \times 100\% \]

Where \( \beta_d \) is damage rate of core matrix permeability, \( k_a \) is core permeability, \( k_b \) is core permeability after injury.

Taking the core matrix permeability as an evaluation index, the calculation formula for reducing the matrix permeability recovery rate after adsorption is as follows:

\[ \beta_e = \left(\frac{k_c - k_b}{k_a - k_b}\right) \times 100\% \]

Where \( \beta_e \) is matrix permeability recovery rate after core reduction adsorption, \( k_a \) is core permeability, \( k_b \) is core permeability after injury, \( k_c \) is core permeability after CND treatment.
2.6. Microscopic SEM structure observation of core
The morphology changes of coal rock before and after being damaged by drag reducer and after CND treatment were investigated by scanning electron microscope (SEM: FEI Quanta 200F, Thermo Fisher Scientific U.S.A.).

3. Results and Discussion

3.1. Static adsorption results
The time-adsorption curve of different drag reducers on the surface of coal powder is shown in Figure 1, and the time-adsorption curve of different drag reducers on the surface of coal powder after CND treatment is shown in Figure 2.

**Figure 1.** Adsorption curves of different drag reducers on the surface of pulverized coal.

**Figure 2.** Adsorption curves of different drag reducers on the surface of coal powder after CND treatment.

The experimental results show that with the increase of time, the adsorption capacity of pulverized coal continues to increase and stabilizes within 60 min. Among them, the adsorption capacity of 5330 W, RY70, NT06, and RY246 decreased with the decrease of molecular weight, and the adsorption values at equilibrium were about 14.9, 14.5, 13.8, and 12.6 mg·g\(^{-1}\). It shows that the main body of coalbed adsorption is controlled by molecular size. The larger the molecular weight, the stronger the van der Waals force and hydrogen bond between slick water and coal, and the greater the adsorption capacity. Therefore, the slick water used for coalbed fracturing should use low molecular weight drag reducers as far as possible without affecting the drag reduction effect of fracturing. After the CND treatment, the adsorption capacity of the four drag reducers were about 7.7, 7.9, 7.3, 6.8 mg·g\(^{-1}\),
respectively, which were reduced by 48.3%, 45.5%, 47.1%, and 46%, which proved that the CND has a good function of reducing the adsorption of drag reducers. Based on the fact that the reduction ratio of adsorption is basically the same, it can be inferred that the reduction of adsorption is caused by the changes in the surface properties of the coalbed, rather than the effect of nanoemulsion and drag reducers molecules. Therefore, it is concluded that nanoemulsion can modify the surface properties of coal powder. Subsequent experiments will be designated to test the modification of the surface properties of coalbed by nanoemulsion through contact angle and other experiments.

3.2. Contact angle test

![Figure 3](image)

**Figure 3.** Contact angle test before and after adsorption and after CND treatment.

According to the result of contact angle (Figure 3), after the coal samples were immersed in the fracturing fluids in the four fracturing fluids, the contact angles became smaller to varying degrees, indicating that the original coal rock contains more organic matter and exhibits neutral wetting characteristics. After coal rock interacts with the slick water drag reducers, a large number of hydrophilic polymers are adsorbed on the surface of the coalbed, which leads to an increase in the hydrophilicity of the coal rock. The contact angle of the pulverized coal after CND treatment becomes larger, implying that the hydrophilic substance adsorbed on the pulverized coal decreases and the hydrophilicity decreases. This is because the nanoemulsion has an oil phase core, which absorbs more lipophilic organic matter on the surface of coal powder and replaces the polymer adsorption, which is consistent with the research conclusions drawn from the adsorption experiment (vide supra).

3.3. Spontaneous imbibition test results

![Figure 4](image)

**Figure 4.** The relationship between the cumulative amount of self-absorbed salt water in the core over time.

Figure 4 shows the relationship between the cumulative amount of self-absorbed brine in the core over time. The air-saturated dry core is displaced by liquid spontaneous imbibition to study the gas wetting
performance of the core samples treated with CND. When the core is wetted by the liquid phase, the capillary force is the main driving force of the liquid phase imbibition, and the spontaneous water imbibition in the core gradually increases with time; When the core is wetted by the gas phase, the capillary force is the resistance of the liquid phase imbibition, and the spontaneous water imbibition in the core is significantly reduced. Measure the relationship between the immersion liquid (salt water) into the saturated air core and the amount of liquid absorption with time to determine the change in core wettability. After the fracturing fluid core, the cumulative imbibition increased from about 3 g to about 4.5 g, which proves that the enhanced water wettability of the core is easy to adsorb water and produce water lock. After CND treatment, the core water wettability decreases, which can prove that CND can be competitively adsorbed on the surface of pulverized coal, reducing the hydrophilicity of pulverized coal and releasing part of the water lock.

3.4. Core damage results
The results of the core matrix damage rate after core flooding and the matrix permeability recovery rate after core reduction adsorption are shown in Table 2, and the dynamic verification of slick water (RY246) core adsorption damage is shown in Figure 5.

| Drag reducers model | Injury rate /% | Permeability recovery rate /% |
|---------------------|---------------|-----------------------------|
| 5330W               | 71.64         | 44.6                        |
| RY70                | 67.35         | 45.5                        |
| NT06                | 63.47         | 45.9                        |
| RY246               | 16.67         | 48.5                        |

Figure 5. Dynamic verification of RY246 core adsorption damage.

After the coalbed gas pressure fracturing operation, the fracturing fluid loss zone is the percolation channel through which the gas and liquid must pass. The fracturing fluid filtrate which enters the pore medium of the formation physically and chemically reacts with the reservoir fluid and clay minerals, resulting in the damage on the permeability of the reservoir [11]. Combined with the results of the damage experiment, the high molecular weight drag reducers 5330W, RY70 and NT06 have higher damage rates, followed by 71.64%, 67.35%, and 63.47%. The lowest molecular weight RY246 exhibited the lowest damage rate of 16.67%. After displacing the CND to reduce the absorption of the drag reducer on the core, the core permeability gradually increased. From the results, it can be found that the core permeability recovery rate corresponding to different molecular weight drag reducers is not apparent, and the core permeability recovery rate corresponding to the low molecular weight drag reducers are the largest among the 4 drag reducers, reaching 48.5%. In Figure 5, the dynamic verification of RY246 core adsorption damage visually shows the change of core permeability. When the permeability of the displacement formation water is stable, the permeability of the formation water
after the slick water is displaced will further decline, and the displacement will be stabilized again. After the CND is displaced, the permeability of the formation water can be recovered.

3.5. **SEM results**

![SEM images](image)

**Figure 6.** SEM images A. Before coal rock damage B. After coal rock damage C. After CND treatment.

As shown in Figure 6, the morphological images of the coal powder before and after the damage of RY246 and after reducing the adsorption are compared. It can be found that the surface of the pulverized coal before the damage is uneven, and there are more granular coal particles of uneven size. The distribution of the pulverized coal is relatively loose. As the damage rate increases, the surface tends to be flat, and the surface particles gradually decrease. The denser distribution indicates that the pulverized coal has adsorbed the slick water drag reducers, and the retained polymer blocks most of the gas-liquid seepage channels, resulting in a decrease in permeability.

3.6. **Slick water adsorption & core damage mechanism analysis**

In view of the fact that the coalbed is composed of a network of macromolecules with excellent connectivity and other macromolecular channels that are not connected to each other, its high specific surface and abundant cleats are developed, which determines that the coalbed has stronger adsorption than sandstone reservoirs, and at the same time, The surface of coalbed is enriched with a large amount of organic matter, which can adsorb a large amount of high molecular polymer [12-14]. By comparing the relationship between the molecular weight of the drag reducers and the amount of adsorption, it can be found that the adsorption value of the coal powder is positively correlated with the molecular weight of the drag reducers. There are physical adsorption and chemical adsorption in adsorption. When the polymer is physically adsorbed on the coal surface (Figure 7), the specific manifestation is that the larger the molecular weight, the easier the adsorption will occur until the dynamic equilibrium of adsorption and desorption is reached.

![Diagram](image)

**Figure 7.** Schematic diagram of the water film of the original coalbed, the adsorption of polymer molecules, and the water film attached to the surface of polymer molecules.
Through the results of the adsorption test and the damage test of the drag reducers, it can be clearly seen that the molecular weight of the drag reducers is positively correlated with the adsorption capacity, and the adsorption capacity is positively correlated with the damage rate, and combined with the recovery of the permeability after the adsorption is reduced, it can be inferred that the drag reducers adsorption is the key factor affecting injury is a reversible process. Considering the molecular polarity relationship, water molecules are easy to adsorb on hydrophilic mineral sites, and drag reducers polymers are organic substances, which are easier to adsorb on the surface of coal organic matter. When the drag reducers are adsorbed, the hydrophobic part is adsorbed on the surface of the organic matter of the coalbed, and the hydrophilic part is exposed outward, which makes the hydrophilic range of the coal surface significantly expand, and the water film on the surface of the crack is significantly expanded [15]. As shown in Figure 6, the hydrophobic group of the drag reducers polymer is combined with the lipophilic organic matter on the surface of the coal, and the water molecule is combined with the hydrophilic group of the drag reducers polymer to expand the hydrophilic range of the surface of the coal powder. Intermolecular interactions such as van der Waals forces are directly proportional to the molecular size. Compared with low molecular weight polymers, high molecular weight polymers adsorb more firmly on the surface of coal powder, and the adsorption water film range is expanded. The influence of the water film on the pore throat is more serious for subsequent drainage and gas production, resulting in a decrease in gas production. Therefore, the high-molecular-weight drag reducers adsorbs more on the surface of the coal powder, which causes the gas-liquid seepage pore and throat channel to be blocked, forming a water film, and leading to the occurrence of water lock. The specific manifestation is that the pressure difference between the front and back increases, the permeability decreases, and the damage increases.

4. Conclusion
1. For four anionic drag reducers with different molecular weights, static adsorption test, contact angle test, spontaneous imbibition test, and core damage test show that the adsorption capacity of 5330 W, RY70, NT06, and RY246 decreased with the decrease of molecular weight, and the adsorption values at equilibrium were about 14.9, 14.5, 13.8, and 12.6 mg·g\(^{-1}\). After the treatment of nanoemulsion on coal powder, the adsorption damage of drag reducers molecules can be significantly reduced. The permeability recovery rate of 5330W, RY70, NT06 and RY246 increased with the decrease of molecular weight, and the permeability recovery rate were about 44.6%, 45.5%, 45.9% and 48.5%. RY246 is the best drag reducers among the selected samples, making it suitable for coalbed methane development.

2. The larger the molecular weight of the drag reducers is, the greater the adsorption capacity of the polymer in the coal powder, as well as the higher damage rate to the coalbed. The polymer forms adhesion in the coalbed, causing the pore throat to shrink, and further there may be a water film to block gas-liquid seepage. The channel forms a water lock, and the ground shows that the working pressure increases and the reservoir permeability decreases.

3. Drag reducers adsorption is the main cause of coalbed damage. Therefore, when selecting a slick water fracturing fluid suitable for coalbed, the molecular weight of the drag reducers should be as low as possible while meeting the basic requirement to reduce the amount of drag reducers adsorption. Meanwhile, adding nanoemulsion properly with stronger adsorption performance to induce competitive adsorption to remove the influence of water lock, thereby increasing the gas permeability and increasing the output.

Acknowledgments
This work was financially supported by National Natural Science Foundation of China (Grant No. 52004306), the Strategic Cooperation Technology Projects of CNPC and CUPB (Grant No. ZLZX2020-01 and ZLZX2020-02), the National Science and Technology Major Projects of China
(Grant No. 2016ZX05030005, 2016ZX05051003) and National Natural Science Foundation of China (No. 52174045).

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