Research on Laboratory Experiment of Acidification and Blockage Removal of Coalbed Methane Gas Well in Block M

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Abstract. The coal reservoir in Block M is the low-permeability coal reservoir, in the process of coalbed gas production, since different degrees of blockage occurs in the fracture and pore of the coal reservoir; as a result, the production of coalbed methane is low or shut down. In this paper, the coal rock reservoir in Block M as the research object, and the acidification and blockage removal acid system was selected, and the acidification and blockage removal effect of the optimal acid liquid was evaluated. The coal core soaking experiment was carried out to test the permeability and porosity of the coal core before and after acidification, the experiment showed that the permeability of the coal core was increased to 1.9 to 15.3 times, and the porosity was increased by 0.25% to 3.56%.

Keywords: acidification, coalbed methane, pore permeability.

1. Introduction
Block M is situated in the northwest of China and has abundant gas resources, but propped fracture is prone to blockage in the production process, which affects the mining effect of coalbed methane.

Acidification is a conventional method to stabilize and increase the output of oil wells and gas wells, it can dissolve the blockage in the rock via acidic solutions, repair and improve the permeability of pore and fracture, so as to stabilize and increase output of gas wells [1]. Therefore, the design of scientific acidification technology has certain practical significance for the development of coalbed methane.

2. The Selection of Acid Formula
For blockage in pore and fracture, hydrochloric acid can be used to remove blockage such as carbonate, hydrofluoric acid can be used to remove siliceous blockage, and organic acid can expand the acidification range; oxidizer can oxidize and dissolve organic matter in coal and rock, release inorganic scale that can be removed by the corresponding acid.

2.1. Experimental analysis of single-component acid solution corrosion
The hydrochloric acid solution, hydrofluoric acid solution, acetic acid solution and hydrogen peroxide solution with different mass fractions are prepared for spare. At room temperature, the acid solution is mixed with coal powder in Block M in a certain proportion, and the mixed solution acts for 1h, 6h and 12h, respectively. After the reaction time is reached, the pulverized coal is filtered and dried; the weight
of the pulverized coal after acid etching is recorded and the corrosion rate of the pulverized coal in acid with different concentrations are calculated.

1) Single-component acid coal dissolution

![Fig. 1](image1.png)

**Fig. 1** Corrosion rate of pulverized coal in Block M under different concentrations of HCl

According to the experimental results, when the HCl concentration is constant, the corrosion rate gradually increases with time, in the same reaction time, the greater the reaction concentration, the higher the corrosion rate.

![Fig. 2](image2.png)

**Fig. 2** Corrosion rate of pulverized coal in Block M under different concentrations of HF

For the hydrofluoric acid solution, the reaction is slower in the first 6h, and the corrosion rate reaction accelerates in 6-12h high concentration, in the same reaction time, the greater the reaction concentration, the greater the corrosion rate.
Fig. 3 Corrosion rate of pulverized coal in Block M under different concentrations of CH₃COOH

It can be seen from the figure that when the concentration of CH₃COOH remains unchanged, as the reaction time increases, the corrosion rate of coal samples gradually increases; the corrosion rate is between 1% and 4%, and the corrosion effect is not obvious.

(2) Corrosion of pulverized coal with different concentrations of H₂O₂

Fig. 4 Corrosion rate of pulverized coal in Block M under different concentrations of H₂O₂

It can be seen from the figure that when the concentration of H₂O₂ is constant, as the reaction time increases, the corrosion rate increases gently, and the corrosion rate is between 2% and 4%, and the corrosion effect is not obvious.

2.2. Experimental analysis of multi-component acid corrosion
According to the reaction characteristics between coal powder in Block M and the single acid solution, moreover, combining factors such as the difference in mineral composition and contents in the coal sample of Block M, the total acid solution with 12% concentration is prepared; it is composed of different proportions of HCl, HF and CH₃COOH, the concentration of H₂O₂ in the oxidizing solution is 3%.
Table 1. Proportion of acid solution with mixed components

| Concentration(%) | A | B | C | D | E | F |
|------------------|---|---|---|---|---|---|
| HCl              | 8 | 8 | 8 | 6 | 6 | 4 |
| HF               | 2 | 4 | 0 | 3 | 4 | 4 |
| CH₃COOH          | 2 | 0 | 4 | 3 | 2 | 4 |
| H₂O₂             | 3 | 3 | 3 | 3 | 3 | 3 |

Corrosion of pulverized coal with different concentrations of mixed acid:

![Fig. 5 Corrosion rate of pulverized coal in Block M in different types of mixed acid liquor](image)

It can be seen from the above figure that the reaction is faster in the first 6 hours and the corrosion rate changes quickly, and the corrosion rate changes slowly after 6 hours; the corrosion effect: A>D>E>C>B>F. According to the corrosion effects of different formulas of acid solution and the actual situation on site, etc., the selection result of acid solution formulas is: 8%HCl + 2%CH₃COOH + 2%HF + 3%H₂O₂.

2.3. Selection of coal rock acid liquid system additives

Some additives need to be added in the coalbed methane acidification operation. The types of additives commonly used in the acidification of coal reservoirs have clay stabilizers, iron ion stabilizers and so on. Clay stabilizers can prevent water-sensitive damage and block seepage channels [2]. The iron ion stabilizer can prevent the precipitation reaction of metal ions and the substances in the acid solution.

2.3.1. Selection of clay stabilizers. The clay minerals in the coal samples of Block M are mainly smectites, kaolinites and other substances; these substances are prone to water-sensitive effects after contact with water and block the seepage channel [3]. In order to prevent the occurrence of water-sensitive reactions, clay stabilizers should be selected when conducting acidification laboratory experiments.

In this experiment, KCl, polyquaternary amine aqueous solution, and NH₄Cl three clay stabilizers are selected, by calculating the expansion ratio of the coal block after the three stabilizers act on it, then analyze its stabilizing effect.
Fig. 6 Expansion ratio of pulverized coal in different types of clay stabilizers

Since K⁺ in KCl will have precipitation reaction with residual acid, and Cl⁻ will reduce the corrosion ratio of acid solution, KCl is not used as clay stabilizer, furthermore, due to environmental and economic reasons, and 0.5% polyquaternary amine solution is selected as clay stabilizer.

2.3.2. Selection of iron ion stabilizers. During the production increase operation of coal reservoir acidification, metal reaction of part of acid liquid and coalbed fluid produce precipitation to block the pore and fracture channels of the reservoir.

Therefore, the selection of iron ion stabilizers is of great significance to the development of coalbed methane acidification.

The titration method was used to evaluate the aqueous solutions of three iron ion stabilizers EDTA, NTA, and ammonium citrate by measuring the iron ion stabilization ability.

Calculation method of iron ion stabilizer stabilization capacity:

Experimental methods of iron ion stabilizers evaluation:

The titration method is used to evaluate the aqueous solutions of three iron ion stabilizers EDTA, NTA, and ammonium citrate by measuring the iron ion stabilization capacity.

Calculation method of stabilization capacity of iron ion stabilizers:

\[ N = \frac{aV_1}{bV_2} \]

Fig. 7 The capacity of iron ion stabilizers to stabilize iron ions
Experiments show that 0.5% NTA iron ion stabilizer has the strongest capacity to stabilize iron ions; therefore, NTA with 0.5% concentration should be selected as the iron ion stabilizer in the acidification operation of coalbed methane wells.

The above experimental results are integrated; the selection results of the main acid solution of the coal samples in Block M are as follows: 88%HCl+2%CH₃COOH+2%HF+3%H₂O₂. For M block, it is recommended to use 0.5% polyquaternary amine solution as clay stabilizer and 0.5% NTA solution as iron ion stabilizer.

3. Experimental Evaluations of Acidification and Blockage Removal

3.1. Experimental evaluation of coal core permeability before and after acidification

3.1.1. Experimental principle and plan of coal core permeability measurement. The coal core permeability before and after acidification is measured to test the anti-reflection effect of the selected acid on the coal reservoir. The gas permeability of the coal core before and after acidification is tested by gas measurement system of reservoir permeability dynamic damage evaluation system.

According to Darcy-Weisbach Formula:

\[ K = 1000 \times \frac{2P \mu L}{A(P_R^2 - P_s^2)} \]

3.1.2. Analysis of experimental results. The permeability test results of coal core before and after acidification are shown in the figure:

![Permeability of coal core before and after acidification](image)

**Fig. 8** Permeability of coal core before and after acidification

The results show that the permeability of the 4 coal cores is significantly improved after acidification. The increasing multiples of h₀₁-h₀₄ are 8.1 times, 1.9 times, 15.3 times, and 3.7 times, respectively.

3.2. Experimental evaluation of coal core porosity before and after acidification

3.2.1. Measurement plan of coal core porosity. The gas measurement system computer is used to automatically calculate the porosity of the coal core before and after acidification.
3.2.2. Analysis of experimental results.

![Fig. 9 Porosity of coal core before and after acidification](image_url)

The results show that the porosity of the 4 coal cores has been improved after the acidification experiment. The porosity of the 4 coal cores increase by 0.25%, 1.78%, 3.56%, and 1.13%, respectively.

Permeability changes: the permeability of the 4 coal cores in Block M has been significantly improved after the acidification experiment, and their increasing multiples are 8.1 times, 1.9 times, 15.3 times, and 3.7 times. Porosity change: the increase of coal core porosity after acidification experiment is 0.25%, 1.78%, 3.56%, 1.13%. The acidification dissolves the blocked minerals in the coal and increases the connectivity in the pore and fracture of the coal reservoir, since the fracture development condition and mineral content distribution of each coal core are different, the anti-reflection multiples are different.

4. Conclusion

In this paper, the static corrosion experiment of pulverized coal is adopted, according to the corrosion effect of acid liquid and pulverized coal, the optimal main acid formula of coal samples in Block M is obtained: 8%HCl+2%CH₃COOH+2%HF+3%H₂O₂. The selected result of the additive is: 0.5% polyquaternary amine solution is selected as the clay stabilizer, and 0.5% NTA solution is selected as the iron ion stabilizer. It is found by laboratory experiment that the coal core permeability of Block M has been improved after acidification experiment.

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