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Experimental Study of the Impact of Chlorine Dioxide on the Permeability of High-Rank Contaminated Coal Reservoirs

Zhou Zhang,* Pengbo Zhou, Lifang Zhao, Jin Yang, Min Zhou, and Baoan Xian

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ABSTRACT: The permeability of high-rank coal reservoirs is generally low, and high-viscosity working fluid can also contaminate the reservoirs and reduce permeability during drilling and fracturing engineering. These two reasons lead to a lot of low-yield CBM wells in the southern Qinshui Basin, China. The impact of chlorine dioxide on the permeability of high-rank coal has been studied in detail. The coal samples with changed characteristics before and after treatment were compared using coal-ash, displacement, immersion, and plug removal experiments. The ash experiment results show that the ash content of the coal samples decreased by 16.35%. The displacement and immersion experiments using chlorine dioxide solution showed that displacement with chlorine dioxide could increase permeability. The permeability of coal samples increased by 3005.77% after 80 h of immersion. The plug removal experiment



results show that the permeability of contaminated coal samples was recovered by 11.10-38.90%, with an average recovery of 27.90%. The experimental results show that chlorine dioxide is effective in improving the permeability of high-rank contaminated coal reservoirs. This research result can be applied to low-yield CBM wells polluted by high-viscous working fluid to increase gas production.

1. INTRODUCTION

Coalbed methane (CBM) is developed and applied as a clean energy source in many countries globally, including the USA, Canada, Australia, and China.¹⁻³ The primary critical technologies of CBM exploration and development are comprehensive geological evaluation technology, drilling and completion technology, fracturing technology, drainage, and production technology.⁴ These technologies are also applied to the southern Qinshui Basin, the most successful CBM development in China.⁵⁻⁷ High-rank coals are mainly developed in this block, and they develop a large number of micropores.^{8,9} Cleats are not developed, and the permeability is generally less than 1 mD.¹⁰

The coal reservoir's initial permeability is very low, and permeability is improved by fracturing technology, which is necessary to obtain industrial gas amounts.¹¹⁻¹³ In the initial stage of CBM development, high-viscosity working fluid (including high-viscosity drilling fluid and fracturing fluid) was used in some CBM wells.^{14,15} Good viscoelasticity is one requirement of the physical properties of the fracturing fluid because it can result in a good sand-carrying capacity and reduce fluid loss.¹⁶ However, the side effect of thickeners is due to gel residues,¹⁷ which leads to network blockage of coal seam fracture and adversely affects reservoir permeability and gas production.^{18–20} In the study area, the gas production of CBM wells using high-viscosity clean fracturing fluid is significantly lower than that of surrounding CBM wells using active water

fracturing fluid. The main reason for this was that this type of fluid contaminates the coal reservoir and reduces permeability and desorption, resulting in decreased production of single wells.^{21,22} Therefore, for these CBM wells, removing contamination of the coal reservoir, restoring permeability, and improving the production of CBM wells are urgently needed.

In terms of the development of CBM, contamination in near-borehole zones is mainly caused by external liquid and bacterial contamination and reservoir blockage.²³ At present, plugging removal technologies of CBM wells include physical and chemical plugging removal. Secondary hydraulic fracturing technology, high-energy gas injection,²⁴ and ultrasonic excitation² are physical plugging removal technologies. These technologies produce a certain amount of energy through the equipment that can promote the formation of the multifracture system in the coal reservoir, induce more natural fractures, and improve the permeability of the coal reservoir. So far, the most common chemical plugging removal

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Figure 1. Geological structure map of the Qinshui Basin, China, and the sampling spot of the study area.

technology is acidizing.²⁶ Acidizing plugging removal in coalbed methane wells is a measure to inject acid into the formation and restore or improve reservoir conductivity in a wide range near wellbores by the acid solution. Some scholars have studied the feasibility of ethanol as a plugging remover.²⁷ Research shows that the pore volume and the porosity of coal increased following ethanol treatment, while the affinity for methane was significantly reduced.

The above techniques have a particular effect on plug removal of CBM wells but also have some limitations. Secondary hydraulic fracturing, ultrasonic excitation, ethanol treatment, and acidizing technologies were applied in the study area, but the application effect was not noticeable. Therefore, it is necessary to find a new plugging remover to remove CBM wells' contamination in this area.

In recent years, chlorine dioxide has been widely used in oil fields as a new type of plug removal agent.²⁸⁻³¹ Chlorine dioxide has a strong oxidization activity. The chlorine dioxide molecule consists of one chlorine atom and two oxygen atoms, i.e., ClO₂. The outer layer of the molecule contains 19 electrons. The two O-Cl bonds are σ bonds; there are two electron pairs around each O atom, one electron pair around the Cl atom, and the other five electrons from a delocalized π bond. There are unpaired active odd electrons in the bonding domain that have a strong ability to capture electrons. Therefore, chlorine dioxide has intense oxidation activity and is commonly used in oil fields to remove various polymers, iron sulfide, and bacteria. A combination of chlorine dioxide and acid solution can be used to treat a formation blocked by iron sulfide, bacterial communities, high-molecular-weight polymers, and inorganic scale in the formation, thus removing the blockage in near-borehole zones.^{32–35} This method has been used in many oil fields, increasing production and efficiency and obtaining excellent economic benefits.^{36,37}

However, few studies have been reported on blockage removal and permeability improvement of CBM wells using chlorine dioxide. The effects of chlorine dioxide on ash and the original permeability and the impact on the permeability of contaminated coal reservoirs are unknown. This paper explores the feasibility of using chlorine dioxide as a plug removal agent for high-rank contaminated coal reservoirs. The study was carried out in three steps. First, the influence of chlorine dioxide on the ash content of coal samples was evaluated through experiments, and whether chlorine dioxide increased or decreased the ash content was discussed. Second, the effects of chlorine dioxide on coal samples' initial permeability were discussed by displacement and immersion experiments. Third, the impact of chlorine dioxide on contaminated coal samples' permeability was evaluated by plug removal experiments. Based on the above three types of experimental results, the systematic evaluation of chlorine dioxide plays an essential role in the recovery of permeability of high-rank contaminated coal reservoirs. The experimental results reference the production restoration and reconstruction of low-yield CBM wells with similar geological conditions and development techniques in the southern Qinshui Basin area.

2. GEOLOGICAL SETTING

Qinshui basin is the most prosperous area of CBM development in China. The study area in the southern part of the Qinshui Basin is the main development area, including the Zhengzhuang and Fanzhuang blocks. The bottom Carboniferous system Taiyuan and Permian Shanxi Formations are the main coal-bearing series in the study area.³⁸ Shanxi Formation is composed of medium sandstone, siltstone, mudstone, and 2–7 coal seams, while Taiyuan Formation is composed of mudstone, limestone, siltstone, and 5–10 coal seams. The Taiyuan and Shanxi Formations together average 150 m in thickness and are the two primary coal-bearing strata.³⁹ The total coal thickness of these formations is about 15 m.

In the study area, the gas content of the coal seams in Fanzhuang and Zhengzhuang blocks in the southern Qinshui Basin of China is generally greater than $20 \text{ m}^3/\text{t}$. The average permeability is 0.05 mD.^{40,41} Coal seam No. 3 and No. 15 are mainly developed in the study area, and the No. 3 coal seam is the main coal seam for coalbed methane development. The average thickness of the No.3 coal seam is 5.9 m, the minimum thickness is 2.4 m, and the maximum thickness is 8.1 m. The

No. 3 coal seam is high rank and average Ro, with the maximum values of 2.6% that range from 1.87 to 4.26%.

The study area belongs to a typical coalbed methane development block with high gas content and low permeability in the southern Qinshui Basin (Figure 1).^{42,43} In this block, some CBM wells were polluted by high-viscosity fluid. Gas production was low in the early stages of development.^{2,44} Therefore, for these CBM wells, removing contamination of the coal reservoir, restoring permeability, and improving the production of CBM wells is a critical problem.

3. SAMPLING AND EXPERIMENTS

3.1. Sampling and Experiment Preparation. The coal samples were obtained from the Qincheng and the Yuxi coal mines adjacent to Fanzhuang and Zhengzhuang blocks (Figure 1). The samples' size was 30 cm \times 30 cm \times 20 cm, and they were carefully packed and quickly delivered to the laboratory for experiments. Coal plugs with a diameter of 25 mm and a length of 50 mm were drilled in each coal block. Coal plugs were used to experiment with permeability change, including standard flooding, immersion, and plug removal experiments. Zhengzhuang, Fanzhuan, and gangue samples were labeled ZZ, FZ, and JG, respectively.

3.2. Preparation of Chlorine Dioxide Solution. The primary agent of chlorine dioxide solution is sodium chlorite, and chlorine dioxide solution is composed of the primary agent and an additive. Chlorine dioxide is generated by activating sodium chlorite under acidic conditions. The primary agent and additive were correctly weighed and added into a narrow-mouth graduated Erlenmeyer flask followed by addition of distilled water and stirred until there were no particles or bulk samples. Sodium citrate was added as an acidifier in a proper proportion. The solution was stirred until it turned light yellow to give chlorine dioxide solution, which was sealed and stored. The concentration of chlorine dioxide solution used in this study was 5000×10^{-6} .

It should be noted that chlorine dioxide solution is corrosive. When using chlorine dioxide solution in construction sites, the staff must protect themselves well to avoid skin and eye contact with the solution. In addition, when using chlorine dioxide solution, contact with iron equipment should be avoided to prevent corrosion. This substance is toxic and cannot be transported, hence the need for on-site production.

3.3. Preparation of High-Viscosity Working Fluid. High-viscous working fluid includes drilling fluid and fracturing fluid. The high-viscous working fluid is prepared in the laboratory according to the formula of the field operation. The high-viscous working fluid formula is a surfactant (0.8% VES), a micelle accelerator (0.4% SYN), and an antiswelling agent (1.0% KCl).

4. EXPERIMENTAL METHOD

The study was carried out in three steps. First, the effect of chlorine dioxide on coal ash was evaluated through experiments. Second, the displacement and immersion experiments were performed. The results of chlorine dioxide's influence on the initial permeability of the coal samples were assessed. Third, chlorine dioxide's effect on contaminated coal samples' permeability was evaluated through plug removal experiments.

4.1. Ash Experiments. Ash experiments determined the changes in the ash content of different coal samples before and after being immersed in chlorine dioxide solution. The ash

content of coal was determined according to the national standard Industrial Analysis of Coal (GB/T 212-2008). After two Zhengzhuang, two Fanzhuang, and two coal gangue samples (200 g each) were ground to 0.2 mm, they were mixed evenly and dried. A total of six coal samples were prepared, and 1 ± 0.1 g of the test sample with a particle size of less than 0.2 mm was selected, weighed precisely to 0.0002 g, and evenly spread into the ash pan. The sample was heated to 815 ± 10 °C at a fixed rate in a muffle furnace, ashed, and burned to a constant weight. The ash content was expressed as the percentage of the residue's weight to the weight of the coal sample. The same weights of the above six coal samples were taken and immersed in chlorine dioxide solution for 48 h.

4.2. Original Permeability-Change Experiment. 4.2.1. Displacement Experiments. Two coal samples from the Zhengzhuang block and one coal sample from the Fanzhuang block were selected to drill small coal pillar samples with a diameter of 25 mm and a length of 30 mm. The gas permeabilities of the three small coal pillar samples were measured using a TCQT-III-type gas-phase displacement stimulation test device for low-permeability coal seams with helium as the fluid medium. This experimental design aimed to test the characteristics of permeability change when water and chlorine dioxide solutions were used for displacement. Therefore, water was first used for displacement; the set confining pressure was 2 MPa, the axial pressure was 1 MPa, and the inlet pressure was 0.6 MPa. After the permeability test values were stabilized, chlorine dioxide solution was used for displacement, and the permeability change was observed. Through the above experiments, the permeability-change characteristics when the coal was displaced with chlorine dioxide solution were analyzed.

4.2.2. Immersion Experiments. Two coal samples from the Zhengzhuang block and one coal sample from the Fanzhuang block were selected to drill small coal pillar samples with a diameter of 25 mm and a length of 30 mm. The gas permeability of three small coal pillar samples was measured using a TCQT-III-type gas-phase displacement stimulation test device for low-permeability coal seams with helium as the fluid medium. The three small coal pillar samples were immersed separately in chlorine dioxide solution for 8, 20, 36, 56, and 80 h, respectively, and the gas permeability was measured. The relationship of the reaction time between coal pillar samples with chlorine dioxide solution and the permeability was determined. In the above permeability measurement, the confining, axial, and inlet pressures were set as 2, 1, and 0.6 MPa, respectively.

4.3. Plug Removal Experiments. High-viscous working fluid includes drilling fluid and fracturing fluid. The highviscous working fluid is prepared in the laboratory according to the formula of the field operation. The high-viscosity fluid was made up of surface-active molecules. Its good breaking ability has been widely used in natural gas wells, and its gradual use in coal seams has achieved specific results. However, sometimes, incomplete gel breaking and severe blockage of the fissure passage lead to decreased coal permeability. The coal sample was drilled with a diameter of 25 mm and a length of 30 mm. The gas permeability of three small coal pillars was measured using a TCQT-III-type low-permeability CBM displacement test device and helium gas as a fluid medium. The experiment was divided into three steps. First, the raw coal sample's permeability was tested. Second, the permeability was tested after immersing the three coal samples in the high-viscous

Table 1. Experimental Results from Ash in Coal Samples

	type	sample number	ash pan (g)	ash pan + sample	weight of the material remaining after combustion (g)	ash (%)
original ash		ZZ1	19.3022	20.3861	19.4661	15.12
		ZZ2	19.0381	20.0711	19.2381	19.36
		FZ1	17.6697	18.6812	17.8561	18.43
		FZ2	18.2318	19.2061	18.3694	14.12
		coal average	18.5605	19.5861	18.7324	16.76
		JG1	17.5629	18.5861	18.4342	85.15
		JG2	20.0567	21.0441	20.9691	92.40
		gangue average	18.8098	19.8151	19.70165	88.775
ash after the san dioxide solutio	nple was immersed in chlorine n	ZZ1-1	19.8348	20.8204	19.9401	10.68
		ZZ2-1	17.6917	18.6139	17.8471	16.85
		FZ1-1	17.7419	18.7794	17.9027	15.50
		FZ2-1	17.7446	18.7584	17.8775	13.11
		coal average	18.2533	19.2430	18.3919	14.04
		JG1-1	18.6422	19.6905	19.5456	86.18
		JG2-1	17.6891	18.6181	18.5278	90.28
		gangue average	18.16565	19.1543	19.0367	88.23
	25 Original ash content		а	95.3	Original ash content b	
Soaking chlorine dioxi		ash content			Soaking chlorine dioxide ash content	
Ash content(%)	20 15 10 5 0 ZZ1 ZZ2	FZ1	FZ2	Ash content(%) 666 066 066 066 066 066 066 06	JG1 JG2	

Figure 2. Comparison of coal-ash experimental results. (a) Coal sample. (b) Gangue sample.

working fluid for 72 h. Finally, the three coal samples were immersed in chlorine dioxide solution for 2 h to test their permeability.

5. RESULTS AND DISCUSSION

During the construction of CBM wells, if the working fluid contains viscous liquids (clean fracturing fluid and guanidine gum), many attachments on the coal surface are retained in the coal reservoir and block the fracture system. This affects permeability improvement and production restoration.

5.1. Analysis of Ash Experiment Results. The ash content exerts a significant influence on the gas content and the permeability of coal reservoirs. An increase in the ash content blocks the fracture system in coal reservoirs and reduces permeability, negatively impacting CBM production. The ash experiment results before and after the reaction between coal samples and chlorine dioxide solution showed that the original ash content of coal was 14.12–19.36%, with an average of 16.76%; the ash content of gangue (carbon mudstone) was 85.15–92.40%, with an average of 88.78%. After immersion in chlorine dioxide solution, the ash content of coal was 10.68–16.85%, with an average of 14.04%, and the ash content of the gangue was 86.18–90.28% with an average of 88.23%. The test results are shown in Table 1.

From the results of ash content before and after soaking chlorine dioxide in coal and rock samples, it is found that the ash content of coal samples decreases after immersion, as shown in Figure 2a. The ash content of the ZZ1 sample decreased by 29.37% and that of ZZ2 decreased by 12.96%. In the Fanzhuang sample, the ash content of FZ1 decreased by 15.90%, and that of FZ2 decreased by 7.15%. In total, the ash average of the coal sample decreased by 16.35%. For gangue samples, the ash content of the JG1 gangue samples increased by 1.21%, and that of JG2 samples decreased by 2.29%, with an average decrease of 0.54%, as shown in Figure 2b.

The gangue samples are mainly carbonaceous mudstone, mainly composed of clay minerals, followed by quartz, Muscovite, and a small feldspar. Carbonaceous mudstone is chemically stable and generally does not react with chlorine dioxide. When the gangue sample is soaked with chlorine dioxide, the ash content of one sample increases by 1.21% and that of the other sample decreases by 2.29%, with an average decrease of 0.54%. The amount of change is minimal. It can be concluded that chlorine dioxide solution does not react with the carbonaceous mudstone, and the ash content does not increase. Therefore, it has no adverse effect on the change of permeability of the coal sample.

After obtaining coal samples in this block, scientists used XRD diffraction experiments and discovered that inorganic minerals are mainly composed of clay minerals, calcite, and pyrite.⁴⁵ As shown by the following formula, pyrite reacts with oxygen to generate sulfur dioxide gas, which reduces the ash content in the coal sample.

$$4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{FeO}_3 + 8\text{SO}_2 \tag{1}$$

$$8ClO_2 + 5FeS_2 + 4H_2O \rightarrow 5FeSO_4 + 8HCl$$
(2)

Chlorine dioxide has strong oxidation activity, and it reacts with hot water to decompose into hypochlorous acid, chlorine gas, and oxygen. Light also easily decomposes chlorine dioxide. The inorganic mineral in the coal sample contains pyrite. Pyrite is a disulfide of iron and reacts with oxygen (formula 1) and chlorine dioxide (formula 2). Therefore, the content of ash in coal samples decreases (Figure 2a). Coal samples contain different amounts of pyrite; therefore, the amount of ash reduced by the reaction of coal samples with chlorine dioxide is also different. Overall, the ash content of the four coal samples decreased by 16.35%. The experimental results showed that chlorine dioxide did not produce new ash content in the coal sample but reduced the ash content, which helped improve the permeability of coal.

5.2. Analysis of Permeability Change of the Displacement Experiments. The gas-permeability values of ZZ1 and ZZ2 in the Zhengzhuang block and FZ1 in the Fanzhuang block were 3.610, 0.197, and 10.684 mD, respectively, and the results are shown in Table 2.

Table 2. Permeability Data Measurements for Coal Samples

sample number	sample length (cm)	sample diameter (cm)	gas permeability (mD)
ZZ1	4.032	2.526	3.610
ZZ2	2.748	2.522	0.197
FZ1	2.936	2.528	10.684

The experiment in which the coal was displaced with chlorine dioxide solution showed that sample FZ1, with high original permeability, exhibited increased permeability after displacement using chlorine dioxide solution. In contrast, the permeability values of ZZ1 and ZZ2, both with a small initial

permeability, were unchanged after displacement using chlorine dioxide solution, as shown in Figure 3.

The gas permeability of sample FZ1 is 10.684 mD, that of sample ZZ1 is 3.610 mD, and that of sample ZZ2 is only 0.197 mD. In the three samples, the water permeability was significantly reduced during the water injection stage. The gas permeability was measured using helium, while distilled water was used in the water injection phase. The permeability of water measurement is much smaller than that of gas measurement. The water injection permeability of samples ZZ1 (Figure 3a) and FZ1 (Figure 3b) is plotted from 1.0 mD, and, in comparison, that of sample ZZ2 (Figure 3c) is plotted from 0.1 mD.

Previous studies suggested that after the coal sample is immersed in chlorine dioxide solution, the aromatic ring structure is destroyed by oxidation. The surface is etched to form pores and cracks; therefore, the permeability increases.^{46–48} In this experiment, the initial permeability of sample FZ1 was relatively high. The fractures were developed, and chlorine dioxide could enter a more extensive range of coal cracks to form pores and fracture permeability. However, while the original permeability values of samples ZZ1 and ZZ2 were relatively low, the coal had a compact structure, cracks were not developed, and the range over which chlorine dioxide solution had an effect was minimal; therefore, the permeability remained unchanged.

It should be noted that this experiment was performed within 4 h, soaking the coal samples with chlorine dioxide for a relatively short time, mainly to compare the permeability changes after injection of water and chlorine dioxide solution. This displacement experiment proves that chlorine dioxide solution does not reduce the permeability of coal samples but increases it. Therefore, chlorine dioxide solution is beneficial to the permeability of high-rank coal samples.



Figure 3. Permeability change of coal samples with displacement with chlorine dioxide solution. (a) ZZ1, (b) FZ1, and (c) ZZ2 samples.

5.3. Analysis of the Immersion Experiments. The three small coal pillar samples were immersed separately in chlorine dioxide solution for 8, 20, 36, 56, and 80 h, respectively, and the gas permeability was measured. The relationship of the reaction time between coal pillar samples with chlorine dioxide solution and the permeability was determined. The three coal pillar samples were reacted with chlorine dioxide solution for

Table 3.	Gas-Permeability	Change	after	Immersion	in
Chlorine	Dioxide Solution				

sample number	reaction time (h)	permeability of rock sample (mD)	permeability change ratio (%)
ZZ3	0	0.468	
	8	0.502	7.26
	20	0.563	20.30
	36	0.649	38.68
	56	0.951	103.21
	80	1.054	125.32
FZ2	0	0.050	
	8	0.149	198.00
	20	0.346	592.00
	36	0.333	566.00
	56	1.802	3504.00
	80	1.921	3742.00
FZ3	0	0.002	
	8	0.005	150.00
	20	0.035	1650.00
	36	0.048	2300.00
	56	0.099	4850.00
	80	0.105	5150.00

different durations, and the test results are shown in Table 3. Through the experiment, the following was observed.

- (1) After the coal sample was immersed in chlorine dioxide solution, the permeability was increased by different degrees. As the immersion time increased, the permeability increased continuously (Figure 4).
- (2) Among the three coal samples, ZZ3 exhibited a relatively high original permeability, which increased to 125.32% after the sample was immersed for 80 h. The initial

permeability values of samples FZ2 and FZ3 were relatively low (0.05 and 0.02 mD, respectively). After the sample was immersed for 80 h, the permeability values increased to 3742 and 5150%, respectively, and the magnitudes of the increases were relatively high. The permeability of coal samples increased by 3005.77% after 80 h of immersion. This shows that the permeability of coal samples soaked with chlorine dioxide can be significantly increased.

(3) When the reaction time was within 36 h, the permeability of sample ZZ3 did not change considerably; at 56 h, the permeability increased to 103%. When the reaction time was within 36 h, the rate of increase in permeability of FZ2 was low; at a reaction time of 56 h, the permeability increased to 2064%. The permeability of sample FZ3 increased to 4850% at a reaction time of 56 h. The permeability values of the three coal samples increased when they were immersed in chlorine dioxide solution from 0 to 36 h. The rates of permeability increase slowed considerably from 56 to 80 h; when the immersion time ranged from 36 to 56 h, the rates of the permeability increase of the three coal samples were the fastest.

Cracks were not developed for the samples with low permeability. The coal had a compact structure, and chlorine dioxide solution needed a long immersion time to enter a broader range of microcracks to increase the permeability. After 56–80 h of immersion, chlorine dioxide solution had already entered most of the fractures to react with the coal, and the magnitude of the increase in permeability became small. When the coal was immersed in chlorine dioxide solution for different durations, the curve of the permeability change was generally slow in the early stage, fast in the middle stage, and slow in the later stage. The trend of the rate of permeability increase was slow–fast–slow.

After being immersed in chlorine dioxide solution, the coal sample exhibited an increase in porosity and a decrease in the specific surface area, indicating that the pores of the treated coal sample expanded. The connectivity was enhanced and the reservoir permeability improved; the decreased specific surface area reduces the capacity of coal to adsorb methane. From the



Figure 4. Curve of permeability change of the coal samples immersed in chlorine dioxide solution for different durations.

experiment studying the permeability change with different durations of chlorine dioxide immersion, it was found that the permeability of coal samples was increased to varying degrees after immersion in chlorine dioxide solution. With increasing immersion time, the permeability increased continuously. After the coal samples were immersed for 0-36 and 56-80 h, the rate of the permeability increase was slow, and after 36-56 h of immersion, the rate of the permeability increase was the fastest.

As shown from the above experimental results, chlorine dioxide solution does not cause solid blockage and deterioration of the coal reservoir's permeability; because of its intense oxidization activity, chlorine dioxide reacts with the coal to form pores and cracks and increases the permeability. For coal reservoirs with high initial permeability, the displacement using chlorine dioxide solution increases the permeability, while coal reservoirs with low original permeability need to be immersed for a long time to increase the permeability.

5.4. Analysis of the Plug Removal Experiments. The initial permeability of the three coal samples is relatively low: 0.251, 0.893, and 0.574 mD, respectively. Three coal samples were immersed in high-viscosity working fluid for 72 h. The high-viscosity working fluid can damage the permeability of the coal sample. It was found through experiments that when the high-viscosity fluid soaks in the coal pillar, the permeability generally decreases, and the permeability damage rate reaches 30.1-52.0%, with an average of 43.8%. After soaking in chlorine dioxide solution, the permeability was recovered to some extent, and the damage rate of the ZZ3 sample decreased from 49.4 to 15.7% and that of FZ3 from 52.0 to 13.1%. The injury rate of FZ4 samples was reduced from 30.1 to 19.0%. It can be seen that chlorine dioxide solution had an excellent decontamination effect on high-viscosity working fluid. The permeability of contaminated coal samples was recovered by 11.10-38.90%, with an average recovery of 27.90%. It should be noted that chlorine dioxide can remove a part of the blockage and improve the contaminated coal reservoir's permeability, but it cannot completely recover the original permeability. The results are shown in Table 4.

 Table 4. High-Viscosity Working Fluid Contamination and

 Release Gas Permeability Change

		high-viscosity fluid		chlorine dioxide	
sample number	permeability of rock sample (mD)	permeability (mD)	injury rate (%)	permeability (mD)	injury rate (%)
ZZ3	0.251	0.127	49.4	0.212	15.7
FZ3	0.893	0.429	52.0	0.776	13.1
FZ4	0.574	0.401	30.1	0.465	19.0

Because of the difficulty of gel breaking in high-viscosity working fluid, it exists in the coal seam's fracture system, which results in contamination of the coal seam and a decrease of permeability and gas production. Using the active oxidation of chlorine dioxide, the blockage of an organic polymer in highviscosity working fluid can be eliminated, and the blockage can be removed. When coal encounters high-viscosity liquid, a macromolecular polymer blocks the fracture passage, and the coal sample's permeability decreases further. After soaking with chlorine dioxide, the active oxidation of chlorine dioxide decomposes the macromolecular polymer and changes the high-viscosity liquid into a low-viscosity liquid, which can discharge CBM well, thereby improving the permeability of the coal sample. This experiment fully illustrates this problem.

According to the test results in the laboratory, chlorine dioxide solution is provided on-site for plugging solution, and the injection volume for industrial applications is $80-120 \text{ m}^3$. The effect is better when the soaking time is more than 80 h after injection.

In summary, chlorine dioxide solution removes blockages and improves permeability and can be applied to operation sites to restore and reconstruct low-yield CBM wells.

6. CONCLUSIONS

Chlorine dioxide has intense oxidation activity and is commonly used in oil fields to remove various polymers, iron sulfide, and bacteria. A combination of chlorine dioxide and acid solution can be used to treat a formation blocked by iron sulfide, bacterial communities, high-molecular-weight polymers, and inorganic scale in the formation, thus removing blockages in near-borehole zones. Previous studies suggested that after the coal sample is immersed in chlorine dioxide solution, the aromatic ring structure is destroyed by oxidation. The surface is etched to form pores and fractures; therefore, the permeability increases. The primary purpose of this study is to use chlorine dioxide as a plugging remover to restore the permeability of contaminated coal samples, which has practical significance for the development of CBM wells. The study was carried out in three steps. First, the effect of chlorine dioxide on coal ash was evaluated through experiments. Second, the displacement and immersion experiments were performed. The results of chlorine dioxide's influence on the initial permeability of the coal samples were assessed. Third, chlorine dioxide's effect on contaminated coal samples' permeability was evaluated through plug removal experiments. A series of experiments proved that chlorine dioxide effectively removed high-viscosity fluid contamination and increased coal samples' permeability.

- (1) Through the ash experiment, it was found that chlorine dioxide did not produce new ash content in the coal sample but reduced the ash content; overall, the ash content of the four coal samples decreased by 16.35%, which helped improve the permeability of coal.
- (2) The displacement and immersion experiments using chlorine dioxide solution showed that for coal samples with high original permeability, displacement with chlorine dioxide solution could increase permeability. In contrast, for coal samples with low initial permeability, a long immersion time was required to increase permeability. The permeability of coal samples increased by 3005.77% after 80 h of immersion. The permeability of contaminated coal samples was recovered by 11.10– 38.90%, with an average recovery of 27.90%. The plug removal experimental results show that chlorine dioxide effectively improves the permeability of high-rank contaminated coal reservoirs.
- (3) The experimental data on chlorine oxide used to remove blockages and improve the permeability of coal reservoirs were systematically obtained. The experimental results show that chlorine dioxide solution had a good effect on the decontamination of high-viscosity working fluid. The experimental results reference the production restoration and reconstruction of low-yield

CBM wells with similar geological conditions and development techniques in the southern Qinshui Basin area.

AUTHOR INFORMATION

Corresponding Author

Zhou Zhang – School of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China; Collaborative Innovation Center of Coalbed Methane and Shale Gas for Central Plains Economic Region, Jiaozuo 454000, Henan, China; Henan International Joint Laboratory for Unconventional Energy Geology and Development, Jiaozuo 454000, China; orcid.org/0000-0001-5530-6574; Email: zhangzhou@hpu.edu.cn

Authors

Pengbo Zhou – School of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China

Lifang Zhao – School of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China

Jin Yang – School of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China

Min Zhou – School of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China; Collaborative Innovation Center of Coalbed Methane and Shale Gas for Central Plains Economic Region, Jiaozuo 454000, Henan, China

Baoan Xian – School of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China; Collaborative Innovation Center of Coalbed Methane and Shale Gas for Central Plains Economic Region, Jiaozuo 454000, Henan, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c01348

Notes

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