Study on the Effect of Iron-Based Deoxidizing Inhibitors for Coal Spontaneous Combustion Prevention

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Abstract: To improve the prevention of spontaneous coal combustion, reduced iron powder and other ingredients should be added together to form an iron-based deoxidizing inhibitor, with the dual effect of oxygen consumption and inhibition. The oxygen consumption rate of the inhibitor was studied through experiments. According to the theory of coordination resistance, the coordination resistance of Fe^{3+} was studied via the density functional method. Subsequently, a comparative experiment of the effects on spontaneous coal combustion was conducted. The research shows that several kinds of common resistance agents that are added to the reduced iron powder can consume oxygen. However, the rate of oxygen consumption varies. Fe^{3+} produced by the reduced iron powder indicates a strong coordination resistance. When compared with traditional inhibitors of Mg^{2+}, Fe^{3+} has a stronger inhibition effect on the N, P, and S reactive groups in coal. The overall inhibitory effect is better than that of traditional inhibitors, because of the increased oxygen consumption and the coordination resistance of Fe^{3+} on the basis of traditional inhibitors.

1. Introduction

The economy of China has developed rapidly and the demand for coal is increasing the intensity of coal mining [1]. This can lead to accidents during coal mining. In coal mines, mine fires are among the most dangerous disasters that affect safe production [2]. Most mine fires are caused by spontaneous coal combustion [3]. Globally, coal mining industries are threatened by spontaneous coal combustion [4], as it causes serious accidents and environmental pollution [5]. Spray inhibitor technology is commonly used to prevent the spontaneous combustion of coal [6]. Presently, the inhibitors that are used in coal mines are mainly inorganic salts [7], such as NaCl, $MgCl_2$, and $CaCl_2$. Their role in preventing spontaneous coal combustion, in the presence of a large amount of water, is mainly water absorption [8], moisturizing, and coordination resistance [9]. Coordination resistance involves the contained metal cation forming a coordination compound with the active group in the coal, thereby preventing contact between the active group and the oxygen molecule and, consequently, the oxidation reaction.

The resistance to different types of coal is relatively fixed, because of the relatively simple composition of commonly used inhibitors. Moreover, it is difficult to meet the needs of coal mines that require the use of higher-resistivity inhibitors, where spontaneous coal combustion fires are more severe. Therefore, it is difficult to guarantee the safe production in such mines.

In response to the shortcomings of commonly used inhibitors, many researchers have tried to improve on the effect of inhibitors by changing or adding ingredients. Li et al. [10] selected six different types of antioxidants (oxygen-scavenger ascorbic acid, butylated hydroxytoluene, triphenyl phosphite, 2,2,6,6-tetramethyl-1-piperidine-noxyl free radical [TEMPO], edetic acid, and phytic acid) as inhibitors for low-temperature oxidation experiments, and found that TEMPO had the greatest inhibition effect. Qi et al. [11] proposed a kind of controlled-release inhibitor that is made from the synthesis of halogen inhibitors, catechin, copolymers, solvents, and surfactants. Tang [12] used phosphates and $MgCl_2$ as synergistic inhibitors for suppressing the self-ignition of coal. Zhang et al. [13] examined nine tetraalkylphosphonium-based ionic liquids and one imidazolium-based ionic liquid (1-allyl-3-methylimidazolium chloride ([AMIm]Cl)) as possible additives to develop a chemical inhibitor that could efficiently suppress coal oxidation. Slovák et al. [14] used urea and $CaCl_2$ as inhibitors for low-temperature coal oxidation. Qin et al. [15] developed a superabsorbent hydrogel–ascorbic acid composite inhibitor for the suppression of coal oxidation. Cheng et al. [16] designed an intelligent gel to control spontaneous coal combustion. In summary, the abovementioned studies have improved the performance of inhibitors to a certain extent. However, their inhibitory effects are still limited and they cannot meet the requirements to effectively prevent spontaneous coal combustion.

If the performance of inhibitors is to be further improved, controlling oxygen—another major factor that causes spontaneous coal combustion—should be considered, as well as changing inhibitor ingredients to reduce the reactivity of coal. As a result, Hao et al. [17] proposed a deoxidizing inhibitor that could inhibit coal oxidation and reduce the ambient oxygen concentration simultaneously. The deoxidizing inhibitor is composed of inhibitors that are commonly used in coal mines and oxygen-consuming compositions, such as reduced iron powders and fillers. The inorganic salts in commonly used inhibitors can be used to suppress spontaneous coal combustion and as active agents for the oxygen consumption of reduced iron powder. He et al. proposed that the oxygen consumption rate of the inhibitor was related to temperature [18], and that the inhibitory effect was related to coal particle size [19]. Wang's experiments [20] have shown that deoxidizing inhibitors could prevent coal oxidation in closed and semi-closed spaces. However, when the deoxidizing inhibitors contained different compositions, the effects of oxygen consumption and inhibition had not been thoroughly researched. Therefore, this study examined the inhibitory effects of deoxidizers that were mixed with different kinds of inhibitors through experimental methods. The inhibitory effect of iron-based deoxidizing inhibitors was analyzed using the theory of coordination resistance combined with the method of quantum chemical calculation. Finally, a comparative experiment of the inhibitory effect was performed.

2. Experimental Preparation

2.1. Preparation of the Experimental Instruments and Chemicals

The chemicals that were used in the experiment were reduced iron powder, several common inorganic salts ($NaCl$, $MgCl_2$, KCl, and $CaCl_2$), diatomite, and Vaseline (for sealing). The instruments that were used were an HH-6 water bath and an AR-800 oxygen meter. The experimental instruments and chemicals that were used are presented in Figure 1.
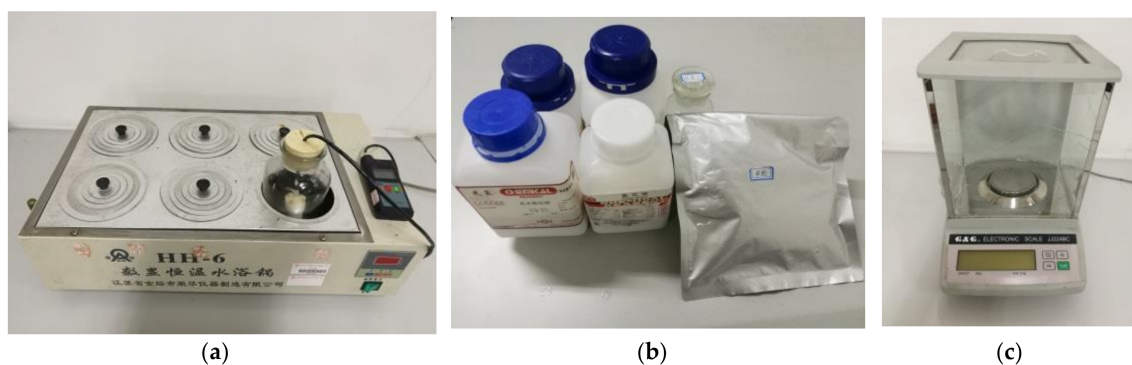
Figure 1. Experimental instruments and chemicals used in this study. (**a**) HH-6 water bath; (**b**) Chemicals; and (**c**) Precision Balance.

2.2. Oxygen Consumption Mechanism of Iron-Based Deoxidizing Inhibitors

Iron-based deoxidizing inhibitors were made by adding reduced iron powder—which consumes oxygen—and fillers to common inhibitors that are used in coal mines, such as $MgCl_2$, KCl, and $CaCl_2$. The reduced iron powder, catalyzed by the inhibitor, consumed oxygen according to the following chemical equation:

$$2Fe + O_2 + 2H_2O = 2Fe(OH)_2$$
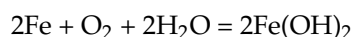
$Fe(OH)_2$ further reacted with oxygen, producing $Fe(OH)_3$:

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3 \rightarrow 2Fe_2O_3 + 3H_2O$$
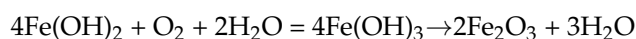
2.3. Experimental Procedures

2.3.1. Oxygen Consumption of Deoxidizers Mixed with Different Kinds of Inhibitors

The deoxidizer mass in the iron-based deoxidizing inhibitor was maintained at 1.5 g, and the temperature was set at 40 °C. Subsequently, 0.6 g of diatomite, and 0.15 g each of $MgCl_2$, NaCl, KCl, and $CaCl_2$, were added to four wide-mouthed containers. The time required to consume the oxygen in the containers was determined, and the effect of the different inorganic salts on the oxygen consumption rate of reduced iron powder was analyzed.

2.3.2. Inhibition of Iron-Based Deoxidizing Inhibitors

(a). Calculation Models for Coordination Resistance

According to the theory of coordination resistance, active groups that contain N, S, and P on the coal surface, react with inhibitive cations to produce coordination complexes, thereby reducing their activity with oxygen. Furthermore, the stability of the resulting coordination complexes can determine the rank of the performance of the inhibitors. $MgCl_2$, a common inhibitor that is used in coal mines, was selected as a representative inhibitor for further research. After the oxidation reaction of the iron-based deoxidizing inhibitor, Fe^{3+} was produced, and $MgCl_2$ was dissolved in water to produce Mg^{2+}. Gaussian 09 was used to establish the model in which the molecular structure of coal was simplified to form a molecular segment of coal, which consisted of one benzene ring, one carbonyl, and one side chain with active groups. This segment was connected with Fe^{3+} and Mg^{2+} through coordination bonds to form ligand structures, and the stability of the resulting coordination complexes that were produced through the reaction between Fe^{3+} Mg^{2+}, and active groups—containing N, P, and S in the coal molecule—was investigated. Based on the valence bond theory, the formation of coordination bonds could be explained by hybrid orbitals. The orbital hybridization consists of internal

and external hybrid orbitals, with the coordination complexes that are formed by more stable internal orbitals, and with the coordination complexes that are formed by relatively unstable external orbits.

(b). Structural Stability of the Coordination Complexes of Iron-Based Deoxidizing Inhibitors

The geometry of the coordination complexes that were generated by reactions between Fe^{3+}, Mg^{2+}, and coal molecules—with side chains containing N, P, and S—was calculated based on a computational optimization of the constructed model and the density functional theory at a B3LYP/6-31G level.

(c). Frontier Orbital Energy and Stability of the Coordination Complex Molecules

We optimized the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) diagrams of the respective Fe^{3+}- and Mg^{2+}-based complexes formed with coal molecule structural models—with side chains containing N, P, and S—at a B3LYP/6-31G level.

(d). Kinetic Stability of the Coordination Complexes

Molecular kinetic stability is related to the energy difference between the frontier orbitals and the absolute value of HOMO energy. An increased energy difference between the frontier orbitals, or a larger absolute value of HOMO energy, could lead to the improved kinetic stability of the resulting coordination complex. Therefore, we also investigated the energy difference between the frontier orbitals and the absolute value of the HOMO energy of the coordination complexes that were formed by reactions between Fe^{3+}, Mg^{2+}, and coal molecules—with side chains containing N, P, and S.

2.3.3. Comparative Experiment of the Inhibitory Effect

Based on the previously described experimental method, an experiment was used to compare and analyze the inhibiting effects of $MgCl_2$ and iron-based deoxidizing inhibitors by analyzing variations in the quantity of CO that was produced by heating the coal samples. The experiment was conducted in three experimental groups (Groups 1–3) using a 0.5 g, 50 mesh, brown coal sample in each group. The experimental temperature was maintained at 70 °C. Subsequently, 0.15 g of $MgCl_2$ was added to the weighing bottle for Group 2, and an iron-based deoxidizing inhibitor (containing 1.5 g of reduced iron powder, 0.15 g of $MgCl_2$, and 0.6 g of diatomite) was added to the weighing bottle for Group 3. Within the first 5 h, the concentration of CO in the wide-mouthed bottles was measured every 0.5 h and then every 1 h. After each measurement of CO concentration, the chemicals were prepared again and the experiment was restarted.

3. Results and Discussion

3.1. Oxygen Consumption Rule of Iron-Based Deoxidizing Inhibitors

Figure 2 indicates the variation of oxygen concentration over the duration of the experiment, which analyzed the effect of identical masses of different inorganic salts on the oxygen consumption rate of reduced iron powder. The relationship between oxygen concentration and time can be expressed as a quadratic function. The R-squared values are presented in Table 1. For identical masses of $MgCl_2$, NaCl, KCl, or $CaCl_2$, the times that were required to consume the oxygen were 3.3 h, 4.9 h, 5.4 h, and 9.1 h, respectively. Therefore, the order of the oxygen consumption rate was $MgCl_2 > NaCl > KCl > CaCl_2$.

Table 1. The R-squared values.

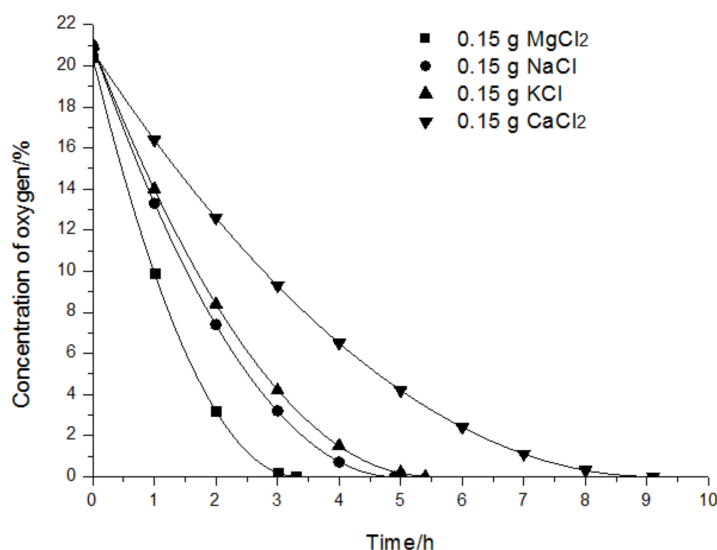| Name	0.15 g $MgCl_2$	0.15 g NaCl	0.15 g KCl	0.15 g $CaCl_2$
R-squared value	0.99999	0.99999	0.99999	1.00000

Figure 2. Variation in oxygen concentration over time.

According to the principle that inorganic salts promote the oxidation of reduced iron powder, it can be deduced that inorganic chloride inhibitors readily dissolve in water, and the metal and chloride ions that are produced from electrolysis accelerate the rate of electron loss from iron atoms. Thus, the speed reaction rate is increased. The four types of ions that are produced from ionization, namely, K^+, Ca^{2+}, Na^+, and Mg^{2+}, play a role in transporting electrons during the reaction that occurs between the reduced iron powder and oxygen in the air. Therefore, the reaction rate is determined by the electron-attracting ability and cation quantity. In this case, although K, Ca, Na, and Mg have a diminishing ability to lose electrons, the ability to attract electrons (i.e., the conductivity of their ionic counterparts, namely, K^+, Ca^{2+}, Na^+, and Mg^{2+}) has an inverse rank. In addition, among the four inorganic salts of identical masses, $MgCl_2$ can attract the most electrons. Hence, the oxygen consumption rate in the experimental group that used $MgCl_2$ was noticeably higher than that of the other groups. Therefore, it can be deduced that the order of the ability to promote oxygen consumption of reduced iron powder among the four inorganic salts is as follows: $MgCl_2 > NaCl > CaCl_2 > KCl$. However, the experimental results indicated that the ability of $CaCl_2$ to consume oxygen was inferior to that of KCl. The reason for this discrepancy was that, upon contact with water, $CaCl_2$ initially formed $CaCl_2 \cdot 2H_2O$, instead of an electrolyte with Ca^{2+} that was produced from ionization. This resulted in a decreased reaction rate.

3.2. Inhibitory Effect of Iron-Based Deoxidizing Inhibitors

3.2.1. Structural Stability of Iron-Based Deoxidizing Inhibitor Coordination Complexes

We performed optimization calculations on the model and adopted the density functional theory at a B3LYP/6-31G level to calculate the geometry of the coordination complex that was produced through reactions between Fe^{3+}, Mg^{2+}, and N-containing side chains. The geometric configurations of the resulting coordination complexes were labelled as Complexes I and II; those generated through reactions between Fe^{3+}, Mg^{2+}, and P-containing side chains were labelled as Complexes III and IV; and those generated through reactions between Fe^{3+}, Mg^{2+}, and S-containing side chains were labelled as Complexes V and VI. The calculated structural models are presented in Figure 3.

Table 2 indicates the bond lengths of the resulting coordination complexes. The bond lengths for N, P, and S increase in sequence for both Fe^{3+} and Mg^{2+}. This means that the coordination complexes that are produced through the reaction with N-containing side chains are the most stable, whereas the complexes that are formed from S-containing side chains are the least stable. This result shows that both

Fe^{3+} and Mg^{2+} have excellent inhibitive effects on N-containing active groups in coal. For coordination complexes that are formed from N-containing side chains, the bond length in the Fe^{3+} complex is shorter than in the Mg^{2+} complex, which indicates that Fe^{3+} has a better inhibiting effect.

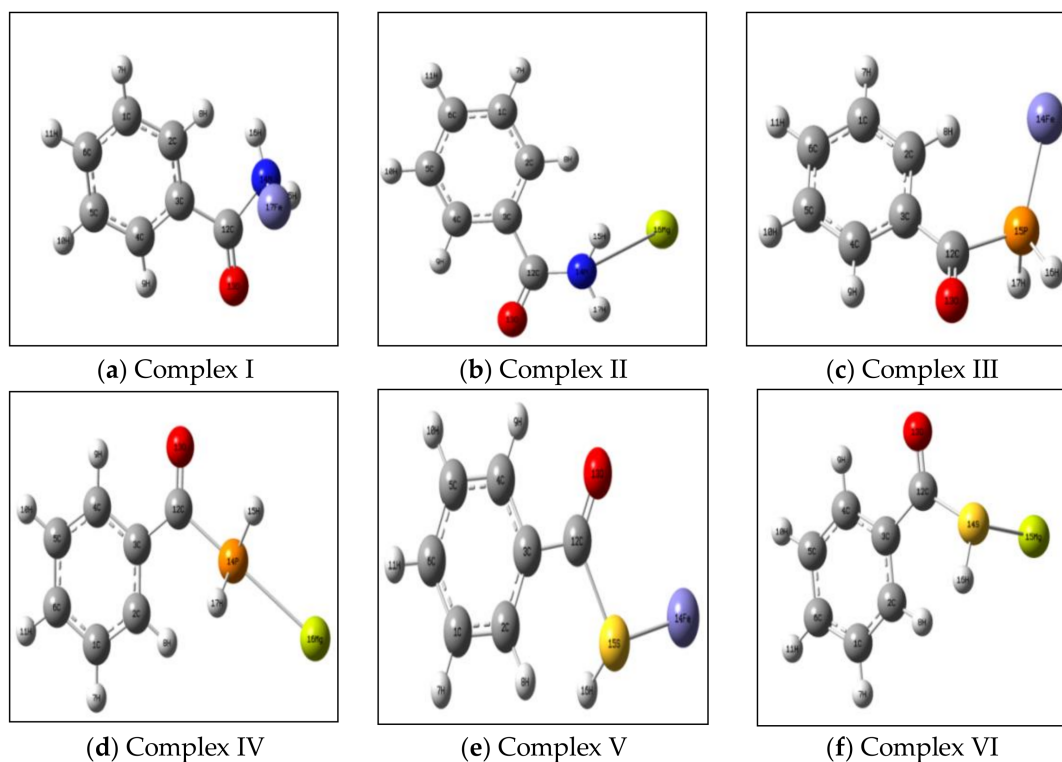| (**a**) Complex I	(**b**) Complex II	(**c**) Complex III
(**d**) Complex IV	(**e**) Complex V	(**f**) Complex VI

Figure 3. Structural models of the six complexes.

Table 2. Bond lengths of coordination bonds in the complexes.

Name	N Side Chain (nm)	P Side Chain (nm)	S Side Chain (nm)	N–C Bond Length (nm)	P–C Bond Length (nm)	S–C Bond Length (nm)
Fe^{3+} coordination complex	0.18969	0.21856	0.221728	0.150674	0.196189	0.195472
Mg^{2+} coordination complex	0.283451	0.293678	0.295896	0.137229	0.194957	0.185771

3.2.2. Frontier Orbital Energy and Stability of Coordination Complex Molecules

Figure 4 presents the optimized HOMO and LUMO diagrams of the coordination complexes that are produced through reactions between Fe^{3+}, Mg^{2+}, and coal molecules—with side chains containing N, P, and S—at a B3LYP/6-31G level.
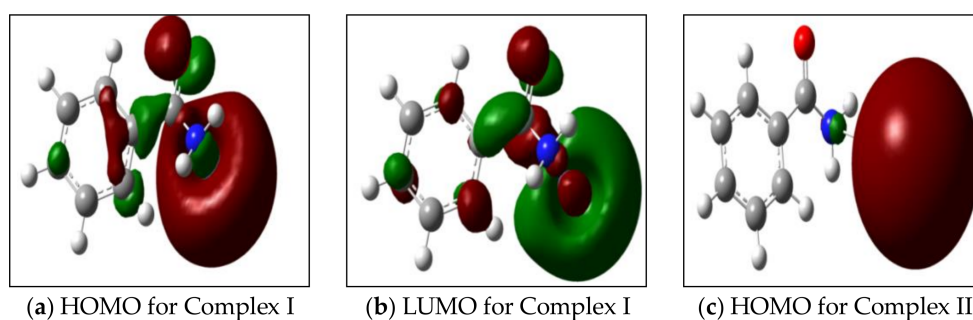
(**a**) HOMO for Complex I	(**b**) LUMO for Complex I	(**c**) HOMO for Complex II

Figure 4. *Cont.*

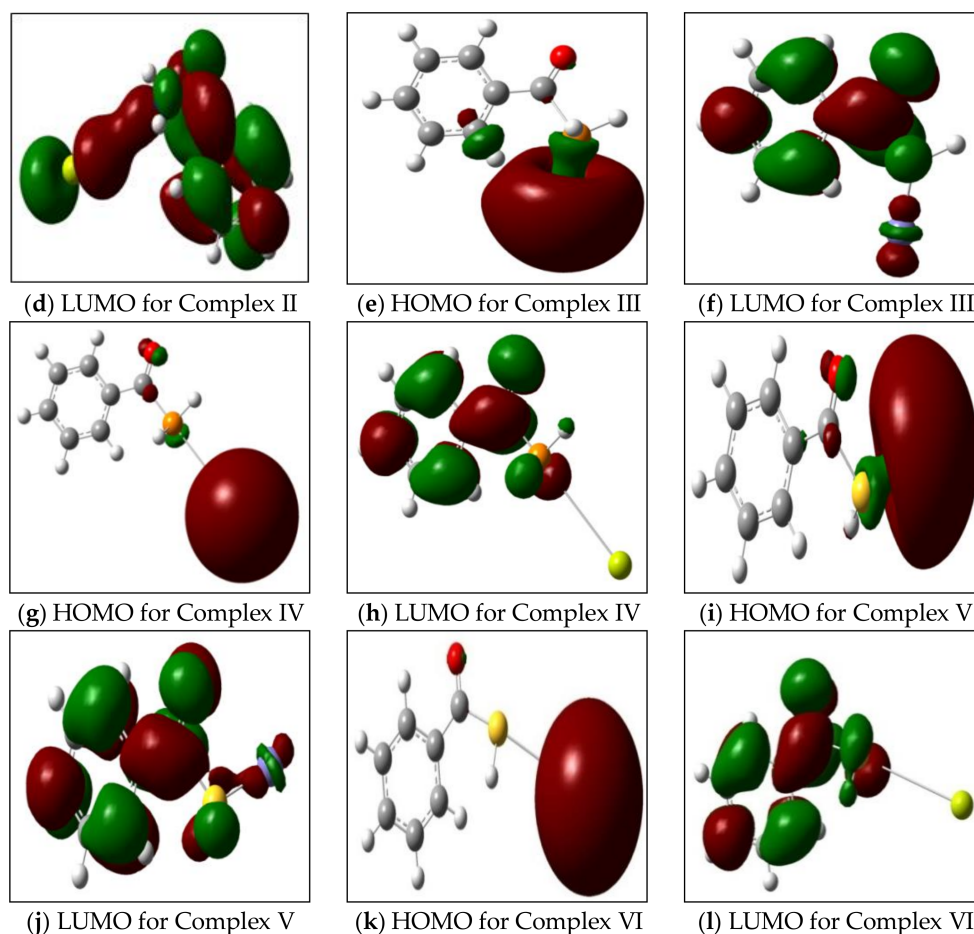|		
(**d**) LUMO for Complex II	(**e**) HOMO for Complex III	(**f**) LUMO for Complex III
(**g**) HOMO for Complex IV	(**h**) LUMO for Complex IV	(**i**) HOMO for Complex V
(**j**) LUMO for Complex V	(**k**) HOMO for Complex VI	(**l**) LUMO for Complex VI

Figure 4. Frontier orbitals of the six complexes.

The red regions in Figure 4 denote positive values, and the green regions denote negative values. The larger regions indicate a greater probability of electron emergence. Iron, being the 26th element, has an electron configuration of 1s2, 2s2, 2p6, 3s2, 3p6, 3d6, and 4s2, and its hybridized orbital configuration in the coordinated complexes is 4s4p4. For HOMO, the difficulty faced by electrophiles when attacking each atomic position is determined by the distribution of the electronic density in each atom, while the inverse is true for LUMO. Interactive forces exist between Fe^{3+} and N atoms in the resulting coordination complex at a HOMO level, while the interactive forces between Mg^{2+} and N, P, and S atoms are relatively weaker. The resulting positive zones have no intersection with their negative counterparts, and the positive zones mainly rely on Mg^{2+}. Therefore, the Mg^{2+} coordination complexes are relatively less stable, which means that Mg^{2+} is inferior to Fe^{3+} in terms of its inhibiting effect.

3.2.3. Kinetic Stability of Coordination Complexes

Table 3 shows the energy differences between the frontier orbitals and the absolute value of HOMO energy for the six complexes. The Fe^{3+} coordination complexes that are formed with coal molecules—that have side chains with N, P, and S—have greater differences in energy between the frontier orbitals when compared with the corresponding Mg^{2+} coordination complexes. The absolute values of HOMO energy for the Fe^{3+} complexes are also higher, indicating that the Fe^{3+}-based coordination complexes have good resistance to oxidation. Hence, it can be deduced that Fe^{3+}—formed from the oxidization of reduced iron powder—when added to inhibitors also has an inhibiting effect, and the effect is superior to that of Mg^{2+} in the original inhibitors.

Table 3. Absolute frontier orbital energy and HOMO energy of the six complexes.

Name	EHOMO-1 (eV)	EHOMO (eV)	ELUMO (eV)	ELUMO+1 (eV)	ΔE (eV)
Molecular coal containing N	−7.02	−6.70	−1.07	−0.24	5.63
Fe^{3+} coordination complex containing N	−7.02	−6.70	−1.07	−0.24	5.63
Mg^{2+} coordination complex containing N	−6.75	−6.32	−2.15	−0.92	4.17
Molecular coal containing P	−7.30	−6.53	−1.99	−0.45	4.54
Fe^{3+} coordination complex containing P	−15.15	−14.13	−7.33	−6.30	6.80
Mg^{2+} coordination complex containing P	−5.58	−5.21	−2.01	−0.86	3.20
Molecular coal containing S	−7.29	−7.16	−1.99	−0.50	5.17
Fe^{3+} coordination complex containing S	−14.99	−13.86	−7.55	−6.08	6.31
Mg^{2+} coordination complex containing S	−7.55	−6.16	−2.57	−0.78	3.59

3.3. Analysis of Inhibitory Effect

Figure 5 compares the inhibiting effects of $MgCl_2$ inhibitors and iron-based deoxidizing inhibitors. The peak values of CO concentration were 53.6 ppm and 63.3 ppm for the container with 0.15 g of $MgCl_2$ added and the container without any reagent, respectively. For the coal sample with an added iron-based deoxidizing inhibitor, the maximum CO concentration was only 16.5 ppm. Therefore, the iron-based deoxidizing inhibitor had a greater inhibiting effect, as it was able to achieve the dual effect of oxygen consumption and resistance.
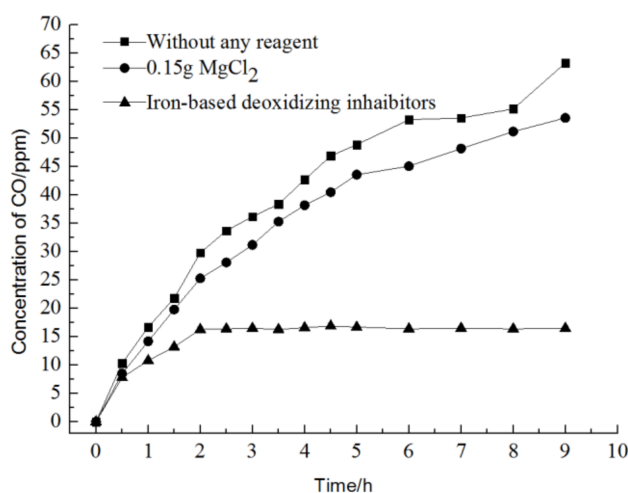
Figure 5. Variation of carbon monoxide concentration at 70 °C.

4. Conclusions

The oxygen consumption and resistance of iron-based deoxidizing inhibitors, to prevent spontaneous coal combustion, was studied via experiments and analytical calculations. The main conclusions are as follows:

(1) Although different kinds of inorganic chloride inhibitors can consume oxygen after reduced iron powder has been added, the oxygen consumption rate varies. The order of the oxygen consumption rate is $MgCl_2$ > NaCl > KCl > $CaCl_2$. Different types of conventional inhibitors are selected to be used as deoxidizing inhibitors with different oxygen consumption rates, according to the actual production needs of a particular mine.

(2) According to the theory of coordination resistance, the complexes formed from Fe^{3+} that are formed after the oxidation of the deoxidizer and coal molecules—that have side chains with N, P, and S—are more stable when compared with the corresponding Mg^{2+} coordination complexes. This shows that Fe^{3+} can better prevent the reaction of reactive groups in the coal with oxygen. However, the product of the oxidation reaction of the deoxidizer is $Fe(OH)_3$, and the solubility is

low. In order to achieve a better inhibitory effect, it is necessary to conduct further research into increasing the solubility of Fe^{3+}.

(3) In the presence of limited oxygen, and via comparative experimentation, the coal sample—to which the deoxidizing inhibitor was added—produced the least amount of CO at a constant temperature of 70 °C, indicating that the "coal–oxygen double resistance" effect is more likely to prevent spontaneous coal combustion. Similarly, under the conditions of continuous oxygen supply, it can improve resistance when compared with conventional inhibitors, provided that the deoxidizing inhibitors can reduce the oxygen content in the supply of air flow.

Author Contributions: For this paper, the design of article ideas and experimental tests was by Chaoyu Hao; Yanling Chen put forwarded study ideas with Jiren Wang and completed the data testing and wrote the paper; Cunbao Deng discussed experimental ideas with Guang Xu; Fengwei Dai completed the data analysis with Rui Si; the laboratory tests and analysis were completed by Hongfei Wang and Haoyu Wang.

Conflicts of Interest: The authors declare no conflict of interest.

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