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Research article

Experimental study on the inhibitory effect of ethylenediaminetetraacetic acid (EDTA) on coal spontaneous combustion

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A R T I C L E I N F O

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A B S T R A C T

The inorganic salts in coal contain a certain number of metal ions, among which transition metal ions can exert a certain catalytic effect on coal spontaneous combustion by reducing the activation energy of coal oxygen reaction. Therefore, the addition of metal chelating agent in coal will definitely reduce the catalytic effect of metal ions, so as to inhibit coal spontaneous combustion. In this paper, the inhibitory effect of a common metal chelating agent ethylenediaminetetraacetic acid (EDTA) on coal spontaneous combustion was studied. Four coal samples were selected in this study. First, basic data such as the types and contents of transition metal elements in coal samples were measured via X-ray fluorescence (XRF). Then, thermal analyses, infrared spectrum experiments, low-temperature oxidation experiments and crossing point temperature experiments were performed on WL coal samples before and after EDTA treatment. The experimental results show that there is no mass gain caused by oxygen adsorption in the EDTA-treated coal sample throughout the heating process. In addition, the treated coal sample exhibit a great reduction in its content of oxygen functional groups, a decrease in the concentration of gas products and a rise of the crossing point temperature, indicating that EDTA has a strong inhibitory effect on coal. The calculation of the apparent activation energy reveals that the activation energies of the inhibited coal sample were 51.18 kJ/mol and 43.42 kJ/mol in the temperature ranges of 30–70 °C and 80–180 °C, respectively, which are 7.94 kJ/mol and 8.28 kJ/mol higher than those of the raw coal. This proves that the metal chelating agent EDTA is able to inhibit coal spontaneous combustion by chelating transition metal ions to increase the activation energy. Finally, experiments were carried out to study the inhibitory effects of EDTA on different coal samples, which suggests that EDTA can exert good inhibitory effects on different coal samples.

1. Introduction

After excavation, the coal exposed to air will absorb oxygen and release heat which accumulates in the coal under appropriate conditions and accelerates the oxidation reaction process of coal, producing more energy and eventually leading to coal spontaneous combustion. The combustion not only causes waste of resources and pollution to the environment, but also acts as the ignition source in many gas explosion accidents. Thus, it is very important to prevent coal spontaneous combustion during coal mining [1–3]. Inhibitors, which are simple and convenient to use for preventing coal spontaneous combustion, are widely applied in coal mines. However, previous researches on inhibitors mainly focus on the inhibitors' physical and chemical properties such as their water absorption and moisture retention properties and their influences on the coal spontaneous combustion are rarely studied, leaving defects of low inhibitory efficiency and short inhibitory time [4–7]. Hence, it becomes particularly important to make an in-depth study on an efficient inhibitor that can suppress coal spontaneous combustion from the perspective of coal's self-ignition factors.

The internal factors causing the occurrence of coal spontaneous combustion include the physical and chemical properties, lithofacies distribution and mineral composition of coal [8–11]. Mineral inorganic salts in coal contain abundant metal ions that can pose different influences on the combustion. As we know, the spontaneous combustion tendency of coal increases with the increase of pyrite content, and the $Fe^{2+/3+}$ can remarkably promote the combustion. On the contrary, NaCl, $CaCl_2$ and $MgCl_2$ can be used as inhibitors to retard the spontaneous combustion of coal in goaf. Na^+, Ca^{2+} and Mg^{2+} in these substances can exert a certain inhibitory effects on the combustion. Relevant scholars have conducted in-depth researches on different effects of metal ions on coal spontaneous combustion, as well as their corresponding mechanisms. Wang [12], who studied the inhibition

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mechanism of Ca^{2+} on coal spontaneous combustion based on the theory of quantum chemistry, revealed that nitrogen, phosphorus, sulfur, oxygen and other active groups contained in coal formed coordination chemical bonds and ligands with metal Ca^{2+}, thus lowering the activity of active groups to react with oxygen. Tang [13] proved that manganese ions could accelerate coal spontaneous combustion by studying the effects of three kinds of manganese salts on the combustion; meanwhile, he found via infrared spectroscopy that manganese ions could promote the decomposition of C—O and alkyl, and obtained via a thermal analysis instrument that manganese could promote the oxidative decomposition to release more heat; moreover, he also pointed out the possible mechanism for its catalysis on the coal oxidation. After studying the process in which different metal ions accelerated the oxidation of Shenfu coal sample, Jiang [14] revealed that rare metal ions Co^{2+}, Ni^{2+} and La^{3+} had a more prominent catalytic effect on oxidation by analyzing the product structure via infrared spectroscopy. Azik et al. [15] found that during the process of oxidation, iron (II) sulfate was formed in 24 h; aliphatic CH_2 and CH_3 groups barely changed during the formation of iron (II) sulfate; then, after the formation, aliphatic CH_2 and CH_3 groups started to oxidize. The above studies show that metal ions (such as Ca^{2+} and Mg^{2+}) in the halide salt can inhibit coal spontaneous combustion to some extent, while transition metal ions (such as Fe^{2+},Co^{2+} and Ni^{2+}) can promote the occurrence of coal spontaneous combustion to a large extent. People often prevent coal spontaneous combustion by adding halide salts in production applications, yet there are very few researches on the prevention of coal spontaneous combustion by means of suppressing metal catalysis. Many oxidation processes take place when metal ions participate in the transfer of electrons during the change of the valence state to shorten the chain initiation period. Therefore, the occurrence of coal spontaneous combustion will be restrained to some extent, if the transition metal ions with a catalytic effect can be reduced and the activation energy of coal oxidation can be increased.

EDTA, as a very strong metal ion chelating agent, can combine with metal ions in the form of coordination bond to form stable six-membered ring chelates, thus inactivating metal ions and raising the activation energy of organic oxidation. This property of metal chelating agents is widely used in the remediation of heavy metal in soils and the extraction of heavy metals in plant waste streams [16–19]. In the food-processing industry, it is used to stop metal ions from catalyzing the oxidative deterioration of food [20–22]. In industries of polymer products like rubber, it is applied to the prevention of occurrence of catalytic aging for maintaining the service life and performance. In the medicine field, it is used as anticoagulant to inactivate calcium ions, so that blood can be stopped from coagulating [23]. Nevertheless, the application of EDTA in coal industry is very limited, as it is used for the titration of metal ion to determine the contents of constant metallic ions in coal.

In this paper, a highly effective inhibitor for coal spontaneous combustion control was studied from the perspective of inactivating transition metal ions. A new idea of inactivating metal ions in coal and increasing activation energy of coal oxidation was proposed considering internal factors that affect coal spontaneous combustion instead of just the nature of inhibitor. The transition metal elements and their contents in coal, the mass and heat release of coal before and after the inhibition, the gas composition and changes of functional groups on coal surface at different temperatures were tested and analyzed using techniques such as XRF, thermal analysis, infrared spectroscopy and gas chromatography. In addition, the apparent activation energy of coal oxidation was calculated.

Table 1
Proximate and metamorphic degree of the coal samples.

Coal samples	Industrial analysis				Metamorphic degree
	M_{ad}/%	A_{ad}/%	V_{ad}/%	FC_{ad}/%	
WL-coal	10.37	13.26	35.56	40.81	Sub-bituminous
BLT-coal	7.31	5.52	37.42	49.75	Sub-bituminous
DFS-coal	6.35	7.74	29.65	56.26	Bituminous
KZD-coal	1.94	13.21	24.56	60.29	Bituminous

2. Experimental

2.1. Coal sample and low-temperature oxidation experimental device

2.1.1. Preparation of coal samples

Four kinds of coal samples were selected for the experiment, namely Wu Lan coal sample, Bu Lianta coal sample, Kou Zidong coal sample and Da Fosi coal sample. The proximate and metamorphic degree of the coal samples are shown in Table 1. The newly exposed coal samples were vacuum-sealed underground and then brought to the laboratory, after which they were crushed in the protective atmosphere of nitrogen and sieved to a particle size range of 0.180–0.380 mm. After 30 g of EDTA water solution with a mass fraction of 10% was prepared, 50 g of coal sample was separately added into it and stirred evenly for inhibitory immersion of 48 h. Then, the samples were dried in a vacuum drying box at 40 °C. The comparative tests were carried out by adding distilled water of the same mass. An obvious knot phenomenon appeared after the treatment of coal samples.

2.1.2. Determination of transition metal ions in coal

The transition metal elements in coal can promote its spontaneous combustion. In this experiment tested, the composition and contents of chemical elements in coal was tested on the X-Ray Fluorite Spectroscopy S8 Tiger instrument produced by Bruker Company, Germany, so as to describe the possible transition metal elements and their contents in coal. First, the four coal samples were subjected to ashing treatment in a muffle furnace and the ash samples were ground to below 74 μm. Next, it was made into a 6 cm^3 flake for the test and analysis. The contents of transition metal elements in coal ash are listed in Table 2.

2.1.3. Diagram of the low-temperature oxidation experimental device

The low-temperature oxidation experimental device consists of a programmed temperature device and a chromatographic analysis device (see Fig. 1). The programmed temperature device is a 2000-type temperature oven for coal spontaneous combustion. The chromatographic analysis device, a FULI9790 chromatographic analyzer made in China, includes three channels and can simultaneously analyze the concentrations of gases such as CO, C_2H_4, CO_2 and O_2 at the outlet. When the margins of error of gas concentration both lie within 0.5% for

Table 2
Contents of transition metal elements in coal samples.

Element	Z	Content (ppm)			
		WL	BLT	DFS	KZD
Sc	21	7.3	8.1	12.1	7.2
Ti	22	117.0	159.2	312.1	208.2
Mn	25	83.7	285.9	158.2	88.9
Fe	26	885.6	4383.2	9256.6	7809.7
Co	27	9.3	11.3	22.4	7.7
Ni	28	11.8	21.2	10.5	8.9
Cu	29	17.2	7.6	8.2	22.2
Zn	30	26.8	16.5	11.1	18.5
Zr	40	134.0	65.2	24.1	38.8