



## Full Length Article

# A chelated calcium-procyanidine-attapulgitite composite inhibitor for the suppression of coal oxidation



Xiaoxing Zhong, Botao Qin\*, Guolan Dou\*, Chen Xia, Feng Wang

Key Laboratory of Gas and Fire Control for Coal Mines (China University of Mining and Technology), Ministry of Education, Xuzhou 221116, China  
School of Safety Engineering, China University of Mining & Technology, Xuzhou 221116, China

## ARTICLE INFO

## Keywords:

Coal oxidation  
Chelated inhibitor  
Radical scavenging activity  
Keep coal hydrated

## ABSTRACT

In this study, the impact of chelated calcium-procyanidine-attapulgitite composite inhibitor on coal oxidation process is studied. The hydroxyl and superoxide anion radical scavenging activity for procyanidine-calcium chloride complexes was measured, and the result show that the complex with ligand-to-calcium ion ratio 1:5 has the highest radical clearing activity. Due to the water adsorption quality of  $\text{CaCl}_2$ , the thermal analysis of samples with/without procyanidine-calcium chloride complexes indicated that the complex can slow down the coal oxidation well and the best ratio of procyanidine and  $\text{CaCl}_2$  should be determined at 1:7. Then the water retention capacity of procyanidine,  $\text{CaCl}_2$ , ATP and composite inhibitors were compared, and the result indicated that ATP can improve the water retention of the composite inhibitor, so ATP as introduced into the composite inhibitor, and the optimal ratio of chelated inhibitor and ATP was determined as 1:5 by TG-DSC curves. Therefore, a chelated calcium-procyanidine-attapulgitite composite inhibitor was chosen as an additive to suppress coal oxidation. The measurements of CPT, oxygen consumption during low temperature oxidation and CO emissions all demonstrated that the addition of the composite inhibitor to coal samples has an obvious suppression effect on the oxidation process. The *in situ* FTIR spectra of coal samples during the oxidation process show that the coal oxidation slows down due to the addition of chelated calcium-procyanidine-attapulgitite composite inhibitor by eliminating free radicals and keeping the coal hydrated.

## 1. Introduction

Spontaneous combustion of coal has become an increasingly serious worry during the coal mining and storage [1–3]. It can result in serious accidents and financial losses for the storage and transportation of coal [4–8]. Adding inhibitors is one way of preventing spontaneous combustion of coal [9–11]. To date, halogen salts (such as  $\text{NaCl}$ ,  $\text{MgCl}_2$  and  $\text{CaCl}_2$ ), three-phase foam, and polymers have been widely used in coal mines for the prevention and extinguishing of fires. They can absorb water or hinder access of oxygen to the coal surface, so their suppression is physical. [12–16]. However, these inhibitors always exhibit low efficiencies and short active lifetimes. Therefore, more and more researchers began to study chemical inhibitors. For example, Wang [17] proposed to use ionic liquids to inhibit the coal spontaneous combustion, and found [Bmim][OTf] and [Bmim][AC] make better effect in depressing the oxidation of bituminous coal. Zhan [18] examined the impact of  $\text{Na}_3\text{PO}_4$  on coal oxidation, the results show that the addition of  $\text{Na}_3\text{PO}_4$  to coal mainly influences the routes for the decomposition of hydroxyl by promoting its conversion into ether linkages, and

subsequently improving the coal thermal stability. Watanabe [11] examined the effect of  $\text{Cu}(\text{Ac})_2$ , and found the effect on low-temperature oxidation is chemical in nature. These chemical inhibitors are highly efficient, although some are expensive or not applicable to all types of coal. Therefore, the development of new inhibitors that are economic and highly efficient is desirable. Moreover, it is useful to investigate the potential of composite inhibitors that may overcome the disadvantages of individual inhibitors discussed above.

As we all know, procyanidine (PA) is an antioxidant, which is present in fruits, seeds, leaves, flowers and bark of many plants [19]. Many studies report that procyanidins can scavenge several forms of free radicals such as superoxide anion, hydroxyl and alkyl peroxy radicals [20]. Attapulgitite clay (ATP) is abundant in nature, and is very cheap. Moreover, ATP is present in a kind of hydrous magnesium-aluminum silicate mineral, which has rich pores and surface group [21,22]. Therefore, it has been widely used as colloidal agents, reinforcing fillers, sealing materials, versatile carriers and adsorbent. This work investigates a composite inhibitor for coal spontaneous combustion which consists of procyanidine, calcium chloride and attapulgitite.

\* Corresponding author.

E-mail address: [gldou@cumt.edu.cn](mailto:gldou@cumt.edu.cn) (G. Dou).

**Table 1**  
Properties of the coal samples.

Coal	Proximate analysis (dry ash free basis)(%)					Ultimate analysis (air dried basis)(%)				Heating (kJ g <sup>-1</sup> ) Q <sub>net, ad</sub>
	M <sub>ad</sub>	A <sub>ad</sub>	V <sub>ad</sub>	FC <sub>ad</sub>	C	H	N	S	O	
ZD	15.92	6.61	20.68	56.79	73.97	3.82	1.37	0.44	20.38	23.30
SD	6.36	4.20	32.04	57.40	78.73	4.54	1.03	0.09	15.61	29.28
PS	6.60	5.79	33.21	54.40	76.88	3.32	0.61	0.35	18.84	21.93

## 2. Material and methods

### 2.1. Experimental reagents and coal samples

The majority of reagents used (including procyanidine (PA) at a purity of 99%, calcium chloride (CaCl<sub>2</sub>, A.R. grade), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, A.R. grade), sodium bicarbonate (NaHCO<sub>3</sub>, A.R. grade), cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>, A.R. grade), pyrogallol (A.R. grade), hydrochloric acid (HCl, A.R. grade), and tri-methylolaminomethane (A.R. grade) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, A.R. grade) were purchased from a local medical station. Attapulgite clay (ATP) is taken from Wuxi, Jiangsu, China.

Coal samples were collected from the Zhundong (ZD) Colliery in Xinjiang Province, the Shendong (SD) Colliery in the Nei Monggol Autonomous Region and the Pingshuo (PS) Colliery in Shanxi Province. During sample preparation, lumps of these coal samples were milled and sieved with fragments in the 0.25–0.80 mm range used for the experimental investigations. Table 1 summarizes the basic characteristics of these coals. All the coal samples were dried at 105 °C in N<sub>2</sub> for 1 h.

### 2.2. Hydroxyl radical scavenging activity

The hydroxyl radical scavenging activity was measured according to the methods of Guo et al. [23] with some modifications. About 2 mL Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> buffer solution (pH = 9.2), 1 mL Co(NO<sub>3</sub>)<sub>2</sub> solution (0.00050 mol/L), 1 mL Nit-R salt (0.00156 mol/L) and 1 mL H<sub>2</sub>O<sub>2</sub> with volume fraction 0.1% were mixed and increased to 10 mL with distilled water. The solution was then added to the test tubes and left at 40 °C for 50 min. Then the absorbance of the mixture was measured at 484 nm by using a UV spectrophotometer and recorded as A<sub>s</sub>. The corresponding blank experiments were taken and the capability to scavenge hydroxyl radical was recorded as A<sub>0</sub>. The percentage of hydroxyl radical scavenging activity was calculated by using the following equation.

$$\text{Hydroxyl radical activity(\%)} = A_s/A_0 \times 100$$

### 2.3. Superoxide anion radical scavenging activity

The superoxide anion radical scavenging activity was measured according to the methods of Guo et al. [23] with some modifications. About 5 mL Tris-HCl buffer solution (pH = 8.2), 30 μL pyrogallol and 1 mL test sample solution were mixed and increased to 10 mL with distilled water was added to the test tubes. Then Tris-HCl buffer solution was used as reference, and the absorbance of the mixture was measured at 325 nm per 30 s in 6 min by using a UV spectrophotometer. The linear variation in absorbance and time was obtained, and the slope was auto-oxidation rate and was recorded as v. The corresponding blank experiments were taken and auto-oxidation rate was recorded as v<sub>0</sub>. The percentage of hydroxyl radical scavenging activity was calculated by using the following equation.

$$\text{Superoxide anion radical activity(\%)} = (v_0 - v)/v_0 \times 100\%$$

### 2.4. Simultaneous TG-DSC measurement

Simultaneous TG-DSC measurement (TA-Q600) was used to evaluate the oxidation behaviors of the raw coal and inhibitor treated coals. A sample of 5–10 mg in mass was quickly and loosely placed on the aluminum crucible. The sample temperatures were raised from room temperature to 800 °C at 2 K/min. 21% oxygen was flowed as the reaction gas, and the flow rate of the air purging into the furnace was set as 100 mL/min.

### 2.5. FT-IR experiment

In situ FTIR was employed to determine changes in the samples' functional groups with a KBr powder background used as a reference. Samples were dried overnight at 105 °C under N<sub>2</sub> for 1 h. Then, during analysis, the sample was placed into the reaction chamber, the dome was installed and dry air was introduced to the chamber from its base (below the coal sample), exiting from the top. The reaction chamber was heated to 220 °C at 1 °C/min. For the exhaust gases, the region from 650 to 4000 cm<sup>-1</sup> was scanned using a 4 cm<sup>-1</sup> resolution. To identify the more active surface aliphatic and oxygen-containing compounds, the Beer-Lambert principle was employed to assess changes over time. Each spectrum composed the summation of 64 scans using a Kubelka-Munk conversion. The spectra were acquired at 30-s intervals and four spectra were collected in series for each coal sample under the same environmental conditions.

### 2.6. Cross point temperature (CPT), oxygen consumption and evolution of CO with increasing temperature

CPT values were measured by an experimental apparatus of our own design consisting of a spontaneous combustion simulation system and a temperature data acquisition system. For each test, 50 g of sample was positioned in the apparatus reactor in such a way as to ensure that there was sufficient airflow within the sample. Dry air with an oxygen concentration of 20.96% was then passed through the sample for half an hour to stabilize the test specimen while the reactor was heated to a predetermined initial temperature. The temperature of the reactor was then set to increase by 0.8 °C/min while dry air was entered the reactor at 8 mL/min until 70 °C, and then switched to 96 mL/min at least for 160 min. During this process, the temperatures of the reactor and the sample were recorded. Because the emission of CO and CO<sub>2</sub> from coal is temperature-dependent, monitoring the evolution of these gases is recognized as an effective means of tracking or predicting the onset of self-heating. Meanwhile therefore, exhaust gases from the reactor outlet were analyzed for CO content by gas chromatography at 10 °C intervals, beginning at 40 °C.

The same apparatus used to measure CO content was also employed to measure the consumption of oxygen by the samples between 40 and 70 °C. Here, the enclosure was set to a constant temperature of 40 °C while dry air entered the reactor at 50 mL/min for 30 min. The temperature was increased at 0.8 °C/min and the flow of air was decreased to 8 mL/min. The oxygen concentration of the gas exiting the reactor outlet was sampled and analyzed when the temperature reached 70 °C. Oxygen consumption at 70 °C was then calculated based on the

Download English Version:

<https://daneshyari.com/en/article/6632091>

Download Persian Version:

<https://daneshyari.com/article/6632091>

[Daneshyari.com](https://daneshyari.com)