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# Phosphorus and Manganese Effect on Oxygen-Consumption of Coal Spontaneous Combustion

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Effects of two kinds of trace elements (manganese and phosphorus) on coal spontaneous combustion are investigated in this paper. The oxygen-consumptions in oxidization of coal samples with reagents are measured. The experimental results suggest that the reagents of manganese can catalyze the coal spontaneous combustion, whereas phosphorus can inhibit the reactions. Moreover, the impact of these promoting and inhibiting regents was strengthened with an increase in the additive loading. This phenomenon can be explained by mechanism of free radical reactions to some extent.

**Key Words: Phosphorus, Manganese, Coal spontaneous combustion, Oxygen-consumption.**

## INTRODUCTION

Ninety-four percent of mine fire is spontaneous mine fire according to the statistics from the year 1953-1984[1]. Spontaneous combustion causes serious problems in coal mine and related industries[2]. Therefore, it is significant to evaluate the potential of spontaneous combustion for preventing fire disasters. Currently, most of the researchers put forward some theories about coal spontaneous combustion[3,4], such as the theory of pyrite is well known.

The composition of coal is extremely complex for it not only contains the major elements (C, H, N, O), but also contains over 80 kinds of trace elements. These trace elements are possibly impact the properties and processes of coal spontaneous combustion. Cole *et al.*[5] reported that the coal which is rich in pyrite is easier to spontaneous combustion because of the presence of $Fe^{2+}$ ions in the pyrite can accelerate the oxidation of coal. The mentioned reaction mechanism has studied explicitly, whereas the other trace elements effect on spontaneous combustion of coal are still not studied.

The manganese, content of 4-100 μg/g and average in 47 μg/g, is prevalent present in the coal of Chinese mine area[6]. The content of 8619 μg/g manganese was detected in Haizhou coal mine, located in Liaoning province, which has serious coal spontaneous combustion problem. This hazard may relate with the high content of manganese in this coalfield. In addition, the manganese content in coal which is liable to spontaneous combustion is generally higher than in the coal that difficult to spontaneous combustion. Such as manganese content in coal of Shendong and Caili mine area (both suffer severe spontaneous combustion disasters) is higher than that in coal of Huaibei mine area (rarely suffer spontaneous combustion disaster)[7]. Diantou mine area, located in Ordos Basin, phosphorus content up to 6360 μg/g in coal seam, has not occurred spontaneous combustion disasters yet. However, Yuheng mine area, also located in Ordos Basin, phosphorus content as low as 10-470 μg/g in coal seam, is suffered serious spontaneous combustion spontaneous disaster[8]. For these mentioned examples, it is necessary to study the influence on coal spontaneous combustion by manganese and phosphorus.

The initial stage of coal spontaneous combustion can attribute to the radical-reactions[9-11]. As we know, many elements have catalytic or inhibitory effect on free radical reactions. Meanwhile, some elements will be directly involved in the reaction. It is significant to study which element can promote or inhibit the spontaneous combustion of coal. Oxygen-consumption is one of indicators which can indicate the reaction characteristics of coal spontaneous combustion. In this paper, the oxygen-consumptions of coal with different elements are measured. Furthermore, the effects of various elements on coal spontaneous combustion are analyzed.

## EXPERIMENTAL

The characteristics of coal spontaneous combustion are directly related to the oxygen-consumption. For the same kind of coal, the spontaneous combustion tendency of the coal is increasing with the oxygen-consumption going up. Five kinds of chemical reagents were added to the coal samples (from Jinshan coal mine) in order to test the impact of trace elements on spontaneous combustion of coal. Reagents of two kinds of

elements (manganese and phosphorus) were added into the coal sample (0.180-0.420 mm). Each 100 g coal sample was added 0.02 mol reagent for experiment.

The reagents were dissolved by 7 mL deionized water to uniform mixed reagents with coal. Reagent solution was added to the coal samples with stirring. Kept the mixture closed for 24 h to make sure the reagents were full combination with coal. Then the oxygen-consumption experiments were carried out after the mixture of coal sample and reagent dried 10 h (40 ºC) under the nitrogen atmosphere.

The coal sample mixed with reagent was put into the sample tank, with the experimental temperature from 30-200 ºC, and the oxygen concentration was tested after the oxidation of coal. The oxygen-consumption in oxidization of drying coal sample with 7 mL deionized water was tested by same experimental condition for experimental comparison.

The SP501N gas chromatograph and 5A molecular sieve were adopted for testing oxygen concentration. Controlling by the mass flow regulate facility, the dry air flow through the sample tank was 20 mL/min. The experimental set-up is shown in Fig. 1.

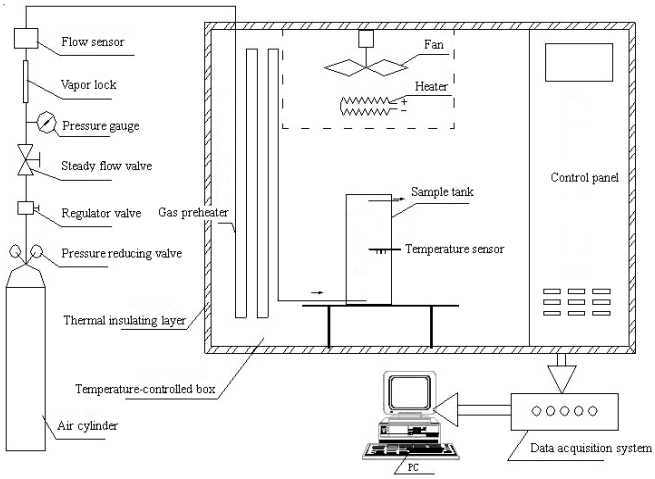
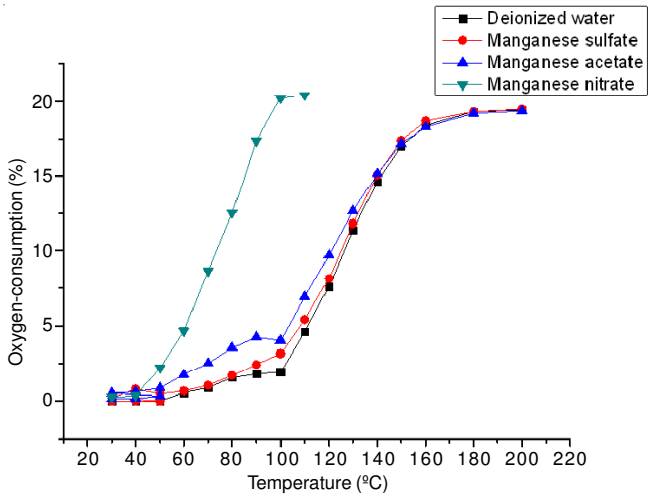



Fig. 1. Experimental set-up

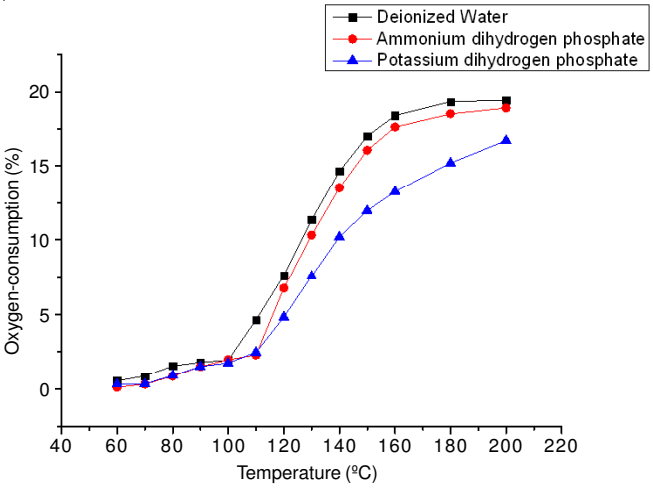
## RESULTS AND DISCUSSION

Fig. 2(a) shows the oxygen-consumption curve of oxidation for coal samples with manganese at different temperatures. General speaking, the oxygen-consumption of oxidation for coal added manganese is more than raw coal. The oxygen-consumption increased slightly between 80 to 120 ºC when the coal sample added manganese sulphate. From room temperature to 150 ºC, especially before 100 ºC, oxygen-consumption increased more obvious while added the manganese acetate in coal sample. The way that add manganese nitrate into coal sample will introduce the fastest speed of oxygen-consumption which before 100 ºC all the oxygen have almost exhaust. Obviously, inorganic manganese or organic manganese can play a catalytic role in the low-temperature oxidation stage of coal.

Fig. 2(b) describes that oxygen-consumption curve of coal samples added phosphorus at different temperatures. Two reagents contained phosphorus element can reduce the oxygen-consumption of coal, whereas potassium dihydrogen phosphate




(a) Manganese




(b) Phosphorus

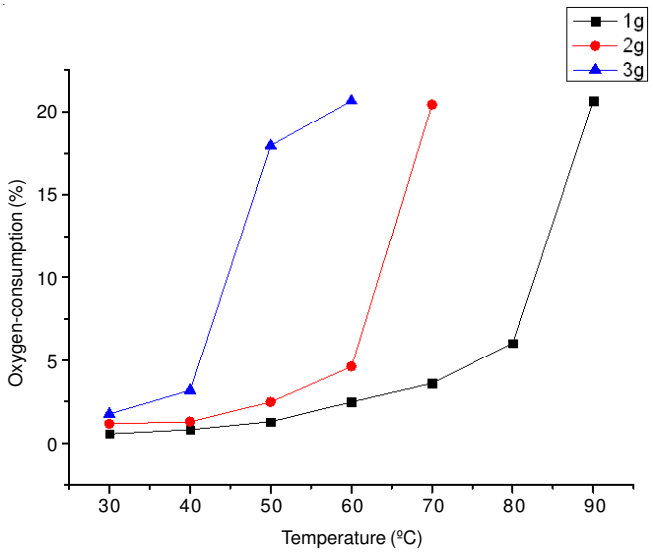
Fig. 2. Oxygen-consumption of coal with manganese and phosphorus additives

has more significant impact. We could learn that the phosphorus element is a disincentive in the coal oxidation process.

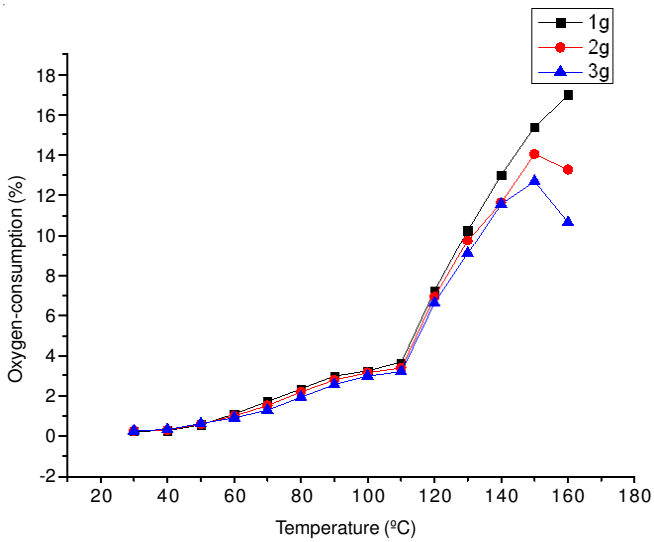
The doses of manganese and phosphorus influence on the coal consumption of oxygen are experimented. The manganese nitrate and potassium dihydrogen phosphate used in this experiment for the effects of these regents on the oxygen-consumption of coal sample are the most obvious.

It can be seen from Fig. 3 that the volume of reagent also impact oxygen-consumption of coal samples. The promoting or inhibiting effects of the reagents are growing with the dosage increasing. The oxygen is depleted at the 90 and 60 ºC in the experiment when add 1 and 3 g manganese nitrate respectively in coal sample. The similar trend is showed in the experiment for potassium dihydrogen phosphate, especially the oxygen-consumption started to decrease till 150 ºC, which indicates that the reagents of phosphorus can effect inhibit coal spontaneous combustion.

**Theories:** Many transition metals act as a catalyst in organic reactions, such as ferrous ions can catalyze the hydrogen peroxide to produce hydroxyl radicals[12]. The catalysis of cobalt ions also allows the C-H structure breaks to generate free radicals[13]. Sometimes, trace amounts of metal




(a) Manganese nitrate




(b) Potassium dihydrogen phosphate

Fig. 3. Oxygen-consumption of coal with manganese nitrate and potassium dihydrogen phosphate in different content

ion have significant catalysis[14]. With similar position in the periodic table, the manganese and iron should have the similar nature.

The nature of metal-catalytic-oxidation is free radical reactions. For transition metals exist multiple valence states, the process of metal valence state change plays the role of electron transfer. The presence of manganese can accelerate the generation of $^{\bullet}OH$ radical. The reactions are as follow:

$$Mn^{2+} + H_2O_2 \rightarrow 2Mn^{3+} + {}^{\bullet}OH + OH^-$$

$^{\bullet}OH$ and $Mn^{3+}$ can further react with the organic structure of coal:

$$R\text{-}H + Mn^{3+} \rightarrow R^{\bullet} + Mn^{2+} + H^+$$

$$R\text{-}H + {}^{\bullet}OH \rightarrow H_2O + R^{\bullet}$$

with presence of oxygen, the reaction of $R^{\bullet}$ radicals generate peroxide for the oxidation reaction.

$$ROOH + Mn^{2+} \rightarrow RO^{\bullet} + Mn^{3+} + OH^-$$

$$ROOH + Mn^{3+} \rightarrow ROO^{\bullet} + Mn^{2+} + H^+$$

$$2ROOH \rightarrow RO^{\bullet} + ROO^{\bullet} + H_2O$$

We can see that the manganese element may play the initiator role in the spontaneous combustion of coal from the mentioned reactions.

A lot of substance contained phosphorus can be used as the flame retardant. Meanwhile, the mechanism of this kind of flame retardant depends on the type of phosphorus compounds, the chemical structure of the polymer and combustion conditions[15]. In general, the detail react theory for phosphorus-contained flame retardant are as follow:

$$H_3PO_4 \rightarrow HPO_2 + HPO + PO^{\bullet}$$

$$H^{\bullet} + PO^{\bullet} \rightarrow HPO$$

$$HPO + H^{\bullet} \rightarrow H_2 + PO^{\bullet}$$

$$PO^{\bullet} + OH \rightarrow HPO + O^{\bullet}$$

$$OH^{\bullet} + H_2 + PO^{\bullet} \rightarrow HPO + H_2O$$

The phosphorus is particularly effective as the flame retardants when the $H^{\bullet} + O_2 \rightarrow OH + O^{\bullet}$ take place in the reaction. The phosphorus can play the flame retardants role only at high temperature condition.

## Conclusion

It is necessary to study the effect of trace elements on coal spontaneous combustion for there are multiple elements can be detected in coal and the abundance of various trace elements in coal is varied. Based on the free radical reactions theoretical, the reaction mechanisms of phosphorus and manganese on coal oxidation are analyzed. In summary, the manganese play a catalytic role in the process of coal oxidization since 40 ºC, whereas the phosphorus element was inhibited the spontaneous combustion of coal after 150 ºC. Other elements effect on coal spontaneous combustion needs further research.

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