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Impact of Sodium and Magnesium on Low-Temperature Oxidation of Coal

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Apart from the elements like C, H, O and N, other mineral elements are also found in the composition of coal, which influence the low-temperature oxidation of coal. Five kinds of inorganic additive (Na and Mg) were added into the coal samples for the programmed-heating experiments. Then the O_2 consumption, CO_2 and CO generation were tested. Interfering by the magnesium or sodium reagent, the concentration on O_2 consuming, CO_2 and CO producing for the treated coal all decreased evidently. Furthermore, some inorganic minerals can react with coal molecules and form stable structure, which resulting in the suppression in the oxidation of coal.

Keywords: Coal, Sodium, Magnesium, Low-temperature oxidation.

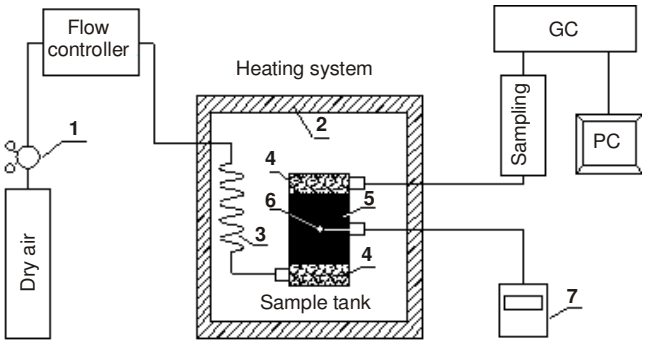
INTRODUCTION

Spontaneous combustion of coal is the major natural disaster in Chinese collieries. According to incomplete statistics, over 60 % of state-owned coal mines have hazards on coal self-ignite and annual economic losses reach up to several million dollars[1-2]. Coal, a kind of polymers, includes many elements, such as carbon, hydrogen, oxygen, nitrogen and sulfur *etc*,. Various organic and inorganic components, like clay, sulfides, sulfates, carbonates, chlorides, silicates, oxides, influence the characteristics of coal together[3,4]. Spontaneous combustion of coal is an extremely complex process with dynamic changes and inorganic mineral in coal is likely to affect its properties and processes, for example, the pyrite Fe^{2+} ions can accelerate the oxidation of coal[5-7]. Many elements can act as a catalyst or inhibit in free radical reactions, some elements even be directly involved in the reaction. Minerals can be used to evaluate the use of coal in a different process behavior, including control of fly ash, cinder and other combustion by-products[8-10].

It is necessary to further examine which elements or inorganic minerals play the significant role in coal spontaneous combustion and which act as a disincentive. Oxygen consumption, CO and CO_2 generation can be used to evaluate the oxidizing intensity in the low-temperature oxidation of coal. How these elements impact the self-ignite of coal not only helps to estimate the combustibility of coal, but also supplies a new way for the inhibition of spontaneous combustion.

EXPERIMENTAL

The coal from seam 3# (Xutuan colliery) was used as the experimental sample. Taking into account the non-homogeneous property of coal, coal with small particles were selected and crushed in order to avoid interference in the test results. The reagent solution was added to the coal samples and prolonged agitation and then sealed 24 h to make it fully mixed with coal. Before experiment, all coal samples were dried in vacuum for 12 h. Each 40 g coal (0.125-0.180 mm) with 0.4 g inorganic sodium or magnesium were prepared as the experimental sample. Besides, coal sample only with deionized water also used in the comparative experiment. Controlling remains a heating rate at 1.2 °C/min for ensuring the heating uniform and slow. Experimental setup is shown in Fig. 1, which includes



1-Valve, 2-Insulated furnace, 3-Preheat pipe, 4-Tank cover, 5-coal sample, 6-Sensor, 7-Temperature display

Fig. 1. Diagram of temperature-programmable experimental device

three parts *i.e.*, the air supply system, programmed heating system and the gaseous products analysis system.

RESULTS AND DISCUSSION

With increasing temperature, the oxygen consumption increased and the oxygen concentration gradually decreased due to the chemical reaction between oxygen and coal. Because the heating rate during the heating process is slower, the temperature inside the sample tank can be considered as equal. As the oxygen content in the entrance of experimental setup is 21 % (mass fraction), the average oxygen consumption rate (unit volume) is:

$$V(T) = -\frac{dC}{d\tau} = -\frac{dC}{dx/u} = -\frac{dC}{dx}\cdot\frac{Q}{S}$$

where, V(T) is oxygen consumption rate [T, mol/(cm^3 s)] at temperature; C is mass fraction of oxygen; τ is time, s; u is air flow rate (cm/s) in the sample tank; x is the distance (cm) of any point (within the sample tank) away from the tank inlet (cm); Q is supplied air volume (cm^3/s); S is the sectional area (cm^2) of sample tank.

According to the chemical kinetics and chemical equilibrium, the oxygen consumption rate is proportional to the mass fraction of oxygen. Therefore, the oxygen consumption rate in fresh air is:

$$V_0(T) = \frac{C_0}{C}V(T)$$

where,$V_0(T)V(T)$ is average oxygen consumption rate in fresh air; C_0 is mass fraction of oxygen in fresh air, C_0 = 21 %.

$$V_0(T) = \frac{Q\cdot C_0}{S\cdot L}\cdot \ln\frac{C_1}{C_2}$$

where, C_1 and C_2 is the mass fraction of oxygen at the inlet and outlet of sample tank, separately, C_1 = 21 %; L is the height of coal sample in the tank.

On the basis of experimental data, the oxygen consumption for coal samples in the low-temperature oxidation process is shown in Fig. 2. Generally speaking, the oxygen consumption of coal decreases after the loading of all three inorganic sodium. For the sodium phosphate, this additive do not play a prohibitive role until the temperature reach 423 K. By contrast, the sodium chloride shows a obvious effect during the temperature range of 393 to 453 K. The performance of sodium sulfate is particularly outstanding, which keep the oxygen consumption not more than 2 % in the whole process. Both magnesium chloride and magnesium sulfate play a remarkable inhibitory effect in the low temperature oxidation of coal. After the treatment magnesium, even at 453 K, the reducing oxygen concentration remains around 2 %.

Figs. 3 and 4 show the curve of CO_2 and CO generation at different temperature. After adding inorganic sodium, the CO_2 and CO producing of coal lower than the data of raw coal. According to the CO_2 and CO data, the sodium chloride and sodium phosphate start to significantly inhibit low temperature oxidation of coal since 393 and 423 K, respectively. However, even when the temperature reach to the 453 K, the sodium sulfate still can make sure the yield of CO_2 and CO below 4100 and 1000 ppm, respectively. Obviously, the dium chloride and sodium

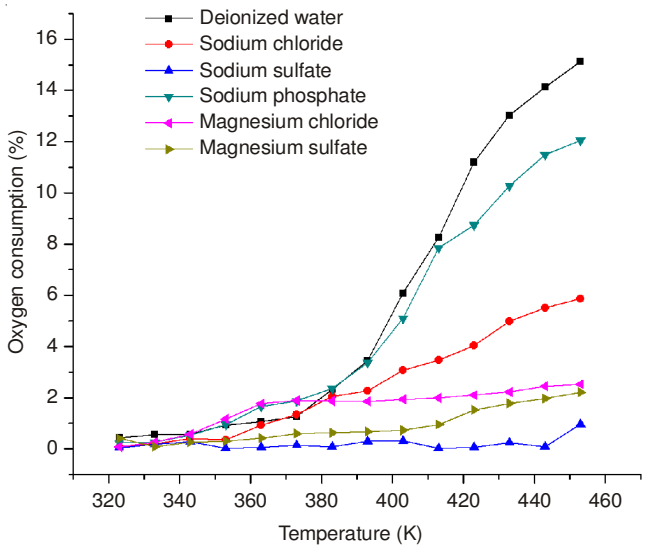


Fig. 2. Changes in the oxygen consumption of coal samples

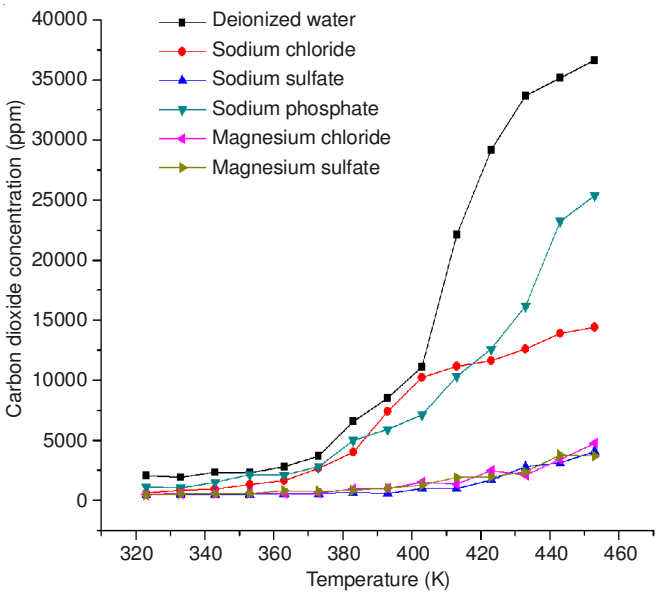


Fig. 3. CO_2 generation of coal samples

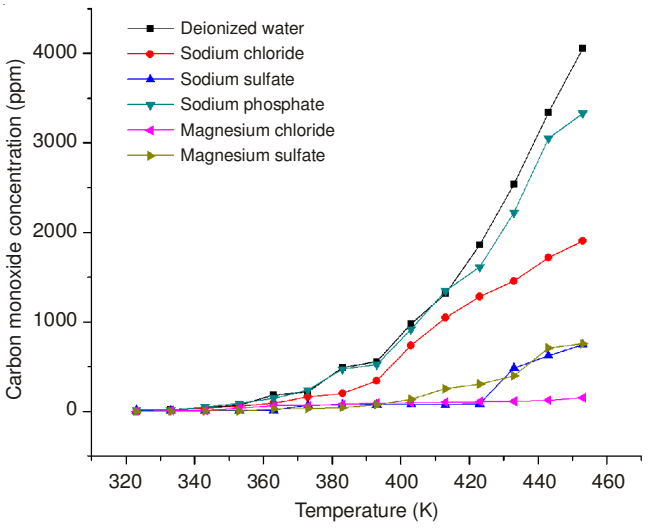


Fig. 4. CO generation of coal samples

sulfate start to work at early stage of the low-temperature process, while the sodium phosphate become effective till the temperature up to 453 K. It is noteworthy that both magnesium chloride and magnesium sulfate remarkably suppress the CO_2 and CO production in the spontaneous combustion of coal. Addition of magnesium chloride or magnesium sulfate can control the CO yield of coal less than 4800 ppm. In comparison, the CO_2 generation is limited within 154 and 755 ppm, respectively.

In the chemical reaction of coal-oxidation, the reaction proceeds mainly determined by the activation energy and probability of effective collision between the molecules. When the sodium and magnesium exist in the coal, the inorganic salts and active substances mutual attract each other and destroy the free force field in coal surface. Thereby the oxygen atom return to the molecular state, which improve the activation energy of oxygen, also reduces the opportunities of effective collision between reactant molecules. Further, the inorganic salts and molecular coal may occur substitution and complexation to form a stable structure, which suppress the rupture rate of bonds in coal molecule, thereby inhibit or slow down the reaction rate of oxygen and active groups in coal surface. Using magnesium chloride as the example, the chemical reaction equations are as follows[11]:

$$R\text{-}O\text{-}O^{\bullet} + MgCl_2 + H_2O \longrightarrow ROCl + Mg(OH)_2 + HCl$$

$$R\text{-}O\text{-}O^{\bullet} + HCl \longrightarrow ROCl + {}^{\bullet}OH$$

In addition, some scholars put forward new ideas, they state that the coal molecule is a polydentate ligand with multiple ligand atoms (N atoms). Through the reaction with metal ions like the Na^+ and Mg^{2+}, the active side chains in coal molecule mutually chelate and form stable ring structures. As a result, the chemisorption of oxygen becomes more difficult and the active of whole coal molecule decrease significantly.

Conclusion

In this paper, the temperature-heating methods and gas chromatograph detecting were used for studying the inorganic sodium and magnesium impacting on spontaneous combustion of coal. According to the data of gaseous products, both inorganic sodium and magnesium can hinder the low-temperature oxidation of coal effectively, while the magnesium usually has better effect than the sodium. In addition, after the loading of these reagents, the formation of stable ring structure may be the main reason for the decreased activity in the coal surface.

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REFERENCES

1. Z. Shi, J. Deng, X.F. Wang and Z.Y. Wen, *J. Fuel Chem. Technol.*, **32**, 652 (2004).
2. W. Xingshen, Prevention and Cure of Fire in Mine, China University of Mining and Technology Press, Xuzhou, China (1988).
3. H. Wang, B.Z. Dlugogorski and E.M. Kennedy, *Combust. Flame*, **134**, 107 (2003).
4. Y.B. Tang, Z.H. Li, Y.L. Yang and D.J. Ma, *Asian J. Chem*., **25**, 3384 (2013).
5. D. Cole, G. Simmons, R. Herman, K. Klier and I. Czakonagy, *Fuel*, **66**, 1240 (1987).
6. Y.B. Tang, Z.H. Li, Y.L. Yang, N. Song and D.J. Ma, *Asian J. Chem*., **25**, 441 (2013).
7. B.B. Beamish and A. Arisoy, *Fuel*, **87**, 125 (2008).
8. X.Y. Tang, Trace Elements in Chinese Coal, The Commercial Press, Beijing, pp. 292-295 (2004).
9. H. Haykiri-Açma, R. Yavuz, A. Ersoy-Meriçboyu and S. Küçükbayrak, *Thermochim. Acta*, **342**, 79 (1999).
10. W. Sujanti and D. Zhang, *Fuel*, **78**, 549 (1999).
11. S. Li, *Inorg. Chem. Ind.*, **3**, 75 (2003).