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# Laboratorial Investigation of Coal Fire Extinguishing and Re-burning Risk in Underground Coal Mines

Dongjuan Ma, Liang Yuan, Sheng Xue, Xianshu Dong,\* Pengwei Guo, and Yibo Tang\*



**ABSTRACT:** The extinguishing and re-burning of the closed fire area in an underground coal mine were investigated by laboratoryscale physical simulation. Temperatures in the center of the fire source were recorded, and the typical cooling process was observed to include the rapid cooling stage (900–400 °C) and dilatory cooling stage (400–100 °C). With the increase of coal mass from 20 to 80 kg, the rate of cooling decreases and the time required for fire extinguishing increases by 69.5%–193.2%. At temperatures ranging between 500 and 100 °C, yields of CO and H<sub>2</sub> show strong correlation with the attenuation of the coal fire, and the trend in the yield of H<sub>2</sub> might be used as the optimal indicator considering the different amounts of coal. A significant difference appears in the concentration of H<sub>2</sub> released by samples of different dosages of coal in the early stage of cooling, especially when the temperature exceeds 200 °C. During the extinguishing process, micropores in coal fused into mesopores and macropores, while the content of Ocontaining groups fluctuated significantly. Variations of elemental C and O also indirectly reflect the combustion state in the fire cooling. Taking the experimental reactor as a physical model, the time required for the fire area from closure to safe re-opening is deduced, that is,  $t = Cm \ln (T_1 - T_{\infty})/(T_2 - T_{\infty})$ . The calculated results were compared with the changes in measured temperatures, providing a theoretical foundation for the re-opening prediction of mine fire areas.

# 1. INTRODUCTION

As a significant source of fossil fuel energy, the production of coal is often accompanied by frequent spontaneous fires, which poses a great threat to the safety of underground miners.<sup>1</sup> Although the existing fire prevention and treatment techniques are multifarious, the control of underground coal fire remains extraordinarily challenging.<sup>5-8</sup> Generally, for underground mines with complex conditions and restricted fire-extinguishing approaches, the method of closure of the fire area is often used to control spontaneous fire hazards.<sup>9–12</sup> However, when re-opening the fire area to normalize coal recovery, re-burning accidents emerge as required, resulting in further casualties and property losses.<sup>13–15</sup> Therefore, research on re-burning of fire areas has become a major issue to be addressed. After the fire area is closed progressively, the coal within is gradually extinguished due to insufficient O2 supply, but the heat hardly dissipates and further accumulates, resulting in the long-term maintenance of a high-temperature regime.<sup>16-19</sup> During the

enclosed period of the fire area in an underground coal mine, it is impossible to see the development of the fire, but it is necessary to investigate the state of the combustion in the fire area.<sup>20-23</sup> At present, as the common practice to understand indirectly the fire condition, we rely on gas indicators, as shown in Table 1.

Even if the gas was to be adopted as the main index to predict mine fires globally, the yield of any index gas is affected by many factors and becomes uncontrollable, especially in an actual large-scale fire area: these unstable indicators also take

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Table	1.	Gas	Indicators	for	Monitoring	the	Closed	Fire	Area i	in	Underground	Coal	Mines
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gas indicators	advantages	disadvantages
СО	sensitive response to coal temperature change	easily affected by varied ventilation conditions; large error and low reliability
$C_2H_2$ ; $C_2H_4$ ; hydrocarbon ratio	accurately predict high-temperature fire areas	insensitive to early spontaneous fire (<100 $^\circ C)$
$\Delta O_2$	describe fire development at the macrolevel	assume that the fire area is an ideal state with complete sealing and without any air exchange
Graham's ratio	remarkable stability and anti-interference	imprecise under low O <sub>2</sub> consumption environment
alkane ratio; C <sub>2</sub> H <sub>6</sub> /CH <sub>4</sub> ; C <sub>3</sub> H <sub>8</sub> /CH <sub>4</sub> ; C <sub>4</sub> H <sub>10</sub> /CH <sub>4</sub> ;	reflect different periods of fire in the underground	not applicable to the fire of newly exposed coal
C/H	high sensitivity and wide application	not applicable to the gassy mine

on the important task of judging the timing of re-opening.<sup>24–27</sup> Systematic and scientific judgment methods for evaluating the re-burning risk are needed urgently for underground fire control; reliable mathematical models are preferred to the single indicator collected from the gas.<sup>28</sup>

Scholars have studied the micro and macroscale characteristics of coal in the fire area, which provides a theoretical reference for predicting the risk of re-burning in the fire area.<sup>25,29-31</sup> Lu et al.<sup>32</sup> studied the change in temperature at the intersection after coal ignition, concluding that coal far from the spontaneous combustion center is more likely to reignite upon re-opening; combustion characteristics of untreated coal samples that underwent a 10%  $\mathrm{O}_{2}$  ,  $\mathrm{N}_{2}$  , and  $\mathrm{CO}_{2}$ environment were compared. After thermogravimetric analysis, infrared testing, and pore analysis, it is shown that the change in spontaneous combustion characteristics of coal samples in low oxygen or inert environments will increase the re-burning risk in the unsealed fire area;<sup>33</sup> Zhou et al.<sup>34</sup> studied the formation of oxidation products (CO,  $CO_{2}$ , and  $C_{2}H_{4}$ ) through 5 groups of spontaneous combustion tests on coal with different  $O_2$  concentrations (21%, 17%, 13%, 9%, and 5.8%) and stated that the result calculated by using the  $O_2$ content in the actual situation is credible. The thermodynamic model of re-burning could also be established, and the change of gas products in the fire area was studied by simulating the re-burning in the fire area; Lu et al.<sup>35</sup> compared the generation and development of index gases of coal with different O<sub>2</sub> concentrations under adiabatic oxidation conditions and explored the functional groups in coal samples by Fourier infrared spectroscopy (FTIR), so as to obtain the tendency of coal spontaneous combustion under different O2 concentrations. At present, many studies mostly rely on the generation of gas products to judge the risk of re-burning in the fire area, but the measurement of gas concentration is often inaccurate, fluctuates greatly, and is vulnerable to the influence of the surrounding environment. Therefore, it is necessary to investigate the combustion characteristics and re-burning mechanism of coal in the underground fire area for predicted re-burning risk accurately. In the paper, the experimental tests were conducted for monitoring the whole process of fire languishment and extinguishment. A mathematical model to predict the extinguishing process of fire area is established according to thermophysical data. Comparison between the measured data and the theoretical prediction data could verify the accuracy of the theoretical model, which also provide a theoretical basis for describing the combustion state in the fire area and evaluating the risk of re-ignition in the fire area.

# 2. EXPERIMENTAL WORK

The experimental coal samples (20-60 mm) collected from Shanxi were prepared and stored at low temperature for standby (Figure 1a). The technical parameters of the coal samples are listed in Table 2.

The simulation device of the closed fire zone is a self-made experimental device, comprising a temperature recorder, temperature probe, control valve, air feeder, and adiabatic furnace (Figure 1b,c). The temperature data were recorded every 60 s; the temperature probe is a screw thermocouple with a measurement range of 0-1300 °C; the external and inner diameters of the experimental furnace are 400 and 250 mm, respectively. The total height is 1600 mm, and the thickness of the insulation layer is 50 mm.

After 4 groups of samples (20-80 kg) were ignited in the furnace and fully burned for 10 min, the experimental device was closed to simulate the extinguishing process. When the temperature dropped to 500 °C, gas samples at each 50 °C drop in temperature were collected and the component concentration was detected by the GC-950 gas chromatograph. Meanwhile, coal samples at different temperature points (interval 100 °C) were collected for later analysis. The infrared spectra of coal samples were measured using a Bruker Vertex-70 Fourier transform infrared spectrum in situ test system. The scanning wave number of the experiment was set to 500-4000 cm<sup>-1</sup>. In the experiment, an Emax energy spectrometer and a Hitachi s-4800 high-resolution field emission scanning electron microscope were used to detect the microstructural and elemental changes of each coal sample. The pore structures were investigated using the Mike ASAP 2020c model specific surface area and pore analyzer. The coal samples collected from the closed fire area at 5 temperature nodes were crushed and put into a vacuum degassing station for degassing at 100 °C to eliminate the influences of other factors. The pore size test range of the experimental device was 0.35-500 nm, the pressure was controlled within the range from 0.050 to 0.995 MPa, the N<sub>2</sub> was used as the adsorption gas, and the temperature was set to 77 K. The full pore of the sample was analyzed, and the experimental data were recorded.

### 3. RESULTS AND DISCUSSION

**3.1. Temperature and Gas.** As an indicator for assessing the situation, the temperature is the most intuitive and obvious criterion, and it is easy to assess the development of the fire area; however, in reality, the temperature at the fire source in the closed fire area cannot be measured directly, and only the atmospheric temperature can be measured. The actual situation of the fire cannot be determined, meaning that no rational criterion for re-opening the fire area can be provided. The self-extinguishing process of real coal fires under natural



(a) Coal samples



(b) Diagrammatic representation of the device



(c) Components comprising the device

Figure 1. Experimental setup and materials.

conditions was simulated through physical experiments. The temperature changes in coal samples of different masses were measured with the passage of time, and the time required for coal from sealing to re-opening in the actual situation was predicted through the data obtained from experiments. As exhibited in Figure 2, the temperature reached using coal samples of different masses showed rapid cooling at first and then decreased slowly as the fire was extinguished. Among



Figure 2. Temperature variation in coal fires with different fire loads in a closed area.

them, the coal sample with the mass of 20 kg underwent the fastest cooling, taking about 16.4 h to cool from 900 to 100 °C. In the process of heat transfer from the fire zone to the surrounding environment, the temperature difference gradually decreases, and the cooling of the coal fire is discriminated into 2 distinct stages. In the rapid cooling stage (900-400  $^{\circ}$ C), with the increase of coal mass, the rate of cooling is kept at 29.6–70.3 °C/h. By contrast, in the slow cooling stage (400– 100 °C), the cooling maintains at 9.4–30.9 °C/h. Obviously, the difference of cooling performance between the 2 stages shows that the extinguishing of fire is a nonlinear process. Cooling from about 400 °C to ambient temperature proves to be a longer process, and the observed data during this process is more susceptible for assessing re-ignition. The scale of coal fire increases with the increase of coal dosage. It's difficult for a large scale fire to self-extinguish. However, people seldom attempt to establish the mathematical relationship between the total amount of residual coal in the fire area and the time of reopening. In coal mine sites, after a fire area is closed, the subsequent problem is to estimate the time required for the fire area to extinguish. Since under the premise that traditional gas indicators cannot fully predict the development of fire, it is of great significance to make sure that we can accurately obtain the appropriate time for re-opening. Generally, after finding the fire, although the location of the fire source and the initial scale of the fire hardly be detected, the total amount of coal left in the fire area and the heat transfer environment in the fire area can be estimated. Therefore, based on the coal dosage involved in the combustion and the heat transfer environment in the fire area, it is possible to establish a prediction model to provide a reference for the actual safety work.

Conventionally, carbon oxide is often regarded as an significant coal fire indicator gas.<sup>36</sup> Figure 3a shows that the CO concentration produced by coal samples of different

Table 2. Technical Parameters of Coal Samples<sup>a</sup>

	_		technical an	alysis	ultimate analysis					
coal sample	$M_{ad}$ %	$A_{ad}$ %	$V_{ad}$ %	$FC_{ad}$ %	Qad MJ/kg	C %	Н%	N %	S %	O %
Shanxi anthracite	2.71	12.56	4.99	79.74	28.36	88.97	4.24	1.31	0.36	5.12

"Note:  $M_{ad}$  is the moisture content;  $A_{ad}$  is the ash content;  $V_{ad}$  is the volatile content;  $FC_{ad}$  is the fixed carbon content.



Figure 3. Variation in gas yield during the extinguishing process.

masses decreases with the temperature, showing a monotonic downward trend. After the experimental reactor is closed, with the decrease of temperature, the CO yield in the closed fire area also decreased from 40,000 ppm to 100 ppm approximately between 500 and 50 °C. The matter that participated in the oxidation reaction is more abundant with the increasing coal dosage, but the production of CO never emerge dramatically increasing. Even in common fire scenarios, the loading of combustibles is the dominant factor governing the development of the fire. Evidently, during the extinguishing of an underground coal fire, the residual  $O_2$  in a closed environment controls the reaction that produces CO, instead of the coal dosage. Therefore, in an underground coal mine, the CO concentration cannot directly reflect the total amount of burned coal and estimate the comprehensive scale of the fire area. Meanwhile, the H<sub>2</sub> concentration has also been regarded as an indicator for predicting the risk of coal fires; it is more reactive than CO but appears later, generally being released at >120 °C.<sup>37</sup> According to Figure 3a, in the development of a fire in a closed area, the yield of H<sub>2</sub> also shows a notable change, contributing to accurate fire-area evaluation. From about 5000 to 5 ppm, variation of the H<sub>2</sub> concentration is first rapid and then becomes moderate. The production of  $H_2$  is largely unaffected by a lean oxygen environment but is positively related to the scale of a coal fire. When the temperature decreases to 300  $^{\circ}$ C, the H<sub>2</sub> concentration of the coal sample with the lowest mass drops to as low as 150 ppm, and H<sub>2</sub> gradually disappears at <300 °C, indicating that, at high temperatures, it is a better indicator of the fire state. At temperatures <300 °C, other available indices should be

considered alternatively; the rapid decline in H<sub>2</sub> yield in the fire area is mainly due to the fact that the low-density H<sub>2</sub> diffuses at a faster rate than other gases. Given that the variation of the H<sub>2</sub> concentration in the cooling process is related to the amount of coal, it can be concluded that H<sub>2</sub> data are preferred compared with the traditional CO index. The  $C_2H_4$  yield also tends to decrease from 50 ppm to almost zero during the fire-extinguishing process, but this trend varies with the temperature. Notably, the mass of coal used in experiments is directly proportional to the  $C_2H_4$  concentration, which indicates that although the concentration remains at a low level,  $C_2H_4$  still could be used as the credible gas index in a closed fire area.

Based on the fact that the number of molecules of combustibles consumed in a fire is proportional to the number of molecules or the volume of gas produced at constant temperature, we used the Trickett's ratio (TR), which is broadly used as an excellent indicator to describe the fire status and to avoid interference as much as possible.<sup>38</sup> As shown in Figure 3b, the change in the Trickett ratio (TR) is between 0.1 and 0.8, which meets the standard of gas reliability and can be used as the indicator for judgment. The TR gradually decreases with the passage of time, indicating that the coal is extinguished, and the fire is reduced. According to the CO/  $CO_2$  ratio,<sup>39</sup> the trend is first climbing to 0.34 and then decreasing, and this ratio is also proportional to the mass of coal. In underground mine sites, this data is often affected by the variation of O2 supply around the closed fire area. The  $C_2H_4/C_2H_6$  ratio of the 4 coal loads shows the same decline as other gas indices. However, data for coal samples with a higher

loading peak at 0.23 and for groups with lower loading only reach 0.05. With the passage of time, this ratio gradually decreases and stabilizes. In addition, by comparing the 4 groups of curves, the growth is sustained longer when adding more coal *ab initio*. The coal consumption affects the variation of the ratio, but the correlation between  $C_2H_4/C_2H_6$  and temperature is weak. Although each gas indicator reflects the combustion state of the fire area to some extent, considering all kinds of interference factors in the coal mine,  $H_2$  should be the preferred indicator to describe the extinguishing process of the fire area.

**3.2. Infrared Spectra.** The corresponding infrared spectra curves of coal samples at temperatures between 500 and 100 °C during coal-fire extinguishing were obtained (Figure 4).



Figure 4. Infrared spectra of coal samples under different conditions.

It can be seen from Figure 4 that the infrared spectrum absorption peak of the sample is mainly concentrated in the wavelength range of the C–O stretching vibration (1300–900 cm<sup>-1</sup>) and aromatic C-H out-of-plane bending vibration  $(900-700 \text{ cm}^{-1})$  in O-containing functional groups.<sup>40</sup> This finding indicated that several main chemical bonds in the C-O wavelength range of oxygen-containing functional groups show an increase as the temperature decreases. After comparison, it is found that the spectral peak intensities of alkene ethers and alcohols are relatively high, indicating that these two structures undergo significant changes in the fire-extinguishing process. In contrast, substituted benzene (C-H) shows a different performance: with the decrease of temperature, different numbers of adjacent hydrogen atoms tend to decline and then rise. Substituted benzene functional groups in the coal sample disappear at 500 °C, which can be attributed to the precipitation of volatile matter leading to the decrease of the

proportion of aromatic structures at high temperatures and the later increase due to their polymerization. It can be seen more intuitively from the peak area variation of functional groups that the changes in C–O functional groups vary to a greater extent than the bending vibration of C–H during extinguishing of coal fire. During the cooling process, the pyrolysis reaction slows down, and the consumption and decomposition of corresponding groups slow down, but active groups are still generated due to the influence of temperature, especially with regard to the abundance of O-containing functional groups that increases. In general, the change of the content of these functional groups corresponds to the critical active structure in coal spontaneous combustion, which is closely related to the risk of re-burning of residual coal in the fire area at the microlevel.

**3.3. Elemental Distribution.** The SEM results of coal samples at different temperature stages are shown in Figure 5.

The macerals of coal include organic components evolved from plant organic matter and inorganics derived from minerals.<sup>41</sup> Coal ash will be gradually generated during the burning and extinguishing process of coal. Figure 5 shows that the number of pores in coal samples is gradually reduced and the pore diameter is gradually increased. The surface structure of coal samples at 500-400 °C is relatively complex, and abundant pores and cracks appear on the surface of the coal. Coal samples at 300-100 °C show a significant reduction in the number of pores and cracks, and the pore classification can also be simplified. Due to the influences of surface material reaction and thermal action, the surface structure of coal will change, and the pores will become larger and the density will decrease. Under these closed conditions, as the early temperature is higher, the ash produced by coal combustion will melt and block some pores. Then, under the low-oxygen and high-temperature environment in the closed fire area, some pores will merge and change from numerous pores to a small number of macropores.

The energy-dispersive X-ray spectrum (EDS) is used to quantify changes in the elemental composition of coal samples at different temperatures during coal-fire extinguishing. According to the EDS analysis (Figure 6), it is known that the 5 groups of coal samples mainly include copious amounts of C and O plus traces of mineral elements such as Al, Si, S, Ca, *etc.* As the temperature of the coal changes, the proportion of elements on the coal surface exhibits different migration trends.

It can be seen from Figure 6 that the contents of C and O show significant changes in the extinguishing of a coal fire. As the temperature decreases, the changes in C and O contents exhibit a significant negative correlation.<sup>42</sup> Monitoring the languishment of the fire area, the proportion of C decreases slowly from 87.56% to 71.34% between 500 and 300 °C and rapidly decreases to 17.35% between 300 and 100 °C. In contrast, the amount of O (as an element) continued to rise, steadily increasing from the initial 7.91% to 52.21%. Under high temperature, the C in coal will continue to be consumed and produce gases such as CO, CO2, and C2H4, and the reaction activity fluctuates at different temperature stages. The increase in amount of O is mainly due to the physical and chemical adsorption of coal samples. Corresponding to the aforementioned SEM results, as the intensity of coal combustion decreases, the number of coal pores increases; thus, the O<sub>2</sub> adsorption on the coal surface intensifies, which results in the increased O content. At the initial stage in the





(a) 500°C





(c) 300°C



(d) 200°C



(e) 100°C

Figure 5. Surface microstructure of coal samples at different temperatures (magnification 10,000 times).

closed fire zone, much residual organic matter remains in the coal sample. On account of the content of C readily

participating in the reaction remaining high, the re-burning risk increases accordingly. In the later stage, with the



**Figure 6.** Changes in elemental proportion of coal samples at different temperatures.

continuous consumption of C on the surface of residual coal, the proportion thereof substituted by O increased, diminishing the risk of re-burning. Decreasing from 11.1-0.33, the ratio of elemental C/O on the surface of residual coal in the fire area also has the potential to be used as an auxiliary index to judge the state of combustion coal and the risk of re-burning in the closed fire area.

**3.4. Pore Structure.** It can be seen from Figure 7 that the area of the hysteresis loop gradually increases with the decrease of temperature, indicating that the physical structure of the coal sample is mainly microporous at the initial stage of cooling and then gradually develops into mesoporous and microporous forms, with relatively weak connectivity, which are not conducive to combustion.<sup>43</sup> After calculation by Brunner–Emmett–Teller (BET) and Barrett–Joyner–Halen-da (BJH) methods, the specific surface area, pore diameter, and pore volume listed in Table 3 were obtained.

As seen from Table 3, the specific surface area decreased from 23.7609 m<sup>2</sup>/g at 500 °C to 10.5199 m<sup>2</sup>/g at 100 °C, and the pore volume decreased from 0.06327 to 0.03326 m<sup>3</sup>/g. The specific surface area decreased with the temperature decline, and the pore volume showed a similar tendency. The size of the mesopores and micropores barely changes (consistent with the law governing such a lag). The average pore size of mesopores increases from 6.1314 to 9.2933 nm. In contrast, the average pore size of micropores decreases from 1.1828 to 1.0404 nm. In the process of fire-area extinguishing, the fine pore structure of the coal sample collapses, resulting in the micropores increasing in number and the mesopores and macropores increasing in number. Explicitly, the dynamic development and evolution of pores, the reduction of specific surface area, and the differentiation of microporous and

mesoporous pore sizes all appear in the extinguishing of a coal fire.

# 4. PREDICTION MODEL

When the experimental setup is closed, the temperature in the process of self-extinguishing presents a certain trend similar to an actual closed fire area in an underground coal mine. Therefore, a mathematical model of the temperature field could be established to predict the change of temperature in the closed fire area. Since the device used in the experimental part is a cylinder, the physical model under the experimental conditions was established from the point of view of consistency. Due to the extremely complex heat and mass transfer process of coal, the model was simplified in all aspects and the following assumptions were made:

- 1. The temperature in loose coal is evenly distributed;
- 2. The influence of radiation heat transfer between coal bodies is not considered;
- 3. The change of the mass of coal in the time period is not considered;
- 4. The changes in the properties of the coal in the time period are not considered;
- 5. The density, specific heat capacity, and other main parameters of the coal and air flow are constant;
- 6. The thermal conductivity *K* and convective heat transfer coefficient *h* are constant.

Taking the area where the loose coal body is located as the control volume, according to the law of energy conservation (eq 1), the change in energy can be quantified.

$$\Delta E_{st} = E_{\rm in} - E_{\rm out} \tag{1}$$

where  $\Delta E_{st}$  is the energy change in the control volume during this time period;  $E_{in}$  is the energy entering the control volume;  $E_{out}$  is the energy leaving the control volume.

After the fire area is closed, the combustion reaction in the fire area lasts a certain time until the extinguishing process begins; therefore, there is no internal heat source in the loose coal, the fire gradually decreases, the temperature gradually decreases, and the heat Q stored in the control volume is radiated into the environment in the form of heat conduction and convection, mainly including the energy Q flowing out of the coal in the form of heat conduction through contact with device 1. The energy Q is dissipated in the form of convective heat transferring between the coal body and the air flow in device 2. The air flow in the device comes into contact with the inner wall of the device and diffuses energy Q to the environment in the form of convection and heat conduction 3. These are substituted into eq 1 giving

$$Q = Q_1 + Q_2 + Q_3$$
 (2)

Since the experimental reactor is a hollow cylinder, the temperature gradient of the cylinder wall presents a logarithmic distribution in the process of radial guide heating, and the insulation layer of the device wall adopts a variety of materials for comprehensive use, including refractory, insulation particles and the iron sheet from inside to outside. The thermal resistance  $R_1$  of coal passing through the composite wall can be expressed using eq 3.

$$R_{1} = \frac{\ln(r_{2}/r_{1})}{2\pi k_{A}L_{1}} + \frac{\ln(r_{3}/r_{2})}{2\pi k_{B}L_{1}} + \frac{\ln(r_{4}/r_{3})}{2\pi k_{c}L_{1}}$$
(3)



Figure 7. N<sub>2</sub> adsorption-desorption isotherms of coal samples at different temperatures.

			average pore size/nm		
temperature/ °C	specific surface area/m <sup>2</sup> ·g <sup>-1</sup>	pore volume/ m <sup>3</sup> ·g <sup>-1</sup>	mesoporous	micropore	
500	23.7609	0.06327	6.1314	1.1828	
400	22.3528	0.0555	7.2769	1.0817	
300	18.6737	0.04135	7.6246	1.044	
200	14.0391	0.04112	8.9545	1.0431	
100	10.5199	0.03326	9.2933	1.0404	

where  $r_1$ ,  $r_2$ ,  $r_3$ , and  $r_4$  represent the radius from the inner wall to the outer wall, m;

 $k_A$ ,  $k_B$ , and  $k_C$  refer to the thermal conductivity of refractory, thermal insulation particles and the iron sheet, W/(m K);  $L_1$  is the height of coal in the unit, m.

Set L 2 is the contact height between the air flow in the device and the furnace wall, which is determined by replacing L in eq 3. The air flow can be expressed through the thermal resistance  $R_2$  of the composite wall as given by eq 4

$$R_{2} = \frac{\ln(r_{2}/r_{1})}{2\pi k_{A}L_{2}} + \frac{\ln(r_{3}/r_{2})}{2\pi k_{B}L_{2}} + \frac{\ln(r_{4}/r_{3})}{2\pi k_{C}L_{2}}$$
(4)

If the temperature drops by amount dT in time dt, then dQ,  $dQ_1$ ,  $dQ_2$ , and  $dQ_3$  can be expressed as

$$\mathrm{d}Q = Cm \; \mathrm{d}T \tag{5}$$

$$dQ_{1} = \frac{T - T_{\infty}}{R_{1} + \frac{1}{2\pi r_{4}L_{1}h_{\infty}}} dt$$
(6)

$$\mathrm{d}Q_2 = h_s(T - T_s) \,\mathrm{d}t \tag{7}$$

$$dQ_{3} = \frac{T_{s} - T_{\infty}}{\frac{1}{2\pi r_{1}L_{2}h_{s}} + R_{2} + \frac{1}{2\pi r_{4}L_{2}h_{\infty}}} dt + \frac{T_{s} - T_{\infty}}{\frac{1}{h_{s}A} + \frac{1}{k_{D}A} + \frac{1}{h_{\infty}A}} dt$$
(8)

where, *c* is the specific heat capacity of coal, J/(kg K); *m* is the mass of coal, kg; *T*, *T<sub>s</sub>*, and *T<sub>∞</sub>* are the temperatures of coal, flue gas, and external environment, K; *R*<sub>1</sub> and *R*<sub>2</sub> denote the thermal resistance of coal and flue gas passing through the cylindrical wall, K/W; *h<sub>s</sub>* and *h<sub>∞</sub>* are the convective heat transfer coefficients of flue gas and air,  $W/(m^2 K)$ ; *k<sub>D</sub>* is the thermal conductivity of flue gas passing through the furnace cover, W/(m K); *A* is the area of the furnace cover,  $m^2$ .

Substituting these 4 equations into eq 2 because the remaining space in the experimental device except for coal is small and the heat storage condition in the closed device is good, it is assumed that the flue gas temperature is the same as that of coal, as  $T = T_s$ , and on this basis, the following formula is obtained after simplification:

$$dT = \frac{1}{cm} \left( \frac{T - T_{\infty}}{R_1 + \frac{1}{2\pi r_4 L_1 h_{\infty}}} + \frac{T - T_{\infty}}{\frac{1}{2\pi r_1 L_2 h_s} + R_2 + \frac{1}{2\pi r_4 L_2 h_{\infty}}} \right)$$
$$+ \frac{T - T_{\infty}}{\frac{1}{h_s A} + \frac{1}{k_D A} + \frac{1}{h_{\infty} A}} = \frac{T - T_{\infty}}{cm} \left( \frac{1}{R_1 + \frac{1}{2\pi r_4 L_1 h_{\infty}}} + \frac{1}{\frac{1}{2\pi r_4 L_1 h_{\infty}}} + \frac{1}{\frac{1}{2\pi r_4 L_2 h_{\infty}}} + \frac{A}{\frac{1}{h_s} + \frac{1}{h_p} + \frac{1}{h_{\infty}}} \right)$$

If

$$K = \frac{1}{R_1 + \frac{1}{2\pi q_L l_1 h_\infty}} + \frac{1}{\frac{1}{2\pi r_1 L_2 h_s} + R_2 + \frac{1}{2\pi q_L l_2 h_\infty}} + \frac{A}{\frac{1}{h_s} + \frac{1}{k_D} + \frac{1}{h_\infty}}$$

then

$$dT = \frac{K}{cm}(T - T_{\infty}) dt$$
<sup>(9)</sup>

It should be noted that under the assumed conditions, the mass is a quantitative variable in an extinguish process, and the mass of coal can be set artificially during calculation. By integrating eq 9, the relationship between temperature and time can be obtained. After calculation, it is found that the relationship between the two conforms to an exponential function. Figure 8 shows the temperature data comparison between the predicting model and experiments using 20–80 kg coal.



Figure 8. Comparison of the theoretical model and measured data in the process of coal fire extinguishing.

Article

The change of temperature under different initial masses of coal is different. The greater the amount of coal, the slower the change in temperature, and the longer the time from closure of the fire area to re-opening. Assuming that the temperature drops from  $T_1$  to  $T_2$  and the time increases from 0 to t, the time required for the temperature drop can be obtained through the definite integral calculation of model eq 9, that is, eq 10.

$$t = Cm \ln \frac{T_1 - T_{\infty}}{T_2 - T_{\infty}} \tag{10}$$

where C is a constant, which is obtained by combining the parameters such as thermal resistance and specific heat capacity with eq 9. Equation 10 can be used to predict the time required for the fire area to progress from closure to reopening. According to Figure 8, fully considering the surrounding environment of coal fire, the extinguish time of 20-80 kg coal fire, which is predicted by the theoretical model, is 20.1, 33.5, 43.2, and 50.5 h. Through observation, it is found that the change in temperature calculated by the model is similar to the experimental results, which can be used as a preliminary reference for predicting the change of temperature in a fire in a coal mine. When the extinguishing time cannot be accurately predicted, it is extremely difficult to obtain the appropriate re-opening time. Relying on traditional evaluation indicators often leads to erroneous judgment. After re-opening and recover ventilation, the development of reignited fires is extremely rapid, probably causing secondary disasters such as explosions and subsequently bringing serious casualties and losses. To a certain extent, the prediction model has a guiding significance because the minimum error between measured and predicted data is controlled at 5% approximately. Nevertheless, an underground coal mine exists in an extremely complex environment; when conducting theoretical calculations, it is also necessary to consider other factors and synthesize other indicators to determine the re-opening time.

As an initial prediction model, this work has taken a landmark forward. However, only a single coal sample was tested and medium-scale simulation was conducted in this paper. Various coal samples from different mining areas should be introduced into the further research. Coal with different ranks usually exhibits different combustion performances in underground fire hazards, especially in the development of spontaneous combustion. Different coal samples may also exhibit different critical parameters in the extinguishing process of closed fire areas. Meanwhile, considering the complex environment in real underground fire area, full-scale simulated experiment undoubtedly be instrumental in the improvement of the prediction model. In addition, the thermal conductivity of the surrounding rock in the coal mine is also more variable than that of a single thermal insulation layer in the experimental device. A modified model based on more experimental data in the future will provide an ultrahigh precision prediction of fire extinguishing time and will have great application potential.

#### 5. CONCLUSIONS

The process of extinguishing a coal fire in an underground mine was investigated by a self-made experimental setup. After the reactor filled with coal was closed, the time required for the temperature of 4 groups of coal samples (20 to 80 kg) to fall from 900 to 100  $^{\circ}$ C was 16.4, 27.8, 37.5, and 48.1 h. The rate

of cooling decreased with the increase in initial mass of coal in the closed fire area. In the process of cooling, data variations in the CO, H<sub>2</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> contents were recorded at different temperatures: CO and H<sub>2</sub> are strongly correlated with the change in temperature. Before the temperature falls to 200  $^{\circ}$ C, the H<sub>2</sub> concentration produced by the 80 kg coal sample was about nine times that of the 20 kg sample, and the  $H_2$ concentration produced by different initial masses of coal was different; due to high-temperature pyrolysis, side-chain fracturing of hydroxyl groups decreased significantly (and even ceased); nevertheless, the content of functional groups such as C-O in coal samples increased from 12.5% to 73.6%, and the proportion of aromatic ring substitution (C-H)structures increased by 15.3%. When the temperature was reduced from 500 to 100 °C, the proportion of elemental C on the surface of the residual coal decreases from 87.56% to 17.35%, and that of elemental O increases from 7.91% to 52.21%; based on the aforementioned experimental results, taking the small cylindrical furnace as the physical model, according to the law of the conservation of energy and Fourier's law, introducing the mass that can be set as the variable, a mathematical model of the change in temperature vs time was established. The change in temperature with time was predicted, and a formula of the time required for the fire area to progress from closure to safe re-opening, namely,  $t = Cm \ln t$  $(T_1 - T_\infty)/(T_2 - T_\infty)$ , was deduced, which provides a certain theoretical foundation for the re-opening of a coal mine after a fire.

# AUTHOR INFORMATION

### **Corresponding Authors**

- Yibo Tang College of Safety and Emergency Management Engineering, Taiyuan University of Technology, Taiyuan 030024, China; orcid.org/0000-0002-8922-0979; Email: tangyibo11@126.com
- Xianshu Dong College of Mining Engineering, Taiyuan University of Technology, Taiyuan 030024, China; Email: xsdong36859@126.com

#### Authors

- **Dongjuan Ma** College of Mining Engineering, Taiyuan University of Technology, Taiyuan 030024, China; orcid.org/0000-0002-8725-2811
- Liang Yuan College of Mining Engineering, Taiyuan University of Technology, Taiyuan 030024, China; Joint National-Local Engineering Research Centre for Safe and Precise Coal Mining, Anhui University of Science and Technology, Huainan 232000, China
- Sheng Xue Joint National-Local Engineering Research Centre for Safe and Precise Coal Mining, Anhui University of Science and Technology, Huainan 232000, China
- Pengwei Guo College of Safety and Emergency Management Engineering, Taiyuan University of Technology, Taiyuan 030024, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c04468

#### Notes

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#### REFERENCES

(1) Tang, Y. B. Experimental investigation of applying  $MgCl_2$  and phosphates to synergistically inhibit the spontaneous combustion of coal. *J. Energy Inst.* **2018**, *91*, 639–645.

(2) Wessling, S.; Kessels, W.; Schmidt, M. Investigating dynamic underground coal fires by means of numerical simulation. *Geophys. J. Int.* **2008**, *1*, 439–454.

(3) Zhai, X.; Ge, H.; Shu, C.; Obracaj, D.; Wang, K.; Laiwang, B. Effect of the heating rate on the spontaneous combustion characteristics and exothermic phenomena of weakly caking coal at the low-temperature oxidation stage. *Fuel* **2020**, *268*, 327.

(4) Li, J.; Li, Z.; Yang, Y.; Zhang, X. Study on the generation of active sites during low-temperature pyrolysis of coal and its influence on coal spontaneous combustion. *Fuel* **2019**, *241*, 283–296.

(5) Ma, L.; Guo, R.; Wu, M.; Wang, W.; Ren, L.; Wei, G. Determination on the hazard zone of spontaneous coal combustion in the adjacent gob of different mining stages. *Process Saf. Environ. Prot.* **2020**, *142*, 370–379.

(6) Lu, Y.; Liu, Y.; Shi, S.; Wang, G. G. X.; Li, H.; Wang, T. Microparticles stabilized aqueous foam for coal spontaneous combustion control and its flow characteristics. *Process Saf. Environ. Prot.* **2020**, *139*, 262–272.

(7) Tang, Y. B.; Guo, Q.; Yerman, L. Experimental Investigation on Using Chloride/Hydroxide Aerosol to Control Spontaneous Combustion of Lignite in Underground Coal Mines. *Energy Fuels* **2020**, *34*, 10607–10618.

(8) Lu, Y.; Yan, Z. H.; Shi, S. L.; Wang, G.; Li, H.; Niu, H. Y.; Guo, Z. G.; Wang, P. Delineation and Prevention of the Spontaneous Combustion Dangerous Area of Coal in a Regenerated Roof: A Case Study in the Zhoujing Coal Mine, China. *Energy Fuels* **2020**, *34*, 6401–6413.

(9) Qin, B.; Li, L.; Ma, D.; Lu, Y.; Zhong, X.; Jia, Y. Control technology for the avoidance of the simultaneous occurrence of a methane explosion and spontaneous coal combustion in a coal mine: A case study. *Process Saf. Environ. Prot.* **2016**, *103*, 203–211.

(10) Ren, X.; Hu, X.; Xue, D.; Li, Y.; Shao, Z.; Dong, H.; Cheng, W.; Zhao, Y.; Xin, L.; Lu, W. Novel sodium silicate/polymer composite gels for the prevention of spontaneous combustion of coal. *J. Hazard. Mater.* **2019**, *371*, 643–654.

(11) Tang, Y. B.; Hu, S. H.; Wang, H. E. Using P–Cl inorganic ultrafine aerosol particles to prevent spontaneous combustion of low-rank coal in an underground coal mine. *Fire Saf. J.* **2020**, *115*, No. 103140.

(12) Tang, Y. B.; Huang, W. Experimental and theoretical study of the effect of particle size on the forward propagation of smoldering coal. *Fuel* **2022**, *312*, No. 122903.

(13) Wang, X. B.; Deng, H. Z.; Deng, C. B.; Cui, C. B.; Shan, Y. F.; Song, Z. Q. Study on the spontaneous combustion and oxidation mechanism of low molecular ketone compounds in coal. *Fuel* **2022**, 321, No. 124022.

(14) Shi, Q.; Qin, B. Experimental research on gel-stabilized foam designed to prevent and control spontaneous combustion of coal. *Fuel* **2019**, *254*, 115558.

(15) Song, Z.; Kuenzer, C. Coal fires in China over the last decade: A comprehensive review. *Int. J. Coal Geol.* **2014**, *133*, 72–99.

(16) Tang, Y. B.; Wang, H. E. Development of a novel bentoniteacrylamide superabsorbent hydrogel for extinguishing gangue fire hazard. *Powder Technol.* **2018**, 323, 486–494.

(17) Ma, L.; Wang, D.; Wang, Y.; Dou, G.; Xin, H. Synchronous thermal analyses and kinetic studies on a caged-wrapping and sustained-release type of composite inhibitor retarding the spontaneous combustion of low-rank coal. *Fuel Process. Technol.* **2017**, *157*, 65–75.

(18) Zhu, C. G.; Wang, J.; Xie, W. X.; Zheng, T. T.; Lv, C. Improving Strontium Nitrate-Based Extinguishing Aerosol by Magnesium Powder. *Fire Technol.* **2015**, *51*, 97–107.

(19) Taraba, B.; Pavelek, Z. Investigation of the spontaneous combustion susceptibility of coal using the pulse flow calorimetric method: 25 years of experience. *Fuel* **2014**, *125*, 101–105.

(20) Taraba, B.; Pavelek, Z. Study of coal oxidation behaviour in reopened sealed heating. *J. Loss Prev. Process Ind.* **2016**, *40*, 433–436.

(21) Xue, D.; Hu, X. M.; Cheng, W. M.; Wei, J. F.; Zhao, Y. Y.; Shen, L. Fire prevention and control using gel-stabilization foam to inhibit spontaneous combustion of coal: Characteristics and engineering applications. *Fuel* **2020**, *264*, No. 116903.

(22) Yang, Y. L.; Li, Z. H.; Si, L. L.; Hou, S. S.; Zhou, Y. B.; Qi, Q. Q. Consolidation grouting technology for fire prevention in minedout areas of working face with large inclined angle and its application. *Fire Mater.* **2017**, *2020*, 700–715.

(23) Zhang, J.; Zhang, H.; Ren, T.; Wei, J.; Liang, Y. Proactive inertisation in longwall goaf for coal spontaneous combustion control-A CFD approach. *Safety Science* **2019**, *113*, 445–460.

(24) Zhang, Y.; Yang, C.; Li, Y.; Huang, Y.; Zhang, J.; Zhang, Y.; Li, Q. Ultrasonic extraction and oxidation characteristics of functional groups during coal spontaneous combustion. *Fuel* **2019**, *242*, 287–294.

(25) Zhang, Y.; Zhang, Y.; Li, Y.; Li, Q.; Zhang, J.; Yang, C. Study on the characteristics of coal spontaneous combustion during the development and decaying processes. *Process Saf. Environ. Prot.* **2020**, *138*, 9–17.

(26) Zhou, C. S.; Zhang, Y. L.; Wang, J. F.; Xue, S.; Wu, J. M.; Chang, L. P. Study on the relationship between microscopic functional group and coal mass changes during low-temperature oxidation of coal. *Int. J. Coal Geol.* **2017**, *171*, 212–222.

(27) Zhou, F. B.; Shi, B. B.; Cheng, J. W.; Ma, L. J. A New Approach to Control a Serious Mine Fire with Using Liquid Nitrogen as Extinguishing Media. *Fire Technol.* **2015**, *51*, 325–334.

(28) Liu, H. G.; Tang, Y.; Ma, D. Experimental investigation of spontaneous combustion of anthracite controlled by the chemical deposition of two-phase (hydroxide and  $CO_2$ ) aerosols. *Fuel* **2022**, 319, No. 123765.

(29) Chao, J.; Chu, T.; Yu, M.; Han, X.; Hu, D.; Liu, W.; Yang, X. An experimental study on the oxidation kinetics characterization of broken coal under stress loading. *Fuel* **2021**, *287*, No. 119515.

(30) Liang, Y. T.; Zhang, J.; Wang, L. C.; Luo, H. Z.; Ren, T. Forecasting spontaneous combustion of coal in underground coal mines by index gases: A review. *J. Loss Prev. Process Ind.* **2019**, *57*, 208–222.

(31) Yutao, Z.; Yuanbo, Z.; Yaqing, L.; Xueqiang, S.; Yujie, Z. Heat effects and kinetics of coal spontaneous combustion at various oxygen contents. *Energy* **2021**, *234*, No. 121299.

(32) Lu, W.; Li, J. H.; Li, J.; He, Q.; Hao, W.; Li, Z.; Li, J. L. Oxidative kinetic characteristics of dried soaked coal and its related spontaneous combustion mechanism. *Fuel* **2021**, 305, No. 121626.

(33) Tang, Y. B.; Xue, S. Laboratory Study on the Spontaneous Combustion Propensity of Lignite Undergone Heating Treatment at Low Temperature in Inert and Low-Oxygen Environments. *Energy Fuels* **2015**, *29*, 150330080647009.

(34) Zhou, F. B.; Li, J. H.; He, S.; Liu, Y. S. Experimental modeling study on the reignition phenomenon when opening a sealed fire zone. *Procedia Earth Planet. Sci.* **2009**, *1*, 161–168.

(35) Lu, X. X.; Zhu, H. Q.; Wang, D. M. Flow characteristic investigation of inhibition foam used for fire extinguishment in the underground. *Process Saf. Environ. Prot.* **2018**, *116*, 159–168.

(36) Wang, Y.; Mei, F.; Xue, S. Comparative analysis of microstructure evolution and oxidation performance of acid-treated lignite. *Fuel Process. Technol.* **2021**, *215*, No. 106750.

(37) Liu, H.; Li, Z.; Yang, Y.; Miao, G.; Li, J. The temperature rise characteristics of coal during the spontaneous combustion latency. *Fuel* **2022**, 326, No. 125086.

(38) Jones, J. H.; Trickett, J. C. Some observations on the examination of gases resulting from explosions in collieries. *Min. Engr.* **1954**, 114.

(39) Ma, D. J.; Tang, Y. B.; Wang, H. E. Laboratory Investigation of Underground Fire Hazard Control in Coal Mines by Use of the Pyrotechnic Aerosol. *Combust. Sci. Technol.* **2021**, 1–15.

(40) Zheng, Y. N.; Li, Q. Z.; Lin, B. Q. Real-time analysis of the changing trends of functional groups and corresponding gas generated law during coal spontaneous combustion. *Fuel Process. Technol.* **2020**, *199*, No. 106237.

(41) Mishra, D. P. Effects of intrinsic properties, particle size and specific surface area on WOP and spontaneous combustion susceptibility of coal. *Adv. Powder Technol.* **2022**, *33*, No. 103454.

(42) Tang, Y. B.; Wang, H. Experimental investigation on microstructure evolution and spontaneous combustion properties of secondary oxidation of lignite. *Process Saf. Environ. Prot.* **2019**, *124*, 143–150.

(43) Sun, L.; Zhang, C.; Wang, G.; Huang, Q.; Shi, Q. Research on the evolution of pore and fracture structures during spontaneous combustion of coal based on CT 3D reconstruction. *Energy* **2022**, *260*, No. 125033.