

Oxidation and Characterization of Low Concentration Gas in High-Temperature Reactor

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Abstract

To achieve efficient utilization of low-concentration mine gas, reduce resource waste, and alleviate environmental pollution, high-temperature oxidation of low-concentration gas at a concentration range of 1.00% to 1.50% that is directly discharged into the atmosphere during coal mine production was oxidized to recover heat for reuse. The gas oxidation equipment was improved for the heating process, and the safety of low-concentration gas oxidation under high-temperature environment was evaluated. Experimental results showed that the reactor could provide a 1000 °C high-temperature oxidation environment for gas oxidation after installing high-temperature resistant ceramics. The pressure variation curves of the reactor with air and different concentrations of gas were similar. Due to the thermal expansion, the air pressure slightly increased and then returned to normal pressure. In contrast, the low-concentration gas exhibited a stable pressure response in the high-temperature environment of 1000 °C. The outlet pressure was significantly greater than the inlet pressure, and the pressure difference between the inlet and outlet exhibited a trend to increase with the gas concentration. The explosion limit varied with the temperature and the blend with oxidation products. The ratio of measured gas pressure to air pressure after oxidation was below the explosion criterion, indicating that the measured concentration gas is still safe after the shift of explosion limit, which provides a safe concentration range for efficient use of low-concentration gas in the future.

Keywords: low concentration; gas; reactor; high-temperature oxidation

1 Introduce

Coal mines emit a large amount of low-concentration gas every year. However, unstable gas source conditions and low long-term utilization rates lead to a waste of energy and large greenhouse gas emissions¹. Therefore, low-concentration gas utilization is an important issue that needs to be resolved currently.

Low-concentration gas emits heat at high temperatures, which not only provides energy for gas oxidation but also affords the remaining heat for utilization. The residual

heat after gas oxidation from a gas concentration of 0.4% or more has economic value³, and the utilized concentration is generally controlled at 1.2%⁴.

However, the intermediates of gas oxidation are complicated⁵, and the mixed gas also affects the gas explosion limit⁶. Depending on its physical properties and chemical suppression performance⁷, CO₂ has the function of suppressing the explosion. Specifically, the upper and lower flammable limits of CH₄ were both reduced by the introduction of CO₂⁸. The flammability limit of gas in mixtures with water vapor was narrower than in dry gas air mixtures⁹. The mitigating effect of ultra-fine water mist on the explosion of hydrogen/gas mixture reduced the flame temperature, and the mitigation effect gradually increased with the increase of the fine water mist flux¹⁰. Water mist could alleviate low-concentration (6%) gas explosion. Under high concentration conditions of 9%, 11%, or 13%¹¹, water mist still exhibited a significant suppressing effect on gas explosion¹². With decreasing initial temperature, the maximum explosive pressure increased, and the density of the flammable mixture increased¹³. The higher the initial pressure or temperature, the higher the upper flammable limit¹⁴. The flammable limit of the natural gas-air mixture at 20 MPa and 100 °C increased significantly from 4.95%-15.51% at room temperature (0.1 MPa and 25 °C) to 2.87% -64.40%. With the increase of pressure and temperature, the change of the upper flammable limit (UFL) was more sensitive than the change of the lower flammable limit (LFL)¹⁵. Within the temperature range of 25 °C-100 °C, with the increase of the initial pressure, UFL and LFL showed logarithmic growth and logarithmic decay, respectively, while the UFL and LFL increased linearly with the change of the initial temperature. The gas system was in an oxygen-depleted state near the upper flammable limit with a generation of CO during the production process. In contrast, the gas system was in an oxygen-rich state near the lower explosion limit, in which the reacted gases were almost all CO₂¹⁵. With the increase of the initial temperature, the peak explosion pressure decreased while the heat release rate accelerated. The addition of the diluent gas significantly reduced the explosion pressure¹⁶. The lower limit of flammability of gas at high pressure was slightly reduced. However, when the gas concentration was above 3 MPa, the upper limit of flammability

was significantly increased. In the meantime, the theoretical limit oxygen concentration required for the explosion was gradually reduced, which increases the explosion hazard¹⁷.

In this paper, 1.00%-1.50% of mine gas was used at a high temperature of 1000 °C. The heating performance of the reactor, the oxidation pressure curve of gas in the reactor, and the gas inlet and outlet pressures were measured. The oxidation reaction of 1.50% gas was evaluated to quantify the gas explosion parameters. This work provides a theoretical basis for the efficient use of low-concentration gas.

2 Theory and experiment

2.1 Gas oxidation equation

The exothermicity of gas oxidation is complicated. The gas oxidation reaction generates various intermediates, but the final products are generally considered to be water and carbon dioxide¹⁸ (Figure 1). Gas oxidation is an exothermic process, releasing 803 KJ of heat per mole of gas.

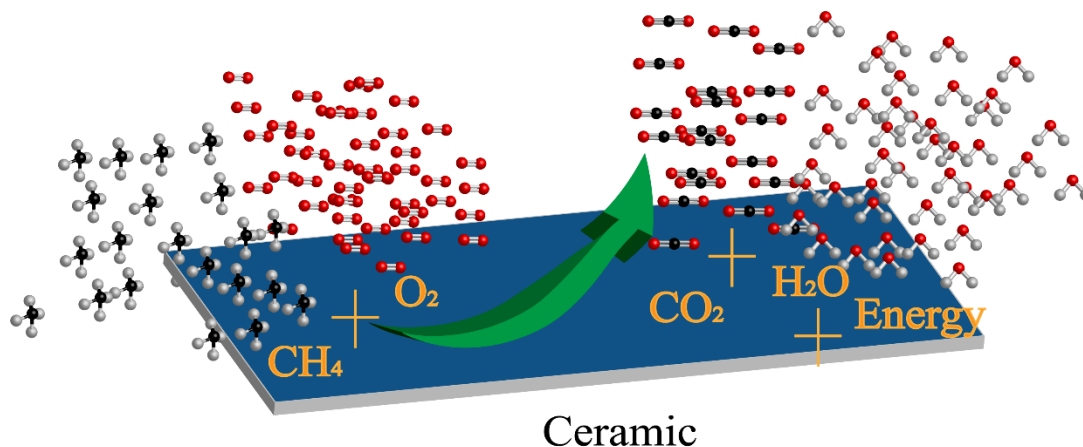
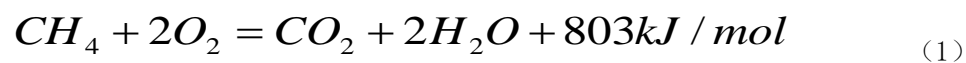


Figure 1 Exothermic oxidation of the gas

2.2 Equipment optimization

To improve the heating capacity of the equipment and ensure that the equipment can provide a stable high-temperature environment, high-temperature ceramics were installed in the reactor (Figure 2). The maximum temperature of this experiment was 1000 °C, and the preheating temperature of the heat storage body should be higher than this temperature. Therefore, the square corundum mullite material was used (Table 1),

which has a maximum service temperature of 1500 °C.

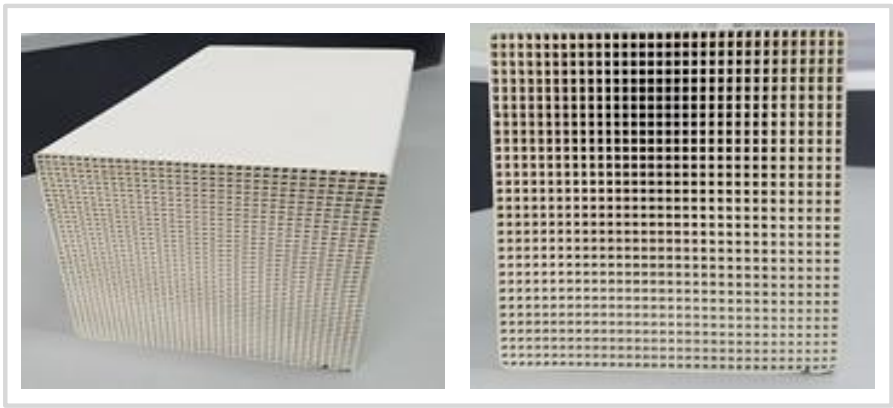


Figure 2 Reactor ceramics

Table 1 Ceramic parameters

Dimension (length, width, height m)	0.15×0.15×0.3	volume m ³	0.00675
Single pore side length m	e=0.003	Single pore side thickness m	a=0.00075
Number of pores	40×40	Porosity	65%
Pore surface area m ²	5.8	Specific surface area m ² /m ³	859
Mass kg	5.71	Heating up to 1000 °C required energy kJ	10352

2.3 Experimental parameters

The control parameters of this experiment are mainly temperature T, combustor cavity volume V, inlet pressure P, ventilation volume flow q_v, ventilation time t, and gas concentration n%. Specifically, the cavity volume of the combustor is V = 35.6L. This experiment is to identify the relationship between the lower flammable limit and temperature, so the inlet pressure is taken as normal pressure, that is, P = P₀ = 101.3KPa. Since the inlet pressure is taken as a fixed value, the measured maximum airflow of the system was q_v = 400L/min. Subsequently, the airflow time was obtained as below:

$$t = \frac{V}{q_v} = \frac{35.6L}{400L / \text{min}} = 5.34s$$

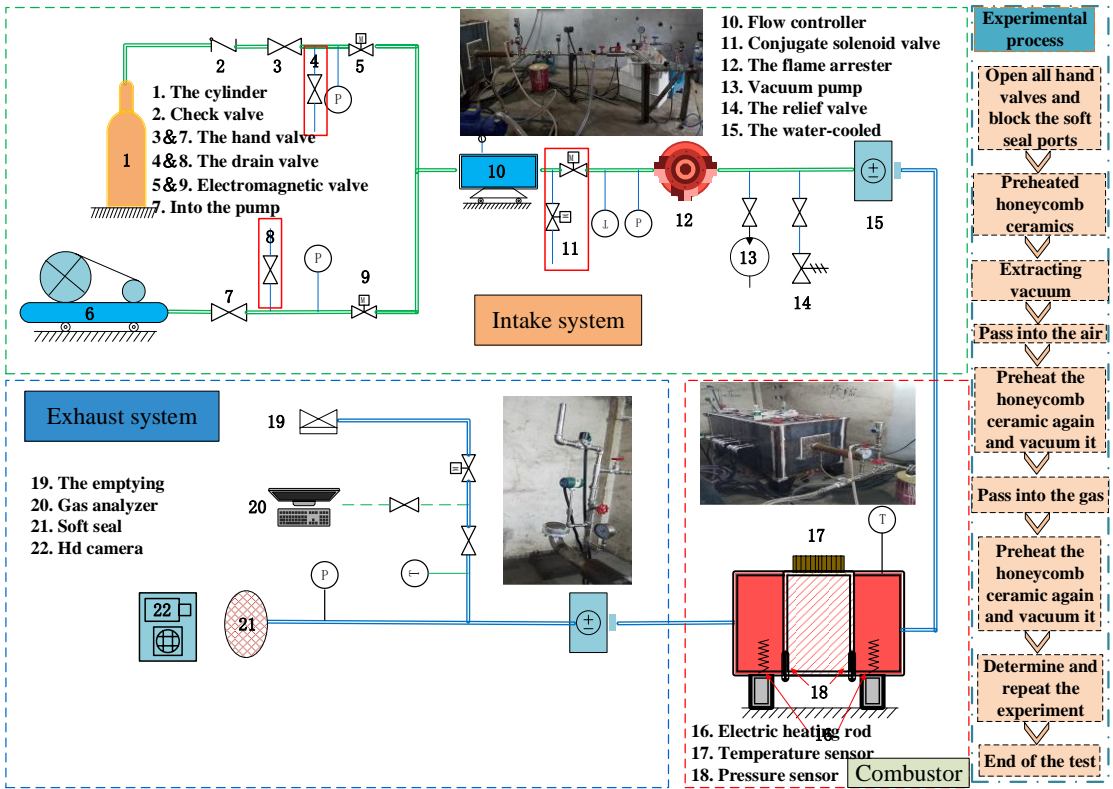
(2)

2.4 Explosion criterion

The gas storage oxidation reaction was carried out at a high temperature of more than 700 °C. The increase in temperature reduces the lower limit concentration of gas explosion. Therefore, under the influence of multiple factors, the high-temperature oxidation of low-concentration gas at 1000 °C will also explode. To achieve the safe and efficient utilization of low-concentration gas, this experiment focuses on the oxidation test for 1.00%-1.50% concentration gas. The explosion criterion of this test is the ratio of the pressure of the gas to the pressure of air after the temperature rising, $P_2/P_1 \geq 1.07$.

2.5 Experimental process

The reaction equipment is mainly composed of three systems: the inlet/exhaust system, the combustor, and the monitoring system (Figure 3). The gas oxidation is mainly completed in the combustor



3 Results and discussion

3.1 Discussion on heating capacity of improved equipment

At the target temperature range of 800 °C-1050 °C, the experiment results of the combustor temperature rising are shown in the Table.

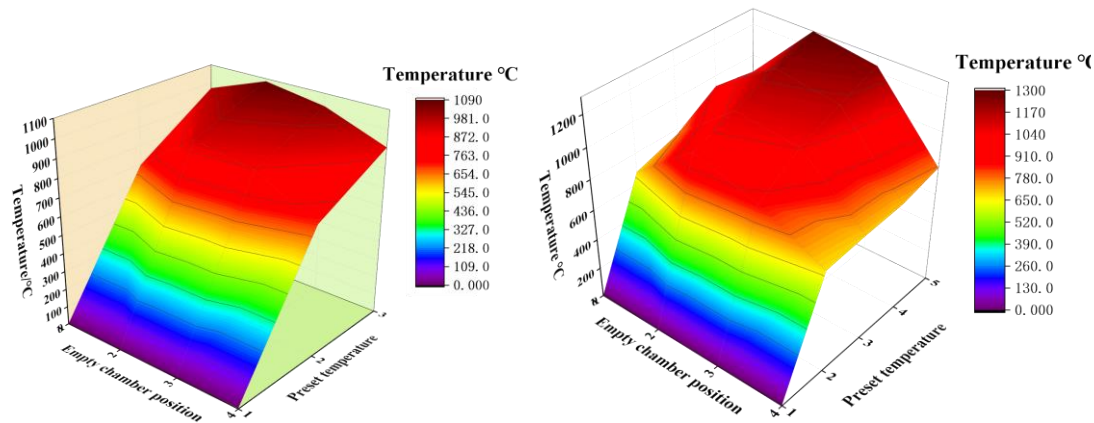


Figure 4 Empty chamber temperature Figure 5 Temperature after installing ceramic

Figure 4 shows the temperature rising of the chamber at a preset temperature (Y-axis) of 800 °C (Y, 2) and 1000 °C (Y, 3). After heating for 23 hours at a preset temperature of 800 °C, the average chamber temperature reached 799 °C, which was 1 °C different from the set temperature. After heating for 28 h at a preset temperature of 1000 °C, the average chamber temperature reached 1000 °C. These results indicate that the heating conditions could reach the preset temperature when the chamber was empty, providing a high-temperature environment for gas oxidation.

Figure 5 shows the temperature rising experiment after installing the ceramic at the preset temperatures (Y-axis) of 800 °C (Y, 2), 900 °C (Y, 3), 1000 °C (Y, 4), and 1050 °C (Y, 5). After heating for 23 h at preset temperatures of 800 °C and 900 °C, the average temperatures of the ceramic reached 806 °C and 899 °C, respectively. After heating for 28 h at a preset temperature of 1000 °C, the average temperature of the ceramic reached 1000 °C. After heating for 30 h at a preset temperature of 1050 °C, the average temperature of the ceramic reached 1050.3 °C. The results showed that after installing the ceramics, the heating experiment met the preset requirements and the test system could increase the temperature to 1000 °C. The discrepancy between the average temperature of the ceramics and the preset temperature was small, which meets the high-temperature environment for continuous low-concentration gas oxidation.

3.2 Measured pressure chart of gas oxidation at 900 °C

At the average ceramic temperature of 968.3 °C and the vacuum of approximately 30 kPa, the air was quickly pumped in, and the pressure of gas oxidation was measured

in real-time. The picture shows the real-time pressure detection chart.

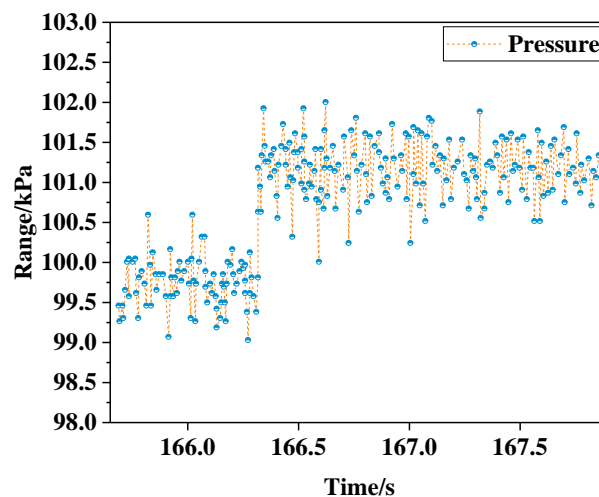
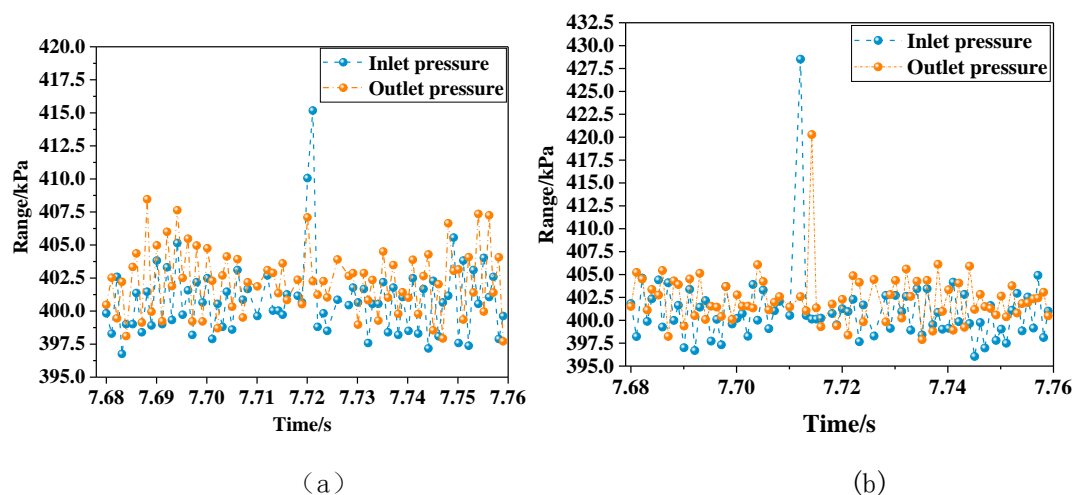


Figure 6 Measured flashover air pressure

Figure 6 is the actual measurement of flashover air pressure. It can be seen from the Figure that the initial measured flashover pressure fluctuated steadily around 99.75 kPa, but the pressure increased significantly around 166.33 s and fluctuated steadily again around 101.25 kPa after the pressure spike. Since the ceramic is affected by the airflow during the evacuation, the temperature will be significantly reduced and recovered in a short time. After flashing air, the pressure in the chamber increased with temperature recovery and air expansion after heating. A spiking value was detected in the pressure. The pressure after the air flashing was 101.4 kPa.

The airflow was set to 400 L/min, and the airflow time was set to 5.3 s. After several tests, the inlet pressure was set to 400 kPa. Figure 7 shows the measured pressure at the ceramic temperature of 900 °C.



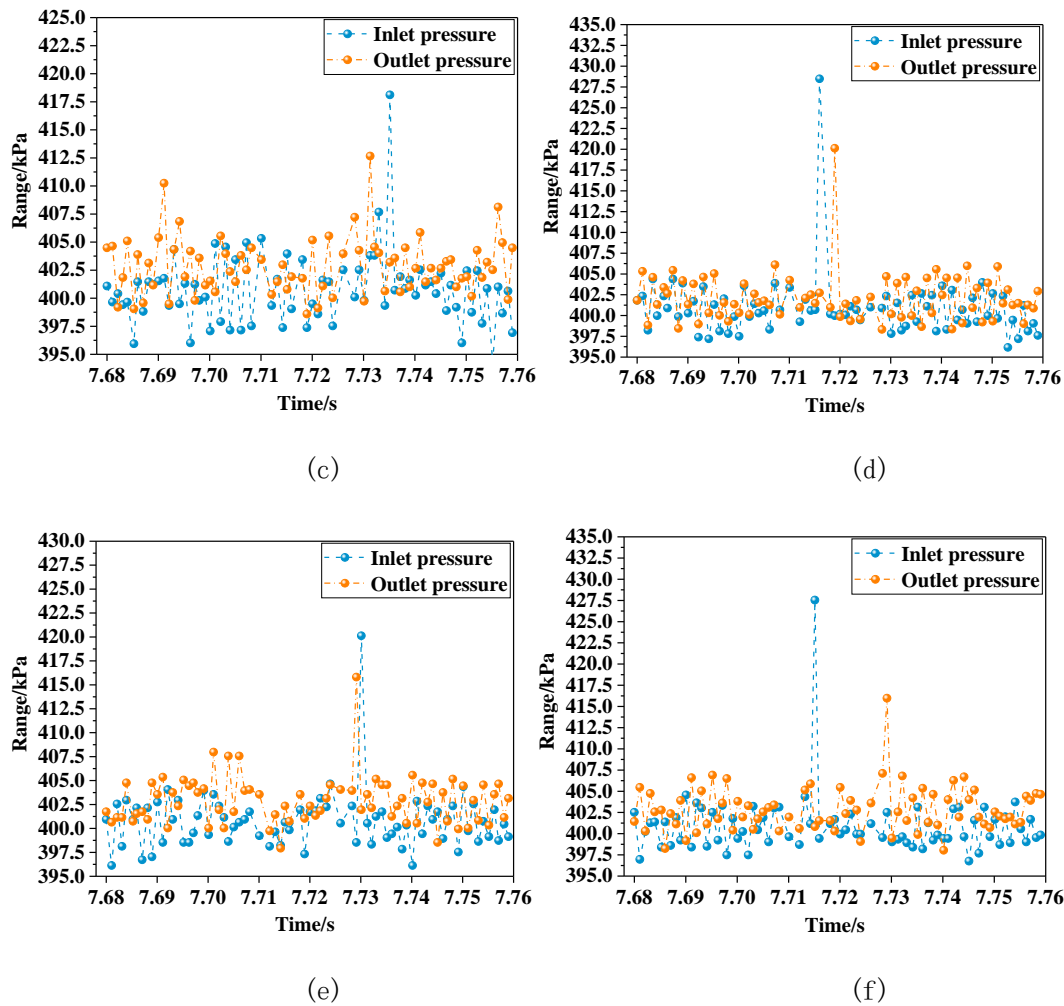


Figure 7 Experimental pressure detection chart

Figure 7 is the experimental pressure chart. Figures a, b, c, d, e, and f shows the pressures of gas concentrations of 1.10%, 1.20%, 1.30%, 1.40%, and 1.50% in the air, respectively, at the inlet pressure of 400 kPa and the measured ceramic temperature of 900 °C. It can be seen that when the inlet pressure was constant, the pressure change when passing air or gas was almost the same without a detected difference. A peak appeared in the air pressure curve, which is ascribed to the rapid air expansion after the ceramic temperature recovered, but the expansion range was small and the inlet and outlet pressures returned to normal as the air concentration increased. The pressure change curves of different concentrations of gas were similar to a maximum peak. Their increase ranges were greater than those of air because gas enters a high-temperature environment and is oxidized to generate water and carbon dioxide and releases heat. The volume of gas expands when absorbing heat. However, the generated carbon

dioxide and water vapor are mixed with gas, which reacts with oxygen at high temperatures to continuously generate more intermediates. As the reaction proceeds, more carbon dioxide and water vapor are generated, which suppresses the increase in pressure and eventually the pressure becomes normal. The overall fluctuation range of the inlet and outlet pressures was small, indicating that the gas in the reactor does not have a sudden volume expansion and a sudden pressure increase caused by oxidation. When gas is exposed to high temperature, it reacts with oxygen to generate carbon dioxide and water vapor. A small amount of carbon dioxide and water vapor are mixed with the gas and continue to react with the gas, affecting the gas explosion limit. Compared with air, it can be seen that the gas reaction mixed with a small amount of carbon dioxide and water vapor proceeded smoothly without a significant increase in pressure, indicating that the gas explosion limit mixed with a small number of impurity gases hardly changed.

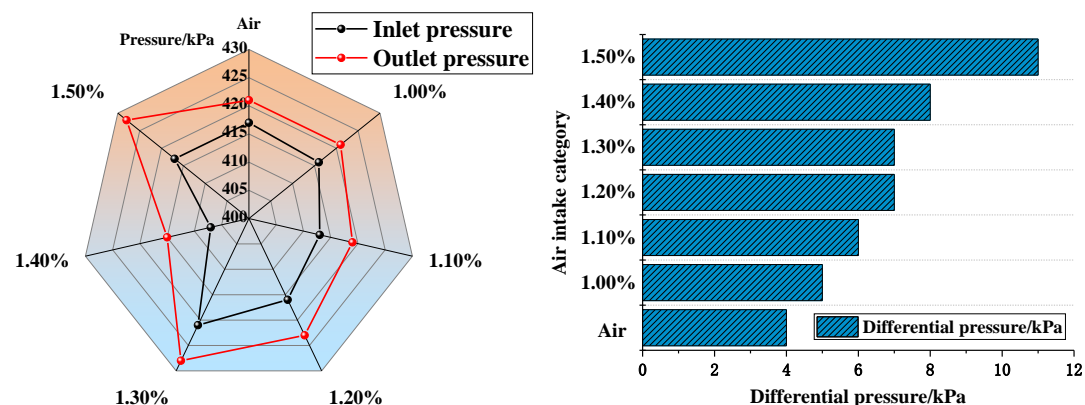


Figure 8 Inlet and outlet pressure Figure 9 Pressure difference between inlet and outlet

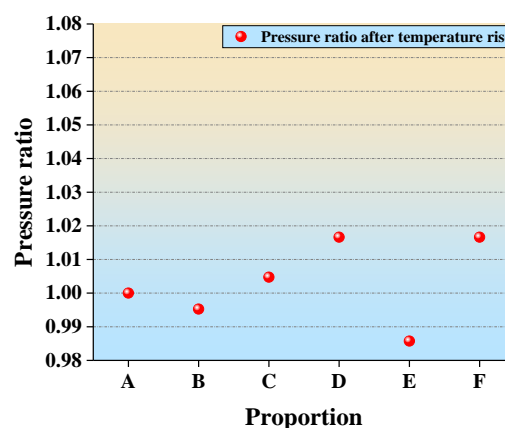


Figure 10 Explosion criteria

Figure 8 shows the gas flow pressures of the inlet and outlet equipment. It can be seen that the gas pressures of different gases increased to varying degrees after passing through the heater. This phenomenon is attributed to the thermal expansion of the gas when passing through a high-temperature environment. When passing through a high-temperature environment, gas occurs oxidation reaction, releasing water vapor and carbon dioxide, which increases the gas pressure in a short time. The pressure of different types of gas is different, which results in different pressure at the outlet. However, the discrepancy between the two curves is small, indicating that the volume of the original gas does not increase sharply after passing through the ceramic heater and the possibility of instant explosion is very slight.

Figure 9 shows the pressure difference between the inlet and the outlet. It can be seen that the air pressure difference was the smallest, indicating that the air has a smaller expansion volume when heated and has a lower risk of explosion. The maximum pressure difference of gas at a concentration of 1.5% indicates that the methane gas was instantaneously heated when passing through a high-temperature heat source. The gas expansion is caused not only by the expansion of its volume but also by the gas reaction that generates water vapor, carbon dioxide, and heat. The volume of gas was significantly increased with a maximum pressure difference of 11 kPa when exiting the reactor. From Figure 2, the pressure difference of gas was greater than the pressure difference of air when passing through the high-temperature heat source. The pressure difference of gas exhibited an increasing trend with the increase of the concentration, which indicates that the increase of the concentration enables the gas to tend to approach the pressure spike when passing through the high-temperature environment of 1000 °C. The difference in the pressure difference between 1.4% and 1.5% gas after thermal oxidation was greater than that when the gas concentration increased by 0.1%, indicating that the pressure difference changed more drastically when the gas concentration exceeded 1.4%. During the gas concentration increased from 1% to 1.5%, the pressure difference did not change much, indicating that the pressure did not spike instantaneously.

Figure 10 shows the ratio of gas outlet pressure to air outlet pressure at different

concentrations. A, B, C, D, E, and F represent the ratios of gas outlet pressure to air outlet pressure at concentrations of 1.00%, 1.10%, 1.20%, 1.30%, 1.40%, and 1.50%, respectively. It can be seen that the ratio of the gas outlet pressure to the air outlet pressure was very different at different concentrations. The minimum value was observed at point E, indicating that the measured gas concentration is the safest at 1.40% and the possibility of gas explosion is the minimum. The same maximum value was observed at points D and F, which indicates that the gas explosion is most likely and the most dangerous when the measured gas concentrations are 1.30% and 1.40%. However, the measured data points are far less than 1.07, indicating that there is no danger of explosion in the measured concentrations of gas. This result demonstrates that there is no explosion risk in the gas concentration range of 1%-1.5%, in which the gas in the reactor is oxidized rather than explosion. The gas is fully oxidized without risk of explosion, which affords a high-temperature heat source. When using low-concentration gas from mines in the future, we can control the gas concentration below 1.5% with mixed air to achieve safe and efficient utilization of low-concentration gas.

4 Conclusion

To accomplish the use of low-concentration gas in coal mines, a self-developed oxidation reactor was used for high-temperature oxidation of the gas. The gas reaction was characterized by the pressure difference between the inlet and outlet. The conclusions of the study are as follows.

1 The reactor has the ability to provide a high-temperature reaction environment at 1000 °C for low-concentration gas oxidation.

2 The pressure variation curves of the reactor with air and different concentrations of gas were similar. The gas in the reactor did not exhibit a sudden volume expansion or a sudden pressure increase due to oxidation. Compared with air, the pressure of gas mixed with a small amount of carbon dioxide and water vapor did not fluctuate significantly during the further reaction.

3 The inlet and outlet pressures of 1.00%-1.50% concentration gas were at similar levels. Their pressure difference was slight, indicating that there was no instant increase in pressure in the gas reactor. The ratio of low-concentration gas outlet pressure to air

outlet pressure was less than 1.07, indicating that no gas explosion occurred in the measured range. The safe oxidation gas concentration in the reactor was from 1.00% to 1.50% and the gas concentration of 1.40% had the minimum explosion probability, which provides the optimal concentration for future low-concentration gas oxidation utilization.

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