Control of spontaneous combustion of coal in goaf at high geotemperature by injecting liquid carbon dioxide: inert and cooling characteristics of coal

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Abstract. The spontaneous combustion of coal in goaf at high geotemperatures is threatening safety production in coal mine. The TG-DSC is employed to study the variation of mass and energy at 4 atmospheres (mixed gases of N₂, O₂ and CO₂) and heating rates (10°C/min) during oxidation of coal samples. The apparent activation energy and pre-exponential factor of coal oxidation decrease rapidly with increasing the CO₂ concentration. Furthermore, its reaction rate is slow, its heat released reduces. Based on the conditions of 1301 face in the Longgu coal mine, a three-dimensional geometry model is developed to simulate the distributions stream field and temperature field and the variation characteristics of CO₂ concentration field after injecting liquid CO₂. The results indicate that oxygen reached to depths of ~120m in goaf, 100m in the side of inlet air, and 10m in the side of outlet air before injecting liquid CO₂. After injecting liquid CO₂ for 28.8min, the width of oxidation and heat accumulation zone is shortened by 20m, and the distance is 80m in the side of working face and 40~60m in goaf in the direction of dip affected by temperature.

1. Introduction

Coal fires are caused by two types of ignition sources: forced and spontaneous. Spontaneous combustion may be the initial cause of a fire which is then spread by conduction or convection to other areas of a mine [1]. Therefore, a large number of researches have been conducted for the evolution of the spontaneous combustion of coal. With respect to the molecular structure of coal, Jones [2] et al. studied the functional groups of coal using FT-IR in the low-temperature oxidation of coal and analyzed the variation of hydroxyl group. Kök [3] et al. studied on the thermal analysis and kinetic characteristics for coal combustion. Numerous researches have conducted numerical simulations for studying the evolution of the spontaneous combustion of coal. Zhu [4] et al. studied the self-ignition characteristics for coal stockpiles by the method of numerical simulation. Wen [5] simulated the change in temperature field and distribution trend in exploitation process under different advancing velocities of working face. Zhang [6] et al. established a three-dimensional (3D) mathematical model for the spontaneous combustion of coal, simulated the distribution of seepage velocity field, concentration field, and temperature field, concluded the relationship between the oxidation zone height with temperature rising time and air supply volume, and calculated the temperature variation regularity under different propulsion velocities.
Compared to the measurements of the pre and post spontaneous combustion of coal, Qin [7] et al. using the injection of liquid nitrogen technology successfully extinguished large-area spontaneous combustible fire in the goaf. Zhu [8] determined the cooling range by injecting nitrogen in working face and applied Fluent to analyze the range and distribution of spontaneous fire zone by pre and post nitrogen injection. Zhu [9], Hao [10] and Zhou [11] et al. simulated O2 concentration field by injecting nitrogen in goaf and original situation and calculated the air leakage quantity of oxidation zone by the inversion method.

In recent years, with the increase in depth and geotemperature, the risk of spontaneous combustion has increased, and the difficulty of control has also increased. The conventional method of injecting nitrogen cannot reduce sufficient amount of heat and injecting colloid cannot stop air leakage. With a high gasification speed and heat absorption of liquid CO2, it can cool and inert coal rapidly and efficiently. In this study, the TG-DSC is employed to study on the variation of mass and energy at 4 atmospheres (mixed gases of N2, O2 and CO2) and different heating rates during oxidation of coal samples, and determines the effect to restrain coal oxidation by CO2. The flow field and cooling region distribution and regulation in goaf at high geotemperature were evaluated by the numerical simulation, thus providing a basis for the prevention and control of the spontaneous combustion of coal.

2. Experimental section

2.1. Experimental conditions

The instrument of Netzsch 449C TG-DSC is selected to measure the characteristics of mass and energy of coal samples at different atmospheres (mixed gases of N2, O2 and CO2) and the reaction kinetics parameters of coal oxidation and decomposition are calculated with it.

(1) The flow rate of the mixed gases: 50 ml/min.
(2) The flow rate of protective gas: 25 ml/min.
(3) The temperature of gas aluminum pool: 190°C.
(4) The quantity of coal sample: 1~3mg.
(5) The range of temperatures: 30~900°C.
(6) Heating rate: 10°C/min.

The sizes of coal sample were 0.074~0.105mm, proximate and elemental analysis of coal samples were shown in Table 1. The detailed experimental conditions were described in Table 2.

| Sample          | Industrial analysis (%) | Elemental analysis (%) |
|-----------------|-------------------------|------------------------|
|                 | Mdaf | Ad | Vdaf | C   | H   | O   | N   | S   | C/H |
| Bituminous coal | 1.16 | 5.56 | 37.17 | 85.81 | 5.80 | 6.58 | 1.11 | 0.70 | 1.23 |

| Experimental conditions | O2(%) | N2(%) | CO2(%) | Temperature rise rate (°C/min) |
|-------------------------|-------|-------|--------|--------------------------------|
| 1                       | 21    | 79    | 0      | 10                             |
| 2                       | 14    | 52.7  | 33.3   | 10                             |
| 3                       | 8     | 30    | 62     | 10                             |
| 4                       | 4     | 18.2  | 77.8   | 10                             |

2.1.1. Effects of CO2 on characteristic temperature of coal oxidation

Figure 1 illustrates the TG-DTG curves of the coal sample with various CO2 concentrations having an apparent effect on oxygen consumption rate. The time of its combustion and oxidation is postponed relative to air atmospheres and the characteristic temperature of coal spontaneous combustion has a significant change. The differences of TG curve for critical temperature are small at different atmospheres, while the differences of TG and DTG curves are gradually greater with increasing CO2 concentration at the temperature of mass loss. The peak of mass loss at high concentration is smoother than at low
concentration of CO$_2$. The spontaneous combustion of coal is inadequate with lower concentration of O$_2$, and its temperature of mass loss is delayed.

**Figure 1.** TG-DTG curves of the coal samples oxidation with various oxygen concentrations. In DTG curve, the temperatures of mass loss for coal oxidation and combustion are 494.8, 516.2, 520.8, and 557.3 °C with 21, 14, 8 and 4% O$_2$ concentration, respectively.

**Figure 2.** The DSC curves of the same coal samples at different CO$_2$ concentration. The peaks of temperatures for heat emission are 493.1, 508.0, 514.2 and 552.6 °C with 21, 14, 8 and 4% concentration of O$_2$, respectively.

2.2. Effects of CO$_2$ on exothermic intensity of coal oxidation

Figure 2 displayed the DSC curves of the coal samples at different CO$_2$ concentration. The curve shows a double step shape, and has two summits during the coal sample release heat, which mainly reflect two stages of the oxidation resolve and severe burning, and its resolve reaction is done in phases. It is related to the coal construction, there is a part of active group with forceful reaction activity but bad heat stability in the coal, it quickly comes into oxidizing reaction in a low temperature, and thus, the first summit occurs by the 350K, with increasing coal temperature, much aromatic construction take part in the process of coal oxidizing burning, which make two summits occur in the process of coal oxidation. With the lower of CO$_2$ concentration, The DSC curve is shaper, and the reaction of coal oxidation is fiercer, furthermore, its intensity of heat emission is greater. The concentration of CO$_2$ is higher which results the DSC curve to change more flat, the quantity of heat emission is smaller. Therefore, the reaction of coal oxidation is effectively restrained, which the peaks of temperatures for heat emission are backward.
2.3. Reaction kinetics for the suppression of coal oxidation with CO₂

The kinetics parameters of coal oxidation can be calculated according to the data from TG curves. In the Coats-Redfern model, we can get the slope and intercept through the function curve of \( \ln \left( \frac{g(a)}{T^2} \right) \) and \( \frac{1}{T} \), which the kinetics parameters of activation energy and pre-exponential factor (Table 3) can be calculated.

**Table 3. The parameters of Coal Oxidation Kinetics at different atmosphere.**

| Condition number | Fitting equation | Temperature range(°C) | Activation energy(E(kJ/mol)) | Pre-exponential factor(A(min⁻¹)) | Correlation coefficient r(•) |
|------------------|------------------|-----------------------|-------------------------------|---------------------------------|-----------------------------|
| 1                | \( y = -20.558x+10.448 \) | 352–542              | 170.91                        | 7.09×10⁶                        | 0.9986                      |
| 2                | \( y = -20.328x+9.602 \) | 370–573              | 169.01                        | 3.07×10⁶                        | 0.9986                      |
| 3                | \( y = -19.711x+8.7059 \) | 370–567              | 163.87                        | 1.19×10⁶                        | 0.9991                      |
| 4                | \( y = -18.878x+6.7111 \) | 359–539              | 156.95                        | 1.55×10⁵                        | 0.9973                      |

Based on the Arrhenius equation, the reaction rate is close dependent on both the activation energy and the pre-exponential factor A. It is concluded that the Arrhenius curves of coal sample combustion under different CO₂ concentration (Figure 3). The activate energy E is decreased with increasing concentration of CO₂, and it at air atmosphere is greater than at filling CO₂. The activation energy and frequency in the process of the coal sample burning reduce with the increase of CO₂ volume fraction; the average apparent activation energy is lower after injecting CO₂ in the coal, and it reduces with the increase of CO₂ volume fraction, which is easier to generate the burning phenomenon in the CO₂ environment. According to the Arrhenius theory, the rate of reaction is closely related to the apparent activation energy E and pre-exponential factor A, average apparent activation energy is lower in the CO₂ environment, but the corresponding pre-exponential factor decreases with the magnitude rate, reaction rate is lower if the CO₂ volume is bigger. The decrease of the average apparent activation energy just indicates that the sensibility of the oxidation burning reaction to the temperature reduces, but pre-exponential factor (frequency factor) A has astrong influence on the reaction rate from. In brief, the activation energy of the same coal sample and the sensibility to the temperature reduce if the CO₂
concentration increases, but the pre-exponential factor changes a lot, however the reaction rate actually reduces soon; with the increasing CO₂ concentration, the characteristic temperature moves backward, and the reaction difficulty increases.

3. Numerical simulation section

3.1. In-situ region of calculation model

The average geothermal gradient of 1301 working face is 3.23 °C/100m, the ground temperature reached 42 °C, the coal face strike was 2700m, and the tendency was 220m. The fully mechanized sublevel caving technology was used in this coal, the height of caving coal was 5m, and the height of goaf was 3.5m. The air volume of working face was 2400m³/min, and the downward ventilation technique was used.

The remaining coal thickness from coal wall to goaf within 10 m was 7.14 m, and that in other place was 1.82 m. The vadose rupture zone was in each side of inlet air and outlet air in goaf, which exceeded the coal seam floor by 15 m range. Because the air flow entered into the goaf from the working face, the width of working face and each lane was 10m, the height of working face was 3.5 m, and the breadth of working face was 220 m. The height of each lane was 3.5 m, and the breadth of each lane was 4 m. The goaf width was 220 m, and its depth was 300 m. The amount of air in the designed face was 2400m³/min, and the oxygen concentration was 20.98%. The calculated region was a wall except two side lanes, \( \overline{Q} = 0 \). The mesh was generated with a grid step of 0.2 m, perpendicular to the working face direction in the infiltration area of air leakage. The grid step in the zone of working face and two lanes was 0.4m. On this basis, a 3D model of calculation area was established as shown in Figure 4.

3.2. Hypothesis and boundary definition

The goaf assumed to be an isotropic and homogeneous medium, and the temperature was set at 42°C, which is close to a stable thermal field. Affected by many factors such as pressure drop and viscous resistance, fresh air and CO₂ reached the goaf by a stable percolation way, with a convection heat transfer and removing some heat from the goaf. Liquid CO₂ was injected into the inlet upper corner, the flow was 1200m³/h, the outlet pressure was 0.6MPa, and the temperature is \( \sim 5^\circ \text{C} \). The relevant physical parameters of coal and rock are shown in Table 4.

**Inlet 1:** Oxygen concentration of exposed surface: volume percentage was 21%; and the quality percentage was 23.0%. Inlet air velocity: \( V = \frac{Q}{S} = 2400m^3/(4m \times 3.5m \times 60s) = 2.86m/s \), Q is the normal air quantity of 1301 working face, and S is the inlet lane area.

**Inlet 2:** Liquid CO₂ concentration: mass percentage was 100%. Pipe line (4 inches) velocity: \( V = 1200m^3/[\pi \times (D/2)^2 \times (60 \times 60)s] = 42.5m/s \).

| Table 4. Physical parameters. |
|------------------------------|
| Item                        | Coal | Rock | O₂  | CO₂  |
|-----------------------------|------|------|-----|------|
| Density (kg/m³)             | 1350 | 1650 | 1.43| 1.78 |
| Specific heat (J/kg K)      | 1250 | 1650 | 920 | 840  |
| Temperature (°C)            | 42   | 42   | 26  | -5   |
| Thermal conductivity (W/m K)| 0.15 | 0.2  | 0.25×10⁻⁵| 0.0145×10⁻⁵|

3.3. Numerical simulation results

3.3.1. Flow field before injecting CO₂: Fresh air permeatethrough the loose porous coal-rock media of goaf from the upper corner, and the residual coal reacted with the oxygen in goaf. Because of the influencing factors such as pressure gradient and viscous resistance coefficient, the pressure drop and percolation resistance increased. The fresh air temperature was low (26 °C), and the thermal exchange in the coal-rock of loose porous media occurred at 42 °C when flowed into the goaf, thus
decreasing the temperature of goaf. By intercepting a bottom plane of 0.5 m at the bottom of the plane, the oxygen concentration field and temperature field are shown in Figure 5 and 6.

The depth of oxygen infiltration in goaf was \( \sim 120 \) m, the input air side was \( \sim 100 \) m, the return air side was only 10 m, and the mass concentration decreased gradually with the increase in depth. The oxygen concentration within the range from 0 to 0.02 was 65%, and that within the range from 0.208 to 0.23 was 20%.

Figure 6 shows that the range of exchanged temperature field in goaf is small. The energy exchange of the fresh air in goaf was limited because of its own limited cooling capacity by the energy conservation law. The energy exchange was obvious in the intake side goaf of 20 ~ 30 m, the temperature was \( \sim 311 \) K (38 \(^\circ\)C), and the temperature of deep goaf area was 314K (41 \(^\circ\)C) and remained constant. The percentage of zone with temperature between 313.4 K and 315 K was 67.5%, and that between 299 K and 300.6 K was 2.5%.

\[\text{Figure 5. Concentration field of oxygen in goaf.}\]
\[\text{Figure 6. Temperature field in goaf.}\]

3.3.2. Flow field after injecting CO\(_2\) The oxygen concentration field and temperature field changed after injecting CO\(_2\). Because of the low temperature of injected CO\(_2\) with a large velocity and momentum, the goaf temperature decreased, the oxygen concentration reduced, the zone narrowed, and the cooling and oxygen reduction effect occurred. The CO\(_2\) relief vent of 10m in the upper corner of goaf was taken as an example. By the numerical simulation of CO\(_2\) components and energy exchange at different times, the CO\(_2\) concentration field, temperature field, and the results of the oxygen concentration field after injecting CO\(_2\) for 12 min and 28.8 min are shown in Figure 7 to 9.
Figure 7 shows that in the area of goaf the CO₂ seepage was large, and the length was ~20 m along the direction of working face and ~30 m along the goaf direction in 12 min. After 28.8 min, the increase in depth was better, along the direction of working face was ~70 m and along the goaf direction was ~40 m. Therefore, after the injection of CO₂, the inerting effect was ideal.

Figure 8 shows that the temperature of goaf was 42 °C and that of CO₂ was ~5 °C, which is a large temperature difference. Therefore, energy exchange occurred easily. After 12 min of injecting CO₂, the cooling range was 25 m along the direction of working face and ~10 m along the goaf direction. After 28.8 min, the cooling range further increased, the length along the working face was ~35 m along the goaf direction, resulting in a significant cooling effect.
Figure 9 shows that the diffusion direction of oxygen concentration in goaf after injecting CO2. After 12 min, the reduction in oxygen concentration and area were limited. After 28.8 min, the inerting effect was ~80 m along the direction of working face and ~70 m along the direction of the goaf. Thus, the effect of inerting and decrease in oxygen was obvious.

4. In-site verification
Using SF6 as the tracer gas, 9L SF6 was released into a pre-buried pipeline with injected CO2 by the transient releasing method. The releasing position and monitoring points are shown in Figure 10, and five sampling points were selected, namely, point No.1 (70 stent), point No.2 (30 stent), point No.3 (down corner), point No.4 (the 20th buried pipe), and point No.5 (the 21th buried pipe). The sample in each point was collected in every 3 min.

Figure 10. Observation points in goaf for testing air leakage and its variation trend

The test results are shown in Figure 10. SF6 gas was detected at three points: 30 min in point No.1, 36 min in point No.2, and 51 min in point No.5. The SF6 concentration was determined at each point except points No.3 and 4, affected by severe air flow, and showed a normal distribution curve by time variation. The SF6 concentrations at points No.1, 2, and 5 were high. SF6 migrated from the lower-
middle part of stents to deep goaf, and the velocity was 3 ~ 4m/min, which is similar to the simulation results.

To determine the temperature variation, the advance speed was maintained slow during the turnaround direction of working face. The CO concentration of the lower-corner angle increased slowly at the beginning, the highest value obtained was 190ppm, and the results are shown in Figure 11. The highest temperature in goaf went up to 58°C. The quantity of continuous CO2 injection was 40,000kg. Then, the CO concentration and temperature decreased steadily, and the temperature decreased after a 40 m distance, similar to the simulation results of CO2 injection diffusion distance and influencing range (40m). The temperature and CO concentration of the suffocating zone after 60m decreased rapidly.

![Figure 11. Variation trend of CO concentration in face corner and temperature in goaf.](image)

5. Conclusions
(1) The activation energy at air atmosphere is greater than filling CO2 for coal sample. With increasing CO2 concentration, the activate energy and the pre-exponential factor are fast small, which restrain the coal combustion.

(2) The depth of oxygen permeation ingoaf is 120 m before injecting CO2, air inlet side is ~100 m, and air outlet side is ~10 m. The mass concentration gradually increases with the increase in goaf depth; the temperature zone of the air inlet side in goaf clearly change to 20 ~ 30 m.

(3) The variation zone of injected CO2 concentration in 12 min is ~20 m along the direction of working face and 30 m along the goaf direction; the cooling zone is ~25 m along the direction of working face and 10 m along the goaf direction. After 28.8 min, the expanding zone is better; the length along the direction of working face is ~70 m, and the depth along the goaf direction is ~40 m. The cooling range further increases, the length along the working face is almost all, and the depth is ~35 m along the goaf direction. The reducing zone of oxygen concentration is ~80 m along the direction of working face and 70 m along the direction of the goaf.

(4) Using SF6 as the tracer gas, the width of oxidation and heat accumulation zone is shortened to 20m. The distance is 80m in the side of working face and 40~60m in the goaf direction affected by temperature, and the affected distance is ~20 m, thus confirming the results of numerical simulation and indicating that the developed model is reliable.

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