Research on the Technology of Fire Prevention and Extinction by Direct Injection of Liquid Carbon Dioxide

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ABSTRACT: Coal spontaneous combustion in goaf, due to the characteristics of good concealment, difficult-to-be determined high-temperature point, and large space area, brings great difficulty to fire prevention and control. Usually, the measures of colloid injection and nitrogen injection have high economic cost and need a long time. Based on physical properties and fire extinguishing mechanism of liquid carbon dioxide, carbon dioxide is inert gas, after being injected into fire area, it can reduce oxygen content in fire area, leading to fire extinction due to lack of oxygen; liquid carbon dioxide and solid carbon dioxide, in the process of evaporation and sublimation, absorb a lot of heat and decrease the temperature of fire area, speeding up fire extinction. This paper has studied the technology of fire prevention and extinction by direct injection of liquid carbon dioxide and safety technology measures; the initial pressure of high-pressure carbon dioxide fire extinguishing system is 5.17 Mpa; this paper has studied the flow velocity, node temperature and clinical detonation formula of liquid carbon dioxide in pipeline. Through field test of 2024 working face in Bajiao Mine, it is proved that the CO concentration in goaf decreases from 900ppm to 0ppm within short period, which produces good effect.

KEYWORDS: Spontaneous combustion of coal seam, Goaf, Liquid carbon dioxide, Direct injection application and prospect is very broad in China[2].

1 INTRODUCTION

The disaster accident of coal seam spontaneous combustion seriously threatens the safe production at coal mine. Once underground fire occurs, national resources and production equipment will suffer severe damage and loss, even the life and safety of mine production personnel are endangered. Especially, with the increase of mining strength in recent years, continuous development of new technology for high yield and high efficiency, relatively complicated ventilation system, coal seam spontaneous combustion have obvious increasing trend[1].

From current technology for preventing coal spontaneous combustion, liquid carbon dioxide is injected to fire area to prevent and extinct fire, the technology has been applied successful both at home and abroad. It is proved, in practice, to be a new and effective fire prevention and extinction technology. With the emergence of fully-mechanized coal mining technology, such fire prevention and extinction technology has strong advantages in terms of investment, fire extinguishing efficiency and other aspects, compared with the technology of fire prevention and extinction by nitrogen injection. Such technology plays an active role in preventing coal spontaneous combustion disaster in goaf, therefore, its

2 PHYSICAL AND CHEMICAL PROPERTIES AND FIRE EXTINGUISHING MECHANISM OF CARBON DIOXIDE

Carbon dioxide is suffocating gas which is colorless and slightly sour at room temperature and normal pressure. It has three forms under different pressure and temperature. It does not burn, nor support combustion in the solid, vapour and liquid state. When the concentration of carbon dioxide in the air exceeds 3%, one will breathe with difficulty and have headaches, when the concentration of carbon dioxide in the air exceeds 25%, one will suffer dysfunction of central nervous system, and death from suffocation. Carbon dioxide is commonly-used fire extinguishing agent. When the concentration of carbon dioxide in air exceeds 29.2%, it can cause combustion extinguishment. When the melting point is -56.6°C (5.2 atm), the critical temperature is 31.3°C, critical pressure is 72.80 atm, carbon dioxide has the sublimation characteristics, and the sublimation point is -78.5°C (1 atm). Under low-temperature and pressurization, CO₂ can turn into liquid state, by using latent heat of evaporation, snowflake-shaped solid can be formed, and can be made into dry ice after further cooling and pressurization (solid carbonate)[3].
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Figure 1 Three-phase Transformer of liquid carbon dioxide

Specific gravity of carbon dioxide in gaseous state relative to air is 1.529, the density is 1.976 kg/m$^3$, (0°C and 1 atm), the density of liquid carbon dioxide varies greatly with temperature change, at -20°C, its density is 1.01 kg/L. At 15°C and 1 atm, 1.56 L liquid carbon dioxide can be converted into 1m$^3$ gas, the volume expands by about 640 times.

### Table 1 Physical Properties of Liquid Carbon Dioxide

<table>
<thead>
<tr>
<th>Relative Molecular Mass</th>
<th>Density (g/l)</th>
<th>Heat of Vaporization (kg/kj)</th>
<th>Gas Volume Increase Multiples after Vaporization</th>
<th>Relative Volume Mass</th>
<th>Liquid Density (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>1.976</td>
<td>137</td>
<td>640</td>
<td>0.967</td>
<td>980</td>
</tr>
</tbody>
</table>

Vaporization of liquid carbon dioxide and sublimation of solid carbon dioxide both absorb a lot of heat. Solid carbon dioxide absorbs heat of 137 kcal/kg during sublimation, dry ice refrigeration capacity is about 2 times that of water ice. Heat absorption of liquid carbon dioxide during vaporization varies with the difference of temperature.

Because carbon dioxide is suffocating gas, it can reduce oxygen content in fire area, and extinct fire due to lack of oxygen. In addition, in the process of evaporation and sublimation, liquid carbon dioxide and solid carbon dioxide will absorb a lot of heat to reduce the temperature in fire area and accelerate fire extinguishment.

The density of carbon dioxide is greater than that of the air. When the fire at the bottom is extinguished, carbon dioxide will quickly sink to the bottom, and drive oxygen out, so the fire extinguishment effect is very good. When the temperature reduces to -56°C, part of carbon dioxide in gaseous phase can turn into fine particles (solid phase) -- dry ice, the dry ice can absorb surrounding heat and sublime, that is, it plays the role in cooling combustion material. On the other hand, when carbon dioxide is released, it is distributed around combustion material to dilute the oxygen content in surrounding air. The decrease of oxygen content will reduce the generation rate of heat during combustion; when the heat generation rate decreases to be lower than heat loss rate, combustion will stop, this is fire extinguishing effect of carbon dioxide$^{[4]}$.  

3 RESEARCH ON THE TECHNOLOGY OF FIRE EXTINCTION SAFETY BY DIRECT RELEASE OF LIQUID CARBON DIOXIDE

Liquid carbon dioxide usually comes from chemical
plants near mines. When mines need liquid carbon dioxide, special transport equipment is used to transport liquid carbon dioxide from chemical plants to mines, and different way is used to transport storage tank used in mine to the place of fire extinction.

Liquid carbon dioxide is transported from chemical plants to mines by means of specific low-temperature tanker. The tanker is mainly composed of storage tank, modified car, operating vehicle, cryogenic liquid pump, pressure-charging unit and metal hose. Storage tank adopts vacuum powder insulation, or high vacuum multi-layer insulation, with small evaporation loss, safe and reliable, but its price is high, and its volume is big, it can only be used in ground transportation.[5-6]

For underground transportation of liquid carbon dioxide, according to the nature of liquid carbon dioxide and national requirements on relevant national regulations, standards and specification, special car used in mine is manufactured, its working pressure is 2.6Mpa, medium temperature is -40℃, the body material is 16 MnDR low-alloy steel, heat insulation material is hard polyurethane foam plastics.

![Photo of Special Mine Storage Tank For Liquid Carbon Dioxide](image)

The main security problems related to the technology of fire extinction safety by direct release of liquid carbon dioxide mainly are reflected in the following aspects: (1) During injection, carbon dioxide condensation easily occurs to form dry ice in pipelines, pore plates, valves and other places, causing block in pipeline, even detonation occurs to cause pipeline burst because flow velocity exceeds local velocity of sound. (2) Because liquid carbon dioxide storage tank is a pressure vessel, special safety technical measure needs to be developed for underground transportation process. (3) When carbon dioxide is injected to fire area, poisonous and harmful gas in fire area or in goaf connecting to fire area may be drove out, or a lot of carbon dioxide in gas phase surges out, which threatens safety production of working face. Therefore, centering around the three problems, the technology of fire extinction safety by direct release of liquid carbon dioxide has been studied.

3.1 Determination of Initial Pressure of Liquid Carbon Dioxide

Storage pressure is about 2.1MPa, and the storage temperature is -19±1℃, and the storage state is liquid. As shown in carbon dioxide three-phase diagram in Figure 1, the phase transition pressure of carbon dioxide under the storage condition of the temperature is 2.07 Mpa, if below this phase transition pressure, carbon dioxide begins to evaporate and gasify, and form gas-liquid two-phase flow in pipeline. Carbon dioxide steam, as drive force, has pushed the movement of two-phase flow, so Chinese regulations sets 2.07 Mpa as initial calculation pressure of low-pressure C02 fire extinguishing system. However, in high-pressure CO2 fire extinguishing system, the storage pressure of fire extinguishing agent is 15 MPa. The phase transition pressure of CO2 under normal temperature is 5.17 Mpa (English unit is 750 PSI). Therefore, in the beginning of injection, carbon dioxide is basically liquid, fire extinguishing agent itself has not enough vapour pressure as initial impetus; therefore, only 15Mpa high-pressure nitrogen prefilled in storage bottle is used to act as initial impetus. After injection is started, pressure decreases; once pressure decreases to below 5.17 Mpa, carbon dioxide begins to evaporate and produces subsequent impetus, and maintains for a period of time under this pressure. Therefore, initial calculation pressure of high-pressure carbon dioxide extinguishing system is 5.17 MPa.

3.2 Basic Rule on Flow of Low-Pressure Carbon Dioxide in Pipeline

(1) Determination of flow velocity in pipeline

When low pressure carbon dioxide begins to be injected, because fire extinguishing agent storage container has very big volume, pressure drop is not as severe as that of high-pressure carbon dioxide fire extinguishing system. However, because the vapour pressure of liquid carbon dioxide under low temperature is close to storage pressure, with pressure drop, a large amount of liquid carbon dioxide will evaporate, and form uniform two-phase flow in
pipeline faster than high-pressure carbon dioxide, and the proportion of gas phase is bigger, closer to single-phase gas flow. On the other hand, with pressure decrease of carbon dioxide, its volume expands so fast, so its flow velocity in pipeline increases rapidly. Because of rapid flow velocity, finite quantity of pipeline length can be ignored. Therefore, from the perspective of thermodynamics, the flow of carbon dioxide in open pipe can be considered as adiabatic opening system steady flow process \(^{(7)}\).

Energy conservation equation of working medium steady flow per unit mass in opening system:

\[
q = (u_2-u_1) + (p_2-v_2) + (V_{22}-V_{21})/2 + g(Z_2-Z_1) + w
\]  

Therefore, according to downstream and upstream node pressure ratio \(P_2/P_1\), upstream node temperature \(T_1\) and velocity of upstream node \(V_1\), the flow velocity of downstream node can be calculated.

(2) Determination of temperature of downstream node

The temperature at downstream node depends on the temperature of upstream node and differential pressure ratio between upstream or downstream nodes: when the pressure is higher than that at triple point, and at the upstream node, the temperature of carbon dioxide and the \(\text{CO}_2\) pressure ratio at upstream and downstream nodes are known, as long as the temperature of carbon dioxide in downstream node calculated is lower than the temperature of triple point (56.6°C), this point will cause dry ice freezing phenomenon.

(3) Icing and detonation phenomenon in low-pressure \(\text{CO}_2\) fire extinguishing system

As seen in three-phase diagram of carbon dioxide, as for low pressure \(\text{CO}_2\) fire extinguishing system, in the process of injection, regardless of gas or liquid state, as long as the temperature of carbon dioxide is lower than 56.6°C, dry ice and freezing phenomenon will occur.

Flow velocity increases when pressure decreases. When flow velocity increases to be local velocity of sound, the flow fails due to “sound barrier”. Once flow velocity breaks through the sound barrier, detonation will occur. The huge power of detonation usually causes icing in pipeline, and the area of orifice at the freezing place will decrease, pressure drop will further increase, so the downstream temperature will decrease further. Therefore, once dry ice is generated, before pipeline has not been fully blocked yet, detonation occurs more easily.

Local velocity of sound during isentropic adiabatic flow:

\[
V_c = \left(\frac{2RT}{k(k+1)}\right)^{1/2}
\]  

\(T\) is the local temperature (K) of downstream node, which can be determined by Formula (6). Because gas constant of carbon dioxide \(R = 188.9 \text{ J/(kg \cdot K)}\), specific heat ratio \(K = 1.285\), so the relationship between local velocity of sound of carbon dioxide and the local temperature is:

\[
V_c = 14.58T^{1/2}(\text{m/s})
\]  

This is critical flow velocity which prevents detonation. The flow velocity obtained from calculation shall not be greater than or equal to critical flow velocity given by the above formula, otherwise, the detonation will occur. For safety’s sake, limit pressure reducing ratio and critical velocity both should have safety factor. Safety factor should not be less than 1.3. Namely, the pressure reducing ratio \(P_2/P_1\) should not be less than 0.6 when carbon dioxide gets through a pipe segment or a part; the flow velocity at any part should not be greater than 11.2\(T^{1/2}\)m/s. In addition, the temperature at any node should not be lower than 223 K (-50°C). As a result, the velocity and temperature of each node shall be calculated, otherwise, we cannot ensure that dry ice or detonation does not occur in injection process.

4 INDUSTRIAL TEST ON FIRE EXTINGUISHING BY USING LIQUID CARBON DIOXIDE

4.1 Overview of Working Face and Spontaneous Combustion Sign

For 2024 Working Face in Baijiao Mine, the strike length is 438m, the inclined length is 2.2m, and the average mining height is 2.2m, recoverable reserves is 190,555T. The coal seam of working face is 448.9-429.0m deep, 4# coal seam (B2) has simple structure, with thickness of 1.1-5.9m and average thickness of 3.5m; 3# coal seam (B3) is lack in this area; for 2# coal seam (B4), the thickness is 1.0-1.8m, and the average thickness is 1.4m. The spacing between 2# coal seam and 4# coal seam is 0.1-4.7m. The coal seam trend: 300-325°, inclination: 210-235°, angle of inclination: 4-8°, average angle of inclination: 7°. The firmness coefficient of coal seam is f=2-4. The working face adopts the stroke longwall retreat mining method and fully caving coal mining method to manage roof. The air distribution quantity is about 360m³/min.

Because the working face is subject to coal seam group mining, with small interlayer spacing, there is large amount of residual coal in goaf, with great threat of spontaneous combustion. Starting from June 10, 2011, CO appears at working face, with increasing trend, see Figure 3.
4.2 Measure of Fire Extinguishment By Using Liquid Carbon Dioxide

From middle shift of June 24 to morning shift of July 6, a total of 271 tons of liquid carbon dioxide is injected to goaf and working face. See Figure 4 for diagram of pore forming through drilling, specific injection, and gas change.

Carbon dioxide fire preventing and extinguishing unit is installed at 20# parking lot (see attached figure), and the unit is connected with pump pipe to 2-inch iron pipe; the 2-inch iron pipe is connected through pathway in 20# area to injection site, and flow confluence device is used to connect to each pipe.

<table>
<thead>
<tr>
<th>Drilling No.</th>
<th>CO2 Injection Amount/T</th>
<th>Coalbed Injection Rate/T</th>
<th>Drilling No.</th>
<th>CO2 Injection Amount/T</th>
<th>Coalbed Injection Rate/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>15.6</td>
<td>66</td>
<td>D3</td>
<td>7.2</td>
<td>33.3</td>
</tr>
<tr>
<td>B4</td>
<td>15.6</td>
<td>24</td>
<td>D4</td>
<td>8.3</td>
<td>8.8</td>
</tr>
<tr>
<td>B6</td>
<td>13.9</td>
<td>46</td>
<td>D1</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>B8</td>
<td>2.6</td>
<td>21.5</td>
<td>D2</td>
<td>4.7</td>
<td>17</td>
</tr>
<tr>
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<td>7.8</td>
<td>D3</td>
<td>4.3</td>
<td>0.8</td>
</tr>
<tr>
<td>C1</td>
<td>13.2</td>
<td>1.5</td>
<td>D5</td>
<td>4.3</td>
<td>6.3</td>
</tr>
<tr>
<td>C2</td>
<td>13.2</td>
<td>E1</td>
<td>7.8</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>39</td>
<td>E3</td>
<td>4.3</td>
<td>3.9</td>
</tr>
<tr>
<td>C5</td>
<td>12.1</td>
<td>13</td>
<td>E2</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>10.8</td>
<td>E4</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>22</td>
<td>D6</td>
<td>6.7</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>5</td>
<td>3.9</td>
<td>D8</td>
<td>3.5</td>
<td>2</td>
</tr>
<tr>
<td>D4</td>
<td>7.2</td>
<td>19</td>
<td>14</td>
<td>6.7</td>
<td>28</td>
</tr>
<tr>
<td>D5</td>
<td>7.2</td>
<td>0.8</td>
<td>15</td>
<td>6.7</td>
<td>23</td>
</tr>
<tr>
<td>D6</td>
<td>7.2</td>
<td>26</td>
<td>Total</td>
<td>271</td>
<td>327</td>
</tr>
</tbody>
</table>

Figure 4 Record on Drilling and Injection of Carbon Dioxide for Fire Preventing and Extinguishing at 2024 Working Face

4.3 Effect Analysis

Through injection of liquid carbon dioxide, the temperature of 2024 working face decreases obviously, the CO gas concentration in airtight machinery roadway at 2024 working face is detected (see Figure 5-6): CO gas inside airtight machinery roadway started to appear in June 19, CO gas concentration reached peak 180ppm on June 24, with injection of liquid carbon dioxide, CO gas concentration began to decrease, until the concentration was zero on July 11; inside airtight area for return air, before injection of liquid carbon dioxide, CO concentration is very high, and is 300ppm on June 19, which indicates that the residual coal in goaf begins to enter the stage of
rapid temperature rise, with serious sign of spontaneous combustion; with injection of liquid carbon dioxide, CO concentration decreased rapidly, and decreased to zero on July 11.

![Figure 5 Curve of Change of Air in Airtight Machinery Roadway at 2024 Working Face](image)

Results show that, as for coal spontaneous combustion hazard in large-area mined-out area, combustion point can not be determined and fire extinction can not be made directly; therefore, the technology of direct injection of liquid carbon dioxide is an effective, fast and convenient means.

5 CONCLUSION

(1) With regard to physical properties and fire extinguishing mechanism of liquid carbon dioxide, carbon dioxide is suffocating gas, it can reduce oxygen content in fire area, and extinct fire due to lack of oxygen. In addition, in the process of evaporation and sublimation, liquid carbon dioxide and solid carbon dioxide will absorb a lot of heat to reduce the temperature in fire area and accelerate fire extinguishment.

(2) Initial calculation pressure of high-pressure CO₂ fire extinguishing system is 5.17 Mpa, flow velocity, node temperature and detonation critical formula have been deduced.

(3) The test on 2024 working face at Baijiao Mine shows that, as for coal spontaneous combustion hazard in large-area mined-out area, combustion point can not be determined and fire extinction can not be made directly, therefore, the technology of direct injection of liquid carbon dioxide is an effective, fast and convenient means.

INTRODUCTION TO AUTHOR

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