Experimental study on compound phase change materials

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Abstract. According to incomplete statistics, the mine heat damage accidents since the 1970s have threatened the safety of mining and the safety and health of underground workers all the time. At present, many mine workers have physical discomfort in high-temperature mines, and then affect the safe mining of mines. As China's shallow coal seam has been basically mined out and gradually mined to deep mines, the underground heat damage is becoming more and more serious. The overall and local cooling of the mine has become a difficult problem in the underground work, which also restricts the production of the mine. The development of individual cooling equipment can effectively alleviate the heat stress of mine workers. Therefore, it is necessary to select non-toxic environmental protection and low-cost cooling materials as the cooling medium of cooling clothing. It is necessary to consider that the cooling medium is harmless to human body and can keep the human body working in a more comfortable micro environment without affecting the working efficiency.

Keywords: mine heat damage, safe mining, heat stress, individual cooling clothing.

1. Introduction

With the improvement of mining mechanization and automation, the mining depth of mine increases gradually. At present, China's mining is extending to the deep with an average speed of 8m-12m per year. The mine extension speed in the middle and East reaches 10m-25m per year, and the mining depth of most mines has exceeded 1000m. According to statistics, the temperature of underground strata with mining depth of more than 1000m in China reaches 35-45℃, and that of underground strata with mining depth of more than 1500m exceeds 45℃. Due to the deep mining of mine geothermal, mechanical heat dissipation caused by high degree of mechanization, ore oxidation and other reasons, the heat damage problems such as high temperature and high humidity in the mine are particularly prominent [2-3]. If the personnel work in high temperature and humidity environment for a long time, the heat balance of heat production and heat dissipation will be damaged, which will cause various adverse physiological reactions of human body, and lead to heatstroke, heart failure or pathological changes, or even death. At the same time, it will also affect the psychological reaction of the human body, resulting in irritability, anxiety and other unstable emotions, which will increase the rate of operational errors, reduce the production efficiency, and even cause safety accidents in serious cases. Some studies have shown that when the temperature of underground driving operation point exceeds 30℃, the probability of accident occurrence increases by 1~1.5 times than that when the temperature is less than 30℃. Because of the
serious heat damage in the mine, the harm to the operators is obvious, so the prevention and control of the mine heat damage is particularly important.

For the coal mine, the investment in the cooling project of underground mining face is generally 2~2.5 million yuan, and the investment of the whole mine cooling system is as high as 10~50 million yuan. In metal mines, due to the scattered underground operation and discontinuous production, the cost of investment in large-scale refrigeration equipment is higher. It is reasonable to believe that in addition to the above cooling technology, personal protection technology has become a development trend, and has been widely used in ground construction industry, horticulture and airport apron, and the effectiveness of cooling clothing in relieving thermal and physical strain has been confirmed. However, the use of personal protective clothing in underground mine still has certain research potential, and it is particularly urgent to develop personal protective clothing for metal heat damage mines. Relevant studies have shown that wearing personal protective clothing on workers has obvious cooling effect and simple follow-up maintenance. In recent years, it has become a research hotspot of domestic and foreign scholars [5]. Inorganic hydrated salt phase change materials have the characteristics of high latent heat, high solubility, high thermal conductivity, low price and rich raw materials, which are widely used in the fields of thermal insulation building materials and industrial waste heat recovery [6]. Shi Qisong et al. [7] developed Na₂SO₄ cooling material which can be used for individual temperature reducing clothing. According to the thermal effect parameters, the phase change temperature of the phase change material is about 15°C and the latent heat of phase change is 170 J/g. Gu et al. [8] studied and analyzed the solidification process and supercooling degree of calcium chloride hexahydrate (CaCl₂ꞏ6H₂O) by differential scanning calorimeter (DSC) and step cooling curve. The results showed that the addition of 1% carboxymethyl cellulose and 2% strontium chloride hexahydrate (SrCl₂ꞏ6H₂O) can effectively reduce the supercooling degree of CaCl₂ꞏ6H₂O and inhibit phase separation. Haibin et al. [9] prepared the phase change energy storage capsule with the best coating rate and coating efficiency, which were 52.84% and 56.27%, respectively. He Qian [10] prepared phase change materials by adding expanded graphite into paraffin. The experimental results show that adding 2% expanded graphite to paraffin can increase the heating time by 39.4%. Xu Yongfeng et al. [11] prepared a new phase change material by adding metal sodium with high thermal conductivity into paraffin. The experimental results show that the thermal conductivity of the phase change material increases by 17.6 times and the heat storage and heat release rate increases by 1 time when adding 5% metal sodium.

2. Materials and methods

2.1. selection of phase change materials
At present, the phase change materials commonly used in low temperature clothing on the market mainly include inorganic phase change materials and organic phase change materials. Inorganic phase change materials include molten salt, sulfate, chloride salt and phosphate, and organic phase change materials include paraffin, fatty acids, polyols and esters. The performance comparison of phase change materials with different components is shown in Table 1.

According to the comparison in Table 1, the advantages of inorganic phase change materials are low cost, phase change temperature close to room temperature, but the latent heat of phase change is small, supercooling is easy to precipitate, and it is corrosive. The phase change latent heat of commonly used inorganic phase change materials, such as Na₂SO₄ꞏ10H₂O, is only 160 J/g, and can only last for about 1 hour during use, which cannot meet the long-term use of operators. Paraffin is a mixture of alkanes with different carbon atom numbers. Its general formula is CₙH₂n+2. Because of its small volume change before and after phase transition, it has a wide range of sources and low price, and has a high latent heat. The phase transition temperature can be obtained by adjusting the proportion of different carbon atoms in alkane.
Table 1. performance comparison of different phase change materials

| Type       | Inorganic phase change materials                                                                 | Organic phase change materials                                                      |
|------------|--------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| component  | Hydrated salt: Na₂SO₄·10H₂O, CaCl₂·6H₂O et al                                                   | fatty acid, lipid, alcohols: PG, NPG, PEG et al                                       |
|            | latent heat:                                                                                   | Paraffins: N-hexadecane, N-octadecane et al                                         |
|            | 150~300 J/g                                                                                   | 120~300 J/g                                                                          |
| Phase transition temperature | 15~36℃                                                                                     | 10~40℃                                                                              |
| advantage  | low price, high thermal conductivity, low latent heat                                          | high thermal efficiency, low phase change undercooling                               |
| shortcoming| high undercooling, easy precipitation, separation, corrosion                                   | volatile                                                                            |
|            | poor heat transfer performance                                                                |                                                                                     |

Through the performance comparison of various phase change materials and the comprehensive consideration of meeting the downhole service conditions, paraffin is selected as the cooling medium in the cooling clothing. In the practical application of paraffin, considering that the phase change temperature is close to the human comfort, the phase change materials are usually compounded. Because the cost of N-alkanes with even number of carbon atoms is lower than that of alkanes with odd number of carbon atoms, and compared with isomers, it has higher latent heat of phase change. Therefore, the paraffin with even number of carbon atoms is selected. The phase transition temperature of N-hexadecane in paraffin wax is 18℃ and that of N-octadecane is 28℃. N-hexadecane and N-octadecane are used as compound raw materials for further analysis and research.

2.2. Compounding of phase change materials

In order to meet the various needs of the research object, it is necessary to maintain the thermal comfort of human body by adjusting the mixture ratio of the two-phase change materials. The phase change temperature of the mixture can be changed by adjusting the compound proportion of the two-phase change materials. It can solve the problem that a single material is difficult to meet the special requirements of the application object, and make the product increase efficiency, modify and expand the application range. When the two kinds of phase change materials are mixed in a certain proportion, new characteristics will appear, and three phase state dynamic equilibria appear, namely A(s)-AB(s)-solution L. Under the condition of constant ambient temperature and pressure, if material A is dissolved in the mixed solution C obtained from material B, the chemical potential of material A in solid and liquid environment should be consistent if the composition of material A is stable. Namely:

$$\mu_A^{(s)}(T, P) = \mu_A^{l}(T, P, x_A)$$  (1)

Where, $\mu_A^{(s)}$— the chemical site of material A when it exists in solid state;
$\mu_A^{l}(T, P, x_A)$— the chemical site of material A when the content of material A in mixture C is $x_A$;
$x_A$— the ratio of the amount of material A to the amount of material C in the mixed solution, i.e. mole fraction.

At the same time, the three phases of the mixture still keep dynamic equilibrium:

$$\mu_A^{(s)} + d\mu_A^{(s)} = \mu_A^{l} + d\mu_A^{l}$$  (2)

Combining formula (1) with formula (2), formula (3) can be obtained:
\[ d\mu_A^{(s)} = d\mu_A^{(l)} \]  

When the ambient pressure of the mixture is stable, the chemical site of material a is only affected by ambient temperature; when material a participates in the mixture, the chemical site of material a is affected by temperature and proportion \( x_A \) respectively:

\[
d\mu_A^{(s)} = \left[ \frac{\partial \mu_A^{(s)}}{\partial T} \right] dT = -S_A^s dT
\]  

Assuming that the mixture is an ideal solution, the chemical potential of the components of the solution follows the following relationship:

\[
\mu_A^{(l)} = \mu_A^{(s)} + RT \ln x_A
\]  

After finishing, we got the following results:

\[
d\mu_A^{(l)} = \left[ \frac{\partial \mu_A^{(l)}}{\partial T} \right] dT + \left[ \frac{\partial \mu_A^{(l)}}{\partial x_A} \right] dx_A = -S_A^l dT + RT \ln x_A
\]  

By introducing formula (4) and formula (6) into formula (3), it is calculated that:

\[
T_A = \frac{1}{\frac{1}{T_f} - \frac{R \ln x_A}{\Delta H_A}}
\]  

Where, \( \Delta H_A \)——the enthalpy of phase change material A, J/mol; \( T_f \)——phase transition temperature of phase change material A, K; \( R \)——gas constant, \( R=8.315J/(K\cdot mol) \).  

Similarly, for material B:

\[
T_B = \frac{1}{\frac{1}{T_f} - \frac{R \ln x_B}{\Delta H_B}}
\]  

After the mixture of material, a and material B, the phase transition temperature of the mixture is as follows:

\[
T = T_A \times x_A + T_B \times x_B
\]  

Where, \( T \)——the phase transition temperature of the mixture when the mass ratio of materials A and B is \( x_A, x_B, K \); \( x_A, x_B \)——the ratio of the amount of material a and material B respectively.  

The physical properties of N-hexadecane and N-octadecane are shown in table 2.
Table 2. physical parameters of two-phase change materials

| Physical parameters       | Phase change materials | C_{16}H_{34}(N-hexadecane) | C_{18}H_{38}(N-octadecane) |
|---------------------------|------------------------|-----------------------------|-----------------------------|
| phase transition temperature(K) | 291.45                 | 301.75                      |
| latent heat(J/g)          | 229.3                  | 244                         |
| relative molecular mass(M) | 226.44                 | 254.49                      |

According to the formula (7) and (8) in the above section, the phase transition temperature of the mixture of materials A and B can be obtained. When N-hexadecane is dissolved into N-octadecane:

\[ T_A = \frac{1}{\frac{R}{T_f} \ln \frac{x_A}{x_A}} \left( \frac{\Delta H_A}{R} - \ln x_A \right) = \frac{6244.461}{21.425 - \ln x_A} \tag{11} \]

When N-octadecane is dissolved into N-hexadecane:

\[ T_B = \frac{1}{\frac{R}{T_f} \ln \frac{x_B}{x_B}} \left( \frac{\Delta H_B}{R} - \ln x_B \right) = \frac{7467.897}{24.749 - \ln x_B} \tag{12} \]

3. Results

The physical parameters of material A and material B are brought into formula (11) and formula (12), and the calculation results are brought into formula (9) according to different proportions. The phase transition temperature of the mixture under different proportions can be obtained, and the temperature change curve is made, as shown in Fig. 1.

**Figure 1.** temperature curves of composite phase change materials with different proportions.
It can be seen from Fig.1 that the phase transition temperature of the mixture is lower than that of N-hexadecane in the mixing experiment of different proportions of two-phase change materials, which is due to the solid-solid phase change in the process of material mixing. Generally, the lowest acceptable comfortable temperature of human trunk skin is 24°C [12]. In the design of cooling clothing, the phase change material is not directly in contact with human skin, so the phase change material with 24°C phase change temperature can be selected. It can be seen from the figure that the molar ratio of N-octadecane to N-hexadecane in the compound mixture is 9:1, so this mixture will be selected in the subsequent performance test of temperature reducing clothing the cooling medium was tested.

4. Conclusion
The most commonly used phase change material is solid-liquid phase change material. The characteristics of this kind of material are: when the temperature is higher than the phase change temperature, the material changes from solid to liquid and absorbs heat (melting process); when the temperature is lower than the phase change temperature, the material changes from liquid to solid, releasing heat (curing process), and the material temperature remains unchanged during the phase change process. What needs to be paid attention to is that the melted phase change material will be naturally frozen into solid and store a large amount of latent heat when it is placed in the environment below its phase change temperature. Imagine that when the surface temperature is very low in winter, the underground environment is still high temperature and high humidity. At this time, the phase change material can be frozen when placed on the ground. Therefore, this kind of low-carbon and environmental protection phase change material is suitable for the cooling medium in the well lowering temperature suit. In this study, through the combination of N-hexadecane and N-octadecane, compared with N-hexadecane, the compound phase change material has more suitable phase change temperature and higher latent heat. Because of the high phase change temperature, it can last for a long time in the downhole individual cooling. It is necessary to use this kind of cooling medium to study the cooling effect of individual clothing.

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