Application techniques for micro capsules on energy security: A case study on Class B fire

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Abstract. At present, with the rapid development of the national economy, China's demand for energy is becoming stronger. It is particularly important to develop an efficient and environmentally friendly fire extinguishing agent to ensure energy security. As a new type of environmentally friendly fire extinguishing agent, dry water has the advantages of both water mist and dry powder fire extinguishing agent. The core-shell structure of dry water extinguishing agent makes it have fluidity and dispersibility similar to powder fire extinguishing agent, while maintaining extremely high-water content, making it of great application value in the field of fire extinguishing agents. In this paper, the preparation, physical and chemical properties of dry water extinguishing agents and the fire extinguishing performance of Class B fires are studied, based on the existing fire extinguishing theories and experimental results, the fire extinguishing mechanism of dry water extinguishing agents is discussed.

1. Introduction

At present, with the rapid development of the national economy, China's demand for energy is becoming stronger and stronger. How to ensure energy security has become an important topic of current research. Among them, oil and natural gas, as the most important basic energy source in the world, is inherently flammable and explosive. In order to reduce the huge economic losses caused by fires and protect the lives and property of the people, it is particularly important to develop efficient and environmentally friendly fire extinguishing agents.

Traditional fire extinguishing agents such as high-efficiency Halon extinguishing agents (mainly Halon 1211 and 1301) have the advantages of high efficiency, low toxicity, stable performance, and no residual traces. They are widely used in various types of fires. However, the subsequent experiments proved that halogenated alkane compounds could cause serious damage to the ozone layer and bring serious consequences to the ecological environment.[1,2,3]. Therefore, many countries signed the "Vienna Convention for the Protection of the Ozone Layer" and the "Montreal Agreement" in the 1980s, and China subsequently formulated a phase-out plan and stopped the production and use of Halon[4,5] fire extinguishing agent. At present, a variety of Halon fire extinguishing agent substitutes have been
formed, such as gas fire extinguishing agent represented by inert gas, liquid fire extinguishing agent based on foam, and solid fire extinguishing agent based on dry powder[6,7]. However, various types of fire extinguishing agents also have many problems. For example, the preparation process of foam fire extinguishing agent is complicated, and there are many fire extinguishing residues, which cannot be applied to fires of live equipment; inert gas fire extinguishing agent has high cost, low fire extinguishing efficiency, poor cooling effect, and cannot effectively suppress smoldering, which limits its use range; dry powder fire extinguishing agents have no cooling effect and have poor resurgence resistance[8,9,10].

Dry water is a new type of environmentally friendly fire extinguishing agent. Its appearance is a solid powder with good dispersibility, but its water content is more than 90%. It is a kind of microcapsule fire extinguishing medium, which has the advantages of both water mist and dry powder fire extinguishing agent[11,12]. As shown in Figure 1, the core-shell structure of dry water fire extinguishing agent makes it have fluidity and dispersion similar to powder fire extinguishing agent, which is convenient for storage and transportation. At the same time, it has a large water content, so it can be used in the field of fire suppression. The dry water fire extinguishing agent has excellent fire extinguishing performance, the fire extinguishing residue is easy to clean, will not pollute the environment, and the cost is low, and almost no pollutants are generated during the production process[13]. Therefore, in recent years, more and more researchers have begun to pay attention to dry water fire extinguishing agents[14,15]. In this paper, the preparation, physicochemical property of dry water fire extinguishing agents and the fire extinguishing performance of Class B fires are studied. Based on the existing fire extinguishing theories and experimental results, the fire extinguishing mechanism of dry water fire extinguishing agents is further discussed.

![Figure 1. Schematic diagram of dry water structure.](image1)

![Figure 2. Dry water sample.](image2)

### 2. Experimental

#### 2.1. Sample preparation

All chemicals and reagents were used as received from commercial sources without further purification. In this experiment, the hydrophobic SiO$_2$ model is AEROSIL R812S, and the chemical additives are KHCO$_3$ (Beijing Chemical Reagent Company, AR), KNO$_3$ (Tianjin Damao Chemical Reagent Factory, AR), NH$_4$H$_2$PO$_4$ (Beijing Tongguang Fine Chemical Company, AR). The high-speed shearing method is used for preparation, and the equipment used is a high-speed disperser (JFS-550). The preparation parameters are: the rotation speed is 6000r/min, the mixing ratio of SiO$_2$ and distilled water is 6:100, and the stirring time is 2min. Among them, the preparation of modified dry water needs to replace distilled water with a corresponding salt solution with a mass fraction of 5%. Prepare white powdery particles, as shown in Figure 2. Four kinds of dry water fire extinguishing agents were prepared: Pure water dry water, KHCO$_3$ dry water, KNO$_3$ dry water, NH$_4$H$_2$PO$_4$ dry water. The appearance is white powdery particles, as shown in Figure 2.

#### 2.2. Characterization

Structure and morphology of the samples were characterized by electron microscope (TM3030PLUS). Refer to the measurement method of dry powder fire extinguishing agent in GB4066-2017 to characterize the bulk density. First, weigh 20g of sample powder and place it in a measuring cylinder
with a stopper, turn the measuring cylinder upside down to make the powder in a boiling state, and finally let it stand for 3 minutes and then read the volume to calculate the bulk density; use the fixed cone method to characterize the fluidity of the sample: Firstly, a glass round table of radius $r$ was placed 50mm directly below the funnel, and 50g samples to be tested were weighed with an electronic balance and poured into the funnel. Turn the funnel upside down five times to fully disperse the powder. Place the funnel on the iron stand, turn on the funnel switch to allow the powder to flow out under the action of gravity. After the powder has completely flowed out, measure the height $h$ from the apex of the stacking cone to the upper surface of the glass round table. The angle of repose of the powder $\theta = \tan^{-1}(h/r)$, repeat three times and take the average value.

2.3. Fire tests

Fire extinguishing efficiency is one of the most important performance indicators of fire extinguishing agents. The special structure of dry water makes it impossible to fully refer to the test standards of water-based fire extinguishing agents or dry powder fire extinguishing agents. Therefore, according to the characteristics of dry water fire extinguishing agents, while referring to domestic and foreign fire extinguishing agent standards such as GA 578-2005, GB 4066-2017, etc., we independently designed a closed fire extinguishing experiment platform suitable for the fire extinguishing performance test method of dry water fire extinguishing agent, and conducted experimental research on Class B fire.

In order to reduce the interference of airflow in the environment, this experiment counts as a fully submerged fire extinguishing in a confined space. The fire extinguishing test box is designed, and the fire extinguishing agent in the powder storage tank is sprayed by the way of carrying flow by driving the spray with high pressure nitrogen gas. Among them, cyclohexane was selected as the experimental fuel. The nozzle of the experiment box is designed in the center of the top of the box, and the fire source is placed in a fixed position outside the nozzle. Use a camera to record the fire extinguishing process.

The fire extinguishing agent storage tank used in the experiment refers to the design of the portable dry powder fire extinguisher. The temperature data acquisition equipment thermocouple used in the experiment is WRNK-191 armored thermocouple from Shanghai Zhenfeng Instrument Factory, and the temperature acquisition range is $0 \sim 1100^\circ$C. The fire extinguishing agent storage tank used in the experiment refers to the design of the portable dry powder fire extinguisher. The temperature collection range of the thermocouple used in the experiment is $0 \sim 1100^\circ$C (Shanghai Zhenfeng Instrument Factory, WRNK-191 armored thermocouple). The temperature data recording equipment used is a paperless recorder (Hangzhou Meikong Automation Technology Co., Ltd., MIK-R5000D). The equipment for controlling the output pressure on the pressure storage tank is a single-stage pressure reducer (Tyco Air (Beijing) Technology Co., Ltd. A-1H model), with an inlet pressure of 15Mpa and an outlet pressure of $0 \sim 1.2$Mpa.

The fire extinguishing device is composed of a pressure storage tank, a single-stage pressure reducing valve, a pipe, a powder storage tank, and a nozzle. The overall situation of the fire extinguishing platform is shown in Figure 3.

![Figure 3. Fire extinguishing experiment platform.](image-url)
Set up an oil pan (square oil pan, 200×200×50mm), pour 600ml water and 150ml cyclohexane into the oil pan during the experiment, and set a cushion block with a height of 130mm under the square oil pan. During the experiment, the thermocouple was fixed on the iron stand, and the end position of the thermocouple was placed in the center of the oil pan. The height of the two thermocouples from the oil pan was 15cm and 30cm respectively. In order to further confirm the effectiveness of the fire extinguishing agent for full-submerged fire extinguishing in a confined space, two combustion tanks (diameter is 80mm, height is 100mm) were placed in the corners of the test box during the experiment. Fill the tank with water and cyclohexane to 1/3 of the height of the combustion tank. In the experiment, the fuel tank is ignited, and a thermocouple is placed above the tank to detect the change of the internal flame[16]. In the experiment, the fire extinguishing agent was sprayed for 30 seconds. If the flame is extinguished and does not re-ignite, it is judged that the fire extinguishing is successful. Record the amount of extinguishing agent and take the minimum amount from the successful fire extinguishing situation in the three experiments. Finally, turn off the camera, and after the experiment box cools down, read the data in the paperless recorder, weigh the remaining fire extinguishing agent in the powder storage tank, and calculate the amount of sprayed fire extinguishing agent. The experiment compared the fire extinguishing efficiency of dry water fire extinguishing agent and commercially available superfine dry powder fire extinguishing agent.

3. Results and discussion

3.1. Structure and morphology

Morphological images of the dry water sample were shown in Figure 4(a-d). The core-shell structure of the sample can be clearly observed. The three samples of pure water dry water, KHCO₃ dry water and KNO₃ dry water have similar microscopic appearances, uniform shapes, and good encapsulation. The particle size is concentrated in 20~50μm; while the NH₄H₂PO₄ dry water structure has a larger particle size, which is concentrated in 100~200μm.

The bulk density and fluidity of the four kinds of dry water are shown in Table 1. The bulk density of dry water fire extinguishing agent is between 0.4~0.6g/ml, among which the bulk density of pure water dry water, KHCO₃ dry water and KNO₃ dry water is about 0.42g/ml; while the NH₄H₂PO₄ dry water has a higher bulk density of 0.55g/ml, which is significantly larger than the other three samples. The fluidity of dry water is good. Among them, the pure water dry water, KHCO₃ dry water and KNO₃ dry water have an angle of repose close to that of ABC dry powder fire extinguishing agent, all at about 38°, indicating that the fluidity of dry water is similar to dry powder and can be used as a fire extinguishing agent. The angle of repose of NH₄H₂PO₄ dry water is about 32°.

![Figure 4. Morphologic images of dry water: (a)pure water dry water, (b)KHCO₃ dry water, (c)KNO₃ dry water, (d)NH₄H₂PO₄ dry water](image)

| Table 1. Performance parameters of four kinds of dry water. |
|-----------------------------------------------------------|
| **Type** | **Particle size distribution (μm)** | **Bulk density (g/ml)** | **Fluidity (°)** |
|----------|-----------------------------------|------------------------|-----------------|
| Pure water dry water | 20 ~ 50 | 0.42 | 38.11 |
| KHCO₃ dry water | 20 ~ 50 | 0.419 | 38.2 |
3.2. Fire extinguishing performance

Before the fire extinguishing experiment, a control combustion experiment must be carried out to determine the initial time of flame stable combustion $T_0$ and the flame out time $T_1$; then a fire extinguishing experiment (N₂, 99.9%) was carried out to obtain the extinguishing time $T_2$; finally, a certain quality of different types of extinguishing agents were added to the powder storage tank, and the extinguishing experiment was carried out to obtain the extinguishing time $T_3$; the above experiments are all carried out under the same working conditions, eliminating the interference of environmental factors. The ideal result: $T_1 > T_2 > T_3$, which can show that the added extinguishing ingredients have positive significance for fire suppression in confined spaces. The fire extinguishing experiment process is shown in Figure 5.

|          |                |     |  
|----------|----------------|-----|  
| KNO₃ dry water | 20 ~ 50 | 0.423 | 38.27 |
| NH₄H₂PO₄ dry water | 100 ~ 200 | 0.553 | 32.52 |

First, carry out a control combustion experiment. After ignition, the flame temperature is recorded by a paperless recorder. The upper and lower thermocouples correspond to channel 2 and channel 1, respectively. Among them, the location of channel 2 is at the center of the flame, the flame shape is stable, and the temperature curve is stable, which can more represent the true state of the flame, so the temperature curve of channel 2 is taken as a reference. As shown in Figure 6(a), after the fuel is ignited, the temperature of the thermocouple rises rapidly and reaches the highest value of 550-580°C after 20s, that is, $T_0=30s$. After a period of time, the temperature fluctuates between 450 and 550°C. The steady state lasts for about 60s. After that, the fuel burns out and the fire potential decreases, and the flame is
extinguished within 10s, that is, \( T_1 = 90s \). Then a control fire extinguishing experiment was carried out. Channels 3 and 4 correspond to the combustion tanks in the lower left corner and the upper left corner respectively. The ignition sequence is 4, 3, 2, 1, and the entire ignition process is completed within 5 seconds. The temperature-time curve of fire extinguishing is shown in Figure 6(b). The spray experiment was carried out three times in succession, and the average of the three times of fire extinguishing time was 35s, that is, \( T_2 = 35s \); After determining \( T_1 \) and \( T_2 \), conduct fire extinguishing experiments with adding fire extinguishing agents, and the fire extinguishing time \( T_3 \) of five fire extinguishing agents including superfine ABC dry powder, Pure water dry water, K\( \text{HCO}_3 \) dry water, K\( \text{NO}_3 \) dry water and NH\( \text{H}_4\text{H}_2\text{PO}_4 \) dry water was obtained, and then \( T_3 \) was compared and analyzed to evaluate the effectiveness of the five fire extinguishing agents for class B fires.

The temperature curves of different fire extinguishing agents are shown in Figure 7-11. All five fire extinguishing agents can successfully extinguish the flame. The temperature curve of the flame can be divided into three stages: pre-ignition, extinguishing, and cooling. After ignition, the thermocouple shows that the temperature rises rapidly. After 30s, the flame temperature reaches and stabilizes at the highest value. Subsequently, due to the release of the extinguishing agent, the temperature above the fuel dropped rapidly, and the flame was extinguished at about 300°C. The flame was effectively controlled and extinguished during this period. After that, as the temperature continues to decrease, the difference between the temperature above the fuel and the ambient temperature becomes smaller, and the temperature of the thermocouple slowly decreases and gradually tends to be gentle, approaching room temperature. Among them, the temperature curves of superfine ABC dry powder, K\( \text{HCO}_3 \) dry water, and K\( \text{NO}_3 \) dry water are similar. These three fire extinguishing agents have similar fire extinguishing efficiency and good fire extinguishing effects. The temperature curves of pure water dry water and NH\( \text{H}_4\text{H}_2\text{PO}_4 \) dry water are similar, and the temperature decreases slowly, so the fire extinguishing effect of these two fire extinguishing agents is slightly worse. After the fire extinguishing agent is released, the flame temperature drops. The flame is generally suppressed and extinguished within a few to ten seconds after the fire extinguishing agent is injected. Therefore, the temperature-time data of this period will be selected for analysis and comparison to study the fire extinguishing effect of the fire extinguishing agent.

![Figure 7. Fire extinguishing curve diagram of five extinguishing agents](image_url)
Use OriginLab software to process and analyze the data of fire extinguishing time and extinguishing agent dosage obtained in the fire extinguishing experiment, and obtain the temperature-time curve, the average cooling rate and the maximum cooling rate in the process of suppressing the flame of different extinguishing agents.

As shown in Table 2, the amount of superfine ABC dry powder is much smaller than that of dry water fire extinguishing agent. The superfine ABC dry powder fire extinguishing agent used in the experiment is a special customized ammonium dihydrogen phosphate coated dry powder, the composition is 90% ammonium dihydrogen phosphate, 10% auxiliary materials (hydrophobic white carbon black, activated clay, etc.). Its effective fire extinguishing ingredients are much higher than those contained in dry water. The dosage of different types of dry water fire extinguishing agents is also different, specifically, pure water dry water < KNO3 dry water < NH4H2PO4 dry water < KHCO3 dry water.

| Number | Superfine powder | KHCO3 dry water | KNO3 dry water | Pure water dry water | NH4H2PO4 dry water |
|--------|------------------|-----------------|---------------|---------------------|-------------------|
| 1      | 10.45g           | 27.8g           | 22.55g        | 16.25g              | 16.80g            |
| 2      | 5.35g            | 25.33g          | 18.05g        | 15.95g              | 20.26g            |
| 3      | 5.89g            | 22.83g          | 16.55g        | 15.05g              | 26.60g            |
| average| 7.23g            | 25.32g          | 19.05g        | 15.75g              | 21.22g            |

The extinguishing time of the five extinguishing agents is shown in Table 3. The extinguishing time is from short to long: KHCO3 dry water < superfine ABC dry powder < KNO3 dry water < pure water dry water < NH4H2PO4 dry water, among them, KHCO3 dry water and superfine ABC dry powder take the shortest time.

Analyzing the temperature-time curve in Figure 7-11, it can be found that the process of extinguishing type B fire by superfine ABC dry powder, KHCO3 dry water and KNO3 dry water is roughly the same. The temperature change curves collected by the four channels are similar, and it is not possible to directly express the effects of the five fire extinguishing agents in the process of extinguishing and cooling. Therefore, the channel 2 curve data temperature drop rate that best represents the flame development process is selected to represent the cooling effect of the extinguishing agent. Use OriginLab software to calculate the rate of temperature decrease per second during the fire extinguishing spray process, that is, the slope of the curve, and find the maximum value of the flame temperature decrease during the period, that is, the maximum value of the slope.

| Number | Superfine powder | KHCO3 dry water | KNO3 dry water | Pure water dry water | NH4H2PO4 dry water |
|--------|------------------|-----------------|---------------|---------------------|-------------------|
| 1      | 6.53s            | 8.41s           | 5.86s         | 13.95s              | 21.17s            |
| 2      | 10.20s           | 7.88s           | 8.15s         | 14.83s              | 15.88s            |
| 3      | 6.97s            | 7.32s           | 11.93s        | 12.68s              | 17.19s            |
| average| 7.90s            | 7.87s           | 8.90s         | 13.82s              | 18.08s            |

Table 4 shows the average cooling rate and the maximum cooling rate during the fire extinguishing process of different extinguishing agents. The average value of the cooling rate from high to low is superfine ABC dry powder = KHCO3 dry water > KNO3 dry water > pure water dry water > NH4H2PO4 dry water; the maximum value of the cooling rate from high to bottom is superfine ABC dry powder = KHCO3 dry water > NH4H2PO4 dry water > KNO3 dry water > pure water dry water, among them, KNO3 dry water, pure water dry water, and NH4H2PO4 have the smallest values.
Table 4. The cooling rate of five fire extinguishing agents

|                     | super fine powder | KHCO₃ dry water | KNO₃ dry water | Pure water dry water | NH₄H₂PO₄ dry water |
|---------------------|-------------------|-----------------|----------------|----------------------|-------------------|
| Mean cooling rate   | 20.1°C/s          | 21.1°C/s        | 13.6°C/s       | 8.7°C/s              | 9.0°C/s           |
| Maximum cooling rate| 28.3°C/s          | 28.3°C/s        | 21.0°C/s       | 20.5°C/s             | 21.6°C/s          |

In summary, the superfine ABC dry powder has a large cooling rate, a short extinguishing time, and a small amount of extinguishing agent, which has a good extinguishing effect. The lowest cooling rate is pure water dry water, which is 8.7°C/s, and its particle size is equivalent to KHCO₃ dry water and KNO₃ dry water, when the fluidity and bulk density of the three are similar, it can be approximately regarded as the fire extinguishing components of the three fire extinguishing agents and the frequency of action of the flame is equivalent. It can be seen that both KHCO₃ and KNO₃ have an inhibitory effect on the flame during the fire extinguishing and cooling process. However, NH₄H₂PO₄ dry water has large particle size, large bulk density and poor fluidity, and the spray effect is different under the same pressure and equipment spraying conditions, resulting in unsatisfactory fire extinguishing. Combining the weight calculation with the analytic hierarchy process, the experimental results show that the order of the dry water extinguishing agent scores from high to low is: KHCO₃ dry water > KNO₃ dry water > pure water dry water > NH₄H₂PO₄ dry water.

4. Conclusion

In this paper, the dry water preparation process and fire-extinguishing experiments are studied, four types of dry water, KHCO₃, KNO₃, NH₄H₂PO₄, and pure water are prepared, and their fluidity, bulk density and other properties are obtained. A fire extinguishing experiment was designed, and the experiment was compared with the superfine ABC dry powder fire extinguishing agent. The experimental data obtained was processed and analyzed, and the following conclusions were drawn:

1. The core-shell structure of dry water fire extinguishing agent makes it have fluidity and dispersibility similar to powder fire extinguishing agent, while maintaining extremely high-water content, making it of great application value in the field of fire extinguishing agents. Therefore, its application in the field of fire extinguishing is of great significance for firefighting and the development of fire extinguishing agents.

2. The physical and chemical properties of the dry water prepared under the optimal preparation conditions are as follows: pure water dry water, KHCO₃ dry water, KNO₃ dry water, the particle size of the three kinds of dry water is concentrated in 20-50µm, and the particle diameter of NH₄H₂PO₄ dry water is concentrated in 100-200µm; pure water dry water, KHCO₃ dry water, and KNO₃ dry water have a bulk density of about 0.40g/ml, an angle of repose of 38°, and good fluidity; NH₄H₂PO₄ dry water bulk density is 0.55g/ml, and the fluidity of the angle of repose is 32°.

3. A fire extinguishing test box was built to conduct fire extinguishing experiments on Class B fires. The four data of fire extinguishing agent consumption, fire extinguishing time, average cooling rate and maximum cooling rate obtained from the fire extinguishing experiment of 5 experimental samples were compared and analyzed. Combining the weight of the analytic hierarchy process, it is concluded that the fire extinguishing efficiency of the five dry water fire extinguishing agents is from good to bad: KHCO₃ dry water > KNO₃ dry water > pure water dry water > NH₄H₂PO₄ dry water.

Acknowledgement

This work was sponsored by the Key K&D Program of Hebei Province (No. 20375503D) and Key Scientific Research Projects in China People’s police University (No. 2019zdgg006).

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