

## Preparation and firefighting performance study of a new AFFF firefighting material based on nano silicon dioxide

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### ABSTRACT

To improve the firefighting performance of aqueous film forming foam (AFFF), a new AFFF formulation containing nano silicon ( $\text{SiO}_2$ ) particles was developed in this study. Nano- $\text{SiO}_2$  (average particle size: 105 nm) was synthesized and incorporated into the standard AFFF formula at a concentration of 5%. The physicochemical properties of modified AFFF were systematically analyzed, and then the new firefighting material was tested in a simulated fire environment to analyse its firefighting performance. The firefighting time of new firefighting materials for solid combustibles, liquid substances, and chemical fires was significantly improved compared to the unoptimized materials, ranging from 0.9 to 1.5 minutes, 0.7 to 1.3 minutes, and 1.1 to 2.3 minutes, respectively. After 7 days of exposure, the quality loss of  $\text{SiO}_2$ -AFFF on steel (ASTM A36) was 0.9%, while the quality loss of the control AFFF was 9.8%, indicating a significant reduction in corrosiveness. Acute toxicity testing showed a significant reduction in toxicity compared to the control group. These results indicate that the addition of nano- $\text{SiO}_2$  significantly raises the fire extinguishing performance of AFFF and reduces its corrosiveness, providing a potential pathway for the development of more effective and safer AFFF firefighting materials.

**Keywords:** Nano silicon; AFFF firefighting agent; Firefighting performance; Firefighting equipment.

### 1. INTRODUCTION

Fire has the characteristics of strong suddenness, rapid spread, and serious harm. Once a fire occurs, it will cause huge property losses and seriously threaten people's life safety. Therefore, timely extinguishing of fires is crucial for preventing the spread of fire, reducing casualties and property damage [1, 2]. Aqueous film forming foam (AFFF), as an efficient and fast fire extinguishing material, takes a vital part in the field of fire protection. The AFFF firefighting agent can quickly cut off the contact between the flame and the fuel by forming a water film on the fuel surface. At the same time, the foam layer can inhibit the release of fuel vapor, so as to achieve the purpose of rapid extinguishing. AFFF is widely used for fire suppression in oil fields, chemical plants, airports, and other places [3, 4]. However, the surface activity of stabilizers and foaming agents in traditional AFFF materials is insufficient, resulting in unsatisfactory fire extinguishing performance. At the same time, their corrosiveness also has a certain impact on firefighting equipment and the environment. Therefore, it is particularly important to build a novel, environmentally friendly, and efficient AFFF formula [5, 6].

In the last few years, massive scholars have optimized the performance of AFFF extinguishing agent, mainly focusing on the following aspects: first, reducing environmental pollution. For example, WANZEK *et al.* [7] studied the method to reduce the pollution of polyfluoroalkyl substances in AFFF, but did not pay attention to the fire extinguishing time; when extinguishing a wood pile with this method, the extinguishing time required was 4.6~6.1 minutes. PINKARD [8] designed an AFFF firefighting material based on methyl sodium hydroxide, which reduces the generation of pollutants but lacks attention to the corrosiveness of the material, resulting in an equipment loss rate of 18.2%. The second was to improve fire extinguishing efficiency. For example, WU *et al.* [9] designed a new type of AFFF firefighting material based on hydrocarbon substances, which reduced firefighting time by 12.4%. However, its mechanism is based on hydrocarbon surfactants, and the stability of the fire extinguishing agent is relatively low (with a half-life of only 12 minutes at 25 °C).

Although the above studies have improved AFFF firefighting materials in different aspects, few studies have optimized the surface activity of the materials, resulting in unsatisfactory firefighting performance of AFFF materials. Nano- $\text{SiO}_2$  is a non-toxic and environmentally friendly nano material with excellent stability and

dispersibility [10]. The surface of the material contains massive hydroxyl groups, which have strong surface activity and are prone to chemical adsorption. Many scholars have analyzed the properties of nano-SiO<sub>2</sub> [11, 12]. For example, ZHANG *et al.* [13] designed an optimization method of firefighting foam based on nano-SiO<sub>2</sub> particles to develop a stable fluoride free firefighting foam. The findings denoted that massive nano-SiO<sub>2</sub> particles can adsorb surfactants, thus forming a network structure on the surface of nano-SiO<sub>2</sub> particles, filling and blocking the foam liquid boundary, thus raising the stability of foam. In addition, YANG *et al.* [14], to explore the impact of nano-SiO<sub>2</sub> particles on the foam performance of mixed surfactant solution, added nano-SiO<sub>2</sub> particles to hydrocarbon surfactant, and analyzed the performance of the foam generated by them. The results showed that due to the three-dimensional network structure of nano-SiO<sub>2</sub> particles, a stable film could be formed on the material surface, which could increase the sealing and spreading of foam on the material surface.

In summary, although there are currently many AFFF optimization materials, they still have problems such as low firefighting efficiency, long firefighting time, and high loss of firefighting equipment. To solve the above problems, a nano-SiO<sub>2</sub> modified AFFF material was prepared in this study, and its firefighting performance, corrosiveness, and toxicity were evaluated to raise the firefighting efficiency of the firefighting agent. The interaction between a large number of hydroxyl groups in nano-SiO<sub>2</sub> particles and the surfactant molecules of AFFF can enhance the mutual attraction of the surfactant molecules of AFFF, promote the formation of micelles, and improve the stability of foam. Moreover, the film-forming properties of nano-SiO<sub>2</sub> particles enable AFFF to effectively isolate air and fuel during fire extinguishing, preventing the spread of fire and improving fire safety. The innovation of the research is to find the best particle size and concentration of nano SiO<sub>2</sub> when the surface activity of foam extinguishing agent is the strongest by controlling the particle size and concentration of nano SiO<sub>2</sub> material, so as to improve the extinguishing performance of foam extinguishing agent.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of AFFF firefighting materials based on nano-SiO<sub>2</sub>

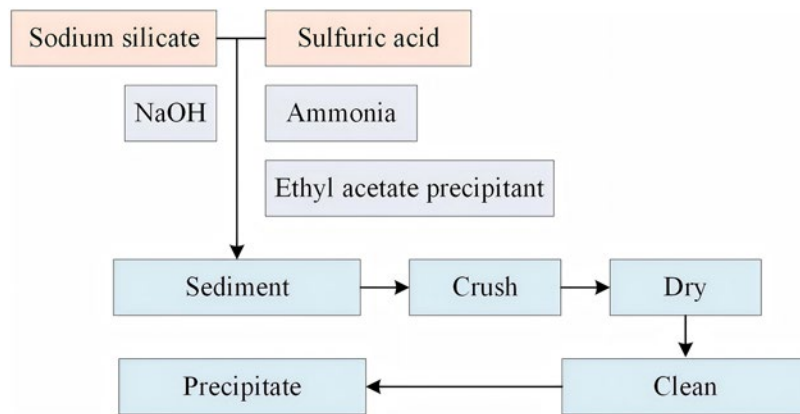
AFFF is a type of firefighting agent based on hydrocarbon surfactants and fluorocarbon surfactants [15]. This firefighting agent forms a water film on the surface of certain hydrocarbon liquids to extinguish fires caused by non water soluble liquid fuels [16]. Nano-SiO<sub>2</sub> particles can interact with the active ingredients in AFFF extinguishing agent in the foam liquid film, thus raising the foam stability of AFFF extinguishing agent and improving the firefighting efficiency [17, 18]. To raise the performance of foam extinguishing agent (FEA), nano-SiO<sub>2</sub> was added to AFFF extinguishing agent to improve it, and the performance of the improved FEA was analyzed. The preparation of SiO<sub>2</sub>-AFFF extinguishing agent requires the preparation of nano-SiO<sub>2</sub> first. The reagents used in the preparation of nano-SiO<sub>2</sub> are shown in Table 1.

During the preparation process, the reaction temperature is maintained within 40–50 °C. The basic process for preparing nano-SiO<sub>2</sub> particles is shown in Figure 1.

The water glass solution was mixed with other auxiliary reagents in a reactor and stirred at 300–600 r/min for 2 h. The pH was kept between 8–9 at the beginning of stirring, and the pH was adjusted to 9–10 by

**Table 1:** Preparation reagents and functions of SiO<sub>2</sub>.

REAGENT	PURITY	SUPPLIER	FUNCTION
Water glass (0.15 m/V)	95%	Xi'an Huachang Water Glass Co., Ltd	Silicon source
Sulfuric acid (0.34 mL/L)	95%	Nanjing Shengqinghe Chemical Co., Ltd	pH adjustment
Ammonia water (0.05 mL/L)	25%~28%	Nanjing Shengqinghe Chemical Co., Ltd	Catalyst
NaOH (3 mL/L)	96%	Shandong Blue Star Chemical Co., Ltd	pH adjustment
Tetraethyl orthosilicate (1 mL/L)	99%	Shanghai Aladdin Biochemical Technology Co., Ltd	Precursor
Ethyl orthosilicate (1 mL/L)	99%	Wuhan Xinyang Ruihe Chemical Technology Co., Ltd	Precursor
Ethyl acetate (1 mL/L)	98%	Kunshan Southeast Chemical Materials Co., Ltd	Precipitant
Cetyltrimethylammonium bromide (0.65 mL/L)	99%	Shanghai Kaiyin Chemical Co., Ltd	Surface modifier, prevents agglomeration



**Figure 1:** Preparation method of nano-SiO<sub>2</sub> particles.

**Table 2:** Preparation reagents and instruments for SiO<sub>2</sub> AFFF firefighting materials.

RAW MATERIAL	PURITY	SOURCE	DEVICE	MODEL	SOURCE
FS-50 surfactant (3 m/V)	99%	Guangzhou Jinshengji Chemical Co., Ltd	Mixer	RDROC-1S laboratory mixer of the same model	Changzhou Quanhe Instrument Manufacturing Co., Ltd
SDS surfactant (5 m/V)	92%	Guangzhou Jinshengji Chemical Co., Ltd	Filter	Needle filter	Changzhou Quanhe Instrument Manufacturing Co., Ltd
Fluorocarbon surfactant (6 m/V)	90%	Produced by Hubei Siweitu New Material Technology Co., Ltd	Reaction kettle	Jacketed Pilot Plant Reactors	Changzhou Quanhe Instrument Manufacturing Co., Ltd
Polyacrylamide (1 m/V)	90%	Anhui Tianrun Chemical Industry Co., Ltd	Storage tank	PTFE anti- corrosion storage tank	Changzhou Quanhe Instrument Manufacturing Co., Ltd

adding NaOH after 15 min. Next, ethyl acetate precipitant was added and stirred thoroughly until no precipitate was produced, keeping the pH between 9–10. The precipitate was then washed three times with warm water at 45 °C containing cetyltrimethylammonium bromide, controlling the pH to about 7. The resulting solid was dried in a vacuum oven at 50–90 °C for 5 hours. The dried SiO<sub>2</sub> solid was then ground using a nano-mill. The nano-grinding was carried out in three stages, gradually decreasing the diameter of the media balls (0.6–0.8 mm → 0.35–0.45 mm → 0.15–0.25 mm) and gradually increasing the stirring rotor linear speed (5–10 m/s → 10–15 m/s → 15–25 m/s), with a total milling time of 4 hours. Finally, the obtained SiO<sub>2</sub> particles were added to AFFF firefighting materials to prepare a novel SiO<sub>2</sub> AFFF firefighting material. The raw materials and preparation equipment for this material are shown in Table 2.

The preparation of SiO<sub>2</sub> AFFF firefighting material is denoted in Figure 2. First of all, 0.1%~1% cetyltrimethylammonium bromide cationic surfactant was used as the modifying agent, which was slowly added to the suspension of nano-SiO<sub>2</sub> particles. The stirring speed was 100 r/min while adding, so as to ensure that the surfactant was evenly covered on the surface of nano-SiO<sub>2</sub> particles and improve the compatibility and stability of nano-SiO<sub>2</sub> particles and foam solution. And within the low concentration range of 0.1% to 1%, the cationic surfactant of hexadecyltrimethylammonium bromide has enough molecules to cover the surface of nanoparticles, neutralize some charges, reduce the absolute value of zeta potential but still maintain a sufficiently high value, and the electrostatic repulsion is still sufficient to maintain dispersion stability without causing particle precipitation. Then the pretreated nano-SiO<sub>2</sub> particles, a variety of surfactants, stabilisers and water

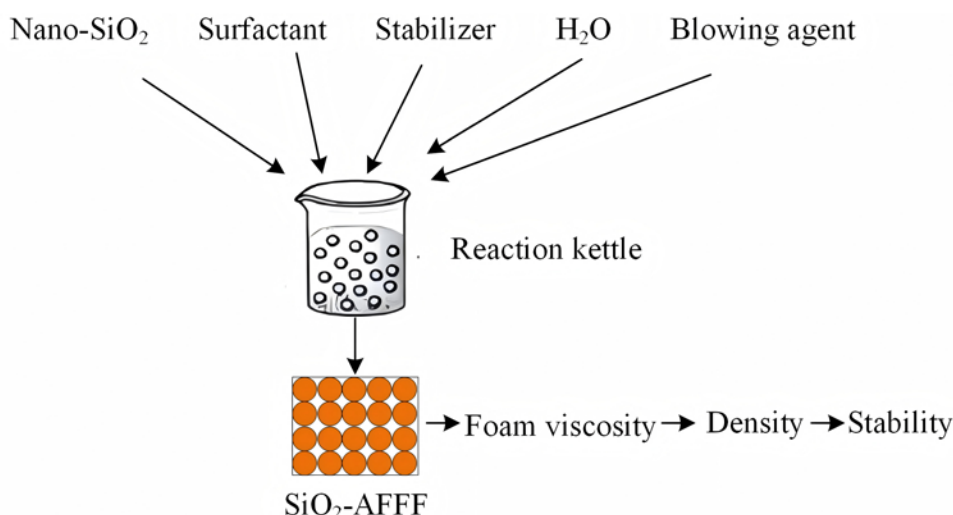


Figure 2: Preparation of  $\text{SiO}_2$ -AFFF material.

were added into the reactor and fully stirred at a stirring speed of 500 r/min for 1.5 h. Then, foaming agent was added to help form foam structure in the reaction kettle. Generally, low-cost air was used as the foaming agent, and air was forcibly injected into the foaming agent solution by blowing air to provide pressure, with an air flow rate of 200 mL/min. The reagent ratio was then adjusted by observing the speed of disappearance of the foam solution to ensure the stability of the foam solution. Viscosity was measured using a rotational viscometer, and the density of the liquid was measured using a liquid densitometer with density target values and viscosity target values initially set to 0.95–1.05 g/cm<sup>3</sup> and 32.6 mPa·s. Finally, the prepared  $\text{SiO}_2$ -AFFF firefighting materials were stored in tanks for subsequent use. And some components in  $\text{SiO}_2$ -AFFF fire extinguishing agent may undergo chemical reactions or physical property changes during the concentration process, which can affect its fire extinguishing performance. Therefore, the silicone based foam extinguishing agent in this study usually exists in a specific and prepared state.

## 2.2. Analysis method for firefighting performance of $\text{SiO}_2$ -AFFF firefighting materials

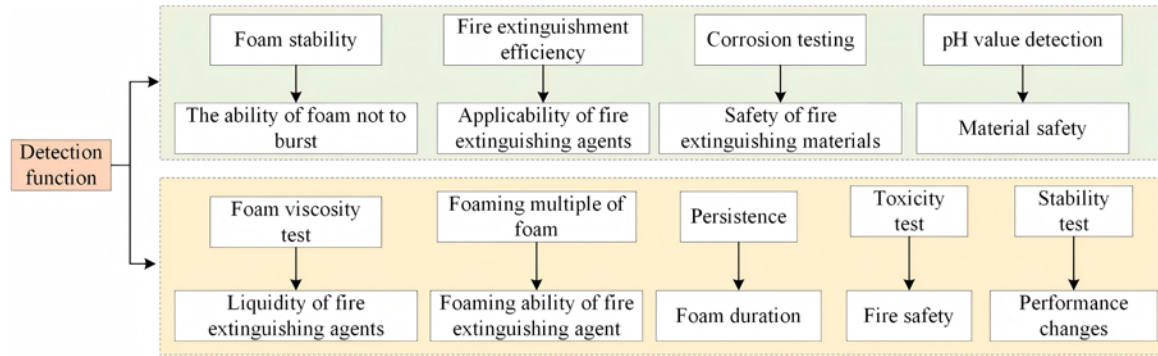
The firefighting performance of  $\text{SiO}_2$ -AFFF firefighting materials can be analyzed from multiple aspects, as shown in Figure 3. The firefighting performance of  $\text{SiO}_2$ -AFFF firefighting material is related to foam stability, firefighting efficiency, corrosivity test, material pH value test, foam viscosity test, foam foaming multiple test, durability test, toxicity test, storage stability test and other aspects.

Foam stability test can evaluate the ability of foam produced by FEA to keep unbroken in air. Firefighting efficiency testing refers to the effectiveness of firefighting agents in extinguishing different types of fires, which can ensure the applicability of firefighting agents. The calculation formula for firefighting efficiency is shown in Equation 1.

$$\begin{cases} C_1 = Q/V \\ C_2 = Q \times P / V \times T \end{cases} \quad (1)$$

In Equation 1,  $C_1$  represents the firefighting efficiency for solid and liquid fires.  $Q$  represents the combustion volume of the fire, which is calculated using the combustion area and combustion depth.  $V$  represents the consumption of foam extinguishers,  $C_2$  represents the firefighting efficiency for gas fires,  $P$  represents the pressure of gas fires, and  $T$  represents the firefighting time.

Corrosion testing is to detect the corrosiveness of firefighting agents on equipment and materials, ensuring that the firefighting agents will not cause damage to firefighting equipment and protective facilities during use, and ensuring the safety of firefighting operations and the integrity of equipment. PH testing is to ensure that the acidity and alkalinity of the firefighting agent are appropriate, reducing the harm of the firefighting agent to firefighting equipment and human health. Foam viscosity test can be used to reflect the fluidity of FEA, and the fluidity will have a direct impact on the transportation and spraying of FEA. Firefighting agents with lower



**Figure 3:** Detection function of different firefighting performance.

viscosity are easier to pass through pipelines and nozzles, ensuring rapid spraying in emergency situations. The detection of foam foaming ratio can evaluate the foaming ability and extinguishing effect of FEA. The higher the foaming ratio, the stronger the foaming ability of FEA, which can quickly generate a large number of foam at the fire scene, effectively cover the fire source and improve the firefighting efficiency. The calculation method for foaming ratio is denoted in Equation 2.

$$M = (V \times \tau) / G_2 - G_1 \quad (2)$$

In Equation 2,  $V$  refers to the volume of the glass bucket used in the test, the volume of the glass bucket is set to 4 L,  $\tau$  refers to the density of foaming agent aqueous solution,  $G_1$  refers to the mass of the glass bucket, and  $G_2$  refers to the total mass of the glass bucket and foam. The diffusion coefficient of foam extinguishing agent is the core index to prove that foam forms a film on the fuel surface, and its calculation formula is shown in Formula 3.

$$S = rc - ri \quad (3)$$

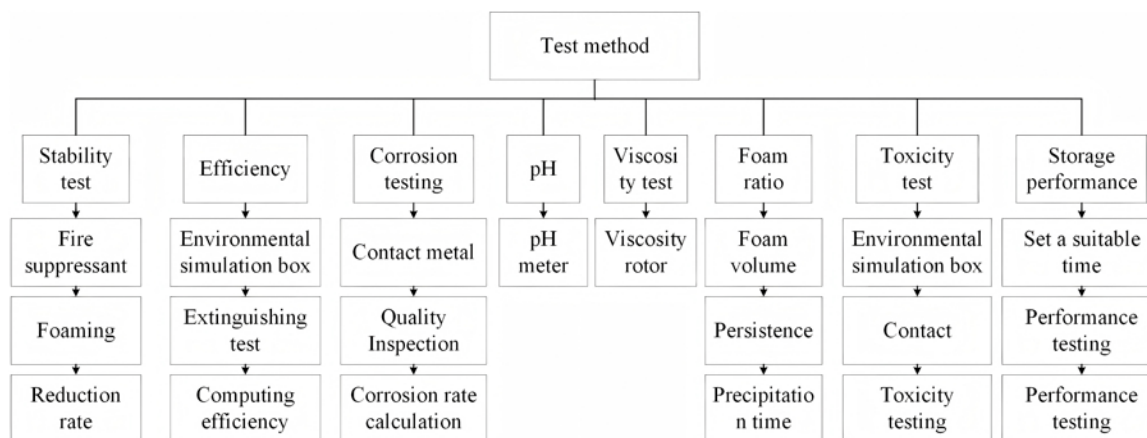
In Formula 3,  $S$  is the diffusion coefficient,  $rc$  is the fuel surface tension, and  $ri$  is the interfacial tension between foam solution and fuel. The durability test can evaluate the duration of FEA on the fire site to judge the effectiveness of extinguishing agent. Then it is necessary to test the potential toxicity of the firefighting agent to the environment and human health, to ensure the safety of the firefighting agent. Finally, the storage stability of FEA is tested to evaluate the performance change of extinguishing agent during storage. When testing the performance of firefighting agent, it is necessary to prepare various testing equipment, use a viscometer to measure the viscosity of foam liquid, and use a foam producer to simulate the production capacity of foam liquid in practical application. Then, pH meter is utilized to detect the pH of foam solution, and environmental simulation box is utilized to test the stability and performance change of foam solution under different environmental conditions. The test methods for various extinguishing properties of FEA are shown in Figure 4.

From Figure 4, the stability test method of FEA is to foam  $\text{SiO}_2$ -AFFF FEA under the standard conditions of GB/T 15308, and measure the reduction rate of foam within a certain time. The reduction rate refers to the percentage of foam volume reduction due to gravity, liquid evaporation, gas diffusion and other factors within a certain period of time. The firefighting efficiency test refers to simulating fire conditions in an environmental simulation box, using firefighting agents for firefighting testing, and calculating the firefighting efficiency using Equation 1 during the testing. The corrosivity test method was to contact  $\text{SiO}_2$ -AFFF FEA with common metal materials. ASTM A36 steel, 6061 aluminum and C11000 copper were selected as experimental materials during the experiment. The selected material was de-oiled and degreased, de-rusted and activated, then cut and sanded to divide it into equal-sized pieces. The corrosion rate of the material was calculated by testing the mass transformation of the metal material before and after corrosion after 7 days of exposure to room temperature by completely submerging the metal material in the solution. The calculation formula is shown in Equation 4.

$$\rho = (m_0 - m_1) / St \quad (4)$$

In Equation 4,  $m_0$  means the mass of the metal before corrosion,  $m_1$  means the mass of the metal after corrosion,  $S$  means the surface area of the metal, and  $t$  means the corrosion time. PH detection is to directly





**Figure 4:** Testing method for firefighting agent performance.

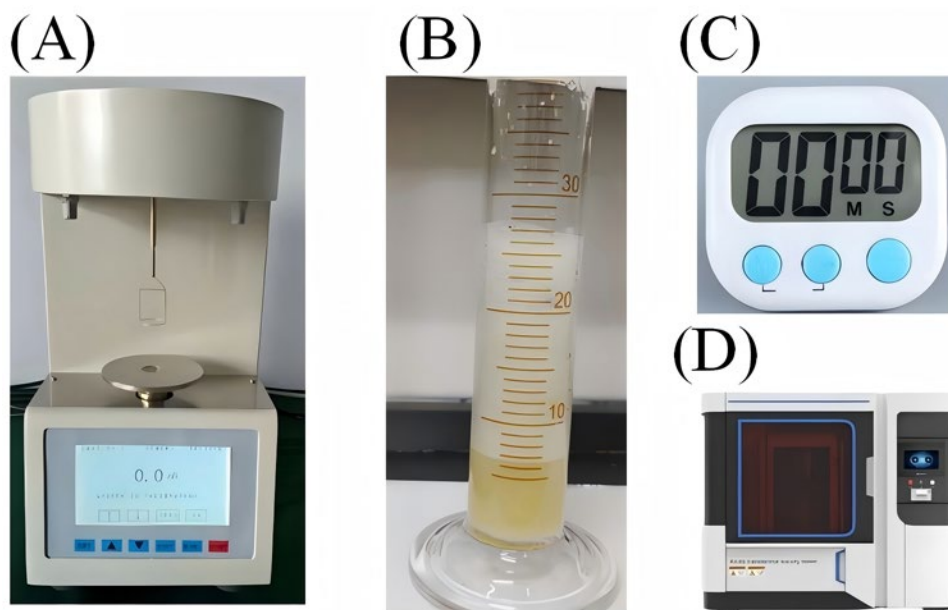
measure the pH of FEA through pH meter. During testing, a PHS-25 solid composite electrode pH meter was used, and during calibration, an automatic calibration method was adopted. A known pH standard buffer was prepared and the electrode was calibrated by immersing it in the buffer and immersing it in the auto-calibration mode. To perform the viscosity test, the sample foam solution was first cooled first to the lowest use temperature, i.e., the lowest temperature at which the foam solution can maintain stable performance, which was set to  $-20\text{ }^{\circ}\text{C}$ . Then, a suitable rotary viscosity rotor was chosen for viscosity measurement. The NDJ-4 rotating viscosity rotor was selected for the measurement and the speed was set to 30 r/min. The foaming ratio test method was to place a certain volume of  $\text{SiO}_2$ -AFFF FEA in a glass bucket, measure the volume of foam produced by FEA, and calculate the foaming ratio. The durability test of FEA can evaluate the durability of FEA by measuring the time of 25% mass liquid releasing after the formation of FEA. The toxicity test of FEA included acute toxicity test, chronic toxicity test, environmental toxicity test, mutagenicity test, etc. During acute toxicity testing, the OECD 202 method was utilized to evaluate the toxicity of fish by observing their survival status after exposure to firefighting agents and calculating the EC50 parameter. Chronic toxicity testing was conducted using the OECD 211 method to observe the reproduction of large fleas after prolonged exposure to firefighting agents, and their no observed effect concentration (NOEC) values were recorded to evaluate toxicity. The environmental toxicity test was conducted using the OECD 201 method to observe the growth of algae after exposure to firefighting agents, and the EC50 values were recorded to evaluate the toxicity of the fire extinguisher. The mutagenicity test was conducted using the OECD 471 method, using *Salmonella typhimurium* to observe whether it undergoes genetic mutations after exposure to chemicals, and the probability of mutations was recorded to evaluate its toxicity. Finally, when testing the storage performance of extinguishing agent, the above test method was used to test the extinguishing efficiency and stability of FEA every time it is stored in the storage tank. The storage temperature should be between  $-5\text{ }^{\circ}\text{C}$  and  $40\text{ }^{\circ}\text{C}$ , and the storage area should be kept dry and ventilated, avoiding exposure to direct sunlight. Testing should be conducted every month. The firefighting performance of  $\text{SiO}_2$ -AFFF-based firefighting materials was tested using the above method to verify that the material can optimize the firefighting effect of the extinguishing agent. The device for detecting the surface tension, foaming rate, extinguishing time and toxicity of extinguishing agent is shown in Figure 5.

During the test, keep the temperature at about  $25\text{ }^{\circ}\text{C}$  during the surface tension test, and record the surface tension value after stabilization. When testing the foaming rate, measure 50 mL of solution for foaming test, and test it in a windless environment with a temperature of  $25 \pm 2\text{ }^{\circ}\text{C}$  and a relative humidity of  $50 \pm 5\%$  RH. When testing the extinguishing time of extinguishing agent, control the amount of extinguishing agent within  $1.5 \pm 0.2\text{ L}$ , and record the extinguishing time.

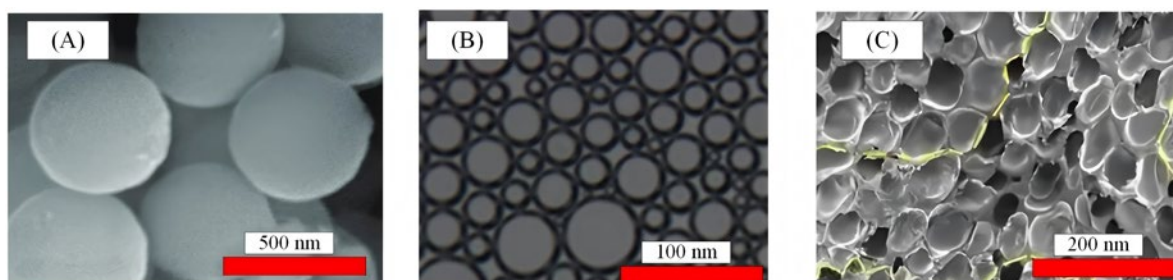
### 3. RESULTS AND DISCUSSION

#### 3.1. Analysis of physical and chemical properties of $\text{SiO}_2$ -AFFF firefighting materials

To verify the effectiveness of the foam firefighting agent based on nano- $\text{SiO}_2$  proposed in the research, the physical and chemical properties of the prepared nano- $\text{SiO}_2$  material and  $\text{SiO}_2$ -AFFF were tested first. The SEM image (Figure 6(A)) shows that the nano- $\text{SiO}_2$  particles are spherical in shape and have good dispersibility. Figure 6(C) shows that the mesh structure of  $\text{SiO}_2$ -AFFF was denser, which can better isolate air and improve



**Figure 5:** The (A) is a surface tension test device, (B) is a foaming rate test device, (C) is a fire extinguishing time test device, and (D) is a fire extinguishing agent toxicity test device.

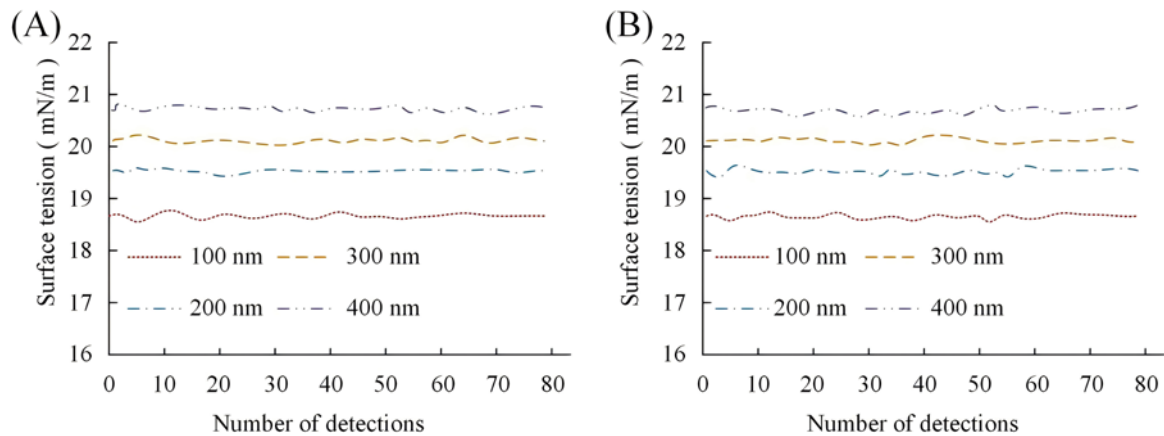


**Figure 6:** The (A-C) SEM images of  $\text{SiO}_2$ , AFFF materials, and  $\text{SiO}_2$ -AFFF at different magnifications.

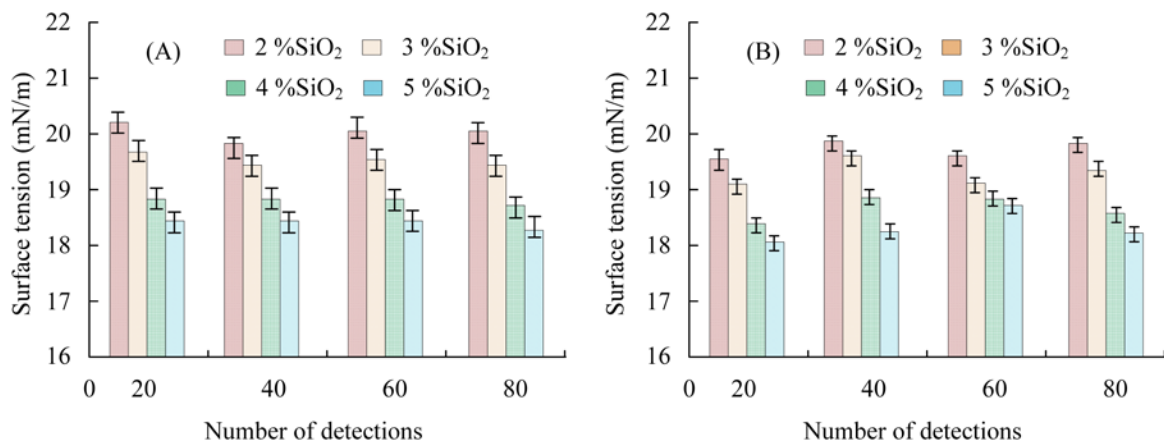
firefighting efficiency during firefighting. And the dispersion coefficient of  $\text{SiO}_2$  nanoparticles was calculated by measuring their particle size to obtain a dispersion coefficient of 0.2.

Then, the influence of nano- $\text{SiO}_2$  materials with different particle sizes on the surface activity of foaming agent and stabilizer in FEA was tested, and the findings are denoted in Figure 7. According to Figure 7(A), the surface tension (ST) of the foaming agent of the firefighting agent formed by nano- $\text{SiO}_2$  particles with particle sizes of 100 nm, 200 nm, 300 nm, and 400 nm was 18.76 mN/m, 19.67 mN/m, 20.78 mN/m, and 20.97 mN/m, respectively. The smaller the particle size of nano- $\text{SiO}_2$  particles, the lower their ST, and the lower the ST, the stronger the surface activity of the foaming agent in  $\text{SiO}_2$ -AFFF firefighting materials. As shown in Figure 7(B), the influence trend of the particle size of nano- $\text{SiO}_2$  particles on the surface activity of stabilizers in firefighting materials was roughly the same. The mechanism by which the particle size of nano- $\text{SiO}_2$  particles affects the surface activity of foaming agents and stabilizers may be that when their particle size is small, the surface area of nano- $\text{SiO}_2$  particles will significantly increase, the number of surface molecules will increase, and surface molecules will require additional energy to maintain stability due to uneven force, which will increase surface energy. To reduce the total energy of the system, the ST will decrease, and the increase in surface area will provide more adsorption sites for surfactants, enhancing their effectiveness and further reducing ST.

Then the surface activity of foaming agent and stabilizer in foam firefighting agent with different nano- $\text{SiO}_2$  concentration at the same particle size was tested, and the results are denoted in Figure 8. From Figure 8(A) and (B), the lower the concentration of nano- $\text{SiO}_2$ , the greater the ST of foaming agent and stabilizer



**Figure 7:** The influence of nano-SiO<sub>2</sub> materials with different particle sizes on the surface activity of the (A) foaming agent and (B) stabilizer of AFFF firefighting agent.



**Figure 8:** The influence of nano-SiO<sub>2</sub> materials with different concentrations on the surface activity of the (A) foaming agent and (B) stabilizer of AFFF firefighting agent.

in the SiO<sub>2</sub>-AFFF firefighting material FEA. This indicates that the lower the concentration, the lower the surface activity of the firefighting agent. When the SiO<sub>2</sub> concentration was 5%, the ST of the foaming agent and stabilizer could reach the lowest, which were 17.67 mN/m and 17.56 mN/m, respectively. This result may be due to the increase in the concentration of nano-SiO<sub>2</sub>, which causes more surfactant molecules to adsorb onto the surface of the nanoparticles, covering the contact surface between the solution and air. Due to the ability of surfactant molecules to reduce ST, an increase in surface coverage will lead to a decrease in solution ST. From the above experimental results, when preparing SiO<sub>2</sub>-AFFF firefighting materials, it needs to control the particle size of nano-SiO<sub>2</sub> materials at 100 nm and the concentration at about 5%, so as to improve the surface activity of foam firefighting agent. And the interfacial tension and viscosity data of SiO<sub>2</sub>-AFFF fire-fighting material based on this concentration and particle size were tested. The results showed that its interfacial tension was 1.09 mN/m, and its diffusion coefficient was calculated to be 16.58 mN/m. The dynamic viscosity of the material is 20~30 mPa·s, and the contact angle of the material is 83° at 5% concentration and 100 nm particle size. The highest separation energy can form the most stable foam.

### 3.2. Analysis of firefighting performance of firefighting materials

After analyzing the performance of the prepared FEA, the extinguishing performance of the new FEA in the actual situation was analyzed. The firefighting performance of the AFFF extinguishing agent not improved

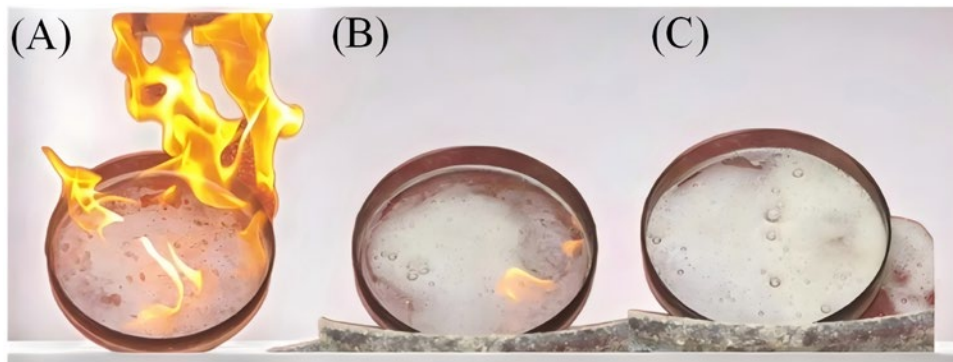


with nano-SiO<sub>2</sub> was compared with that of the proposed nano-SiO<sub>2</sub> FEA in the environmental simulation box to simulate an actual fire, so as to verify the superiority of the agent. The flame extinguishing situation during SiO<sub>2</sub>-AFFF fire extinguishing agent test is shown in the Figure 9.

First, the foaming rate of different foam extinguishing agents was tested, and the results are shown in Table 3.

It can be seen from Table 3 that the foam foaming rate of SiO<sub>2</sub>-AFFF foam extinguishing agent is the highest in different fire extinguishing scenarios. Compared with the traditional AFFF extinguishing agent, the foaming rate was significantly improved ( $p < 0.01$ ). Then, the extinguishing time of two different materials of firefighting agents on flames under the same fire situation was tested, and the results are denoted in Table 4. SiO<sub>2</sub>-AFFF extinguishing agent took the shortest time to extinguish the flame in various fire situations. Among them, the extinguishing time for solid combustibles was within 0.9–1.5 minutes, with an average time of 1.2 minutes. This firefighting agent had a slower extinguishing speed and took a longer time to extinguish fires caused by gas, with an average time of 3.75 minutes. Compared to fires caused by solid combustibles, the extinguishing time was extended by about 2.5 minutes. It may be that the gas itself has fluidity and is difficult to be fixed or limited in a small range, which makes it difficult for FEA to cover the gas fire source and quickly form an effective insulation layer. When the AFFF extinguishing agent made of nano-SiO<sub>2</sub> material was not used to extinguish the fire caused by solid combustibles, it took 2.1–3.3 minutes. When other FEAs were used to extinguish various fires, the time consumption was higher than that of SiO<sub>2</sub>-AFFF extinguishing agent.

Then, the corrosiveness of the four firefighting materials to common metals was tested to ensure the effectiveness of firefighting materials in the storage process, the use of firefighting agents in the process of firefighting materials, to protect the firefighting performance of firefighting agents. Four types of firefighting materials were subjected to corrosion testing in three types of ASTM A36 steel, 6061 aluminum, and C11000 copper metals. After 7 days of contact at room temperature, their corrosion effects were tested, and the results are denoted in Figure 10. From Figure 10(A), the corrosion of SiO<sub>2</sub>-AFFF extinguishing agent to common steel, aluminum and copper metals was low, and the mass loss was only 0.9%, 1.1% and 0.8%. In Figure 10(B) and (C), although fluoroprotein FEA and aluminum sulfate FEA were less corrosive to metals, they were slightly



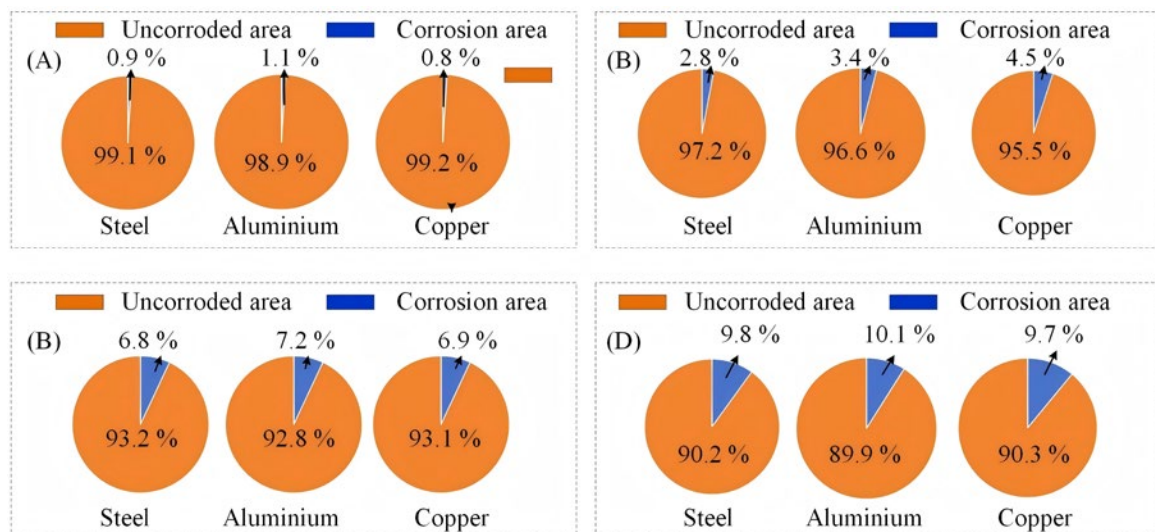
**Figure 9:** The (a) is the flame condition at the beginning of extinguishing, (b) is the flame condition in the process of extinguishing, (c) is the flame condition that has been extinguished.

**Table 3:** Comparison of foaming rate of fire extinguishing agent.

FIRE TYPE	AFFF (ml/g)	ALUMINUM SULFATE FEA (ml/g)	FLUOROPROTEIN FEA (ml/g)	SiO <sub>2</sub> - AFFF (ml/g)	P (VS. AFFF)
Solid combustibles (0.5 m <sup>3</sup> firewood pile fire)	380 ± 30	420 ± 32	450 ± 40	610 ± 45	$p < 0.01$
Liquid substance (1 m <sup>2</sup> heptane pan fire)	410 ± 35	480 ± 10	500 ± 45	720 ± 50	$p < 0.01$
Gas fire (0.5 m <sup>2</sup> Hydrogen fire)	310 ± 20	350 ± 20	380 ± 35	520 ± 40	$p < 0.01$
Chemical fire (0.5 m <sup>2</sup> Methanol fire)	360 ± 10	400 ± 10	420 ± 40	580 ± 45	$p < 0.01$

**Table 4:** Time consumption of firefighting with different FEAs.

FIRE TYPE	AFFF (min)	ALUMINUM SULFATE FEA (min)	FLUOROPROTEIN FEA (min)	SiO <sub>2</sub> -AFFF (min)
Solid combustibles (0.5 m <sup>3</sup> firewood pile fire)	2.1~3.3	1.8~3.1	1.5~2.9	0.9~1.5
Liquid substance (1 m <sup>2</sup> heptane pan fire)	1.9~2.4	1.6~2.8	1.8~3.2	0.7~1.3
Gas fire (0.5 m <sup>2</sup> Hydrogen fire)	5.1~8.1	4.8~7.3	4.5~6.9	3.2~4.3
Chemical fire (0.5 m <sup>2</sup> Methanol fire)	2.3~3.7	2.8~3.2	2.3~4.1	1.1~2.3

**Figure 10:** Corrosion test results of (A) SiO<sub>2</sub>-AFFF extinguishing agent, (B) fluoroprotein FEA, (C) aluminum sulfate FEA and (D) AFFF extinguishing agent.

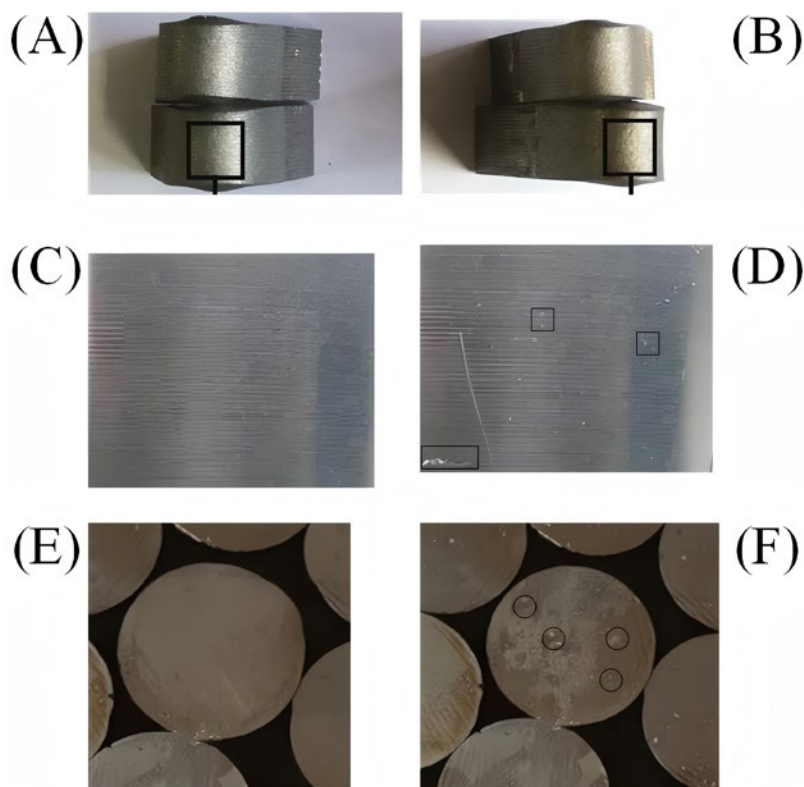
higher than SiO<sub>2</sub>-AFFF extinguishing agent. The mass loss of fluoroprotein FEA to three metals was 2.8%, 3.4% and 4.5% respectively, and that of aluminum sulfate FEA to three metals was 6.8%, 7.2% and 6.9% respectively. As shown in Figure 10(D), the AFFF extinguishing agent that is not improved by nano-SiO<sub>2</sub> was highly corrosive to three metals, which is not conducive to the storage and transportation of extinguishing agent, and is easy to damage items when extinguishing a fire.

The corrosion of SiO<sub>2</sub> AFFF extinguishing agent on the three metals is shown in Figure 11.

Finally, the toxicity of the four types of firefighting agent materials was tested, and the outcomes are denoted in Table 5. Among the four FEAs, SiO<sub>2</sub>-AFFF extinguishing agent had the highest EC50 and NOEC. In the acute toxicity test, its EC50 was 6000.68 mg/L, much higher than the 3956.55 mg/L of AFFF extinguishing agent. In chronic toxicity testing and environmental toxicity testing, its NOEC value and EC50 value were also the highest among the four firefighting agents, at 7343.68 mg/L and 8764.32 mg/L, respectively. From the toxicity test results, SiO<sub>2</sub>-AFFF has the lowest toxicity, while AFFF has the highest toxicity.

#### 4. DISCUSSION

To improve the performance of the existing AFFF extinguishing agent and enhance the extinguishing effect of the extinguishing agent, this study improved the AFFF extinguishing agent by using the prepared nano-SiO<sub>2</sub> particles to improve the extinguishing effect of the extinguishing agent. The surface activity of foaming agent and stabilizer in SiO<sub>2</sub>-AFFF firefighting material was tested. The outcomes denoted that the ST of foaming agent and stabilizer in SiO<sub>2</sub>-AFFF firefighting agent was less than 20 mN/m when the particle size of nano-SiO<sub>2</sub> particles was 100 nm and the concentration was 5%, and the surface activity was the strongest. In the AFFF



**Figure 11:** The (A) And (b) are before and after corrosion of steel block, (c) and (d) are before and after corrosion of aluminum, and (E) and (f) are before and after corrosion of copper block

**Table 5:** Toxicity testing of firefighting agents.

FIRE SUPPRESSANT	ACUTE TOXICITY EC50 (mg/l)	CHRONIC TOXICITY NOEC (mg/l)	ENVIRONMENTAL TOXICITY EC50 (mg/l)	PROBABILITY OF GENE MUTATION (%)
SiO <sub>2</sub> -AFFF	6000.68	7343.68	8764.32	0.008
Fluoroprotein FEA	4898.67	6567.93	7752.41	0.012
Aluminum sulfate FEA	3978.88	5623.65	6732.98	0.019
AFFF	3956.55	4567.71	5798.65	0.045

material modified by LIU *et al.* [19] using Y-shaped fluorinated surfactants, the minimum ST of the material was 35.8 mN/m, and the surface activity of the firefighting agent was significantly lower than that of SiO<sub>2</sub>-AFFF. After analysis, it is found that the reason for this phenomenon is that the nano-SiO<sub>2</sub> particles have a large specific surface area, which can increase the number of atoms on the surface and the surface energy. In SiO<sub>2</sub>-AFFF, the surface of nano-SiO<sub>2</sub> particles can adsorb foaming agent and stabilizer for analysis. This adsorption changes the distribution of foaming agent and stabilizer molecules on the surface of the solution, making them more inclined to enrich at the gas-liquid interface, effectively reducing the surface tension of the liquid. In addition, the longer molecular chains and more branches of Y-shaped fluorinated surfactants can hinder their movement in the solution, thereby reducing their ability to reduce ST. And in order to suppress the firepower of the swimming pool and protect the environment, the QIU team has developed a new type of fluorine free material to replace AFFF fireproof material, and tested the material. The results showed that the interfacial tension of the fire extinguishing agent was very low, at 1.5 mN/m. The interfacial tension of the SiO<sub>2</sub>-AFFF fire extinguishing agent proposed in this study is 1.09 mN/m, which is lower than the new fluorine free fire extinguishing agent proposed by QIU *et al.* [20]. This indicates that SiO<sub>2</sub> AFFF fire extinguishing agent is prone to spreading and forming a

dense water film on the fuel surface, quickly covering, effectively isolating air, and suppressing reignition. In addition, YU *et al.* [21] designed a double template fire safety gel based on ice and bubbles in order to improve the fire performance of buildings. Through testing, it was found that the safety gel could provide sustainable fire air gel for buildings in combination with biodegradation when managing the high heat effect of buildings, ensuring fire extinguishing efficiency. The SiO<sub>2</sub>-AFFF fire extinguishing agent proposed in this study has a shorter extinguishing time and can extinguish flames in a timely manner. And YU *et al.* [22] designed a heterostructure based on the combination of gelatin and kosmotropic anions to enhance the environmental stability of two-dimensional black phosphorus in flame retardancy, thereby improving the flame retardancy and fire resistance of the material. The SiO<sub>2</sub>-AFFF fire extinguishing agent proposed in this study can also enhance its surface activity and foaming rate, thereby isolating flames and improving its fire resistance.

In addition, QIU *et al.* [23], in order to improve the stability of foam and its fire resistance, adjusted the stability of foam by actively switching the state of the liquid film interface. Eventually, the viscosity of the foam was only 1.2 mPa·s, while the viscosity range of SiO<sub>2</sub>-AFFF extinguishing agent was within the range of 20~30 mPa·s. Although QIU *et al.*'s viscosity was extremely low, the low viscosity would lead to the high fluidity of foam, which would lead to the easy rupture of foam. The viscosity range of SiO<sub>2</sub>-AFFF extinguishing agent covered the demand range of conventional extinguishing agent, which could balance the fluidity and stability of foam according to different fire scenarios. In addition, YU *et al.* [24] adjusted the stability of foam by adding nanofibers to adjust the fluidity of foam. The results showed that the contact angle of this material was 79°, lower than that of SiO<sub>2</sub>-AFFF material. Therefore, the stability of SiO<sub>2</sub>-AFFF material was good. The reason is that the SiO<sub>2</sub>-AFFF material is more hydrophobic, and the liquid film is not easy to be wetted and destroyed by water, so it is more stable in thermodynamics, thus improving the stability of foam. YU *et al.* [25] built a light responsive intelligent foam through the Hoffmeister effect and 2D black phosphorus to improve the stability of foam. The team's results show that the interfacial tension of foam is 5.76 mN/m, while the interfacial tension of SiO<sub>2</sub>-AFFF foam is 1.09 mN/m. The results show that SiO<sub>2</sub>-AFFF material can rapidly expand on the combustion surface to form a continuous water film, so as to more effectively isolate oxygen and block the combustion chain reaction.

To test the extinguishing performance of the prepared SiO<sub>2</sub>-AFFF extinguishing agent, this study compared the performance of this FEA with that of other FEAs. The results showed that the extinguishing time of SiO<sub>2</sub>-AFFF extinguishing agent for different fires was the shortest, and the extinguishing time for solid fires such as liquid substances, gas fires and chemical fires was 0.9~1.5 min, 0.7~1.3 min, 3.2~4.3 min and 1.1~2.3 min, respectively, which was significantly lower than other extinguishing agents. After the SNIPES *et al.* [26] modified the AFFF material with hydrophilic polymer, the firefighting agent produced by SNIPES took more than 4 minutes to extinguish the fire under the same conditions, and the firefighting time was higher than that of SiO<sub>2</sub>-AFFF extinguishing agent. According to the specific analysis, the reason for this result is that nano SiO<sub>2</sub> particles can be inserted into the micelle structure formed by surfactant molecules, making the arrangement between micelles more loose and orderly. This structural change reduces the viscosity of the foam liquid film, improves the fluidity of the foam, enables it to quickly cover the entire combustion area, reduces the contact area between the source of goods and air, and effectively inhibits the combustion reaction. When hydrophilic polymers form a water film, it takes a longer time. However, the research results showed that FEA took a long time to extinguish gas fires, which is similar to the research results of ZHANG *et al.* [27]. This is due to the diffusivity and fluidity of gas, and it is hard for foam to form an effective covering layer. Even if the foam can temporarily cover part of the fire source, it will soon be blown away or diluted by the gas, thus reducing the fire extinguishing effect and prolonging the fire extinguishing time.

## 5. CONCLUSION

In view of the low firefighting efficiency of AFFF and the problem of harmful substances, this study optimized the AFFF material by using nano-SiO<sub>2</sub>, and proposed a new SiO<sub>2</sub>-AFFF extinguishing agent. The research also tested the performance of the FEA. The results showed that the extinguishing time of SiO<sub>2</sub>-AFFF extinguishing agent was short, and its corrosivity and toxicity were low. It can be seen from the results that the SiO<sub>2</sub>-AFFF extinguishing agent proposed in the study could effectively improve the efficiency of the firefighting agent and ensure the safety of the extinguishing process. Future work can focus on optimizing the particle size and surface modification of nano-SiO<sub>2</sub>, and conducting large-scale firefighting tests to promote the renewal and development of firefighting materials. However, the extinguishing effect of FEA on gas fires in this study is not ideal. In the future, it is necessary to further research and develop effective formulas for gas fires. It may be possible to guarantee the extinguishing effect by combining nano-SiO<sub>2</sub> with other additives, or by modifying the foam conveying system.



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## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon request.