



## Temperature effects of the artificial accelerated ageing of aqueous film-forming foam agent on the foam structural stability

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### ABSTRACT

Aqueous film-forming foam (AFFF) fire extinguishing agent is widely used in petrochemical and other fields because of its excellent fire extinguishing performance. However, it will gradually deteriorate under the influence of ambient temperature changes during long-term storage. This study investigates the ageing behavior of AFFF under temperature variations by designing an artificial accelerated ageing experiment with alternating temperature cycles. The results show that under the experimental conditions, there is no significant change in the surface tension of the foam, but its stability significantly decreased. The foam expansion ratio decreases by more than 10.00 %, and the drainage time is reduced by an average of 47.78 %. Additionally, the uneven distribution of components in the solution led to an increase in the Sauter mean diameter of the bubbles and thickening of the liquid film, indicating a weakening of the microstructural integrity of the foam. An empirical model for performance prediction is developed in this study. The model provides an important theoretical basis and technical support for the storage management and formulation optimization of fire extinguishing agents.

### 1. Introduction

Over the past few decades, aqueous film-forming foam (AFFF) has been widely used in the fire protection industry for its excellent fire extinguishing effectiveness [1,2]. The combination of fluorocarbon and hydrocarbon surfactants enables AFFF to have a relatively low surface tension, allowing it to form a water film on the liquid surface. The polymer-based foam stabilizers contribute to the efficient coverage of foam layer in the fire scene [3–5]. The outstanding oil fire suppression capability of AFFF makes it an indispensable part of fire prevention in the petrochemical industry.

However, long-term storage of fire extinguishing agents is required for economic reasons. Changes in ambient temperature, light and chemical reactions will inevitably lead to the ageing and failure of the active ingredients of the extinguishing agent [6,7]. Specifically manifested as a decline in fire extinguishing performance, insufficient spray distance, and other comprehensive problems. Furthermore, the ageing process of the fire extinguishing agent may also lead to the release of

harmful gases or the formation of precipitates, which can cause potential risks such as pipe blockage. The failure of the extinguishing agent during its service life severely hinders the effectiveness of emergency response during the critical window of fire rescue, potentially resulting in larger-scale casualties and economic losses.

The countries for the foam fire extinguisher inspection cycle and qualification standards have developed strict specifications. In China, the technical standard for foam extinguishing systems (GB50151-2021) mandates that foam with a shelf life of no more than two years must undergo annual testing, while foam with a shelf life exceeding two years is required to be tested biennially [8]. The National Fire Protection Association (NFPA 10) stipulates that fire extinguishers need to be inspected for external maintenance once a year, and according to the type of extinguishers, an internal inspection should be carried out every 1–6 years [9]. The inability to determine the failure time of the extinguishing agent makes it impossible to establish a precise schedule for its renewal. Frequent replacement of the fire extinguishing agent not only incurs higher economic costs but also exacerbates resource waste.

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Therefore, it is particularly important to study the stability of the performance of the fire extinguishing agent during storage and its evolution mechanism.

Currently, systematic research on the ageing of fire extinguishing agents is still relatively limited. Previous studies have evaluated the effectiveness of expired foam extinguishing agents (fluoroprotein, AFFF, and alcohol-resistant foams). The results show that some agents experience performance changes, with longer extinguishing times and shorter re-ignition times [10]. It has been shown that AFFF undergoes significant thermal ageing at high temperatures [11]. Based on liquid chromatography-mass spectrometry coupled with nuclear magnetic resonance hydrogen spectroscopy, it is found that the short-chain components of hydrocarbon surfactants are significantly degraded during thermal ageing. The degradation process can be accelerated by either acidic or alkaline environment. For the quantitative analysis of the ageing mechanism, high-temperature accelerated ageing experiments combined with the Arrhenius equation and time-temperature superposition method can effectively predict the performance evolution and service life of surfactants under ambient temperature conditions [12]. Current research mainly focuses on the development of new fire extinguishing agents, with less attention given to the performance changes of already developed agents within their designated life.

This paper aims to investigate the key performance and micro-structural changes of AFFF after artificial accelerated ageing. The experiment followed international standards and adopted an alternating high-temperature and low-temperature method that better matched the actual storage environment. Periodic freeze-thaw cycles were used to accelerate the ageing behavior of the fire extinguishing agent. By observing parameters such as surface tension, liquid release time, and Sauter mean radius under different cycles, the mechanism of performance evolution after ageing was compared and analyzed. Based on data analysis, an empirical model for predicting foam life was proposed. This research can provide data support and theoretical basis for the storage management and applicability assessment of AFFF.

## 2. Method and material

### 2.1. Experimental material

The formulation of AFFF is so effective in fire suppression that it is widely used worldwide. However, due to the restrictions imposed by the Stockholm Convention on perfluorooctane sulphonate, long-chain fluorocarbon components are no longer used in commercial foam fire extinguishing agents nowadays [13,14]. This study used aqueous film-forming foam extinguishing agent (6 % AFFF), purchased from Jiangsu Suolong Fire Technology Company. The main components include hydrocarbon surfactants and polymeric foam stabilizers (specific substances are proprietary). Additional additives, such as urea and ethylene glycol, are incorporated to enhance antifreeze and solubilizing properties. The structures of common hydrocarbon surfactants and foam stabilizers are shown in Fig. 1 [15,16].

### 2.2. Alternate high and low temperature ageing

This experiment adheres to the Chinese national standards GB15308 and GB27897, as well as the International Maritime Organization (IMO) testing standards for fixed foam fire suppression systems and EN1568. These standards specify testing requirements that involve freeze-thaw cycles achieved through alternating high and low temperatures, with the observation of solution changes after multiple cycles. The low temperature is set at  $-45\text{ }^{\circ}\text{C}$ , which is lower than the freezing point of the extinguishing agent solution. The purpose is to freeze the solution and then heat it to melt, to assess its stability and performance changes during repeated freeze-thaw cycles. The high temperature is set to  $55\text{ }^{\circ}\text{C}$ , which exceeds the standard of  $25\text{ }^{\circ}\text{C}$  in the GB15308 specification. Examine its chemical stability under high temperature conditions. The

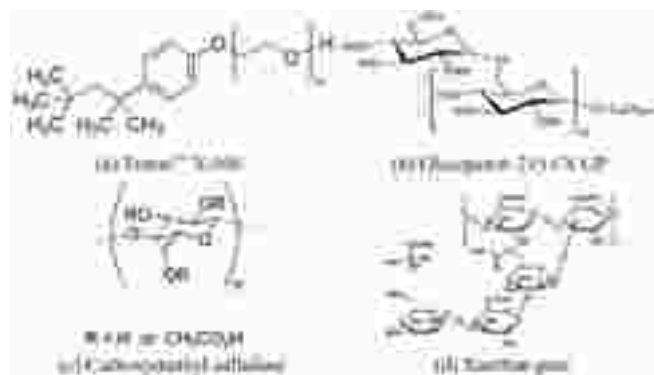


Fig. 1. The common surfactants and foam stabilizers (a) Triton™ X-100 (b) Glucopon® 215 CS UP (c) Carboxymethyl cellulose (d) Xanthan gum. (The image is sourced from Wikipedia.)

temperature variation range reaches  $100\text{ }^{\circ}\text{C}$ , which helps to fully simulate the temperature fluctuations that may occur in practical applications.

After dispensing the foam liquid samples, the test is placed in an oven at a temperature set to  $55\text{ }^{\circ}\text{C}$  for 12 h of continuous high temperature heating. Subsequently, the samples are rapidly transferred to a freezer at  $-45\text{ }^{\circ}\text{C}$  for quick cooling. Once cooling is complete, the samples are immediately returned to the oven for another 12 h of continuous heating. The above process is repeated to accelerate the ageing of the foam through high and low temperature and rapid high and low temperature transition. Three foam samples are sampled at 336 h intervals, starting with the first heating. In total, the test procedure is carried out for 2352 h and eight sets of samples are taken, as detailed in Fig. 2.

### 2.3. Foam analyzer

As shown in Fig. 3, the DFA100 Foam Analyzer is a highly specialized instrument for a wide range of foam research applications from KRUSS in Germany. The instrument can dynamically measure the volume of foam during its formation and track its decay process. The FSM module utilizes optical sensors to measure the size distribution of bubbles and track their variation over time. The LCM module is capable of measuring liquid content within the foam at multiple vertical levels. Additionally, the system allows the performance of tests under temperature-controlled conditions. The Line sensor of the instrument has a Spatial resolution of

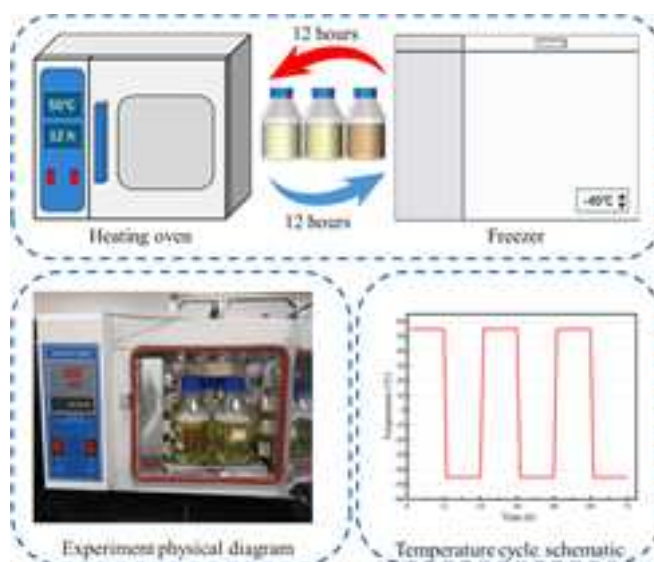


Fig. 2. Schematic diagram of temperature cycling test.

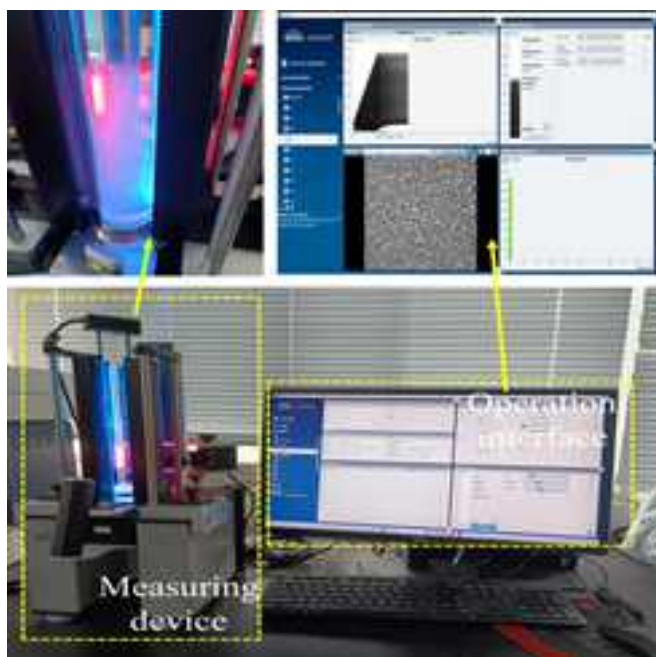


Fig. 3. Foam analyzer physical drawing and operation interface.

200 dpi, a temporal resolution of 20 fps, and the performance of the camera system is 2 fps at  $1280 \times 1240$  px, which can observe bubbles as small as  $50 \mu\text{m}$  in size.

The aged foam solution is removed and diluted with pure water in the ratio of 6:94, and inject the foam solution into the foaming chamber while ensuring that the instrument is dried.

To ensure that the foam solution is fully foamed, the test is conducted by quantitatively blowing 120 ml of air at a flow rate of 0.30 L/min.

#### 2.4. Advanced extended surface tension meter

The surface tension is measured using an advanced Sigma 700 extended-range tensiometer (as shown in Fig. 4). A platinum ring is used for the measurement, which is flame-cleaned to a red-hot state with an alcohol lamp before each test to remove surface contaminants. During



Fig. 4. Surface tensiometer and testing principle.

the test, when the platinum ring is in contact with the liquid surface, the liquid surface exerts a force on the ring due to surface tension, and the instrument realizes equilibrium by applying a reverse force to accurately determine the surface tension value. Measurement accuracy is up to 0.001 mN/m.

#### 2.5. pH meter

Measurements are taken using a pH meter calibrated with a standard buffer (as shown in Fig. 5). During the test, the electrode is immersed vertically in the liquid phase of the foam solution. The single measurement is recorded after the value has stabilized, and the value can be accurately recorded in two decimal places. To eliminate electrode memory effects, the electrode is sequentially rinsed with ultrapure water and dried with filter paper between consecutive measurements.

#### 2.6. Calculation of the sauter mean radius

The distribution of bubbles in foams is highly polydisperse and the performance of the bubble population can be described comprehensively by the sauter mean radius. It can intuitively reflect the combined characteristics of the volume and surface area of the particle population [17,18]. The specific calculation formula is as follows:

$$d_{32} = \frac{\sum_{i=1}^n n_i d_i^3}{\sum_{i=1}^n n_i d_i^2} \quad (1)$$

Where  $n_i$  and  $d_i$  represent the amount and radius of particulate matter in the particle size fraction, respectively. The calculation results are detailed in Fig. 10.

#### 2.7. Calculation of the foam liquid film thickness

The foam liquid film is the thin layer of liquid between the bubbles in the foam structure. The thickness of the liquid film affects the rate of bubble coalescence and the drainage rate of the foam, thereby determining the stability of the foam. The thickness of a single liquid film can be calculated by resistance calculation, and the thickness of the foam film can be roughly calculated by comparing it with the number of bubbles in the measuring range [19]. The specific formula is as follows:

$$d = \frac{h}{N} = \frac{1}{N} \frac{\rho L}{Rw} \tau \quad (2)$$

Where  $h$  is the thickness of the monolayer film;  $N$  is the number of



Fig. 5. Benchtop pH Meter.

bubbles;  $\rho$  is the resistivity of the solution;  $L$  is the electrode spacing;  $R$  is the resistance;  $w$  is the width of the film; and  $\tau$  is the curvature of the path between the electrodes, which can be approximated to be 1.00. See Fig. 6 and Fig. 10 for details.

### 3. Result and discussion

#### 3.1. Effects of thermal cycling on solution homogeneity

During the heating process, there is minimal loss of solvent components due to the well-sealed container. After freezing, the sample undergoes a phase transition from liquid to solid. The color of the solution shows no obvious change before and after ageing. During the test, there is no obvious solid precipitation found in the container, but an oil-like substance is observed floating in the solution. This could be attributed to the precipitation and aggregation of the solution components into oil droplets, indicating that the homogeneity of the solution has been compromised to some extent. Details are shown in Fig. 7.

#### 3.2. Effects of temperature cycling on the physicochemical properties of foam solution

Surface tension is one of the key factors in the efficient firefighting performance of AFFF. Lower surface tension contributes to the formation of a more homogeneous and stable foam as well as an improved diffusion coefficient. Surfactants, which are amphiphilic compounds, play a crucial role in maintaining the surface tension of the foam solution at lower levels. The variation in surface tension of the foam solutions at different ageing times is shown in Fig. 8. The overall trend remains stable, with fluctuations within the allowable error range, indicating no significant changes in surface tension. The common surfactant components are highly stable and undergo pyrolysis only at temperatures exceeding 400 °C [20,21]. Therefore, given that the test temperature is much lower than the pyrolysis temperature, it can be concluded that no surfactant loss occurred in the solution.

The pH of AFFF exhibits a continuous increase over time, as shown in Fig. 8. A comparison of the pH variations among the three foam samples reveals distinct differences. The pH of Sample 1 and Sample 2 increases significantly, with Sample 1 rising from 8.99 to 9.58 and Sample 2 rising from 8.86 to 9.73. In contrast, the pH change in Sample 3 is minimal, with only 0.05. The pH is determined by the hydrogen ion concentration in the solution, and considering the effective sealing of containers, pH

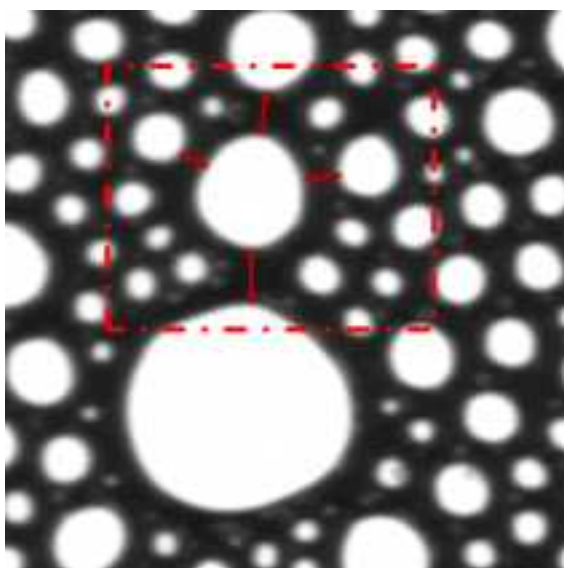


Fig. 6. Schematic diagram of liquid film.



Fig. 7. The apparent changes and phase transitions of the sample.

fluctuations caused by water evaporation can be excluded. The overall trend observed in samples suggests that the non-surfactant components in the solution undergo degradation, leading to an alkaline shift in pH. On the other hand, Sample 3 exhibits a relatively stable pH, suggesting the presence of a pH buffer that helps maintain the pH during storage. Previous studies indicate that both acidic and alkaline environments accelerate the degradation of foam solution components, thereby shortening the service life of foam and potentially causing foam failure even within the shelf life. This underscores the importance of avoiding ingredients that cause significant pH changes or adding pH buffers to stabilize the solution. In summary, although the pH values of all three samples increase over time, the extent and rate of this change vary. Effectively regulating pH during storage to ensure the long-term stability and performance of fire extinguishing agents remains a critical area for future research.

#### 3.3. Effects of thermal cycling on foam performance

Alternating high and low temperatures have an irreversible impact on the physicochemical properties of AFFF, demonstrating its excellent ageing performance, as shown in Fig. 9. The foam expansion ratio characterizes the expansion volume ratio of foam concentrate and determines the coverage efficiency. The 25 % drainage time reflects the stability of the foam system and is directly related to the key time parameter for maintaining the integrity of the coverage layer and the anti-reignition ability. After 2352 h of ageing, the drainage time of the samples decreased by 64.45 %, 29.26 %, and 49.63 % respectively, and the foam expansion ratio decreased by more than 10.00 %. As analyzed in the previous text, there is a phenomenon of component aggregation and uneven concentration distribution in the foam solution. In areas with excessively high concentration, the solution viscosity increases, resulting in greater resistance to bubble formation and fewer bubbles being generated. In areas with excessively low concentration, the liquid film strength of the generated bubbles is low, making it difficult to maintain. At the same time, the uniformity of the generated bubbles is greatly affected. This further accelerates the gravitational drainage and bubble rupture rate, leading to an increase in the drainage rate. The decline in foam performance is also related to the changes in foam stabilizer. Foam stabilizer plays a dominant role in the stability and foaming performance of foam. They can combine with surfactants to form a weakly interacting polymer-surfactant system (usually including neutral polymers and charged surfactants), or form a strongly interacting system (containing oppositely charged surfactants and polymers). These systems enhance foam stability by generating strong spatial repulsive forces. The heterogeneous distribution of components and the degradation of the polymer foam stabilizer lead to a decrease in the quantity of the composite system. As a result, nearly half of the total decline in AFFF performance can be observed during the first ageing cycle, as shown in Fig. 9 [22]. The failure of the foam layer barrier,

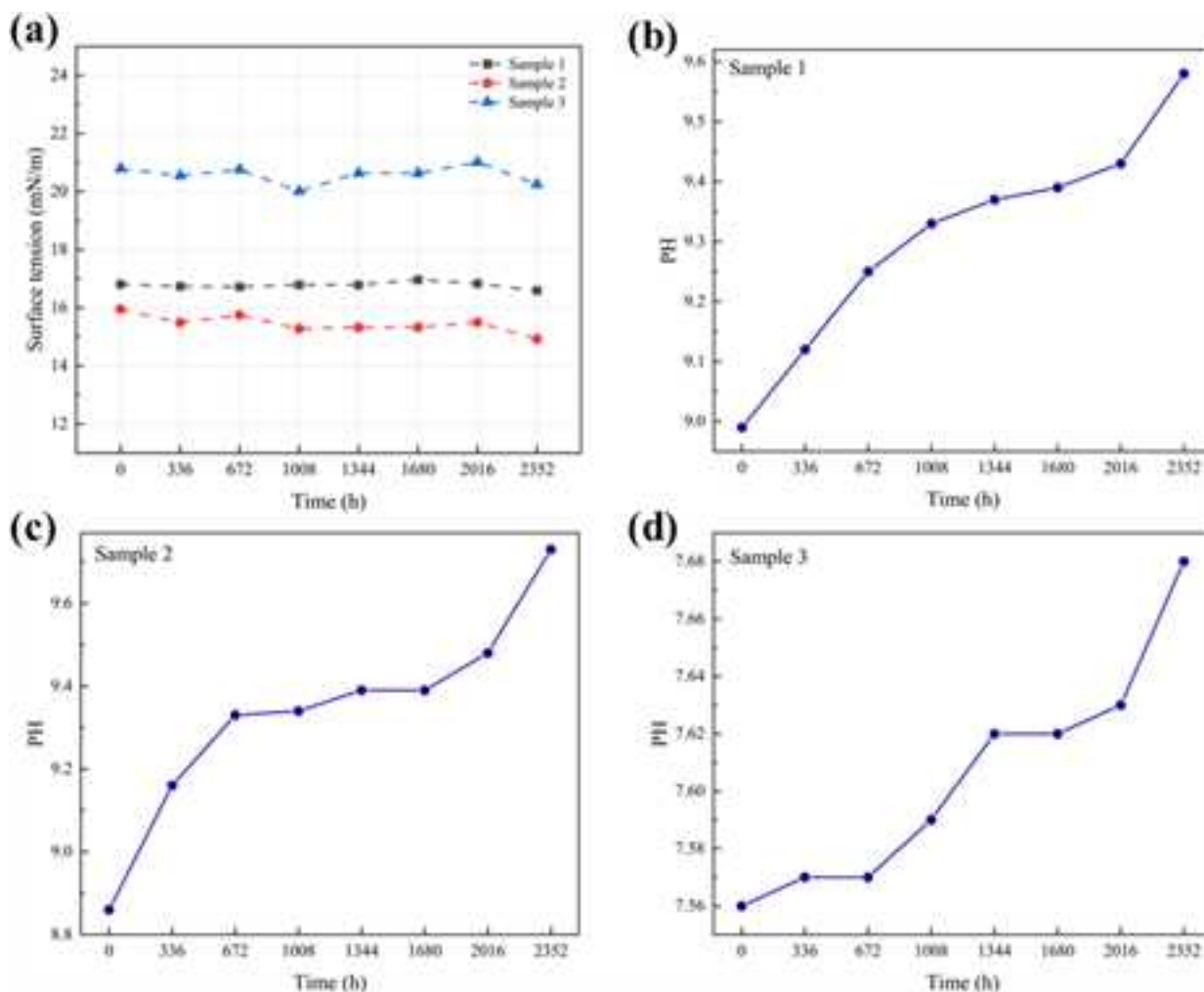


Fig. 8. (a) Variation of surface tension with ageing time (b-d) Variation of pH with ageing time.

caused by the deterioration of stability and insufficient foam expansion rate, will directly lead to a sharp increase in the risk of fuel vapor penetration and re-ignition during firefighting operations.

### 3.4. Effects of thermal cycling on foam microstructure

After foaming reaches a steady state, the initial sauter mean radius of the foam increases gradually with the ageing time. The sauter mean diameter of the foam in the intermediate state also shows the same trend. In the previous studies, low surface tension represents a lower interfacial energy consumption for bubble generation and incorporation, resulting in denser foams. As observed in earlier research, the surface tension of the foam does not change significantly. Therefore, the increase in the mean diameter can be attributed to the uneven distribution of surfactants in the solution. This further proves the uneven distribution of solute components in the solution. In practical applications, it is difficult to form a dense foam layer that effectively isolates the transfer of heat.

As shown in Fig. 10, it can also be observed that the rate of radius growth gradually increases within the same testing phase. This indicates that the foam coalescence and coarsening behaviors are becoming more pronounced. Bubble coalescence depends on the adsorption rate of surfactants at the bubble surface and the competition between bubble drainage. The hydrolysis, depolymerization, and precipitation losses of the polymer during the ageing process weaken the foam-stabilizing effect of the polymer-surfactant composite system. It becomes difficult for

the liquid to be maintained in the liquid film, and it precipitates under the influence of gravity and other forces. Meanwhile, the uneven distribution of surfactants in the solution also weakens the resistance of active molecules on the liquid film surface, enhancing the drainage of the foam. This ultimately leads to the intensified rupture of the liquid film and the coalescence process.

From the Fig. 10, it is found that the thickness of the liquid film under the same moment keeps getting thicker as the ageing cycle proceeds. The foam stabilizers are all used to enhance the stability of the foam structure. When it becomes inactive or depleted, the foam is more likely to break up and the bubble size and distribution become uneven, resulting in a thicker and more unstable foam layer. The thickening of the foam film usually means that the structure of the foam becomes weak. The uneven distribution of the surfactant in the foam is also a key factor in the thickening of the liquid film. During the ageing process, the surfactant may accumulate excessively in certain areas of the solution. This uneven distribution results in localized areas with excessive liquid film thickness, further reducing foam stability. Especially when exposed to a heat source, the overly thick liquid film cannot effectively isolate the fire source from the air, reducing the foam's fire extinguishing effectiveness.

### 3.5. Performance prediction model

The key characteristics of AFFF in fire extinguishment applications are its stability and liquid film isolation capability, which are primarily controlled by foam stabilizers and surfactants. Experimental results

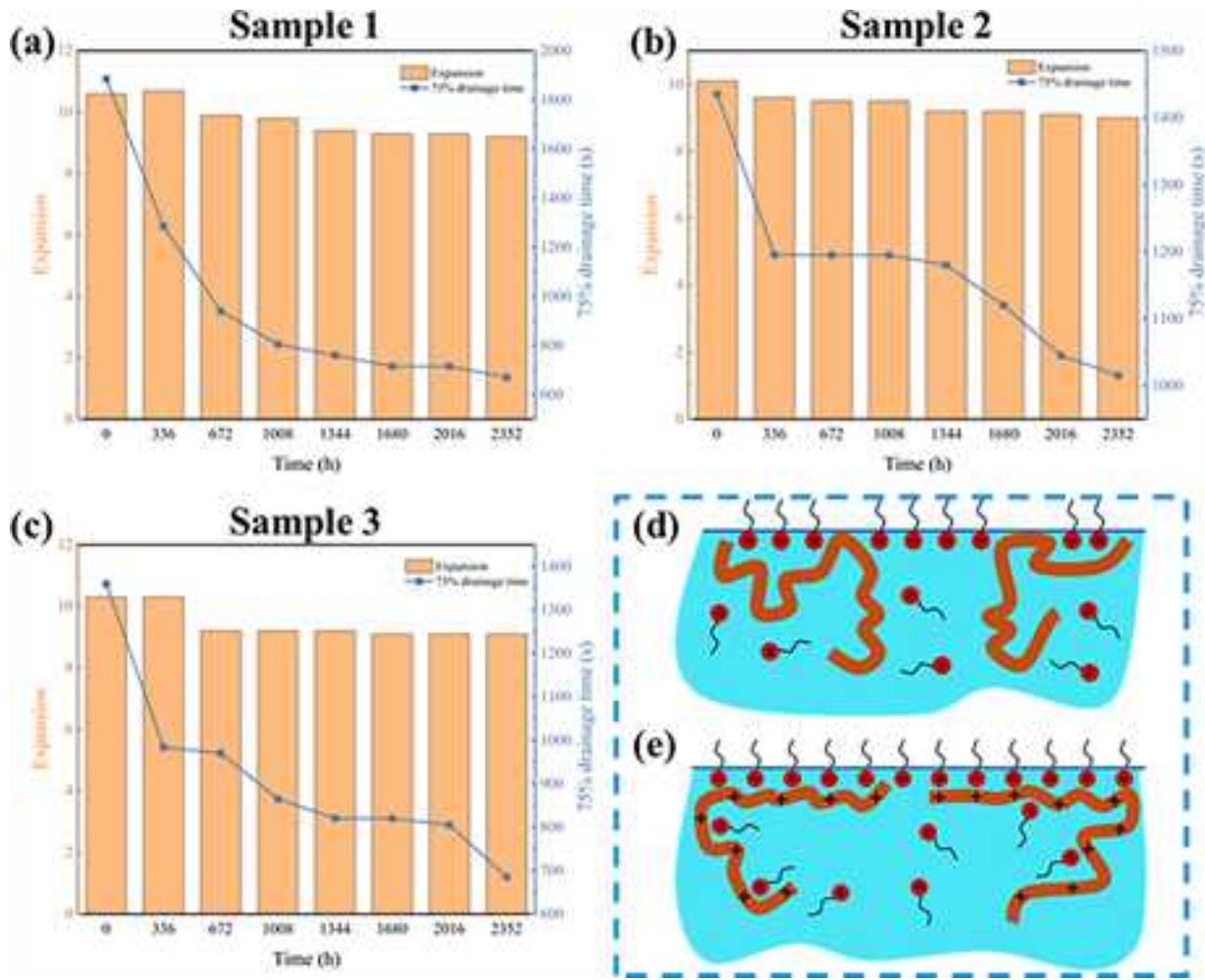


Fig. 9. (a-c)Variation of foam performance (d)Surfactant-polymer weak interaction system (e)Surfactant-polymer strong interaction system (a) Sample 1 (b) Sample 2 (c) Sample 3.

indicate that while the surface tension remains relatively unchanged, there is a significant loss in foam performance. To systematically quantify the effects of temperature cycling on foam performance, this study proposes a comprehensive analysis of drainage time and foam expansion ratio to characterize the overall stability and strength of the foam.

The index for calculating the comprehensive performance of foam is proposed by the previous authors based on the volumetric decay curve of the foam after stopping the mixing [23,24], and the calculation formula is as follows:

$$FSI = 0.75 \cdot V_{foam} \cdot t_{1/2} \rightarrow FSI = 0.75 \cdot E \cdot t_{1/2} \quad (3)$$

$$E = \frac{V_{foam}}{V_{liquid}} \quad (4)$$

Where,  $FSI$  is the comprehensive index of the foam system;  $V_{foam}$  is the foam volume;  $t_{1/2}$  is the liquid drainage half-life. Since the volume of liquid used for foaming is the same in each test, it is calculated by replacing  $V_{foam}$  with foaming expansion  $E$  according to the formula of foaming expansion. The details are shown in Fig. 11.

As shown in the Fig. 11, the integrated strength of the foam shows a significant decreasing trend with the increase of cycling cycles. In order to accurately predict the  $FSI$  of foams under different ageing cycles, this study used the least squares method combined to optimize the experimental data.

The model underlying the least squares method is commonly used in

linear, logarithmic, and logarithmic forms. Based on the given data, the exponential function is processed as an example:

$$y = A \cdot e^{-t/B} + C \quad (5)$$

The goal of fitting the curve based on the least squares method is to find the optimal parameters  $A$ ,  $B$ , and  $C$  by minimizing the sum of squared errors. For each data point  $(t_i, y_i)$ , the predicted value based on the fitting model is:

$$\hat{y}_i = A \cdot e^{-t_i/B} + C \quad (6)$$

Then the residual is:

$$\varepsilon_i = y_i - \hat{y}_i = y_i - (A \cdot e^{-t_i/B} + C) \quad (7)$$

On the basis of the residual sum of squares, the objective function is constructed as:

$$S(A, B, C) = \sum_{i=1}^8 (y_i - A \cdot e^{-t_i/B} - C)^2 \quad (8)$$

To minimize the objective function, it is necessary to calculate the partial derivatives of the function with respect to  $A$ ,  $B$ , and  $C$ , and use these derivatives to update the parameters. We define the learning rate as  $\alpha$ , and then iteratively update the parameters until convergence.

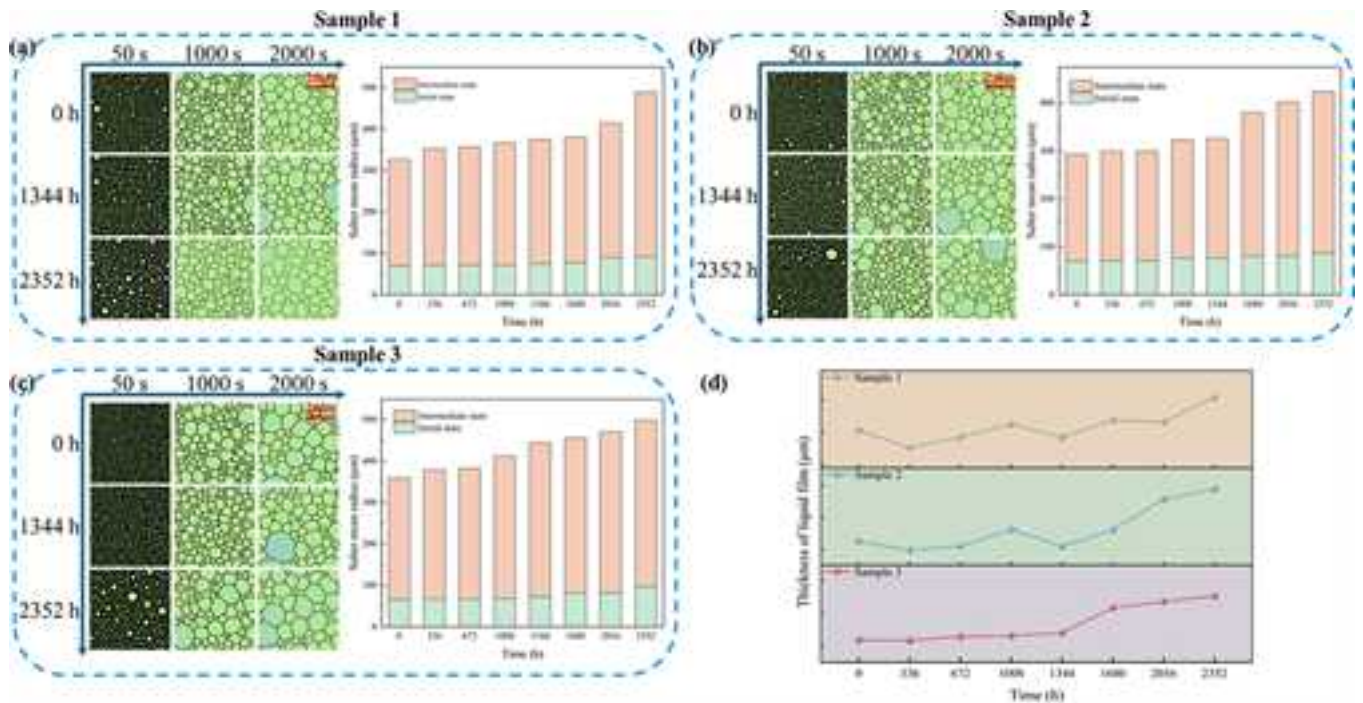


Fig. 10. (a-c) Periodic Variation of Foam Microstructure and Sauter Mean Radius (e) Foam film thickness variation curve (a) Sample 1 (b) Sample 2 (c) Sample 3.

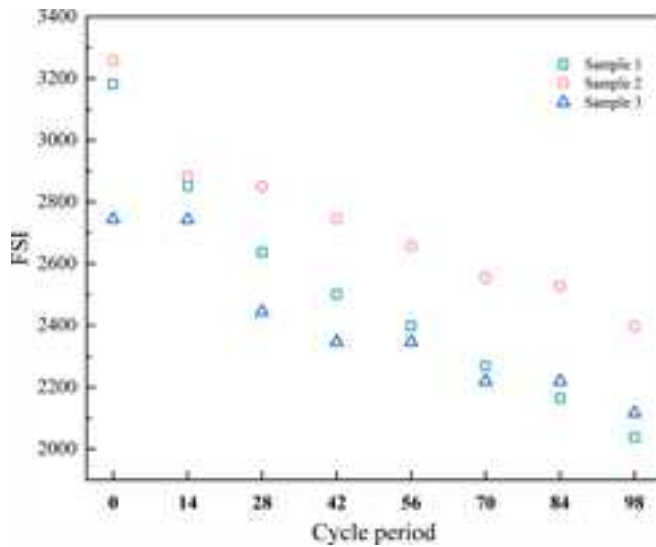


Fig. 11. The FSI of the sample under different periods.

$$\begin{aligned} \frac{\partial S}{\partial A} &= -2 \sum_{i=1}^8 (y_i - A \cdot e^{-t_i/B} - C) \cdot e^{-t_i/B} \\ \frac{\partial S}{\partial B} &= 2 \sum_{i=1}^8 (y_i - A \cdot e^{-t_i/B} - C) \cdot A \cdot t_i \cdot e^{-t_i/B} \cdot \frac{1}{B^2} \\ \frac{\partial S}{\partial C} &= -2 \sum_{i=1}^8 (y_i - A \cdot e^{-t_i/B} - C) \end{aligned} \quad (9)$$

The parameters A, B, and C are first initialized as random or estimated values. In each iteration, update each parameter until the objective function converges.

$$\begin{aligned} A_{new} &= A_{old} - \alpha \cdot \frac{\partial S}{\partial A} \\ B_{new} &= B_{old} - \alpha \cdot \frac{\partial S}{\partial B} \\ C_{new} &= C_{old} - \alpha \cdot \frac{\partial S}{\partial C} \end{aligned} \quad (10)$$

By iteratively updating the parameters A, B, and C, the objective function  $S(A, B, C)$  converges to a minimum value, resulting in the optimal fitting parameters A, B, and C. In accordance with the theory, three functions are selected to process the data in this study, and the specific results are shown in Table 1. From the Fig. 12, it can be observed that the exponential function fitting presents a smaller error and accurately reflects the trend of the numerical changes, thereby predicting the overall strength of the foam under different cycles. This also indirectly indicates that the integrated intensity of the foam follows a somewhat similar pattern in different cycles during the temperature cycling process. However, this phenomenon still needs to be explored in depth through further research. The details of the fitting curve are shown in Fig. 12 and Table 2.

Based on the properties of the exponential function, an attempt can be made to interpret the meaning of the parameters. The parameter A represents the initial stability of the foam, B shows the rate of decline in the strength of the foam, and C represents the level of stability of the foam after a long period of ageing. A smaller value of B means that the foam deteriorates more quickly; a larger value means the foam has a stronger ability to maintain stability over time. This parameter can be used to assess the sensitivity of the foam extinguishing agent to

Table 1  
Comparison of model fit.

NO.	The sum of squared minimum errors		
	Linear function	Exponential function	Logarithmic function
1	44247.94	7416.34	117935.19
2	46136.67	22587.85	42275.23
3	37638.58	23800.16	98770.21

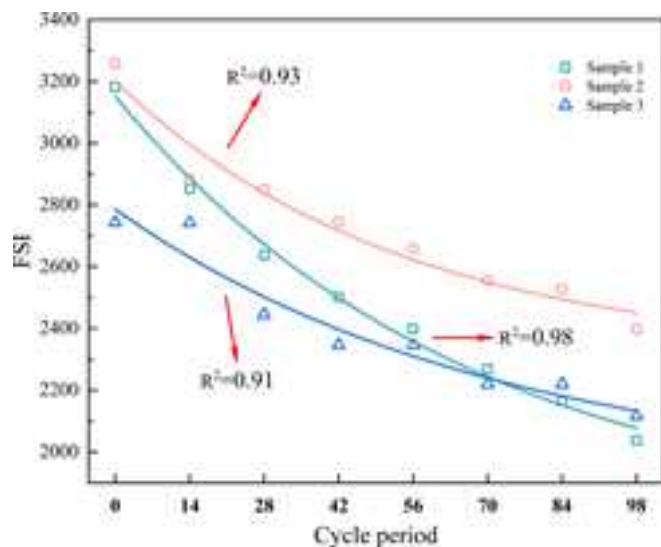


Fig. 12. The figure of foam stability fitting curve.

**Table 2**  
Fitting empirical equations.

NO.	Fitting curve equation	Limiting value
1	$y = 1393.10\exp(-x/66.34) + 1759.26$	1759.26
2	$y = 894.05\exp(-x/53.72) + 2307.43$	2307.43
3	$y = 873.34\exp(-x/71.24) + 1912.80$	1912.80

temperature changes. The value of  $C$  can help evaluate whether the foam extinguishing agent can still maintain a certain fire extinguishing effect under extreme conditions.

The fitted curve mathematically reveals the nonlinear relationship between the performance of the foam extinguishing agent and ageing time, further clarifying the differences in stability exhibited by different samples during ageing. From the fitting equation, it can be seen that various foam extinguishing agents have different tolerance levels to temperature cycles, and each foam has a final limit value. This limit value reflects the minimum stability that the foam performance can maintain after prolonged exposure to alternating high and low temperatures. Specifically, the limit values for the three samples are 1759.26, 2307.43, and 1912.80, respectively. By comparing these limit values, it can be observed that Sample 1 initially exhibits superior overall performance compared to Sample 3, but its stability decreases at a significantly faster rate, and its final limit value is the lowest among all the samples. This indicates that although Sample 1 provides a stronger fire-extinguishing effect at the beginning of use, its stability deteriorates more quickly over time. Therefore, Sample 1 may be more suitable for short-term use, while long-term application would require more frequent maintenance and inspection to ensure the effectiveness of the extinguishing agent. The limit values derived from the fitting equation not only provide a theoretical basis for evaluating the storage life of foam extinguishing agents but also have important practical significance for optimizing extinguishing agent formulations, predicting performance during long-term use, and establishing reasonable inspection cycles. Based on these analyses, researchers and engineers can more accurately select and adjust the formulations of foam extinguishing agents to extend their effective service life and ensure fire-extinguishing performance under various environmental conditions.

#### 4. Conclusion

This paper designs an artificial accelerated ageing experiment involving alternating high and low temperatures, investigating the

changes in the fundamental properties of AFFF after ageing. The total duration of the experiment is 2352 h, with eight sampling intervals. The study reveals the ageing trends of AFFF, from microstructure alterations to changes in basic physical and chemical properties, as well as foam performance. Through the comprehensive performance indicators of the foam and equation fitting, the evolution mechanism of foam quality under different ageing periods is quantified. The main conclusions are as follows:

- (1) Under temperature cycling, the samples repeatedly undergo freezing and thawing processes. The uniformity of the solution is disrupted, and the aggregation of oil-like components floats on the surface.
- (2) The surface tension remains stable under artificial accelerated ageing conditions, maintaining its excellent stability without significant loss. The pH of AFFF increases significantly with ageing.
- (3) The uneven distribution of solution components and changes in foam stabilizer result in a significant decline in foam performance. After 2352 h of ageing, the foam expansion ratio decreased by more than 10.00%, and the average defoaming time was shortened by 47.78 %.
- (4) At the microscopic level, the heterogeneity of bubbles increased after ageing, significantly weakening their stability. This resulted in an increase in the Sauter mean radius, a faster radius growth rate, and an increase in the liquid film thickness.
- (5) A performance prediction model is established in this study. It is found that different AFFFs exhibit varying levels of tolerance to temperature cycling, with a certain limit reached after prolonged cycles. Therefore, for different foam solutions and varying storage conditions, it is recommended to develop appropriate storage and performance evaluation schemes.

#### CRediT authorship contribution statement

**Kai Wang:** Writing – original draft, Project administration. **Qihang Yue:** Writing – review & editing, Formal analysis. **Junyi Zhang:** Formal analysis, Data curation. **Peiyao Chen:** Methodology. **Zhengyang Wang:** Investigation. **Wei Wang:** Investigation. **YaFei Zhou:** Methodology. **Biao Zhou:** Writing – review & editing, Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

Data will be made available on request.

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