

Article

Reaction Model and Optimization of the Alkaline Hydrolysis of SF-3 Double-Base Propellant Wastes Using Analysis of Response Surface Methodology

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Abstract

The alkaline hydrolysis process is a promising method for treating SF-3 double-base propellant waste. This study aimed to validate the SF-3 waste alkaline hydrolysis reaction model and optimize its reaction conditions, thereby promoting the industrial application of alkaline hydrolysis treatment of double-base propellant wastes. Thus, the SF-3 alkaline hydrolysis reaction model was developed based on theoretical assumptions, derivations, and experimental validation. A central composite design coupled with response surface methodology was used to optimize the operational conditions, including reaction temperature, liquid–solid ratio, and reaction time. The results showed that the SF-3 alkaline hydrolysis conformed to a shrinking particle reaction model. The relationship between the x_{SF} and the t is $x_{SF} = [(\alpha + 2)t/(\alpha t_e') - 2t^2/(\alpha t_e'^2)] \times 100$, where the limiting step is the alkaline hydrolysis process on the particle surface. In addition to reaction temperature and reaction time, the liquid–solid ratio influenced the SF-3 alkaline hydrolysis process. Furthermore, the results of Pareto and analysis of variance analyses revealed that the regression model equation was obtained as $x_{SF} = 48.91 + 8.32_1 + 13.11X_3 - 3.49X_1^2 - 2.162X_2^2 - 4.179X_3^2 + 2.78X_1X_2$. Meanwhile, the optimal reaction temperature, time, and liquid–solid ratio were 86.5 °C, 70.8 min, and 6.0, respectively. Under the optimal reaction conditions, the predicted x_{SF} using the regression model was 99.80%, while the experimental value was $95.01 \pm 1.87\%$, demonstrating the accuracy of the regression model. Therefore, this study provides theoretical and technical support for the industrial-scale safe disposal and resource utilization of waste double-base propellants.

Keywords: double-base propellant wastes; shrinking particle reaction model; response surface methodology (RSM); liquid–solid ratio; optimization of reaction conditions

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1. Introduction

To enhance national military reserves and strengthen military capabilities, countries worldwide are continuously developing and producing new types of weapons and ammunition. However, the safe disposal of obsolete ammunition that has reached the end of its shelf life is also a critical phase in the entire ammunition lifecycle [1]. High energy, high

strength, and stable combustion are the basic requirements of propellants [2]. Shuangfang-3 (SF-3) is a double-base propellant composed of nitrocellulose (NC) and nitroglycerin (NG), which has been widely used in many types of munitions due to its high energy density and thermal stability [3–5]. However, SF-3 double-base propellants have limited storage life due to the consumption of stabilizers through the self-decomposition of NC and NG [6,7]. The safety and stability during storage and utilization of SF-3 double-base propellants, which have reached the end of their storage life, and their application may significantly deteriorate, rendering them waste propellants [8]. Waste SF-3 double-base propellants contain NG and NC with a nitrogen content exceeding 12.5%, both of which are flammable and highly explosive compounds [9–11]. If not treated properly, waste SF-3 may pose a direct threat to human and property safety [12].

The traditional treatment methods for waste explosives include deep-sea dumping/deep-soil burial, and open burning/detonation. Among them, deep-sea dumping/deep-soil burial pollutes the natural environment and has hidden dangers due to latent energy [13]. Open burning/detonation generates a large amount of high-concentration carcinogenic particles and gases. These primary and secondary pollutants can further pollute the environment, thereby endangering human health [14,15]. Traditional treatment methods cause resource waste and generate a large amount of environmental pollutants [4,16]. To replace traditional treatment methods, some researchers have proposed molten salt destruction [17], advanced oxidation [18–20], solvent extraction [21], biodegradation [22,23], synthesis of industrial-grade explosives [24,25], and alkaline hydrolysis [6,26–29]. Among these methods, in alkaline solutions (such as NaOH, KOH, $\text{Ca}(\text{OH})_2$, and NH_4OH), nitrate ester compounds (such as NC and NG) can be easily de-nitrated to form nitrates or nitrites, thereby achieving the purpose of de-energization [3,6,30–32]. Additionally, KNO_3 and KNO_2 are generated through alkaline hydrolysis of waste SF-3 double-base propellants with KOH solution, while NH_4NO_3 and NH_4NO_2 are generated through alkaline hydrolysis of waste SF-3 double-base propellants with NH_4OH . These products can be used as nitrogen and potassium fertilizers in agricultural production and as industrial and military explosives, achieving resource utilization and energy neutralization [6]. Therefore, alkaline hydrolysis is a promising alternative to traditional treatment methods for the safe disposal and resource recovery of waste double-base propellants [3].

To date, many studies have been conducted on alkaline hydrolysis of waste explosives, and propose possible mechanisms for the alkaline hydrolysis reaction of NC and NG [6,33–36]. However, no large-scale application of alkaline hydrolysis has been reported. The study of the alkaline hydrolysis reaction model of double-base propellants enhances understanding of the reaction process and limiting steps, determining the conditions affecting the reaction. It also serves as the foundation for optimizing the parameters of the industrialized process [37,38]. The optimization of alkaline hydrolysis reaction conditions represents the basis for its industrial design. The alkaline hydrolysis reaction of double-base propellants is a typical liquid–solid reaction; the properties of the solid (such as porosity, particle size, and geometry) are the main factors affecting the modeling of its liquid–solid reaction [37]. SF-3 is a typical long-grain double-base propellant, with granules in the form of hollow cylinders [1]. However, the hydrolysis reaction model for long-grain double-base propellants has yet to be studied. Therefore, it is critical to clarify its alkaline hydrolysis reaction model before optimizing the reaction conditions for SF-3.

In previous studies, the effects of reaction temperature, types and concentrations of the bases, and reaction time were examined [30,33]. However, as a liquid–solid reaction, the liquid–solid ratio (i.e., the mass ratio of alkali solution to SF-3 granules) is an important factor affecting the alkaline hydrolysis reaction of SF-3 double-base propellant. However, this important factor has been neglected to date [39]. The liquid–solid ratio affects the SF-3 degradation rate and the subsequent treatment of alkaline hydrolyses, including detox-

ification, evaporation, and concentration to produce fertilizer. Response surface methodology (RSM) is an effective method for optimizing process conditions and can be used to determine the impact of various factors and their interactions on response values during process operations [40]. Central composite design (CCD)-RSM is widely used for optimizing process conditions in various fields, such as medicine, chemical engineering, biology, and the environment [41–44].

This study aimed to optimize the alkaline hydrolysis conditions of SF-3 double-based propellants. Based on experimental results and theoretical derivations, an alkaline hydrolysis reaction model of SF-3 double-based propellants was established to determine the conditions affecting their alkaline hydrolysis reaction. Then, RSM was used to design and analyze experiments for the alkaline hydrolysis reaction of SF-3 double-based propellants. It was also used to determine the optimum conditions for the three selected main influencing factors. Moreover, the corresponding regression model was fitted to determine the optimal reaction conditions, which were then validated through experiments. This study provides theoretical and technical support for the safe industrial disposal and resource utilization of waste SF-3 double-based propellants and other waste long-grain double-based propellants containing NC and NG as the main energy components.

2. Materials and Methods

2.1. Materials and Chemicals

Waste SF-3 double-base propellant granules were obtained from a Chinese People's Liberation Army (PAL) unit, which were mainly composed of NC and NG. A hollow-cylinder SF-3 granule, round with uniform specifications, was selected. The inner diameter, outer diameter, and length were 2, 5, and 5 mm, respectively. SF-3 double-based propellant was composed of 56.0% NC, 25.6% NG, 9.0% dinitrotoluene (DNT), and 12.4% other ingredients. KOH (analytical reagent grade, AR) was purchased from Damo Chemical Reagent Factory (Tianjin, China). KNO₃ (guaranteed reagent grade, GR) and NaNO₂ (AR) were sourced from Huada Chemical Reagent Factory (Guangzhou China). NH₂C₆H₄SO₂NH₂ (AR) and amionsulfonic acid (AR) were supplied by Fuchen Chemical Reagent Factory (Tianjin, China), and N-(1-naphthyl)-ethylenediamine hydrochloride (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Alkaline Hydrolysis of SF-3 Double-Base Propellant

The experimental procedure of the alkaline hydrolysis reaction of SF-3 double-base propellant granules is shown in Figure 1. First, 15 mL of 20 wt% KOH aqueous solution was added to a 150 mL single-neck flat-bottomed flask and then stirred. To ensure the safety and stability of the alkaline experiment, the flat-bottomed flask was placed in an SHJ-6A digital magnetic stirring water bath (Xinrui Instrument Factory, Changzhou, China). Then, the spherical condenser tube was connected to the top of the flat-bottomed flasks. A BT100-2J peristaltic pump (Longer Precision Pump Co., Ltd., Baoding, China) was used to pump cooling water to the spherical condenser tube to cool the moisture evaporated from the flat-bottomed flasks during the alkaline hydrolysis reaction, thereby maintaining a constant volume of the solution [26]. Following the procedure of previous research, the alkaline hydrolysis reaction temperatures were set to 50 ± 0.5, 60 ± 0.5, 70 ± 0.5, 80 ± 0.5, and 90 ± 0.5 °C, respectively [6,10,26,33,45], while the stirring speed was set at 120 rpm to investigate the effect of the reaction temperature on the degradation rate of SF-3 double-based propellant granules. To investigate the effect of stirring rate on the degradation rate of SF-3 double-based propellant granules, the alkaline hydrolysis reaction temperature was set to 80 ± 0.5 °C, and the magnetic stirring speeds were set to 50, 120, 200, and 300 rpm, respectively. When the temperature of the water bath reached the set

value, an ME204E analytical balance (Mettler Toledo, Zurich, Switzerland) was used to weigh 2.0 ± 0.01 g of SF-3 granules (accurately record the mass). The weighed samples were transferred to a flat-bottomed flask, and a timer was started. Aliquots (0.5 mL) of the reaction solution were withdrawn at alkaline hydrolysis reaction times of 2, 5, 10, 20, 30, 40, 50, and 70 min, using a 1.0 mL pipette, and the concentrations of nitrate–nitrogen and nitrite–nitrogen were determined.

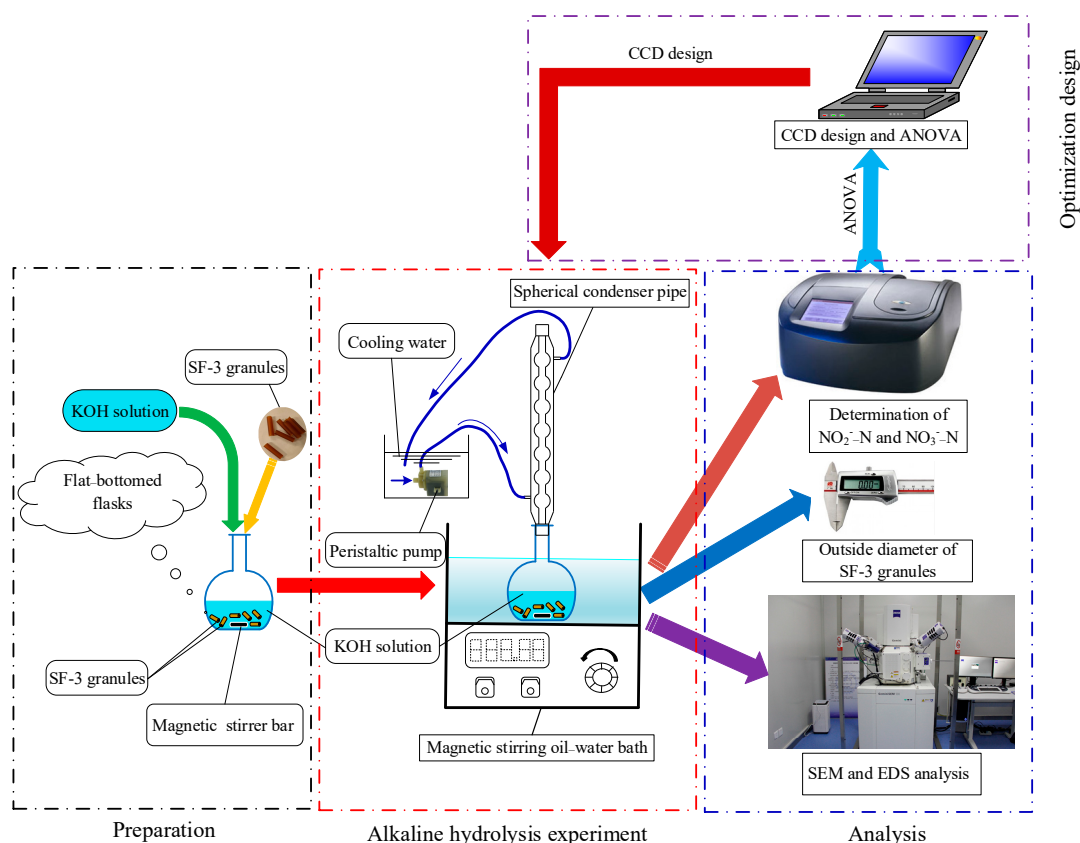


Figure 1. Experimental process of alkaline hydrolysis of SF-3 double-base propellant.

To investigate the effect of liquid–solid ratio on the degradation rate of SF-3 double-based propellant granules, 2.0 ± 0.01 g of SF-3 granules were set aside. The amount of KOH consumed was determined based on the composition of its energetic components. Then, the theoretical mass of KOH consumed was calculated based on the mass of the SF-3 granules. The theoretical mass of KOH was then weighed out and dissolved in deionized water to prepared KOH solutions at liquid–solid ratios (i.e., the mass ratio of alkali solution to SF-3 granules) of 1, 2, 3, 4, 7, 9, 11, and 13, and transferred to flat-bottomed flasks. The alkaline hydrolysis reaction temperatures were set to 80 ± 0.5 °C. When the temperature stabilized at 80 ± 0.5 °C, the weighed SF-3 granules were added to the flat-bottomed flask and the timer was started. At the alkaline hydrolysis reaction time of 20 min, a 1.0 mL pipette was used to withdraw a 0.5 mL aliquot of the reaction solution, and the concentrations of nitrate–nitrogen and nitrite–nitrogen were determined.

As the reaction temperature increases, the alkaline hydrolysis reaction rate of SF-3 granules accelerates. Rapid changes in SF-3 granules occur under high temperature conditions, which make it difficult to observe changes in particle size and microstructure during the alkali hydrolysis reaction process [12]. Therefore, to analyze the changes in particle size of the SF-3 granules before and after alkaline hydrolysis, approximately 70 SF-3 granules were selected and subjected to alkaline hydrolysis at a reaction temperature of 50 ± 0.5 °C and a liquid–solid ratio of 7 for 50 min. The outside diameters of all SF-3 granules

before and after alkaline hydrolysis were measured using digital calipers (Guilin Guanglu Measuring Instrument Co., Ltd., Guilin, China) with an accuracy of 0.01 mm. The SF-3 double-based propellant granules were analyzed before and after alkaline hydrolysis at a reaction temperature of 50 ± 0.5 °C and a liquid–solid ratio of 7 for 50 min. The morphology and structure of the SF-3 granules were investigated using field emission scanning electron microscopy (FE–SEM) with a GeminiSEM 500 instrument (Carl Zeiss AG, Oberkochen, Germany). Then, energy-dispersive X-ray spectroscopy (EDS) coupled with a GeminiSEM 500 instrument (Carl Zeiss AG, Oberkochen, Germany) was used for qualitative and semi-quantitative analysis of the main elements (N, C, and O) on the surface of SF-3 granules.

Based on the above alkaline hydrolysis experiment results, three main influencing factors were determined to optimize the alkaline hydrolysis reaction conditions of SF-3 granules. Then, 20 sets of experiments were designed using the CCD method, and the alkaline hydrolysis reaction experiments of SF-3 granules were conducted under the 20 sets of experimental conditions. The samples were collected to measure nitrate–nitrogen and nitrite–nitrogen, and the experimental results were analyzed using analysis of variance (ANOVA).

2.3. Determination of Nitrate–Nitrogen and Nitrite–Nitrogen

SF-3 is a double-based propellant containing NC and NG as its main energetic components and a small amount of DNT. The alkaline hydrolysis of NC and NG mainly led to denitrification, while nitrate and nitrite ions were the main nitrogen-containing compounds in the alkaline hydrolysis reaction solution [9,10,46,47]. The main alkaline hydrolysis product of DNT was nitrite ion [34–36]. Therefore, the degradation rate of the SF-3 double-base propellants was determined by measuring the concentrations of nitrate–nitrogen and nitrite–nitrogen in the alkaline hydrolysis reaction solution [26]. The concentrations of nitrate–nitrogen and nitrite–nitrogen were determined according to GB 7493–87 (Water Quality-Determination of Nitrogen (Nitrite)-Spectrophotometric Method) and HJ/T 346–2007 [(Water Quality-Determination of Nitrite–Nitrogen-Ultraviolet Spectrophotometry), respectively. A DR-5000 ultraviolet–visible (UV–Vis) spectrophotometer (Hach Company, Loveland, CO, USA) was used to measure the concentrations of nitrate–nitrogen and nitrite–nitrogen [6,26]. The alkaline hydrolysis degradation rate of waste SF-3 double-base propellants x_{SF} was calculated using the following equation [26]:

$$x_{SF} = \frac{m_i(\text{NO}_3^- - \text{N}) + m_i(\text{NO}_2^- - \text{N})}{m} \times 100, \quad (1)$$

where i denotes the number of samples; m is the total nitrogen content of waste SF-3 double-base propellant samples added to flat-bottomed flasks, mg; $m_i(\text{NO}_3^- - \text{N})$ is the mass of the nitrate–nitrogen produced by the alkaline hydrolysis reaction of the SF-3 double-based propellants at the i -th sampling point, mg; and $m_i(\text{NO}_2^- - \text{N})$ is the mass of the nitrite–nitrogen produced by the alkaline hydrolysis reaction of the SF-3 double-based propellants at the i -th sampling point, mg.

Since the volume of the alkaline hydrolysis reaction solution decreases slightly with each sampling, Equations (2) and (3) are used to correct for $m_i(\text{NO}_3^- - \text{N})$ and $m_i(\text{NO}_2^- - \text{N})$, respectively.

$$m_i(\text{NO}_3^- - \text{N}) = c_i(\text{NO}_3^- - \text{N}) \times [V - (i-1)V_0] + \sum_{i=2}^i [c_{i-1}(\text{NO}_3^- - \text{N}) \times V_0], \quad (2)$$

where $c_i(\text{NO}_3^- - \text{N})$ represents the nitrate–nitrogen concentration of the i -th sample, mg/L; $c_{i-1}(\text{NO}_3^- - \text{N})$ is the nitrate–nitrogen concentration of the $i - 1$ -th sample, mg/L; V is the initial volume of the alkaline hydrolysis reaction solution, L; and V_0 is the sample volume per sampling, L.

$$m_i(\text{NO}_2^- - \text{N}) = c_i(\text{NO}_2^- - \text{N}) \times [V - (i-1)V_0] + \sum_{i=2}^i [c_{i-1}(\text{NO}_2^- - \text{N}) \times V_0], \quad (3)$$

where $c_i(\text{NO}_2^- - \text{N})$ represents the nitrite–nitrogen concentration of the i -th sample, mg/L, and $c_{i-1}(\text{NO}_2^- - \text{N})$ is the nitrite–nitrogen concentration of the $i-1$ -th sample, mg/L.

By combining Equations (1)–(3), the alkaline hydrolysis degradation rate of waste SF-3 double-base propellants x_{SF} can be rewritten as:

$$x_{\text{SF}} = \frac{[c_i(\text{NO}_3^- - \text{N}) + c_i(\text{NO}_2^- - \text{N})] \times [V - (i-1)V_0] + \sum_{i=2}^i [(c_{i-1}(\text{NO}_3^- - \text{N}) + c_{i-1}(\text{NO}_2^- - \text{N})) \times V_0]}{m} \times 100. \quad (4)$$

2.4. Experimental Design and Statistical Analysis

Statistical analysis was performed using the Minitab V.18 statistical package (MINITAB Inc., State College, PA, USA). A total of 20 experiments were designed based on a 2^3 full factorial CCD, consisting of eight factorial points (coded to the usual ± 1 notation), six axial points ($\pm\alpha, 0, 0$), $(0, \pm\alpha, 0)$, $(0, 0, \pm\alpha)$, and six replications at the center point $(0, 0, 0)$ [43]. The value of α for rotatability depends on the number of points in the factorial portion of the design, which is given in Equation (5) [43]:

$$\alpha = (N_F)^{1/4}, \quad (5)$$

where N_F is the number of points in the cube portion of the design ($N_F = 2^k$, where k is the number of factors). Therefore, α is equal to $(2^3)^{1/4} = 1.682$ according to Equation (5).

First, the 20 experimental runs from the CCD were performed according to the SF-3 granules alkaline hydrolysis reaction steps described in Section 2.2. The concentrations of nitrate–nitrogen and nitrite–nitrogen in the samples were measured, and the degradation rates were calculated using Equation (4). Then, the experimental results were analyzed using ANOVA, and a regression model was obtained by regressing the experimental results [48]. The quadratic equation model predicting the optimal conditions can be expressed as Equation (6) [42,49]:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j, \quad (6)$$

where Y is the percentage of SF-3 degradation rate; X_i and X_j are the coded variables; β_0 is the intercept term; and β_i , β_{ii} , and β_{ij} are the first-order term, the quadratic term, and the interaction between X_i and X_j , respectively.

Pareto analysis was used to provide deeper insight into the CCD results and identify the main influencing factors. ANOVA was used as a diagnostic test, revealing the adequacy of the proposed model. ANOVA and Pareto analysis were also performed using Minitab V.18, and the three-dimensional (3D) response surface and contour plots were drawn using Matlab V.16a (Math Works Inc., Natick, MA, USA). The accuracy of the polynomial model fit is represented by the coefficient of determination R^2 . The R^2 value measures the variability in the observed response values that can be explained by the experimental factors and their interactions. These analyses were performed using Fisher's test and p -values, and the model terms were evaluated using p -values at the 95% confidence level. To validate the model's accuracy, five parallel experiments were conducted under optimal conditions, and the experimental results were compared with the predicted values.

3. Results and Discussion

3.1. Analysis of the Alkaline Hydrolysis Mechanism of Main Energetic Components in SF-3 Granules

The main energetic components in SF-3 double-base propellant are NC, NG, and DNT, of which NC and NG are nitrate compounds [6,12,27,50]. FE-SEM images (Figure 2a,b) reveal that the surface of the SF-3 granules was relatively smooth before the alkaline hydrolysis reaction, and the appearance of small cracks might be attributed to the sample cutting process. However, after the alkaline hydrolysis reaction, depressions and a small cavity were observed on the surface of the SF-3 granules. The EDS image (Figure 2c,d) reveals that oxygen content on the surface of the SF-3 granules significantly decreased after the alkaline hydrolysis reaction. The oxygen content reduced because the oxygen primarily exists in the functional groups $-O-NO_2$ and $-NO_2$, both of which undergo reactions during the alkaline hydrolysis process [9,10,26,30]. After the alkaline hydrolysis reaction, the carbon content on the surface of SF-3 granules significantly increased due to the skeleton remaining after NC denitration [26].

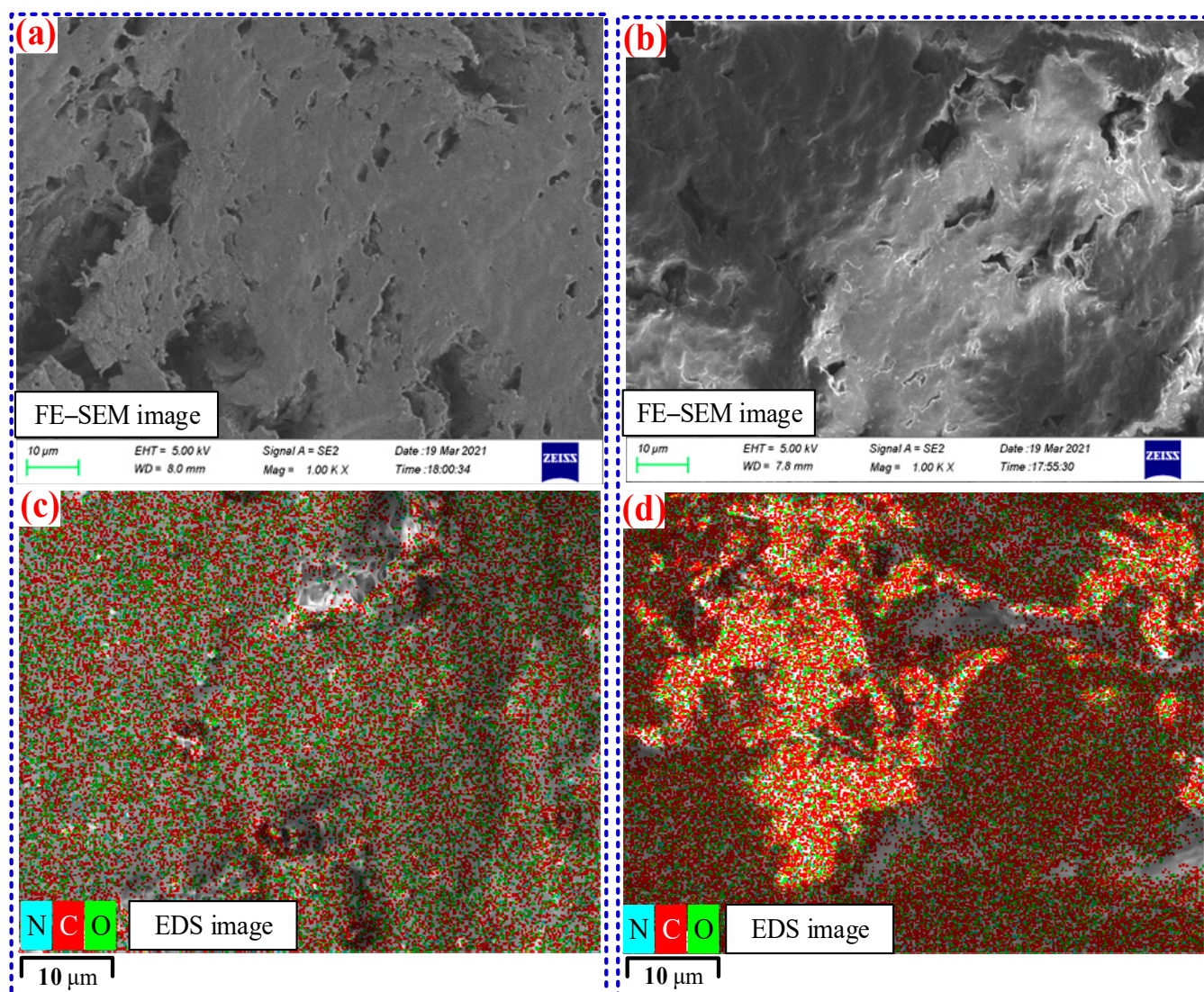


Figure 2. FE-SEM and EDS images of the SF-3 double-base propellant before and after the alkaline hydrolysis reaction. (a) FE-SEM image before the alkaline hydrolysis reaction; (b) FE-SEM image after the alkaline hydrolysis reaction; (c) EDS image before the alkaline hydrolysis reaction; (d) EDS image after the alkaline hydrolysis reaction.

3.2. Verification of the Alkaline Hydrolysis Reaction Model of SF-3 Double-Base Propellant

As shown in Figure 3, although a skeleton remains after NC denitration, NG was physically embedded within the fibrous structure of NC in the double-based propellant [51]. Studies have shown that the skeleton remains after the alkaline hydrolysis reaction [6]. However, NG undergoes denitration and even hydrolysis to form smaller compounds (such as oxalic acid, formic acid, and glutaric acid) during the alkaline hydrolysis process [47]. Therefore, it is difficult for NC to maintain a structural skeleton on the surface of SF-3 granules to form an ash layer after the alkaline hydrolysis reaction. As the alkaline hydrolysis reaction proceeded, the skeleton on the surface of SF-3 granules detached, reducing the size of SF-3 granules. To further prove that no ash layer was formed on the surface of SF-3 granules after the alkaline hydrolysis reaction, the outer diameter of the SF-3 granules before and after the alkaline hydrolysis reaction was measured, and the results are shown in Figure 4. As shown in Figure 4, the outer diameter of SF-3 granules significantly decreased after the alkaline hydrolysis reaction at $50 \pm 0.5^\circ\text{C}$, with an average decrease of 0.4 mm. Therefore, the alkaline hydrolysis reaction of the SF-3 granules conforms to the characteristics of the shrinking particle reaction model of liquid–solid reactions [52]. Therefore, the alkaline hydrolysis of SF-3 granules includes three steps: the mass transfer of OH^- from the bulk liquid to the particle surface, alkaline hydrolysis on the particle surface, and the mass transfer of alkaline hydrolysis products from the particle surface to the bulk liquid [12].

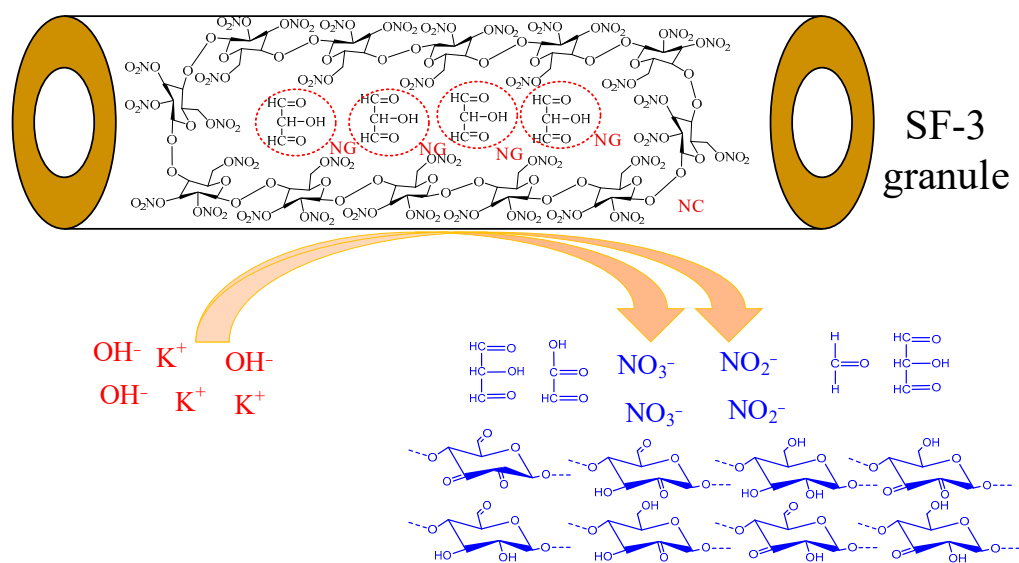
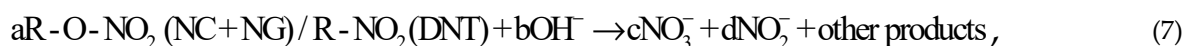


Figure 3. The alkaline hydrolysis reaction process of SF-3 double-base propellant granules.

According to the possible mechanism of the alkaline hydrolysis reaction of double-base propellants containing NC, NG, and DNT as the main energetic components, as shown in Figure 3, the alkaline hydrolysis reaction equation of the SF-3 double-base propellant was expressed as follows:



where a , b , c , and d denote stoichiometric coefficients, and R is the hydrocarbon group.

For the alkaline hydrolysis reaction of double-base propellants, where the particle surface reaction is the rate-limiting step, Li et al. [26] expressed the alkaline hydrolysis reaction rate r_{SF} of double-base propellant granules per unit area as:

$$r_{\text{SF}} = -\frac{1}{S_c} \frac{dn_{\text{SF}}}{dt} = -b' \frac{1}{S_c} \frac{dn_{\text{KOH}}}{dt} = b' A e^{\frac{-E_a}{RT}} (\gamma C_{\text{As}})^m, \quad (8)$$

where b' denotes the stoichiometric ratio of nitrate esters (NC and NG) to KOH, namely a/b ; S_c is the surface area of unreacted SF-3 granules, cm^3 ; dn_{SF}/dt is the rate of alkaline hydrolysis of SF-3 granules, mol/s ; dn_{KOH}/dt is the reaction rate of KOH, mol/s ; γ is the activity coefficient of KOH in the solution; m is the reaction order; A represents a pre-exponential factor, d^{-1} ; E_a is the activation energy of the alkaline hydrolysis of SC granules, J/mol ; R is the universal gas constant, $8.314 \text{ J/(mol}\cdot\text{K)}$; T is the absolute temperature, K ; and C_{AS} is the KOH concentration, mol/cm^3 .

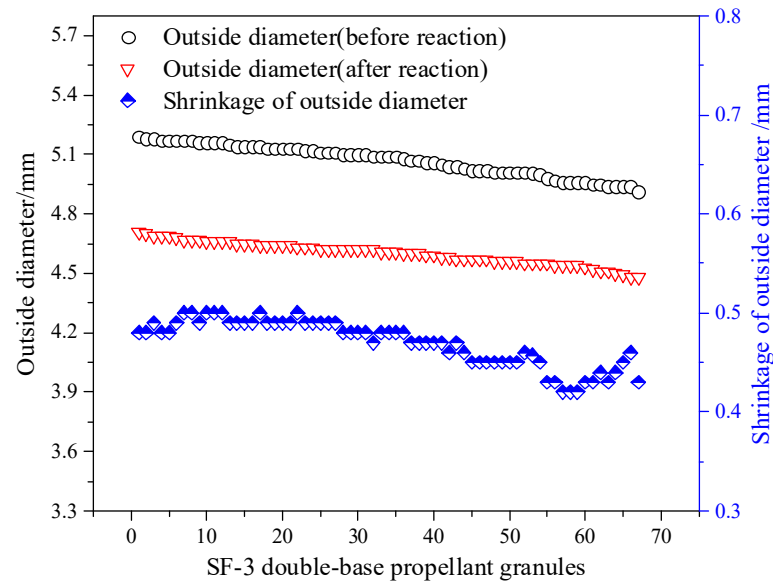


Figure 4. Change in the outside diameter of SF-3 granules before and after alkaline hydrolysis.

The schematic illustrations of the shrinking particle reaction model of the SF-3 double-base propellant alkaline hydrolysis are shown in Figure 5. As SF-3 double-base propellant is a hollow-cylinder granule, the average radius of the bottom surface of SF-3 granules is assumed to be R_m , and the inner and outer diameters of the granules can be expressed as $R_m - l$ and $R_m + l$, respectively.

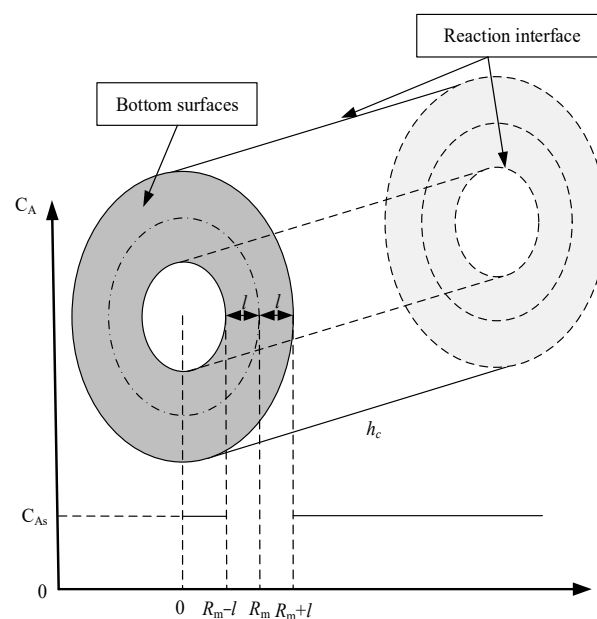


Figure 5. Schematic illustrations of the shrinking particle reaction model of SF-3 double-base propellant alkaline hydrolysis.

Based on the characteristics of the shrinking reaction model, SF-3 particles were assumed to shrink uniformly during the alkaline hydrolysis process [53]. The particle height is assumed to be $h = \alpha l$, where l is the outer diameter minus 1/4 of the inner diameter of SF-3 double-based propellant granules at reaction time 0 [26]. As both SF-3 and SC double-based propellant granules are homogeneous solid propellants with NC and NG as the main energetic components [54–56], their particles are ring-shaped. Therefore, the expression for reaction time t can be derived based on a double-base propellant alkaline hydrolysis reaction model, proposed by Li et al. [26].

$$t = \frac{\rho_m}{b'Ae^{\frac{-E_a}{RT}} (\gamma C_{As})^m} (l - l_c), \quad (9)$$

where ρ_m denotes the density of SF-3 granules, g/cm³, and l_c represents 1/4 of the outer diameter minus the inner diameter of SF-3 granules at reaction time t . The range of l_c is $(1 - \alpha/2)L \leq l_c \leq l$.

As SF-3 granules are hollow-cylinder double-based propellants, the height $h > 2l$. As a result, when the l_c of unreacted SF-3 granules is 0, the alkaline hydrolysis reaction is complete. Therefore, assuming that the time required for the alkaline hydrolysis reaction of SF-3 granules to complete is t_e' , the calculation formula is as follows:

$$t_e' = \frac{\rho_m}{b'Ae^{\frac{-E_a}{RT}} C_{As}^m} l. \quad (10)$$

By combining Equations (9) and (10), the relationship between t and t_e' can be obtained, as shown in Equation (11).

$$t/t_e' = \frac{l - l_c}{l} = 1 - \frac{l_c}{l}. \quad (11)$$

As the alkaline hydrolysis reaction of SF-3 particles is characterized by a decrease in particle volume, the alkaline hydrolysis degradation rate x_{SF} of SF-3 double-based propellant granules can be expressed using Equation (12).

$$1 - x_{SF} = \frac{V_p}{V_s} = \frac{4\pi R_m [(\alpha - 2)ll_c + 2l_c^2]}{4\alpha\pi R_m l^2} = \frac{\alpha - 2}{\alpha} \frac{l_c}{l} + \frac{2}{\alpha} \left(\frac{l_c}{l}\right)^2, \quad (12)$$

where V_s denotes the volume of SF-3 granules at an alkaline hydrolysis reaction of 0, cm³, and V_p is the volume of SF-3 granules at an alkaline hydrolysis reaction of t , cm³.

The relationship between the alkaline hydrolysis reaction rate x_{SF} (%) of SF-3 granules and the reaction time t can be obtained by combining Equations (11) and (12), resulting in Equation (13).

$$x_{SF} = \left(\frac{\alpha + 2}{\alpha t_e'} t - \frac{2}{\alpha t_e'^2} t^2 \right) \times 100. \quad (13)$$

The main energetic components of SF-3 double-based propellant are NC and NG. The alkaline hydrolysis reaction of NC and NG mainly leads to a denitrification reaction, while nitrate and nitrite ions are the main nitrogen-containing compounds in the alkaline hydrolysis reaction solution [6,9,10,30,45,47]. Many studies have shown that nitrogen content in NC can be determined by measuring the concentrations of nitrate–nitrogen and nitrite–nitrogen in the alkaline hydrolysis reaction solution [9,10,30]. Halasz et al. [47]. found that under conventional heating conditions, the total content of nitrate–nitrogen and nitrite–nitrogen in the alkaline hydrolysis reaction solution accounted for 98% of the nitrogen content in NG. Therefore, the SF-3 alkaline hydrolysis degradation rate x_{SF} can be calculated by measuring the concentrations of nitrate–nitrogen and nitrite–nitrogen in the alkaline hydrolysis reaction solution.

The experimental results revealed that the alkaline hydrolysis rate x_{SF} of SF-3 granules at different temperatures was obtained as a function of reaction time and then fitted

using Equation (13) (Figure 6a). As shown in Figure 6a, at reaction temperatures of 50 ± 0.5 , 60 ± 0.5 , 70 ± 0.5 , 80 ± 0.5 , and 90 ± 0.5 °C, the relationship between x_{SF} and t conforms to Equation (13), and the variance R^2 is greater than 0.99. Figure 6b shows the relationship between the SF-3 alkaline hydrolysis degradation rate x_{SF} and reaction time t at different stirring speeds. As shown in Figure 6b, the stirring speed slightly affected the alkaline hydrolysis reaction of SF-3 granules. This indicates that the alkaline hydrolysis is unrelated to mass transfer on the surface of SF-3 granules. Therefore, the alkaline hydrolysis reaction of SF-3 double-base propellant can be proven to conform to the particle surface reaction-controlled shrinking particle reaction model.

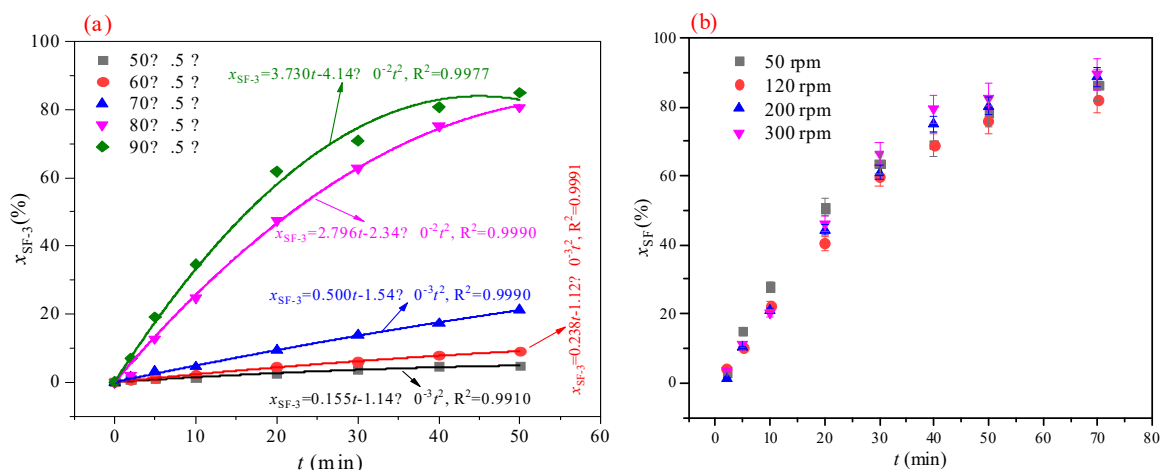


Figure 6. Relationship between x_{SF} and t at (a) different temperatures and (b) different stirring speeds.

3.3. Optimization of Alkaline Hydrolysis Reaction Conditions for SF-3 Double-Based Propellants

3.3.1. Determination of Influencing Factors and Scope

RSM is an effective method for optimizing process conditions, and its accurate optimization results depend on the proper determination of the influencing factors and the scope of the experiment. The research results of the alkaline hydrolysis reaction model of SF-3 double-base propellant in Section 3.1 and previously reported results reveal that the main factors affecting the alkaline hydrolysis reaction include reaction temperature, reaction time, and alkaline solution concentration [30,33,57]. As a typical liquid–solid reaction, the liquid–solid ratio is also an important factor affecting the alkaline hydrolysis reaction of double-based propellants [39], and the alkaline concentration changes with variations in the liquid–solid ratio. Therefore, in this study, the alkaline hydrolysis reaction temperature, reaction time, and liquid–solid ratio were selected as the influencing factors, and a single-factor experimental range was conducted for RSM optimization.

(1) Alkaline hydrolysis reaction temperature

The alkaline hydrolysis reaction of the main energetic components (NC and NG) in SF-3 double-base propellant is an exothermic reaction that follows the Arrhenius equation, and it releases enormous heat [44,58]. To ensure safety during the alkaline hydrolysis reaction process, the reaction temperature range was set to 50–90 °C [9,26,33]. The research results of the SF-3 double-base propellant alkaline hydrolysis reaction model reveal that the limiting step of the alkaline hydrolysis reaction is the reaction process on the particle surface. An increase in reaction temperature accelerates the molecular motion of OH⁻, thereby increasing the effective collisions between molecules and accelerating the reaction. Therefore, as the reaction temperature increased, the rate of alkaline hydrolysis reaction of SF-3 double-base propellant increased (Figure 6a).

(2) Alkaline hydrolysis reaction time

Due to the irreversibility of the alkaline hydrolysis reaction of NC and NG, the alkaline hydrolysis degradation rate x_{SF} of SF-3 double-base propellant will inevitably increase as the reaction time increases [30,39]. As shown in Figure 6a, the alkaline hydrolysis degradation rate of SF-3 at 80 °C and 90 °C was relatively fast in the first 20 min and then slowed down. This phenomenon may be attributed to the high alkaline concentration (i.e., high OH^- concentration), which leads to a higher probability of effective collisions between molecules. As the reaction progressed, the alkaline concentration decreased, reducing the probability of effective collisions between molecules.

(3) Liquid–solid ratio

In industrial applications, the liquid–solid ratio is an important factor affecting both reaction efficiency and subsequent treatment efficiency of the reaction liquid [30,58]. The hydrolysis reaction between SF-3 double-base propellant granules and KOH solution is a typical liquid–solid reaction [12]. Therefore, the alkaline hydrolysis reaction rate of SF-3 granules is influenced by the effective liquid–solid contact area and the initial concentration of KOH in the liquid phase. As shown in Figure 7, at a reaction time of 20 min, the alkaline hydrolysis degradation rate x_{SF} of SF-3 double-base propellant increased as the liquid–solid ratio increased from 1 to 4. This is because as the liquid–solid ratio increases, the volume of the KOH solution increases, thereby increasing the effective contact area between the SF-3 granules and the KOH solution. At a liquid–solid ratio of 4, the x_{SF} reached its maximum of 86.90%. However, when the liquid–solid ratio increased from 4 to 13, the x_{SF} decreased. This is because to the same theoretical consumption value of KOH, an increase in the liquid–solid ratio reduces the initial concentration of KOH, leading to reduced effective intermolecular collisions between KOH molecules and SF-3 granules.

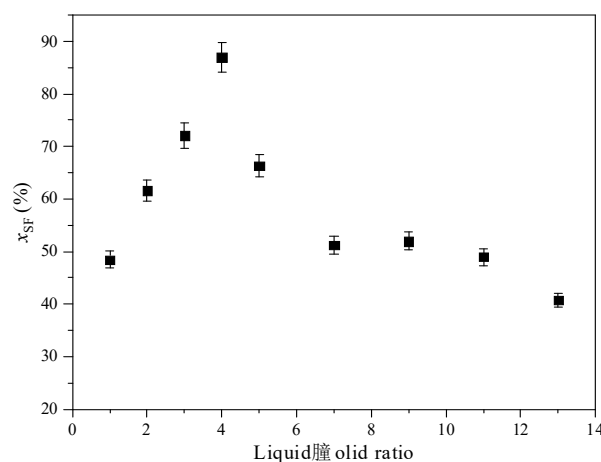


Figure 7. Relationship between x_{SF} and t liquid–solid ratio.

3.3.2. Response Surface Method Optimization of SF-3 Double-Base Propellant Alkaline Hydrolysis Reaction Conditions

(1) Experimental range and levels of the independent test variables

RSM is used when a few significant factors are involved in optimization [59]. It is also used to determine the relationship between one or more responses and factors [60]. In this study, SF-3 degradation rate was monitored as the response. The experiment results of the various factors affecting the SF-3 degradation rate and their corresponding levels are listed in Table 1.

Table 1. Experimental range and levels of the independent test variables.

Variables	Factor	Unit	Range and Level				
			$-\alpha$	-1	0	$+1$	$+\alpha$
Reaction temperature	X_1	°C	53.2	60	70	80	86.8
Liquid–solid ratio	X_2	-	2.32	3	4	5	5.68
Reaction time	X_3	min	6.36	20	40	60	73.64

(2) Overall performance

The CCD method was used to design 20 experimental runs based on the range and levels of the independent test variable, and the results are shown in Table 2. As shown in Table 2, the first column shows the number of runs, the next three columns are the values of the analyzed factors, and the rest are the experimental and predicted values for the SF-3 alkaline hydrolysis degradation rate. The highest SF-3 alkaline hydrolysis degradation rate (96.68%) was achieved in run 17 at a reaction temperature of 80 °C, liquid–solid ratio of 5, and reaction time of 60 min. As shown in Table 2, the predicted values for SF-3 hydrolysis degradation rates in runs 3, 4, 6, 7, 10, 11, 12, 14, and 18 are quite different from the experimental removal values. Errors were recorded in the range of 0–18.35%. Approximately 18.35% of the error was recorded in run 12.

Table 2. Full factorial CCD matrix for SF-3 degradation rate.

Experiment Run	Reaction Temperature (X_1 , °C)	Liquid–Solid Ratio (X_2)	Reaction Time (X_3 , min)	SF-3 Degradation Rate x_{SF} (%)		
				Measured	Predicted	Errors
1	80.00	3.00	20.00	50.09	50.92	−1.66
2	53.18	4.00	40.00	36.24	37.84	−4.42
3	60.00	5.00	60.00	65.51	68.27	−4.21
4	70.00	4.00	40.00	71.34	73.90	−3.59
5	70.00	4.00	40.00	74.38	73.90	0.65
6	70.00	5.68	40.00	70.87	67.08	5.35
7	80.00	5.00	20.00	48.05	56.03	16.61
8	70.00	4.00	40.00	70.96	73.90	−4.14
9	60.00	5.00	20.00	19.11	17.51	8.37
10	60.00	3.00	60.00	72.00	67.62	6.08
11	70.00	4.00	40.00	76.98	73.90	4.00
12	70.00	4.00	6.36	25.01	20.42	18.35
13	70.00	2.32	40.00	63.53	62.23	2.05
14	86.82	4.00	40.00	86.81	80.12	7.71
15	60.00	3.00	20.00	25.79	29.22	−13.30
16	70.00	4.00	40.00	75.98	73.90	2.74
17	80.00	5.00	60.00	96.68	96.85	−0.18
18	80.00	3.00	60.00	74.17	79.37	−7.01
19	70.00	4.00	73.64	87.53	87.03	0.57
20	70.00	4.00	40.00	72.87	73.90	−1.41

(3) ANOVA

The coefficients of the response function (Equation (6)) and the t and p -values for the SF-3 alkaline hydrolysis degradation rate were calculated from experimental data, and the results are presented in Table 3. Regression analysis can be used to simultaneously solve multivariate equations [61]. The experimental results were used to fit the following second-order polynomial equation to the SF-3 alkaline hydrolysis degradation results in terms of coded factors:

$$Y = 48.91 + 8.32X_1 + 0.95X_2 + 13.11X_3 - 3.49X_1^2 - 2.16X_2^2 - 4.18X_3^2 + 2.78X_1X_2 - 1.65X_1X_3 + 2.05X_2X_3 \quad (14)$$

where “+” denotes a synergistic effect and “−” is an antagonistic effect.

The SF-3 alkaline hydrolysis degradation rate results predicted using Equation (14), at each experimental point, are presented in Table 2.

Table 3. ANOVA for SF-3 hydrolysis degradation rate (%) ($R^2 = 0.9730$, $R^2(\text{adj}) = 0.9486$).

Source	DF	Adj. SS	Adj. MS	F-Value	p-Value
Model	9	8912.98	990.33	39.97	0.000 ^s
Linear	3	7541.76	2513.92	101.47	0.000 ^s
X ₁	1	2156.99	2156.99	87.06	0.000 ^s
X ₂	1	28.29	28.29	1.14	0.310 ^{ns}
X ₃	1	5356.48	5356.48	216.21	0.000 ^s
Square	3	1103.78	367.93	14.85	0.000 ^s
X ₁ ²	1	400.75	400.75	16.18	0.000 ^s
X ₂ ²	1	153.84	153.84	6.21	0.032 ^s
X ₃ ²	1	732.80	732.80	29.58	0.000 ^s
Interaction	3	267.43	89.14	3.60	0.054 ^{ns}
X ₁ X ₂	1	141.49	141.49	5.71	0.038 ^s
X ₁ X ₃	1	49.49	49.49	2.00	0.188 ^{ns}
X ₂ X ₃	1	76.45	76.45	3.09	0.109 ^{ns}
Residual error	10	247.75	24.77	-	-
Lack-of-fit	5	217.57	43.51	7.21	0.025 ^s
Pure error	5	30.17	6.03	-	-
Total	19	9160.72	-	-	-

^s = significant at $p < 0.05$; ^{ns} = not signification at $p > 0.05$.

As the ANOVA was established with a confidence interval of 95%, the significance of the first-order term, second-order term, and interaction term in influencing the SF-3 double-base propellant alkaline hydrolysis reaction was evaluated using p -values [62]. As shown in Table 3, the coefficients for the reaction temperature (X_1), reaction time (X_2), and the square terms (X_1^2 , X_2^2 and X_3^2) as well as the interaction terms (X_1X_2) ($p < 0.05$ for all) were highly significant, whereas the liquid–solid ratio (X_3) and the interaction terms (X_1X_3 , X_2X_3) were insignificant to the response.

Two fitted lines are used to illustrate the reliability of the prediction [62]. The first line represents the perfect fit (where experimental data equals predicted data), with all ideal model data falling on this perfect fitting curve. The other curve is the best-fit line (with equation $y = ax + b$) for the scattered data points, obtained through regression analysis based on the least squares method. The reliability of the model is confirmed when the predicted response factor values agree with experimental data within an acceptable margin of accuracy [43]. Figure 8 shows the comparison between the experimental values of the alkaline hydrolysis degradation rate x_{SF} (%) of SF-3 double-base propellant and the predicted values obtained from the model. As shown in Figure 8, good agreement was observed between the experimental and predicted values for the SF-3 alkaline hydrolysis degradation rate ($R^2 = 0.9730$). The closer the value of variance R^2 is to 1, the more accurate the second-order polynomial model [41]. Additionally, as shown in Table 3, the p -value of the regression model equation is 0.000 ($p < 0.05$), indicating that the second-order polynomial model fits well with the experimental results.

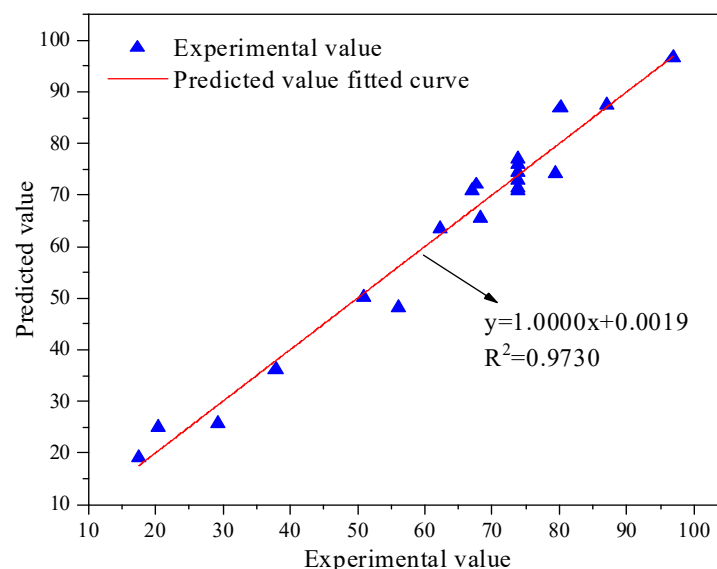


Figure 8. Verification chart of experimental and predicted values for SF-3 hydrolysis degradation rate.

The R^2 value of 0.9730 obtained from Figure 8 indicates that the regression model (Equation (14)) exhibits a good fit to the experimental results. This model equation can account for 0.9730 of the variation in the response variable observed in the experiment. This result shows that 97.30% of the variation in SF-3 alkaline hydrolysis degradation rate is influenced by the primary, secondary, and interaction terms of the three independent variables: alkaline hydrolysis reaction temperature, reaction time, and liquid–solid ratio. However, for the model with different independent variables, R^2 is usually adjusted for sample size and number of terms in the model through a degree-of-freedom correction, referred to as the adjusted R^2 ($R^2(\text{adj})$). When the model contains multiple terms and the sample size is not large, $R^2(\text{adj})$ may be significantly smaller than R^2 [63,64]. However, the $R^2(\text{adj})$ value of 0.9486 in this study is close to the corresponding R^2 value of 0.9730.

The significance and adequacy of the model require ANOVA testing [49,65]. AVOVA was used to divide the total error results into two parts, including model-related errors and experimentally related errors (Table 3). The F-value indicates whether the model-related error is significant compared with the error associated with residual error. When the F-value of the model in the confidence interval α is greater than the lack-of-fit F-value, it indicates that the model can effectively predict experimental results. The lack-of-fit is calculated using experimental error (pure error) and residuals. The F-value of this model at the 95% confidence interval was 39.97, which is significantly greater than the F-value of the lack-of-fit (7.21). This disparity indicates that the model has strong predictive ability for experimental results.

The ANOVA results showed that the coefficients for reaction temperature (X_1), reaction time (X_3), the interaction term X_1X_2 , and the squared terms of the independent variables (X_2^2 and X_3^2) (all with p -values less than 0.05) significantly influenced the alkaline hydrolysis reaction of SF-3. The order of importance of the influence of different variables on the alkaline hydrolysis degradation rate of SF-3 can be observed in the standardized Pareto graph (Figure 9).

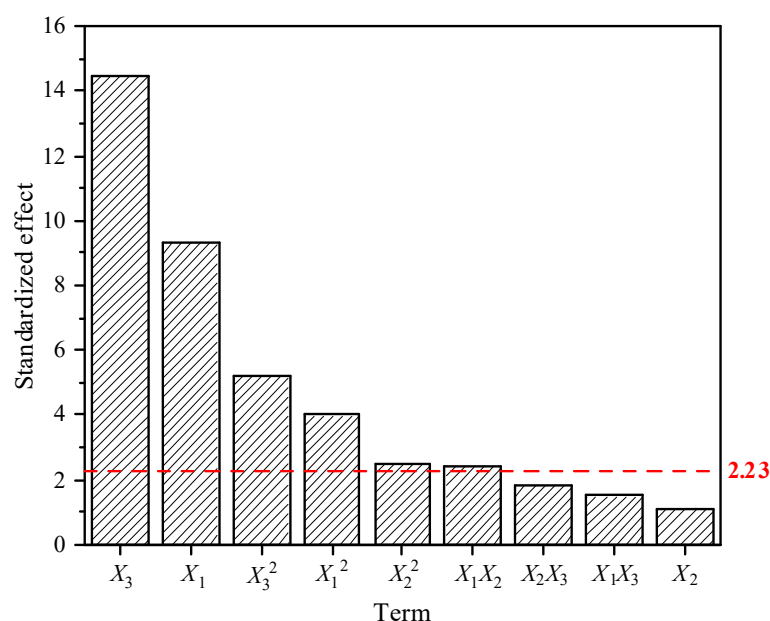


Figure 9. Graph of the Pareto analysis ranking the effect of individual factors on the SF-3 alkaline hydrolysis degradation rate.

As shown in Figure 9, the order of importance of variables on the SF-3 hydrolysis degradation rate was as follows: $X_3 > X_1 > X_3^2 > X_1^2 > X_2^2 > X_1X_2 > X_2X_3 > X_1X_3 > X_2$. The interaction terms between reaction time and liquid–solid ratio (X_2X_3), reaction temperature and reaction time (X_1X_3), and liquid–solid ratio (X_2) all exceeded the 95% confidence interval, making them statistically insignificant. The analysis results above show that reaction time and reaction temperature are the two most significant variables influencing the alkaline hydrolysis reaction of SF-3, which are consistent with previous research results [30,33,45,57]. The quadratic terms of reaction time, reaction temperature, and liquid–solid ratio are also important influential variables in the alkaline hydrolysis process of SF-3 and cannot be neglected.

To determine whether the influence of variables on the response variable is statistically significant, the original quadratic model can be modified to some extent to obtain an optimal model with only significant influence variables [65]. Based on the Pareto analysis graph and ANOVA results, variables without significant influence ($p > 0.05$) were removed from the original quadratic model (Equation (14)), as shown in the following equation:

$$x_{\text{SF}} = 48.91 + 8.32X_1 + 13.11X_3 - 3.49X_1^2 - 2.16X_2^2 - 4.18X_3^2 + 2.78X_1X_2. \quad (15)$$

(4) Optimization of parameters

To elucidate the independent variables and their interactive effects on the SF-3 hydrolysis degradation rate, three-dimensional (3D) plots and their corresponding contour plots are presented in Figure 10. They provide a method for visualizing the relationship between response and experimental level of each variable and the type of interactions between the test variable [60]. Reaction temperature played a crucial role in the SF-3 alkaline hydrolysis process. Figure 10a,b describe the interaction of the reaction temperature with the liquid–solid ratio at a constant alkaline hydrolysis reaction time of 40 min. Figure 10c,d represent the interaction of the reaction temperature and time at a liquid–solid ratio of 4. Figure 10e,f represent the interaction of the liquid–solid ratio with the reaction time when the reaction temperature is 70 °C.

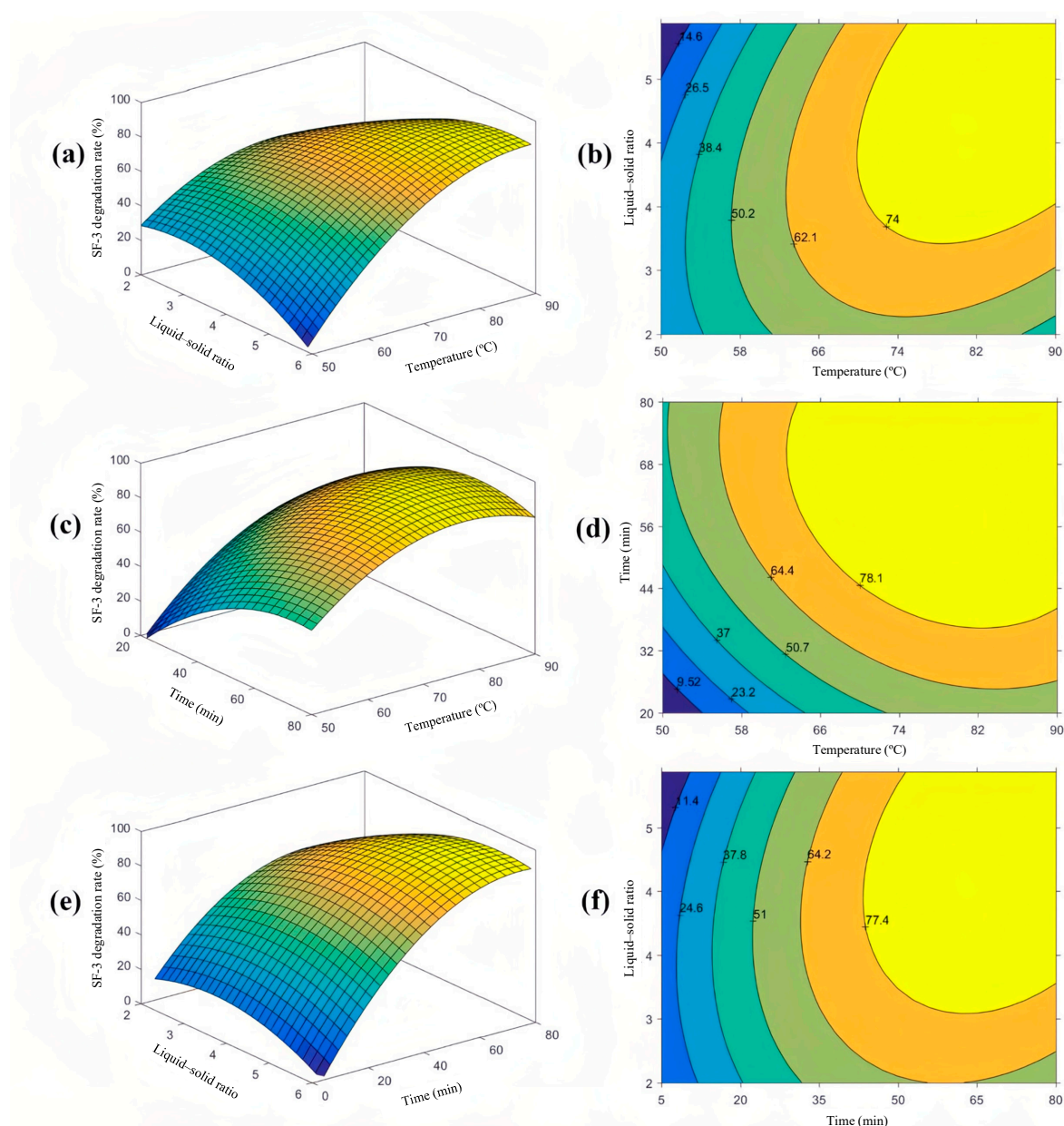


Figure 10. Surface and contour plots of the hydrolysis degradation rate of SF-3 granules as a function of reaction temperature, liquid–solid ratio, and reaction time. (a,b) Reaction temperature and liquid–solid ratio; (c,d) reaction temperature and time; (e,f) reaction time and liquid–solid ratio.

A peak observed in Figure 10a,c,e indicates that the optimum point is well-defined within the design boundaries [66]. According to previous reports, contour maps reflect the intensity of interactions between variables [30]. If contour lines are almost circular, interactions can be neglected. However, elliptical contour lines indicate strong interaction [67]. As shown in Figure 10b,f, the elliptical contour lines indicate a strong interaction between reaction temperature (X_1) and liquid–solid ratio (X_2), and between liquid–solid ratio (X_2) and reaction time (X_3). Although the liquid–solid ratio (X_2) has no significant effect on the response function, its interaction with reaction temperature and reaction time is strong, indicating that the liquid–solid ratio is the main influencing factor in the SF-3 alkaline hydrolysis reaction process. As shown in Figure 10d, the contour lines are closer to circular, indicating that although both reaction temperature and reaction time are the main influencing factors in the SF-3 alkaline hydrolysis reaction, their interaction is relatively weak.

(5) Verification of models

To maximize the SF-3 hydrolysis degradation rate, the optimum parameters were used according to RSM. The reaction temperature, reaction time, and liquid–solid ratio were 82.0 °C, 70.8 min, and 6.0, respectively. The RSM prediction and experimental results of the SF-3 hydrolysis degradation rate at optimal conditions are shown in Table 4. To confirm the actual prediction ability of the model, five sets of parallel experiments under optimal conditions were performed. As shown in Table 4, the optimal hydrolysis degradation rate under optimal conditions reached 99.80%, and the mean rate of the experimental results was $95.01 \pm 1.87\%$. The experimental verification results under optimum conditions in this study were consistent with the predicted results, indicating that the model obtained through experimental design had reliable predictive ability.

Table 4. Optimal values of the independent variables, experimental results, and RSM prediction of the SF-3 hydrolysis degradation rate.

Temperature (°C)	Liquid–Solid Ratio	Time (min)	SF-3 Hydrolysis Degradation Rate (%)	
			Predicted	Measured $\pm$ SD *
82.0	6.0	70.8	99.80	95.04 ± 1.87

* SD: Standard deviation of the five replicates.

4. Conclusions

In this study, based on FE–SEM and EDS analysis results, the relationship between the alkaline hydrolysis degradation rate x_{SF} of SF-3 double-base propellant granules and the reaction time t was obtained through theoretical reaction model derivation and experimental verification, where $x_{SF} = [(\alpha + 2)t/(\alpha t_e') - 2t^2/(\alpha t_e'^2)] \times 100$. The fitting variance R^2 of the experimental results exceeded 0.99 at 50 ± 0.5 , 60 ± 0.5 , 70 ± 0.5 , 80 ± 0.5 , and 90 ± 0.5 °C. This result shows that the alkaline hydrolysis reaction of SF-3 granules conforms to the shrinking particle reaction model, in which the limiting step is the alkaline hydrolysis process on the particle surface. Meanwhile, the experimental results of alkaline hydrolysis at different stirring speeds showed that the stirring speed did not affect the alkaline hydrolysis rate of SF-3 granules. However, the results showed that KOH concentration, reaction temperature, and reaction time were the main factors influencing the alkaline hydrolysis degradation rate. Moreover, as a typical liquid–solid reaction, the liquid–solid ratio significantly influenced the hydrolysis reaction of SF-3 granules, while the liquid–solid ratio affected the concentration of KOH. Therefore, using the alkaline hydrolysis reaction temperature, reaction time, and liquid–solid ratio as independent variables, RSM was used to optimize the SF-3 granules alkaline hydrolysis reaction conditions. Thus, the optimal reaction temperature, reaction time, and liquid–solid ratio are 86.5 °C, 70.8 min, and 6.0, respectively. The regression model equation obtained through ANOVA was $x_{SF} = 48.91 + 8.32X_1 + 13.11X_3 - 3.49X_1^2 - 2.162X_2^2 - 4.179X_3^2 + 2.78X_1X_2$. ANOVA showed a high R^2 value of the regression model equation ($R^2 = 0.9730$), thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. Under optimal conditions, the predicted value of the regression model equation and experimental value were 99.80% and $95.01 \pm 1.87\%$, respectively. Therefore, RSM effectively predicted the SF-3 alkaline hydrolysis degradation rate of the alkaline hydrolysis process and optimized the process conditions. This study provides theoretical and technical support for the large-scale application of alkaline hydrolysis of double-base propellant wastes.

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dition, Project administration. Z.G.: Supervision, Visualization, Conceptualization, Investigation, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

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