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Optimizing Wet Hydrolysis for Nitrogen Removal and Alumina Recovery from Secondary Aluminium Dross (SAD)

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Abstract: Secondary aluminum dross is a solid waste generated after removing aluminum from industrial aluminum slag (primary aluminum dross), which is included in the European Hazardous Waste List because of harmful substances such as aluminum nitride. More and more SAD is being directly disposed of in landfills, which will not only harm the ecological environment and human health, but also cause resources. Under the background of green and low-carbon circular economy, nitrogen removal and resource recycling of SAD are very important environmental pollution, resource and the economic benefits of the aluminum industry. In this study, a new method was introduced to explore the interaction between various factors in the denitrification process by using the response surface method, and the optimal denitrification process conditions were predicted and determined by a regression equation that is, the denitrification rate of SAD was 99.98% at the reaction time of 263 min, reaction temperature of 95 ℃ and concentration of 6.5 wt.%. Furthermore, the content of Al₂O₃ in SAD was successfully elevated to 98.43% through the reaction carried out in a 10 wt.% NaOH solution system at the controlled temperature of 90 ℃ for 5 h. It was summarized that the wet treatment methodology can efficiently eliminate aluminum nitride (AlN) from SAD and heighten the Al₂O₃ grade to meet metallurgical standards. This research is expected to eliminate the adverse impact of SAD on the environment and its safety risks, and provide an innovative method for the sustainable resource utilization of SAD.

Keywords: SAD; hydrolysis; AlN; denitrification rate; Al₂O₃; recycling

1. Introduction

A large amount of aluminum dross is generated during the production of electrolytic aluminum, aluminum products and recycled aluminum; on average, the melting of 1 tonne of primary aluminum produces approximately 15 to 25 kg of aluminum dross [1]. There are two categories of aluminum dross: primary aluminum dross (PAD) and secondary aluminum dross (SAD) [2]. Usually, PAD is generated during the first stage of the melting process and contains about 15–80 wt.% metallic aluminum. By re-smelting PAD by mechanical crushing or adding flux, metallic aluminum can be recovered and SAD powder can be obtained, reducing the aluminum content to 5–10 wt%. Approximately 4 million tonnes of PAD and 1 million tonnes of SAD are generated globally per year [3]. During the formation of aluminum dross, nitrogen in the air reacts with molten aluminum to yield the hazardous substance aluminum nitride (AlN) [4,5]. AlN is a covalently bonded, hexagonal crystal lattice structure known for its high thermal conductivity, electrical insulation properties and hardness. Aluminum nitride is often encountered in the aluminum melting process as an impurity, which can affect the quality of the final aluminum product. In aluminum dross, AlN is a significant component that requires efficient removal to achieve the desired purity standards for recycling and reuse purposes. AlN can react with airborne moisture to produce toxic and hazardous ammonia gas, which has
a risk of ignition and explosion, along with a corrosive and irritating odor. Additionally, the reaction between AlN and acid gases in the atmosphere can lead to the formation of aerosol ammonium salts, causing atmospheric pollution [6]. Owing to inadequate recycling techniques, 95% of SAD is disposed of in landfill sites and waste dumps. SAD is classified as a form of dangerous solid waste, featuring both the reactive component, AlN, and the toxic component, which appear on the National Hazardous Substances List. Proper disposal measures are necessary to avoid severe environmental pollution and potential safety risks [7,8]. Therefore, the first priority in the treatment of SAD should be harmlessness, with denitrification as a potential option [9]. The denitrification of SAD can be achieved through dry roasting or wet hydrolysis [10–13]. However, dry roasting denitrification demands a high temperature and advanced equipment, whereas wet hydrolysis denitrification requires only low equipment investment and can be easily industrialized [14–16]. The denitrification rate in the SAD hydrolysis process is higher in an alkaline system. Nonetheless, the impact of hydrolysis denitrification in the alkaline system is greater in terms of nitrogen removal rate, owing to the significant composition variability stemming from different sources of aluminum dross. In contrast, the difference in composition of aluminum dross from different sources leads to an insignificant effect on hydrolysis denitrification. The hydrolysis of SAD in an alkaline system yields high denitrogenation rates. However, differences in the sources and compositions of aluminum dross greatly affect the denitrogenation effect of hydrolysis [17]. At present, the studies of SAD hydrolysis for denitrogenation mainly focus on the optimization of the parameters and process of hydrolysis, and the improvement of the denitrification rate is still the main problem in hydrolysis treatment[18,19].

Researchers from various countries have conducted a lot of studies on the recycling and utilization of SAD, including the utilization of SAD for the preparation of water purifiers, steel refining agents, construction and road materials, refractory materials, etc. [20–22]. However, the industrial-scale application of SAD has not been realized yet due to its complex production processes and high production costs. SAD is a potential source of secondary aluminum, with an alumina content that can exceed 60% [7,23]. Recycling it as a raw material for aluminum smelting by increasing its alumina content could significantly reduce recycling costs and fulfill enterprise expectations [24–26]. In this study, the effects of hydrolysis factors, including temperature, time, liquid–solid ratio, additive type and additive dosage, on the removal rate of aluminum nitride in SAD during wet treatment were studied with the goal of reduction and harmless treatment. However, because the relationship between the factors is not simple or linear, the response surface model was used to explore the influence of the interaction between the factors, and the model was used to predict the optimal process conditions of wet nitrogen removal. The analysis of the composition and the principle of the reaction in wet nitrogen removal shows that recycling SAD as a raw material in aluminum smelting is feasible in theory. The AlN in SAD was reduced to a very low level by regulating the reaction conditions, and the alumina content was greatly increased to achieve the goal of recycling. This not only solves the problems of the harmful nature and accumulation of SAD, but also promotes the development of the aluminum industry in a more environmentally friendly and efficient direction, and achieves a transformation and upgrading of the aluminum industry and its sustainable development.

2. Materials and Methods

2.1. Materials

This experiment utilized raw materials sourced from an aluminum factory situated in Chuzhou, Anhui Province. The raw materials were black and gray, irregular in shape and contained massive solids. The raw materials were ground and dried and then placed in sealed bags for use. The phase composition analysis, element analysis and microscopic morphology analysis of the treated SAD were carried out, respectively, by a Riken Electric
D-MAX2550VB-X-ray diffractometer, a Netherlands ZETIUM-X-ray fluorescence spectrometer and a Hitachi-SU8220 scanning electron microscope from Japan. The results are shown in Figure 1, Table 1 and Figure 2, respectively. The main phases of the SAD are Al₂O₃, AlN, Fe₃N, NaSiO₄ and NaCl. The diffraction peak intensity of alumina is the highest, and the diffraction peak of AlN can be obviously observed. The micromorphology of the samples was characterized by means of a scanning electron microscope. It can be observed from Figure 2a that the morphology of the SAD was irregular and the particle size was different. The block in Figure 2b may be aluminum oxide, with AlN and some salts embedded in the aluminum oxide in smaller particles. Combined with Table 1, it is evident that the SAD comprises O, Al, N, Na, Cl and Si as well as other elements. The percentage of AlN in the SAD was determined to be 11.14% through the Kjeldahl nitrogen determination technique.

![Figure 1. XRD pattern of SAD.](image)

![Table 1. Main chemical element composition of SAD (mass fraction, %).](table)

2.2. Methods and Principles

For AlN powders or ceramics, the hydrolysis process consists of three interdependent phases: an initial hydrolysis phase, the formation and transformation phase of AlOOH and the formation and growth phase of Al(OH)₃ [27]. At the beginning of the reaction, the resulting thin hydrobauxite layer will hinder the hydrolysis of the reaction, so there is an
induction period. The induction period decreased with increasing temperature and increased with decreasing solution pH. In addition, the hydrolysis product of AlN is closely related to the temperature. When the temperature is higher than 351 K, the hydrolysis tends to produce amorphous meta-aluminic acid; when the temperature is lower than 351 K, Al(OH)₃ is the hydrolysis product. The corresponding reaction equation [28] is as follows:

\[ AlN + 3H_2O = Al(OH)_3 + NH_3 \quad (T < 351K) \]  

\[ AlN + 2H_2O = AlOOH_{amorph} + NH_3 \quad (T > 351K) \]  

\[ NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \]  

However, due to the complex composition of SAD, the hydrolysis process of AlN in SAD differs from that of AlN powder or AlN ceramics in that there is no induction period and the hydrolysis product has only an Al(OH)₃ phase and no AlOOH phase. Considering that the hydrolysis behavior of AlN in SAD may be influenced by several factors and that AlN may interact with other components, it is important to investigate the hydrolysis behavior of AlN in SAD and its optimal denitrification process conditions. The influence of each factor on the hydrolysis reaction can be investigated independently by the influence factor evaluation test, and then the response surface model can be applied to analyze the rate of denitrification, which can lead to a more comprehensive understanding of the interactions between the factors and to find the conditions to achieve the best denitrification effect. The model can predict the effect of different combinations of factors on the nitrogen removal effect, and the model can be validated and optimized through several experiments [29]. While optimizing the denitrification process conditions, appropriate process control is explored to increase the alumina content to meet the demand of recycling it as a raw material for aluminum smelting, and to achieve the goal of simultaneous nitrogen removal and resource recycling, thus realizing an environmentally friendly treatment of SAD, rational resourceful recycling and comprehensive utilization.

The hydrolysis procedure was conducted in a constant-temperature magnetic stirring oil bath. The reaction temperature and rotational speed were controlled by this device, and when the conditions of the preset values were reached, a round-bottomed flask containing a quantitative amount of SAD and solution was placed in the oil bath, waiting for the end of the reaction to be quickly vacuum-extracted and filtered; the filter residue was placed in a drying box at 50 °C for 1 h to determine the AlN and Al₂O₃ content.

Determination of AlN content: A sample weighing 0.5000 g was placed in a long-necked flask, followed by adding 200 mL of sodium hydroxide solution (1.5 mol/L) and 50 mL of boric acid solution (20 g/L) into the conical flask. The long-necked flask was then heated in an oil bath to reach a temperature of 130 °C, resulting in an increase in liquid volume to 150 mL as the reaction proceeded. Subsequently, a few drops of methyl red-methylene blue indicator were added to the conical bottle, and titration with a standard hydrochloric acid solution commenced until the solution changed from green to purple-red at the titration end point. The volume of the standard hydrochloric acid used for titration was recorded accordingly [30,31].

AlN content calculation formula:

\[ \omega(AlN) = \frac{c \times (V_1 - V_2) \times M}{1000 \times m} \times 100\% \]  

where \( c \) is the HCl standard titration solution concentration, mol/L; \( m \) is the sample mass, g; \( M \) is the AlN molar mass, g/mol; \( V_1 \) is the volume of HCl standard solution used in the titration, mL; and \( V_2 \) is the volume of HCl standard solution used in the blank, mL.
Determination of Al$_2$O$_3$ content: Accurately weigh 0.5000 g sample in a silver crucible, add a few drops of anhydride CH$_3$OH and 4 g NaOH solids, and melt at a low temperature, gradually rising to 700 °C in a high-temperature furnace for 15 min; when taking out, shake well, cool and soak with 40mL boiling water, and wash the crucible; add 20 mL HCl, boil until the solution is clear, cool, transfer to a 250 mL volumetric bottle, dilute with water to scale and shake well to be measured. Remove 25 mL of the solution into a 250 mL triangle bottle, add 10 mL 200 g/L tartaric acid solution, 12 mL 0.1 mol/L EDTA solution and a few drops of xylene orange indicator; neutralize with NH$_3$·H$_2$O until the solution is purple, adjust with HCl until yellow, then add an excess 8 drops, dilute with H$_2$O to 100 mL, heat and boil for 1 min, add 10 mL 200 g/L C$_6$H$_{12}$N$_4$ solution while hot and cool under running water to room temperature; add 4 drops of 5 g/L xylene orange indicator, titrate with Pb(NO$_3$)$_2$ standard solution to turn purple and do not fade for 15 s, regardless of the reading. Immediately add 10 mL 200 g/L KF solution, heat and boil for 3 min and cool to room temperature with running water; add 3 drops of xylene orange indicator, titrate with Pb(NO$_3$)$_2$ standard solution to reach a stable purple color; that is, the end point, and record the reading. Perform a blank test at the same time.

Al$_2$O$_3$ content calculation formula:

$$\omega(\text{Al}_2\text{O}_3) = \frac{(V_0 - V) \times c \times M/2}{1000 \times m \times V_1/V_A} \times 100\% \quad (5)$$

where $V_0$ is the volume of the Pb(NO$_3$)$_2$ standard titration solution which is consumed in the blank test, mL; $V$ is the volume of the Pb(NO$_3$)$_2$ standard titration solution which is consumed by the sample, mL; $c$ is the Pb(NO$_3$)$_2$ standard titration solution concentration, mol/L; $M$ is the value of the molar mass of Al$_2$O$_3$, g/mL; $m$ is the mass of the sample, g; $V_1$ is the volume of sample solution removed, mL; and $V_A$ is the total volume of the sample solution, mL.

3. Results and Discussion

3.1. Single-Factor Experiment

3.1.1. Reaction Time

The experimental results of the effect of hydrolysis time on the denitrification rate of SAD are shown in Figure 3a under the conditions of a deionized water system, 50 °C, 10/1 liquid–solid ratio, and a rotational speed of 400 rpm for a SAD particle size of 18 mesh. From the figure, it can be seen that with an increase in hydrolysis time, the more adequate the AlN hydrolysis and the higher the denitrification rate. When the hydrolysis time exceeds 8 h, the denitrification rate tends to be stable, and the maximum denitrification rate does not exceed 80%.

![Figure 3](image-url)
3.1.2. Reaction Temperature

In the deionized water system, the experimental results of the effect of hydrolysis temperature on the denitrification rate of SAD when the reaction time is 3 h and the other conditions remain unchanged are shown in Figure 3b. In the range from room temperature to 50 °C, the denitrification rate increases faster with increasing temperature; this may be due to the fact that increasing temperature both accelerates the reaction and facilitates the diffusion of the reaction medium, which promotes the hydrolysis of AlN [32]. When the temperature rises to 90 °C, the denitrification rate increases little, and the maximum denitrification rate is less than 75%. This may be due to the fact that the hydrolysis products cover the surface of AlN, which hinders further hydrolysis reaction. Therefore, it is necessary to explore the effect of other reaction systems on the denitrification rate.

3.1.3. Reaction System

This experiment investigates the impact of the degree of AlN hydrolysis in three different reaction systems: a deionized water system, a 6% mass concentration Na$_2$CO$_3$ solution system and a 6% mass concentration NaOH solution system. According to Figure 4, the AlN hydrolysis efficiency demonstrates the lowest rate in the deionized water system, while the NaOH solution system yields the highest AlN hydrolysis. Related studies support the consistent occurrence of the shrinking unreacted nucleus model during AlN removal, with inner diffusion being the rate-controlling process [33].

![Figure 4](image_url)

**Figure 4.** Effect of time on the denitrification rate in different solution systems.

In an alkaline solution, the hydrolysis of AlN can be strengthened. The reaction process and principle are shown in Figure 5. When the hydrolysis reaction has just started, the AlN is in sufficient contact with water, and the hydrolysis rate is increased. With the continuous progress of the reaction, the surface of AlN is gradually covered by insoluble solid aluminum hydroxide products, and the hydrolysis of aluminum nitride inside is hindered. The addition of NaOH, in which OH$^-$ can destroy the Al(OH)$_3$ product layer on the surface of AlN, leads to the surface of AlN being exposed again, and the hydrolysis reaction continues. The rate control step was changed from inner diffusion to chemical reaction control, which greatly improved the degree of AlN hydrolysis [34].
3.1.4. NaOH Solution Concentration

The impact of NaOH solution concentration on the extent of AlN hydrolysis was investigated under the following conditions: reaction temperature of 50 °C, reaction time of 3 h, liquid–solid ratio of 10/1, rotational speed of 400 rpm and SAD particle size of 18 mesh. The results are presented in Figure 6a. As the NaOH concentration rises, the rate of AlN removal increases rapidly. However, when the concentration exceeds 6%, the rate of denitrification decreases slowly with further increases. As the concentration of OH⁻ in the solution increases, the pH of hydrolysis rises, leading to the AlN hydrolysis reaction equilibrium shifting leftwards. This transformation from the rapid chemical reaction control stage to the diffusion control stage results in a certain degree of suppression of the AlN hydrolysis in SAD.

3.1.5. Liquid–Solid Ratio

In the reaction with a 6% mass concentration NaOH solution, while keeping the other conditions unchanged, Figure 6b shows the effect of the liquid–solid ratio. The decomposition rate of AlN increases with the increase in the liquid–solid product mass ratio. The denitrification rate does not change much after increasing the liquid–solid product mass ratio to 8 mL·g⁻¹, because the sludge viscosity and internal diffusion transfer resistance of
the hydrolytic process decrease with an increasing liquid–solid ratio. The rate of AlN hydrolysis increases gradually; nevertheless, the increase in the liquid–solid ratio does not result in a significant improvement of the denitrification rate, because the alkaline environment formed by dissolving ammonia is favorable to AlN hydrolysis, and increasing the liquid–solid ratio reduces the concentration of ammonia in the solution [35]. Based on these findings, the optimal liquid–solid product mass ratio was determined to be 8 mL·g⁻¹.

3.1.6. Other Factors

The experiment results displaying the effects of rotational speed and SAD particle size on the reaction system with the NaOH solution at 6% mass concentration can be seen in Figure 6c,d. The rate of denitrification has a variation range of 5%, suggesting a relatively insignificant impact on the removal rate of AlN.

3.2. Analysis of Response Surface Experiment Results

Response surface methodology (RSM) is a technique for optimizing results that involves integrating experimental design and mathematical modeling. The experiments are carried out at local points, with regression used to fit the functional relationship between factors and results on a global scale. This enables optimal levels to be obtained for each factor [35,36]. Based on the results of the single-factor experiments, the denitrification rate (Y) response value was used to explore the interactions between A: reaction time (min), B: reaction temperature (°C) and C: sodium hydroxide solution mass concentration (%) in the hydrolysis process and their effect on Y. The response surface method was used to explore the interactions between A: reaction time (min), B: reaction temperature (°C) and C: sodium hydroxide solution mass concentration (wt.%) in the hydrolysis process and the effect on Y. The factors and corresponding level coding values chosen for the response surface method experiment are presented in Table 2. The experiment involves three variables and necessitates the design of 17 experimental groups, including 5 groups of central repeated experiments, to establish the response surface model; the specific experimental design and results are presented in Table 3.

Table 2. Coding of experimental factors and levels.

<table>
<thead>
<tr>
<th>Coded Variable</th>
<th>A: Time/min</th>
<th>B: Temperature/°C</th>
<th>C: Concentration/wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>−1</td>
<td>180</td>
<td>80</td>
<td>4</td>
</tr>
<tr>
<td>0</td>
<td>240</td>
<td>87.5</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>300</td>
<td>95</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 3. RSM arrangement and results.

<table>
<thead>
<tr>
<th>Run</th>
<th>A: Time/min</th>
<th>B: Temperature/°C</th>
<th>C: Concentration/wt.%</th>
<th>Y: Denitrification/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>80</td>
<td>6</td>
<td>98.16</td>
</tr>
<tr>
<td>2</td>
<td>240</td>
<td>87.5</td>
<td>6</td>
<td>98.53</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>95</td>
<td>6</td>
<td>96.69</td>
</tr>
<tr>
<td>4</td>
<td>240</td>
<td>87.5</td>
<td>6</td>
<td>98.16</td>
</tr>
<tr>
<td>5</td>
<td>240</td>
<td>95</td>
<td>8</td>
<td>98.9</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>95</td>
<td>6</td>
<td>99.26</td>
</tr>
<tr>
<td>7</td>
<td>240</td>
<td>95</td>
<td>4</td>
<td>98.9</td>
</tr>
<tr>
<td>8</td>
<td>180</td>
<td>87.5</td>
<td>4</td>
<td>93.38</td>
</tr>
<tr>
<td>9</td>
<td>240</td>
<td>87.5</td>
<td>6</td>
<td>98.16</td>
</tr>
<tr>
<td>10</td>
<td>300</td>
<td>87.5</td>
<td>4</td>
<td>96.69</td>
</tr>
<tr>
<td>11</td>
<td>180</td>
<td>80</td>
<td>6</td>
<td>92.64</td>
</tr>
</tbody>
</table>
Table 4 shows the ANOVA results of the quadratic model for the denitrification rate. The model F-value is 86.43, which indicates that the model is significant. A p-value (Prob > F) of less than 0.05 indicates a significant impact of the experimental parameters on the experimental results, and a value less than 0.0001 indicates a highly significant impact. Thus, A, B, C, A², and C² are significant model terms. The p-value of the interaction terms AB and AC is less than 0.05, while that of BC is more than 0.05, indicating that the interactions of reaction time and temperature, and of reaction time and sodium hydroxide concentration, are significant, while the interaction between reaction temperature and caustic concentration is insignificant. The misfit term’s F-value is insignificant, indicating accurate model fitting over the entire regression range. The rate of denitrification’s multiple quadratic regression equation is as follows:

\[
Y = 20.46508 + 0.395499A + 0.184667B + 3.41637C - 0.001639AB + 0.003083AC - 0.018500BC - 0.000493A^2 + 0.002773B^2 - 0.190375C^2
\]

Table 4. ANOVA for denitrification rate.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F-Value</th>
<th>p-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>66.57</td>
<td>9</td>
<td>7.40</td>
<td>86.43</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>A</td>
<td>32.76</td>
<td>1</td>
<td>32.76</td>
<td>382.82</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>B</td>
<td>12.35</td>
<td>1</td>
<td>12.35</td>
<td>144.30</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>C</td>
<td>2.05</td>
<td>1</td>
<td>2.05</td>
<td>23.96</td>
<td>0.0018</td>
</tr>
<tr>
<td>AB</td>
<td>2.18</td>
<td>1</td>
<td>2.18</td>
<td>25.42</td>
<td>0.0015</td>
</tr>
<tr>
<td>AC</td>
<td>0.5476</td>
<td>1</td>
<td>0.5476</td>
<td>6.40</td>
<td>0.0393</td>
</tr>
<tr>
<td>BC</td>
<td>0.3080</td>
<td>1</td>
<td>0.3080</td>
<td>3.60</td>
<td>0.0986</td>
</tr>
<tr>
<td>A²</td>
<td>13.29</td>
<td>1</td>
<td>13.29</td>
<td>155.26</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>B²</td>
<td>0.1025</td>
<td>1</td>
<td>0.1025</td>
<td>1.20</td>
<td>0.3101</td>
</tr>
<tr>
<td>C²</td>
<td>2.44</td>
<td>1</td>
<td>2.44</td>
<td>28.53</td>
<td>0.0011</td>
</tr>
<tr>
<td>Residual</td>
<td>0.5991</td>
<td>7</td>
<td>0.0856</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>0.4348</td>
<td>3</td>
<td>0.1449</td>
<td>3.53</td>
<td>0.1273</td>
</tr>
</tbody>
</table>

Table 5 shows the results of the statistical analysis of the regression equation error. The CV value (0.3010%) is less than 10%, indicating a high degree of confidence and accuracy in the model. The Adeq precision value (29.114) is the effective signal-to-noise ratio, which is greater than 4, which suggests that the model can be used for predictive purposes. The \( R^2 \) value is very close to 1, and the values of \( R^2_{adj} \) and \( R^2_{pre} \) are very high and the difference is less than 0.2, demonstrating that the model fits well and the measured and predicted values of denitrification rate have high correlation.

Table 5. Error statistical analysis.

<table>
<thead>
<tr>
<th>( R^2 )</th>
<th>( R^2_{adj} )</th>
<th>( R^2_{pre} )</th>
<th>Adeq Precision</th>
<th>CV/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9911</td>
<td>0.9796</td>
<td>0.8926</td>
<td>29.114</td>
<td>0.3010</td>
</tr>
</tbody>
</table>

This study conducts an analysis on the response surface of AlN hydrolysis in SAD by fixing one influential factor and investigating the interaction between two other factors. Figure 7 presents the response surface and contour plots depicting the impact of hydrolysis temperature and time on denitrification rate at a sodium hydroxide concentration of...
6%. Specifically, Figure 7a demonstrates that reaction time and temperature exert significant effects on the nitrogen removal rate while exhibiting an interactive relationship. By maintaining a constant reaction temperature, prolonging the reaction time resulted in a consistent increase in denitrification rate, subsequently leading to a gradual decline in hydrolysis rate. On the other hand, by keeping the reaction time constant, the denitrification rate experiences a slow increase with an increase in the reaction temperature. Based on Figure 7b, the denitrification rate is more greatly influenced by changes in reaction time than changes in reaction temperature, as indicated by the higher contour density observed along the direction of reaction time change.

The response surfaces and contour plots of reaction time and sodium hydroxide concentration on the denitrification rate at a reaction temperature of 87.5 °C are shown in Figure 8. In this case, the reaction time and sodium hydroxide concentration have a significant effect on the denitrification rate, and the reaction time has a greater effect on the denitrification rate. With the increases in time and concentration, the rate of denitrification increases, but when the time and concentration increase to a certain level, the rate of denitrification decreases instead, which is due to the interaction impact.

When the reaction time is 240 min, the influence of temperature and the concentration of the NaOH solution on the denitrification rate is shown in Figure 9. With an increase in temperature, the denitrification rate increases, but with an increase in solution concentration, the denitrification rate increases first and then decreases, indicating that there is an optimal value of the concentration. As shown in Figure 9b, reaction temperature has a greater effect on the denitrification rate than the solution concentration, and the interaction between the two is not significant.

Figure 7. Interactive effects of reaction time and temperature. (a) Response surface plot  (b) contour plot.

Figure 8. Interactive effects of reaction time and NaOH solution concentration. (a) Response surface plot; (b) contour plot.
Figure 9. Interactive effects of reaction temperature and NaOH solution concentration. (a) Response surface plot; (b) contour plot.

The optimal reaction conditions of wet denitrification by response surface optimization are as follows: the denitrification rate was predicted to be 99.984% when the reaction temperature was 95 °C, the concentration of the NaOH solution was 6.489% and the reaction time was 263.243 min. To verify the feasibility of the optimal processing parameters, the preparation conditions were modified to the reaction temperature of 95 °C, the NaOH solution concentration of 6.5% and the reaction time of 263 min, taking into account the actual experimental operation. After three experiments, the actual value of denitrification rate was determined to be 99.63%, and the relative error was 0.35%, which confirm the feasibility of the experimental design using the response surface method.

3.3. Recycling

During the hydrolysis process, magnetic compounds containing iron attach themselves to the magnets. This phenomenon can be exploited to separate these compounds by filtration, thus effectively removing them from the mixture. The salts and soluble substances in the SAD are dissolved in the sodium hydroxide solution and are separated from the SAD during filtration. The dried solid residue was analyzed using X-ray diffraction (XRD), which confirmed the presence of only the Al₂O₃ phase. It can subsequently be reused as a raw material for aluminum smelting, streamlining the procedure and saving treatment costs. The thermodynamic data for reactions (7)–(9) were calculated by HSC Chemistry, as shown in Figure 10. The Gibbs free energies (∆G°) of the three reactions are negative, suggesting that they occur spontaneously. The AlN hydrolysis reaction is easier to carry out than the reaction between Al₂O₃ and NaOH in the SAD, which is a slow process. Therefore, the thermodynamic difference can be employed to regulate the reaction conditions to maximize the hydrolysis of AlN in SAD and further enrich Al₂O₃. Based on the diagram, it is evident that there is minimal variation in the Gibbs free energy of the reaction between 25–100 °C. Therefore, the effects of various factors should be investigated according to the actual experiments.

\[
\begin{align*}
\text{AIN} + 3\text{H}_2\text{O} & = \text{Al(OH)}_3 \downarrow + \text{NH}_3 \uparrow \\
\text{Al}_2\text{O}_3 + 2\text{NaOH} & = 2\text{NaAlO}_2 + \text{H}_2\text{O} \\
\text{Al(OH)}_3 + \text{NaOH} & = \text{NaAlO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]
3.3.1. Effect of Time on Al₂O₃ Content

Under the given conditions, the reaction temperature was set to 50 °C and the liquid–solid ratio was 8/1 in the 6 wt.% NaOH solution system; the experimental results of the effect of time on the content of Al₂O₃ and AlN in SAD are shown in Figure 11a. The content of Al₂O₃ increases rapidly with an increase in the reaction time, increases slowly to 5 h and then tends to be stable, while the content of AlN decreases rapidly and then tends to be stable, and the reaction time of 5 h is the best choice for comprehensive consideration.
3.3.2. Effect of Temperature on Al\(_2\)O\(_3\) Content

Under the condition that the reaction time is 3 h and the other conditions remain unchanged, the experimental results of the effect of hydrolysis temperature on the content of Al\(_2\)O\(_3\) and AlN in SAD are shown in Figure 11b. When the temperature is lower than 80 °C, the Al\(_2\)O\(_3\) content gradually increases with the elevation of temperature, and reaches the maximum value at 80 °C, but the AlN content exceeds 1%, which does not reach the ideal range. When the temperature exceeds 80 °C, the Al\(_2\)O\(_3\) content has a downward trend, which may be caused by the reaction of partial Al\(_2\)O\(_3\) with NaOH. With an increase in temperature, the AlN content first rapidly decreases and then slowly decreases. At 90 °C, the AlN content is at a low level, and the Al\(_2\)O\(_3\) content is at a high level. Considering the overall consideration, the temperature of 90 °C is appropriate.

3.3.3. Effect of NaOH Solution Concentration on Al\(_2\)O\(_3\) Content

When the other conditions remain unchanged, the influence of the NaOH solution concentration on the content of Al\(_2\)O\(_3\) is explored. As shown in Figure 11c, with increasing concentration of NaOH solution, the Al\(_2\)O\(_3\) content shows an overall upward trend; however, when the concentration is over 6%, the AlN content rises slowly with an increase in the solution concentration, which may be due to the decrease in solute diffusion efficiency caused by the increase in concentration. The reaction rate changes from the rapid chemical reaction control stage to the diffusion control stage. The concentration of the NaOH solution was chosen to be 10% based on comprehensive consideration.

In the 10% NaOH solution system, after undergoing a reaction at 90 °C for 5 h, the content of Al\(_2\)O\(_3\) in SAD is 98.43%, while the denitrification rate is 95.58%, and the content of AlN is only 0.492%, which is at a low level and in accordance with the expected value. According to the requirements of metallurgical-grade alumina and the Chinese non-ferrous metal industry standard YS/T 803-2012 [37], the content of Al\(_2\)O\(_3\) reached the YAO-3 level (≥98.4%). The XRD results in Figure 11d show that the product is composed primarily of Al\(_2\)O\(_3\) with a small amount of other materials, probably Al(OH)\(_3\) or salts, indicating that the treated SAD can be used as a feedstock for aluminum refinement.
3.4. Evaluation and Prospect

3.4.1. Environmental Benefit Assessment

In this study, by hydrolyzing SAD in an alkali solution, not only was the effective recovery of aluminum resources realized, but also the risk of environmental pollution was significantly reduced. The hydrolysis process converts the AlN in the SAD into a relatively harmless form, reducing the release of ammonia and other harmful gases, and effectively curbing the potential pollution of soil and water bodies. In addition, the reuse of recovered alumina reduces the mining of original aluminum ore resources, in line with the principle of resource recycling for sustainable development. Compared to traditional aluminum production methods, our proposed process has a lower carbon footprint, mainly due to reduced energy consumption and material waste [38,39]. This not only reduces the burden of the aluminum industry on the environment, but also reduces the greenhouse gas emissions generated by the mining of new ores, which has a positive impact on the mitigation of climate change.

3.4.2. Economic Benefit Evaluation

From an economic point of view, the recycling method proposed in this study has significant cost-effectiveness. By converting SAD into raw materials for smelting aluminum, enterprises can obtain alumina at a lower cost, reduce dependence on the raw material market and improve the utilization efficiency of resources. In addition, the reuse of recycled alumina reduces energy consumption, reduces the carbon footprint in the smelting process and brings the double benefits of energy conservation and emission reduction for enterprises. As the global demand for green and sustainable products increases, recycled alumina is expected to open up new market opportunities, bringing economic gains and market competitiveness to companies.

3.4.3. Future Prospect

The market demand for SAD resource products is expected to continue growing due to increasingly strict environmental regulations and improved public awareness of environmental protection. Furthermore, technological innovation and process optimization have led to more stable alumina content in SAD products, which is anticipated to enhance recovery efficiency, reduce costs and improve the market competitiveness of SAD resource products in the future.

In summary, the recycling of hydrolyzed products from SAD presents a positive outlook in terms of both environmental and economic benefits. It is recommended to increase R&D investment in this field, optimize process flow and improve recovery efficiency. Additionally, it is suggested that relevant enterprises and research institutions strengthen cooperation to jointly explore more efficient and environmentally friendly utilization technology for SAD resources in order to achieve green transformation and sustainable development within the aluminum industry.

4. Conclusions

In this study, the influence of different factors on the nitrogen removal rate of SAD was first studied. The response surface model was used to optimize and determine the optimal nitrogen removal process conditions, and the resource utilization was carried out. The results are as follows:

(1) Among the three systems of deionized water, Na$_2$CO$_3$ solution and NaOH solution, the NaOH solution system has the best nitrogen removal effect. In the NaOH reaction system, the effect of reaction temperature and reaction time on the denitrification rate is very significant, followed by the concentration of the NaOH solution.

(2) According to the response surface model, the optimal process parameters were a reaction temperature of 95 $^\circ$C, reaction time of 263 min and NaOH solution concentration
of 6.5 wt.%. Under these conditions, the nitrogen removal rate is 99.63% and the relative error is 0.35%.

(3) The reaction was carried out in the 10% NaOH solution system, the reaction temperature was controlled to 90 °C, the reaction time was 5 h and the Al₂O₃ content was significantly increased to 98.43% during the SAD treatment process, reaching the YAO-3 standard of metallurgical-grade alumina in the Chinese non-ferrous metal industry standard YS/T 803-2012. Moreover, the content of Al₂O₃ is only 0.492%, which achieves the recycling of SAD into raw materials for smelting aluminum while removing nitrogen.

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