Study on the Absorption of Nitrous Tetroxide Waste Gas by Foaming Agent

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Abstract. The problem of waste gas treatment of nitrogen tetroxide (N\textsubscript{2}O\textsubscript{4}) has long been a difficult problem for researchers. This paper determines the combination liquid formula of N\textsubscript{2}O\textsubscript{4} waste absorption system by screening absorbent, foaming agent and foaming method, and finds a new method to deal with N\textsubscript{2}O\textsubscript{4} waste gas. In addition, the paper measures nitrate and nitrite content respectively by UV-visible spectrophotometry, and obtains the absorption rate and the nitrite emission of absorption system in order to judge the overall absorption effect. The research results show that using the new method in the actual waste gas absorption, absorption rate can reach more than 93% under the simple exposure device, while nitrite content is lower than the national surface water discharge standard, which can solve the problem of waste gas harm.

1. Introduction
As a liquid rocket propellant, N\textsubscript{2}O\textsubscript{4} has been widely used in missile weapons and space vehicles\textsuperscript{[1]} but N\textsubscript{2}O\textsubscript{4} is highly toxic, and it can cause poisoning or even death through the respiratory tract or skin. Contacting with most organic matter, it may cause burning or even explosion, and has the risk of fire and explosion\textsuperscript{[2]}. Because of the low boiling point of N\textsubscript{2}O\textsubscript{4} (21.2°C)\textsuperscript{[3]}, once leaking, it will quickly evaporate from the liquid into nitrogen dioxide gas, which has a strong irritating odor, and the density is larger than air\textsuperscript{[4]}, causing red brown smoke on the surface which can cause different degrees of harm to operators and the environment.

The packed tower water absorption method is a common method for small and medium-sized chemical enterprises to treat N\textsubscript{2}O\textsubscript{4}\textsuperscript{[5]}. The method is simple and low in investment cost, and can convert most of N\textsubscript{2}O\textsubscript{4} into nitrates, but due to a small amount of NO hardly soluble in aqueous solution, the absorption efficiency is not too high; the combustion treatment method has better treatment effect, but the absorption device is bulky and difficult to move, and can only be used in fixed places. It is difficult to effectively treat N\textsubscript{2}O\textsubscript{4} under the existing conditions in the laboratory. It is urgent to develop a new method that not only can efficiently treat N\textsubscript{2}O\textsubscript{4} and its products, but also meets the requirements of portability, easy operation, low cost and promotion for waste gas absorption.

In view of the fact that liquid N\textsubscript{2}O\textsubscript{4} reacts violently and easily splashes, this study intends to convert the N\textsubscript{2}O\textsubscript{4} liquid into gas, and try to achieve safe and efficient absorption of N\textsubscript{2}O\textsubscript{4} gas (hereinafter referred to as waste gas). In the early stage, after adding a small amount of foaming agent into the absorbent solution, it was found that the foam layer was formed to achieve dense coverage of the waste gas, and no waste gas was detected to escape, and a significant absorption effect was obtained, so it is feasible as a research direction.
2. Experimental

The experimental device is mainly composed of two parts: one part is the source of waste gas, and its function is to keep the sample cylinder to provide continuous and stable $\text{N}_2\text{O}_4$ waste gas, which can be realized by heating the cylinder containing $\text{N}_2\text{O}_4$ at a constant temperature. The other part is the absorption system of waste gas, which is mainly composed of a combination of water, foaming agent, absorbent and the like. The schematic figure of the experimental device is shown in Figure 1.

![Figure 1. Schematic figure of experimental device.](image)

2.1. Selection of foaming agent

The initial volume of the aqueous foaming agent was set at 1L. To the same volume (2L), the foaming rate of the different foaming agents was measured by the time of foaming. The time taken for the volume of the solution to fall from 2L to 1L of the scale line was recorded, and the foam stability was evaluated by the defoaming time. Five groups were measured in parallel. A foaming agent with fast foaming rate and long foam stabilization time is selected.

2.2. Selection of absorbent and determination of its dosage

Prepare sodium hydroxide, hydrogen peroxide, potassium permanganate, aqueous urea solution of similar concentration, and then add 3mL of foaming agent respectively. The waste gas is passed into the absorption liquid to compare the compatibility and synergy between the different absorbents and the foaming agent.

The waste gas was continuously supplied to the absorption system, and the quality of the waste gas consumed within 1 minute was recorded. Ten sets of parallel assays were performed under the same conditions.

2.3. Foaming design

Prepare 4 2L beakers, each of which is filled with 1L of water, 10g of urea, 3mL of foaming agent, and numbered 1, 2, 3, and 4. Each beaker was filled with waste gas, the No. 1 beaker was stirred in the same direction with a glass rod, the No. 2 beaker was stirred with a magnetic stirrer, the No. 3 beaker was continuously blasted into the gas through the air bottle, and the No. 4 beaker was sequentially added with 5 g of sodium bicarbonate and 4.5 mL of hydrochloric acid. (Exactly complete reaction), then stirred evenly with a glass rod. Observe and record the blistering in each beaker.

2.4. Determination of nitrate nitrogen content in absorption liquid

The absorption time was set to 1 min, and the masses of the sample cylinders before and after absorption were recorded as $m_0$ and $m_1$ respectively. Pipette 1 mL of the supernatant and measure the absorbance according to the standard method [6]. The absorbance value is recorded as $A_m$.

2.5. Determination of nitrite nitrogen content

After the absorption experiment, the appropriate amount of the absorption liquid was transferred to a 25 mL colorimetric tube, and the absorbance $A'_{m}$ was measured at 540 nm according to the usual standard method [5], and the nitrite-nitrogen content $\rho'_{m}$ was obtained.
3. Results and discussion

3.1. Foaming agent selection results and analysis

The defoaming time of the six foaming agents is shown in Figure 3. F-type and P-type foaming agents have the longest foam stabilization time, both above 400s(mean). The S-type foaming agent has the shortest settling time and can only maintain 143s (mean), and the foam is loose.

![Figure 2. Foaming time of different foaming agents.](image)

![Figure 3. Defoaming time of different foaming agents.](image)

Analysis of Figure 2 and Figure 3 can be concluded: (1) The foaming rate of the foaming agent is closely related to its foaming multiple and composition. The G and Z foaming agents exhibit a higher foaming rate due to their higher foaming multiple. Although the F-type foaming agent is a low-multiple foaming agent, it has greatly enhanced its foaming ability because it contains an appropriate amount of fluorocarbon surfactant. (2) Large bubbles are the main factors determining the life of the foaming agent. Due to the thin film wall of the large bubble, it is extremely easy to be crushed and broken \[7\]. Moreover, large bubbles are susceptible to factors such as evaporation and vibration, so the life is generally not long. While the dense foam layer is different, the foam is arranged tightly and the gap is small, so the solvent evaporation on the surface of the bubble film is reduced. The foam molecules complement each other and interact synergistically, and the foam life is prolonged, so the foam is stable for a long time.

It can be seen from the above analysis that the F-type foaming agent has a fast foaming rate, a dense foam layer and good foam stability, and is a foaming agent having the best comprehensive performance among the six foaming agents. The foaming agents used below all refer to such foaming agent. In combination with the foaming agent's own use characteristics (adding a small amount can significantly improve the solution interface state) \[8\], the amount of foaming agent in this study is set to 3mL.

3.2. Selection of absorbent and analysis of its dosage

3.2.1. Absorber selection results and analysis

The direct addition of foaming agent in water does not last for a long time, and the foaming difficulty is gradually increased in the later stage. Some large bubbles are formed, which are easily crushed and broken, resulting in continuous escape of waste gas. Sodium hydroxide inactivates protein molecules in the foaming agent. Lack of performance such as foaming, the foaming agent can not foam normally. The potassium permanganate can absorb the waste gas in a short time, and it is limited by the solubility in practical application. Hydrogen peroxide and water are mutually soluble in any ratio, and the absorption effect is slightly better than potassium permanganate. The large amount of gas generated in the urea solution accelerates the uniform growth of the foam, which is favorable for forming a dense foam, and can greatly improve the absorption effect of the solution.

Comparing the above five kinds of absorbents, the absorption effect of urea is the best. Not only urea is cheap and easy to obtain, but also its combination with foaming agent has fast foaming, large foaming
capacity, strong foam stability, good compatibility and synergy. It can be used for continuous absorption of N$_2$O$_4$ waste gas.

3.2.2. Quantitative analysis of absorbent

The amount of absorbent is directly related to the amount of N$_2$O$_4$ waste gas treated. The reaction formula of N$_2$O$_4$ and urea is shown in formula (1) [5].

\[
N_2O_4 + CO(NH_2)_2 \rightarrow N_2↑ + CO_2↑ + NH_4NO_3 \tag{1}
\]

By using the stoichiometric relationship of N$_2$O$_4$ and urea in the formula (1), the formula for calculating the absorbent can be obtained as shown in formula (2).

\[
m_a = \frac{60m_n}{92} \tag{2}
\]

Where: $m_a$ is the mass of urea, g; $m_n$ is the mass of N$_2$O$_4$, g; 60, 92 are the relative molecular masses of urea and N$_2$O$_4$.

The amount of waste gas generated and the theoretical amount of absorbent used are shown in Table 1. It can be seen from the table that under the same gas supply condition, the output of waste gas is generally stable, and the average value of the measurement can be used as a reference value for the amount of waste gas generated. The theoretical amount of urea can be calculated from the formula (2). Taking into account the excess principle of the absorbent and the high solubility, the amount of the absorbent is now calculated in an excess of about 10%, and the actual amount of the absorbent is selected to be 10 g.

| No | Waste gas consumption | Absorbent dosage | Average amount of absorbent |
|----|-----------------------|------------------|-----------------------------|
| 1  | 14.4                  | 9.4              | 9.2                         |
| 2  | 14.8                  | 9.6              |
| 3  | 13.6                  | 8.8              |
| 4  | 14.2                  | 9.2              |
| 5  | 15.0                  | 9.8              |
| 6  | 13.2                  | 9.0              |
| 7  | 13.0                  | 8.4              |
| 8  | 14.6                  | 9.6              |
| 9  | 14.4                  | 9.4              |
| 10 | 13.4                  | 8.8              |

3.3. Foaming method selection and discussion

The glass rod stirring method can only produce a thin layer of foam above the liquid surface, and the foam cannot continue to grow, so this method is not recommended. Magnetic stirring can only drive local agitation, resulting in less foam generation. The stirring power is insufficient, and the air cannot be introduced into the solution in a large amount, so the foaming effect is not good. Although the gas blasting method can introduce gas into the solution to accelerate the uniform dispersion of the foaming agent, the solubility of the air in water is poor, causing uneven bubble size, and the foam is easily broken and faded.

The chemical reaction foaming method forms the foam layer which is dense and uniform, and the foam has long stabilization time and fast foaming rate. The main reasons for the analysis are as follows: First, a large amount of gas released by the reaction of hydrochloric acid and sodium bicarbonate accelerates the uniform distribution of the foaming agent. The time for forming the orientation of the foam layer is shortened [9], and the surface tension of the liquid is lowered, leading to the foam more likely to be formed; the second is that the reaction of urea and N$_2$O$_4$ also generates gas which rises smoothly in the solution, and the foaming agent is evenly stressed, which is conducive to the formation of dense and delicate foam layer [10].

It can be seen from the above analysis that the chemical reaction foaming method has a fast foaming rate, a simple foaming method, and good foam stability, and synergistically exerts a covering absorption effect with urea, so it is the preferred method for the four foaming methods.

3.4. Absorption formula determination

The amount of water in the absorption liquid is 1L; from the above analysis, the actual dosage of the absorbent is 10g; the dosage of the foaming agent is 3mL; thefoaming method is chemical reaction
foaming method, and the reaction reagents of sodium bicarbonate and hydrochloric acid are respectively 5g and 4.5mL.

3.5. Absorption rate measurement results and discussion

3.5.1. Nitrate nitrogen content calculation

The standard solution volume corresponding to the absorbance value is found from the standard working curve, and the standard solution concentration is converted into the mass of the nitrate-nitrogen. The nitrate-nitrogen content is calculated as:

\[ \rho_m = \frac{A_m}{k} \frac{\rho_k}{V_i} \frac{25}{V_0} \times 1000 \]  

Where: \( \rho_m \) is the nitrate-nitrogen content, mg/L; \( k \) is the proportional constant; \( V_0 \) is the volume taken from the colorimetric tube; \( \rho_k \) is the standard solution concentration; \( C_k=0.1\text{mg/mL} \); \( V_t \) is the volume of the sample taken from the absorption liquid; \( V_t = 1 \text{ mL} \).

3.5.2. Absorption rate calculation and analysis

From the stoichiometric relationship between \( \text{N}_2\text{O}_4 \) and nitrate in formula (1), the amount of \( \text{N}_2\text{O}_4 \) actually participating in the reaction can be derived, and the calculation formula is as shown in formula (4):

\[ m_N = \frac{92 V_L \rho_m}{14 \times 1000} = \frac{23 \rho_m}{3800} \]  

Where: \( m_N \) is the actual absorption of \( \text{N}_2\text{O}_4 \); \( V_L \) is the volume of the absorption liquid, \( V_L = 5\text{ L} \); 92, 14 are the relative molecular mass of \( \text{N}_2\text{O}_4 \) and the relative atomic mass of nitrogen.

The absorption rate of the absorption system can be obtained from the ratio of the actual absorption of \( \text{N}_2\text{O}_4 \) to the theoretical absorption. The theoretical absorption is the difference in mass of the sample cylinder before and after the reaction, which can be expressed as \( m_0-m_1 \). The calculation formula of the absorption rate is shown in formula (5).

\[ \eta = \frac{23 \rho_m}{3800(m_0-m_1)} \]  

The calculation results of nitrate-nitrogen content and absorption rate of the absorption liquid are shown in Table 2. It can be seen from the table that the calculation results of each absorption rate are relatively close, the standard deviation is 0.01, and the relative standard deviation is 1.06%, which indicates that the establishment of this method can better ensure the parallelism and reproducibility of the determination of nitrate-nitrogen content.

| No | \( A_m \) | \( A_m/k \text{ /mL} \) | \( V_0/\text{mL} \) | \( 25/V_0 \) | \( \rho_m/\text{mg/L} \) | \( m_N/\text{g} \) | \( m_0-m_1/\text{g} \) | \( \eta \) |
|----|----------|-----------------|---------|-------------|------------------|-----------------|-----------------|------|
| 1  | 0.2043   | 0.813           | 1       | 25          | 2032.5           | 13.4            | 14.2            | 0.941 |
| 2  | 0.1961   | 0.781           | 1       | 25          | 1952.5           | 12.8            | 13.6            | 0.943 |
| 3  | 0.2142   | 0.853           | 1       | 25          | 2132.5           | 14.0            | 14.7            | 0.953 |
| 4  | 0.2033   | 0.809           | 1       | 25          | 2022.5           | 13.3            | 14.1            | 0.943 |
| 5  | 0.1975   | 0.786           | 1       | 25          | 1965.0           | 12.9            | 13.8            | 0.936 |
| 6  | 0.2027   | 0.807           | 1       | 25          | 2017.5           | 13.3            | 14.3            | 0.927 |
| 7  | 0.1922   | 0.765           | 1       | 25          | 1912.5           | 12.6            | 13.5            | 0.931 |
| 8  | 0.2066   | 0.822           | 1       | 25          | 2055.0           | 13.5            | 14.7            | 0.919 |
| 9  | 0.2028   | 0.807           | 1       | 25          | 2017.5           | 13.3            | 14.2            | 0.934 |
| 10 | 0.2011   | 0.800           | 1       | 25          | 2000.0           | 13.1            | 13.9            | 0.946 |
| Mean| 0.2021  | 0.804           | 1       | 25          | 2010.0           | 13.2            | 14.1            | 0.937 |
The determination of the absorption rate of N\textsubscript{2}O\textsubscript{4} by water and sodium hydroxide solution has been studied in previous studies\textsuperscript{[11]}. By shaking the ampoule ball sample of known purity N\textsubscript{2}O\textsubscript{4} and changing the amount of water added, the highest absorption rate of water to N\textsubscript{2}O\textsubscript{4} can reach 75% within 5 min, and the absorption rate can reach up to 82% within 10 min. Under the condition of sufficient oscillation of sodium hydroxide for 5 min, the average absorption rate can reach 90.9%. The research method in this paper is different. The dense foam layer formed by the foaming agent can complete the high-efficiency absorption of waste gas under the open condition. The absorption rate of 93.7% can be achieved within 1 min, which significantly improves the absorption effect.

3.6. Determination and discussion of nitrite-nitrogen content

The nitrite-nitrogen content can be determined by the corresponding volume on the standard working curve. The calculation formula of nitrite-nitrogen content is shown in formula (6).

\[
\rho_m' = \frac{A_{m'} \cdot \rho_k'}{V_0} \times 1000
\]

Where: \( \rho_m' \) is the content of nitrite-nitrogen, \( \mu \text{ g/L} \); \( k' \) is the proportional constant; \( \rho_k' \) is the concentration of the standard solution, \( \rho_k' = 1 \ \mu \text{ g/mL} \); \( V_0 \) is the volume taken from the absorbing solution.

The measured value of nitrite-nitrogen was calculated from the formula (6), and a histogram as shown in Fig.4 was produced accordingly. The results of multiple measurements show that the nitrite-nitrogen content is relatively close, which can basically ensure the reproducibility of nitrite content determination. Nitrite is a carcinogenic toxic substance that must be strictly controlled and treated. The national standard stipulates that the mass concentration of nitrite-nitrogen in surface water is not higher than 0.2 mg/L\textsuperscript{[12]}. It is known from the measurement results that the method is lower than surface water discharge standard of the national standard after absorption treatment. This is because as the absorption progresses, the solution is acidic, and urea can rapidly reduce nitrite to nitrogen under acidic conditions, which is not conducive to its large amount of stability\textsuperscript{[7]}

![Figure 4. Nitrogen content of nitrite.](image)

4. Conclusion

This study established a new method for the absorption of N\textsubscript{2}O\textsubscript{4} waste gas by foaming agent. The foam layer is dense and uniform, and has good coverage and absorption of waste gas. Through screening, comparison, and index determination, the best formula for the absorption composition was obtained. After 1 min of continuous absorption, the average absorption rate reached 93.7%, and the average nitrite-nitrogen content was 32.3 \( \mu \text{ g/L} \), which was lower than the national surface water discharge standard (200 \( \mu \text{ g/L} \)). In the true sense, high efficiency absorption and non-toxic emission of N\textsubscript{2}O\textsubscript{4} are realized.
The safety and reliability of the treatment of N₂O₄ waste gas by the method are obviously improved, which have high environmental protection benefits and promotion value.

References

[1] Yang L. G. (2014) Preparation and Corrosion Resistance of Aluminum-based Amorphous Protective Coatings. Shenyang: Northeastern University. pp. 1-5.
[2] Hu J. Y. & Huang Z. Y. (2017) Risk Assessment of N₂O₄ Storage Tanks. J. Safety and Environmental Engineering. Commun., 24: 129-131.
[3] Liu D.C. (2010) Discussion on the leakage accident of hazardous chemicals and preventive measures. J. Hunan Safety and Disaster Prevention. Commun., 3: 46-47.
[4] Luo F., Huang Z. Y., Liu B., et al. (2011) Saltwater Simulation Analysis of N₂O₄ diffusion in Confined Space. J. Safety and Environmental Engineering. Commun., 18: 93-96.
[5] Jiang W., Zhang J. T., Zhang K. Z. (1993) Rocket propellant monitoring protection and pollution control. National University of Defense Technology Press, Changsha.
[6] Wang Y. F. (2010) Biodegradation of NO in Waste Gas by Hollow Ceramic Ball Filler. Qingdao: Qingdao Technological University. pp. 18-27.
[7] Xin Z. (2010) Material Additive Chemistry. Chemical Industry Press, Beijing.
[8] Liang Z. Q. (2005) Handbook of Practical Cleaning Technology. Chemical Industry Press, Beijing.
[9] Wang M. M. & Guo D. H. (2007) Foaming Properties of Foaming Agents and Its Influencing Factors. J. Progress in Fine Petrochemicals. Commun., 8: 40-44.
[10] Tong W., Wang W. Q., Zhao B., et al. (2018) A new method for the absorption of N₂O₄ waste gas. J. Chemical Propellants Polymers. Commun., 16: 66-71.
[11] Cong R. M., Yan A. K., Jiao T. S. (2011) Study on the mechanism of absorption of N₂O₄ from water and sodium hydroxide solution. In: The 5th National Conference of Chemical Propellants in Chinese Chemical Society. Dalian. pp. 500-504.
[12] GB 3838-2002, Surface Water Environmental Quality Standards.