Available Online: 26 May 2025 DOI: 10.54254/2977-3903/2025.23518

Study on the performance of sodium borohydride-containing emulsion explosives

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Abstract. This study developed a novel emulsion explosive containing sodium borohydride ($NaBH_4$). The effects of $NaBH_4$ content on the performance of the emulsion explosive were investigated using methods such as brisance, density measurements, and theoretical calculations. Additionally, the thermal decomposition characteristics of the emulsion explosive samples were examined through thermogravimetric analysis. Results indicated that as the $NaBH_4$ content increased, the density of the explosive initially increased and then decreased, while the heat of explosion continuously increased. The brisance of the emulsion explosives is stable under different temperature conditions ranging from 20 ℃ to 30 ℃. At 25℃, the brisance initially increased and then decreased, reaching a maximum value of 22.4 mm at a $NaBH_4$ content of 5%, which represents a 50.33% improvement compared to ordinary emulsion explosives. The TG curves of all samples exhibited consistent trends. Under the same heating rate, the initial decomposition temperature of the emulsion explosive increased with the addition of $NaBH_4$.

Keywords: emulsion explosive, detonation performance, high-brisance

1. Introduction

Emulsion explosives, widely used in industrial applications, are known for their water resistance, high safety, and environmental friendliness. However, due to the presence of approximately 10% water in their composition, the proportion of combustible components is reduced, limiting the energy output of these explosives [1]. Therefore, improving the blasting performance of emulsion explosives and developing high-brisance formulations has been a key focus of research worldwide.

In the process of researching high-brisance emulsion explosives, hydrogen storage materials have been found to serve as both sensitizers and energetic additives [2, 3]. Cheng et al. demonstrated that MgH_2-based hydrogen storage emulsion explosives significantly improve brisance and work capacity [4]. In addition to hydrogen storage materials, high-energy metal powders can also effectively enhance the performance of emulsion explosives. Mishra et al. noted that emulsion explosives maintain stable detonation performance at an aluminum content of 5% [5]. Cheng et al. found that with a boron powder content of 16%, the detonation performance was optimal. And with the boron powder content from 0% -20% gradually increased, the average explosion temperature, explosion pressure, positive impulse and heat of explosion containing boron emulsion explosives first increased and then decreased [6].

Although the aforementioned materials can effectively enhance the detonation performance of emulsion explosives, they also face issues such as high costs, reduced stability of emulsion explosives, and complex processes. This study, through theoretical analysis and preliminary experimental research, has found that $NaBH_4$ has a hydrogen content of 10.6%. It generates a significant amount of heat and gaseous products during the explosion reaction, which can improve the detonation performance of emulsion explosives. Moreover, its cost is only 10% of that of metal powders. Therefore, this paper proposes to select $NaBH_4$ as a high-energy additive to develop a new type of high-brisance emulsion explosive. The study will conduct brisance experiments to test the detonation performance of the samples and explore the relationship between $NaBH_4$ content and the detonation performance of emulsion explosives. Additionally, it will investigate the impact of $NaBH_4$ on the thermal stability of emulsion explosives through thermal decomposition experiments. The ultimate goal is to develop a new type of high-brisance emulsion explosive that is cost-effective, powerful, and safe. This work will provide a basis for further theoretical and experimental research as well as for large-scale production.

2. Experimental part

2.1. Preparation of emulsion explosives

In order to clarify the material properties of industrial grade sodium borohydride and pure sodium borohydride and their applicability, this study was tested using XRD ray diffraction experiments and the results are shown in Figure 1.

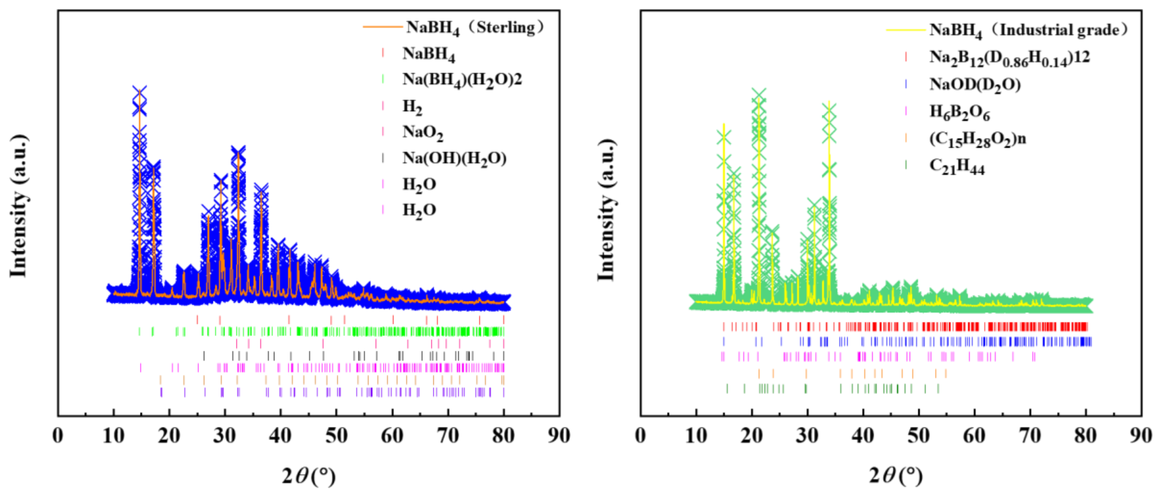

Figure 1. XRD curves of industrial-grade sodium borohydride and pure sodium borohydride

As shown in Figure 1, both materials primarily consist of sodium borohydride, sodium borohydride hydrate, and sodium hydroxide hydrate. Pure sodium borohydride is highly reactive at room temperature and readily reacts with moisture in the air, leading to premature reactions during sample preparation. In contrast, industrial-grade sodium borohydride is coated with carbon-hydrogen organic compounds, which enhance its chemical stability and reduce its cost. Therefore, industrial-grade sodium borohydride is more suitable as an energetic additive.

The composition and mass percentage of the emulsion matrix are as follows: Ammonium Nitrate (AN): Sodium Nitrate (SN): composite oil phase: urea: water = 73:10.7:5.3:2:9. Different mass fractions of $NaBH_4$ were then added to the emulsion matrix to prepare $NaBH_4$-containing emulsion explosives.

The formulations and Oxygen Balance (OB) of the samples are shown in Table 1.

Table 1. Sample formulations and oxygen balance

Samples	1#	2#	3#	4#	5#	6#
$NaBH_4$ Content/ %	0%	1%	3%	5%	7%	9%
OB/ (g·g-1)	0.0157	-0.0014	-0.0361	-0.0697	-0.1039	-0.1381

2.2. Brisance experiment

The brisance was tested using the lead column compression method as specified in GB12440-90. A 50 g explosive column was prepared in a paper tube, fixed on a lead column with a spacer, and detonated in an explosion container. Experiments were conducted at temperatures of 20 ℃, 25 ℃, and 30 ℃ to compare the changes in brisance under different environmental conditions. The diagram of the brisance experiment is shown in Figure 2.

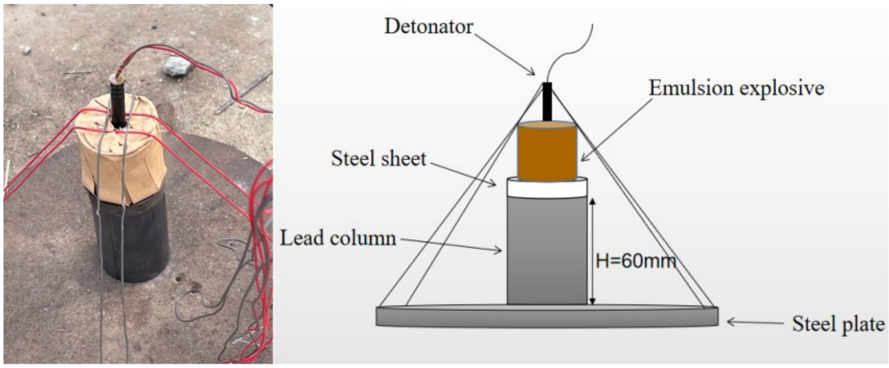

Figure 2. Schematic diagram of the brisance experiment

2.3. Thermal decomposition characteristics experiment

The thermal decomposition experiments were conducted using a TGA2 thermogravimetric analyzer manufactured by Mettler Toledo, Switzerland. Alumina crucibles were used during the experiments, with nitrogen (N_2) as the experimental atmosphere at a flow rate of 50 mL/min. Approximately 2.5 mg of each sample was placed into the alumina crucibles. Heating rates of 10 °C/min and 15 °C/min were applied, with the temperature range set between 30 °C and 400 °C. The mass changes of the samples before and after the experiments were recorded and compared to analyze the thermal decomposition characteristics.

3. Results and discussion

3.1. Effect of $NaBH_4$ content on the brisance of emulsion explosives

To further analyze the mechanism of the detonation performance of $NaBH_4$ emulsion explosives, this paper also calculates the theoretical heat of explosion of the emulsion explosive samples using MATLAB software, based on the detonation parameters of the Becker-Williams Method and the calculation method of Hess's Law. Theoretical calculation of heat of explosion and the actual heat of explosion comparison figure is shown in Figure 3 below.

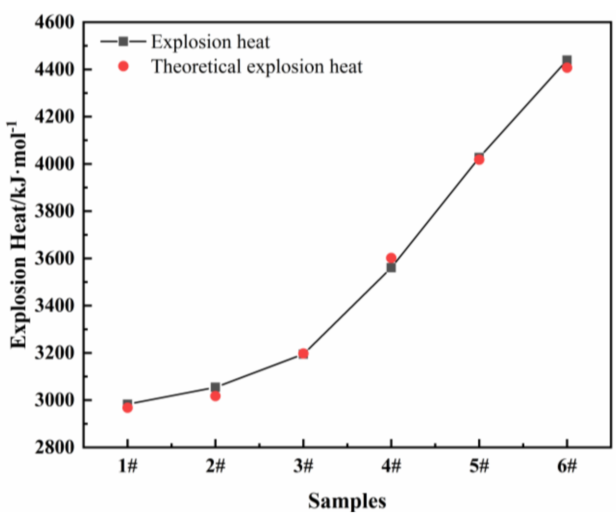

Figure 3. Comparison of actual heat of explosion and theoretically calculated heat of explosion

As can be seen from the comparison figure, the explosion heat value calculated according to the detonation equation is basically consistent with the actual explosion heat of the emulsion explosives samples, indicating that the actual detonation performance of $NaBH_4$-containing emulsion explosives is basically consistent with the predictive theoretical model. The results of the brisance experiment and the calculated heat of explosion for emulsion explosive samples with varying $NaBH_4$ contents are presented in Table 2.

Table 2. Detonation parameters of emulsion explosive samples

Samples	1#	2#	3#	4#	5#	6#
Density/g·cm-3	1.32	1.36	1.41	1.59	1.48	1.35
Heat/kJ·mol-1	2982.69	3054.83	3194.92	3560.75	4027.46	4439.57
aBrisance/mm	14.6	18.0	20.0	21.8	18.9	17.3
bBrisance/mm	14.9	18.6	20.3	22.4	19.8	17.2
cBrisance/mm	15.8	19.1	20.8	22.7	20.6	18.4

a. The brisance of the emulsion explosive sample at an experimental temperature of 20 ℃. b. The brisance of the emulsion explosive sample at an experimental temperature of 25 ℃. c. The brisance of the emulsion explosive sample at an experimental temperature of 30 ℃.

The experimental results indicate that the brisance of emulsion explosive samples containing $NaBH_4$ is higher than that of ordinary emulsion explosives. As the $NaBH_4$ content increases, the brisance and density of the explosives initially increase and then decrease. Under the three different temperatures, the trend of brisance change of the emulsion explosive samples is consistent. It can be seen that within the temperature range from 20 ℃ to 30 ℃, the brisance performance of the emulsion explosive samples is stable, without significant fluctuations.

The brisance of emulsion explosives containing 1%, 3%, 5%, 7%, and 9% $NaBH_4$ increased by 24.83%, 36.24%, 50.33%, 32.89%, and 15.44%, respectively, compared to Sample #1 (ordinary emulsion explosive) at 25 °C. The brisance reaches its maximum value of 22.4 mm in Sample 4# (with a $NaBH_4$ content of 5%), representing a 50.33% increase compared to Sample 1#. Additionally, the heat of explosion of the emulsion explosive samples increases progressively with the addition of $NaBH_4$.

The analysis reveals that the brisance of emulsion explosives is closely related to their density. When the $NaBH_4$ content ranges from 0% to 5%, the density of the explosive gradually increases. The relatively high hydrogen content in $NaBH_4$ leads to the release of more heat during the detonation reaction, which in turn raises the temperature within the explosion reaction zone. This elevated temperature enhances the work capability of the detonation products on the surrounding medium, thereby gradually increasing the brisance of the explosive. However, when the $NaBH_4$ content exceeds 5%, the density of the explosive begins to decrease. Although the heat of explosion continues to increase, an excessive amount of $NaBH_4$ drives the explosive towards a negative oxygen balance, disrupting the stoichiometric ratio between oxidizers and fuel within the system. This imbalance hinders the complete release of energy from the explosive, resulting in a decline in brisance.

3.2. Effect of $NaBH_4$ on the thermal decomposition characteristics of emulsion explosives

Emulsion explosives are hazardous materials with enormous energy stored in a metastable state. When subjected to external stimuli, thermal decomposition reactions occur within the explosive, releasing a large amount of heat in a very short time [7]. If the generated heat accumulates within the explosive and is not released promptly, it may lead to severe consequences such as detonation. While improving the explosive performance of emulsion explosives, changes in their thermal stability must not be overlooked.

To study the effect of $NaBH_4$ on the thermal decomposition characteristics of emulsion explosives, thermal decomposition experiments were conducted on the samples containing different mass fractions of $NaBH_4$. The TG curves of the samples are shown in Figure 4.

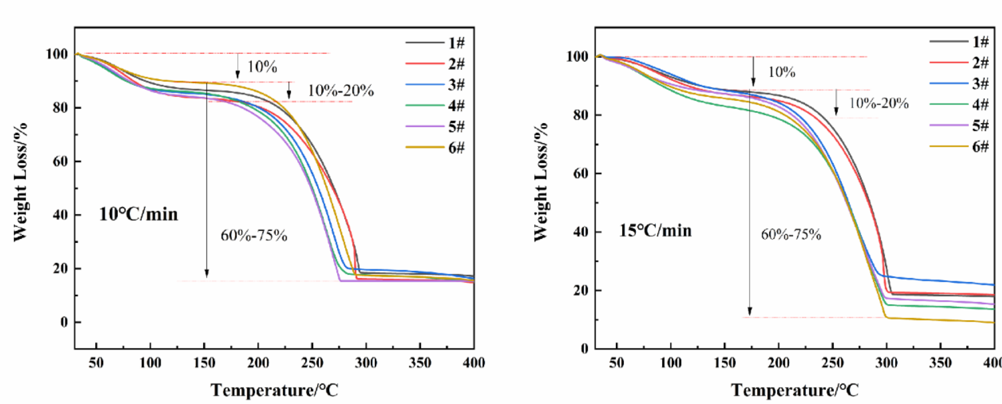

Figure 4. TG curves of emulsion explosives with different $NaBH_4$ contents

From Figure 4, the TG curves of the emulsion explosive samples with varying $NaBH_4$ contents exhibit a consistent trend. Based on theoretical analysis, the thermal decomposition characteristics of the emulsion explosives can be divided into three distinct stages. In the first stage, from 30 °C to 175 °C, the mass loss of the samples is approximately 15%, primarily attributed to the evaporation of water from the emulsion matrix and the decomposition of a small fraction of unstable emulsion components. In the second stage, from 175 °C to 300 °C, the mass loss is between 60% and 75%, mainly resulting from the vigorous decomposition reactions of ammonium nitrate, sodium nitrate, and the composite oil phase within the emulsion explosive system. In the third stage, from 300 °C to 400 °C, the TG curve remains stable with no further mass loss, indicating that the decomposition process has been completed. To further investigate the influence of $NaBH_4$ on the thermal stability of emulsion explosives, the thermal decomposition parameters of the samples were determined under two different temperature conditions based on the TG curves. The data are presented in Table 3.

Table 3. Thermal decomposition parameters of emulsion explosive samples

Heating Rate	Initial Decomposition Temperature /℃					
	1#	2#	3#	4#	5#	6#
10 ℃/min	153.16	157.46	161.76	164.43	167.50	173.66
15 ℃/min	151.30	153.16	158.90	165.14	169.86	176.53
Heating Rate	Maximum decomposition rate temperature /℃					
	1#	2#	3#	4#	5#	6#
10 ℃/min	274.96	276.42	276.97	284.17	275.96	262.01
15 ℃/min	262.25	286.82	281.62	288.82	286.82	276.97

According to Table 3, the initial decomposition temperatures of $NaBH_4$-containing emulsion explosives are all higher than those of ordinary emulsion explosives. Furthermore, at the same heating rate, the initial decomposition temperature increases progressively with the increasing $NaBH_4$ content. Emulsion explosives are water-in-oil multiphase systems where interfacial properties play a critical role. The BH_4-ion of $NaBH_4$ is strongly reducing, and the hydrogen atoms in its structure can participate in the chemical reaction, prompting the formation of hydrogen bonds in the system [8]. Hydrogen bonding helps stabilize the interfacial membrane between the water and oil phases. The hydrogen bonds derived from sodium borohydride act in the interfacial region, enhancing the strength and toughness of the interfacial membrane. Under thermal shock, a stable interfacial membrane prevents the separation of the oil and water phases, thereby avoiding the aggregation of active components and uncontrolled reactions caused by phase separation. This provides a safeguard for thermal stability.

As a result, during thermal decomposition experiments, the emulsion explosive system requires higher energy to disrupt the intermolecular forces, leading to an increase in the initial decomposition temperature. In conclusion, $NaBH_4$ enhances the thermal stability of emulsion explosives.

4. Conclusion

- Comparison of the theoretical computational model with the actual results concluded that the predicted detonation model is consistent with the actual. The brisance performance of the emulsion explosives samples is stable in the temperature range of 20-30℃. $NaBH_4$ significantly improves the brisance of emulsion explosives. The brisance of emulsion explosives containing 1%, 3%, 5%, 7%, and 9% $NaBH_4$ increased by 24.83%, 36.24%, 50.33%, 32.89%, and 15.44%, respectively, compared to Sample #1 (ordinary emulsion explosive) at 25 °C. At a $NaBH_4$ content of 5%, the brisance reached a maximum value of 22.4 mm.
- The TG curves of emulsion explosive samples exhibit consistent trends. The initial decomposition temperatures of $NaBH_4$ emulsion explosives are higher than ordinary emulsion explosives. $NaBH_4$ enhances the thermal stability of emulsion explosives to a certain extent.

Acknowledgments

The work is supported by the Foundation of Anhui Engineering Research Center of New Explosive Materials and Blasting Technology of Anhui University of Science and Technology (AHBP2023B-03).

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