Full Paper

Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.202000105

Influence of Different Gases on the Performance of Gas-Storage Glass Microballoons in Emulsion Explosives

Yixin Wang,[a] Honghao Ma,*[a, b] Zhaowu Shen,[a] Jiping Chen,[a] and Liangliang Huang[a]

Abstract: A new type of emulsion explosive sensitized by hydrogen-storage has been invented previously. To better understand the role of hydrogen in emulsion explosives, the detonation experiments with different gas storage were conducted. Several gases, such as helium, oxygen, and nitrogen, were taken into account. Brisance tests, detonation velocity tests, and underwater detonation experiments showed that the high-pressure hydrogen can improve the power and energy of emulsion explosive. The adiabatic compression of different gases was calculated. The pressure and temperature of the gas in GMs were obtained. Hydrogen has better compression performance than the other gases. Combining experiments and theoretical calculations can obtain that, hydrogen plays an important role in hot spots formation rate and emulsion explosive energy, and nitrogen and oxygen have little contribution to the energy of emulsion explosive, while helium is difficult to store in GMs and has a negative influence on the performance of emulsion explosive.

Keywords: Emulsion explosive · Gas storage · Glass microballoons · Underwater explosion · Adiabatic compression

1 Introduction

Emulsion explosives are the most commonly used industrial explosive [1]. They are composed of emulsion matrix and sensitizer. The main component of the emulsion matrix is ammonium nitrate that provides the detonation capability [2]. The sensitizer makes the emulsion matrix sensitive to a detonator. The common sensitizer is the glass microballoon (GM), which is a hollow spherical shell structure [3]. When the GMs are subjected to shock, the internal gas is adiabatically compressed and the temperature rises to form hot spots [4,5].

The energy of emulsion explosives is not high enough and this has become the limitation of its development [6]. We have invented an emulsion explosive sensitized by hydrogen-storage GMs, to enhance the power of emulsion explosive [7]. The experiments illustrated that introducing hydrogen into GMs can improve the detonation performance of emulsion explosives.

Gas storage in GMs was first proposed in the 1970s [8]. Researchers at Lawrence Livermore National Laboratory (LLNL) filled GMs with deuterium and tritium for the inertial confinement fusion program. The study proved that GMs could serve as containers for high-pressure gas. Most researchers focused on storing hydrogen in GMs rather than other gases because hydrogen has a wide range of applications [9]. Hydrogen-storage GMs were commonly used for nuclear fusion, new energy vehicles, or hydrogen transport [10,11].

In previous studies, we have confirmed that hydrogen-storage in GMs can improve the detonation performance of emulsion explosives [7]. There are two conjectures about the reasons for the energy increase of emulsion explosives. One is high-pressure property of hydrogen and the other is combustible property. High-pressure may make it easier for more GMs to form hot spots, while the combustion of hydrogen may contribute more to the increase in the energy output.

In this study, we carried out detonation experiments of other gas-storage for comparing with hydrogen in order to better understand the role of hydrogen in hydrogen-storage emulsion explosive. Nitrogen, oxygen, and helium are considered.

In addition, the theoretical calculation of compression of different gas in GMs is carried out. The pressure and temperature profiles of internal gas are calculated. Hydrogen has better compression performance than the other gases.

Finally, we can obtain that, hydrogen plays an important role in hot spots formation rate and emulsion explosive energy, and nitrogen and oxygen do not contribute to the energy of emulsion explosive, while helium is difficult to store in GMs and has a negative influence on the performance of emulsion explosive.

[a] *Y. Wang, H. Ma, Z. Shen, J. Chen, L. Huang*
CAS Key Laboratory of Mechanical Behavior and Design of Materials (LMBD)
Department of Modern Mechanics
University of Science and Technology of China
**e-mail: hhma@ustc.edu.cn*
[b] *H. Ma*
State Key Laboratory of Fire Science
University of Science and Technology of China
Hefei, Anhui 230026, P.R. China

2 Experimental Section

The experimental section includes the production of gas-storage GMs and detonation experiments. The detonation experiments include brisance tests, detonation velocity tests, and underwater explosion experiments. Here, we just briefly describe the experimental process, of which the details and data processing have been introduced in reference [7].

2.1 Explosives Preparation

The GMs were purchased from Bengbu Glass Industry Design & Research Institute (Bengbu, Anhui, China). The average particle size is 55 μm and the effective density is 0.25 g/cm^3. The compressive strength is about 10 MPa which is enough for hydrogen storage.

Considering that the GMs are sealed spherical shell structure and permeable only at high temperature, the reaction kettle which provides high temperature and pressure was selected. Its design temperature and pressure are 400 °C and 17 MPa. After the purification of GMs by density separation with alcohol, the broken GMs were removed. The complete GMs were put into the reaction kettle and filled the kettle with high-pressure gas. The gas-storage GMs would be obtained after storing for a while at high temperature.

According to Cheng (2013) [12], the emulsion explosives energy reaches a maximum when the mass ratio of GMs and emulsion matrix is 4:100. Three gases were chosen to compare with hydrogen and they were oxygen, nitrogen, and helium. In addition to conventional emulsion explosives and hydrogen-storage emulsion explosives, there were five types of emulsion explosives under consideration in total, which are listed in Table 1.

Table 1. Five kinds of emulsion explosives samples.

Sample	Type of stored gas	Density (g/cm^3)
EE–H2	hydrogen	1.128
EE-He	helium	1.127
EE–O2	oxygen	1.132
EE–N2	nitrogen	1.130
EE	no gas	1.120

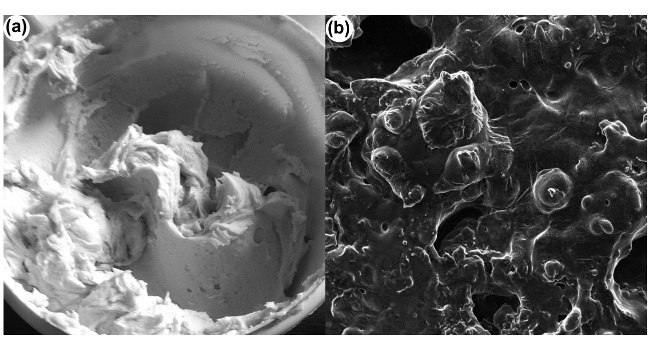

Figure 1. Emulsion explosives: (a) macroscopic image, (b) SEM image.

The emulsion matrix is composed of ammonium nitrate, whose mass ratio is 75%, and sodium nitrate, a small amount of water and wax. Figure 1 is the macroscopic and microscopic image of emulsion explosives. Due to the different gases are stored inside the GMs and there is no difference in appearance, there is no difference in the images of different samples, so we only list the image of sample EE.

According to Zygmunt [13], the detonation velocity of emulsion explosives is affected by the density. In our experiments, the density difference of different samples is very small, as shown in Table 1, tested in the detonation velocity testing. The reason is that the content of gas-storage GMs in emulsion explosives is very small. According to previous research [7], 10 grams of GMs can store 0.088 grams of hydrogen. That is to say, when the volume does not change obviously, the density of emulsion explosives change at most about 0.88%, which is consistent with the experimental measurement results. Therefore, the effect of density on the performance of emulsion explosives can be ignored in our researches.

2.2 Explosion Experiment System

The lead cylinder compression test is a commonly used method to evaluate the brisance of explosives. 50 grams of emulsion explosive was placed on a lead cylinder, separated by a thin steel cylinder. The amount of compression of the lead cylinder tested to express the brisance value.

Detonation velocities were measured by the electric probe off-on method. After the explosives detonated, the detonation wave knocked off the paint on the surface of the probe, making the probe conductive, and the timer recorded the time. Then the velocities of detonation wave can be calculated.

The underwater explosion can fully evaluate the detonation performance of explosives by measuring the shock wave in water. Underwater experiments were conducted in a steel water tank with 4.9 m in diameter (*D*) and 5.0 m in depth (*H*). 30 grams of explosive sample was fixed 3.0 m underwater and in the center of the steel water tank. The shock wave was captured by two PCB-W ICP138A25 type pressure sensors (PCB Piezotronics, Inc. USA.), which were placed 3.0 m underwater and 1.0 m and 1.2 m away from the charge. The signal was collected and stored by a Tektronix 4104 digital oscilloscope (Tektronix, Inc. USA.).

2.3 Detonation Data Processing

The pressure signal of the shock wave was obtained from the underwater explosion experiments and the schematic diagram is shown in Figure 2. The impulse (I), specific shock energy (E_s), specific bubble energy (E_b) and specific total energy (E_t) were calculated based on pressure signal by the following equation [14–16]:

$$I = \int_0^{6.7\theta} p(t)\mathrm{d}t \tag{1}$$

$$E_s = \frac{4\pi R^2}{W\rho_w C_w}\int_0^{6.7\theta} p^2(t)\mathrm{d}t \tag{2}$$

$$E_b = \frac{1}{8WC^3K_1^3}\left(\sqrt{1+4Ct_b}-1\right)^3 \tag{3}$$

$$E_t = K_s(\mu E_s + E_b) \tag{4}$$

The explanation of the variables in the above formulas: p(t) is the pressure of shock wave; θ is the attenuation time of shock wave, that is the time from the peak pressure (P_m) decays to the 1/e times of P_m; R is the distance from the charge to the sensor; W is the mass of the charge; ρ_w is the density of water; C_w is the velocity of a shock wave in water; C is a fitted constant, equals to $-0.332\ s^{-1}$ [17]. K_1 is determined by the equation:

$$K_1 = 0.135\rho_w^{1/2}\Big/P_h^{5/6} \tag{5}$$

where P_h is the total hydrostatic pressure at charge depth; K_s is the shape parameter of explosive, which equals to 1.00 in this study; μ is the attenuation coefficient of a shock wave and associated with the detonation velocity by the following equation:

$$\mu = 1 + 1.3328\times10^{-1}p_{CJ} - 6.5775\times10^{-3}p_{CJ}^2 + 1.2594\times10^{-4}p_{CJ}^3 \tag{6}$$

where p_{CJ} (Pa) is the CJ pressure, γ is the heat capacity ratio, ρ is the density of charge and D_v is the detonation velocity.

All the data are listed in Table 2 after the above calculations. Since multiple gas-storage experiments were not conducted at the same time, a control group experiment was carried out at each experiment, which is sample EE.

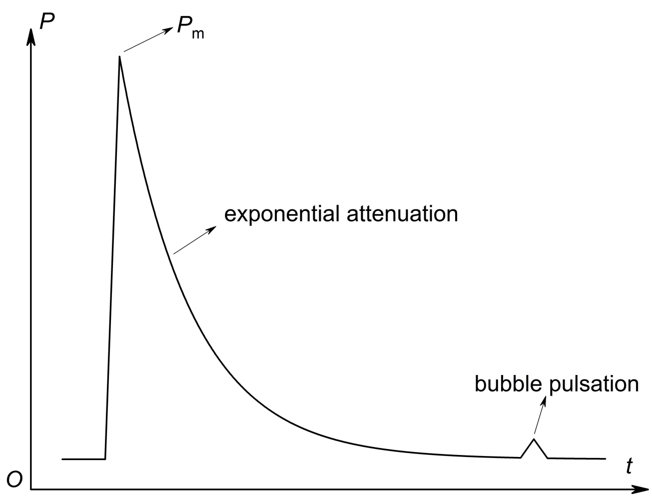

Figure 2. The schematic diagram of the underwater explosion pressure profile.

2.4 Discussion

Figure 3 provides the relative change rate of parameters of the emulsion explosives after gas storage, expressed as a percentage. What is striking in this figure is the rapid decrease in the brisance and detonation velocity of sample EE–He, which is different from the other three samples. The most likely reason for this phenomenon is that helium is a single atom molecule. This feature will cause the helium to have good permeability in the GM shell and the permeability is little affected by temperature. This is different from diatomic molecules, such as hydrogen, oxygen, and nitrogen.

According to Tsugawa (1976) [8], the permeability of helium is much greater than that of hydrogen under the same conditions. At room temperature, high-pressure hydrogen can be stored in GMs for days to weeks, while high-pressure helium can only be stored for an hour or two. Therefore,

Table 2. Experimental data of different samples.

Sample	h_b/cm	D_V/(m/s)	P_m/MPa	I/(Pa·s)	E_s/(MJ/kg)	E_b/(MJ/kg)	E_t/(MJ/kg)
EE	19.8	4784	10.054	482.75	0.497	1.844	2.647
EE–H2	23.0	5036	10.013	526.79	0.531	1.867	2.741
EE	19.8	4784	10.514	807.11	0.572	1.877	2.802
EE-He	11.8	4332	10.702	778.05	0.561	1.993	2.834
EE	19.3	5013	10.759	503.59	0.600	1.882	2.874
EE–O2	21.5	4923	11.233	491.39	0.601	1.911	2.903
EE–N2	21.4	5005	10.889	501.58	0.561	1.954	2.893

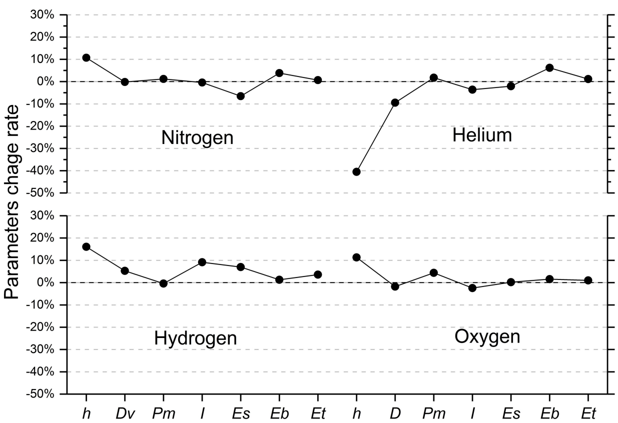

Figure 3. The parameters change in four kinds of samples.

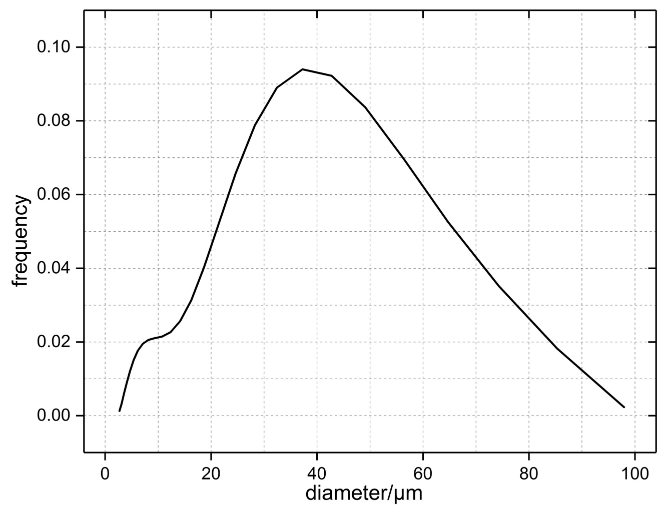

Figure 4. The size distribution of GMs.

the helium-storage GMs will quickly release helium in the explosive before its initiation, expanding the explosive and reducing the density, which can be seen in the experiment. The density reduction of explosives will significantly reduce the detonation velocity and power of explosives. Therefore the parameters *h* and D_v of sample EE–He will decrease.

For hydrogen, oxygen, and nitrogen, their permeability is almost the same and the amount stored in the GMs is the same. What can be seen in Figure 3 is that the brisance (*h*) of sample EE–H2 has a larger increase more than that of samples EE–N2 and EE–O2. This shows that the gas stored in the GMs contributes to the brisance of the emulsion explosive. The extra part of the brisance of sample EE–H2 is because hydrogen can participate in the reaction and release energy, which can be verified by the improvement of the impulse (*I*), specific shock energy (E_s), and specific total energy (E_t) of sample EE–H2.

In a word, it can be seen from the experiment. On one hand, the high-pressure gas in the GMs can increase the brisance of the emulsion explosive, while it has little contribution to the energy. On the other hand, the combustion of hydrogen can additionally increase the energy of emulsion explosives.

3 Theoretical Calculation

3.1 Equations Preparation

In order to understand the role of high-pressure gas on hot-spot generation, the impaction of different gas by the shock is calculated theoretically. Because the GM is very small, the time for the detonation wave to pass through the GM is sufficiently short and ignorable. Therefore, we can consider the compression process of the bubble as spherically symmetric.

The size distribution of GMs is 10–100 μm, as shown in Figure 4, and the average size is 50 μm. The thickness of the GM shell is only 1–2 μm, which is so thin that the fracture of the shell can be ignored. The schematic diagram of bubble compression is shown in Figure 5.

We only study the changes in pressure, temperature, the radius of bubbles under external impaction, regardless of the chemical reaction of explosives and hydrogen.

The conservation equations of the internal gas are:

$$\frac{\partial \rho_g}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(\rho_g r^2 u_g\right) = 0 \tag{8}$$

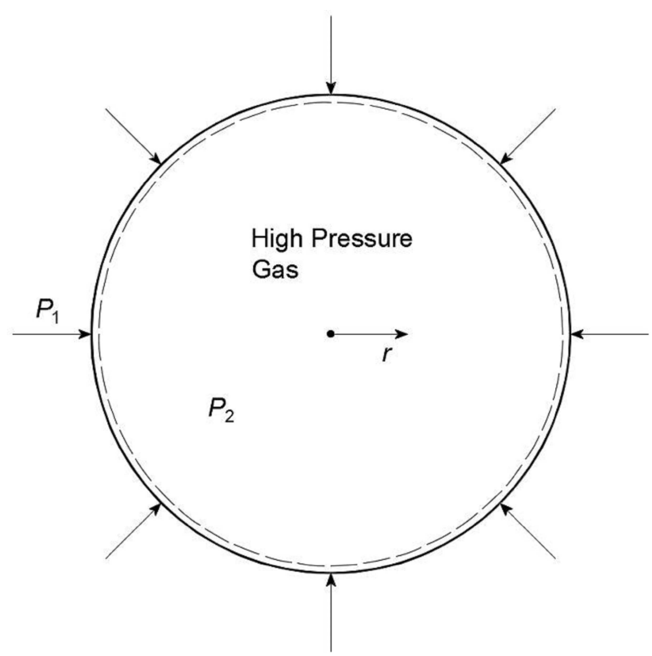

Figure 5. The adiabatic compression model of the bubble.

$$-\int_0^{R_g} 4\pi\rho_g r^2 u_g \mathrm{d}r = \int_0^t 4\pi R_g^2 (P_1 - P_2)\mathrm{d}t \tag{9}$$

$$\frac{4}{3}\pi\rho_g R_g^3 \frac{e_g - e_g0}{M_g} + \frac{1}{2}\int_0^{R_g} 4\pi\rho_g r^2 u_g^2 \mathrm{d}r = -\int_{R_g0}^{R_g} 4\pi r^2 (P_1 - P_2)\mathrm{d}r \tag{10}$$

In the above equations, ρ_g, u_g, R_g, P_2, M_g and e_g represent density (g/cm^3), velocity (m/s), radius (m), pressure (Pa), molar mass (g/mol) and molar internal energy (J/mol) of internal gas, respectively. The pressure outside the bubble (P_1) is the detonation pressure of the detonator, which is approximately equal to 12 GPa. The pressure inside the bubble (P_2) is the pressure of high-pressure gas, of which the initial value is 5.0 MPa.

The BKW state equation is selected to describe the state of gas [18,19]:

$$\begin{cases} \frac{P_2 V_g}{RT_g} = f_B(w) = 1 + we^{\beta w} \\ w = \frac{\kappa k}{V_g}\left(T_g + \theta\right)^{-\alpha} \end{cases} \tag{11}$$

R, V_g, and T_g are the gas constant, molar volume (cm^3/mol), and temperature (K) of internal gas. α, β, θ, and κ are the adjustable parameters, which are 0.5, 0.16, 10.91, and 400, respectively. k is the covolume of gas (80 for hydrogen, 380 for nitrogen, and 350 for oxygen). There is another equation about internal energy and temperature, according to thermochemical theory [20,21]:

$$\begin{cases} e_g = \left(H^0 - H_r^0\right) - RT_g + RT_g\left[\alpha T_g \tfrac{f_B(w)-1}{T_g+\theta}\right] \\ \left(H^0 - H_r^0\right) = At + \tfrac{1}{2}Bt^2 + \tfrac{1}{3}Ct^3 + \tfrac{1}{4}Dt^4 - \tfrac{E}{t} + F \end{cases} \tag{12}$$

In this equation,$(H_0 - H_r^0)$ is the standard enthalpy (kJ/mol) under 0.1 MPa and $t = T/1000$. The coefficients A, B, C, D, E, and F were obtained from JANAF tables and tabulated in Table 3 [21].

There are five variables u_g, R_g, P_2, e_g, and T_g, and five equations (8), (9), (10), (11), and (12). Therefore, this system can be solved by numerical calculation. The fourth-order Runge-Kutta method is a very good choice.

Emulsion explosives start to react at a few hundred degrees Celsius, so we set 1000 K as the endpoint of the calculation and a temperature greater than 1000 K has no meaning.

3.2 Calculation Results

The calculation results are shown in Figures 6 and 7, which show the temperature and pressure in the GM with time, respectively.

Table 3. The coefficients in equation(12).

T/K	H_2			N_2			O_2		
	298–1000	1000–2500	2500–6000	100–500	500–2000	2000–6000	100–700	700–2000	2000–6000
A	33.066	18.563	43.414	28.986	19.506	35.519	31.322	30.032	20.911
B	−11.363	12.257	−4.293	1.854	19.887	1.129	−20.235	8.773	10.721
C	11.433	−2.860	1.272	−9.647	−8.599	−0.196	57.866	−3.988	−2.020
D	−2.773	0.268	−0.097	16.635	1.370	0.015	−36.506	0.788	0.146
E	−0.159	1.978	−20.534	0.0001	0.528	−4.554	−0.007	−0.742	9.246
F	−9.981	−1.147	−38.515	−8.672	−4.935	−18.971	−8.903	−11.325	5.338

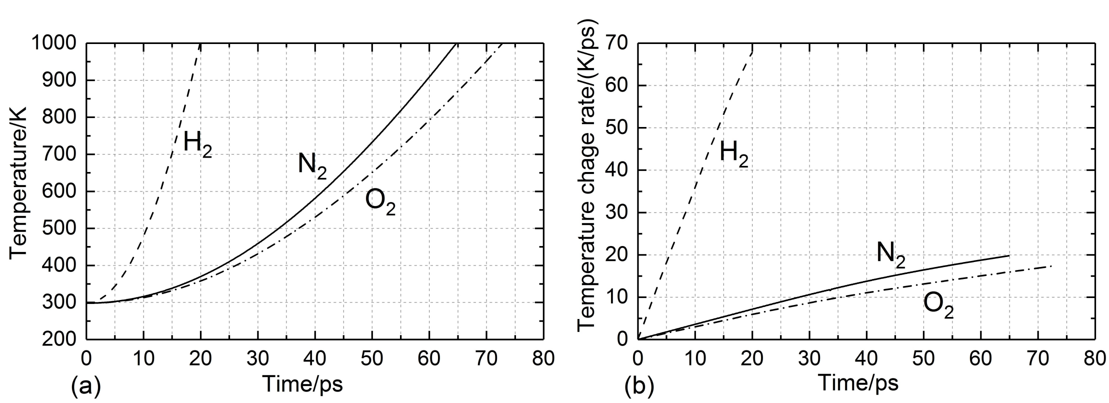

Figure 6. Temperature profiles. (a) is temperature profiles, (b) is temperature change rate profiles.

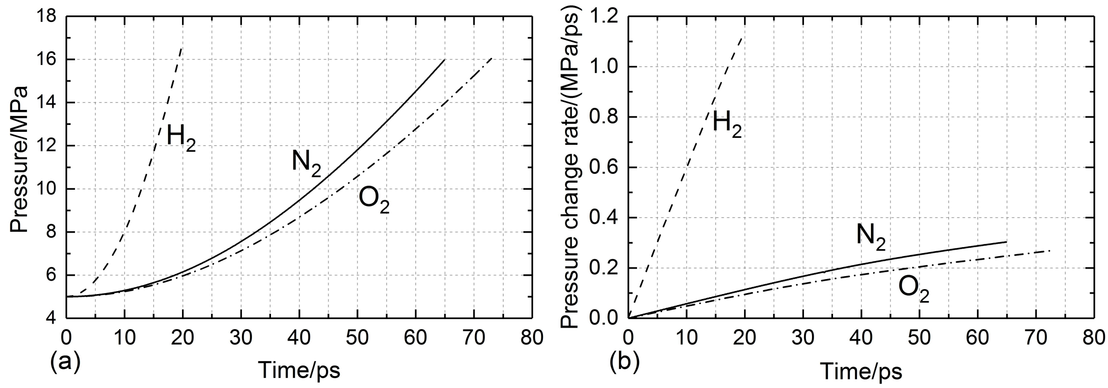

Figure 7. Pressure profiles. (a) is pressure profiles, (b) is pressure change rate profiles.

As can be seen from Figures 6 and 7, the temperature and pressure of hydrogen rise significantly faster than those of nitrogen and oxygen under the same conditions. Although the time difference is only picoseconds, thousands of such GMs in the emulsion explosive are impacted at the same time and the cumulative effect is obvious. And, the calculation is only a simple estimate, just to illustrate the difference between hydrogen nitrogen and oxygen.

Therefore, from the calculations, we can obtain that hydrogen is more suitable for gas-storage in GMs than other gases. When the hydrogen bubble is impacted, the temperature and pressure rise faster and it is easier to form hot spots than other gases. This will also make the explosives react more fully and have more power.

The calculation results are consistent with the experimental results. The power and energy increase for emulsion explosives sensitized by hydrogen-storage GMs is obvious, while nitrogen and oxygen make little contribution to the power of emulsion explosives and helium will reduce the power.

4 Conclusions

In this investigation, the aim was to assess the differences between four kinds of gases in the detonation of emulsion explosives. The experiments and theoretical calculations confirmed that:

1. Helium is difficult to store in GMs, which has a negative influence on the performance of emulsion explosives. Nitrogen, oxygen, and hydrogen can be stored in GMs, which contributes to the improvement of the power of emulsion explosives. Hydrogen can also participate in the combustion, which also contributes to the energy enhancement of emulsion explosives.
2. Hydrogen is more suitable for gas-storage in GMs than other gases. Under the same impact pressure, the temperature and pressure of hydrogen-storage GMs rise faster and it is easier to form hot spots than other gases.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (Grant No. 51874267 and No. 51674229). The authors would like to thank these foundations for financial support.

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Manuscript received: April 25, 2020
Revised manuscript received: May 29, 2020
Version of record online: July 31, 2020

