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Numerical Simulation of Propellant Diffusion Considering Chemical Reaction

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Abstract. Gas phase diffusion process of UDMH and NTO in confined space was investigated and the mechanism of the reaction between the propellants was analyzed in order to study the diffusion process considering chemical reaction between propellants based on numerical simulation. According to the results of numerical simulation, the propellant concentration distribution, resultant of reaction distribution, as well as temperature distribution was obtained. Results showed that the leakage diffusion process can be divided into three stages: heavy gas deposition stage, rapid reaction stage and equilibrium diffusion stage. In the heavy gas deposition stage, propellants are mainly affected by gravity. During the rapid reaction stage, the chemical reaction between propellants plays a certain role in the diffusion process. In the equilibrium diffusion stage, the bottom temperature of the confined space increased significantly, the highest temperature reached 306K.

1. Introduction

The liquid propellants used in large rockets in the aerospace field in China are mainly hydrazine fuels (UDMH) and nitrooxidants (N₂O₄). These substances are highly toxic, corrosive, hygroscopic, flammable, explosive and volatile[1]. In the process of propellant transfer and regular maintenance, staff members' lax thinking, work fatigue, operation failure or irregular operation often lead to leakage accidents. The probability of accidents caused by human error is more than 50% [2]. Due to a series of protective measures adopted in the storage process of propellant, the possibility of large-scale leakage is relatively small, and the main leakage problems are leakage or drip [3,4]. In the process of leakage or dripping, unsymmetrical dimethylhydrazine diffuses mainly in the form of vapor, while nitrous oxide decomposes spontaneously into nitrogen dioxide vapor diffusion.

When unsymmetrical dimethylhydrazine and nitrogen tetroxide exist in space, chemical reactions between propellants may lead to explosion in addition to the toxic hazard of propellant itself [5,6,7]. Therefore, the concentration distribution law of propellant leaking at the same time is studied to provide valuable reference for the formulation of emergency treatment measures.

2. Another Section of Your Paper

Ernesto C[8] gives the reaction process of unsymmetrical dimethylhydrazine and nitrogen dioxide under the conditions of no light, room temperature (15 C), gas phase, and gives the reaction path according to the test products. As shown in Figure 1, the reaction equation is given in combination with the consumption rate of reactants and the rate of biosynthesis.



The experiment was carried out under the conditions of no light and room temperature (15 C). It is the environmental condition for most propellants to be stored. Therefore, the reaction mechanism can represent the gas phase reaction process of UDMH and N₂O₄ propellants under leakage.

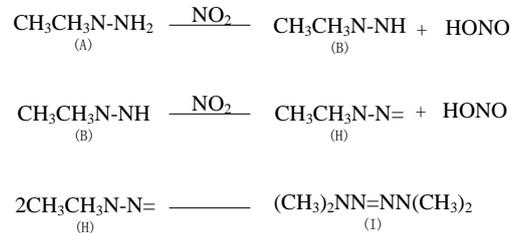


Figure 1. Reaction mechanism under room temperature and without illumination

3. Numerical Simulation

There are three sets of leaking conditions, one is simultaneous leaking of propellant, the other is 60 s leaking of UDMH and the other is 60 s leaking of nitrous oxide.

The toxicity of N₂O₄ and NO₂ mixed vapors released after N₂O₄ leakage is considered as the same component[13,14], and N₂O₄ is mainly hydrazine oxide[15] in the form of nitrogen dioxide. Therefore, N₂O₄ vapor is calculated as a single NO₂ in this paper.

In emergencies, when personnel are exposed to propellant vapor, the maximum allowable concentration of unsymmetrical dimethylhydrazine in the air at different times and in the working area[14] is shown in Table 1.

Table 1. The limit of propellant emergency exposure

Exposure limit concentration	UDMH mg/m ³ (ppm)	NTO mg/m ³ (ppm)
Maximum permissible concentration in working area	1.34(0.5)	5(2.43)
10 min emergency exposure limit concentration	268(100)	62(30)
30 min emergency exposure limit concentration	134(50)	41(20)
60 min emergency exposure limit concentration	80(30)	21(10)

Taking unsymmetrical dimethylhydrazine(UDMH) as an example, the lowest concentration limit is 5.00×10^{-7} (1.34 mg/m³), which is the maximum allowable concentration in the working environment. The propellant vapor will have a toxic effect on the long-term resident, while the upper concentration limit is 1.00×10^{-4} (268 mg/m³) for emergency exposure for 10 minutes, and the air. If the vapor concentration of medium propellant reaches or exceeds this value, it will cause serious toxic damage to unprotected personnel in a short time.

3.1. Simultaneous Leakage of Propellant

According to the propellant concentration distribution, chemical reaction between propellants and temperature distribution, the whole leakage process can be divided into heavy gas deposition stage, rapid reaction stage and equilibrium diffusion stage.

The concentration distribution in the rapid reaction stage is shown in Fig. 2. High concentration of unsymmetrical dimethyl hydrazine began to diffuse upward after covering the bottom of the enclosed space during the gas deposition stage. Nitrogen dioxide met unsymmetrical dimethyl hydrazine in the process of downward deposition under the influence of gravity. Subsequently, the transverse section of nitrogen dioxide sinking gas becomes smaller and smaller, and the upward diffusion of high concentration UDMH gas is blocked by nitrogen dioxide and diffuses to both sides. During this period, the interface between high concentration UDMH and nitrogen dioxide became larger and larger, and the whole interface presented V-shaped. Different from the heavy gas deposition stage, the reaction

rate of the two high-concentration propellants is higher than that of the low-concentration reactions in the heavy gas deposition stage.

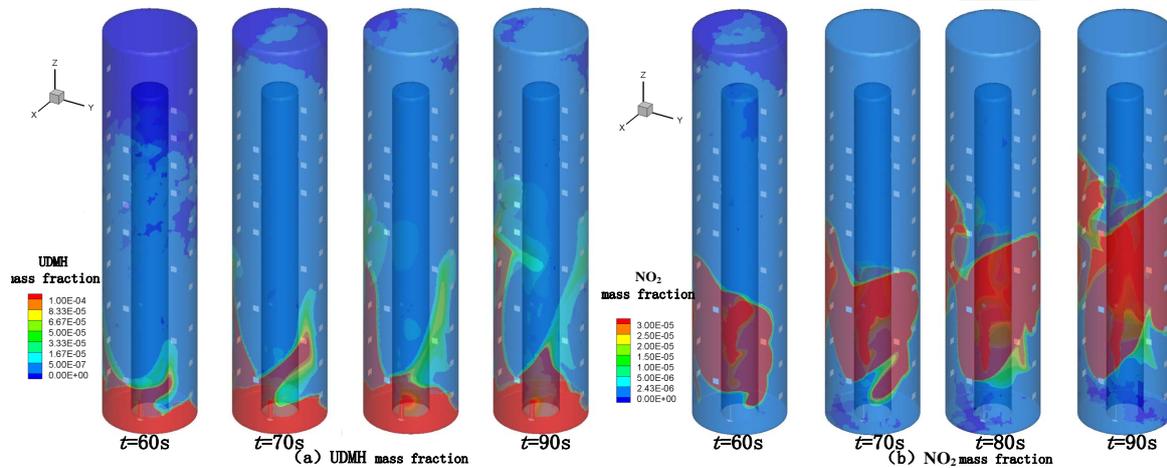


Figure 2. The schematic diagram of propellant distribution at the rapid reaction stage

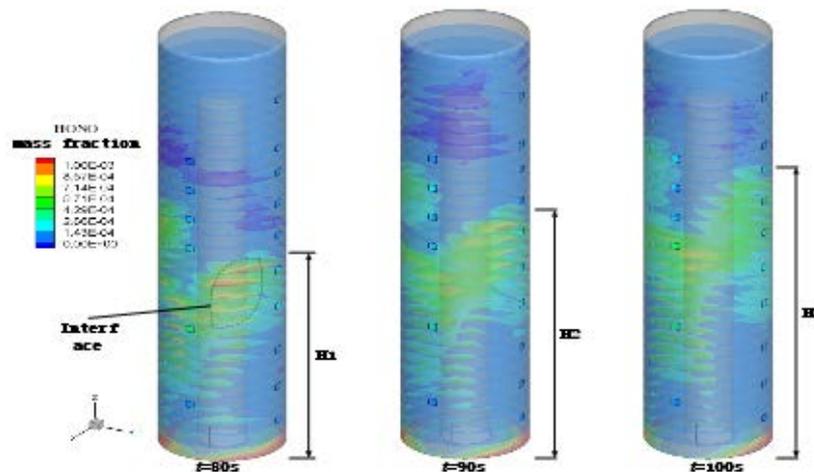


Figure 3. HONO multi slice concentration distribution at $t=80s$

The concentration distribution of reactants in multiple sections is shown in Fig. 3. Compared with the heavy gas deposition stage, the high concentration products occur not only at the bottom of the launching well, but also in the middle of the launching well. Comparing with Figure 6, it can be seen that the region where the high concentration products occur coincides with the position of the interface between the two propellants. The high concentration products in the space of launch wells basically present V-shaped. Considering the concentration distribution at different time, the high concentration area of high concentration products is climbing continuously. It can be seen from Figure 7 that: $H1 < H2 < H3$. In the process of diffusion, the high concentration area disappears slowly. There are two main reasons. One is that the high concentration product itself diffuses and dilutes slowly. The other is that the high concentration product area diffuses to the Y axis direction of the enclosed space and is diluted by the air inlet.

The propellant vapor in the equilibrium diffusion stage has occupied different heights of the enclosed space, and its distribution is shown in Fig. 4. At this time, unsymmetrical dimethylhydrazine is mainly at the bottom of the enclosed space. The unsymmetrical dimethylhydrazine slightly extends upward at the leakage, while nitrogen dioxide occupies the rest of the enclosed space. The two propellants are in dynamic equilibrium, and the interface between the propellants is very stable. At this

time, it can also be considered that UDMH is equivalent to the heavy gas in the space and deposits at the bottom of the enclosed space, while nitrogen dioxide is relatively lightly distributed in the upper half of the enclosed space. The interface height between propellants is about 4.8m. At this time, the whole enclosed space is filled with propellant vapor, and the concentration of propellant is greater than the emergency exposure limit concentration of 10 minutes, which belongs to high-risk areas. People without third-class protective clothing should evacuate as soon as possible.

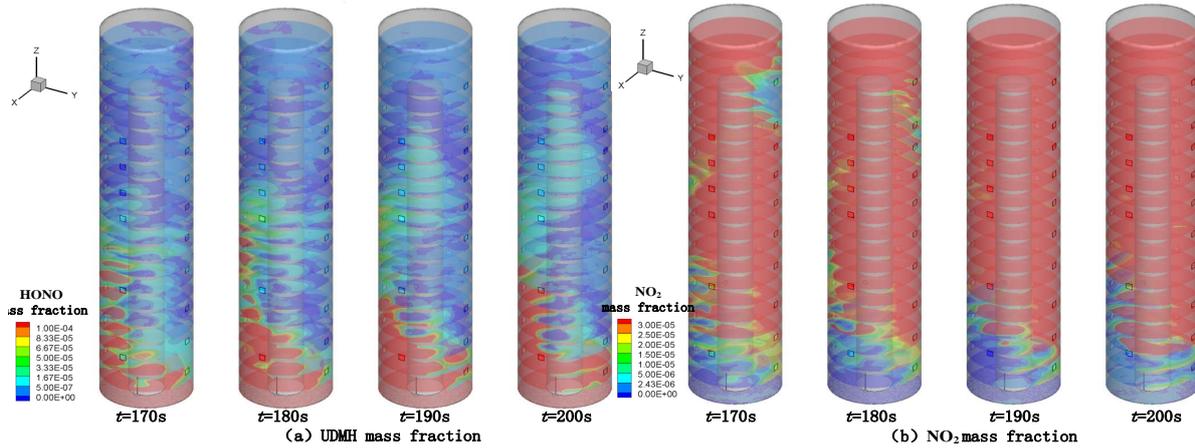


Figure 4. Distribution of propellant concentration over time in stable diffusion stage

3.2. Effect of Leakage Relative Time on Diffusion

Considering that there is a certain interval between the leakage time of two propellants in the leakage accident, the spatial distribution of propellants will affect each other, so the influence of leakage time difference on diffusion is analyzed.

Unsymmetrical dimethylhydrazine (UDMH) diffusion is mainly deposited at the bottom of the launch well without disturbance of nitrogen dioxide. At this time, the poisoning area is smaller. The height of the emergency exposure limit concentration is about 2m at 10min at 60s, and the X and Y axes are evenly distributed. When the diffusion of UDMH is not affected by nitrogen dioxide, the vapor mainly deposits at the bottom of the launch well.

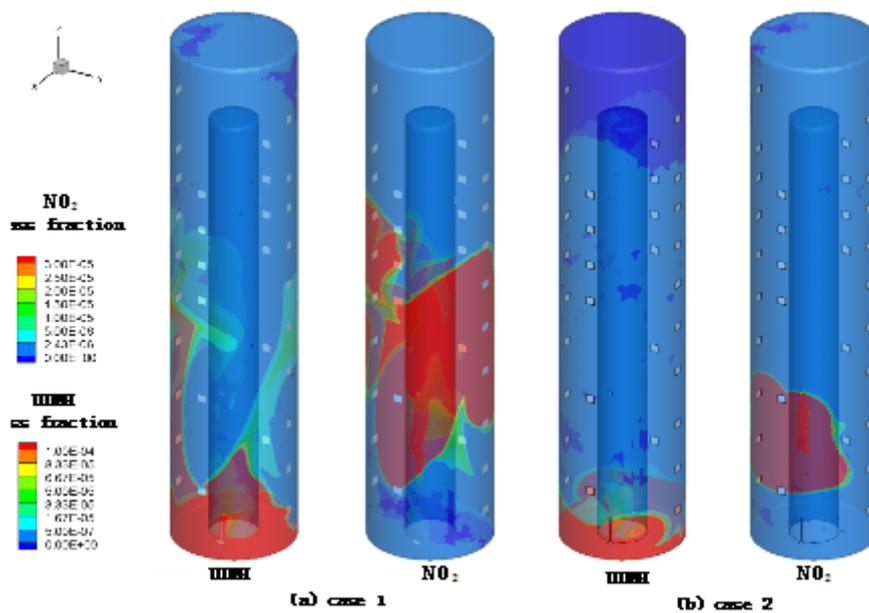


Figure 5. Temperature Curve with Height on Monitoring Line

The nephogram of propellant distribution at 90s working conditions 1 and 2 is shown in Fig. 5. When there is time difference between propellant leaks, the distribution of unsymmetrical dimethylhydrazine which leaks first is more stable and concentrated than that in case 1. In case 2, the reaction interface between propellants is smaller and the reactants are more concentrated than the V-shaped interface in case 1. When unsymmetrical dimethylhydrazine leaks first, it will occupy the bottom of launching well preferentially because of the influence of heavy gas. When nitrogen dioxide diffuses, the interface with unsymmetrical dimethylhydrazine is approximately flat. With the passage of time, the diffusion of nitrogen dioxide to the bottom of the launch well will be consumed by chemical reaction, so the concentration of nitrogen dioxide is only significant in the upper half of the launch well. Compared with condition 1, unsymmetrical dimethylhydrazine leakage accelerates the stratification of propellant in launch well space. During the diffusion process, the interface between UDMH and N₂O did not bend at a large angle, but steadily entered the equilibrium diffusion stage similar to that in case 1.

When nitrogen dioxide leaks, it is affected by gravity. The diffusion direction of high concentration of nitrogen dioxide is towards the bottom of the launching well as the upward diffusion of nitric oxide which is lighter than unsymmetrical dimethylhydrazine. After the propellant contacts with each other, the V-shaped interface is formed after the propellant contacts with each other, and the angle is about 23 degrees, as shown in Fig. 6.

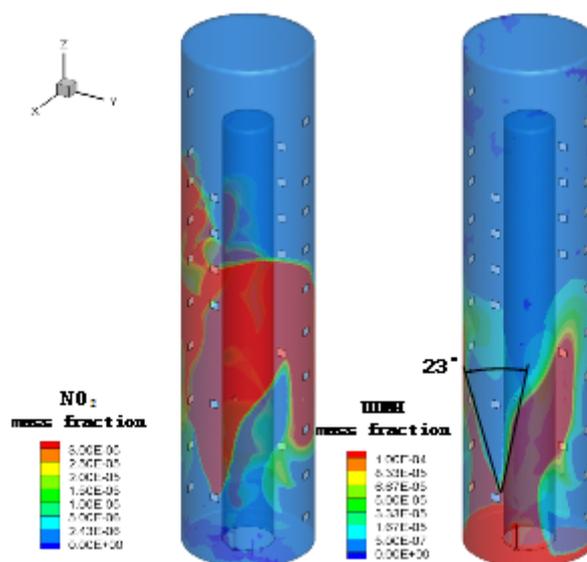


Figure 6. Propellant concentration distribution under condition 3

4. Conclusion

In this paper, the problem of propellant leakage and diffusion in enclosed space is studied based on numerical simulation method. The effects of different factors on diffusion are compared and analyzed, and the following conclusions are obtained.

1) According to the diffusion and reaction of propellant in different time periods, the process of propellant leakage and diffusion can be divided into three main stages: heavy gas deposition stage, rapid reaction stage and equilibrium diffusion stage. In the gas deposition stage, the diffusion of propellant is mainly dominated by gravity. Under the influence of gravity, the high concentration propellant deposits below the enclosed space after leaking, and a part of the low concentration propellant diffuses rapidly to the upper half of the enclosed space under the action of upward flow field. When the downward deposition of high concentration nitrogen dioxide gas and upward diffusion of high concentration unsymmetrical dimethyl hydrazine gas meet, the leak diffusion process enters a rapid reaction stage. In this stage, the reaction changed from low concentration to high concentration. After the two propellants met, the contact area increased continuously, showing V-shaped. After the

rapid reaction stage, the distribution between the two propellants remained basically stable, unsymmetrical dimethyl hydrazine was distributed in the area below 4.8m in the enclosed space, and the rest of the space was occupied by nitrogen dioxide gas. At this stage, the high concentration propellant occupies all the space in the enclosed area, and the toxicity hazard reaches its peak.

2) When there is a certain time difference in propellant leakage, the process of propellant diffusion will be different. When unsymmetrical dimethyl hydrazine leaks first, there will be no sharp V-shaped interface between high concentration propellants. Instead, it will be replaced by a smooth surface, which will advance to the equilibrium diffusion stage relative to the simultaneous leakage of propellant. When nitrogen tetroxide leaks ahead of time, a sharper interface will be formed between high concentration propellants. Higher concentration of UDMH will diffuse higher in the enclosed space. In either case, the flow field in the enclosed space will eventually stabilize at the equilibrium diffusion stage of the relative equilibrium of propellant distribution.

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