Analysis of ‘7.23’ hydrogen cylinder explosion accidents of three quartz products companies

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Abstract. On July 23, 2004, three quartz manufacturing companies’ hydrogen cylinders exploded during operation in the same county of China. Six people were killed and several buildings collapsed. In this paper, the cause of hydrogen cylinder explosions is analyzed by introducing the production and operation process of hydrogen. The energy and the overpressure generated by the explosion are estimated through quantitative analysis. In order to safely release hydrogen, corresponding methods are designed. The lessons learned from chemical process safety are also presented to prevent similar accidents from occurring, which is helpful to prevent personal injury and loss of property.

1. Introduction
On July 23, 2004, three quartz manufacturing companies’ hydrogen cylinders exploded during operation in the same county of China. Six people were killed and several buildings collapsed. It is understood that the hydrogen cylinders used by the three companies were filled by the same company. After the accident, the local safety supervision department immediately stopped the hydrogen production enterprises and all the gas consumers.

According to investigation, three accident companies were producing quartz rods at the time of the accident. In order to reach the melting point of quartz, tungsten crucibles are used for melting. However, Tungsten is easily oxidized at high temperatures, which will make it unusable. Therefore, nitrogen is selected as the protective gas for tungsten. At the same time, a small amount of hydrogen is required as the reducing gas to protect the tungsten crucible.

2. Investigative Process
The qualitative process of the accident is necessary for the accident analysis. It is very important to determine whether the cylinder is a physical explosion or a chemical explosion.

2.1. Detection of cylinder fragments
Fragments of a hydrogen cylinder at the explosion site were detected.
Table 1. Chemical composition test results of exploded hydrogen cylinders

| Chemical composition | Fragments measurement (average)/% | Standard value/% |
|----------------------|----------------------------------|-----------------|
| Carbon               | 0.29                             | 0.40            |
| Sulfur               | 0.006                            | 0.04            |
| Phosphorus           | 0.009                            | 0.04            |
| Phosphorus and Sulfur| 0.015                            | 0.07            |
| Manganese            | 1.46                             | 1.4~1.75        |
| Silicon              | 0.22                             | ≤0.37           |
| Chromium             | 0.03                             | 0.8~1.1         |
| Nickel               | 0.03                             | ----            |
| Vanadium             | 0.07                             | ----            |

Table 2. Mechanical character of hydrogen cylinders

| Mechanical behavior | Sample measured value (average) | Standard value |
|---------------------|---------------------------------|----------------|
| Tensile strength /MPa | 797.6                           | ----           |
| Yield point /MPa     | 619.2                           | ----           |
| Elongation/%         | 19.5                            | 14~16          |

Table 3. The thickness of the fragments

| Cylinder number | Measured Fragments thickness (average)/mm | Design thickness / mm |
|----------------|------------------------------------------|-----------------------|
| 577234         | 6.5                                      | 5.7                   |
| 163275         | 8.4                                      | 5.7                   |
| 193156         | 7.0                                      | 5.8                   |
| 122041         | 6.8                                      | 5.8                   |

2.2. Explosive property.

According to the investigation at the explosion site, the following facts were discovered:

- The gas cylinders exploded in the three accidents were filled by the same company, and the gas cylinders in the three explosion accidents almost at the same time.
- Cylinders show large deformation, and both the fragments are at an angle of 45° to the direction of the principal stress, and some are perpendicular to the end face. The section of the cross section is irregular.
- Several gas cylinders exploded at the same time as the valve was opened.
- The power of the explosion was huge. There was a rapid pressure increase in the gas cylinder before the explosion. There were many fragments of steel cylinders at the scene of the accident. The building a few meters away was seriously damaged, causing casualties.
- The cylinder has a certificate of conformity, and the steel stamp on the cylinder is complete. There is no corrosion on the surface, and the cylinder itself is measured without explosion defects. The minimum burst pressure of the hydrogen cylinder is 39.65MPa via calculations. According to the fragments generated by the explosion of the gas cylinder on the site and the damage to the surrounding gas cylinders and buildings, the instantaneous pressure of the explosion should be several times higher than 39.65MPa.
- Cylinders were randomly sampled from each accident unit and analyzed for gas composition. It was found that a large amount of air was mixed into many cylinders, and the air accounted for 50% of the total volume.

Based on the above statement, it is inferred that a chemical explosion occurred in this accident.
2.3. Gas mixing

A few days before the accident, the company's hydrogen production process was relatively normal. The produced hydrogen was tested without any problems. Part of the produced hydrogen was sent to other process parts of the company, so the hydrogen production process can be ruled out. Possibility of mixing in air. Next, the company's compression link was investigated. According to the test results and analysis, it can be basically determined that the gas mixture occurred in the compression processing.

![Process flow chart of compression](image)

Figure 1. Process flow chart of compression

1- gas cabinet; 2- sink; 3, 4- Water ring pump; 5, 6-valve; 7, 8- Buffer tank (with explosion-proof membrane in the tank); 9, 10- Hydrogen compressor; 11- Cylinder filling row

According to investigations after the incident, it was found that the power supply department had limited power to the company the night before the accident. In order to ensure process power consumption, the watchkeeper ordered to close valves 5 and 6 after confirming that the compressor had stopped working. However, when the hydrogen compressor is started, valve 5 is still closed and valve 6 is already open. This makes the vacuum in front of the No. 9 hydrogen compressor continuously increase with the extension of the driving time. In addition to the rain the night before, the explosion-proof membrane in the No. 7 buffer tank has been dampened, and its reliability cannot be guaranteed. After the difference reached a certain level, the explosion-proof film cracked, a large amount of oxygen was inhaled, and was filled into a hydrogen cylinder, mixed with hydrogen to form explosive gas.

2.4. Gas mixing

According to the accident investigation report, static electricity can be identified as the direct ignition source of this explosion accident. When the operator opened the valve of the hydrogen cylinder, the friction between the air flow and the bottle valve generated static electricity, which directly detonated the cylinder. Gas cylinder operators died on the spot. The overpressure generated by the explosion caused the walls of the hydrogen cylinder storage room to collapse, causing injuries to many people.

3. Quantitative analysis

3.1. Calculation of explosion energy

In this accident, the explosion occurred in a hydrogen cylinder. Under high pressure, the explosion will be more destructive than under normal pressure. The ignited high-pressure combustible gas undergoes a chemical reaction in the hydrogen cylinder. The high pressure generated instantly ruptures the cylinder, and the high-pressure gas is quickly released into the air and is ignited quickly. In this process, the release of energy is divided into two phases, one is the adiabatic expansion of the gas, and the other is the combustion of the gas. The generated energy E can be expressed as:

\[ E = E_m + E_c \]  \hspace{1cm} (1)

Where, \( E_m \) is factual mechanical energy, kJ; \( E_c \) is actual chemical explosion energy, kJ.
There are generally four methods for estimating the explosion energy of compressed gases: the Brode method, the isothermal expansion method, the isentropic expansion method, and the thermodynamic effective energy method. However, both the isothermal expansion method and the thermodynamic effective energy method are based on the isothermal assumption. It is generally believed that the isentropic expansion method can better predict the explosion energy in the distance, and the Brode method can predict the explosion energy near the source of the explosion. In this accident, the deaths were all operators of hydrogen cylinders, more accurately estimate the energy near the explosion source is needed. At the same time, the Brode method is the most realistic method available, because it has fewer limiting assumptions than the isentropic model.

\[ E_i = \frac{(p_g - p_s) \times V}{\gamma} \]  

(2)

Where, \( p_g \) is absolute pressure of gas in the cylinder before explosion, MPa; \( p_s \) is surrounding pressure, MPa; \( V \) is Volume, m\(^3\), \( \gamma \) is ratio of specific heats, 1.41.

Due to the explosion of the cylinder on the ground, the reflection, absorption and consumption of ground energy should be considered. The actual mechanical energy equation can be written as \( E_m = 1.8E_1 \). The energy of a chemical explosion is estimated by:

\[ E_2 = VQ_v \]  

(3)

Where, \( Q_v \) is the combustion heat of hydrogen, 12770 kJ / m\(^3\).

In this accident, the filling pressure of the hydrogen cylinder was 10 MPa, the volume of the hydrogen cylinder was 40 L, the volume ratio of hydrogen to oxygen was exactly 1:1, and the initial temperature was 310 K. When converted to a standard atmospheric volume, it was approximately 1.77 m\(^3\). In actual conditions, about 90% of the energy generates shock waves, and the rest is used to project fragments and tear steel cylinders. The actual chemical energy equation can be written as \( E_c = 0.9E_2 \).

The total energy of the pressure vessel rupture and hydrogen explosion is:

\[ E = E_m + E_c = 505.47kJ + 20342.61kJ = 20848.08kJ \]

The blasting energy is converted into TNT equivalent \( q = 20848.08 / 4500 = 4.63\) kgTNT.

3.2. Calculation of overpressure caused by explosion

Explosion experiments have shown that overpressure can be estimated from the distance between TNT equivalent and the origin of the explosion on the ground. The rule of proportional relationship obtained from experience is:

\[ z_e = \frac{r}{m_{TNT}^{1/3}} \]  

(4)

Where, \( z_e \) is proportional distance, m/kg\(^{1/3}\); \( r \) is distance from origin of explosion, m; \( m_{TNT} \) is TNT equivalent, kg.
Figure 2 shows the relationship between proportional overpressure and proportional distance. The proportional overpressure \( p_0 \) is given by:

\[
p = \frac{p_0}{p_s}
\]

Where \( p \) is proportional overpressure, dimensionless; \( p_0 \) is the lateral overpressure peak overpressure; \( p_s \) is the surrounding pressure.

The curve in Figure 3 can also be described by the following empirical equation:

\[
p = \frac{1616 \left[ 1 + \left( \frac{z_e}{4.5} \right)^2 \right]}{\sqrt{\left[ 1 + \left( \frac{z_e}{0.048} \right)^2 \right] \left[ 1 + \left( \frac{z_e}{0.32} \right)^2 \right] \left[ 1 + \left( \frac{z_e}{1.35} \right)^2 \right]}}
\]

4. Safety disposition

In this accident, more than 1,000 cylinders filled in the same batch may be problematic cylinders and become a major source of danger that needs urgent disposal.

The main disaster forms during venting are gas cloud explosion, jet fire and hydrogen cylinder explosion. The commonality is the existence of combustible and explosive substances, and the second is that it has an ignition source when it has the energy to trigger an explosion. Since flammable explosive substances are now available, it is necessary to start with controlling ignition energy. The most uncontrollable factor is electrostatic.

Friction is the most important cause of static electricity. Because the released gas is mixed with floating solid and liquid particles, when the gas is ejected at high speed, the particles and the tube wall rub against each other, contact each other and quickly separate, making the positive and negative atoms electrical imbalance causes redistribution of electric charges, causing particles and inner walls of pipes to have equal amounts of electric charges of different signs, respectively. According to
engineering experience, when the air velocity is less than 8 m/s, generally no electrostatic discharge will occur. The following formula is used to estimate the flow rate when the gas is vented:

\[
c = \sqrt{\frac{2}{k-1} \frac{k}{k-1} \frac{RT}{k} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]}
\]  

(7)

Where, \(c\) is Gas flow speed, m/s; \(k\) is Boltzmann's constant, 1.4; \(p_2\) is Outlet gas pressure, 0.1MPa; \(p_1\) is inlet gas pressure, 10MPa.

Through calculation, when the valve is fully opened, the gas flow rate reaches 114.90 m/s, which can completely cause the phenomenon of electrostatic discharge.

In order to ensure the safety of the emptying process, the electromechanical arm is designed to operate through a SPST switch. Sandbags were placed on hydrogen cylinders as an explosion-proof measure, and the operation was performed 20 meters away. No explosion accident occurred during operation.

5. Conclusion
This accident is a very typical accident because it is a reaction in a pressure vessel. The destructive force of the explosion is much greater than the physical explosion of a hydrogen cylinder. Therefore, preventing such accidents will prevent great losses to enterprises. This paper proposes the following countermeasures:

- Strictly control the inspection before filling the hydrogen cylinder. The gas in the cylinder is randomly sampled for detection to determine the type of gas.
- Enterprises should not combine two pipelines into one pipeline. An additional hydrogen filling row should be installed. Each pipeline should be filled separately. At the same time, change management should be done.
- Strengthen the maintenance and repair of equipment. Maintain the integrity of the equipment. Unqualified products cannot be used. Special personnel should be arranged to repair the equipment.
- Operators should keep records of shifts and strictly implement the process regulations.
- Units using pressure vessels should be equipped with reinforced concrete explosion-proof walls and lightweight ceilings. In this accident, it was because of the use of a reinforced concrete ceiling that some companies could not release pressure in time, which caused the explosion-proof wall to collapse and cause secondary injuries.

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