An Experimental Study on High-Pressure Hydrogen Compatibility of Rubber Seals at FCV Refuelling Receptacles

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Abstract. A method is proposed to test the sensitivity of high-pressure hydrogen compatibility of rubber O-ring seals at FCV refuelling receptacles based on a long-term high-pressure pure hydrogen full-immersion environment testing, in combination with such Chinese standards as the determination of the effect of liquids of rubber and FCV refuelling receptacles. Through an aging property test system, the high-pressure pure hydrogen full-immersion testing is conducted for 5 groups of rubber O-ring seals to be measured. Before and after the testing, an electronic balance is used to measure the mass of the rubber O-ring seals, obtaining changes in mass and volume. At last, on the basis of the changes, the sensitivity of the seals of various models and in diverse experimental groups to the high-pressure hydrogen compatibility is obtained through our analysis.

Keywords: Hydrogen compatibility, sensitivity, high-pressure environment, mass and volume changing rate.

1. Introduction

As a new type of green energy resource, hydrogen features cleanness, high-efficiency and ease of mass production. For the past few years, it has been strongly supported in different counties on the market. By the end of 2019, over 50 countries have issued lots of incentive policies about applied research on hydrogen energy sources [1]. However, the building of hydrogen fuelling stations is a huge obstacle to the development of hydrogen fuel cell vehicle (HFCV) industry, the key of the technological progress in hydrogen energy [2]. Particularly, rubber O-ring seals are of great importance to the refuelling receptacle sealing. During sealing, rubber O-ring seals are directly exposed to high-pressure pure hydrogen, thus leading to hydrogen compatibility. Because of penetration and diffusion of the high-pressure hydrogen, non-linear volume expansion may occur in the rubber O-ring seals. In addition to the influence on tensile properties, it also lowers the actual fracture stress of the materials [3] and has a strong influence on sealing effects. In this case, it is very necessary to explore the compatibility of rubber O-ring seals with hydrogen.

At present, hydrogen compatibility research is focused on metal and rubber materials. For example, a finite element model (FEM) was established by Looney et al. [4] to simulate three ISO 11114-4 material compatibility testing methods applicable to hydrogen gas cylinders; they also made use of an...
experimental measurement approach to calibrate monotonic constitutive models of cyclic deformation and constitutive models of cyclic deformation. It is proved that such a method can predict critical damage of materials. As far as Dadfarnia et al. [5] are concerned, a new approach was constructed through methods including the finite element analysis and thermodynamic theories of decohesion, for the coupled hydrogen transport problem with hydrogen-assisted elastoplastic deformation. The proposed approach is used to confirm internal correlations between degradation mechanism characteristics obtained by microscopic observations and first-principles calculations of macroscopic indices of embrittlement. Regarding rubber materials, Zhou et al. [6] probed into low-amplitude reciprocating motions of rubber seals in a hydrogen environment.

It turned out that rubber seals in hydrogen are more inclined to micro-motions in a viscous state, leading to more serious fatigue failure and fretting wear. By observing changes of network-chain density of nitrile-butadiene rubber (NBR) during dehydrogenation after the exposure to high-pressure hydrogen, the Debye-Bueche equation was utilized by Ohyama et al. [7] to estimate dimensions and volume fractions of non-homogeneous structures. Additionally, the thermal desorption analysis was conducted to evaluate residual hydrogen content in samples exposed to the high-pressure hydrogen and look into relationships between hydrogen content and spatial heterogeneity of rubber. However, specific experimental investigations on relationships of hydrogen and volume/mass changes of rubber O-ring seals are still rather scarce at home and abroad. In this paper, an experimental study is designed, by combining Chinese standards on determining the effect of liquids of rubber and FCV refuelling receptacles, to explore mass and volume change sensitivity of rubber O-ring seals at refuelling receptacles in a high-pressure hydrogen environment. In this way, the quality performance of rubber O-ring seals of diverse models can be distinguished.

2. Experiments

2.1. Testing principles

According to testing procedures stipulated in Chinese standards of determining the effect of liquids of rubber, rubber O-ring seals fully immersed in high-pressure pure hydrogen are subjected to the influence of hydrogen intrusion, diffusion and dissolution. As a result, both mass and volume of them may alter. In line with Fick's Second Law, a diffusion-controlled equation expressing compatibility of hydrogen and rubber can be written as follows [8]:

\[ \frac{\partial c_H}{\partial t} = \frac{\partial^2 c_H}{\partial x^2} + \frac{\partial^2 c_H}{\partial y^2} + \frac{\partial^2 c_H}{\partial z^2} \]

(1)

Where, \( c_H \) stands for hydrogen concentration, \( \frac{\partial c_H}{\partial t} \) for partial differential of hydrogen concentration to time (i.e., a hydrogen diffusion rate), and \( D_H \) for hydrogen diffusion coefficient.

Based on Equation (1), the hydrogen diffusion rate forms a positive correlation with hydrogen concentration provided that the hydrogen diffusion coefficient remains stable; in addition, such a relation is affected by the thickness in different directions inside the rubber and material properties. For this reason, the diffusion rate of hydrogen in a rubber O-ring seal reaches its peak in a full-immersion environment of 99.999% high-pressure pure hydrogen. This may lead to changes in physical properties, such as mass and volume of a material. Here, mass variations before/after the high-pressure pure hydrogen full-immersion environment testing can be quantified as follows:

\[ \Delta m_{100} = \frac{m_f - m_0}{m_0} \times 100\% \]

(2)

Where, \( \Delta m_{100} \) refers to a mass change rate, \( m_f \) to mass (unit: gram) of the rubber seal in the air before the full-immersion testing, and \( m_0 \) to its mass (unit: gram) in the air after the full-immersion testing.

Regarding volume changes of rubber seals, they are generally quantified by the water displacement method expressed in the following Equation (3):
\[ \Delta V_{100} = \left( \frac{m_1 - m_{0,w}}{m_0 - m_{0,w}} - 1 \right) \times 100\% \]  

Equation (3)

Where, \( \Delta V_{100} \) is the volume change rate of rubber seals; \( m_0 \) and \( m_1 \) represent the mass of rubber seals in the air before and after the high-pressure full-immersion testing, respectively; and, \( m_{0,w} \) and \( m_{1,w} \) are the rubber seal mass (unit: gram) in distilled water prior and subsequent to the high-pressure full-immersion testing.

If material density is below 1 g/cm\(^3\), weights should be adopted for measurement during the testing, and the weights and samples must be all immersed in water. A specific calculating method is expressed below:

\[ \Delta V_{100} = \left( \frac{m_1 - m_{1,w} + m_{s,w}}{m_0 - m_{0,w} + m_{s,w}} - 1 \right) \times 100\% \]  

Equation (4)

In Equation (4) above, \( m_{s,w} \) represents the mass of a weight in distilled water and its unit is gram (g for short).

In accordance with performance requirements for non-metallic parts directly exposed to hydrogen at refuelling receptacles, as provided in China National Standards on FCV hydrogen refuelling receptacles, the volume expansion ratio of a rubber O-ring seal shall be no more than 25% after the compatibility test; furthermore, its volume shrinkage rate and mass change rate shall not be greater than 10% in this case.

2.2. Testing system

An aging property test system is shown in Figure 1. In rated conditions, the system can apply a gas pressure up to 70 Mpa at the maximum on samples in a closed container and maintain a constant pressure state for a long time. Such a system is used to carry out high-pressure full-immersion testing for samples. Under constant high pressure for a long time, it is guaranteed by this system that the tested gas can be sufficiently exposed to and compatible with samples to be tested.

Before/after the high-pressure hydrogen full-immersion testing, the mass of samples to be tested is measured by an electronic balance (see Figure 2). More particularly, the electronic balance can measure the mass of samples in the air and in the distilled water. The relationship between the mass in water and that in the air can be expressed in Equation (5) below.

\[ m_w g = m g - f \]  

Equation (5)

Where, \( m_w \) refers to the mass of samples in distilled water, \( m \) to the mass of samples, and \( f \) to buoyancy applied to the samples. In conformity with Archimedes’ physical law of buoyancy, that is, \( f = \)
\( \rho g V \), and based on the fact that the volume of samples is equal to the volume of the distilled water displaced, Equations (3) and (4) can be derived out in conjunction with Equation (5). Accordingly, the volume change rate of samples can be obtained.

![Figure 2. An electronic balance](image)

### 2.3. Testing procedures and methods

A total of 15 rubber O-ring seals were divided into 5 groups, with seals of the same model in the same group. On this basis, an experimental analysis was conducted on the sensitivity of high-pressure hydrogen compatibility. Grouping conditions have been listed in Table 1. Firstly, the electronic balance was employed to measure the mass of all seals in the air and the distilled water respectively, and the initial value of their mass was preserved. Then, the rubber O-ring seals were placed in a testing container of the aging property test system. In this system, 99.999% high-purity hydrogen was supplied; and the pressure was maintained at 70 MPa for 168 hours, to approximately simulate a practical working environment of rubber O-ring seals at refuelling receptacles. After the high-pressure hydrogen full-immersion testing, the electronic balance was used again to measure the mass of the seals in the air and the distilled water respectively; and relevant data were noted down. Finally, the data were substituted into Equations (2) and (3) for the purpose of separately calculating mass and volume change rates of rubber O-ring seals in each group and exploring the hydrogen compatibility. Here, a rubber O-ring seal used as a testing sample is presented in Figure 3.

#### Table 1. Experimental grouping for rubber O-ring seals

| Group No.       | Model No. |
|-----------------|-----------|
| Experimental group 1 | A-1  |
|                 | A-2  |
|                 | A-3  |
| Experimental group 2 | B-1  |
|                 | B-2  |
|                 | B-3  |
| Experimental group 3 | C-1  |
|                 | C-2  |
|                 | C-3  |
| Experimental group 4 | D-1  |
|                 | D-2  |
|                 | D-3  |
| Experimental group 5 | E-1  |
|                 | E-2  |
|                 | E-3  |
Figure 3. A rubber O-ring seal

3. Result analysis

3.1. Standard deviation analysis
Before the high-pressure hydrogen compatibility testing, the mass of rubber O-ring seals in the air and the distilled water is listed in Table 2. Products of the same model have the same manufacturing and technological procedures, and therefore their mass differences are minor before the testing. Furthermore, mass differences of products of the same model manifest accuracy and stability of the manufacturing techniques.

Standard deviation, defined as a root-mean-square deviation of discrete values and respective mean values, is used to describe the dispersion degree of data. The standard deviation $\sigma$ can be expressed in the following equation:

$$
\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \mu)^2}
$$

Where, $N$ stands for the number of discrete data, $x_i$ for values of discrete data, and $\mu$ for the mean value of $N$ discrete data.

Table 2. The mass of rubber O-ring seals before the testing

| Group No. | Model No. | Mass in the air ($m_0/g$) | Mass in the distilled water ($m_{0,w}/g$) |
|-----------|-----------|---------------------------|------------------------------------------|
| 1         | A-1       | 0.0326                    | 0.0061                                   |
|           | A-2       | 0.0326                    | 0.0064                                   |
|           | A-3       | 0.0327                    | 0.0068                                   |
| 2         | B-1       | 0.0310                    | 0.0041                                   |
|           | B-2       | 0.0310                    | 0.0044                                   |
|           | B-3       | 0.0309                    | 0.0038                                   |
| 3         | C-1       | 0.0260                    | 0.0050                                   |
|           | C-2       | 0.0270                    | 0.0049                                   |
|           | C-3       | 0.0273                    | 0.0047                                   |
| 4         | D-1       | 0.0328                    | 0.0059                                   |
|           | D-2       | 0.0328                    | 0.0059                                   |
|           | D-3       | 0.0335                    | 0.0063                                   |
| 5         | E-1       | 0.0327                    | 0.0052                                   |
|           | E-2       | 0.0326                    | 0.0058                                   |
|           | E-3       | 0.0327                    | 0.0055                                   |

Regarding rubber O-ring seals in diverse experimental groups, the standard deviation values of their actual mass before the testing have been shown in Figure 4. As can be observed from this figure, the maximum standard deviation is found in Experimental Group 3, at $6.807 \times 10^{-4}$; comparatively, standard
deviations of Experimental Groups 1, 2 and 5 are rather small and close to each other. Therefore, it can be inferred that rubber O-ring seals in the Experimental Group 3 have the most significant mass dispersion. This suggests that seals of this model are inferior to those of other models in other groups in terms of stability and accuracy of the manufacturing processes.

![Figure 4](image-url)

**Figure 4.** Standard deviation values for the mass of rubber O-ring seals in the air before the testing.

The mass of rubber O-ring seals in the air and the distilled water after the high-pressure hydrogen compatibility testing is given in Table 3 for various groups. In this case, the same method is used to calculate standard deviation values of the mass of rubber O-ring seals in the air after the testing; and the acquired values are compared with those before the testing, in order to explore the effect of the high-pressure hydrogen compatibility testing on discrete changes of mass data (as Figure 5 shows).

As shown in Figure 5, dispersion of rubber ring mass in Experimental Groups 3 and 4 drops slightly, while that in Experimental Groups 2 and 5 increases. Among them, the increase in mass dispersion from $5.774 \times 10^{-5}$ to $5.292 \times 10^{-4}$ is the most significant in group 5. After the high-pressure hydrogen compatibility testing, rubber seals in Experimental Group 5 have their mass changed; and differences in such changes are rather significant, leading to a sharp rise of dispersion. On this basis, it becomes clear that the mass stability of rubber seals in group 5 is rather poor when compared with that in other groups. Moreover, mass dispersion of rubber seals in Experimental Group 1 does not dramatically change and remains at low levels. Therefore, it is proved that the mass stability of rubber seals in group 1 is rather high.

3.2. Mass and volume change rates

Measured values of rubber seal mass in the air and the distilled water before/after the testing are substituted into Equations (2) and (3), so as to work out volume change rates of rubber O-ring seals in different groups prior/subsequent to the high-pressure hydrogen compatibility testing.

Mass change rates of all rubber O-ring seals before/after the testing have been presented in Figure 6. Obviously, mass increase is found in 8 types of rubber seals; 4 types have no obvious changes; and 3 types show mass reduction. Seals of the same model still have mass change rates different from each other. Regarding seals of diverse models, they have different mass change rates as well. In terms of rubber seals in Experimental Group 1, their mass climbs. The mass of some rubber seals in Experimental Group 3 drops, and that of others increases. In groups 4 and 5, the rubber seal mass greatly declines or increases. Thus, it can be summarized that mass changes remain stabler in Experimental Groups 1 and 2.
Table 3. The mass of rubber O-ring seals after the testing

| Group No. | Model No. | Mass in the air (m_i/g) | Mass in the distilled water (m_{i,w}/g) |
|-----------|-----------|-------------------------|----------------------------------------|
| 1         | A-1       | 0.0328                  | 0.0062                                 |
|           | A-2       | 0.0327                  | 0.0061                                 |
|           | A-3       | 0.0328                  | 0.0064                                 |
| 2         | B-1       | 0.031                   | 0.0038                                 |
|           | B-2       | 0.031                   | 0.0038                                 |
|           | B-3       | 0.0308                  | 0.0035                                 |
| 3         | C-1       | 0.0264                  | 0.0046                                 |
|           | C-2       | 0.0269                  | 0.0055                                 |
|           | C-3       | 0.0274                  | 0.0053                                 |
| 4         | D-1       | 0.0328                  | 0.0058                                 |
|           | D-2       | 0.0328                  | 0.0053                                 |
|           | D-3       | 0.0329                  | 0.0053                                 |
| 5         | E-1       | 0.0337                  | 0.006                                  |
|           | E-2       | 0.0327                  | 0.0053                                 |
|           | E-3       | 0.0329                  | 0.0052                                 |

Figure 5. Comparison of standard deviations for the actual mass of rubber seals before/after the testing
In Figure 7, the volume of rubber seals with two different model numbers in Experimental Group 3 declines; however, that of other rubber seals increases after the testing. A possible reason is that high-pressure hydrogen penetrates in rubber seals and fills their volume, resulting in an expansion of interior space of the rubber seals. In Experimental Group 3, both increase and decline in the volume of rubber seals can be found, generating rather high change rates. Therefore, it is proved that the stability of volume changes is rather poor.

Through an analysis on the experimental results, it is clear that rubber O-ring seals of all models conform to international criteria. With respect to mass changes of rubber O-ring seals used as samples, their sensitivity to hydrogen reaches the highest level in Experimental Groups 3 and 5 in a high-pressure pure hydrogen full-immersion environment; and, both the mass change range and data discreteness in the two groups are above those in other groups. Mass changes of rubber O-ring seals in Experimental Group 2 are slightly sensitive to hydrogen; and such changes are rather stable. From the perspective of volume changes, the volume of rubber seals in Experimental Group 3 declines sharply; and these seals are the most sensitive to high-pressure hydrogen. To sum up, the sensitivity of rubber O-ring seals of various models to high-pressure hydrogen reaches its maximum level in Experimental Group 3, and
their working performance is below that of other rubber seals. The sensitivity of rubber O-ring seals in Experimental Group 5 takes the second place, and the lowest sensitivity is found in Experimental Group 2. Group 2 features the highest stability, followed by Experimental Group 1.

4. Conclusion

In combination with two sets of Chinese national standards, an experimental method is proposed to test the sensitivity of rubber O-ring seals at refuelling receptacles to high-pressure hydrogen compatibility. Through a 168-hour high-pressure hydrogen full-immersion test, the mass and volume changes of the seals before and after the testing are analysed, exploring standard deviation variations for mass, and mass and volume change rates of rubber seals of diverse models. The findings are that rubber O-ring seals in Experimental Group 3 are the most sensitive to high-pressure hydrogen, indicating that their stability is the worst. Rubber seals least sensitive to such hydrogen are found in Experimental Groups 1 and 2, and this suggests that rubber seals in the two groups feature good working stability.

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