Study on the Permeability of Nonmetallic Materials in the Hydrogen-Doped Pipeline

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Abstract. As the most efficient way to transport large quantities of hydrogen over long distances, Hydrogen-doped NG pipeline has been actively promoted and developed. Hydrogen into the pipeline will have a variety of effects, as the smallest gas molecules, hydrogen on the pipeline valve, and other key equipment non-metallic materials have a stronger penetration than natural gas, which is bound to increase the leakage of equipment, there are huge security risks. In this paper, the permeability of non-metallic materials in hydrogen-doped NG pipelines is studied by permeability experiments. Seven common non-metallic materials for natural gas pipeline valves and key equipment are compared and selected. The numerical simulation model of hydrogen permeation in non-metallic materials was established to explore the permeability of non-metallic materials under different pressures, temperatures, and mixing ratios of hydrogen. The non-metallic sealing materials suitable for the hydrogen-doped environment are optimized, which can furnish reference for the engineering promotion and technology development of hydrogen-doped natural gas pipeline transportation.

1 Introduction

Hydrogen energy is a kind of green renewable energy, which has been widely promoted and used. To realize the further large-scale application of hydrogen energy, many countries are carrying out the test and promotion of hydrogen-doped natural gas pipeline [1-3]. Nowadays, many experts and scholars have compared and studied several common hydrogen transportation modes, and it has been generally believed that pipeline hydrogen transportation is the optimal way to realize large-scale, long-distance, safe, and efficient transportation of hydrogen [4-6]. It is proposed that the use of existing natural gas pipelines for hydrogen transportation is a fast and economical means to achieve large-scale utilization of hydrogen energy. However, the properties of hydrogen and NG are not the same. Hydrogen entering the NG pipeline will cause hydrogen embrittlement and other adverse effects on pipeline pipes and welded joints [7-11], and can easily penetrate the non-metallic sealing materials in the natural gas pipeline system [12, 13], causing hydrogen blistering and hydrogen absorption expansion and other adverse effects [14-17], which brings new problems and challenges to the safe transportation of pipelines.

At present, many scholars have carried out research on the hydrogen embrittlement of hydrogen-doped natural gas pipeline materials, but research on non-metallic sealing materials for valves and other key equipment in hydrogen-doped NG pipeline systems is still very scarce. As the smallest gas in the molecule, hydrogen can easily diffuse in various locations in the hydrogen-doped natural gas pipeline system [18]. In particular, it is easier to penetrate the non-metallic sealing materials of pipeline valves and some key equipment, which causes the performance degradation of non-metallic sealing materials such as hydrogen bubbling and hydrogen absorption expansion. Therefore, it will increase the leakage of sealing equipment, which has a great potential safety hazard.

2 Penetration experiment of non-metallic sealing materials

2.1 Experimental apparatus and methods

For the test of gas permeability of different gases to non-metallic sealing materials, relevant standards and methods have been established at home and abroad. To explore the permeability of non-metallic sealing materials used in common hydrogen-doped natural gas pipelines, based on the standard-recommended differential pressure gas permeability test method, this paper uses a differential pressure gas permeation device (Experimental device and experimental device principle shown in Fig. 1). Seven different rubber non-metallic materials used in natural gas pipeline valves and key equipment were used to carry out gas permeation experiments of methane hydrogen.

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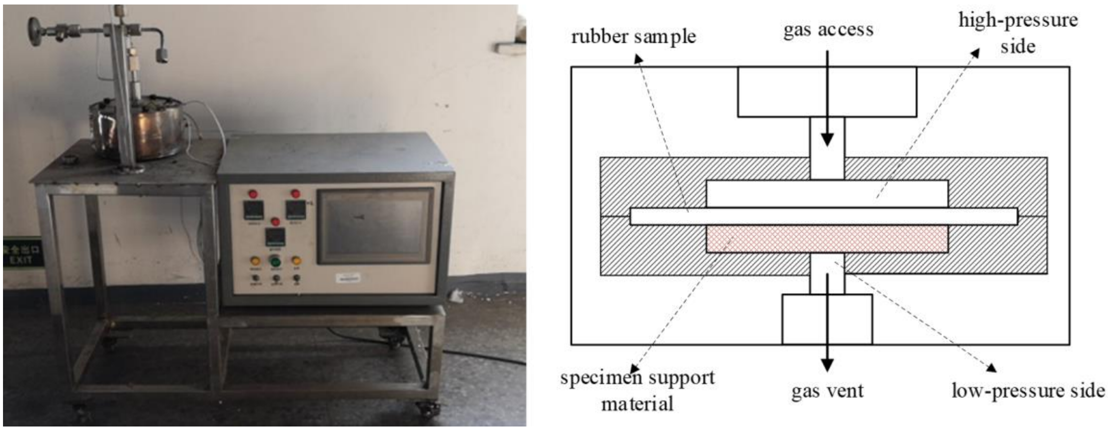

Fig. 1. Differential pressure gas permeation device.

2.2 Non-metallic sealing material penetration experimental data

According to the gas permeation experiment of differential pressure method, the law of gas pressure variation with time on the low pressure side is obtained, that is, the gas permeation curve, and then the parameters of the material are calculated (as shown in the following Table 1). In this study, gas permeation experiments under 6MPa, 60 °C, and 5 % hydrogen content were carried out for seven different rubber non-metallic materials. The diffusion coefficient, solubility, and the permeability coefficient of the resulting material is recorded in the table below. As you can see from the table, among the seven different types of rubber, tetrafluoroethylene rubber has excellent gas permeability under the conditions of 6MPa, 60 °C and 5 % hydrogen content. The diffusion coefficient is 1.04 × 10-10m^2 / s, the solubility is 2.75 × 10-6mol / (m^3 · Pa), and the permeability coefficient is 2.87 × 10-16mol · m / (m^2 · s · Pa).

To further explore the permeability of tetrafluoroethylene rubber with excellent permeability under different hydrogen doping conditions, this study carried out more permeability experiments under different working conditions for tetrafluoroethylene rubber. The test conditions are: pressure 6,9,12 MPa, temperature 60,80 and 100 °C, hydrogen content 5 %, 15 %, 30 %, 100 %, a total of eight groups of experiments. The diffusion coefficient, permeability coefficient, and solubility coefficient of tetrafluoroethylene rubber under eight different experimental conditions were obtained as shown in the following Table 2, Table 3 and Table 4.

Table 1. Gas permeability of sealing materials under the condition of 6MPa, 60 °C and 5 % hydrogen content.

Rubber types	Neoprene	Ethylene-propylene rubber	Polyester polyurethane rubber	Low nitrile nitrile Butadiene Rubber	Tetrafluoroethylene rubber	Butyl rubber	Fluororubber
Diffusion coefficient $\times10^{-10}$m^2/s	4.14	23.8	8.18	13.4	1.04	49.9	4.14
Solubility $\times10^{-6}$mol/(m^3·Pa)	3.62	5.51	3.35	3.5	2.75	4.39	3.62
Permeability coefficient$\times10^{-16}$mol·m/(m^2·s·Pa)	15	131	27.4	46.8	2.87	219	15

Table 2. The effect of different pressures on the gas permeability of tetrafluoroethylene rubber material at 60 °C and 15 % hydrogen content.

Pressure/MPa	Diffusion coefficient $\times10^{-10}$m^2/s	Solubility $\times10^{-6}$mol/(m^3·Pa)	Permeability coefficient $\times10^{-15}$mol·m/(m^2·s·Pa)
6	2.79	4.64	1.29
9	3.34	9.24	3.09
12	3.41	9.73	3.32

Table 3. The effect of different temperatures on the gas permeability of tetrafluoroethylene rubber material under the condition of 6MPa and 15 % hydrogen content.

Temperature/℃	Diffusion coefficient $\times10^{-10}$m^2/s	Solubility $\times10^{-6}$mol/(m^3·Pa)	Permeability coefficient $\times10^{-15}$mol·m/(m^2·s·Pa)
60	2.79	4.64	1.29
80	3.51	13.3	4.68
100	5.23	23.4	12.2

Table 4. The effect of different hydrogen content on gas permeability of tetrafluoroethylene rubber material at 6 MPa and 60 °C.

Hydrogen content/%	Diffusion coefficient $\times 10^{-10} m^2/s$	Solubility $\times 10^{-6} mol/(m^3 \cdot Pa)$	Permeability coefficient $\times 10^{-15} mol \cdot m/(m^2 \cdot s \cdot Pa)$
5	1.04	2.75	0.287
15	2.79	4.64	1.29
30	3.80	11.4	4.32
100	3.69	27.1	10.0

According to the above experiments, temperature, pressure, and hydrogen doping ratio will affect the permeability of hydrogen in non-metallic sealing materials. With the increase of temperature, pressure, and hydrogen doping ratio, the diffusion coefficient, solubility and permeability coefficient of hydrogen in materials will increase.

3 Numerical simulation model of non-metallic sealing material penetration

3.1 Numerical simulation modeling

In this paper, based on the permeation experiment of hydrogen-doped natural gas to non-metallic sealing materials, a numerical simulation model that can accurately simulate the permeation process of gas to non-metallic materials under different hydrogen-doped conditions is established by using the dilute material transfer method of numerical simulation software. The permeability simulation of non-metallic materials of hydrogen-doped natural gas pipeline valves and key equipment was carried out.

According to the infiltration equipment and materials used in the experiment, the rubber material is a standard disc shape, so a two-dimensional axisymmetric model is used for simulation. The model geometry is as follows. The sample is a circular tetrafluoroethylene rubber sheet with a radius of about 40 mm and a thickness of about 2 mm.

The initial boundary conditions in the penetration numerical simulation model are set as no flux and no convection conditions. The upper side of the model is the high-pressure side gas space, which is filled with a mixture of methane and hydrogen. The concentration of the mixed gas can be calculated according to the experimental conditions and the ideal gas state equation. The rectangle in the middle of the model is a non-metallic sealing material, and the initial concentration of the mixed gas in the material is 0 mol / m^3. The lower rectangle of the model is the low-pressure side gas space, and the initial value of the mixed gas concentration in the space is set to 0 mol / m^3. To simulate the stable concentration conditions on the high-pressure side of the gas in the experimental conditions, it is necessary to set the gas inflow conditions on the upper boundary of the model, select the concentration constraints, and set the gas concentration. The concentration is also converted according to the experimental conditions and the ideal gas state equation.

When hydrogen enters the non-metallic sealing material, it will first dissolve on its surface and then penetrate the non-metallic material. To simulate the process of gas dissolution in non-metallic sealing materials, the distribution conditions can be set on the surface of non-metallic sealing materials in the model. The distribution concentration is obtained by Henry's law according to the gas solubility obtained by experiment.

The key parameter of hydrogen permeation in non-metallic sealing materials is the diffusion coefficient. In this model, the diffusion coefficient of the model is set in the transfer property of the rare material transfer. The upper and lower rectangles of the model are gas spaces, and the diffusion coefficient of hydrogen in the mixed gas is set to $0.22 \times 10^{-4} m^{\wedge 2}/s$; the rectangle in the middle of the model is a non-metallic sealing material, which is input according to the real diffusion data of non-metallic materials obtained by the non-metallic material penetration experiment of the valve in the hydrogen-doped environment (Tables 2-4). To simulate the gas permeation process as accurately as possible, the model is divided by the quadrilateral regular grid, and the grid at the non-metallic sealing material is encrypted.

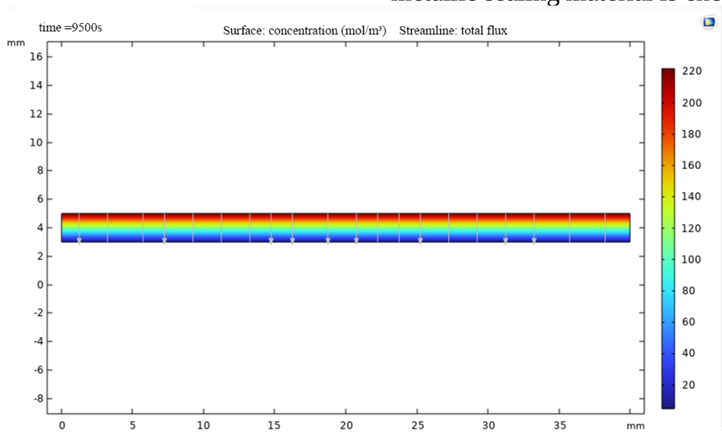

Fig. 2. Numerical calculation results cloud chart.

3.2 Numerical simulation model validation

The numerical simulation model was established for the calculation. The experimental data under different pressure conditions are compared with the data obtained from the numerical model. It can be seen from Fig. 2 and Fig. 3 that the two are basically consistent, which proves that the numerical model established in this study can well simulate the penetration process of hydrogen in non-metallic sealing materials.

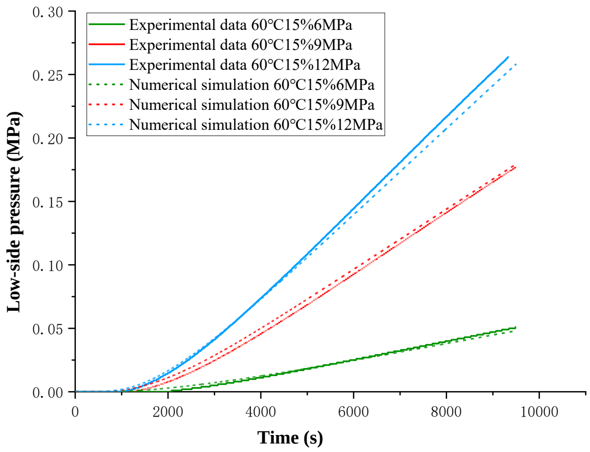

Fig. 3. Comparison and verification of experimental data and simulation data of tetrafluoro propylene rubber.

4 Study on the permeability law of non-metallic sealing materials

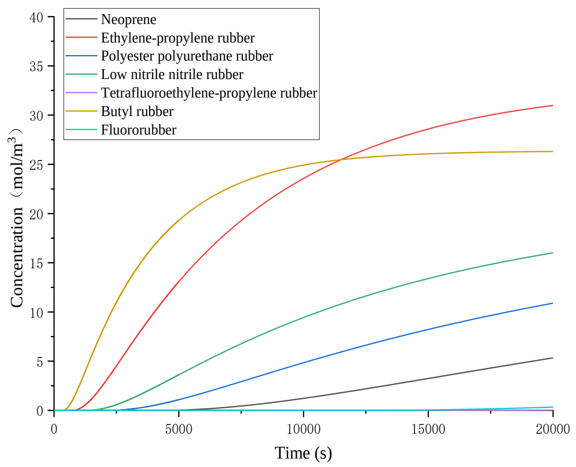

Fig. 4. Comparison of the permeability of seven different rubber materials.

Based on the diffusion coefficient and solubility parameters of seven different rubber materials obtained from the penetration experiment, the numerical simulation model was used to simulate the penetration process of the seven rubber materials. It can be seen from Fig. 4 and Fig. 5 that the comprehensive permeation rate of hydrogen in butyl rubber and ethylene-propylene rubber is the fastest, and the two are different. The diffusion rate of hydrogen in butyl rubber is greater than that in ethylene-propylene rubber, but with time, the gas permeation amount of hydrogen in ethylene-propylene rubber will be greater than that in butyl rubber, which is caused by the different solubility of the two. On the whole, the permeation rate of hydrogen in tetrafluoro propylene rubber is the slowest, and the tetrafluoro propylene rubber used in this study has the best performance in blocking hydrogen permeation.

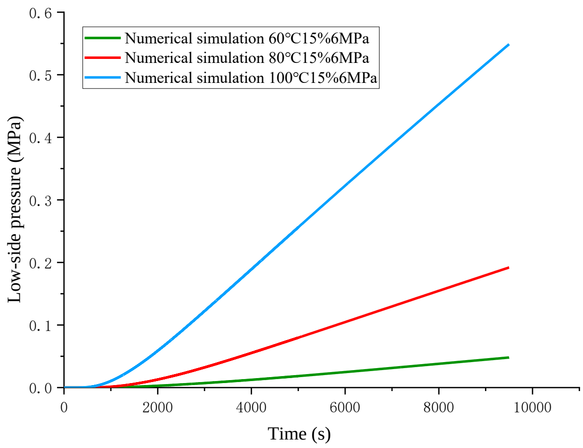

Fig. 5. Comparison of the permeability of tetrafluoroethylene rubber under different temperature conditions.

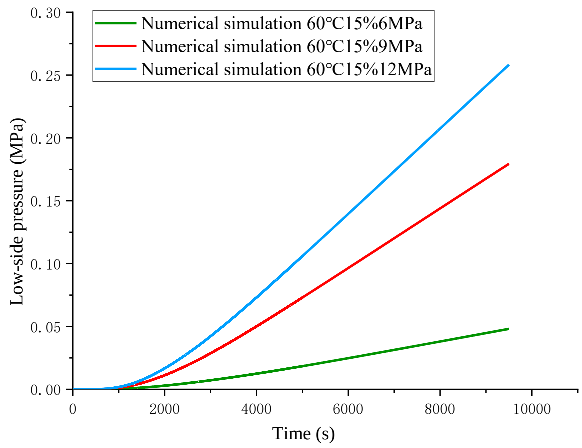

Fig. 6. Comparison of the permeability of tetrafluoroethylene rubber under different pressure conditions.

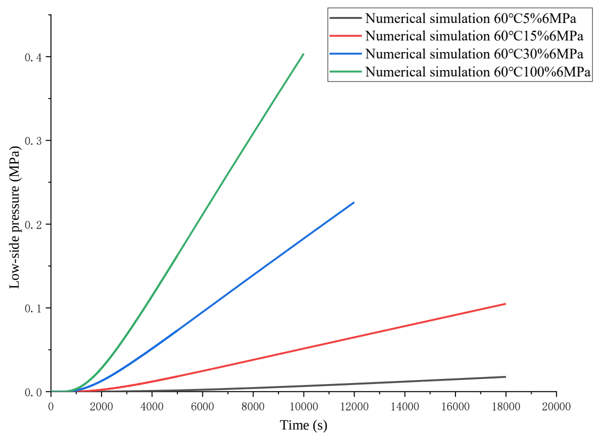

Fig. 7. Comparison of permeation properties of tetrafluoroethylene rubber under different hydrogen blending ratios.

Due to the excellent performance of tetrafluoroethylene rubber, more in-depth research was carried out under different working conditions of temperature 60 °C, 80 °C, 100 °C, pressure 6 MPa, 9 MPa, 12 MPa, hydrogen blending ratio 5 %, 15 %, 30 %, 100 %. The permeation curves of tetrafluoroethylene rubber under different operating environments are as follows Fig. 6 and Fig. 7. It can be clearly obtained that temperature, pressure, and hydrogen doping ratio will affect the permeation process of hydrogen in tetrafluoroethylene rubber, and with the increase of temperature, pressure, and hydrogen doping ratio, the permeation rate of hydrogen in tetrafluoroethylene rubber will increase. Among them, the temperature has the greatest influence on the process of its penetration, and the pressure has less influence.

5 Conclusions and recommendations

In this paper, the permeation experiment of non-metallic materials of valves and key equipment of hydrogen-containing NG pipeline is carried out. Among the seven common rubber materials in natural pipeline systems, tetrafluoroethylene rubber with the best performance was selected, and its permeation performance under different temperatures, pressures, and hydrogen blending ratios was further studied. By the numerical simulation model, the penetration process of hydrogen-doped natural gas in tetrafluoroethylene rubber was simulated, and the penetration performance of non-metallic materials under hydrogen-doped conditions was explored. Combined with the current status of related technologies in China, it is suggested that the following points should be paid attention to in the selection and research of hydrogen-doped natural gas pipeline valves and key non-metallic materials:

(1) Hydrogen will degrade the non-metallic materials used in common natural gas pipeline valves and key equipment, and will significantly increase their penetration. It is necessary to evaluate the applicability of the non-metallic materials used in the key equipment before the pipeline is mixed with hydrogen to ensure that the permeability of the non-metallic materials is within an acceptable range.

(2) There are many factors affecting the permeability of hydrogen in non-metallic sealing materials. Temperature, pressure, and hydrogen blending ratio will affect it. Based on this study, with the increase of temperature, pressure, and hydrogen blending ratio, the diffusion coefficient, solubility and permeability coefficient of hydrogen in the material will increase. It is necessary to standardize the permeability index of non-metallic sealing materials in hydrogen-doped NG pipelines to ensure the safety of pipeline transportation.

(3) Among the seven kinds of non-metallic materials for natural gas pipeline valves and key equipment in this paper, the performance of tetrafluoroethylene rubber used in the experiment to block hydrogen permeation is excellent, but the ratio of tetrafluoroethylene rubber from different manufacturers is not the same exactly, and the performance is also different. If the hydrogen-doped natural gas pipeline is repaired or replaced. When equipment such as pipeline valves, it can give priority to the use of tetrafluoroethylene rubber pipeline equipment, but it is also necessary to test the performance of the materials used in advance to ensure their safety under hydrogen conditions.

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