Airtight Butyl Rubber Under High Pressures in the Storage Tank of CAES-G/T System Power Plant

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ABSTRACT: The compressed air up to the maximum pressure of 8 MPa is stored in the storage facility of the Compressed Air Energy Storage Gas Turbine (CAES-G/T). The interior of the storage facility is covered by air-tight sheets to prevent a leak of this compressed air. Electricity by a power-generating system using such a facility is the first of its kind in the world. So, we have examined the materials of the airtight sheet and found that polymeric materials were suitable. Then, a normal pressure gas permeation test was done on several synthetic resins and rubbers. Butyl rubber (IIR) was found to show the smallest gas permeability. Moreover, a high-pressure gas permeation test was done on IIR and natural rubber (NR). The permeability of IIR at 10 MPa was estimated, and it was clear that IIR was a suitable air-tight material for CAES-G/T. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 173–177, 2005

Key words: barrier; gas permeation; rubber

INTRODUCTION: CAES-G/T SYSTEM POWER PLANT

The Compressed Air Energy Storage Gas Turbine (CAES-G/T) power generating system utilizes low-cost electricity available during off-peak hours (mainly at night) to compress air, which will be stored in an underground rock cavern and subsequently used to generate electricity through gas turbines to meet peak demand, especially on a bright day, especially in summer. Thus, the power-generating system CAES-G/T is composed of underground tanks (cavern), the surface power house, and the pipeline that connects these. The outline of CAES is shown in Figure 1 and Table I. This system contributes to the reduction of the exhaust as well as energy because it reduces the use of the fossil fuel to about 1/3 the amount of a usual gas turbine generating electricity.[1] The storage tanks are required to bear air pressure up to a maximum of 8 MPa. Therefore, storage facilities should have the strength and be airtight against this pressure.

In Germany and the USA, an underground rock salt stratum was chosen; compressed air storage tanks were built, and a CAES-G/T system was put to practical use for electrical load leveling purposes. When compressed air is stored in the cavern, a rock salt stratum bears high pressure without any airtight linings. However, there are no such rock salt layers in Japan. Caverns must be built in the soft stratum.[2,3] We designed a new structure that consists of rock cavern and reinforced concrete (RC) segments covered by butyl rubber lining. When compressed air is stored, the tank expands, as shown in Figure 2. Therefore, the lining sheet is required to have the flexibility and airtightness to prevent trouble by expanding. Gas permeation under pressure as high as 8 MPa was not reported on the rubber sheet as far as we are aware. Therefore, we chose some soft materials as the airtight lining material, which showed enough deformability, and their gas permeabilities under normal and high pressures were investigated in this article.

EXPERIMENTAL

Selection of materials

Airtight sheets are required to have the above-mentioned character, in addition to processibility and cost performance in manufacturing. Test samples were chosen from the sheet materials that were used in the civil engineering field. All seven polymer samples were commercially available: CSM was purchased from TOSOH Co., PVC from CHISSO co., EVA from TOSOH Co., EPDM from SUMITOMO Chemical Co., IIR from JSR Co., CR from DENKI KAGAKU Industrial Co., and NR was RSS#1 from Thailand. Because inorganic materials such as metals and ceramics are

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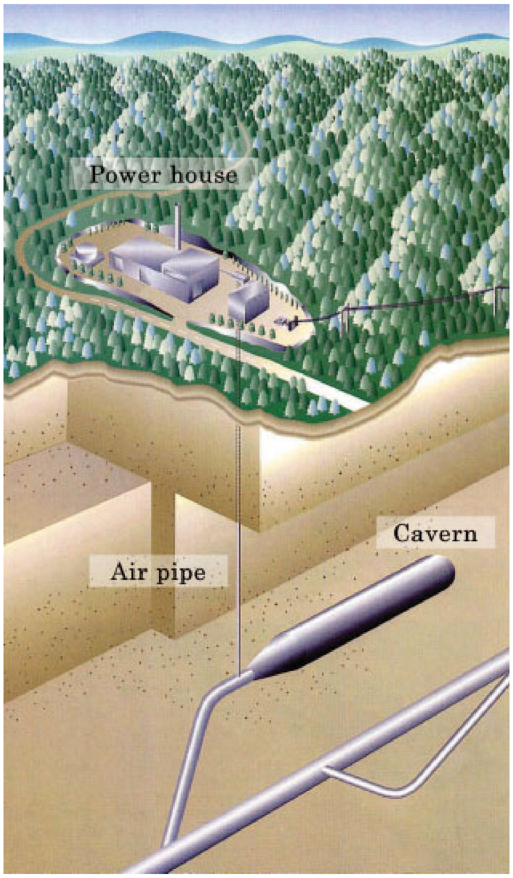

Figure 1 Conceptual drawing of CAES-G/T Power Generating System.

hard and brittle, they cannot follow deformation of the cavern. One organic materials (i.e., asphalts) seemed to be difficult to apply to the construction of in a cavern. On the other hand, polymer materials, especially amorphous ones, seem suitable to lining the RC segments became of its flexibility, airtightness and low density.

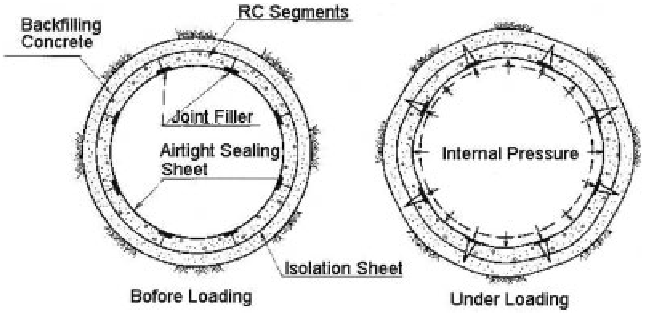

Figure 2 Concept of air-tight lining structure in CAES-G/T Power Generating System.

The gas permeations

The gas permeation was studied on polymers for the package material. The device and the way of measuring it were well established. The ways of measuring were the gas permeation measurements at low pressure, <1 atmospheric pressure. Recently, several polymers were actively used as gas separation film. For selective gas permeation, pressure dependence of permeability is to be elucidated. Therefore, the research of the permeation at a high pressure is important. The permeation at a low pressure is investigated first, and the permeation at a high pressure is studied on the selected materials.

TABLE I
Basic Design Parameters of the Pilot Plant of CAES-G/T System

Item	Parameters
Capacity	2,000 kW
Power generating time	4 h
Compressed air charging time	10 h
Storage system	Variable pressure system
Sealing system	Rubber lining method
Storage pressure	4–8 MPa
Storage air volume	$\sim 1{,}600\ \text{m}^3$
Storage air temperature	50°C or lower

Gas permeability at the normal pressure

The gases used for this experiment were nitrogen and oxygen, which occupy ~ 78 and $\sim 20\%$ of the atmosphere, respectively. The measurement was per JIS K 7126 (Testing Method for Gas Transmission Rate through Plastic Film and Sheeting). The test device (Gas Transmission Rate Tester M-C of instrument Toyo Seiki Seisaku-sho, Ltd.) is shown schematically in Figure 3. The sample was installed in the permeation cell, and the inside of the device was evacuated by a vacuum pump. A test gas of 1 atmospheric pressure was supplied to the high-pressure side of the permeation cell. A change in the pressure of the high-pressure side and that of the low-pressure side of the cell was recorded. The test temperature was 23°C. Gas permeability and gas transmission rate were calculated as.

$$P = 1.523 \times 10^{-12} \times GTR \times d \tag{1}$$

$$GTR = (273 \times V_c \times 24)/(T \times P_u \times A) \times (d_h/d_t) \tag{2}$$

where P is gas permeability (cm^3 cm s cm^2 cmHg), GTR is gas transmission rate (cm^3/m^2 24 h atm), d is thickness of test sample (mm), V_c is low pressure side capacity (mL), T is testing temperature (K), P_u is the difference pressure of the supply gas (mmHg), A is permeation area (m^2), and d_h/d_t is a change in pressure on the low pressure side in an hour (mmHg).

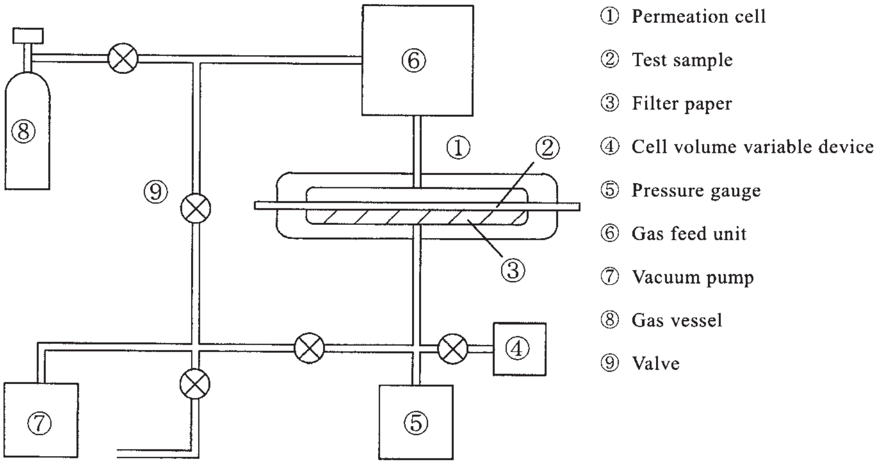

Figure 3 Test equipment of gas permeability at the normal pressure.

Gas permeability at the high pressure

Gases used were nitrogen and oxygen. Test samples were butyl rubber (IIR) and natural rubber (NR) vulcanizates, which were 0.5, 1.0, and 2.0 mm thickness. The test device is shown in Figure 4.[4] This device used a porous sintered stainless plate for the support of test sample inside the permeation cell. Additionally, a filter paper was inserted between the test sample and the support medium, and this prevented the deformation of test samples by the pressure. A test sample was installed in the permeation cell. The inside of the device was evacuated first. Thereafter, test gas was introduced into the permeation cell. Measurements were conducted at 1.0, 3.9, and 9.8 MPa of feed gas pressure. Temperatures of the water bath are 25 and 50°C. Changes of the pressure in the high-pressure side and in the low-pressure side were recorded. Gas permeability was calculated as

$$P = (Q \times L)/(\Delta p \times A \times t) \qquad (3)$$

where P is gas permeability (cm^3 cm/cm^2 s cmHg), Q is gas transmission volume (cm^3), L is thickness of test sample (mm), Δp is the pressure of the supply gas in high pressure side (cmHg) (the pressure of low pressure side $\fallingdotseq 0$), A is permeation area (cm^2), and t is testing time (s).

RESULTS AND DISCUSSION

Selection of materials

The results of gas permeability at the normal pressure are shown in Table II. Polymeric materials have a possibility of materials for airtight sheets. Therefore, test samples were selected from the polymer materials. Among polymeric materials, amorphous ones are preferred, because crystalline ones are generally not flexible and not very deformable. Consequently, chlorosulfonated polyethylene (CSM), poly(vinyl chloride) (PVC), and ethylene–vinyl acetate copolymer (EVA) were selected from the plastics, and ethylene–pro-

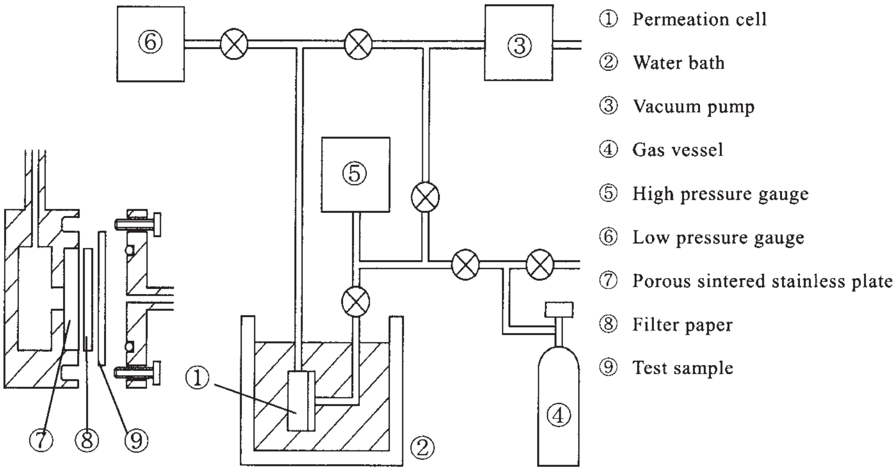

Figure 4 Test equipment of gas permeability at high pressure.

TABLE II
Consideration for Airtight Material on Various Materials

Type	Example of material	Evaluation	Suitability
Inorganic material	Concrete, glass, ceramics	Generally very hard. It cannot cope with the deformation of the surrounding bedrock.	×
Metallic material	Steel	The strain is about 0.2% at the time of yield. It does not follow the deformation of the storage facilities in the compressed air storage.	×
Asphalt material	Asphalt combination material Special asphalt	Construction under ground is difficult.	×
Polymeric material	Synthetic rubber Synthetic resin Synthetic fiber	Promising despite the limited number of previous examples in the area of airtight applications for high-pressure air storage.	○

pylene rubber (EPDM), IIR, chloroprene rubber (CR), and NR were selected from the rubbers. These materials were subjected for the examination. The thicknesses of the sheets are shown in Table III.

Gas permeability at the normal pressure

The results of the selected polymers are shown in Table IV. IIR has the smallest value of gas permeability among seven samples. Based on its chemical structure, it is supposed that the steric hindrance of two methyl groups on a main-chain carbon in IIR prevents gaseous diffusion in the sample. It is noticed that the permeability of nitrogen is smaller than that of oxygen. This behavior is common in gas permeation in polymers, became the former gas has lower solubility and diffusivity in polymer than the latter. It is reasonably assumed that the difference of molecular size affects the diffusivity because the diameter of nitrogen molecule (3.1–3.3 Å) is larger than that of oxygen molecule (2.9 Å).[5] Furthermore, the difference in gas permeability by the thickness of IIR was not recognized. IIR and NR are selected for the high-pressure permeability test because they are estimated to have better barrier properties than the others, as well as excellent mechanical properties.

TABLE III
The Thickness of the Test Sample of Air-Tight Materials

Samples	Thickness (mm) The normal pressure test	 The high pressure test
CMS	3.0	—
PVC	3.0	—
EVA	3.0	—
EPDM	3.0	—
IIR	1.0, 2.0, 3.0	0.5, 1.0, 2.0
CR	3.0	—
NR	3.0	2.0

Gas permeability at high pressure

The results for IIR are shown in Figure 5. The gas permeability of IIR slightly but definitely decreased with increasing pressure up to 10 MPa. This behavior is similar to that of semicrystalline polymers such as low-density polyethylene and polypropylene above glass transition temperature.[6] It is considered that the compression of the test sample by high pressures reduces the distance between polymer chains and impedes the passage of gas molecule through the membrane regardless of being amorphous or semicrystalline. Gas permeability coefficient increased with increasing temperature. It is considered that gas molecules pass through polymer easily because the mobility of polymer and gas molecules increases with increasing temperature.

The results of the NR are shown in Figure 6. Pressures and temperature dependence of gas permeability of the NR show the same tendency as that of IIR. However, gas permeability of NR was about 10–15 times larger than that of IIR. In other words, IIR is the better choice in terms of gas barrier properties.

TABLE IV
Results of Measured Permeability at the Normal Pressure

Material	Thickness (mm)	Gas permeability[a] at the normal pressure [eq. (1)] N_2	 O_2
CSM	3.0	2.18×10^{-11}	1.08×10^{-10}
PVC	3.0	8.02×10^{-11}	2.95×10^{-10}
EVA	3.0	2.02×10^{-10}	4.97×10^{-10}
EPDM	3.0	8.88×10^{-11}	2.36×10^{-10}
IIR	1.0	1.26×10^{-11}	3.79×10^{-11}
	2.0	1.11×10^{-11}	2.17×10^{-11}
	3.0	1.80×10^{-11}	2.18×10^{-11}
CR	3.0	3.62×10^{-11}	1.21×10^{-10}
NR	3.0	3.78×10^{-10}	9.33×10^{-10}

[a] cm^3 cm/cm^2 s cmHg.

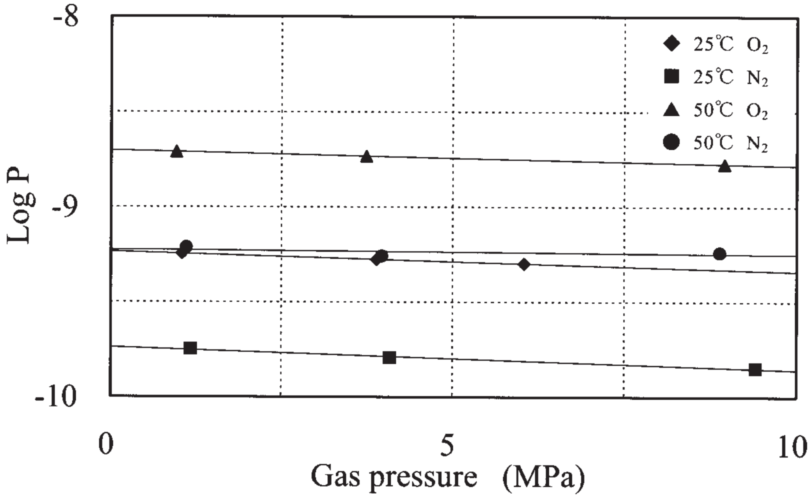

Figure 5 Gas permeability of IIR vulcanizate at high pressures.

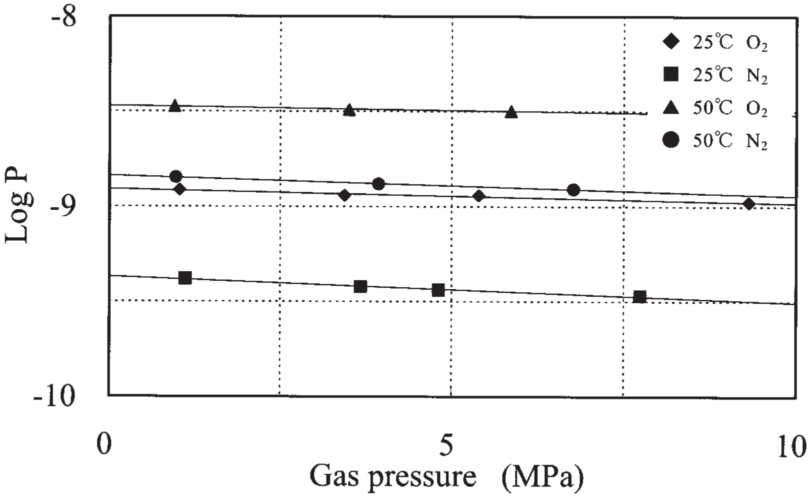

Figure 6 Gas permeability of NR vulcanizate at high pressures.

CONCLUSION

IIR showed the smallest gas permeability among seven polymer samples at both normal and high pressures. Moreover, the gas permeability decreased slightly with increasing pressure up to 10 MPa. IIR is the best gas barrier material among them even at high pressures. Therefore, it is concluded IIR is the best in flexibility, is air-tight, and is best applicable to the lining sheets in a CAES-G/T power-generating system.

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