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PERMEABILITY OF MOLECULAR HYDROGEN AND WATER VAPOR THROUGH BUTYL RUBBER AT AMBIENT TEMPERATURE

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SUMMARY

The preparation of the Safety Analysis Report for the 233-H Replacement Tritium Facility (RTF) requires permeation constants of hydrogen isotopes through butyl rubber, to estimate possible worker exposure given a certain level of tritium in the confinement gloveboxes. Literature values of the permeability constants for hydrogen isotopes and water vapor through butyl rubber at ambient temperature (22-25°C) have been converted to common units and are tabulated (Tables I and II). Permeation rates of tritiated species are the same as that of protium species, within experimental error. Thus, molecular protium and normal water vapor data serve to estimate tritium permeation rates. Because of vendor-to-vendor variability of permeability, especially of water vapor, vendor measurements of water vapor permeability should continue to be used to estimate permeation in SRS processes.

INTRODUCTION

Butyl rubber is the material selected for gloves in the confinement boxes of the 233-H Replacement Tritium Facility (RTF) at the Savannah River Site. It is a good choice for this application because butyl rubber has relatively low permeability to many volatile species, including molecular hydrogen and water vapor[1] and tritium oxide[2]. This report describes results of a literature survey of experimentally determined values of permeability. Methods of calculating flux are described, and the different values of permeability found in the literature are compared. This report does not address the useful lifetime of gloves in the RTF or the radiation damage of butyl rubber gloves by tritium.

Mathematics Of Steady-State Permeation Of Gases Through Polymers

When one side of a polymer membrane is exposed to a species that can permeate through it, the flux, or amount of permeating species exiting the reverse side of the membrane per unit time per unit area, is initially zero. After a time termed the breakthrough time, the exit flux increases with time, and ultimately reaches a maximum steady state value. Steady state permeation of simple gases through polymers is described by[3]:

$$J = \Phi\,(p_1 - p_2)/L \qquad (1)$$

in which J is the flux (quantity of permeating species per unit membrane area per unit time), Φ is the permeability (quantity of permeating species across unit thickness per unit area per unit time per unit pressure drop), p_1 is the partial pressure of the permeating species on the high-pressure side of the membrane, p_2 is the partial pressure of the permeating species on the low pressure side, and L is the thickness of the membrane. The permeability (also termed permeability coefficient) can be calculated using:

$$\Phi = D\,S \qquad (2)$$

where D is the diffusivity (in area per unit time) and S is the solubility (in amount of species contained per unit volume of polymer). The permeability, diffusivity and solubility are material properties; that is, they depend on the state of the material and not on the size or geometry of the membrane or the pressure of the permeating species. These material properties depend on the polymer type and morphology, temperature, diffusing species type, and diffusing species concentration in the polymer. The flux depends on both these material properties and geometrical properties, such as membrane thickness and the partial pressure of the permeating species.

The total quantity of material permeating through a polymer glove (or any polymer part) at steady state is calculated using:

$$\text{Quantity} = J\,A\,t \qquad (3)$$

where A is the total surface area of the glove and t is the time of permeation. Thus, the material property (Φ) is combined with the system properties (p_1, p_2, L, A and t) using Eqs. 1, 2 and 3 to calculate the maximum total quantity of species diffusing through a given glove. The amount of tritiated species in Curies can be found from Eq. 3 using the conversion constant appropriate for the units used.

Literature Values For Molecular Hydrogen And Water Vapor Permeability Through Butyl Rubber

Many units are employed for the quantities in Eqs. 1, 2 and 3. The flux, J, can also be termed the Vapor Transition Rate[4] or Water Vapor Transition Rate[5]. Reports in the literature normally contain information (pressure drop and membrane thickness) enabling calculation of the permeability from the flux. Table I gives values for the permeability Φ of molecular hydrogen through butyl rubber near ambient temperature, after conversion to the dimension:

$$[\Phi] = \frac{\text{cc}H_2\text{-cm}}{\text{cm}^2\text{-s-atm}} \qquad (4)$$

where ccH_2 is cubic centimeters of hydrogen at Standard Temperature and Pressure (273 K, 1 atmosphere or atm). Table II gives similarly converted values for the permeability of water vapor through butyl rubber, near ambient temperature.
Values of hydrogen and water vapor permeability given in Ref. 1 come from other references[6,7]. Also, another source of data[8] cites permeability measurements[9] at ambient temperature and has additional original experimental data for moisture permeability through butyl rubber at 41°C not given in Table II.

Vendor Water Vapor Permeability Values And SRS Specifications

Results of water vapor transmission tests by the vendor of RTF confinement box gloves are also presented in Table II[10]. In converting the values to the given units, 22°C and 50% relative humidity were assumed[5]. These values agree with one of the studies in the literature[11] and are significantly larger than those of other studies[9,12,13,14]. The maximum allowable water vapor permeability value at SRS is also converted and given in Table II[15]. This value is seen to be larger than all of the permeabilities measured in the literature and by the vendor. The butyl rubber gloves have acceptable values of water vapor permeabillity[15].

DISCUSSION

Several investigators have experimentally verified Eq. 1 for many polymers[1,3,8]. Variations in materials properties manifest themselves in variations in the permeability constant. The permeability varies with many factors, and tabulated data should be used cautiously in predicting material behavior in a given application. Some of these factors include the concentration of diffusing species[16], polymer morphology (varied by degree of cross-linking or type and amount of fillers)[13], and temperature[11].

The amount of water soluble in a given polymer is, in general, greater than that of other simple gases such as hydrogen[20]. The solubility of water depends on the type and concentration of hydrophillic and hydrophobic impurities existing in a given polymer blend. It is likely that the variability of measured value of water vapor permeation (Table II) through a given polymer reflect real differences in material structure in nominally similar polymers. (The variability of measured permeabilities for other simple gases through polymers is much less than that of water). The same polymer procured from different manufacturers, or different batches from the same manufacturer, can have differing permeabilities at the same temperature[17]. Vendor permeability measurement[5,10,15] of products being procured by SRS is an effective method of assessing permeation properties.

If vendor measured permeabilities are unavailable for estimation of permeation rates, suggested values for estimating hydrogen and water vapor permeabilities through butyl rubber at 22°C. are: H_2 $\Phi = 0.6 \cdot 10^{-7}$ $ccH_2\text{-}cm/cm^2/s/atm$ and H_2O $\Phi = 15 \cdot 10^{-7}$ $ccH_2O\text{-}cm/cm^2/s/atm$. (Tables I and II). These suggested values fall within the range of values in the tables, and have been reproduced in several investigations.

High pressures (10,000 atm) have also been shown to affect the measured value of permeability[12]. In the RTF, the partial pressure of tritium in the glove boxes will be in the low-pressure range, where permeability is independent of pressure (that is, the steady-state flux is given by Eq. 1 with a pressure-independent permeability Φ). Eq. 1 has been experimentally verified for water vapor permeation through butyl rubber[20].

Investigations of tritiated water (HTO) and molecular tritium (HT) permeation through polymers reveals no significant difference in permeability compared to species having only protium[18]. Protium data can therefore be used to evaluate permeation of tritiated species in polymers.

REFERENCES

1) S. Pauly. "Permeability and Diffusion Data". in *Polymer Handbook*, ed J. Brandrop and E.H. Immergut. Wiley-Interscience, pp.VI/435-VI/449 (1989).

2) C. Wiernicki. *Tritium Oxide Permeation of Ten Glove Materials*. E.I. Du Pont de Nemours & Co. Memorandum HPM-86-100, Savannah River Site, Aiken SC 29808 (July 24, 1986).

3) V. Stannett. "Simple Gases", Chapter 2 in *Diffusion in Polymers*, ed. J. Crank and G.S. Park. Academic Press, pp. 41-73 (1968).

4) ASTM D 314-86. "Standard Test Method for Rubber Property-Vapor Transmission of Volatile Liquids". *1991 Annual Book of ASTM Standards, vol. 9.01*. American Society for Testing and Materials, Philadelphia, PA (1991).

5) ASTM E 96-90. "Standard Test Methods for Water Vapor Transmission of Materials". *1991 Annual Book of ASTM Standards, vol. 4.06*. American Society for Testing and Materials, Philadelphia, PA (1991).

6) G.J. Van Amerongen. *Influence of Structure of Elastomers on Their Permeability to Gases*. J. Poly. Sci. 5(3), pp. 307-332 (1950).

7) P.E. Cassidy, J.M. Aminabhari, and J.C. Brunson. Rubber Chemistry and Tech 56, p. 357 (1983), cited in Ref. 1.

8) J.E. Ayer, D.R. Schmitt and R.M. Mayfield. *Permeation of Water Vapor Through Polymeric Films*. J. Appl. Poly. Sci., 3(7), pp. 1-10 (1960).

9) J.H. Rowan. *Moisture Permeability of Glove Materials for Controlled Atmosphere Boxes*. Analytical Chemistry 28(3), pp. 402-403 (March 1956).

10) North Hand Protection, PO Box 70729, Charleston, SC 29415. Test reports for batch sold to WSRC for RTF.

11) J.M. Kolyer. *Rate of Moisture Permeation Into Elastomer-Sealed Electronic Boxes*. SAMPE Journal, 22(3), pp. 41-44 (May-June 1986).

12) A. Lebovitz. *Effect of High Hydrostatic Pressure on the Permeability of Elastomers to Water*. Rubber Chem. Tech. 39(4), pp. 1298-1307 (1966).

13) P.E. Cassidy, T.M. Aminabhari, and C.M. Thompson. *Water Permeation through Elastomers and Plastics*. Rubber Chemistry and Technology: Rubber Reviews for 1983, 56(3), pp. 594-618 (July-August 1983).

14) C.E. Rogers. "Permeation of Gases and Vapors in Polymers", in J. Comyn, ed., *Polymer Permeability*. Elsevier Applied Science Publishers, Essex, UK, p. 63 (1985).

15) Westinghouse Savannah River Company Manual 5Q1.11, Procedure 101, Rev. 1, Protective Clothing Specifications, section 7.2.2 "Batch Qualification Testing",

paragraph 2 "Water Vapor Permeability". Maximum water vapor transmission rate allowable is 1.5 gram/m^2/day, permeability value calculated for conditions used in Ref. 9.

16) H. Vromans and J.A:H. van Laarhoven. *A Study on Water Permeation through Injection Vials.* Intl. Journ. of Pharmaceuticals, 79(2-3), pp. 301-308 (1992).

17) P. Nau, Equipment Engineering, Savannah River Technology Center, Westinghouse Savannah River Co., private communication 4/29/92.

18) R.H. Steinmeyer and J.D. Braun. *Hydrogen Isotope Permeation In Elastomeric Materials*, in "Radiation Effects and Tritium Technology for Fusion Reactors", Proceedings of the International Conference held at Gatlinburg, TN October 1-3 1975. Conf-750989, ed. J.S. Watson and F.W. Griffen, Volume IV, Oak Ridge National Laboratory, Oak Ridge, TN (March 1976).

19) *O-Ring Handbook.* Precision Rubber Products Corp., Hartmann Drive, Lebanon TN 37087, p. 2-12 (March 1982).

20) D. H. Doughty. The Measurement of Water Vapor Permeability of Glove Materials Using Dilute Tritiated Water. J. Nuclear Materials 103-104, pp. 1595-1600 (1981).

Temperature (°C)	Permeability, Φ ($\cdot 10^{-7}$ $\frac{ccH_2\text{-}cm}{cm^2\text{-}s\text{-}atm}$)	Reference
25	0.55	5
22	0.7	19

Table I.

Steady State Permeability of Molecular Hydrogen Through Butyl Rubber

Temperature (°C)	Permeability, Φ ($\cdot 10^{-7}$ $\frac{ccH_2O\text{-}cm}{cm^2\text{-}s\text{-}atm}$)	Reference
22	3.5	11
~22	5.8 (1 atm pressure)	12
24	5.5 (density 1.21) 4.6 (density 1.21) 7.3 (density 1.06) 5.4 (density 1.06)	8
38	10.0	13
25	0.99	14
23	15.9 37.1	6
22	13 80 16	9 (RTF Vendor Measurements)
22	85	15 (SRS Specification)
39	8.6 6.6	20

Table II.

Steady State Permeability of Water Vapor Through Butyl Rubber

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