Apparatus for determining permeability of hydrogen isotopes in molten-salt (Postprint)

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Abstract

In order to provide data on diffusion coefficients and solubility constants of tritium in molten salts for the critical issue of tritium control in the Thorium Molten Salt Reactor (TMSR) program, a two-chamber permeability apparatus separated by a nickel plate had been developed for determining the permeability of hydrogen isotope in molten salts. Descriptions on the permeability apparatus, experimental procedure and the analytical method for determining the diffusivity and solubility of hydrogen isotope in molten salts were presented in this paper. To assess the performance of the apparatus, the blank tests without molten salt were conducted at 300–700 ℃. The results showed that the nickel plate acting as the window for hydrogen isotope permeation in the apparatus seemed to have less effect on experiments of determining the permeability of hydrogen isotope in molten slat at 500–700 ℃. Furthermore, the applicability of the apparatus with molten salt was also evaluated experimentally, with test experiments of molten Flinak (LiF-NaF-KF) at 500 ℃, 600 ℃ and 700 ℃. Diffusion coefficients and solubility constants of hydrogen in molten Flinak can be derived from those test experiments, which were correlated toDFlinak−H=7.06\$×10$-5e-54.9/(RgT)m2/sandSFlinak-H=$1.67×\$10−7e27.0/(RgT)mol-H2/(m3 Pa).

Full Text

Preamble

Apparatus for Determining Permeability of Hydrogen Isotopes in Molten Salt

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Abstract. To provide data on diffusion coefficients and solubility constants of tritium in molten salts for the critical issue of tritium control in the Thorium Molten Salt Reactor (TMSR) program, we developed a two-chamber permeability apparatus separated by a nickel plate for determining the permeability of hydrogen isotopes in molten salts. This paper presents detailed descriptions of the permeability apparatus, experimental procedures, and analytical methods for determining the diffusivity and solubility of hydrogen isotopes in molten salts. To assess the apparatus performance, we conducted blank tests without molten salt at 300–700 °C. The results showed that the nickel plate acting as the window for hydrogen isotope permeation had minimal effect on experiments to determine hydrogen isotope permeability in molten salt at 500–700 °C. Furthermore, we experimentally evaluated the apparatus applicability with molten Flinak (LiF-NaF-KF) at 500 °C, 600 °C, and 700 °C. From these tests, we derived diffusion coefficients and solubility constants of hydrogen in molten Flinak, which correlated to DFlinak-H = 7.06 × 10−5e−54.9/(RgT) m2/s and SFlinak-H = 1.67 × 10−7e27.0/(RgT) mol-H2/(m3 · Pa).

Keywords: Molten salt, Permeability, Diffusivity, Solubility, Hydrogen isotope
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Introduction

Molten salt systems are widely used in nuclear reactor technology as fuel solvents and heat transfer media due to their advantages of low-pressure operation, radiation stability in liquid phase, sufficient thermal conductivity, and resistance to structural material corrosion. For example, UF4/ThF4-based salts were proposed for molten salt breeder reactors (MSBRs) [1]. Additionally, Flibe, the 2:1 molten mixture of LiF-BeF2, was considered as tritium breeding material in fusion reactors and used in conceptual designs for High-Yield Lithium Injection Fusion-Energy II (HYLIFE-II) [2] and Force-Free Helical Reactor (FFHR) [3]. Another mixed molten salt comprising LiF, NaF, and KF (referred to as Flinak) was proposed as a heat-transfer fluid for molten salt nuclear reactors [4, 5]. The use of molten salts as fuel solvents or heat-transfer fluids is complicated by inherent tritium production as a fission product and through neutron absorption by lithium in the salts. At high temperatures, tritium diffuses through structural materials and may escape to the environment in significant quantities, requiring special consideration in applications [6]. Experimental studies on tritium behavior in molten salts and its permeability through structural materials have been reported [7–15].

In China, research on applying molten salts as fuel solvents and heat-transfer fluids for thorium-based molten salt reactors (TMSR) has been launched, requiring data on the solubility and diffusivity of tritium in fluorine salts and the development of appropriate apparatus designs. The two-chamber design has been applied to determine hydrogen permeability through Flinak molten salt [9], the solubility, diffusivity, and isotopic exchange rates of hydrogen isotopes in Li-Pb [8], and tritium permeation in Flibe [16]. However, limited data are available on the solubility and diffusivity of hydrogen isotopes in molten salts. Furthermore, due to differences in experimental apparatuses, analytical methods, and impurity controls in the salts, literature results are hardly comparable. To obtain valid data on solubility and diffusivity of hydrogen isotopes in molten salts, one must evaluate the performance of the experimental apparatus and analytical method for determining hydrogen isotope permeability. This paper describes the permeability apparatus and analytical method based on the two-chamber concept and evaluates the performance and applicability of the apparatus through blank tests and molten Flinak tests.

Methodology

A. The Permeability Apparatus

A schematic diagram of the apparatus for permeability determination is shown in Fig. 1 Figure 1: see original paper. The system can be divided into functional components: the gas supply system, permeation pot and heating system, diagnostics system, and auxiliary components. The gas supply system delivers uniform flows of research-grade Ar, H2 (D2), or their mixtures with adjustable pressures and flow rates. The heater maintains the permeation pot at a uniform temperature between 500 °C and 700 °C (depending on the molten salt). The diagnostics system measures H2 concentration in the sweeping Ar gas of the permeate side using a gas chromatograph (Shimadzu model GC-2014 coupled with a pulsed discharge helium ionization detector). Auxiliary components include gas delivery systems necessary for experiments, such as gas lines, valves, mass flow controllers, and pressure gauges.

The permeation pot (Fig. 1(b)) is constructed from 316L stainless steel and separated into two chambers by a 2.0-mm thick nickel plate. Both 316L stainless steel and nickel were chosen for their compatibility with the salts of interest. The relatively low diffusion coefficient of hydrogen isotopes in 316L stainless steel at high temperature provides favorable conditions for the nickel plate to serve as an effective window for hydrogen isotope permeation. Penetrations in the 316L stainless steel tubing serve as entrance and exit ports for experimental gases, the molten salt charging port, and the temperature measurement port with a chromel-alumel thermocouple. The charging port is sealed after loading the molten salt, while the temperature measurement port is sealed at its upper end (above the molten salt).

The permeation pot is housed within a larger 316L stainless steel vessel that can be argon-swept or evacuated to minimize effects from hydrogen isotope leakage from the permeation pot. Otherwise, H2 permeating the sidewalls (especially above 500 °C) into the outer vessel could permeate the sidewall again and return to the inner vessel, causing longer times to reach steady-state permeation and higher steady-state H2 concentrations in the downstream Ar gas. Since it was impractical to maintain vacuum in the outer vessel continuously, the inner compartment of the chamber was maintained in Ar gas at atmospheric pressure to protect the salt from contamination by impurities.

B. Experimental Procedures

Under an argon gas atmosphere in a glove box, the upper chamber of the permeation pot was initially charged with molten salt to yield a known liquid thickness (in this case, 20–40 mm) over the specified temperature range. During the heating period, the outer vessel was swept with Ar gas flow or evacuated by a molecular pump while purified Ar gas continuously purged both chambers. During this period, Ar gas swept across the molten salt surface and carried gases released from the molten salt to the diagnostic system for H2 (D2) concentration measurement. When the H2 (D2) concentration in the upper chamber reached zero, H2 (D2) flow was introduced into the lower chamber (upstream side) at constant pressure and flow rate. Meanwhile, Ar gas swept the upper chamber (downstream side) at a constant flow rate (typically ~20 cm^3 (NTP)/min). Hydrogen isotopes diffusing through the molten salt were swept out by the Ar gas and introduced into the diagnostic system for concentration determination, while diffusivity and solubility in the molten salt could be calculated using the one-dimensional diffusion equation discussed in Sec. II C.

After charging hydrogen isotope into the lower chamber, a reversal experiment was conducted under the same operating conditions: H2 (D2) gas was introduced into the upper chamber (upstream side) and the permeating H2 (D2) was swept out by an Ar flow from the lower chamber (downstream side). Surface effects between molten salt, nickel plate, and hydrogen isotope could be investigated by reversing the direction of hydrogen isotope permeation through the molten salt.

C. Theoretical Analysis

Figure 2 [Figure 2: see original paper] graphically illustrates typical models of hydrogen isotope permeation in molten salt: Model a (Fig. 2(a)) for atomic (ionic) migration and Model b (Fig. 2(b)) for molecular migration. The transport mechanism of hydrogen isotopes in molten salt depends on the salt conditions. In molten Flibe, deuterium and tritium diffuse as D+ and T+ species [10]. In molten Flinak, hydrogen diffuses as molecular H2, while H+ ions diffuse when free fluorine ions are present in the salt [9]. In liquid Li-Pb, hydrogen diffusion behavior is based on Li-H binding interactions (the charge state of hydrogen is close to H–) and dissolved hydrogen atoms [17].

The transport process in both models can be described by a one-dimensional diffusion equation for nickel and molten salt:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2}$$

where subscript i denotes nickel or molten salt; c_i and D_i are the molar concentration (in mol/m^3) and diffusivity (in m^2/s) of hydrogen isotope, respectively; x is distance (in m) perpendicular to the nickel plate; and t is time (in s). This is based on assumptions that overall hydrogen isotope permeation is diffusion-limited and the permeation resistance of the nickel plate is much smaller than that of the molten salt layer. These assumptions were verified by experiments with molten Flinak and Flibe using the same permeability apparatus design [9, 16].

The initial and boundary conditions were as follows:

At $t = 0$: c_{Ni} = 0, c_{molten} = 0
At $x = 0$: c_{Ni} = c_{Ni},0 = k_{Ni}P^1/^{2}
At x = L_{Ni}: c_{Ni} = c_{Ni},s = k_{Ni}P^1/^{2}; c_{molten} = c_{molten},s = k_{molten}P^1/^{2} (Model a) or c_{molten} = c_{molten},s = k_{molten}P (Model b)
At x = L_{Ni} + L_{molten}: j = WP_{down} = -D_{molten} c_{molten}/ x

where subscript i denotes nickel or molten salt; L_i is thickness (in m); k_i is solubility constant (in mol/(m^3·Pa^1/^{2}) or mol/(m^3·Pa)); P is hydrogen isotope pressure (in Pa); W is purging gas mole flow rate (in mol/s); A is cross-sectional area (in m^2); and j is hydrogen isotope permeation flux (in mol/(m^2 · s)).

The solutions for steady-state permeation flux (j_{steady}) at the molten salt surface are:

$$j_{steady} = \frac{D_{molten} \cdot k_{molten}}{L_{molten}} \left(\sqrt{P_{up}} - \sqrt{P_{down}} \right) \quad \text{(Model a)}$$

$$j_{steady} = \frac{D_{molten} \cdot k_{molten}}{L_{molten}} (P_{up} - P_{down}) \quad \text{(Model b)}$$

The solutions for transient permeation flux (j_{tra}) are:

$$j_{tra} = \frac{D_{molten} \cdot k_{molten}}{L_{molten}} \left(\sqrt{P_{up}} - \sqrt{P_{down}} \right) \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{(2n-1)^2 \pi^2 D_{molten} t}{4L_{molten}^2} \right) \right] \quad \text{(Model a)}$$

$$j_{tra} = \frac{D_{molten} \cdot k_{molten}}{L_{molten}} (P_{up} - P_{down}) \left[1 + 2\sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{(2n-1)^2 \pi^2 D_{molten} t}{4L_{molten}^2} \right) \right] \quad \text{(Model b)}$$

By fitting the time-dependent variations of transient permeation flux using these equations, the diffusion coefficient of hydrogen isotopes in molten salt can be determined independently. Additionally, the product *D_{molten}* • *k_{molten}* can be determined from the steady-state equations, allowing calculation of the solubility constant.

Results and Discussion

A. Permeation Measurements Without Molten Salt

We investigated H2 permeation through the nickel plate of the apparatus without molten salt at 300–700 °C to verify the apparatus performance and measure the diffusivity and solubility of hydrogen isotopes in the nickel plate for comparison with the molten salt layer's permeation resistance. The experiments charged hydrogen in the lower chamber (upstream) at 1.01×10^5 Pa with a flow rate of 20 SCCM (standard-state cubic centimeter per minute). The upper chamber (downstream) was swept with Ar flows at 1.01×10^5 Pa under the following conditions: 20 SCCM at 300 °C; 20 SCCM at 400 °C; 50 SCCM at 500 °C; 80 SCCM at 600 °C; and 100 SCCM at 700 °C. Simultaneously, the outside vessel was evacuated.

Figure 3 [Figure 3: see original paper] shows the H2 molar flux permeated from the nickel plate. The square data points represent experimental results, while the curves represent numerical calculations using Eq. (1) with nickel replacing the molten salt. The calculations agree well with experimental results at each temperature. By fitting the data in Fig. 3, we determined diffusivity and solubility from the H2 molar flux curves and obtained the product *D_{Ni}-H* • *S_{Ni}-H*, i.e., the hydrogen permeability in nickel.

Figure 4 [Figure 4: see original paper] plots the measured diffusivity, solubility, and permeability values, which correlate to the following Arrhenius equations:

$$D_{Ni-H} = 4.69 \times 10^{-8} e^{-23.9/(R_g T)} \ \mathrm{m^2/s}$$

$$S_{Ni-H} = 59.1 e^{-9.39/(R_g T)} \ \mathrm{mol/m^3}$$

$$P_{Ni-H} = 1.0 \times 10^{-16} e^{-33.3/(R_g T)} \ \mathrm{atom/(m \cdot s \cdot Pa^{1/2})}$$

For comparison, Robertson's correlations [18, 19] for hydrogen diffusivity, solubility, and permeability in nickel are also plotted in Fig. 4. Our diffusion results are comparable with Robertson's data above 500 °C but deviate significantly at 300 °C and 400 °C. The solubility measured in this work is lower than published data across 300–700 °C, with deviation increasing with temperature. This discrepancy may be caused by a surface oxide film on the nickel plate formed during welding. The fact that measured diffusivity and solubility follow Arrhenius relationships demonstrates that the permeability apparatus meets basic requirements for determining hydrogen isotope permeability in molten salt. At 500–700 °C, H2 permeability through the nickel plate agrees closely with reference data, indicating the apparatus is suitable for molten salt working temperatures.

B. Test with Molten Flinak

We conducted experiments on the apparatus to determine H2 permeability in molten Flinak at 500 °C, 600 °C, and 700 °C. Figure 5 [Figure 5: see original paper] shows H2 concentrations in the downstream Ar flow as a function of time. The curves (red lines) calculated by adjusting hydrogen diffusivity and solubility in Eqs. (6)–(9) agree well with experimental data under all conditions except for a small deviation at 500 °C. This disagreement may be due to H+ ion diffusion effects in molten Flinak at 500 °C, potentially caused by mass-transfer processes at the Ni-molten Flinak and Ar gas-molten Flinak interfaces or by impurities in the molten Flinak. However, H+ diffusion effects were limited at lower temperatures, while hydrogen diffusion in molten Flinak at higher temperatures occurred primarily in molecular form. Despite the small deviation at 500 °C, the test results demonstrate that the permeability apparatus and analytical method are applicable for determining hydrogen isotope permeation in molten salts at 500–700 °C.

Table 1 compares the hydrogen diffusivity and solubility in molten Flinak measured at 500 °C, 600 °C, and 700 °C with data from Fukada and Morisaki [9]. Our data correlate to:

$$D_{Flinak-H} = 7.06 \times 10^{-5} e^{-54.9/(R_g T)} \ \mathrm{m^2/s}$$

$$S_{Flinak-H} = 1.67 \times 10^{-7} e^{27.0/(R_g T)} \ \mathrm{mol/(m^3 \cdot Pa)}$$

However, our measured hydrogen diffusivity and solubility in molten Flinak differ significantly from Ref. [9] data. This discrepancy may be attributed to impurity content in molten Flinak, which depends on the salt source and experimental conditions and can chemically react with H+ to change interaction energies between hydrogen and neighboring molecules in the molten salt, thereby affecting diffusivity and solubility under different experimental conditions. Further investigations are needed, and additional tests with hydrogen and deuterium in molten Flinak are in progress at 500–700 °C.

Conclusion

The application of fluorine salts as fuel solvents and heat-transfer fluids for the Thorium Molten Salt Reactor (TMSR) program currently underway in China faces a serious tritium issue, as tritium is produced at high rates in molten salt and causes permeation leakage and structural material corrosion. We have developed a two-chamber apparatus for determining hydrogen isotope permeability in molten salt based on the need for data on tritium solubility and diffusivity in fluorine salts. This paper provides detailed descriptions of the developed permeability apparatus, experimental procedures, and analytical methods for determining hydrogen isotope diffusivity and solubility in molten salt.

We evaluated the performance of the experimental apparatus and analytical method for determining hydrogen isotope permeability in molten salt through blank tests. The nickel plate acting as the window for hydrogen isotope permeation had minimal effect on permeability determination experiments in molten salt at 500–700 °C. We also experimentally evaluated the apparatus applicability with molten salt through tests using molten Flinak (LiF-NaF-KF) at 500 °C, 600 °C, and 700 °C. From these tests, we derived diffusion coefficients and solubility constants of hydrogen in molten Flinak, which correlated to $D\_\{Flinak\}\text{-}H = 7.06\$\times 10^{\{\text{-}5\}e}\{\text{-}54\}^{.\{9\}/(RgT)m}\{2\}/sand * S_{Flinak} - H* = 1.67\times 10^{\{\text{-}7\}e}\{27\}^{.\{0\}/(RgT)mol - H2/(m}\{3\}\$ \cdot \mathrm{Pa})$. However, large discrepancies exist between our data and previous literature values for hydrogen diffusivity and solubility in molten Flinak, possibly due to impurities in the molten salt that require further investigation.

References

[1] Grimes W R. Nucl Appl Technol, 1970, 8: 137–155.
[2] Moir R W, Bieri R L, Chen X M, et al. Fusion Technol, 1994, 25: 5–25.
[3] Sagara A, Motojima O, Watanabe K, et al. Fusion Eng Des, 1995, 29: 51–56.
[4] Hoffman H W. ORNL Technical Report, CF-53-8-106, 1953.
[5] Sherman S R. 2005 DOE H2 Annual Review, Project ID # PD31, 2005.
[6] Briggs R B. Reactor Technol, 1971–1972, 14: 335–342.
[7] Fukada S. J Plasma Fusion Res SERIES, 2013, 10: 22–26.
[8] Maeda Y, Edao Y, Yamaguchi S, et al. Fusion Sci Technol, 2008, 54: 131–134.
[9] Fukada S and Morisaki A. J Nucl Mater, 2006, 358: 235–242.
[10] Anderl R A, Fukada S, Smolik G R, et al. J Nucl Mater, 2004, 329–333: 1327–1331.
[11] Nishimura H, Suzuki A, Terai T, et al. Fusion Eng Des, 2001, 58–59: 667–672.
[12] Suzuki A, Terai T, Tanaka S. J Nucl Mater, 1998, 258–263: 525–529.
[13] Terai T, Suzuki A, Tanaka S. Fusion Technol, 1996, 30: 911–915.
[14] Terai T, Suzuki A, Tanaka S. J Nucl Mater, 1997, 248: 159–163.
[15] Reimann J. Fusion Eng Des, 1991, 14: 413–425.
[16] Calderoni P, Sharpe P, Hara M, et al. Fusion Eng Des, 2008, 83: 1331–1334.

[17] Masuyama D, Oda T, Fukada S, et al. Chem Phys Lett, 2009, 483: 214–218.
[18] Robertson W E. Z Metallkd, 1973, 64: 436–443.
[19] Reiter F, Forcey K S, Gervasini G. EUR-15217-EN, 1993.

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