Journal of Nuclear Materials 447 (2014) 304–313

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Isotope exchange between gaseous hydrogen and uranium hydride powder ☆

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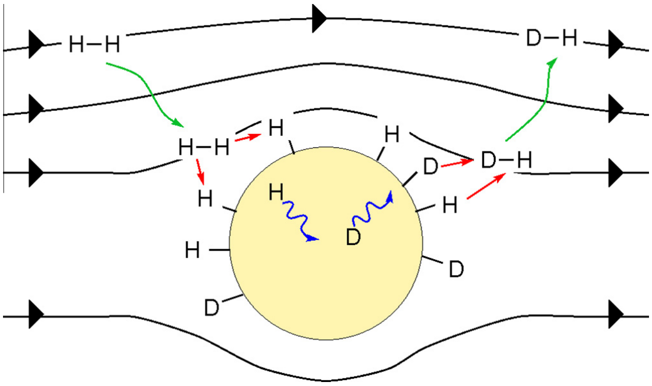
HIGHLIGHTS

- Isotope exchange between hydrogen gas and uranium hydride powder can be rapid and reversible.
- Gas–solid exchange rate is controlled by transport within ~0.7 μm hydride particles.
- Gas chromatographic separation of hydrogen isotopes using uranium hydride is feasible.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 May 2013
Accepted 18 September 2013
Available online 25 September 2013

ABSTRACT

Isotope exchange between gaseous hydrogen and solid uranium hydride has been studied by flowing hydrogen (deuterium) gas through packed powder beds of uranium deuteride (hydride). We used a residual gas analyzer system to perform real-time analysis of the effluent gas composition. We also developed an exchange and transport model and, by fitting it to the experimental data, extracted kinetic parameters for the isotope exchange reaction. Our results suggest that, from approximately 70 to 700 kPa and 25 to 400 °C, the gas-to-solid exchange rate is controlled by hydrogen and deuterium transport within the ~0.7 μm diameter uranium hydride particles. We use our kinetic parameters to show that gas chromatographic separation of hydrogen and deuterium using uranium hydride could be feasible.

1. Introduction

Hydrogen isotope separation is a necessary operation in facilities that handle and process mixtures of hydrogen, deuterium, and tritium; including light/heavy water nuclear power plants [1], tritium production and recycling facilities [2], and proposed thermonuclear power plants [3]. In facilities where large quantities of gaseous tritium are present, it can be advantageous to perform the separation operations in the gas phase, and thereby avoid the additional radiological hazards associated with tritiated water. Various gas phase separation methods have been considered including: cryogenic distillation [2,4,5], thermal diffusion [1,2], membrane permeation [6], and varied techniques using metal hydride beds [2,7–9].

Of the common metal hydrides, palladium has received the most attention [10–21] and is the most widely used [2,22–26]. Uranium hydride can store more hydrogen per unit volume than palladium and can do so with lower gaseous overpressures; consequently it is widely used for hydrogen isotope storage. These

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http://dx.doi.org/10.1016/j.jnucmat.2013.09.037

properties could also have practical benefit in a separation system. However, to design an optimal separator, one must know the rates of adsorption and desorption of each isotope as a function of operating conditions such as pressure, temperature, and mole fraction. Previous studies of isotopic exchange between gaseous hydrogen and solid uranium hydride [27–29], have not produced the needed kinetic data. This may be why uranium hydride, a commonly used hydrogen isotope storage material, has received little attention as an isotope-separation material.

In this paper, we present the first quantitative and experimentally validated model of isotope exchange between gaseous hydrogen and uranium hydride powder. We have performed a set of hydrogen–deuterium isotope exchange tests on a uranium hydride fixed-bed reactor at temperatures between 25 and 400 °C. We extract the kinetic parameters from these tests by fitting an exchange and transport model to the experimental measurements. Our results suggest that the gas-to-solid exchange rate is controlled by hydrogen and deuterium transport in the $\sim$0.7 μm diameter uranium hydride particles. We compare our effective diffusion coefficients with results from earlier gas–solid isotope exchange studies [29], and nuclear magnetic resonance investigations [30,31]. Finally, we use our kinetic parameters to show that a gas chromatographic hydrogen–deuterium separation system based on uranium hydride could be feasible.

2. Methods – Experiment

In general, our experiments (exchange tests) involve flowing either pure H_2 or pure D_2 gas through a porous UD_3 or UH_3 bed and collecting the effluent gas. We monitor the reactor effluent composition using a real-time residual gas analyzer (RGA). Initial bed temperatures are controlled and held between 25 and 400 °C. During a test, approximately 1.4 times more gas flows through the bed than is contained within the solid hydride.

2.1. Apparatus and test procedure

This article's supporting information, [32], contains a detailed description of the apparatus and procedures used in this work. In essence, the apparatus consists of a 45.0 cm^3 source volume, gas pre-heater, uranium hydride fixed-bed reactor, RGA sampling tee, and 166.7 cm^3 receiver volume. Pneumatic valves isolate the source and receiver volumes from the other components.

Prior to a test, the source volume is filled with pure H_2 or D_2 to approximately 1.93 MPa (280 psia); gas purities are given in [32]. When the pneumatic valves open, gas flows from the source volume, through the pre-heater, and into the reactor. Upon exiting the reactor, gas flows through the RGA sampling tee (past a crimped-capillary sampling probe), and into the receiver volume. The final system-equilibrium pressure, which is reached after about 100 s, is approximately 520 kPa (75 psia).

Pressures and temperatures are measured continuously during a test (the instruments are specified in [32]). The reactor effluent flow rate is computed from the receiver pressure–volume–temperature (PVT) data, using a first-order backward-differencing scheme with a 0.75 s time-step.

We also record the RGA ion-current signals. These are converted to mole fractions using methods described in [33]. Calibrations with known $H_2 + HD + D_2$ mixtures showed that the RGA-derived mole fractions are accurate to ±1 mol% for upstream pressures above 34 kPa (5 psia) [33].

Earlier work [33] showed that the RGA's transient response is well approximated by a single-pole low-pass filter. When responding to a step change in hydrogen isotope mixture composition, the RGA requires 2.0 s to reach 90% of the steady-state value. The impact of this transient response on our mole fraction measurements is discussed more fully in Section 4.

At the end of a test, a portion of the receiver gas was collected and analyzed with a calibrated mass spectrometer (MS). The measured gas composition and measured pressure, volume, and temperature were used to compute the amount of H and D in the collection volume. These are compared to the amount of isotope stored on the hydride bed, yielding the extent of bed conversion.

Our PVT measurements were validated by mass closure checks. The apparatus is a closed system and the uranium hydride bed remains fully loaded under these conditions (i.e., it is always $U(H + D)_3$). Consequently, the total moles of gas in the system should be constant. We found this to be true to within the specified uncertainty of our instruments. Our measurements were able to account for all but 2–3% of the total gas used in any test. This implies that the accuracy of our bed conversion measurement is about ±5% (±3% uncertainty from mass closure errors and ±2% uncertainty from MS analysis errors). Repeat-tests have shown that the precision (repeatability) of bed conversion measurement is somewhat better, approximately ±1%.

Multiple exchange tests were run on the reactors. Following an exchange test, two or three additional exchange sweeps were performed at 250 °C to reset the bed to a single isotope in preparation for the next test. The reactor overpressure was sampled after the reset sweeps to confirm that the bed was indeed a single isotope.

In this paper we present results from one individual reactor. Between the first test, $UD_3 + H_2$ at 250 °C and the final test, a repeat of $UD_3 + H_2$ at 250 °C, the bed was swept 37 times. Between tests 1 and 37, the bed's global exchange rate (the bed's overall rate of

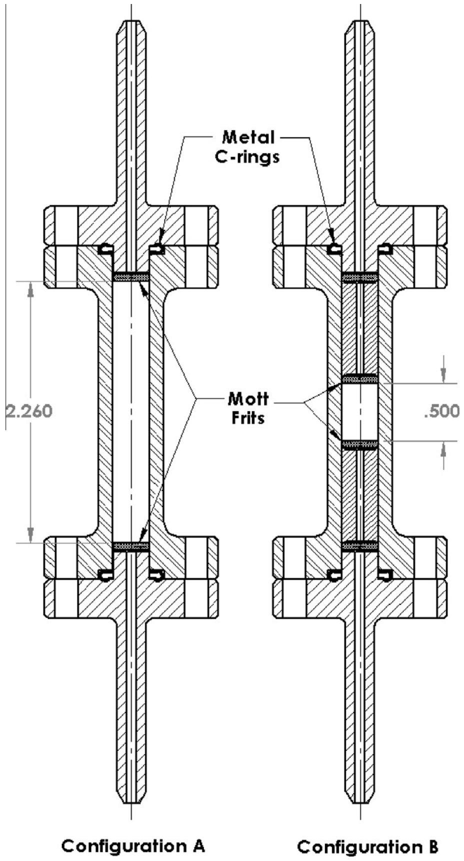

Fig. 1. Uranium hydride reactor assembly (dimensions are in inches). Reactor is in configuration A for loading uranium metal pieces and their decrepitation to hydride powder. Following this, the frits are pressed to 0.500 inch separation, and then spacers and secondary frits are installed (configuration B).