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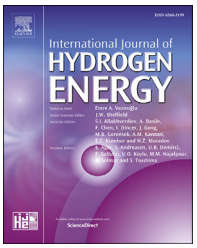

Adsorption kinetics on the recovery of hydrogen isotopes from helium using palladium particle bed

K.C. Sandeep [a,c], Sarika S. Shinde [a], Krunal Mistry [a], Kalyan Bhanja [a], Sadhana Mohan [a], D. Mandal [b,c], Sanjay Mahajani [d,*]

[a] Heavy Water Division, Bhabha Atomic Research Centre, Mumbai, India
[b] Alkali Materials and Metal Division, Bhabha Atomic Research Centre, Mumbai, India
[c] Homi Bhabha National Institute, Mumbai, India
[d] Department of Chemical Engineering, Indian Institute of Technology, Bombay, Mumbai, India

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ABSTRACT

The recovery and separation of hydrogen isotopes from helium purge gas is one of the critical steps in nuclear fusion based fuel cycle. In the present study, the adsorption kinetics of hydrogen and deuterium from helium using palladium particle bed is generated at different temperatures varying from 30 °C to 150 °C in a recirculating packed bed batch adsorption system. The system is modeled as a combination of packed bed adsorber and a mixing vessel connected in closed loop. The overall mass transfer coefficient is estimated at different temperatures by minimizing the error between the simulated results and the experimental data. The apparent activation energy is estimated for both the hydrogen isotopes using Arrhenius plot. Based on the estimated values of apparent activation energies, it is concluded that the overall adsorption rate is limited by internal diffusion for both hydrogen and deuterium.

Introduction

The recovery and separation of hydrogen isotopes from helium purge gas is one of the critical steps in the sustained operation of International Thermonuclear Experimental Reactor (ITER) [1–3]. The different methods reported in literature for this purpose are oxidative adsorption, cryogenic distillation, membrane separation and adsorption [4,5]. In oxidative adsorption, the hydrogen isotopes are converted to their respective water form and adsorbed. Subsequently, the water is converted into gaseous hydrogen isotopes by electrolysis, water gas shift reaction or reduction in the presence of metals like Mg [6–8]. This is a multi-step process and the major limitation of this process is the conversion of useful form of diatomic hydrogen isotopes into less useful water form. Moreover, the tritiated water is more hazardous than tritium in gaseous state. In cryogenic distillation, the operating temperature is very low (~20 K), which results into a highly energy intensive process for this application [9–11]. Moreover, the presence of impurities such as nitrogen, water vapor or oxygen in the helium purge gas can cause freezing in the pipelines and this may eventually lead to plugging of the lines. The membrane separation process using palladium

* *Corresponding author.*
E-mail address: sanjaym@iitb.ac.in (S. Mahajani).
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Nomenclature

a	Interfacial area per unit volume of bed $m^2\,m^{-3}$
$C_{i,b}$	Concentration of species i (hydrogen or deuterium) in helium in the bed $mol\,m^{-3}$
$C^*_{i,b}$	Equilibrium concentration of species i (hydrogen or deuterium) in helium in the bed $mol\,m^{-3}$
$C_{i,m}$	Concentration of species i (hydrogen or deuterium) in helium in the mixing vessel $mol\,m^{-3}$
$C_{i,m,initial}$	Initial concentration of species i (hydrogen or deuterium) in helium in the mixing vessel $mol\,m^{-3}$
$C_{i,m_{exp}}$	Experimental concentration of species i (hydrogen or deuterium) in helium in the mixing vessel $mol\,m^{-3}$
d_p	Diameter of the particle m
Di	Internal diffusivity of species i (hydrogen or deuterium) in solid phase $m^2\,s^{-1}$
$D_{i,M}$	Diffusivity of species i (hydrogen or deuterium) in Helium $m^2\,s^{-1}$
D_o	Pre exponential factor for internal diffusivity $m^2\,s^{-1}$
E_D	Activation energy for diffusivity $J\,mol^{-1}\,K^{-1}$
$K_{c,i}$	Overall mass transfer coefficient for species i (hydrogen or deuterium) ms^{-1}
$k_{f,i}$	External mass transfer coefficient for species i (hydrogen or deuterium) ms^{-1}
$k_{r,i}$	Dissociation rate constant for species i (hydrogen or deuterium) ms^{-1}
$k_{s,i}$	Internal mass transfer coefficient for species i (hydrogen or deuterium) ms^{-1}
m	Average slope of equilibrium curve Dimensionless
M_{Pd}	Molecular weight of palladium $mol\,g^{-1}$
N_{exp}	Number of experimental data points Dimensionless
$p^*_{H_2}$	Equilibrium partial pressure for hydrogen atm
$p^*_{D_2}$	Equilibrium partial pressure for deuterium atm
q_i	Mol of atomic species i (hydrogen or deuterium) adsorbed per kg of Pd $mol\,kg^{-1}$
Q_b	Volumetric flow rate through the bed $m^3\,s^{-1}$
r_{ads}	Rate of adsorption species i (hydrogen or deuterium) $mol\,m^{-3}\,s^{-1}$
R_p	Radius of particle m
R	Universal gas constant $J\,mol^{-1}\,K^{-1}$
R^2	Coefficient of determination Dimensionless
$SS_{residual}$	Sum of Square of residuals Dimensionless
SS_{total}	Total sum of squares Dimensionless
t	Time s
T	Temperature K
u	Superficial velocity through bed ms^{-1}
V_b	Bed volume m^3

Greek letters

ε_b	Bed void fraction Dimensionless
ρ	Density of gas mixture kgm^{-3}
ρ_b	Bulk density of the bed kgm^{-3}
$\sigma^2(C_{i,m_{exp}})$	Variance Dimensionless

Suffix

i	Species hydrogen or deuterium
m	Mixing vessel
b	Adsorber bed

based alloys shows high selectivity for hydrogen isotopes [12–14]. However, the process is limited by the low permeation flux at relatively low partial pressures of hydrogen isotopes as in the present case, which may lead to a large permeation area and less compact system. The operating temperature in Pd based membrane is also as high as 400 °C. The permeability of hydrogen isotopes is an exponentially increasing function of temperature and this can cause significant permeation issues of tritium through structural materials at higher temperatures [15,16]. This may result in tritium loss from the system leading to high environmental impact by providing higher dose to the personnel working in this environment [17]. In case of adsorption process, there are various reported literature, indicating the different studies by either using physical adsorbents such as molecular sieves, activated carbon or using materials which form metallic hydrides, such as U, Ti, Zr, Zr-Ni, ZrV_2 and Zr-Co [18–29]. In physical adsorption process, the adsorption capacity for hydrogen isotopes at room temperature is relatively low and in order to achieve reasonably good adsorption capacity, the bed has to be operated at low temperature close to 77 K, leading to intensive energy demands. Among the metallic hydride based materials, the selection is generally done based on the available equilibrium capacity at relatively low partial pressures of hydrogen isotopes and good adsorption kinetics even at ambient temperature. Moreover, in general, the helium purge gas contains the impurities such as O_2, H_2O, CO, CO_2 and hydrocarbons. The adsorbent should be compatible with the above impurities. The preferred operating temperature of the adsorber bed is close to ambient temperature so as to minimize the tritium permeation issues. Among the above hydriding materials, uranium and zirconium alloys were used at relatively mild operating temperatures (<200 °C), where as zirconium, titanium and yttrium have to be operated at higher temperatures (400 °C) [30]. Fukada et al. have studied the recovery of hydrogen isotopes from argon gas using yttrium and titanium particle bed [30,20]. Tanabe et al. and Shmayda et al. have reported the recovery of hydrogen isotopes using uranium [27,28]. Nobuo et al. investigated the performance of Zr_3Al_2 particle bed using H_2-Ar gas mixture to recover hydrogen [24]. Ashida et al. reported that, in many of the reported candidate materials, such as U, Zr-Ni, Zr-Al and Zr-Co, the oxidation and carburization can decrease the adsorption and desorption kinetics and the coating of palladium is effective to minimize the effect of these impurities in helium [21]. Moreover, the operating temperature for palladium bed is close to ambient and the separation factor for hydrogen isotopes among themselves on Pd is also higher in comparison to

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