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ScienceDirect

Fusion Engineering and Design 83 (2008) 39–44

Fusion Engineering and Design

www.elsevier.com/locate/fusengdes

Determination of the order of surface reactions in Li_2O

A. Badawi

Nuclear Engineering Department, Alexandria University, Egypt

Received 28 September 2006; received in revised form 22 April 2007; accepted 1 May 2007
Available online 21 June 2007

Abstract

An analysis of the different surface reactions taking place in Li_2O was performed in order to determine whether adsorption and desorption of tritium are first or second order reactions. Data from BEATRIX-II Phase I and CRITIC-I were used as basis for calculations.

It was found that only second order adsorption/desorption on the surface of Li_2O can predict the tritium behavior observed experimentally.

Keywords: Li_2O; Adsorption; Desorption; Surface processes

1. Introduction

Lithium oxide is considered to be one of the candidate solid breeder materials for blankets in D–T fusion reactors. Therefore it is important to fully understand the release behavior of the tritium bred inside this material. This is not an easy task because of the complexity of processes occurring inside the grains, on the grain surfaces and inside the pores [1]. Among these processes, different surface reactions (such as adsorption, desorption and dissolution) need to be accurately described in order to determine the tritium release and inventory in Li_2O.

One of the problems that face modeling is that no experimental results are present to determine the order of surface adsorption and desorption processes in solid breeder materials, with the exception of $LiAlO_2$ [2]. This led some models to consider them to be second order [3], while others use empirical equations to overcome this problem [4]. Some theoretical work was done to analyze the surface reactions in Li_2O [5]. However, this work assumed the reactions were second order and did not investigate first order reactions.

In this paper the order of the surface reactions is investigated to examine how it affects the steady state tritium inventories in the grain and on the surface at different conditions, thus deducing the correct order of surface adsorption and desorption.

2. The tritium inventory

The tritium inside Li-based breeders is divided mainly into two components: the surface inventory and the grain inventory, which is usually due to the tritium diffusion inside the grain. In Li_2O, an additional factor contributes to the grain inventory. This is the trapping of tritium atoms in the form of LiOT inside the grains.

2.1. The surface inventory

The surface inventory is controlled by four processes occurring on the surface. These are:

1. Adsorption of the atoms from the pore to the surface of the grains. The flux, R_{ads} is equal to [6]:

$$R_{ads} = k_{ads,i}\frac{C_p}{\sqrt{M}}(1-\theta)^i \tag{1}$$

$$k_{ads,i} = \frac{\sigma z}{\sqrt{8\times 10^{-3}\pi}}\sqrt{RT}\exp\left(\frac{-iE_{ads}}{RT}\right) \tag{2}$$

where C_p is the concentration of the adsorbed species in the pore, θ is the total surface coverage (i.e. the fraction of filled surface sites). The term $(1-\theta)$ represents the number of empty sites available for adsorption. E_{ads} is the activation energy of adsorption, R is the universal gas constant, T is the temperature, σ is the sticking coefficient, z is the number of sites adjacent to each atom and M is the molecular weight of

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E-mail address: alyabadawi@yahoo.com.

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doi:10.1016/j.fusengdes.2007.05.001

the adsorbing gaseous species. $i = 1$ for first order reactions and $i = 2$ for second order reactions.

2. Desorption of atoms from the surface to the pore. The desorption flux, R_{des}, is equal to [6,7]:

$$R_{\mathrm{des}} = k_{\mathrm{des},i}\theta_j^i \tag{3}$$

$$k_{\mathrm{des},i} = \frac{RN_s zT}{A_v h}\exp\left(\frac{-iE_{\mathrm{des}}}{RT}\right) \tag{4}$$

where E_{des} is the activation energy of desorption, θ_j the surface coverage of the desorbing species (j), N_s the number of sites on the surface of the grain, A_v the Avogadro's number, and h is the Planck's constant.

3. Dissolution of atoms from the surface to the grain. This flux, R_{diss}, is equal to [8]:

$$R_{\mathrm{diss}} = k_{\mathrm{diss}}\theta_j \tag{5}$$

$$k_{\mathrm{diss}} = \frac{RN_s zT}{A_v h}\exp\left(\frac{-E_{\mathrm{diss}}}{RT}\right) \tag{6}$$

E_{diss} is the activation energy for dissolution.

4. A flux of atoms, R_β, going from the grains to the surface [6]:

$$R_\beta = k_\beta C_b(1-\theta) \tag{7}$$

$$k_\beta = \frac{1\times 10^{13}}{\sqrt{N_s}}\exp\left(\frac{-E_\beta}{RT}\right) \tag{8}$$

where C_b is the tritium concentration in the grains just below the surface and E_β is the activation energy for adsorption from the bulk to the surface.

The tritium surface inventory, I_s, is related to the tritium surface coverage, θ_T, by

$$I_s = \theta_T N_s S_{\mathrm{BET}}\rho V_{\mathrm{br}}(1-\varepsilon) \tag{9}$$

where V_{br} and ε are the breeder volume and porosity, respectively, ρ is the theoretical density of the Li_2O and S_{BET} is the total BET surface area.

2.2. The grain inventory

The tritium inventory is divided into two parts: the inventory due to tritium diffusion and that due to trapping as LiOT:

The tritium inventory, I_D, due to diffusion is equal to [9]:

$$I_D = \left[C_b + \frac{gr_g^2}{15D}\right]V_{\mathrm{br}}(1-\varepsilon) \tag{10}$$

where g is the rate of tritium generation, r_g is the grain radius and D is the diffusion coefficient of tritium. The tritium inventory, I_{tr}, due to trapping is equal to [9]:

$$I_{\mathrm{tr}} = \left[C_b + \frac{gr_g^2}{15D}\right]\frac{k_{\mathrm{for}}}{k_{\mathrm{dsn}}}V_{\mathrm{br}}(1-\varepsilon) \tag{11}$$

where k_{for} and k_{dsn} are the reaction rate constants for formation and dissociation of LiOT [8]. Eqs. (10) and (11) can be combined together to give

$$I_g = \left[C_b + \frac{gr_g^2}{15D}\right]V_{\mathrm{br}}(1-\varepsilon)(1+K_{\mathrm{eq}}) \tag{12}$$

where I_g is the tritium inventory inside the grain due to both diffusion and LiOT formation. K_{eq} is the equilibrium constant for the reaction $2LiOH = Li_2O + H_2O$ [8].

3. Surface coverage and grain concentration

As seen from Eqs. (9) and (12), both the grain and surface inventories depend on the tritium surface coverage and tritium concentration in the grain. These in turn depend on the surface reactions. As will be shown, whether adsorption and desorption are first or second order reactions will greatly influence the tritium behavior and inventory on the surface and inside the grains.

Some observations were made when performing the following analysis. The first is that when protium is added to the purge gas, most of it is found in the form of H_2, whereas most of the tritium is found in the form of HT [10]. This is due to the fact that the amounts of tritium are much less than those of protium. This is also the reason why the surface coverage of the protium is usually much larger than that of the tritium [5]. These observations can be used to make the following assumptions:

1. $C_{\mathrm{pH2}} \gg C_{\mathrm{pHT}}$;
2. $C_{\mathrm{pHT}} \gg C_{\mathrm{pT2}}$;
3. $\theta_H \gg \theta_T$, or $\theta_{\mathrm{tot}} \approx \theta_H$.

where θ_{tot}, θ_H and θ_T, are the total, protium and tritium surface coverage, respectively.

The analysis was based on obtaining expressions for θ_T and C_b using first and second order surface reactions and steady state conditions. This was done using the three assumptions mentioned above in addition to the following equations:

$$R_{\mathrm{des,T}} - R_{\mathrm{ads,T}} = g \tag{13}$$

and

$$R_{\mathrm{diss}} - R_\beta = g \tag{14}$$

For steady state tritium generation and release, the following equations were obtained for first order surface reactions:

$$\theta_T = \frac{1}{k_{\mathrm{des},1}}\left[g + k_{\mathrm{ads},1}\frac{C_{\mathrm{pT}}}{\sqrt{M_{\mathrm{HT}}}}(1-\theta_{\mathrm{tot}})\right] \tag{15}$$

$$C_b = \frac{g + k_{\mathrm{diss}}\theta_{\mathrm{tot}}}{k_\beta(1-\theta_T)} \tag{16}$$

And for second order reactions:

$$\theta_T = \frac{g + k_{\mathrm{ads},2}(C_{\mathrm{pT}}/\sqrt{M_{\mathrm{HT}}})(1-\theta_H)^2}{k_{\mathrm{des},2}\theta_H} \tag{17}$$