ISSN : 0974 - 7443 Volume 10 Issue 1
CHEMICAL TECHNOLOGY
An Indian Journal
Full Paper
CTAIJ 10(1) 2015 [001-017]

Heat transfer study of a uranium based getter bed for hydrogen storage

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ABSTRACT

Adsorption of hydrogen on a metal getter bed in the form of a reversible metal hydride is one of the most compact methods of storing hydrogen. Heat transfer analysis of a uranium based getter bed for storage of small quantities of hydrogen (upto 5 gm) has been performed in this work. The storage bed has been considered as a batch reactor with an initial charge of hydrogen and uranium. The optimal bed dimensions for a given quantity of hydrogen have been determined. The temperature-time characteristics of the tubular bed in both horizontal and vertical orientation have been evaluated through a simplified analysis. Inside the vessel the main radial heat transfer mode is taken as conduction since the gas inside is stagnant while from the outer surface of the vessel heat losses due to natural convection and radiation have been considered. A combination of dynamic and pseudo-steady state heat transfer analysis has been used in the study to derive suitable linearised expressions for the multi-modal heat loss rate from the bed during hydriding.

KEYWORDS

Hydrogen storage;
Uranium;
Getter bed;
Hydriding;
Batch reactor;
Natural convection;
Dynamic model.

INTRODUCTION

The storage of hydrogen in the form of a metal or alloy hydride has been proven to be a very effective and compact technique for both stationary and mobile applications[1]. For storage of hydrogen, a wide variety of different hydride forming metals and alloys have been extensively studied. Uranium metal is one such material studied, mainly because of its favorable thermodynamic and kinetic properties with respect to hydriding and dehydriding reactions[2,3]. Low temperature operations are favored during hydriding because of the low equilibrium pressure of hydrogen over uranium at low temperatures, thus enabling a safe and compact storage method. But above ambient temperatures allow us to take advantage of faster reaction kinetics and hence quicker hydriding operation.

In the present work, a simplified heat transfer analysis of a getter bed for storing small quantities (i.e. up to 5 gm) of hydrogen in the form of uranium hydride is carried out. More detailed thermal analyses have recently been reported in literature[4,5,6] but a simple gross analysis of the system can also yield useful design information without compromising on accuracy, as demonstrated in this work. The optimal bed dimensions (i.e. the length to diameter ratio) for a given quantity of hydrogen to be stored are evaluated and the dynamic heating and cooling performance of the vessel is studied through a simple

model. This model predicts the time-temperature characteristics of the bed during hydriding reaction phase. It is shown here that for small quantities of hydrogen to be stored in properly designed and insulated beds, special forced cooling arrangements for the getter bed is not necessary as convective and radiation losses can be significant and hence sufficient to prevent excessive surface temperature rise during hydriding reaction.

DESIGN BASIS CALCULATIONS FOR A HYDROGEN STORAGE GETTER BED

The hydriding process is represented by the following chemical reaction[7]:

$$U + 1.5H_2 = UH_3, \quad \Delta H_{Rx} = 97.5 \text{ kJ mol}^{-1} H_2 \qquad (1)$$

This reaction is used to estimate the stoichiometric quantity of uranium necessary for storing a given amount of hydrogen. The mass of solid actually to be loaded into the vessel is decided by the percentage loading of hydrogen on uranium, which is taken as 60% in this work. Thus hydrogen is allowed to be the limiting reactant. The volume expansion of uranium and change in powder density on hydriding are considered in estimating the maximum solid volume. The design pressure is selected as 60 bar (a) and design temperature is taken as 800 K. The highly conservative value of design pressure is selected for a compact system and also for enabling the vessel to withstand stresses and accidental mechanical impact during transportation. At the maximum design temperature of 800 K, the equilibrium dissociation pressure of hydrogen over uranium is about 8 bar (a) only[12]. So even at this temperature the pressure will never rise to 60 bar (a) as considered in the design. This determines the gas volume as the number of moles of gas is fixed. The vessel volume thus consists of the solid volume and the gas volume taken together. Considering an initial temperature of 300 K, this corresponds to an initial fill pressure of 22.5 bar (a) in the vessel for all cases considered here.

The pyrophoricity of metallic uranium causes difficulties in handling it in the open. Depending on the particle size of the metal there is a particular ignition temperature. Thus for handling uranium turnings in the open (i.e. at ambient temperature) they should have a size greater than 1.6 mm (1600 micron), based on correlations available in literature[8]. In this work, uranium turnings with dimensions greater than or equal to 1.6 mm have been considered.

Once the vessel volume is fixed, the dimensions i.e. the diameter, height and wall thickness are determined. In this study, the getter bed studied is designed to lose heat by natural convection and radiation without any provision of forced circulation cooling, since it is expected that there would be only small heat effects associated with the small amounts of hydrogen are to be loaded on to it. Thus the available heat transfer area is an important design parameter and it depends on the value of the length to diameter ratio chosen for the bed. The selection of the length to diameter ratio for the storage vessel is governed by factors like the chosen bed configuration (horizontal or vertical), batch operation or recirculation operation and the heat transfer area available at different length to diameter ratios. For batch operations, a shallow bed which presents greater surface area of the solid to the gas for adsorption and for recirculation mode operations, a narrow diameter vessel which allows for higher superficial gas velocity through the bed and better heat removal are recommended. The bed height or length should be sufficient to allow external heating coils or tapes to be wound properly while the diameter should be sufficient to allow nozzles for gas inlet and outlet ports, ports for thermocouples to be placed on the top closure. For horizontal vessels with recirculation of gas, inlet and outlet ports have to be on opposite ends of the vessel, while in vertical vessels they can both be on one side. With all these considerations, an L/D ratio of 2 to 3 is generally taken to be most favourable and the value of 2.0 is chosen for all the calculations reported in this work unless otherwise stated.

The bed considered in this study is designed to operate in such a way that a certain known amount of hydrogen can be introduced into it and it can be allowed to react with the getter material till the pressure drops to the equilibrium pressure at the operating temperature. At this point the reaction stops and

TABLE 1 : Algorithm for design calculations and simulation of the hydrogen storage getter bed

Step	Calculation
1	The mass of hydrogen to be stored in the getter bed is fixed.
2	60% of stoichiometric loading of the getter material (i.e. uranium) by hydrogen is assumed.
3	Mass of uranium required for hydrogen storage is calculated from stoichiometric equation (Eqn 1) and its volume is calculated after considering expansion on hydriding.
4	The vessel design pressure and design temperature are conservatively selected and it is assumed that all hydrogen adsorbed on the getter material is evolved at this temperature.
5	The volume of gas to be accommodated in vessel is calculated and total bed volume is determined.
6	A particle size for getter material and a length to diameter ratio for the getter bed vessel are selected.
7	The length and diameter of the vessel are evaluated and the wall thickness is calculated based on calculated diameter and design pressure.
8	The bed performance is evaluated under adiabatic conditions to arrive at the adiabatic temperature rise and adiabatic heat generation rate during hydriding.
9	Pseudo steady state analysis is done to arrive at surface temperature of insulation corresponding to the peak heat generation rate, considering heat generation to be equal to radiant energy loss and natural convection energy loss at steady state from the vessel outer surface.
10	The wall heat transfer coefficient for packed beds, the natural convection coefficient at outer wall and the linearised radiation heat transfer coefficient are evaluated over the range covering ambient temperature and the adiabatic bed temperature.
11	The overall multimodal heat transfer coefficient is calculated as a function of temperature and represented by a least squares regression line for the chosen conditions.
12	Using the expression for the overall multimodal heat transfer coefficient to represent total thermal energy loss from the getter bed during hydriding, the dynamic temperature and pressure profiles for the getter bed are obtained by modeling the bed as a batch reactor operating with an initial charge of hydrogen corresponding to the mass of hydrogen to be stored and solving the coupled material and energy balance equations.

there is no more uptake of hydrogen by the getter bed. This is essentially a batch operation. The heat release rate during hydriding is governed by the amount of hydrogen introduced and the kinetics of the hydriding reaction. To enhance heat dissipation during hydriding, a flow-through arrangement in which the hydrogen is recycled through the bed may be used but this configuration is not considered here. To limit temperature rise during this phase, the total amount of hydrogen to be stored may be introduced into the bed in smaller batches instead of all at once.

Once an optimal length to diameter ratio is chosen, the length and diameter of the vessel are calculated and based on the design conditions and material of construction chosen for it, the wall thickness is evaluated from standard formulae for pressure vessel design[9]. Wall thickness evaluation helps decide the schedule number of the pipe section which should be selected for fabrication of the vessel shells. Thus the most pertinent dimensions for evaluating the thermal analysis of the bed are obtained. TABLE 1 shows the essential steps followed in this work to perform design calculations and simulations while the data used for these exercises are reported in TABLE 2. The results of the design calculations for various masses of hydrogen are shown in TABLE 3 below.

For different particle sizes, or different L/D ratios the entire analysis has to be repeated. In this manner, parametric analyses can be carried out for different selected conditions.

MATHEMATICAL ANALYSIS OF THERMAL BEHAVIOUR OF THE GETTER BED

A simple mathematical model of the bed involving overall material and energy balances for the getter bed vessel, using the design data and parameters obtained from literature was made in order to simulate the heat transfer behaviour of the getter bed system. The details are presented in the following sections.

Model equations

The bed was modeled as a batch reactor with an initial charge of hydrogen and uranium inside at a

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TABLE 2 : Base case data used for design calculations and simulations

Parameter	Value
k_o	0.51
E_a	25216 J mol^{-1} K^{-1}
d_p	12 mm
S_s	$0.3141/d_p$ m^2 gm^{-1}
ρ_{Updr}	6000 kg m^{-3}
T_∞	300 K
ΔH_{Rx}	-97.5 kJ mol^{-1}
A	11.492
B	4471 K
Cp_{H2}	14.4 kJ kg^{-1} K^{-1}
Cp_U	0.12 kJ kg^{-1} K^{-1}
k_f	$4.185 * 10^{-3}(20.37 + 8.2 * 10^{-2}T + 3.56 * 10^{-6}T^2)$ W m^{-1} K^{-1}
k_s	27.5 W m^{-1} K^{-1}
k_{ins}	0.08 W m^{-1} K^{-1}
k_w	45 W m^{-1} K^{-1}
ε	0.78

TABLE 3 : Design data for getter beds to store different quantities of hydrogen

Mass of hydrogen(gm)	Mass of uranium for 60% loading(gm)	Total Vessel Volume(m^3)	Length(m)	Inside Diameter (m)	Wall thickness (mm)
1	131.2	$6.13*10^{-4}$	0.146	0.073	3.79
2	262.3	$1.23*10^{-3}$	0.184	0.092	4.77
3	393.5	$1.84*10^{-3}$	0.211	0.105	5.47
4	524.7	$2.45*10^{-3}$	0.232	0.116	6.02
5	655.9	$3.07*10^{-3}$	0.250	0.125	6.74

given initial temperature, which is taken as ambient temperature of 300 K. Typically for finely activated powdered uranium, hydriding takes place at ambient temperature but for turnings or chips temperatures around 100°C to 120 °C will be required. The heating is generally accomplished by electrical means. In this study the charging of hydrogen and the beginning of adsorption at ambient temperature itself is assumed for the purpose of simulations. A pseudo-homogeneous condition was assumed for the bed contents at any time. Thus inside the vessel, no distinction was made between the solid and gas phase i.e. they were assumed to have the same temperature. Heat transfer from the bed was modeled through the use of an overall heat transfer coefficient that accounts for radial heat transfer through several thermal resistances in series as well as radiation heat loss from the outermost surface of the vessel which is the layer of insulation. Figure 1 shows the model

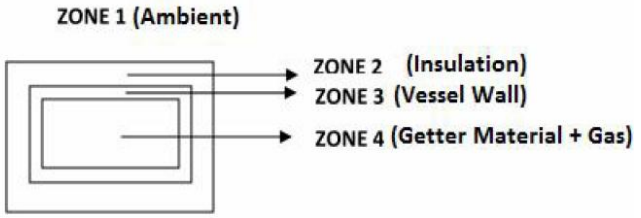

Figure 1 : Model of the getter bed for heat transfer calculation

of the vessel for the heat transfer calculations. Zones 1 to 4 represent the ambient air, the insulation layer, the vessel wall and finally the contents of the packed bed which act as series resistances to heat transfer. Radiant energy transfer to the ambient was also considered from the insulation surface to the ambient air. Variation of thermo-physical properties of the solid with temperature was neglected while for the gas phase these variations were considered.

Hydriding rate equation[10]:

$$(-r_{H_2}) = kp^{0.5} S_s \rho_{Updr} \frac{V_{solid}}{V_{bed}} \quad (2)$$

Overall mole balance on hydrogen:

$$\frac{dn_{H_2}}{dt} = (-r_{H_2}) V_{bed} \quad (3)$$

Overall energy balance[11]:

$$\frac{dT}{dt} = \frac{U_{total} A_s (T - T_\infty) + (-r_{H_2} V_{bed})(-\Delta H_{Rx})}{\sum n_i Cp_i} \quad (4)$$

Equilibrium pressure of hydrogen over uranium[12]:

$$\ln P_o = A - \frac{B}{T} \quad (5)$$

The wall heat transfer coefficient was calculated from Equations 6, 7, 8 using an approximate initial particle dimension (typically 12 mm)[13] to account for radial heat loss. Axial heat transfer was neglected in this analysis by assuming perfect insulation. The bed voidage was evaluated from Equation 9[14].

$$Nu_w = \frac{h_w d_p}{k_f} = 2.4\left(\frac{k_e^o}{k_f}\right) + 0.054\left(1 - \frac{d_p}{d_t}\right) Re_p Pr^{\frac{1}{3}} \quad (6)$$

$$\frac{k_e^o}{k_f} = \left(\frac{k_s}{k_f}\right)^m \quad (7)$$

$$m = 0.28 - 0.757 \log(\varepsilon_b) - 0.057 \log\left(\frac{k_s}{k_f}\right) \quad (8)$$

$$\varepsilon_b = 0.4 + .05\left(\frac{d_p}{d_t}\right) + 0.412\left(\frac{d_p}{d_t}\right)^2 for \frac{d_p}{d_t} < 0.5 \quad (9)$$

The overall convective heat transfer coefficient U_o based on outside area was then calculated as in Eqn 10, considering resistance of the packed bed, the steel wall, the asbestos fabric insulation layer and the ambient air to which there is natural convection induced heat loss[15].

$$\frac{1}{U_o A_s} = \frac{1}{h_w A_i} + \frac{\ln\left(d_{bo}/d_t\right)}{2\pi k_w L} + \frac{\ln\left(d_{ins}/d_{bo}\right)}{2\pi k_{ins} L} + \frac{1}{h_o A_s} \quad (10)$$

The outside heat transfer coefficient h_o for a vertical cylindrical vessel is evaluated from the correlation expressed in Eqn 11[15],

$$Nu_L = \left(0.825 + \frac{0.387 Ra_L^{\frac{1}{6}}}{\left(1 + \left(\frac{0.492}{Pr}\right)^{\frac{9}{16}}\right)^{\frac{8}{27}}}\right)^2 \quad (11)$$

where $Ra_L = \frac{g\beta(T_s - T_\infty)L^3}{\alpha\nu}$, $Nu_L = \frac{h_o L}{k_{air}}$, and $\Pr = \frac{Cp_{air}\mu_{air}}{k_{air}}$

The outside heat transfer coefficient h_o for a horizontal cylindrical vessel is calculated from the correlation shown in Eqn 12[15],

$$Nu_D = \left(0.60 + \frac{0.387 Ra_D^{\frac{1}{6}}}{\left(1 + \left(\frac{0.559}{Pr}\right)^{\frac{9}{16}}\right)^{\frac{8}{27}}}\right)^2 \quad (12)$$

where $Ra_D = \frac{g\beta(T_s - T_\infty)D^3}{\alpha\nu}$ and $Nu_D = \frac{h_o D}{k_{air}}$

The reaction rate constant is obtained from an Arrhenius relationship as shown in Eqn 13[10].

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) \quad (13)$$

Values of parameters used for the simulations are presented in TABLE 3. The overall heat transfer coefficient was found to be relatively insensitive to the value of bed temperature, as shown in Section 3.3 and was thus taken as a constant during the simulation with a given initial temperature, hydrogen pressure and given quantity of hydrogen to be stored. The equations were solved using a simple, explicit finite difference scheme to obtain average bed temperature, composition and pressure profiles as functions of time.

Calculation of natural convection heat transfer coefficient and insulation surface temperature

The calculation of h_o requires a knowledge of the insulation surface temperature. An estimate of the surface temperature was obtained by an iterative steady state calculation in which the sum of the peak heat generation rate due to chemical reaction was equated to the heat loss from the insulation surface by radiation and natural convection. The peak heat generation rate was estimated by assuming adiabatic conditions during the hydriding step and evaluating the bed temperature and hence the rate of reaction heat release as a function of time by solving the material and energy balance equations together. The

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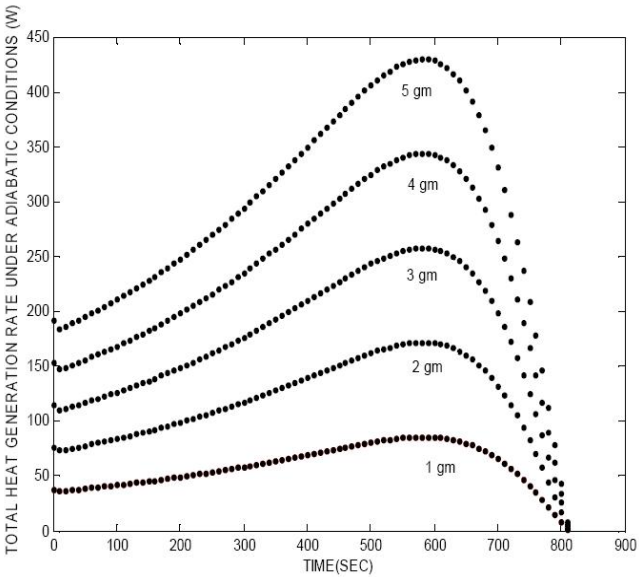

Figure 2 : Adiabatic heat generation rates during hydriding reaction of 12 mm uranium turnings

peak values corresponding to different masses of hydrogen to be stored in a vessel with length to diameter ratio of 2, as shown in Figure 2 were used for further calculations. A surface temperature was assumed, the air properties were evaluated at the arithmetic mean temperature of the surface and the ambient temperatures and the convective heat transfer coefficient was evaluated from Eqn 11 or 12. The insulation surface temperature was then evaluated from the thermal energy balance in Eqn 14.

$$(q_s R)' = h_o A_s (T_s - T_\infty) + \sigma A_s F_{12} \varepsilon (T_s^4 - T_\infty^4) \quad \textbf{(14)}$$

$$[max[(-r)]_{(H_2)} V_{bed} (-(H_R x)]$$

The assumed and calculated values of T_s were checked and depending on the error in the values, further iterations were carried out with revised guess values of T_s till convergence was attained. This is repeated for various heat generation rates over the range of values considered in the present case. The view factor F_{12} was taken as unity in this study. The results of these iterative calculations are presented in TABLE 4.

The dynamic variation of the temperature and gas pressure inside the bed during adiabatic hydriding is shown in Figure 3A and 3B. In each case (i.e. corresponding to different masses of hydrogen being stored) the adiabatic temperature rise during hydriding is about 70 K, starting from an initial ambient temperature of 300 K. While the total heat to be released during hydriding depends on the quantity of hydrogen being stored, the design methodology presented in this study leads to the sizing of the bed in such a way that the actual temperature rise remains same in each case. If the size of the bed is fixed and different quantities of hydrogen have to be stored in it, the adiabatic temperature rise would be different. There would also be a difference if the length to diameter ratio of the bed is varied for a given quantity of hydrogen, as shown in Figure 4. The difference arises because for the same total volume of the bed, selection of different diameters and hence lengths will lead to different calculated wall

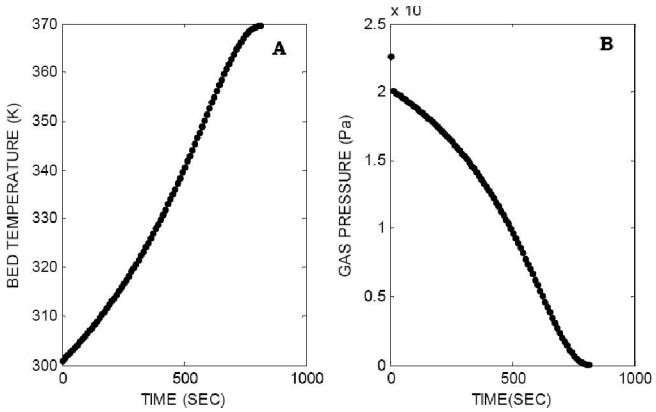

Figure 3A-3B : Dynamic variation of adiabatic bed temperature and pressure during hydriding reaction for 1 gm to 5 gms of hydrogen (A: Temperature profile, B: Pressure profile, L/D=2, d_p = 12 mm)

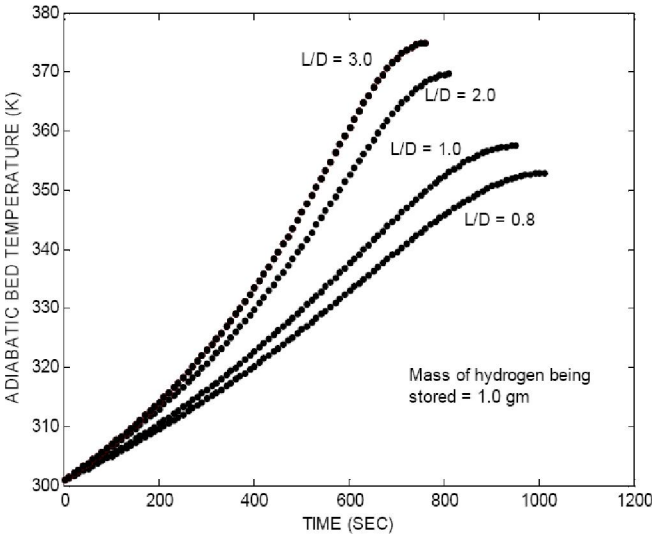

Figure 4 : Dynamic variation of adiabatic bed temperature during hydriding reaction at different length to diameter ratios (d_p = 12 mm)

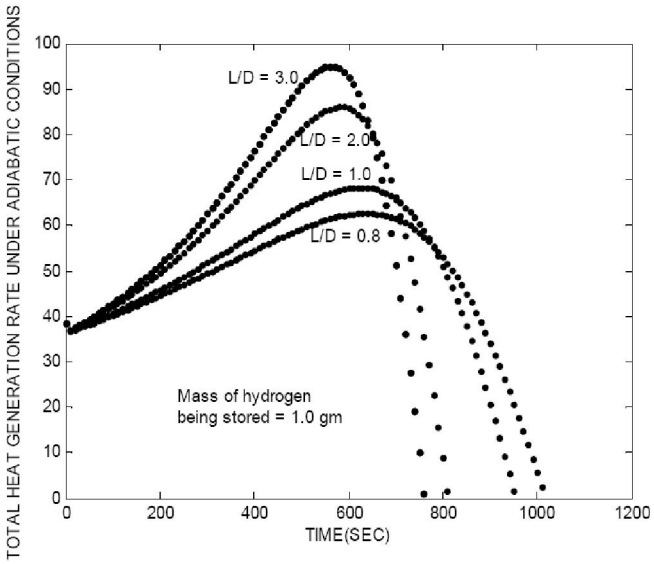

Figure 5 : Variation of adiabatic heat generation rate due to hydriding reaction with length to diameter ratio of the getter bed (d_p = 12 mm)

thicknesses for the same design pressure and temperature. Thus the total weight of the vessel and its closures are different and hence the total thermal capacity of the system is also different. The peak heat release rate also varies with the variation in L/D ratio for a given mass of hydrogen, as shown in Figure 5. Because of differing thermal capacities of the system arising out of differing system masses, the temperature profiles change with change in L/D ratio, for a given weight of hydrogen. This leads to a different reaction rate profile and a heat release rate for every L/D ratio.

Calculation of the skin temperature is practically important from the point of getter bed handling. Too high a skin temperature means difficulty in manual operations pertaining to the bed and possible injury to the operating personnel. Thus it is important to select the proper insulation material and thickness to ensure that the insulation surface temperature is below 60°C even at the maximum envisaged heat generation rates. In each case considered in Figure 2, the insulation thickness was taken as 3 inches and for hydrogen mass upto 5 gm this is determined to be sufficient to keep the surface temperatures of the vertically oriented bed below 60°C, as shown in TABLE 3. This is an important consideration for manual handling of the getter bed system. For the horizontally placed bed, 3 inch thick insulation is not sufficient, as seen from the calculated surface temperatures. Calculations with different insulation thicknesses indicate that 4.5 inch thick asbestos insulation layer would be sufficient to keep the temperatures below 60°C for the horizontal vessels.

It is seen from Figure 2 that the peak heat release rate occurs at about 600 seconds from the start of the reaction and the reaction is complete within 900 seconds when it starts from ambient conditions. After a few cycles of hydriding and dehydriding, the uranium particle size decreases and as the solid becomes more powdery the rates are expected to be much higher and thus the peak heat release rates in that case as well as the insulation surface temperatures would also be higher than the ones reported here. Higher insulation thickness would be needed in that case. In case it is not feasible to use thicker layers of insulation, a layer of material having higher emissivity can be provided over the insulation layer of lower thickness

The knowledge of the maximum steady surface temperatures enables calculation of the natural convection heat transfer coefficient and then the overall heat transfer coefficient, as well as radiation heat loss from the vessel.

Variation of overall heat transfer coefficient U with temperature

TABLE 4: Peak heat generation rates and bed surface temepratures during hydriding reaction (L/D=2, d_p = 12 mm)

Mass of hydrogen (gm)	Peak heat generation rate under adiabatic condition (W)	Maximum insulation surface temperature for vertical vessel at steady state considering both radiation and natural convection heat loss (°C)	Maximum insulation surface temperature for horizontal vessel at steady state considering both radiation and natural convection heat loss (°C)
1	85.22	39.3	45.2
2	172.10	46.7	54.2
3	258.10	52.2	60.8
4	344.10	56.8	66.1
5	430.20	60.7	70.4

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The evaluation of overall heat transfer coefficient is a crucial step since this along with radiation heat loss is what governs the rate of heat loss from the getter bed during hydriding, when no forced cooling arrangements for the bed are provided to limit temperature rise. The overall heat transfer coefficient is calculated from the four thermal resistances in series, as expressed in Eqn 10. The thermal conductivity of the steel and the insulation material are very nearly constant over the temperature range of interest in the present study, thus they were taken to be temperature invariant in the calculations. The temperature dependent fluid properties govern the wall heat transfer coefficient and the natural convection coefficient, so their variations were taken into consideration to calculate the dependence of U on the getter bed temperature.

From the results of calculations reported in sections 3.1 and 3.2, it is evident that during the hydriding reactions, the maximum bed temperature will be about 370 K (97°C) based on the design philosophy adopted in this study, while the maximum surface temperature will vary from about 40 to 60°C for an insulation thickness of 3 inches. In this section, bed temperature is taken as 97°C and for each surface temperature in the range from 40°C to 97°C, the overall heat transfer coefficient is evaluated for the horizontal and vertical orientations of the bed having L/D ratio of 2. The effect of radiation is taken into account by defining a radiation heat transfer coefficient as[16]

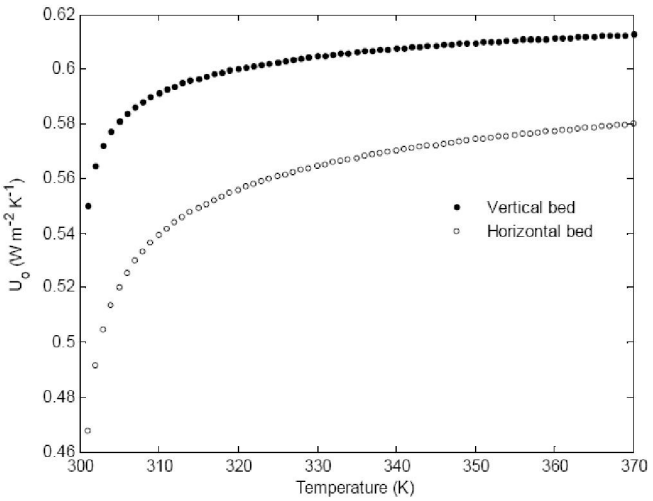

Figure 6 : Variation of the overall convective heat transfer coefficient of a cylindrical getter bed for 1 gm hydrogen with temperature (d_p = 12 mm, L/D = 2)

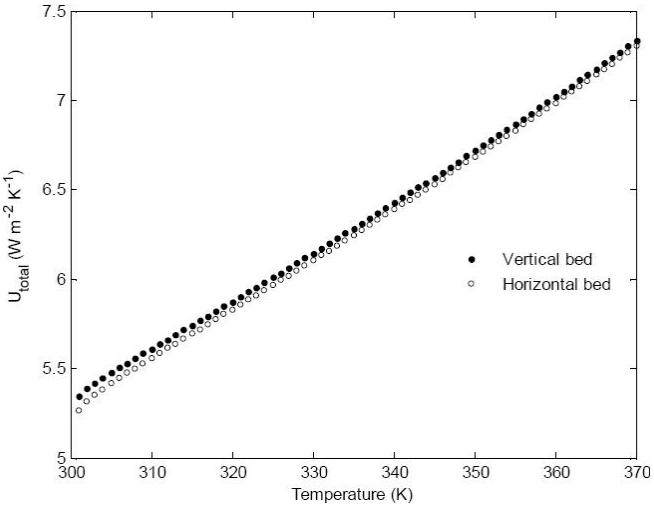

Figure 7 : Variation of the total heat transfer coefficient of a cylindrical getter bed for 1 gm hydrogen with temperature (d_p = 12 mm, L/D = 2)

$$h_R = \sigma\varepsilon \frac{[(T]_S^4 - T_\infty^4)}{(T_S - T_\infty)} \quad (15)$$

The radiant heat transfer term can now be expressed in a linearised form as

$$\dot{q_{Rad}} = h_R(T_S - T_\infty)$$

Hence the total heat loss term in the energy balance equation can be written as

$$\dot{Q_{total}} = \dot{q_{Rad}} + \dot{q_{conv}} = U_o(T - T_\infty) + h_R(T - T_\infty) = U_{total}(T - T_\infty) \quad (16)$$

where $U_{total} = U_o + h_{Rad}$ is the multimodal heat transfer coefficient to account for both convective and radiation heat transfer from the getter bed.

The representative results for a vessel to store 1 gm hydrogen are shown in Figures 6 and 7 and discussed in the following paragraphs. Similar analyses were performed for the larger vessels and some general conclusions were arrived at.

From Figures 6 and 7 it is clearly seen that the total heat loss from the getter bed will be strongly dominated by radiant heat transfer as the total multimodal heat transfer coefficient is more than 10 times larger than the overall convective heat transfer coefficient alone. Moreover, the difference between the multimodal heat transfer coefficient for a vertical and a horizontal vessel is not very large, the difference being about 1.57 % at 300 K (i.e.

ambient condition) and decreasing to 0.45 % at 370 K. If only the overall convective heat transfer coefficient is considered, the maximum and minimum variations between the values for horizontal and vertical vessels are respectively 17.68 % and 5.63 %. But this is not likely to have significant impact upon the heat loss from the vessel since the major heat loss will be due to radiation, which is similar for both types of vessels.

For the getter beds of different dimensions considered in this work, the numerical value of the multimodal heat transfer coefficient at a given temperature shows very little variation i.e. the vessel dimensions do not exert a strong influence on the heat transfer behaviour when radiation is the dominant energy transfer mechanism. But there is significant variation in the values of the overall convective heat transfer coefficient for the different vessels. This is because convective coefficients are strongly influenced by the system geometry (e.g. length and diameter of the vessels in this case) and this is reflected in the difference in values of U_o for the different vessels, in either orientation.

The multimodal heat transfer coefficient was subsequently used in the complete simulation of the getter bed performance. Figure 7 indicates a very nearly linear variation of U_{total} with temperature for both orientations of the bed. A least squares linear regression was thus performed to obtain an equation that mathematically expresses U_{total} as a function of temperature for both horizontal and vertical vessels for different masses of hydrogen to be stored. The regressed equations for the getter beds are shown in TABLE 4 and these were used as inputs to the computer code for simulating dynamic bed performance. Values of the correlation coefficient show clearly the linear dependence of U_{total} on temperature. From TABLE 4, it can be easily understood that at a given value of temperature, the values of U_{total} for the different beds do not show any significant difference and any one of the equations expressing the dependence of U_{total} on temperature can be used for the simulations. Such equations can be derived for beds having any L/D ratio and using any initial particle size of uranium turnings based on the analysis discussed in the previous sections.

Dynamic simulation of getter bed performance and analysis of results

The performance of the getter bed for storage of hydrogen as a function of time was numerically simulated using the methodology discussed above. The profiles of bed temperature, heat generation rate and gas pressure along with the heat generation rate due to reaction were evaluated by solving the coupled material and energy balance equations. Typical profiles for vessels with length to diameter ratio of two and particle size of 12 mm are presented in Figures 8A to 8D.

It is seen from Figure 8 that for this set of conditions, the reaction completion time ranges from about 1000 to 1400 seconds as mass of hydrogen to be stored varies from 1 gm to 5 gm, as compared to 900 seconds under adiabatic conditions. This is due to the higher temperatures and hence higher reaction rates when the system is under adiabatic conditions. The heat release rates are consequently slower and peak heat release rates are less under conditions of heat transfer than under adiabatic conditions. The heat generation rate shows a relatively sharp peak for higher masses of hydrogen to be stored while the curve for 1 gm hydrogen shows a nearly flat region around the highest heat generation rate. The pressure drops monotonically in all cases studied here though it is possible that pressure rises initially due to temperature rise and subsequently drops as the

TABLE 5 : Equations of U_{total} as a function of temperature for different getter beds with L/D = 2 and particle size = 12 mm

Mass of hydrogen(gm)	Linear Regression Equation	Correlation coefficient
1	U_{total} (W m^{-2} K^{-1})=-3.221+0.028*T(K)	0.999
2	U_{total} (W m^{-2} K^{-1})=-3.242+0.028*T(K)	0.999
3	U_{total} (W m^{-2} K^{-1})=-3.259+0.028*T(K)	0.999
4	U_{total} (W m^{-2} K^{-1})=-3.272+0.028*T(K)	0.999
5	U_{total} (W m^{-2} K^{-1})=-3.283+0.028*T(K)	0.999

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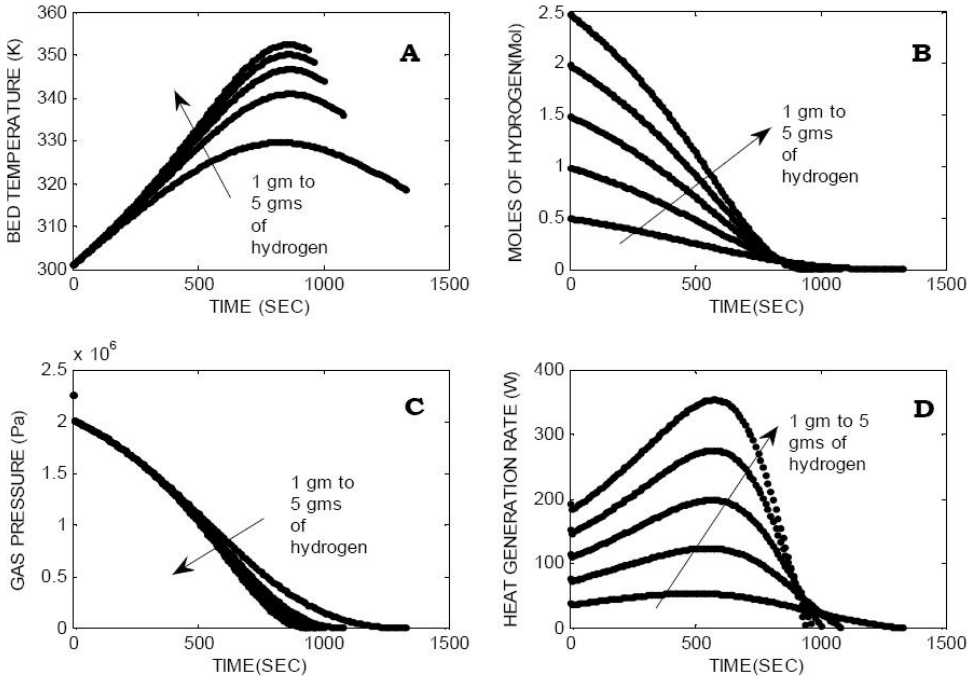

Figure 8A-8D : Dynamic getter bed performance (A: Temperature profile, B: Consumption of hydrogen, C: Gas pressure profile, D: Heat generation rate for vessel with L/D = 2 and d_p = 12 mm)

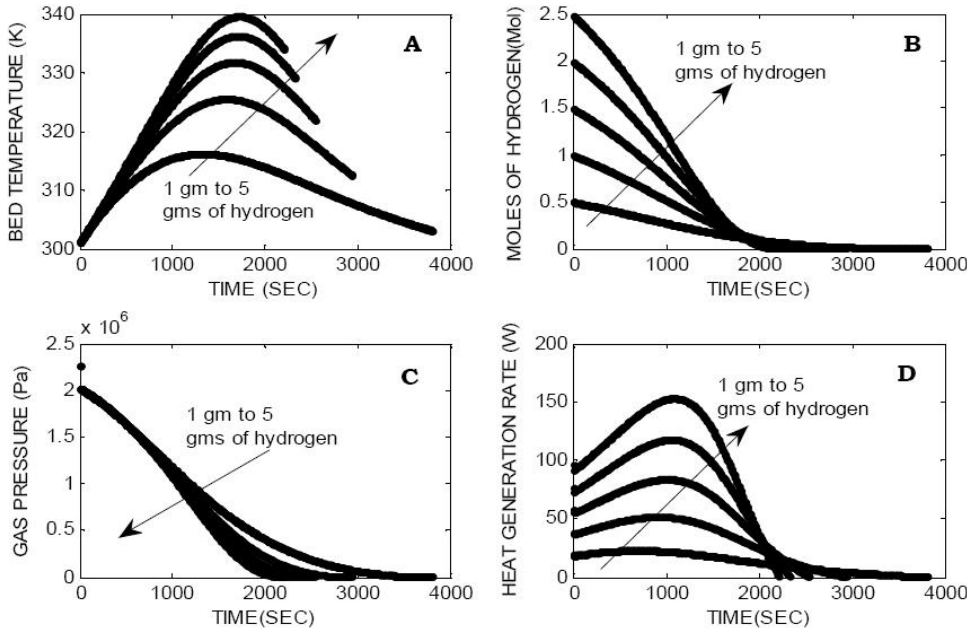

Figure 9A-9D : Dynamic getter bed performance (A: Temperature profile, B: Consumption of hydrogen, C: Gas pressure profile, D: Heat generation rate for vessel with L/D = 2 and d_p = 25 mm)

depletion in the quantity of gas outweighs the pressure rise due to a more rapid increase in temperature (viz. the case considered in Figure 11). The temperature shows an initial rise followed by a drop. Higher the mass of hydrogen to be stored, greater is the peak temperature in each case.

Figure 9 qualitatively shows the same features as Figure 8 but there are quantitative variations arising out of the difference particle size of uranium (25 mm) considered while simulating bed performance. A larger particle size and hence smaller surface are per unit volume have been considered in this case, which automatically leads to smaller reaction rates, lower peak heat generation rates and thus surface

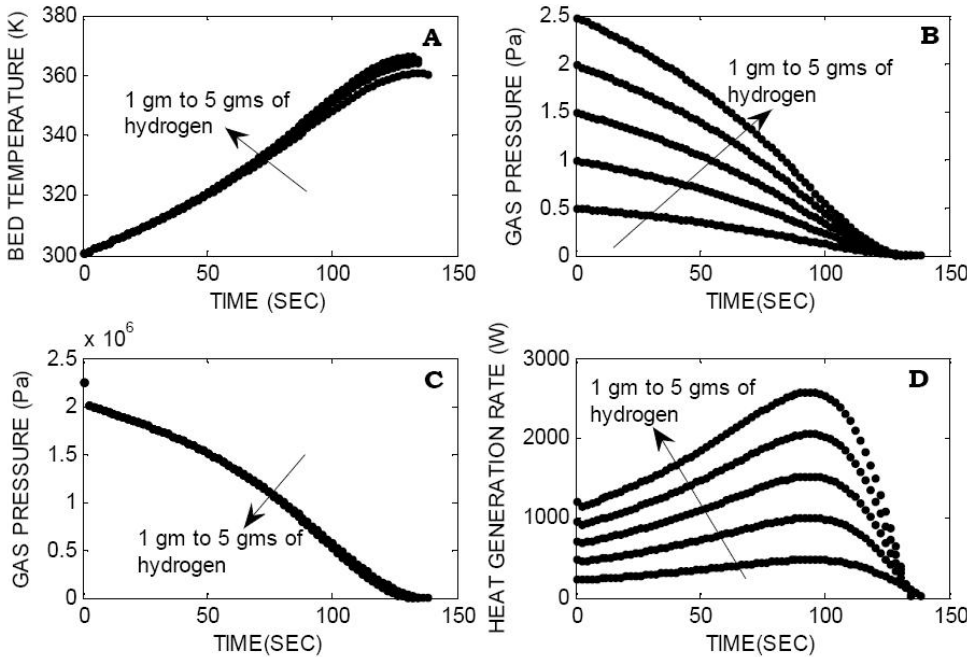

Figure 10A-10D : Dynamic getter bed performance (A: Temperature profile, B: Consumption of hydrogen, C: Gas pressure profile, D: Heat generation rate for vessel with L/D = 2 and d_p = 1.6 mm)

temperatures. The reaction takes about 2500 seconds to 4000 seconds for completion and the peak temperatures occur in between 1000 to 1500 seconds from start of the reaction. The other features remain similar to the case represented in Figure 8.

In the case represented in Figure 10, a much smaller particle size (i.e. 1.6 mm) has been considered. This size is the smallest uranium particle size that can be handled under ambient temperature and pressure without the hazard of metal fire[8]. This leads to much faster reaction rates and very large peak heating rates. The evaluation of the surface temperatures by the pseudo-steady state analysis as done in the previous two cases is not a very effective method since the rate of heat loss is small compared to the very high rate of reaction heat generation and this will not allow a pseudo steady state approximation to be made. For the sake of completion, the approximation was made despite this restriction and results are shown in Figure 10. The nearly adiabatic nature of the hydriding process is clearly indicated in the dynamic bed temperature and pressure curves (Figures 10A and 10C) which are almost coincident for hydrogen mass of 3 gm and above. There are no sharp peaks observed in the temperature profiles and the ultimate bed temperature on completion of the reaction tends to be quite close to the adiabatic bed temperature during hydriding. For such cases, with very high peak heat release rates, forced cooling of the bed will be essential during the hydriding reaction.

Successive hydriding and dehydriding cycles with the same charge of solid getter material causes the getter to break up into smaller particles and thus after every cycle, the bed's characteristics change and as a result its thermal behaviour also changes. Thus it is important to study the effect of particle size on bed performance, as has been carried out in this section. Empirical equations may be developed to track the changes in uranium particle size as a function of hydriding reaction time which may then be used in the rate equation itself.

For large particle sizes of the getter material the reaction rate will be very slow at ambient temperatures. The hydriding will then have to be carried out at higher temperatures attained by the use of an externally or internally placed electric heater or by an induction coil. To simulate this condition, an additional heat input term has to be included in the energy balance equation for the getter bed. A representative case is shown in Figure 11 considering 1 gm of hydrogen to be stored in a vessel with L/D ratio of 2 and particle size of 50 mm. The tempera-

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ture profiles only are shown from the start to the end of the reaction for three cases-when adiabatic conditions are maintained, when heat losses are considered based on the analysis discussed before and when a heater is also present, dissipating on an average 10 W, 50 W or 100 W of electrical energy into the bed. It is seen in Figure 11A that under adiabatic conditions (curve 1), the maximum reaction rates are obtained and the reaction is completed within the least time. With multimodal heat losses present, the reaction is quite slow and takes about 3.5 hours for completion (curve 2). With additional electrical energy input of 10 W, the reaction rates increase, as is seen by the steeper initial temperature rise (curve 3) and a decrease in reaction time is observed. With further increase in the heat input to 50 W, the rate is much faster and the reaction is com-

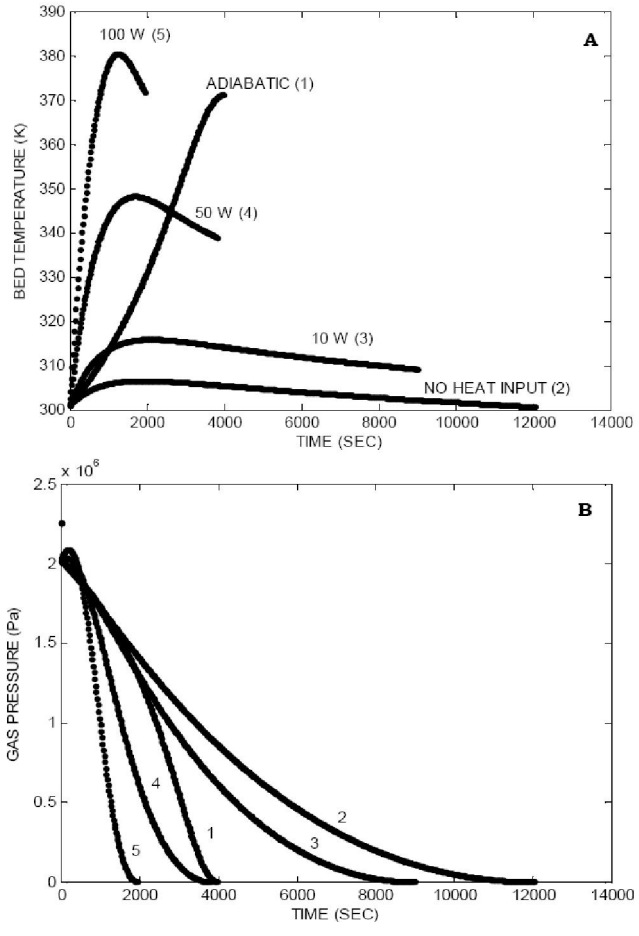

Figure 11A-11B : Effect of electrical heat input on getter bed performance (A: Temperature profile, B: Gas pressure profile)(L/D = 2, d_p = 50 mm, initial charge of hydrogen = 1 gm)

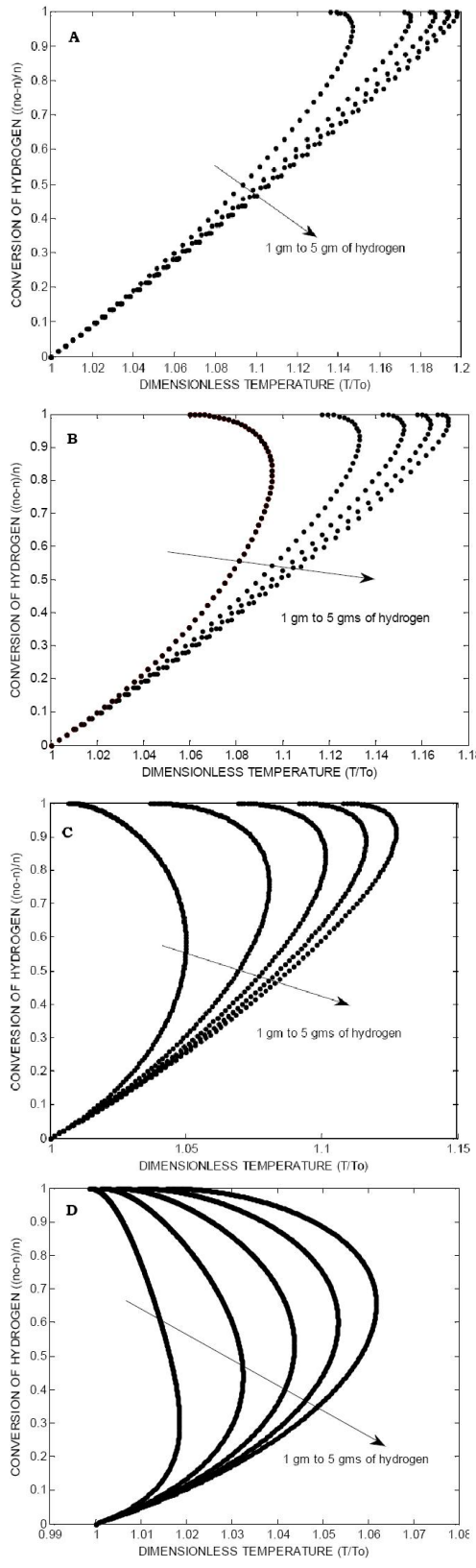

Figure 12A-12D : Phase plane representation of getter bed behaviour during hydriding reaction (A: d_p = 6 mm, B: d_p = 12 mm, C: d_p = 25 mm, D: d_p = 50 mm, L/D = 2 in all cases, no electrical energy input)

pleted within almost the same time as the adiabatic case. Thus for this particular case, about 50 W heat input from external source just about balances the heat loss but does not raise the temperature beyond the adiabatic bed temperature. A temperature controller can even be implemented to act according to a heating policy that allows nearly isothermal conditions to be maintained during hydriding. The high initial rates enable the reaction to be completed within the same time as in the adiabatic case. At 100 W, the rate is very fast as seen by the steep curve 5 and the peak temperature attained is even greater than adiabatic temperature rise of the bed. For high heat input rates, the gas pressure inside the bed also shows an initial rise due to large temperature rise at the outset which compensates the pressure drop occurring due to consumption of the gas by reaction. This is shown in Figure 11B (Curves 4 and 5) for the cases when the electrical heat input is 50 W and 100 W respectively. This analysis therefore helps one to select an optimal electrical energy input for the getter bed for the chosen design and operating conditions.

In Figures 12A to 12D, a phase plane representation of the getter bed behaviour (i.e. plots of number of moles of gas versus bed temperature, as obtained from the simultaneous solution of the coupled material balance equation and energy balance equation) has been presented for the conditions mentioned in the figure captions. Phase plane plots are an alternative way of representing the performance curves of the getter bed system[17].

It is seen that when uranium particle size is small and hydriding reactions are high, leading to high reaction heat release rates, the plots of conversion versus temperature are very nearly straight lines, as would be expected of a reactor behaving adiabatically. The nature of the phase plot however changes significantly when the behaviour departs from adiabatic conditions. The slopes of the curves change sign after a certain degree of conversion and the value of conversion at which this occurs decreases as we have higher particle size and hence lower hydriding rates, for the same mass of hydrogen to be stored. In all phase plane plots shown above, the initial temperature was taken to be the same (i.e. 300 K) and each curve corresponds to a different initial mass of hydrogen charged to the reactor.

Phase plane plots are typically used in the design and analysis of control systems for second order dynamic systems. The lumped capacitance approach followed in this work enables representation of the getter bed as a system with two dependent variables viz. the number of moles of gas and the bed temperature. Thus in studying the effect of a feedback temperature control system on the behaviour of the bed, such plots are expected to be valuable. This problem will be addressed in a future publication.

Analysis of some anticipated abnormal occurrences during getter bed operation

In the dynamic simulations of the getter bed reported in the previous section, it was assumed that the hydrogen fed to the reactor vessel was absolutely pure and there was no ingress of air or water vapour from the ambient into the vessel. Thus side reactions of uranium with oxygen or water vapour were not considered in the analysis. But it is well known that these gases also react with uranium and also uranium hydride exothermically under even ambient conditions[18]. Thus the vessel temperature and pressure characteristics will be affected by these reactions and a part of the uranium will also become unavailable for hydrogen storage. Uranium oxide is a highly stable compound thus once it is formed it permanently reduces the hydrogen adsorption capacity of uranium. Despite all care taken to prevent air or moisture incursion into the getter bed, it is possible that some leakage of air or some air with the feed hydrogen enters into the bed and causes the side reactions. Rapid heat release due to these reactions can raise the getter bed temperature so much that the uranium itself starts burning violently, depending on its particle size[8]. In this section, the effect of these reactions on the peak bed temperature is analyzed.

The reaction of moisture and oxygen with uranium can be represented by Equations 17 and 18 respectively[18]:

$$U + 2H_2O = UO_2 + 2H_2,\ \Delta H_{Rx} = -260\ kJ\ mol^{-1}\ H_2O \quad (17)$$

$$U + O_2 = UO_2,\ \Delta H_{Rx} = -1085\ kJ\ mol^{-1}\ O_2 \quad (18)$$

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TABLE 6 : Adiabatic temperature rise (K) of the getter bed (L/D = 2) during hydriding in presence of oxygen and water vapour

H_2O mole%	O_2 mole %							
	0.0	0.001	0.005	0.01	0.05	0.1	1.0	10.0
0.0	69.77	69.77	69.80	69.84	70.12	70.46	76.75	138.85
0.001	69.77	69.77	69.80	69.84	70.12	70.47	76.75	138.86
0.005	69.77	69.78	69.81	69.84	70.12	70.47	76.75	138.86
0.01	69.78	69.78	69.81	69.85	70.13	70.48	76.76	138.87
0.05	69.82	69.83	69.86	69.89	70.17	70.52	76.80	138.91
0.1	69.88	69.89	69.91	69.95	70.23	70.58	76.86	138.96
1.0	70.89	70.89	70.92	70.96	70.24	71.59	77.86	139.93
10.0	80.94	80.94	80.97	81.00	81.28	81.63	87.86	149.51

The adiabatic temperature rise of the bed under different concentrations (i.e. mole percentage) of oxygen and moisture (ranging from 0.001% to 10% of each gas) present with hydrogen and independently undergoing reaction with uranium is reported in TABLE 6. The adiabatic condition is considered here since it represents the worst case scenario during bed operation and can potentially lead to the most hazardous situation likely to be encountered with respect to bed heating and internal pressure rise. It is further assumed that uranium is always present in excess, thus allowing hydrogen and the contaminant gases to react completely.

It is observed from TABLE 6 that even when oxygen and water vapour concentrations are up to about 0.1 mole % and about 1 mole % respectively with the rest being hydrogen, the adiabatic temperature rise on reaction is only about 3 K more than the case when only hydrogen is reacting with uranium. From the point of view of safety, this rise in temperature is not very significant. Beyond these limits, the temperature rise is more drastic. As oxygen level increases from 0 mole % to 10 mole % in absence of moisture, there is a 99% increase in the adiabatic temperature rise whereas there is only 16% increase when moisture levels vary from 0 mole % to 10 mole % in the absence of oxygen. It appears that with respect to safety and prevention of unmanageable temperature rise in the getter bed, up to 0.1 mole % oxygen and up to 1 mole % water vapour could be allowed with hydrogen during hydriding reactions. This of course would lead to the wastage of uranium available for hydrogen storage, since the oxide formed in both side reactions is very stable and its layers can only be removed from the metal surface by chemical treatment with nitric acid[19]. From literature[18], the rates of reaction of uranium with oxygen and moisture can be compared with the rate of hydriding reaction. It can easily be observed that the reactions with the contaminant gases are several orders of magnitude slower than the hydriding process, thus the heat release due to them would also be very slow and would not affect the total heat release in any appreciable manner. Hence the dynamic bed temperature and pressure profiles will remain practically unaffected over the time duration for the hydriding reaction to be completed. After that, the profiles would be governed by the side reactions and these would evolve very slowly with time. The slow heat release from these side reactions can easily be dissipated by the natural heat loss modes of the bed, depending on the design of the bed and adiabatic conditions and abnormally high temperatures are not likely to occur.

SUMMARY AND CONCLUSION

A simple mathematical model of a uranium based getter bed for storage of small quantities of hydrogen has been presented with emphasis on the overall heat transfer behavior of such a system. The preliminary sizing of the reactor for a given mass of hydrogen to be stored has been carried out based on reaction stoichiometry and optimal vessel dimensions have been obtained for it. The system has then been modeled as a batch reactor and dynamic tem-

NOMENCLATURE

A	Constant in the Van't Hoff equation for hydrogen-uranium system, dimensionless
A_i	Outer surface area of the getter bed, m^2
A_s	Outer surface area of the vessel insulation layer for heat transfer, m^2
B	Constant in the Van't Hoff equation for hydrogen-uranium system, K
Cp_{air}	Specific heat capacity of air, J kg^{-1} K^{-1}
Cp_{H2}	Specific heat capacity of hydrogen, J kg^{-1} K^{-1}
Cp_U	Specific heat capacity of uranium, J kg^{-1} K^{-1}
d_{bo}	Bed outside diameter, m
d_{ins}	Diameter of insulation layer, m
d_p	Uranium particle diameter, m
d_t	Bed inside diameter, m
D	Outside diameter used to define Rayleigh number, m
E_a	Activation energy for hydriding reaction, J mol^{-1}
F_{12}	View factor for radiant energy transfer from vessel to the ambient, dimensionless
g	Acceleration due to gravity, m s^{-2}
h_o	Natural convective heat transfer coefficient from cylindrical vessel, W m^{-2} K^{-1}
h_R	Radiation heat transfer coefficient from cylindrical vessel, W m^{-2} K^{-1}
h_W	Convective wall heat transfer coefficient in packed bed, W m^{-2} K^{-1}
$\triangle H_{Rx}$	Heat of reaction, kJ mol^{-1}
i	Index to component number (i=1 to 3)
k	Reaction rate constant for hydriding, mol H_2 m^{-2} s^{-1}
k_{air}	Thermal conductivity of ambient air, W m^{-1} K^{-1}
k_o	Pre-exponential factor for hydriding reaction of uranium,
k_e^o	Thermal conductivity of bed at zero flow, W m^{-1} K^{-1}
k_f	Thermal conductivity of hydrogen, W m^{-1} K^{-1}
k_{ins}	Thermal conductivity of insulation material, W m^{-1} K^{-1}
k_s	Thermal conductivity of uranium, W m^{-1} K^{-1}
k_w	Thermal conductivity of wall material, W m^{-1} K^{-1}
L	Height of storage vessel, m
L/D	Length to diameter ratio for getter bed, dimensionless
m	Empirical index, dimensionless
n_i	Number of moles of species i at a given time, dimensionless
n_{H2}	Number of moles of hydrogen at a given time, dimensionless
n_o	Initial number of moles of hydrogen inside the vessel, dimensionless
Nu_D	Nusselt number for natural convection heat loss from horizontal bed, dimensionless
Nu_L	Nusselt number for natural convection heat loss from vertical bed, dimensionless
Nu_W	Wall Nusselt number for the packed getter bed, dimensionless
p	Pressure of hydrogen in the vessel at any time, Pa
P_o	Equilibrium pressure of hydrogen over uranium, Pa
Pr	Prandtl number, dimensionless
$\dot{q}_{conv}$	Convective heat transfer rate from getter bed, W
$\dot{Q}_R$	Peak heat generation rate inside getter bed due to hydriding reaction, W
$\dot{q}_{Rad}$	Radiation heat transfer rate, W
$\dot{q}_{total}$	Total heat loss rate, W

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r_{H2}	Rate of hydriding reaction with respect to hydrogen, mol m^{-3} s^{-1}
Ra_D	Rayleigh number based on outside diameter for horizontal vessel, dimensionless
Ra_L	Rayleigh number based on length for vertical vessel, dimensionless
Re_p	Reynolds number, dimensionless
S_s	Specific surface area of uranium turnings or powder, m^2 gm^{-1}
t	Time, sec
T	Average bed temperature, K
T_8	Ambient temperature, K
T_s	Insulation surface temperature, K
U_o	Overall convective heat transfer coefficient based on area A_s, W m^{-2} K^{-1}
U_{total}	Overall heat transfer coefficient based on area A_s, W m^{-2} K^{-1}
V_{bed}	Total internal volume of the vessel, m^3
V_{solid}	Total volume of solid in the vessel, m^3
α	Thermal diffusivity of air, m^2 s^{-1}
β	Volumetric thermal expansion coefficient of air, K^{-1}
ε	Emissivity of the insulation material, dimensionless
ε_b	Bed voidage, dimensionless
μ_{air}	Viscosity of air, Pa s
ν	Kinematic viscosity of air, m^2 s^{-1}
ρ_{Updr}	Density of uranium powder, gm cm^{-3}
σ	Stefan Boltzmann constant, $5.67*10^{-8}$ W m^{-2} K^{-4}

perature profiles have been evaluated using material and energy balance equations for both vertical and horizontal orientations of the bed.

The vessel design philosophy considered here does not include a separate forced cooling system for the hydriding operation; instead it only depends on heat losses due to conduction and convection within the bed and natural convection and radiation from the outermost vessel surface to keep the bed surface temperature within reasonable limits. For the purpose of system performance simulation, all the various modes of heat transfer through various resistances in series have been combined into one multimodal heat transfer coefficient and used in the energy balance equation to account for the radial heat loss from the bed during hydriding. Thus the design method and the analysis presented here apply to compact getter bed systems, suitable for transportation and long term storage of hydrogen or its isotopes. This is made feasible by selection of appropriate vessel dimensions, proper insulation material and layer thickness and vessel orientation. The design procedure is inherently conservative since the maximum design pressure of 60 bar (a) and maximum design temperature of 800 K will never occur simultaneously.

A combination of a pseudo steady state lumped capacitance energy balance analysis and dynamic analysis of the bed's thermal behaviour has been used to derive information like peak heat generation rate during hydriding (which must necessarily be the heat load for which the cooling system of the bed has to be designed in case of larger beds) and maximum surface temperature of the insulation (which is important from the point of view of safety in handling and operating the bed). The information obtained from a dynamic study of the thermal behaviour of the bed under adiabatic condition is used to obtain these parameters and ultimately estimate heat loss rates from the vessel over the temperature range which it is likely to encounter during the hydriding phase. Thermal dynamics of the vessel wall or the insulation layer have not been considered separately, as would have been done in a more detailed, multicapacity heat transfer model but their effect on the time-temperature dynamics of the getter bed has been included by the use of an overall heat transfer coefficient that accounts for convection, conduction and

radiation.

The most pertinent design information for a getter bed for hydrogen storage can be obtained by the simplified analysis presented here. In calculating the wall heat transfer coefficient, a single particle size for the uranium turnings has been considered while in reality the solid getter material will neither have a monodisperse size distribution nor uniform spherical or cylindrical shapes throughout. For large chips or turnings, initially the rate of reaction is expected to be very slow, especially if they are also covered by a layer of uranium oxide or other surface contaminants. In that case the reaction will have to be carried out at above ambient temperature achieved by electrical or induction heating of the bed. The energy balance equation for the vessel will then have to be modified by addition of a heat input term.

A preliminary accident analysis has also been performed by considering air and moisture ingress into the getter bed by leakage or as feed impurity. The effect of the reactions of uranium with oxygen and water vapour alongside the main reaction of uranium and hydrogen on the adiabatic temperature rise of the bed has been considered.

In this work, the focus has been on the hydriding process of uranium and the associated thermal effects in the getter bed. A similar exercise can be carried out for the dehydriding process considering a dehydriding rate equation. There the emphasis would be on preventing heat losses and supplying external heat optimally as opposed to cooling the bed during hydriding reactions.

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