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On the Optimisation of Hydrogen Storage in Metal Hydride Beds

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Abstract

This work presents a systematic approach for the optimal design and control of metal hydride beds used for hydrogen storage. A detailed 2-D mathematical model is developed and validated against experimental and theoretical literature results. Based on recent advances in dynamic optimization, the objective is then to find the optimal process design (e.g. cooling system design) and operating strategy (e.g. cooling fluid flowrate profile over time, hydrogen charging profile, etc) so as to minimize the storing time, while satisfying, a number of operating constraints. Optimization results indicate that almost 60% improvement of the storage time can be achieved, over the case where the system is not optimized, for a minimum storage capacity 99% of the total bed capacity. Trade-offs between various objectives, alternative design options and optimal cooling control policies are systematically revealed illustrating the potential offered by modern optimization techniques.

Keywords: Hydrogen Storage; Dynamic Optimization

1. Introduction

The need for a worldwide conversion from fossil fuels to hydrogen requires the elimination of several barriers imposed along the different steps involved in hydrogen technology. One of the main problems in large usage of hydrogen energy in automotive

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industry is the storage problem. Conventional storage methods such as gas compression and liquidification are impractical since the former requires very heavy gas tanks and the latter is too expensive to be employed in public vehicles. Storing hydrogen in metal hydrides beds as a chemical compound appears to be a promising, cost effective and safe method of hydrogen storage in the near future (Kaplan and Veziroglou 2003). This can be attributed to the reduced operating pressure compared to compress gas technology, thus ensuring less weight and better security. The modelling of hydrogen storage in metal hydride beds has received some attention over the past ten years and several theoretical and experimental works appeared in the literature (Nasrallah and Jemni 1997; Nakagawa et al. 2000, Mat and Kaplan 2001, Mat et al. 2002). The operation of hydrogen storage tank using metal hydrides presents distinct challenges such as the possible appearance of a maximum in the temperature profile (hot spot) and the possibility of temperature runaway. The occurrence of excessive temperatures (often due to parametric sensitivity) can obviously have detrimental consequences on the storage management of the tank such as potential explosions, limited storage capacity, etc. These considerations motivate the need for effective heat management strategies for such systems and novel design options (e.g. design of cooling systems, tank diameter, etc). In this vein, control strategies that regulate the magnitude of the hot spot temperature, while ensuring a maximum storage capacity at minimum total costs are of paramount important. Research indicates that attempts to address this problem directly and systematically are rather rare.

This work presents a systematic optimisation-based strategy for the design and control of metal hydride beds for hydrogen storage. The design of the cooling system, the optimal profile of the cooling medium flowrate and the charging profile of the bed, in order to increase storage efficiency at minimum costs while satisfying a number of safety and operating constraints, are systematically derived.

2. Dynamic Modelling of Metal Hydride beds for Hydrogen Storage

A detailed 2-D mathematical model has been developed taking into account of the physical and chemical phenomena taking place in the bed. The model has been properly integrated with several cooling system models assuming that such systems are located to various radial positions in the bed. Due to space limitations the details of the model is not presented here but the interested reader can refer to Kikkinides et al (2004). The general objective is to suppress the thermal gradients in order to improve the sorption-desorption cycle times and also satisfy potential safety concerns and other design and operating constraints. To this end the following case are considered in details:

- ❖ Introduce a concentric tube, filled with flowing cooling fluid, at the center of the reactor from $r=0$ to $r=r_0$, where $r_0=r_0^*/R<<1$. A typical value used in the present study is $r_0=0.1$.
- ❖ Introduce a concentric annular ring of thickness $\delta r=r_2-r_1$, where $r_1=r_1^*/R$, $r_2=r_2^*/R$, filled with flowing cooling fluid.

Significant modifications and extensions in the original model are required in order to model the above cases. The developed models have been validated againsts experimental and theoretical literature results and have been found to be in excellent agreement. A typical metal hydride reactor with heat exchangers arranged according to the above configurations is shown in Figure 1.

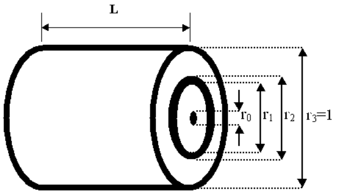

Figure 1. A metal hydride reactor with heat exchangers (in black) inside and outside of the bed

3. Simulation Results

It is interesting to explore the effect of the additional heat exchange configurations on the original design. Thus we consider the following cases:

- Case 1: this is a typical base case with heat exchangers only at r=1 and at z=1.
- Case 2: Here an inner tube is also employed resulting in additional heat exchange at $r=r_0$.
- Case 3: The same as case 2 with the addition of an inner annular ring resulting in additional heat exchange at $r=r_1$ and $r=r_2$.

In Figure 2 we compare the resulting hydrogen uptakes for the three different cases assuming that potential process constraints are not taken into account. As expected both cases 2 and 3 reduce the total hydrogen storage time. It is important to notice that placing an inner annular ring with a heat exchanging fluid at constant temperature, T_c, results in a dramatic improvement in the process performance. More specifically, the time required for 99% storage, drops to about 620 sec, representing a 60% improvement over the base case 1 that requires a total time of 1450 sec for 99% storage.

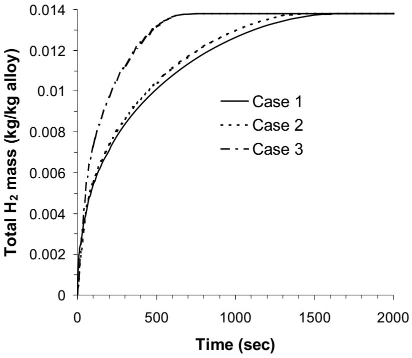

Figure 2. Hydrogen storage profile for three different cooling system designs

A further step along this study was to examine if there is an "optimal" radial position in placing the annular ring. Hence we compared three different cases with r_1=0.4,0.5 and 0.6 while keeping δr=0.1 in all cases. The results (in terms of total hydrogen mass stored and average bed temperature) are shown in Figures 3a and 3b, respectively. It appears that the best position among the three studied cases is the one where the ring is placed close to *r*=0.5. Following a formal optimisation procedure the optimal position is found to be at r_1=0.5137. for r_0=0.1. This position can be explained by the fact that placing the ring close to r=0.5 a more uniform depletion of the temperature fronts at each bed region (inner core or outer core) is achieved.

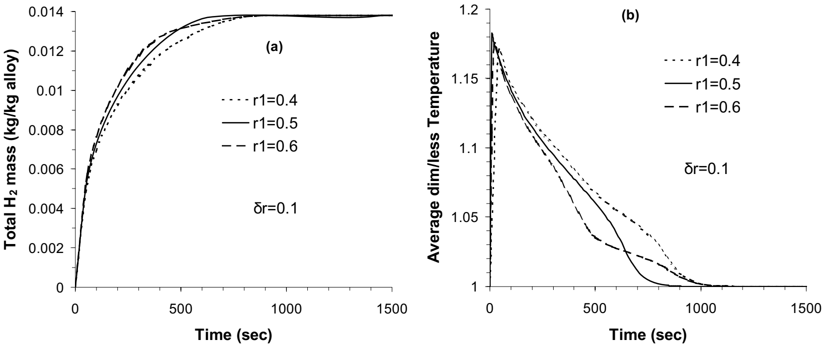

Figure 3. Time evolution (a) of the total H_2 mass and (b) the average temperature in the metal hydride reactor for three different radial positions of the annular ring (T_c=290 K).

4. Optimal Design and Control of Metal Hydride Beds for Hydrogen Storage

4.1 Optimal control of the bed

From the discussion so far it has been evident that there are certain parameters that must be optimally decided in order to achieve an economic and safe process performance. Such parameters can be related to the fixed bed reactor characteristics and/or the heat exchanging system. Here for illustrative purpose only and with no loss of generality we concentrate on the case where only an inner tube with cooling fluid is included and we formally optimize its performance by properly selecting some of the key parameters. Such parameters are, for example, the volumetric flow rate of the cooling fluid, its inlet temperature, the type of the cooling fluid, etc. Because some of these parameters can affect the operation performance in many ways we often end up with a dynamic optimization problem, since the effect is not always monotonic (either positive or negative). A typical example is that of the flow rate of the cooling medium. As we increase the flow rate we expect a more isothermal-like behavior of the cooling fluid, and thus faster storage times. There are two main issues, which must be taken into consideration when establishing optimal control strategies for this system. The first is to ensure that the maximum process storage efficiency is achieved. The second issue is to seek for the best economic performance which can be expressed by the total required storage time since this is proportional to the high compression costs. However, because of the complexity of the underlying process, is it often difficult to define simple heuristic strategies in order to address these two issues and take into account all the operating constraints such as pressure drop limitations, minimum requirements on the total mass hydrogen storage, availability of the cooling medium, maximum temperature due to safety considerations, etc. The overall problem is formulated as a dynamic optimization problem and solved using gPROMS optimization capabilities (Process Systems Enterprise, 2004). Optimization results for the case of 10 control intervals are depicted in Figures 4 for the parameters involved. The results indicate that the optimum time required for 99% H_2 storage in the bed, under the constraints imposed on pressure drop and cooling fluid availability, is 1281 sec. Note that in order to satisfy all the operating constraints, an optimal cooling medium flow rate policy should be used.

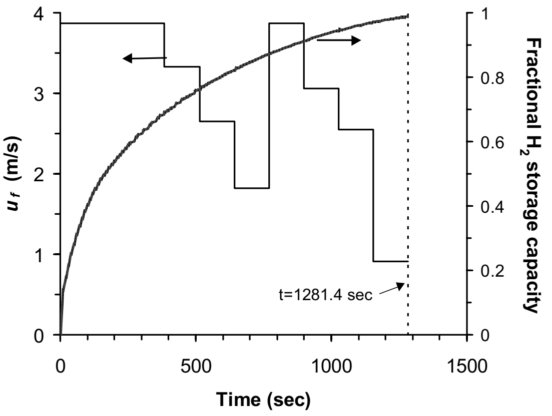

Figure 4. Optimal profile of cooling fluid velocity and fraction of hydrogen storage capacity.

4.2 Optimal Control of temperature gradients in the metal hydride bed

A major problem that often appears in H_2 storage is the excessive amount of heat produced due to the highly exothermic nature of the storage (adsorption-absorption) process. As a result, we have the appearance of extremely high temperature gradients in the reactor bed that can be of the order of 30-60 degrees. In the present base-case study, it was found that the maximum temperature difference is around 65 degrees. Such high temperature differences should be avoided for safety and operability concerns. Past experience has shown that in order to decrease these large temperature differences the system design must be optimized along with the rate of the charging process (inlet pressure history). In general the pressure history at z=0 is determined through a valve equation. Nevertheless for the shake of simplicity we chose to explore the shape of the pressure history curve, which should be controlled by appropriate choice of the various parameters in the valve equation. The dynamic optimisation capabilities of gPROMS have been employed using a total number of 10 time intervals. We employ a piecewise linear approximation of pressure (control variable) by using different optimized slopes at each time interval. In addition a constraint has been imposed on the average bed temperature , ΔT_{avg} , such that this value is always kept below a certain bound value, potentially expressing safety considerations. In order to explore the features of the dynamic optimization algorithm we applied the optimal control procedure for four different temperature constraints: ΔT_{avg}=3 K, 2K, 1.5K and 1K. Thus at the end of the process we have come up with 4 different optimal control profiles for the inlet pressure history, one for each respective temperature constraint and similarly four different profile of the fraction of hydrogen stored.. The results are shown in Figure 5.

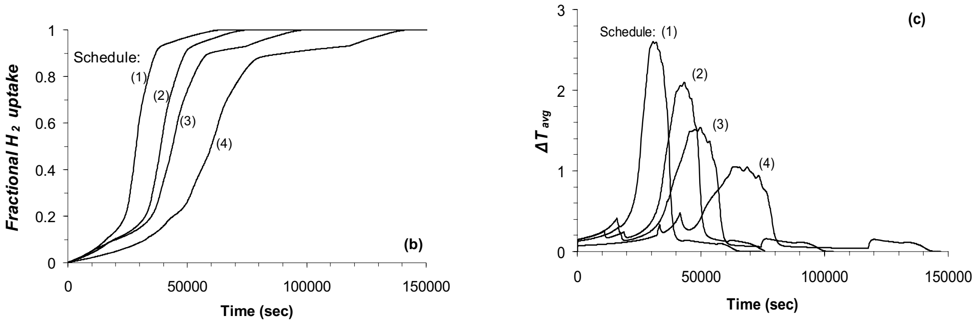

Figure 5. Time evolution of H_2 mass uptake and average temperature difference (dimensionless) profile for four different constraints

5. Conclusions

This work addresses the optimal design and operation of a hydrogen storage hydride bed. The dynamic optimization approach adopted, based on control vector parameterization techniques, identifies the optimal cooling medium control policy so as to achieve a maximum storage efficiency at a minimum storage time horizon, while ensuring satisfaction of complex operating constraints. Furthermore, optimal design decisions include, among others, the radial position of a concentric annular ring in the tank. Optimization results indicate that significant improvement of the storage time can be achieved compared to the case where the system is not optimized.

Acknowledgments

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