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Two Dimensional Model for the Design of Metal Hydride Hydrogen Storage Systems

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Abstract. A 2-D mathematical description of a metal hydride hydrogen storage vessel was developed. This 2-D model was calibrated against experimental discharge data obtained from a commercially viable system containing $Lm_{1.06}Ni_{4.96}Al_{0.04}$ metal hydride. The model was capable of predicting the performance of the vessel for both the discharge and charge processes over a wide range of conditions. This model should thus be very useful for the design and development of the next generation of metal hydride hydrogen storage systems.

Keywords: hydrogen storage, metal hydride, mathematical modeling

Introduction

Hydrogen is being seriously considered as an alternative energy source for use in internal combustion engines or fuel cells; however, despite some recent advancement, hydrogen storage is still a major concern, not only with respect to cost and safety, but also with respect to achieving sufficient gravimetric and volumetric densities for both stationary and especially mobile applications (Ritter et al., 2003). Among the three hydrogen storage options that currently exist, i.e., as a highly compressed gas, as a cryogenic liquid and in a metal hydride solid matrix, metal hydrides still remain attractive, at least for applications that can deal with their low gravimetric hydrogen density, as they store hydrogen relatively safely in the solid form at reasonable temperatures and pressures. For example, the Savannah River National Laboratory (SRNL) used the commercially viable $Lm_{1.06}Ni_{4.96}Al_{0.04}$ metal hydride (Lm = La 55.7, Ce 2.5, Pr 7.7, and Nd 34.1 atomic%) in their design of an on-board hydrogen storage system for a hybrid electric bus (Heung, 1997).

A schematic of the SRNL metal hydride hydrogen storage vessel is shown in Fig. 1. It contains aluminum foam and a U-tube heat exchanger to improve heat transfer. The Al foam is only three-fourths filled with metal hydride powder to compensate for expansion during hydrogenation. A sintered metal feed tube runs axially along the top of the container to ensure a uniform flux of hydrogen into the vessel. These complications present quite a challenge to the development of a mathematical model that can be used for design and optimization.

There are numerous descriptions of mathematical models in the literature (Mat and Kaplan, 2001; Mungole et al., 2000; Nakagwa et al., 2000; Jemni and Nasrallah, 1997; Gopal and Murthy, 1995; Isselhorst, 1997); however, few if any of these studies have validated their models against experimental data, especially from a viable commercial system like the SRNL system. This obviates the use of these models until validation. An exception is the recent works by Gadre et al. (2003, 2005) and Gadre (2003), where mathematical models of increasing complexity were developed that describe the performance of the SRNL system quite well.

These models include: an isothermal-equilibrium model with an analytical solution (Gadre et al., 2003); a 1-D axial gradient model that proved to be suitable for describing the overall behavior of the SRNL system

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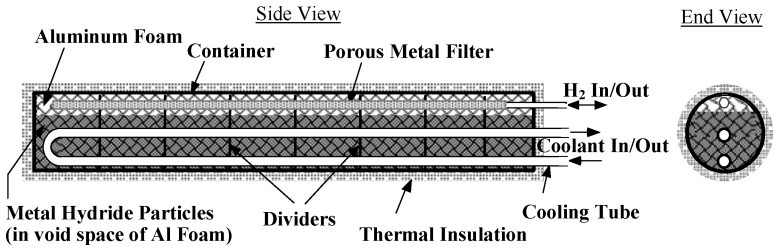

Figure 1. Schematic of the Savannah River National Laboratory metal hydride hydrogen storage vessel.

when including heat and mass transfer effects from the simplest point of view (Gadre et al., 2003); a 1-D axial flow radial energy (AFRE) gradient model, which proved to be better and more insightful than the simpler axial flow model (Gadre et al., 2005); and a AFRE model with a loading dependent thermal conductivity, which further improved the predictive ability of the AFRE model (Gadre et al., 2005). All these models are quite simple and hence useful for incorporating into more complete system integration modeling platforms, like that done recently with a fuel cell unit (Zhenhua et al., 2005). However, a better understanding of this and other systems in terms of the design of a metal hydride hydrogen storage vessel cannot be achieved until a more rigorous 2-D model representing the actual cross-section of the bed is developed.

Therefore, the objective of this study is to extend the works by Gadre et al. (2003, 2005) by developing a 2-D description of the SRNL metal hydride hydrogen storage system. Since mass transfer was shown to have little effect in their previous works, there are only three fitting parameters in this new 2-D model, two for the bed thermal conductivity and one for the overall heat transfer coefficient. The model is calibrated against experimental discharge data obtained from the SRNL system and used to predict its performance over a wide range of conditions, including charge data obtained at relatively high hydrogen flow rates. The results from the 2-D model are also contrasted against those from the simpler 1-D models. Model details and a limited comparison with experimental data are reported. More information and results are given elsewhere (Gadre, 2003).

Theoretical

Only a brief description of the model is given here without any of the equations, as they are provided elsewhere (Gadre, 2003). The 2-D model is based on the following assumptions: The heat exchanger temperature is assumed to be constant and does not vary axially in the U-tube. The hydrogen liberated during discharge flows across the cross-section of the bed under a pressure gradient and then is carried away in the axial direction through the metal feed tube. There is no axial flow at any location in the bed except in the feed tube, where the molar flux is assumed to vary linearly. The outside of the bed is perfectly insulated.

First, the cross-section of the vessel shown in Fig. 1 was divided into three sub-domains. Sub-domains I, II and III, respectively, corresponded to the top of the bed which contained only aluminum foam, the bottom of the bed which contained both aluminum foam and metal hydride, and the feed tube. The U-tube heat exchanger was submerged in sub-domain II. Then, based on these assumptions and assuming ideal gas behavior, 2-D mass and energy balances were written independently for sub-domains I, II and III. The 2-D directional velocities in sub-domains I and II were described by the Blake-Kozeny equation; and in sub-domain III they were described by the equations of motion. The mass transfer resistance was based on a linear driving force (LDF), solid diffusion mechanism in sub-domain II. The heat transfer resistance was based on an overall heat transfer coefficient between the heat exchanger fluid and the aluminum foam/metal hydride particles. The bed thermal conductivity was assumed to be a linear function of loading. Finally, a composite Langmuir (CL) isotherm, with a loading and temperature dependent heat of adsorption (or phase change enthalpy), was chosen as the P-C-T relationship for its ease of use (Gadre et al., 2003).

These equations were solved by first specifying the discharge flow rate at STP through the feed tube. Then, all the relationships were input to the FEMLAB platform and solved simultaneously with the appropriate initial and boundary conditions for discharge. The

initial temperature, pressure and metal hydride loading were specified, along with the boundary condition that equated the heat flux on either side of the heat exchanger and the boundary condition that set the heat flux equal to zero at the perfectly insulated outside vessel wall. This discharge model converted to a charge model simply by changing the initial conditions and the sign of the flux term.

Results and Discussion

A description of the experimental system is provided by Gadre et al. (2003), including the system dimensions, operating conditions, and other model parameters (including the CL isotherm parameters). The same six experimental runs used to calibrate the earlier models (Gadre et al., 2003, 2005) were used here to obtain the heat (h_w) and mass (k_m) transfer coefficients and the thermal conductivity (λ), i.e., the fitting parameters in the 2-D model. Again, one of the six experimental runs, i.e. the 20 SLPM discharge run, was chosen arbitrarily for this purpose. Since mass transfer had little effect compared to heat transfer in the previous work (Gadre et al., 2003), a large k_m was chosen to be close to the equilibrium conditions (i.e., $k_m = 1.0$). Also, since λ was assumed to be a linear function of loading, the two linear coefficients, λ_0 and κ, along with h_w were the actual fitting parameters. Their values were determined to be $\lambda_0 = 2.78$ W/m/K, $\kappa = 0.0005$ and $h_w = 150$ W/m^2/K. It was encouraging that the bed thermal conductivity at zero loading (λ_0) was similar to that obtained in the AFRE model, as it corroborated the validity of these estimated parameters. However, the conductivity variation with respect to loading was significantly less than that predicted with the AFRE model, probably due to the AFRE model not accounting for the 2-D variation in temperature.

Figure 2 compares the experimental pressure and temperature profiles obtained during the 5 and 20 SLPM discharge runs with those predicted from the 2-D model, as well as the other 1-D models. Since predictions of the pressure histories with the previous 1-D models (i.e., the axial flow, AFRE and AFRE with variable conductivity) were already quite good, it was not surprising to obtain good predictions with the 2-D model for all the flow rates. The simpler 1-D and new 2-D models also did reasonably well in predicting the average experimental temperature histories shown in the bottom set of figures, which were obtained by averaging 16 thermocouples (TCs) located axially (4 TCs) and circumferentially (4 TCs) on the external surface of the vessel. However, only the 2-D model was capable of providing accurate predictions of the temperature histories at short times during discharge for the higher flow rate runs, like the 20 SLPM hydrogen discharge run.

Clearly, a cross-section of the bed would be expected to exhibit an asymmetric variation in temperature in going from the top to the bottom of the bed, due to it being only three-fourths filled with metal hydride (Fig. 1). Also, a cross-section of the bed would be expected to exhibit a plane of symmetry in going from the left to the right side of the bed. However, little or no variation in temperature would be expected axially, which was experimentally observed (Gadre et al., 2003). These experimental temperature variations are shown in the middle set of figures by the top, RHS, bottom and LHS temperature histories, which were obtained by averaging the four TCs placed axially at these respective circumferential locations. This circumferential temperature variation was not possible to predict with the 1-D models. In contrast the 2-D model did a satisfactory job in predicting them (middle set of figures). However, the experimental bed had an apparent asymmetry, which caused the temperature on the RHS to be significantly lower than that on the LHS. Since the 2-D model assumed RHS and LHS to be exactly symmetrical, the two curves overlapped each other. Nevertheless, the predictions of the temperature profiles from the 2-D model were reasonably accurate for all discharge flow rates.

The 2-D model was also examined to determine whether it could predict fairly rapid charging of the bed with the same fitting parameters; a typical comparison of the resulting pressure and temperature histories with experiment are shown in Fig. 3. The bed was initially at 328 K and then cooled by passing cold water through the heat exchanger at 295 K and 5 gpm, while feeding hydrogen at 90 SLPM into the bed initially at 2.0 atm until 20 atm was reached. Clearly, this 2-D model also did a good job in predicting, not only the performance of the bed during charge, but also the subtle characteristics associated with its unique geometry.

A major reason for developing the 2-D model was to gain an appreciation and detailed understanding of the heat transfer phenomena occurring in different parts of the bed. The cross-sectional bed profiles of temperature and loading shown in Fig. 4 during a typical discharge run at $t = 0.0$, 1.47 and 2.94 hrs into the

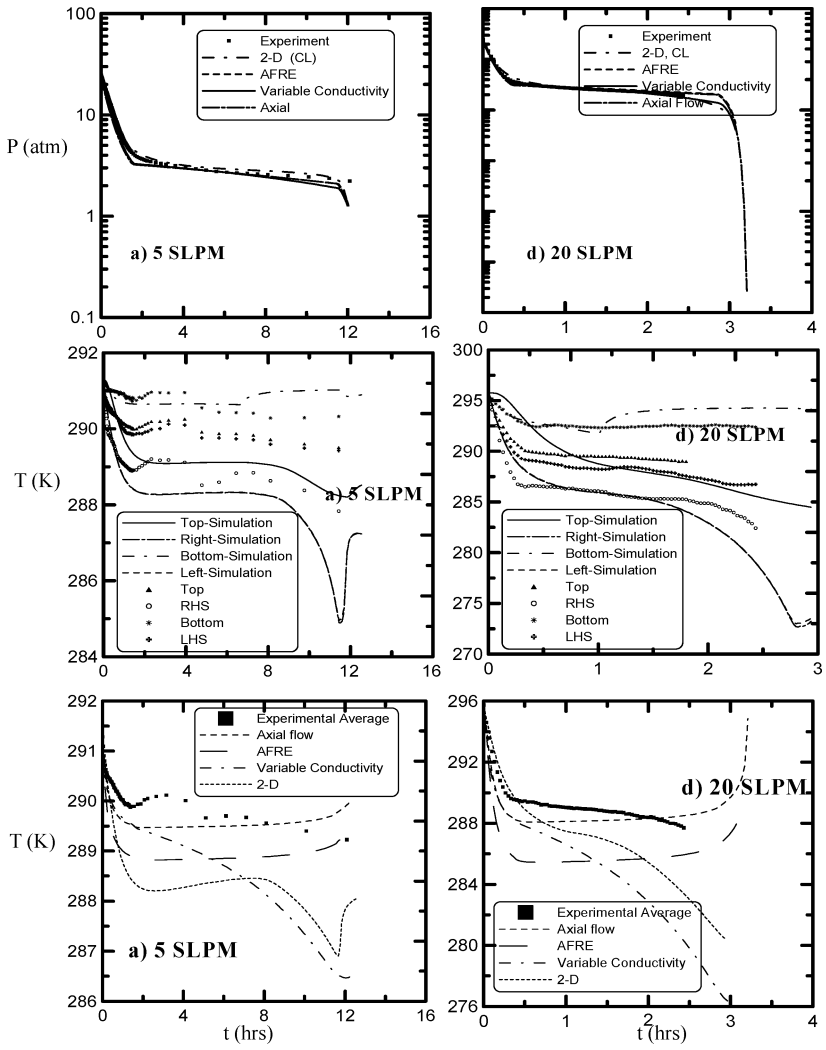

Figure 2. Comparison of predictions from various models with the experimental pressure and temperature histories for 5 and 20 SLPM hydrogen flow rates: initial conditions of 25 atm and 295 K; and heat exchanger water at 295 K and 5 gpm.

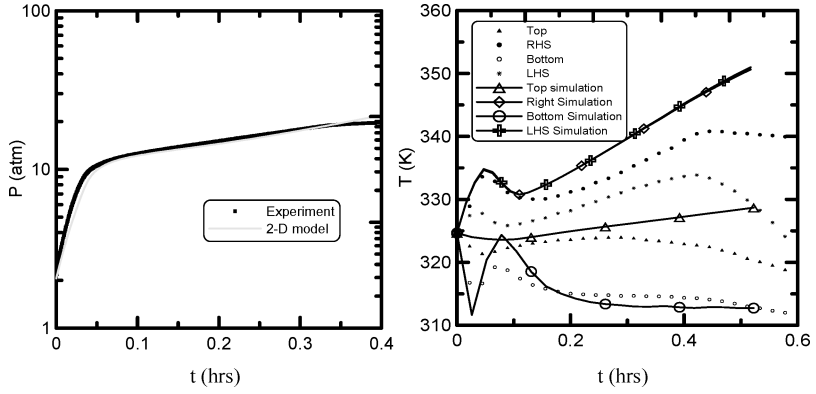

Figure 3. Comparison of 2-D model predictions with the experimental pressure and temperature histories for charging at 90 SLPM hydrogen flow rate; initial conditions of 25 atm and 295 K; and heat exchanger water at 295 K and 5 gpm.

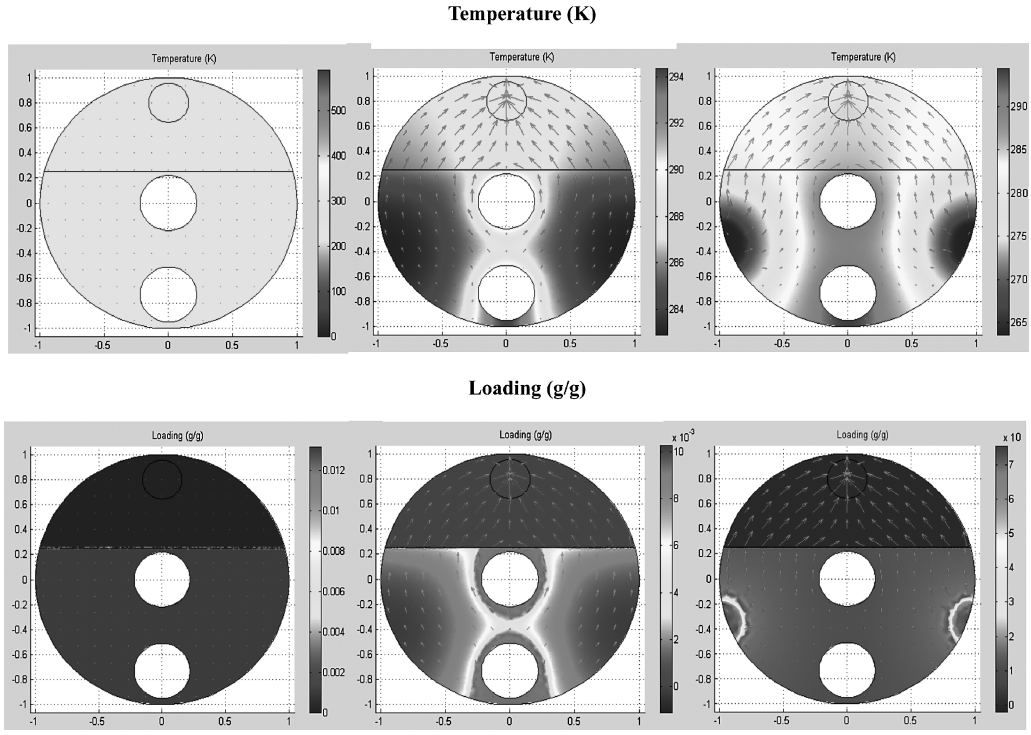

Figure 4. Cross-sectional bed profile predictions of temperature and metal hydride loading from the 2-D model for a 20 SLPM hydrogen discharge: initial conditions of 25 atm and 295 K; and heat exchanger water at 295 K and 5 gpm; and $t = 0.0$ hrs, 1.47 hrs and 2.94 hrs during discharge from left to right.

run reveal this complex behavior. The arrows cutting across the cross-section of the bed represent the flow of hydrogen, with the length of the arrow corresponding to its velocity. The bed, initially ($t = 0$ hrs) at a uniform temperature of 295 K and 25 atm, cooled down significantly on both sides, as hydrogen was released from the metal hydride (endothermically). Note how the arrows emanate from the cooler regions of the bed where hydrogen was still remaining, and how they grow in length as they approached the feed tube. The temperatures close to the heat exchanger always remained higher, since the heat exchanger water was set at 295 K. When the discharge was almost complete ($t = 2.94$ hrs), huge temperature gradients existed inside the bed with the RHS and LHS being significantly cooler than the center of the bed. Also, since higher temperatures correspond to lower metal hydride hydrogen loadings, the hydrogen was depleted much faster near the heat exchanger tubes, where the temperatures were always higher. In contrast, the RHS and LHS of the bed, where the temperatures were always much cooler, still contained significant amounts of hydrogen even when the discharge was almost complete ($t = 2.94$ hrs).

The results in Fig. 4 clearly show the usefulness of the 2-D model for understanding the behavior and predicting the performance of current and next generation metal hydride hydrogen storage bed designs. For example, the placement and number of heat exchanger tubes can readily be studied with such a model. The effect of the relative volumes of sub-domains I, II and III, i.e., the top of the bed containing only Al foam, the bottom of the bed containing both Al foam and metal hydride, and the feed tube, can also be studied.

Conclusions

A 2-D mathematical description of a very intricate metal hydride hydrogen storage vessel was developed in the FEMLAB platform. This commercially viable, Savannah River National Laboratory, patented system contains $Lm_{1.06}Ni_{4.96}Al_{0.04}$ metal hydride dispersed within an aluminum foam matrix, but only three-fourths filled with the metal hydride powder to compensate for expansion during hydrogenation. In addition

to the Al foam, the system also contains a U-tube heat exchanger to improve heat transfer. A sintered metal feed tube also runs axially along the top of the bed to ensure a uniform flux of hydrogen into and out of the vessel.

In contrast to the many complex models in the literature, and in spite of the geometric intricacies of this metal hydride hydrogen storage vessel, the 2-D model developed here has only three fitting parameters. These are the bed thermal conductivity in terms of two coefficients (λ_o and κ) that describe the loading dependence on the thermal conductivity, and the heat transfer coefficient (h_w) at the heat exchanger wall. It is noteworthy that since previous studies showed that this metal hydride bed was severely heat transfer limited, the mass transfer coefficient (k_m) (potentially another fitting parameter, but not here) was chosen to be very high (i.e., $k_m = 1.0$) so that the metal hydride was essentially performing under equilibrium conditions. It is noteworthy that no reaction kinetic expressions were employed in this 2-D model, which greatly simplified its implementation with respect to parameter estimation. The values of the fitting parameters were determined to be $\lambda_o = 2.78$ W/m/K, $\kappa = 0.0005$ and $h_w = 150$ W/m^2/K, by calibrating the 2-D model to a single discharge run from the experimental system. From a physical point of view, the magnitudes of these parameters were quite reasonable.

This 2-D model was capable of predicting the performance of the metal hydride hydrogen storage vessel over a wide range of conditions. Pressure and temperature profiles predicted from the model during both discharge and charge runs compared well with the experimental data. It was also shown how this model could be used to study complex temperature variation within the system that is caused by the endothermic and exothermic effects of discharge and charge being compensated for by the heat exchanger. Overall, this model should be very useful for the design, development and understanding of current and next generation metal hydride hydrogen storage systems, especially because it has few fitting parameters and is easy to implement.

Acknowledgments

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References

Gadre, S.A., "Experimental Design and Simulation of a Metal Hydride Hydrogen Storage System," PhD Dissertation, The University of South Carolina 2003.

Gadre, S.A. et al., "Practical Modeling of Metal Hydride Hydrogen Storage Systems," *Ind. Eng. Chem. Res*., **42**, 1713–1722 (2003).

Gadre, S.A. et al., "One Dimensional Axial Flow Radial Energy Model for the Design of Metal Hydride Hydrogen Storage Systems," *Int. J. Hydro. Energy*, submitted (2005).

Heung, L.K., "On-Board Hydrogen Storage System Using Metal Hydride," in *Hypothesis II Conference Proceedings,* Norway, pp. 251–256, 1997.

Gopal, M.R. and S.S. Murthy, "Studies on Heat and Mass Transfer in Metal Hydride Beds," *Int. J. Hydro. Energy*, **20**, 911–917 (1995).

Isselhorst, A., "Heat and Mass Transfer in Coupled Hydride Reaction Beds," *J. Alloys and Compounds*, 871–879 (1995).

Jemni, A. et al., "Experimental and Theoretical Study of a Metal-Hydrogen Reactor," *Int. J. Hydro. Energy*, **24**, 631–644 (1999).

Mat M.D and Y. Kaplan, "Numerical Study of Hydrogen Absorption in an Lm-Ni_5 Hydride Reactor," *Int. J. Hydro.. Energy*, **26**, 957–963 (2001).

Mungole, M.N. and R. Balasubramaniam, "Effect of Hydrogen Cycling on the Hydrogen Storage Properties of $MmNi_{4.2}Al_{0.8}$," *Int. J. Hydrogen Energy*, **25**, 55–60 (2000).

Nakagwa, T. et al., "Numerical Analysis of Heat and Mass Transfer Characteristics in the Metal Hydride Bed," *Int. J. Hydro. Energy*, **25**, 339–350 (2000).

Ritter, J.A., A.D. Ebner, J. Wang and R. Zidan, "Implementing a Hydrogen Economy," *Materials Today*, **9**, 18–23 (2003).

Zhenhua, J. et al., "Simulation of a Dynamically-Coupled Metal Hydride Hydrogen Storage and Fuel Cell System," *J. Power Sources*., on-line (2005).