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Hierarchical Methodology for Modeling Hydrogen Storage Systems. Part I: Scoping Models

Bruce J. Hardy*, Donald L. Anton
Savannah River National Laboratory, Aiken, SC 29808 USA

ABSTRACT

Detailed models for hydrogen storage systems provide essential design information about flow and temperature distributions, as well as, the utilization of a hydrogen storage media. However, before constructing a detailed model it is necessary to know the geometry and length scales of the system, along with its heat transfer requirements, which depend on the limiting reaction kinetics. More fundamentally, before committing significant time and resources to the development of a detailed model, it is necessary to know whether a conceptual storage system design is viable. For this reason, a hierarchical system of models progressing from scoping models to detailed analyses was developed. This paper, which discusses the scoping models, is the first in a two part series that presents a collection of hierarchical models for the design and evaluation of hydrogen storage systems.

Keywords: Hydrogen Storage Modeling, Hydrogen Storage Systems, Metal Hydrides, Hierarchical Modeling System

* Corresponding author. Tel.: (803) 725-7310; Fax: (803) 725-8829;
E-mail address: bruce.hardy@srnl.doe.gov

NOMENCLATURE

C_{eqv} = $C_{10} + 3C_{20} + C_{30}$

= Concentration of $NaAlH_4$ [moles/m^3] if all metal hydride species were converted to this form. This term is used to convert concentration fractions in the empirical kinetics model to species concentrations.

$C_{p\,f}$ = Specific heat of heat transfer fluid[J/(kg- K)]

C_1 = Concentration of $NaAlH_4$ [moles/m^3]

C_2 = Concentration of Na_3AlH_6 [moles/m^3]

C_3 = Concentration of NaH [moles/m^3]

$C_{1\,0}$ = Initial concentration of $NaAlH_4$ [moles/m^3]

$C_{2\,0}$ = Initial concentration of Na_3AlH_6 [moles/m^3]

$C_{3\,0}$ = Initial concentration of NaH [moles/m^3]

D = Inner diameter of coolant tube [m]

f = Friction factor

G = Mass flux, or mass flux of liquid and gas phases of coolant [kg/m^2-s]

G_{cap} = Gravimetric capacity of the system [kg H_2/kg total]

$h_{conv\ cool}$ = Convection heat transfer coefficient for heat transfer fluid [W/m^2- K]

$h_{2\phi}$ = Two phase convection heat transfer coefficient [W/m^2 K]

k_f = Thermal conductivity of the heat transfer fluid [W/(m- K)]

$L_{hyd\&fins}$ = Length of the bed, including hydride and fins [m]

m_{H_2} = Mass of recoverable hydrogen sorbed in the bed [kg]

m_{system} = Total mass of storage tank, including the bed loaded with H_2, fins, liner gaps and pressure vessel. The mass of the heat transfer fluid is not included.

M_{H_2} = Molecular weight of H_2 [kg/g-mol]

M_{NaAlH_4} = Molecular weight of $NaAlH_4$ [kg/g-mol]

$Nu_D = \frac{hD}{k}$ = Nusselt number based on diameter, D

P = Pressure [Pa]

$P_{eq1}(T)$ = H_2 pressure in equilibrium with $NaAlH_4$ at temperature T [Pa]

$P_{eq2}(T)$ = H_2 pressure in equilibrium with Na_3AlH_6 at temperature T [Pa]

$Pr = \frac{\nu}{\alpha_{diff}}$ = Prandtl number

q" = Heat flux, a scalar, [W/m^2]

R = Gas constant = 8.314 $\frac{J}{mol\ K}$

r_{1F} = Hydriding (forward) reaction rate coefficient for reaction 1 [$mole/(m^3\ s)$]

r_{1B} = Deydriding (backward) reaction rate coefficient for reaction 1 [$mole/(m^3\ s)$]

r_{2F} = Hydriding (forward) reaction rate coefficient for reaction 2 [$mole/(m^3\ s)$]

r_{2B} = Deydriding (backward) reaction rate coefficient for reaction 2 [mole/(m^3 s)]

$Re_D = \frac{GD}{\mu}$ = Reynolds number based on diameter, D

t = Time [s]

T = Temperature [K]

T_{bulk} = Bulk temperature of the heat transfer fluid [K]

T_{wall} = Tube wall temperature [K]

V_{cap} = Volumetric capacity of the system [kg H_2/L]

V_{system} = Total volume of storage tank, including the bed, fins, liner gaps and pressure vessel [m^3]

Greek

α_{diff} = Thermal diffusivity of coolant [m^2/s]

ΔH_i = Enthalpy of reaction on a molar basis of species i [J/(mol of i)]

ΔH_{rx} = Overall heat (enthalpy) of reaction for uptake of H_2 by the hydride [J/g-mol].

$\Delta H_{rxn\ 1}$ = Enthalpy change per mole of H_2 consumed going to left for reaction 1

$\Delta H_{rxn\ 2}$ = Enthalpy change per mole of H_2 consumed going to left for reaction 2

ΔP = Pressure drop across the length of the tube [Pa]

ΔS_i = Entropy change on a molar basis for reaction i [J/mol-K]

ΔT = Change in bulk temperature of coolant over the heated length of the cooling tube [°C]

ν = Kinematic viscosity of coolant [m^2/s]

ρ_f = Mass density of heat transfer fluid [kg/m^3]

ρ_V = Density of saturated vapor [kg/m^3]

μ = Viscosity [Pa-s]

τ = Time required for H_2 charging [s].

INTRODUCTION

Hydrogen storage is a key technical obstacle to the realization of hydrogen fueled vehicles. One method of storing hydrogen in a volumetrically dense form, with acceptable gravimetric density, is through the use of a media that either absorbs, adsorbs or reacts with hydrogen in a nearly reversible manner. However, the complex processes occurring during the onboard charging and discharging of hydrogen from the media make it necessary to utilize detailed numerical models for system evaluation and design. Because detailed models require significant time to develop and run, much effort can be wasted identifying and analyzing poor design concepts. Clearly, it is much more efficient to begin a modeling effort with a good system design and to progress from that point. It is, therefore, useful to employ scoping models that can quickly assess the viability of a coupled media and storage system concept prior to conducting a detailed study. For viable systems, an accurate prediction of system performance is then obtained from detailed models that rigorously integrate the physical chemical processes. Further, the

scoping models can be used to provide input parameters for the detailed models including:

- System size required to store a given mass of hydrogen
- Coolant flowrates and temperatures required to remove the heat generated during hydrogen uptake or discharge.
- Pressures and temperatures that optimize reaction kinetics.
- Upper bounds on the hydrogen charging rate.

As evidenced by the literature review in [1] and [2], prior modeling efforts have focused on predicting the behavior of particular design concepts rather than developing a systematic, quantitative methodology for identifying and analyzing storage system designs (storage vessel and media combinations) that satisfy specific performance criteria. If, as is presently the case, a large number of coupled media and vessel designs require evaluation, a prohibitive amount of time will be consumed by directly applying detailed models without a systematic screening methodology.

Three scoping models were developed to assess the kinetics, the length scales and heat removal requirements of the system, respectively. The kinetics scoping model is used to evaluate the effect of temperature and pressure on the charge and discharge kinetics. The model determines the transient mass of stored hydrogen per mass of hydride, the optimal charge and discharge rates for a particular hydride, and the maximum mass of recoverable hydrogen that can be stored over a long time interval. The kinetics model,

developed with the Mathcad® solver [3], runs in a matter of seconds and can be used to quickly identify the optimal temperature and pressure for either the charge or discharge processes. The geometry scoping model is used to calculate the size of the system, the optimal placement of heat transfer elements, and the gravimetric and volumetric capacities for a particular geometric configuration and hydride. This scoping model was developed in Microsoft Excel® [4] and inputs the mass of hydrogen to be stored, mass of stored hydrogen to mass of hydride (from the kinetics model), component densities, etc. The heat removal scoping model, also based on Microsoft Excel®, is used to calculate coolant flowrates, pressure drops and temperature increases over the length of the cooling channels, and convection heat transfer coefficients. The model inputs system length scales and the mass of hydrogen to be stored directly from the geometry scoping model. Additional inputs consist of the heats of reaction for hydrogen uptake/discharge, the thermal properties of the coolant and the time required to charge the bed.

The system of scoping models is general and can be applied to any storage material and bed configuration. In this document, the models are applied to $TiCl_3$ catalyzed $NaAlH_4$ storage media in a cylindrical shell and tube storage configuration that has axially spaced fins, similar to the system developed by the United Technologies Research Center™, East Hartford, Connecticut, Mosher, et. al. [5]. This configuration is the left illustration in Figure 1. The cross-section of the actual vessel analyzed in the model is shown in the illustration on the right in Figure 1.

KINETICS SCOPING MODEL

Chemical kinetics based hydrogen charging and discharging rates for a particular storage media are evaluated with the chemical kinetics scoping model, which addresses dependence on temperature, pressure and initial composition. The model is used to identify potential discrepancies in kinetics data, optimize charging rates, and determine the gravimetric and volumetric capacities of the hydride.

In this document the kinetics scoping model is applied to $TiCl_3$ catalyzed sodium alanate, $NaAlH_4$, which was chosen for two reasons. First, the kinetics equations for this hydride pose a significant challenge for numerical models. Second, $NaAlH_4$ is one of the few complex hydrides for which kinetics equations are available. It bears repeating, however, that the kinetics scoping model may be applied to any storage media, once its hydrogen uptake and discharge kinetics have been characterized.

Sodium Alanate Kinetics

The United Technologies Research Center™ (UTRC™) developed an empirical kinetics model for hydrogen uptake and discharge reactions in $TiCl_3$ catalyzed $NaAlH_4$, see Attachments 3 and 4 in [6]. The chemical balance equation for the reaction is

$$\underbrace{NaAlH_4}_{\text{Species 1}} \underbrace{\leftrightarrow}_{\text{Reaction 1}} \underbrace{\frac{1}{3}Na_3AlH_6}_{\text{Species 2}} + \frac{2}{3}Al + H_2 \underbrace{\leftrightarrow}_{\text{Reaction 2}} \underbrace{NaH}_{\text{Species 3}} + Al + \frac{3}{2}H_2 \qquad (1)$$

To use the kinetics model, define the expressions:

$$r_{1F} \equiv C_{eqv} A_{1F} \exp\left[-\frac{E_{1F}}{RT}\right]\left[\frac{P(C,T) - P_{eq1}(T)}{P_{eq1}(T)}\right] \tag{2a}$$

$$r_{1B} \equiv -C_{eqv} A_{1B} \exp\left[-\frac{E_{1B}}{RT}\right]\left[\frac{P_{eq1}(T) - P(C,T)}{P_{eq1}(T)}\right] \tag{2b}$$

$$r_{2F} \equiv -C_{eqv} A_{2F} \exp\left[-\frac{E_{2F}}{RT}\right]\left[\frac{P(C,T) - P_{eq2}(T)}{P_{eq2}(T)}\right] \tag{2c}$$

$$r_{2B} \equiv C_{eqv} A_{2B} \exp\left[-\frac{E_{2B}}{RT}\right]\left[\frac{P_{eq2}(T) - P(C,T)}{P_{eq2}(T)}\right] \tag{2d}$$

The equilibrium H_2 pressures $P_{eq1}(T)$ and $P_{eq2}(T)$ are given by the van't Hoff equations:

$$P_{eq1}(T) = 10^5 \exp\left[\frac{\Delta H_4}{RT} - \frac{\Delta S_4}{R}\right] \tag{3a}$$

$$P_{eq2}(T) = 10^5 \exp\left[\frac{\Delta H_2}{RT} - \frac{\Delta S_2}{R}\right] \tag{3b}$$

Values for the constants used in Eqs. 2a-d, and 3a-b are listed in Table 1.

Table 1
Constants for the Rate and Equilibrium Expressions, see Attachment A-1 of [6].

Constant	Value
A_{1F}	10^8
A_{1B}	4×10^5
A_{2F}	1.5×10^5
A_{2B}	6×10^{12}
E_{1F}	80.0 kJ/mol
E_{1B}	110.0 kJ/mol
E_{2F}	70.0 kJ/mol
E_{2B}	110.0 kJ/mol
χ_{1F}	2.0
χ_{1B}	2.0
χ_{2F}	1.0
χ_{2B}	1.0
$\frac{\Delta H_1}{R}$	-4475
$\frac{\Delta S_1}{R}$	-14.83
$\frac{\Delta H_2}{R}$	-6150
$\frac{\Delta S_2}{R}$	-16.22

The reference for this model, contained in Attachments 3 and 4of [6], proposes the kinetics equations

$$\frac{dC_1}{dt} = \begin{cases} r_{1F}\left[\frac{3C_2(t)}{C_{eqv}} - C_{2sat}(T)\right]^{\chi_{1F}} & \text{if} \quad P \geq P_{eq1}(T) \\ r_{1B}\left[\frac{C_1(t)}{C_{eqv}}\right]^{\chi_{1B}} & \text{if} \quad P < P_{eq1}(T) \text{ and } C_1(t) \geq 0 \end{cases} \tag{4a}$$

and

$$\frac{dC_3}{dt} = \begin{cases} r_{2F}\left[\frac{C_3(t)}{C_{eqv}} - C_{3sat}(T)\right]^{\chi_{2F}} & \text{if} \quad P \geq P_{eq2}(T) \\ r_{2B}\left[\frac{3C_2(t)}{C_{eqv}}\right]^{\chi_{2B}} & \text{if} \quad P < P_{eq2}(T) \text{ and } C_2(t) \geq 0 \end{cases} \tag{4b}$$

By Eq. 3.1-1

$$\frac{dC_2}{dt} = -\frac{1}{3}\left(\frac{dC_1}{dt} + \frac{dC_3}{dt}\right) \quad \text{or} \quad C_2 = C_{2\,0} - \frac{1}{3}\left[\left(C_1 - C_{1\,0}\right) + \left(C_3 - C_{3\,0}\right)\right] \tag{4c}$$

Based on data for the charging of NaH, expressions for $C_{2\,sat}(T)$ and $C_{3\,sat}(T)$ were fit by Mosher, UTRC™, see Attachment 4 of [6], as

$$\begin{aligned} C_{2\,sat}(T) &= 0 \\ C_{3\,sat}(T) &= r_{sat}\left(1 - \frac{wf_{iso}^{sat}(T)}{0.056}\right) \end{aligned} \tag{5}$$

where: $r_{sat} = Max\left[1, \left(1 - \frac{0.0373}{0.056 - wf_{iso}^{sat}(T)}\right)\right]$ (6)

The values for the empirical fitting term, $wf_{iso}^{sat}(T)$, vs. temperature are listed in Table 2.

Table 2
Values for $wf_{iso}^{sat}(T)$, see Attachment A-1 of [6].

T (K)	$wf_{iso}^{sat}(T)$
353.15	0.021
363.15	0.023
373.15	0.029
393.15	0.022
413.15	0.018

The kinetics scoping model uses a spline fit to this data with extrapolation fixed at the endpoint values.

The weight fraction of H_2 contained in the sodium alanate metal, based on Eq. 1, is defined as

$$wf = \frac{\text{Mass of } H_2 \text{ in Metal}}{\text{Equivalent Mass of } NaAlH_4} = \frac{1.5C_1 + 0.5C_2}{C_{eqv}} \frac{M_{H_2}}{M_{NaAlH_4}} \quad (7)$$

GEOMETRY AND HEAT TRANSFER SCOPING MODELS

The size of a hydrogen storage system, the location of particular components and its gravimetric and volumetric capacities are calculated with the geometry scoping model. Operating parameters for the heat removal system are calculated with the heat removal

parameter scoping model. The heat transfer scoping model inputs data from the geometry scoping model and, is therefore, run afterwards. Details of the calculations made in the geometry and heat transfer scoping models are given in [6].

Geometry Scoping Model

The storage system modeled in this report consists of a cylindrical bed with a circular array of axial coolant tubes and a central axial coolant tube, see Figure 2. Fins used to enhance heat transfer, are positioned normal to the vessel axis. The arrangement of fins is similar to that of the UTRC™ storage vessel shown in Figure 1, see [5]. The storage media ($TiCl_3$ catalyzed $NaAlH_4$) is layered between the fins. Hydrogen is assumed to be introduced to the bed by a circular array of axial tubes. The pressure vessel itself is assumed to be cylindrical with hemispherical end caps.

Radius of Outer Coolant Tube Ring

Consider a cylindrical bed having a cross-sectional geometry similar to that in Figure 1, but with a variable number of coolant and hydrogen feed tubes. Figure 1 represents a cross-section of the hydride bed only. The pressure vessel, liner and radial gaps are not included in the drawing. Area A_1 in the figure represents the cross-sectional surface area extending from the center of the bed to the circle passing through the centers of the coolant tubes. Area A_2 represents the area of the bed extending from the circle passing through the centers of the coolant tubes to the outer edge of the bed.

Let

S_1 = The arc length of tubes in contact with coolant, lying within area A_1.

S_2 = The arc length of tubes in contact with coolant, lying within area A_2.

To obtain similar rates of heat removal for the inner and outer volumes of the bed, which are the volumes formed by projecting areas A_1 and A_2 along the axis of the bed, it is desirable to have

$$\frac{A_1}{S_1} = \frac{A_2}{S_2} \tag{8}$$

Equation 8, which gives the radius, r, of the ring of outer coolant tubes is equivalent to requiring the ratio of heat-generating volume to cooled surface area to be the same for both regions. This can easily be seen by multiplying the numerator and denominator of both sides of the equation by the bed length, L_{bed}.

The arc lengths of the surfaces in contact with the coolant, S_1 and S_2, are calculated by considering the geometries shown in Figures 1 and 2.

For a given total number of coolant and hydrogen feed tubes and their associated radii, Equation 8 is used as an objective function to obtain a value for r.

System Length Scaless and Masses

Given a volume of hydride, the fin thickness and the approximate fin spacing, the number of plate fins is calculated by the geometry scoping model. The model calculates the total length of the bed, including hydride and fins, and the actual spacing between the fins. The outer vessel length scales are then calculated from the thicknesses of the vessel and liner, the widths of internal gaps and the characteristics of the vessel end caps.

Input Parameters for System Length Scales

The input parameters required to calculate the length Scales of the storage vessel are listed in Table 3.

Table 3
Input for Calculation of System Length Scales

Parameter	Value
Mass of recoverable H_2 to be stored in vessel	1000.00 g
Effective ratio of moles H_2 to moles $NaAlH_4$ that can be stored	1.500
Bulk density of $NaAlH_4$ powder, from [5]	0.72 g/ cm^3
Hydride bed diameter, no walls	23.00 cm
Diameter of coolant tubes	1.91 cm
Diameter of H_2 injection tubes	1.27 cm
Number of coolant tubes	9
Number of H_2 injection tubes	8
Thickness of fin plates	0.0313 cm
Approximate spacing between fin plates	0.64 cm
Tube wall thickness	0.12 cm
Density of tube material (6061-T6 Al from table on pg 6-11 of Avallone and Baumeister [7])	2.70 g/ cm^3
Density of fin material (6061-T6 Al from table on pg 6-11 of Avallone and Baumeister [7])	2.70 g/ cm^3
Material density of porous insert for H_2 delivery (6061-T6 Al from table on pg 6-11 of Avallone and Baumeister [7])	2.70 g/ cm^3
Void fraction of porous insert for H_2 delivery	0.70
Density of tank material (Composite @ 0.05419lbm/in^3)	1.50 g/ cm^3
Density of liner material (6061-T6 Al from table on pg 6-11 of Avallone and Baumeister [7])	2.70 g/cm^3
Assume 1/16 in gap between bed & liner	0.159 cm
Assume 1/32 in thick liner	0.079 cm
Tank wall thickness at 50 bar w/ safety factor	0.132 cm

Storage System Characteristics

The Department of Energy has set goals for the system volumetric capacity, V_{cap}, and the system gravimetric capacity, G_{cap}, which are respectively defined as

$$V_{cap} \equiv \frac{m_{H_2}}{V_{system}} \tag{9}$$

and

$$G_{cap} \equiv \frac{m_{H_2}}{m_{system}} \tag{10}$$

Within the geometry scoping model, the volume and mass of the system are computed from the length scales and component densities to give the volumetric and gravimetric capacities, V_{cap} and G_{cap}, respectively.

Heat Transfer Scoping Model

The purpose of the heat transfer scoping model is to determine the operating parameters required to transfer heat to and from the storage media during charging and discharging operations. Parameter values calculated with this scoping model provide insight into whether a proposed heat removal system is practical. The exothermic chemical reactions occurring during the charging of the bed and the requirement that the bed be heated to release hydrogen necessitate the use of a heat management system. Since a shell and tube

configuration is assumed for the heat transfer system, the principal heat transfer parameters are those related to convection heat transfer for the coolant tubes.

The required rate of heat removal is determined by dividing the total heat generated during the charging of the bed by amount of time required for charging to occur. In this calculation, it is tacitly assumed that heat transfer to the coolant tubes is instantaneous and that the bed uptakes the full charge of hydrogen over the time allotted for charging. The system modeled in this report was evaluated for Dowtherm T® heat transfer fluid. Data sheets, from the respective vendors are listed in Attachment 1 of Hardy [6].

The Dittus-Boelter correlation was used to predict the mass flowrate required to remove the heat of reaction. From Holman [8] the Dittus-Boelter correlation is

$$\mathrm{Nu}_D = 0.023\,\mathrm{Re}_D^{0.8}\,\mathrm{Pr}^{0.4} \tag{11}$$

Therefore, the convection heat transfer coefficient is

$$h_{\text{conv cool}} = 0.023\left(\frac{GD}{\mu}\right)^{0.8}\mathrm{Pr}^{0.4}\,\frac{k_f}{D} \tag{12}$$

The local heat flux, q'', from the wall of the coolant tube is then

$$q'' = h_{conv\ cool}\left(T_{wall} - T_{bulk}\right) = \left(0.023\left(\frac{GD}{\mu}\right)^{0.8} Pr^{0.4}\,\frac{k}{D}\right)\left(T_{wall} - T_{bulk}\right) \tag{13}$$

Based on the mass of hydrogen to be stored, m_{H_2}, and the duration, τ, of the charging process, the average heat flux required to remove heat released while charging the hydride is

$$q'' = \frac{\left(m_{H_2} / M_{H_2}\right)\Delta H_{rx}}{A_{tube}\,\tau} \tag{14}$$

For constant q'' along the axis of the cooling tube, and consequently a constant value of $\left(T_{wall} - T_{bulk}\right)$, Equations 13 and 14 give the mass flux, G, required to remove the heat generated during charging.

$$G = \frac{\left(q''\right)^{1/0.8}}{\left[0.023\frac{k_f}{D} Pr^{0.4}\left(\frac{D}{\mu}\right)^{0.8}\left(T_{wall} - T_{bulk}\right)\right]^{1/0.8}} \tag{15}$$

The pressure drop over the length of a coolant tube (length of the bed), required to drive coolant through the tube at a mass flux G, is

$$\Delta P = f \frac{L_{hyd\&fins}}{D} \frac{G^2}{2\rho_f} \quad (16)$$

The rise in the bulk coolant temperature over the length of a coolant tube (length of the bed) is approximated as

$$\Delta T \approx 4 \frac{q'' L_{hyd\&fins}}{DGC_{p\,f}} \quad (17)$$

Input for Heat Transfer

The input required to calculate heat transfer requirements for the system are listed in Table 4.

Table 4
Input for Calculation of Heat Transfer Parameters

Parameter	Value	Reference
ΔH_{Rxn1}	37.00 kJ/mol H_2	Heat of reaction from species 2 to species 1, see Eq. 3.1-1, Gross [9]
ΔH_{Rxn2}	47.00 kJ/mol H_2	Heat of reaction from species 3 to species 2 , see Eq.3.1-1, Gross [9]
Charging Time	180.00 sec	
Wall Temp	90.00 °C	
Coolant Density	820 kg/m^3	Dowtherm T®, see Attachment 1 in [6]
Coolant Themal Cond	0.104 W/(m K)	Dowtherm T®, see Attachment 1 in [6]
Coolant Viscosity	0.003 kg/(m s)	Dowtherm T®, see Attachment 1 in [6]
Coolant Specific Heat	2300 J/(kg K)	Dowtherm T®, see Attachment 1 in [6]
Coolant Prandtl No.	66.52	Dowtherm T®, see Attachment 1 in [6]

RESULTS

Kinetics Model

In this report, the kinetics scoping model was applied to $TiCl_3$ catalyzed $NaAlH_4$. Charging and discharging rates calculated by the kinetics model were idealized because the temperature and pressure remained fixed throughout the process; quite different from what would occur in an actual storage bed. In an actual storage bed, there will be a pressure transient when the bed is charged or discharged. Further, thermal inertia coupled with heat generated by chemical reactions will result in spatial variation in the temperature of the bed. The difference between the fixed pressure and temperature assumed in the kinetics scoping model and those in the actual bed will result different reaction rates. These effects are the primary reason that a 3-dimensional model, which couples thermal, mass and momentum transport, is required to provide an accurate assessment of bed performance. However, because the temperature and pressure can be fixed in the kinetics scoping model, it can be used to predict the upper limit for charging and discharge of hydrogen from a particular storage media.

$TiCl_3$ Catalyzed $NaAlH_4$

To verify that the kinetics scoping model functioned correctly, hydrogen charging curves for pure NaH were generated at 68 bar for various temperatures using the UTRC™ kinetics model for $TiCl_3$ catalyzed $NaAlH_4$, see Figure 3. Charging rates in this figure are expressed in terms of the weight fraction of hydrogen stored in the hydride, as given by Equation 7. Figure 4 compares the charging rates calculated by UTRC™, using its

kinetics model, with data. Comparing the solid curves in Figures 3 and 4 shows that the kinetics scoping model gave rates that closely follow those obtained from UTRC's™ application of its model. Unfortunately, a tabulation of the values used to generate the UTRC™ plot was not available, so a more precise comparison could not be made.

Charging a bed initially composed of pure NaH, with a stoichiometric ratio of Al, at 50 bar and 100°C, gives the loading curve shown in Figure 5. The pressure was based on prior concepts for hydrogen refueling stations and the temperature was selected to optimize the rate of hydrogen charging, allowing for some temperature overshoot in an actual bed due to the exothermic charging reactions and thermal resistance in the bed. By convention, see Equation 7, the weight fraction in Figure 5 is the mass of recoverable H_2 divided by the mass of $NaAlH_4$ that would occur if the monohydride and hexahydride were all converted to the tetrahydride form. From the kinetics model, the gravimetric capacity, which is the maximum weight fraction of recoverable H_2, approaches 0.029 at the long time limit rather than 0.056, which is the theoretical limit obtained from Equation 7 for the chemical balance in Equation 1. The limited conversion is due to the empirical saturation terms $C_{sat\ i}(T)$ in the kinetics equations. Because the saturation terms depend on temperature, the fraction of monohydride that can be converted to tetrahydride for long times varies with the system temperature during loading. The transient weight fraction of stored hydrogen depends on both the temperature and pressure during the charging process.

Figure 7 shows the curve of Figure 5 on the time interval from 0 to 720 seconds. From this figure it can be seen that, starting with pure NaH, the media loads to hydrogen weight fractions of 0.00238 $\frac{\text{kg } H_2}{\text{kg Total}}$ and 0.00794 $\frac{\text{kg } H_2}{\text{kg Total}}$ in 3 and 12 minutes, respectively.

These values represent the effective gravimetric capacities of the *media* for the corresponding charging times. The U. S. Department of Energy (DOE) 2010 technical targets for onboard refueling, Attachment 3 of [1], require the entire *storage system* (including the mass of the storage vessel and internal components) to load to a hydrogen weight fraction of 0.06 $\frac{\text{kg } H_2}{\text{kg Total}}$ in 3 minutes. Hence, the *media* weight fraction alone is about 4.0% of the DOE target *system* value for a charging time of 3 minutes and approximately 13.2% of the target *system* value if a 12 minute charging time were allowed. As noted earlier, the hydrogen weight fraction loaded in an actual storage bed is expected to deviate from these values because the kinetics model calculates rates at a fixed temperature and pressure. Heat transfer resistance coupled with the exothermic uptake reactions will result in differences between the transient temperature in an actual storage system and the fixed temperature assumed in the kinetics scoping model. Additionally, the pressure in an actual storage system will differ from the assumed value used in the kinetics scoping model during transient operation.

Given the kinetics for $TiCl_3$ catalyzed $NaAlH_4$ at 50 bar and 100°C, approximately 421 kg of $NaAlH_4$ would be required to charge 1 kg of hydrogen into pure NaH in 3 minutes. Because the loading curves are non-linear in time, approximately 126 kg of $NaAlH_4$

would be required to charge 1 kg of hydrogen into pure NaH in 12 minutes under these conditions. If these quantities of $NaAlH_4$ were loaded into the storage vessel, the first discharge would release approximately 23.6 kg and 7 kg of hydrogen, respectively, if the $NaAlH_4$ were converted entirely to NaH. Subsequent charging and discharging of the bed, however, would only involve 1 kg of hydrogen.

Based on the bulk density of $NaAlH_4$, taken as 0.72 g/cm^3 [9] and assuming a 56% powder packing density, the molar density is approximately 13,333 mole/m^3. By Equation 1, each mole of $NaAlH_4$ converts to a mole of NaH. Thus, upon discharge of the hydrogen the NaH concentration would also be 13,333 mole/m^3. Cycling a bed having an initial concentration of 13,333 mole/m^3 of NaH, and 0 mole/m^3 of the other hydrides, with a stoichiometric quantity of Al, between charging conditions of 100°C at 50 bar and discharging conditions of 120°C at 1 bar gives the concentration curves shown in Figure 8.

Bed Geometry

Hardy [6] contains a copy of the full input and output for the geometry scoping model as applied to sodium alanate in the modified shell and tube vessel. In this sample calculation, however, the ratio of *moles* of recoverable H_2 to *moles* of $NaAlH_4$ in the fully converted bed was input as the theoretical value of 1.5 rather than 0.213, which is the value calculated by the kinetics scoping model for a 12 minute charging time, see Table 3. Based on the model input, the parameters in Table 5 were obtained.

Table 5
Calculated Bed and Vessel Parameters

Required length of hydride alone (no structural members, fins or vessel)	0.6562 m
Total number of fin plates, including ends	105
Total length of bed (with fins but no vessel)	0.6890 m
Actual spacing of plates	0.0063 m
Mass of bed; including fins, tubes & $NaAlH_4$	24.643 kg
Volume of bed with vessel & liner	0.0362 m^3
Overall length of vessel (assumed semi-spherical ends)	0.9264 m
Radial distance from axis of storage vessel to center of cooling tube circle. The distance r in Figure 2.	0.0855 m
Gravimetric capacity of storage system	0.041 (kg H_2)/(kg Total)
Volumetric capacity of storage system	0.028 (kg H_2)/(L Total)

Even under the most favorable charging conditions the kinetics scoping model showed that the charging rate was slow and the maximum weight fraction of stored hydrogen was below the theoretical limit. To meet the DOE 2010 target refueling time of 3 minutes, the mass of hydride and the system will need to be increased to the point that the gravimetric capacity of the *system* will be 0.00175 $\frac{\text{kg } H_2}{\text{kg Total}}$. The volumetric capacity of the *system* will be 0.00142 $\frac{\text{kg } H_2}{\text{Liter Total}}$. Both the gravimetric and volumetric capacities for the system, for a 3 minute recharging time, are far below the DOE 2010 technical target gravimetric

and volumetric capacities[1] of 0.06 $\frac{\text{kg } H_2}{\text{kg Total}}$ and 0.045 $\frac{\text{kg } H_2}{\text{Liter Total}}$, respectively, see Attachment 3 of [1]. Increasing the recharging time to 12 minutes gives a *system* gravimetric capacity of 0.00584 $\frac{\text{kg } H_2}{\text{kg Total}}$. For this recharging time the system volumetric capacity is

0.00465 $\frac{\text{kg } H_2}{\text{Liter Total}}$.

Bed Heat Transfer

The spreadsheet used to compute the operating requirements of the bed heat transfer system during charging is listed in Hardy [6]. Based on the chemical reaction equation and heats of reaction for $NaAlH_4$, the 2010 DOE target recharging time of 3 minutes and the inner surface area of the coolant tubes, the surface heat flux at the interior wall of a coolant tube was calculated to be 3.45×10^5 W/m^2. Table 6 lists the heat transfer system operating parameters, required to remove the heat of reaction during charging, when Dowtherm T® is used as the transfer fluid. From the values in Table 6, it can be seen that the operating parameters for the heat exchange system are reasonable.

[1] Gravimetric and volumetric capacities for the *system* are calculated for a graphite composite pressure vessel and under assumptions regarding internal components. The volumetric capacity of the *media* is based on an assumed sodium alanate bulk density of 0.72 g/cm^3 [9].

Table 6
Bed Heat Removal Parameters for a Single Coolant Tube Using DowTherm-T®

Mass Flux	10,300.4 kg/(m^2 s)
Mean Flow Velocity	12.61 m/s
Tube Reynolds Number	58,861.02
Pressure Drop Over Length of Tube	8.134×10^4 Pa
Increase in Temperature Over Length of Tube	2.42 °C
h_{DBL}	4,921.78 W/(m^2 °C)

The heat transfer scoping model assumes that all heat released during the hydrogen charging process is immediately transferred to the coolant tubes. However, in reality reaction rates would not be as fast as assumed, requiring more than 3 minutes, and the low thermal conductivity of the hydride impedes the transfer of thermal energy. Thus, the heat transfer system operating parameters calculated by the heat transfer scoping model are very conservative, and provide more than sufficient heat removal capacity.

CONCLUSIONS

The kinetics, geometry and heat transfer, scoping models are a part of a comprehensive hierarchical methodology used to determine whether or not a storage media together with a corresponding storage system meets operational requirements and merits evaluation with a more detailed model. In addition to the evaluation of storage system performance, the scoping models can be used to identify and test design modifications at a preliminary level. While the scoping models do not perform detailed, coupled physics calculations, as would the detailed numerical model discussed in Hardy [1] and Hardy and Anton [2],

they provide sufficient information to estimate nominal length scales and heat transfer parameters required for the storage system.

To assess a particular hydride and bed configuration the kinetics, geometry and heat transfer scoping models are applied in the following sequence. First, the kinetics scoping model is used to evaluate the equations describing the chemical kinetics for potential discrepancies. Temperatures and pressures that optimize reaction kinetics for the charging and discharging of hydrogen are determined. Under the optimal conditions, the ratio of moles of stored hydrogen to the moles of hydride, attained over a specified refueling time, is calculated. Second, the molar ratio of stored hydrogen, along with other system parameters, see Table 3, are input to the geometry scoping model and the length scales of the storage system, along with its volumetric and gravimetric capacities are calculated. Third, for a particular heat transfer fluid, the operating parameters of the heat transfer system are determined from the heat transfer scoping model.

The scoping analysis clearly demonstrates the need for a hydride that has faster kinetics and a higher hydrogen storage capacity. The low thermal conductivity of the hydride, coupled with the high reaction enthalpy for charging, suggests the need to either reduce the thermal transport length to cooling elements or to otherwise increase the thermal conductivity of the media. Also, hydrides with a lower reaction enthalpy should be investigated. Further, in a more subtle sense, the elementary analysis performed in this

document demonstrates the need for engineering properties for the storage media, which are largely lacking at present.

ACKNOWLEDGEMENTS

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DISCLAIMER

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FIGURES

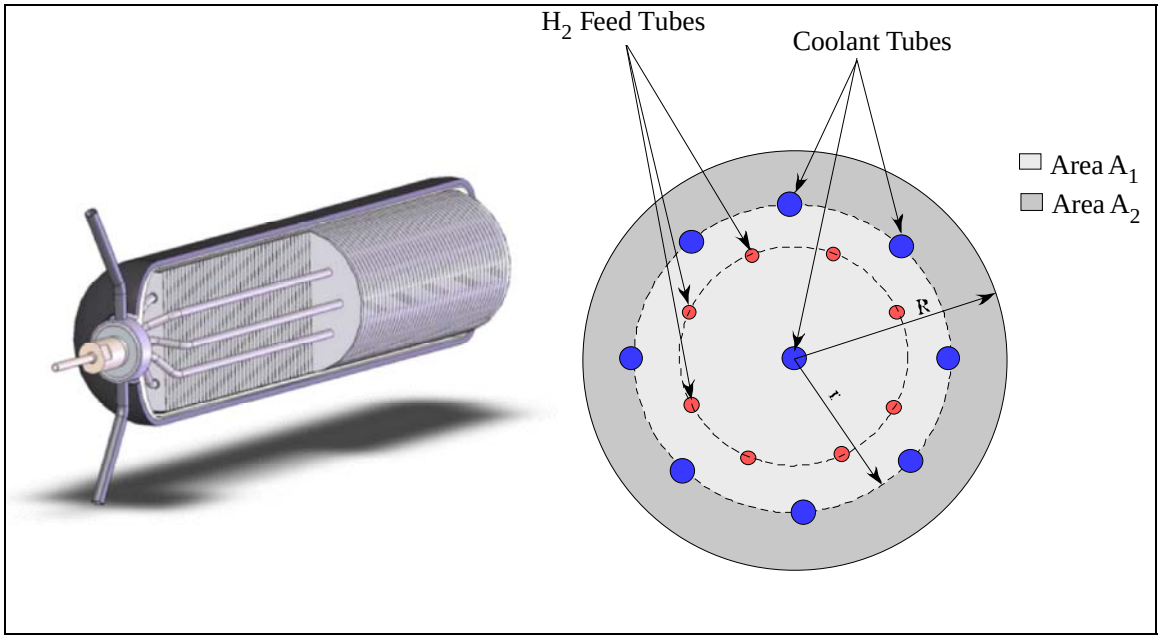

Figure 1 Left illustration is a shell, tube and fin hydride bed configuration, Mosher, et. al. [5], that is similar to the modeled system. The right illustration is a cross-section of the storage system actually analyzed in the model.

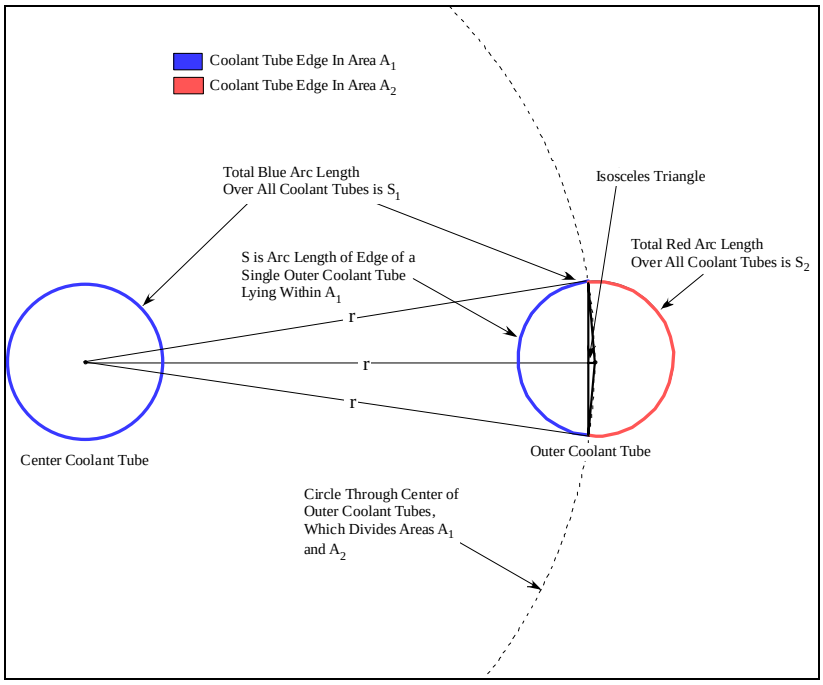

Figure 2 Geometry for the partition of the cooled tube surface with respect to the inner and outer areas of the bed. The figure is not to scale.

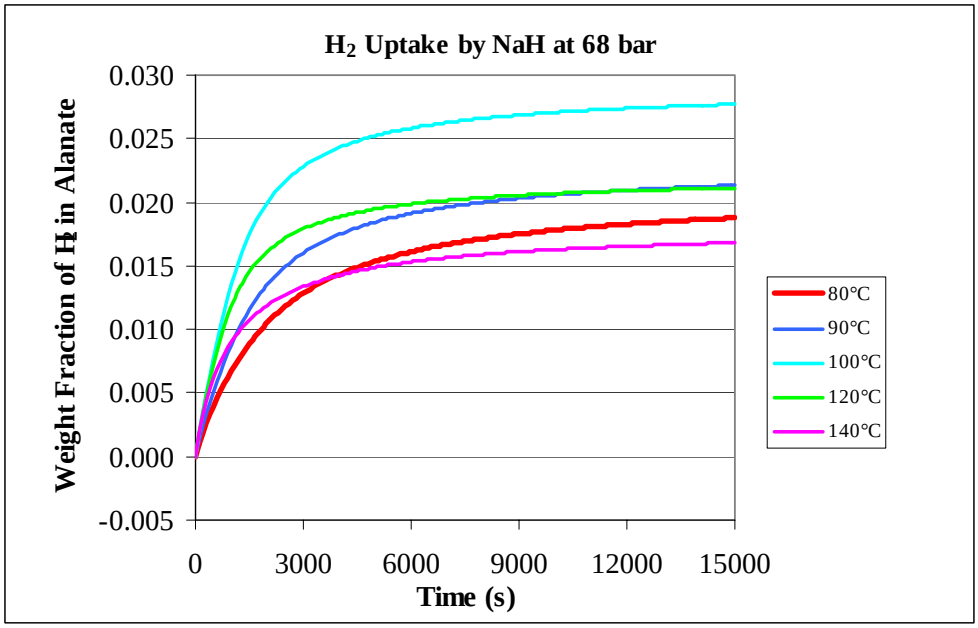

Figure 3 Hydrogen charging rates at 68 bar from the reaction kinetics scoping model.

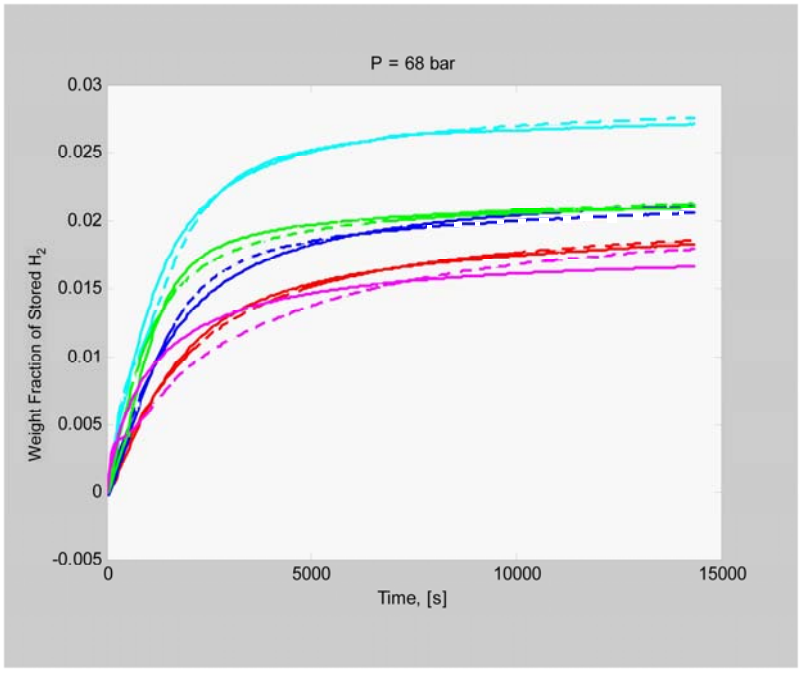

Figure 4 Hydrogen charging rates at 68 bar obtained by UTRC™ using its reaction kinetics model, see Attachments 3 and 4 of [6]. Solid lines represent

model predictions and dashed lines represent data. The legend of Figure 5 gives the charging temperatures.

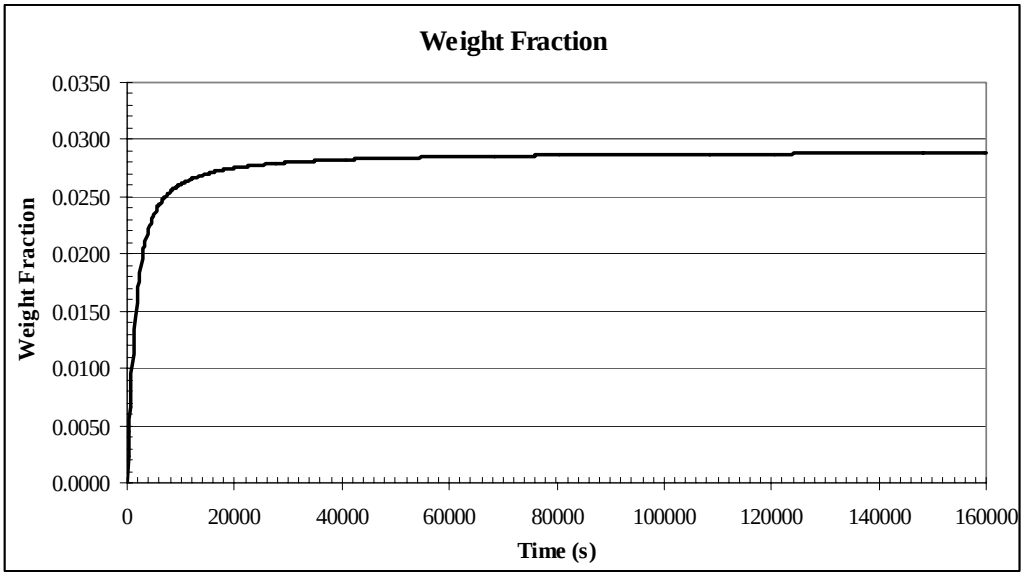

Figure 5 Charging of hydrogen in the hydride at 50 bar and 100°C. The weight fraction is based on Equation 7. Recoverable hydrogen stored in both NaAlH4 and Na3AlH6 are included.

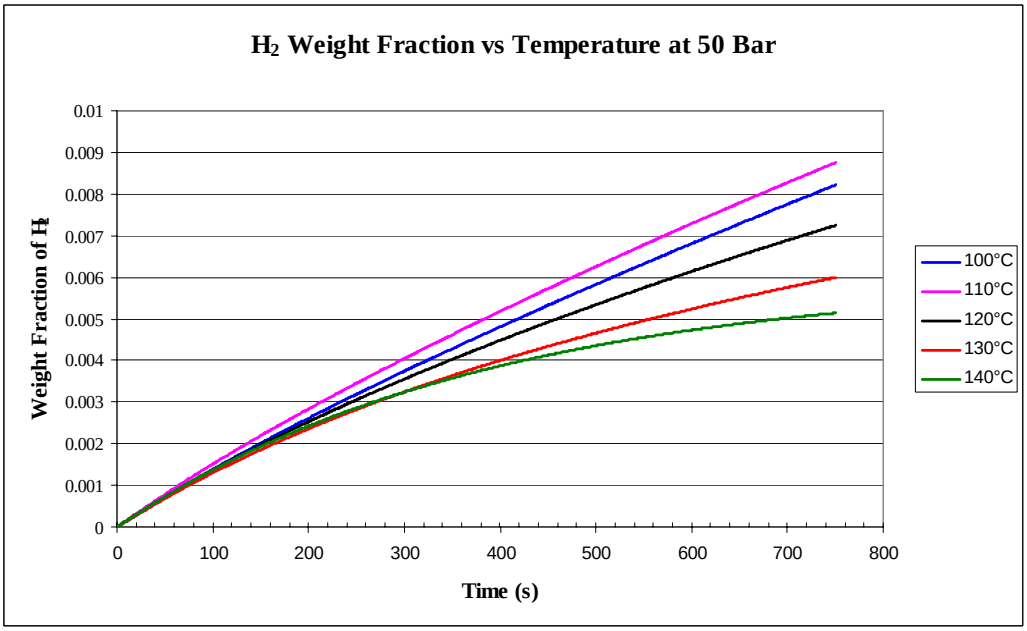

Figure 6 Charging of hydrogen in the hydride at 50 bar as a function of temperature. The weight fraction is based on Equation 7. Recoverable hydrogen storage in both NaAlH4 and Na3AlH6 are included.

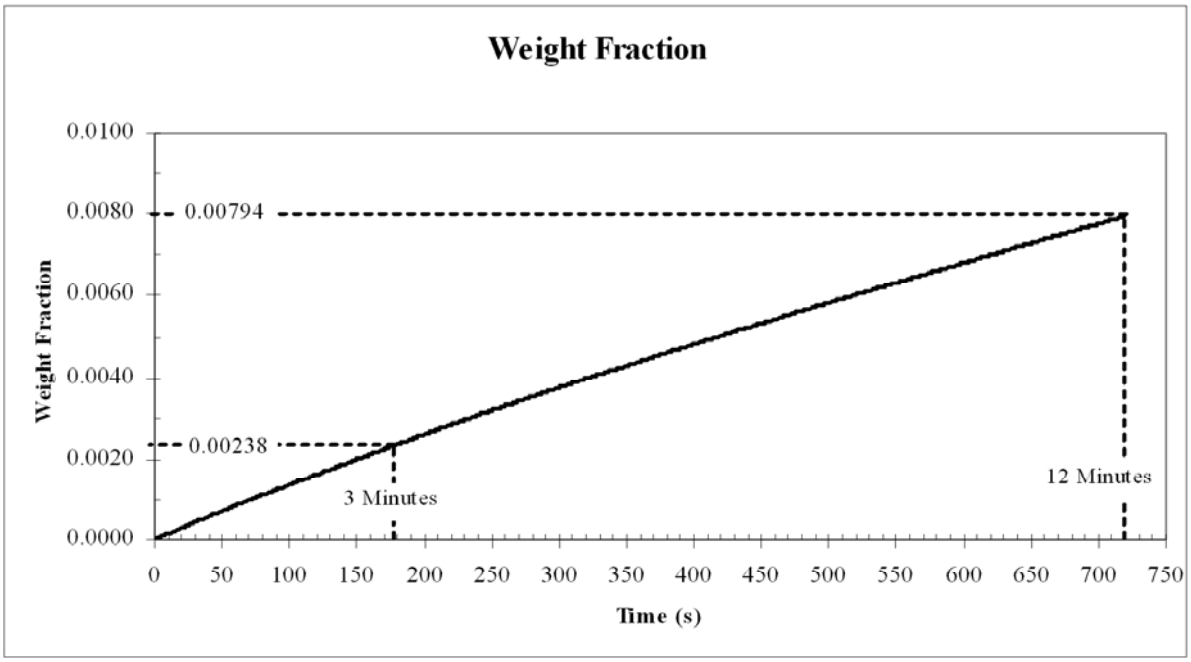

Figure 7 Charging curve of Figure 5 expanded over a time period characteristic of onboard refueling. Charging conditions were 50 bar and 100°C.

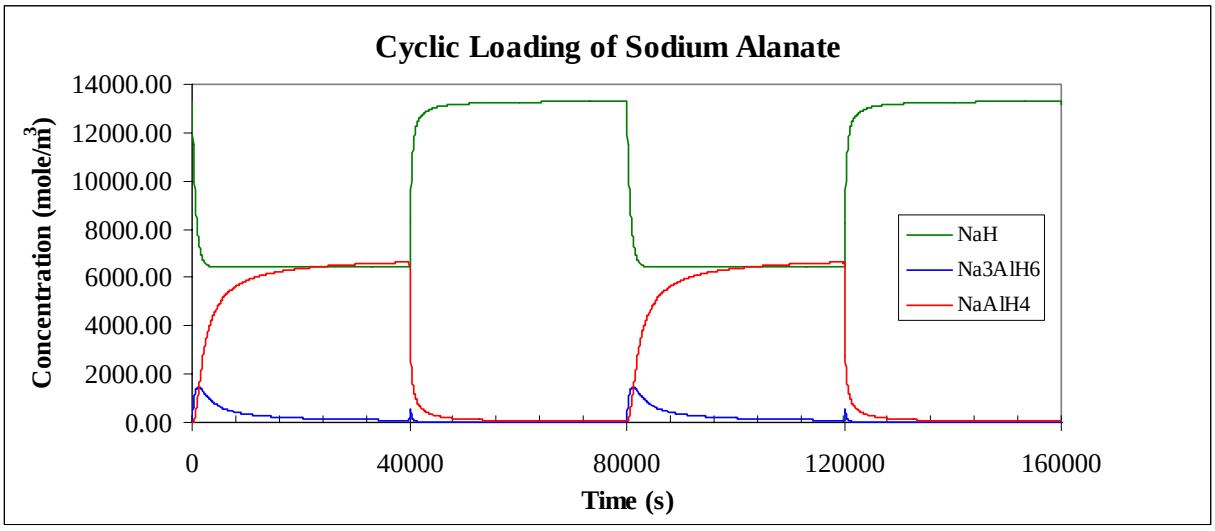

Figure 8 Concentration of all species in the sodium alanate reaction. The initial concentration of NaH was approximately13,333mole/m3 and 0 mole/m3 for the other hydrides. Charging conditions are 100°C at 50 bar and discharging conditions are 120°C at 1 bar.