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# A MASS TRANSPORT MODEL FOR HYDROGEN GENERATION DURING LITHIUM-LEAD/WATER INTERACTIONS

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## Abstract

A mass transport chemical reaction model is presented to predict the rate of hydrogen generated in the interaction of lithium-lead alloy ( $Li_{17}Pb_{83}$ ) with water. This model makes use of experimental data to determine the rate of hydrogen generation from such an interaction. The model is used to determine diffusion rate constants for the lithium-lead/water interaction. The results from the model indicate that the chemical reaction can be represented by a linear rate law, for the later times of the reaction ( $> 10$  s). However, the early stage of the chemical reaction does not follow a linear rate law. The results also indicate that for initial liquid metal temperatures below  $590^\circ C$ , the activation energy is not a function of the initial liquid metal temperature.

## Introduction

Current conceptual designs of fusion power reactors envision the use of tritium as a fuel. Of the possible breeding materials (including liquid lithium, lithium lead compound  $Li_7Pb_2$ , lithium oxide  $Li_2O$ , and lithium based ceramics) a particular alloy of lithium-lead,  $Li_{17}Pb_{83}$ , is being considered for tritium breeding, neutron multiplication and as a coolant within the reactor blanket region. This alloy is receiving more attention because of its ability to act both as a breeder and neutron multiplier. In addition, the alloy does not show a vigorous chemical reaction with water (as demonstrated in scoping experiments by Finn [1], Jeppson et al. [2], and Herzog et al. [3]) or air, one of the important criteria in the choice of a breeder material. In the design of such fusion power reactors, water could be present as an auxiliary cooling fluid or as the working fluid for the power cycle. Thus, one must consider accidental contact of this liquid metal alloy and water, with its possible consequences; i.e., hydrogen generation and local overheating. The hydrogen production from interaction with metal/water, though moderate compared to other blanket materials, is still a safety concern that must be addressed. In this regard, Herzog performed a series of experiments to determine the amount of hydrogen produced under different initial liquid metal alloy and water temperatures.

The objectives of this paper are: (1) to present an improved version of the one-dimensional liquid metal transport model for the Li-Pb/water interaction initially proposed by Herzog, (2) to use this model in conjunction with additional data collected by Lomperski [4] (using Herzog's experimental setup); (3) to analyze the test data and provide estimates of the empirical chemical reaction rate, and (4) to investigate the effects of the initial liquid metal temperatures on these rate coefficients.

## Liquid Metal Transport Reaction Model

This model, proposed by Herzog [3], is based on the premise that the rate of reaction during Li-Pb/water interaction is controlled by the the rate of diffusion of lithium atoms and products ( $Li_2O$  or

$LiOH$ ) at the liquid metal surface. Under such a liquid metal diffusion model, the rate of reaction at the interaction interface will be far greater than the rate of diffusion of lithium to the interaction surface, thus lithium atoms that diffuse into the interaction surface instantaneously react to produce hydrogen.

## Basic Assumptions

The liquid metal transport reaction model is based on the following assumptions: (1) reaction occurs only at the surface, (2) system is assumed to be one dimensional since the driving force of diffusion will result in an axial variation of the molar concentration of reactants and products, (3) concentration of lead is assumed to be constant throughout the interaction since there are 83 atoms of lead to 17 atoms of lithium in the alloy and lead is chemically inactive during the interaction, (4) liquid metal is incompressible, (5) gases produced during the reaction are ideal, (6) once reaction begins, the concentration of lithium at the interaction surface is zero, and (7) there is no bulk mixing within the liquid metal pool or at its surface since the diameter of the liquid metal surface was made smaller than the Taylor unstable wavelength thus stabilizing the reaction surface area.

Figure 1 shows the reference coordinate system used for the model. In the figure, the interaction surface is shown located a distance  $s$  from the bottom of the liquid metal pool. Qualitative concentration profiles of the products and reactants are also indicated in the figure. A vapor film of thickness  $\delta$  is shown above the interaction surface and a pool of subcooled water above the vapor film.

## Model Equations

### Continuity Equations

For a multicomponent system the continuity equation is given [5] by:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial}{\partial z}(C_i V + J_i) \quad (1)$$

which when applied to the reactant and product results in the following two equations:

$$\frac{\partial C_{Li}}{\partial t} = D_{lm} \frac{\partial^2 C_{Li}}{\partial z^2} - C_{Li} \frac{\partial V}{\partial z} - V \frac{\partial C_{Li}}{\partial z} \quad (2)$$

$$\frac{\partial C_{pd}}{\partial t} = D_{lm} \frac{\partial^2 C_{pd}}{\partial z^2} - C_{pd} \frac{\partial V}{\partial z} - V \frac{\partial C_{pd}}{\partial z} \quad (3)$$

The boundary conditions for the continuity equations are: at  $z = 0$ ,  $\partial C_{Li}/\partial z = 0$ ; at  $z = s$ ,  $C_{Li} = 0$ ; and the initial condition is  $C_{Li}(z, 0) = C_{Li_{max}}$ . As will be shown shortly, this equation can be replaced by a simplified equation.

### Energy Equation

Under assumptions 3 and 4, the equation of energy for the liquid

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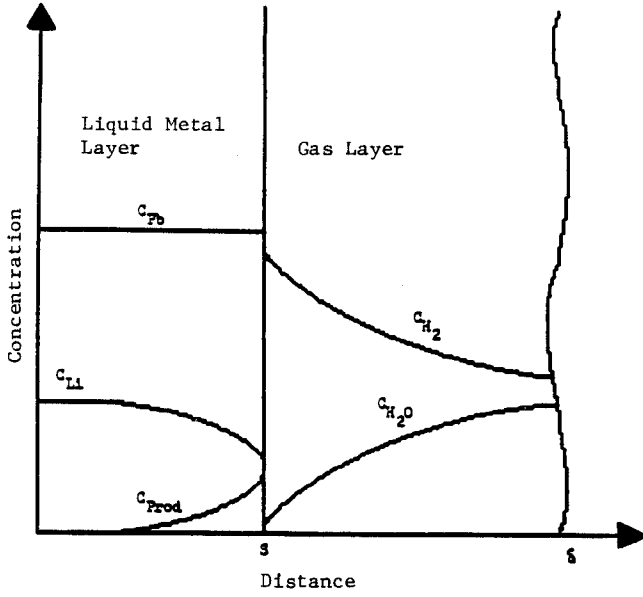


Figure 1. Model coordinate system.

metal pool is given [5] by the equation

$$\rho \frac{DH}{Dt} = -\frac{\partial}{\partial z} (k_{im} \frac{\partial T}{\partial z} + M_i H_i J_i) + \frac{DP}{Dt}. \quad (4)$$

Substituting the relation  $H = U + PV$  and simplifying we obtain the equation:

$$\rho c_p \left( \frac{\partial T}{\partial t} + V \frac{\partial T}{\partial z} \right) = k_{im} \frac{\partial^2 T}{\partial z^2} - ((J_{Li} M_{Li} c_{pLi} + J_{pd} M_{pd} c_{pPd}) \frac{\partial T}{\partial z} + M_{Li} H_{Li} \frac{\partial J_{Li}}{\partial z} + M_{pd} H_{pd} \frac{\partial J_{pd}}{\partial z}) \quad (5)$$

where  $J_i = -D_{im} \partial C_i / \partial z$  and the liquid metal diffusivity  $D_{im}$  is assumed to be of the Arrhenius form:

$$D_{im} = D_o \exp\left(-\frac{\Delta E_d}{RT}\right). \quad (6)$$

The boundary conditions for the energy equation are:  $T(0, t) = T_c(t)$ , a known temperature at the base of the metal pool; at  $z = s$ ,  $q_{cond} + q_{gen} = q_{conv}$  where  $q_{cond}$  is the heat transfer by conduction from the base to the surface,  $q_{gen}$  is the heat generated at the surface as a result of the exothermic reaction and  $q_{conv}$  is the heat transfer by convection from the reaction surface to the vapor film given respectively by:

$$q_{cond} = -k_{im} \frac{\partial T}{\partial z} \quad (7)$$

$$q_{gen} = -R_{Li} (n_{pd} h_{pd} - n_{react} h_{react}) \quad (8)$$

$$q_{conv} = h_{fb} (T(s, t) - T_{sat}). \quad (9)$$

The stable film boiling heat transfer coefficient  $h_{fb}$  is obtained from the theory of film boiling on a flat horizontal surface. Collier [6] suggests the following model for estimating this coefficient:

$$h_{fb} = h_c + 0.75 h_{rad} \quad (10)$$

where

$$h_c = 0.62 \left[ \frac{g(\rho_f - \rho_g) \rho_g k_g^3 i'_{fg}}{\lambda_c \mu_g (T_s - T_{sat})} \right]^{\frac{1}{4}} \quad (11)$$

and  $\lambda_c$  in equation 11 is the unstable Taylor wavelength given by

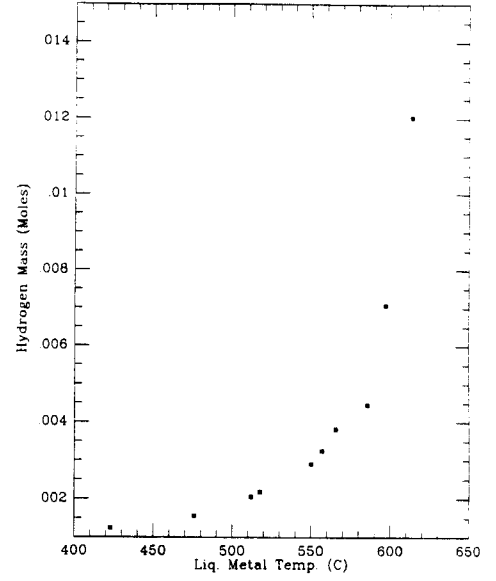


Figure 2. Mass of hydrogen as function of initial metal temperature.

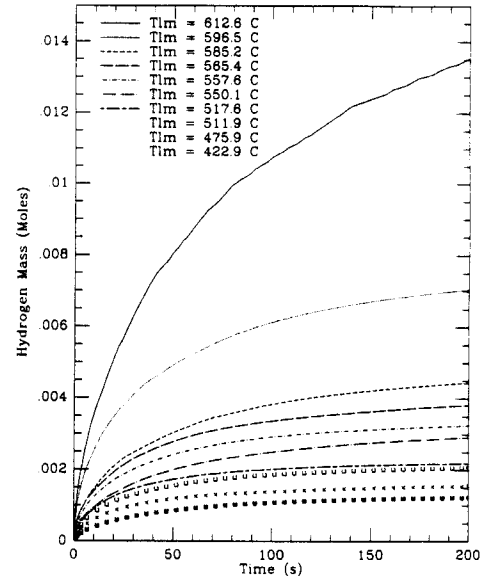


Figure 3. Time history of hydrogen generation.

$$\lambda_c = 2\pi \left[ \frac{\sigma}{g(\rho_f - \rho_g)} \right]^{\frac{1}{2}}. \quad (12)$$

The corrected latent heat of vaporization  $i'_{fg}$ , is given by:

$$i'_{fg} = i_{fg} \left[ 1 + 0.68 \left( \frac{c_{pg} \Delta T}{i_{fg}} \right) \right]. \quad (13)$$

The radiation coefficient  $h_{rad}$  is given by

$$h_{rad} = \sigma_s \left( \frac{T_s^4 - T_{sat}^4}{T_s - T_{sat}} \right). \quad (14)$$

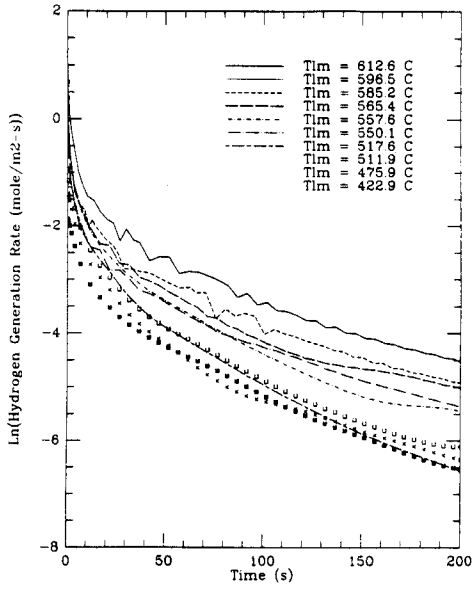


Figure 4. Time history of hydrogen generation rate.

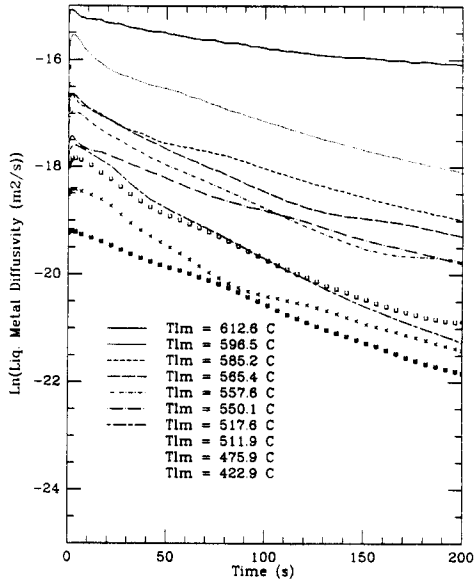


Figure 5. Time history of liquid metal diffusivity.

The two continuity equations and the one energy equation constitute three equations with five unknowns:  $T(z, t)$ ,  $C_{Li}(z, t)$ ,  $C_{pd}(z, t)$ ,  $D_o$  and  $E_d$ . Assumptions 2 and 3 imply that the molar flow rates of lithium and product ( $LiOH$ ) are equal but opposite in direction. Thus the sum of the molar concentrations will be a constant equal to the initial lithium concentration in the alloy  $C_{Li_{max}}$ . Thus equation 3 can be replaced with

$$C_{pd}(z, t) + C_{Li}(z, t) = C_{Li_{max}} \quad (15)$$

Finally, the model is made to match two other conditions obtained from experimental results, namely the initial rate of hydrogen production and a steady state amount of hydrogen generated 200 seconds into the reaction. These last two conditions bring the set of equations to 5 with 5 unknowns.

#### Modifications of Original Model

The expressions for the film boiling heat transfer coefficient orig-

inally used by Herzog [3] greatly overestimated the film coefficient. As a result, the vapor film thickness  $\delta$  was very small and that made the numerical solution unstable. This was corrected by using equations 10 through 14 in the calculation of  $h_{fb}$ . Since the model is based on stable film boiling, Wu [7] and Dhir's [8] work on the minimum film boiling temperature was included in the computer model to check this condition. Furthermore, the properties of the vapor film are all evaluated at the mean temperature, and are all made to vary with temperature. A quasi Newton-Raphson method was used to improve convergence in the numerical scheme. These changes greatly improved the model's ability to converge and to match the experimental value of hydrogen at the end of the 200 seconds. Finally the differential equations are replaced by their Crank-Nicholson finite difference equivalents and solved numerically.

#### Application of Model to Experimental Data

Lomperski [4] slightly modified the experimental apparatus first developed by Herzog [3] to develop a set of data that was used to calculate the amount of hydrogen produced as a function of time for several different initial liquid metal temperatures and liquid metal mass. In Lomperski's experiments, the pool of liquid water above the vapor film was maintained at 30 °C subcooled. This decreased the possibility of any water vapor generated from reaching the gas chamber above the pool of water. Lomperski also repositioned the thermocouple for measuring the temperature of the gas above the water pool to ensure a more accurate reading. Figure 2 shows the actual amounts of hydrogen generated at the end of 200 s. A plot of the amount of hydrogen produced with time was used to determine the initial hydrogen generation rate. This experimentally determined rate and the total amount of hydrogen at the end of 200 seconds were supplied to the liquid metal transport reaction model and the diffusion rate constants  $D_o$  and  $\Delta E_d$  were determined. Figures 3, 4 and 5 show the model's prediction of hydrogen generation, the log of the hydrogen generation rate per unit area and the liquid metal diffusion coefficient respectively as a function of time for different values of initial liquid metal temperature. Figure 6 shows the model's prediction of the liquid metal diffusion coefficient as a function of the inverse liquid metal surface temperature for different values of initial liquid metal temperature.

The hydrogen generation rate is written in the form

$$\frac{1}{A} \frac{dN_H}{dt} = D_H \exp\left(-\frac{\Delta E_H}{RT}\right) = D_{lm} C_{Li_{max}} \quad (16)$$

The mean values predicted by the model are  $D_H = 6.6 \times 10^6$  moles/m<sup>2</sup>·s and  $\Delta E_H = 1.233 \times 10^5$  J/mole. At a liquid metal temperature of 612.6°C, the values  $D_H$  and  $\Delta E_H$  are 338.0 moles/m<sup>2</sup>·s and  $1.496 \times 10^5$  J/mole respectively. Figure 5 shows the dependence of the hydrogen generation rate on time.

As alluded to earlier in the model description, the liquid metal diffusion coefficient is assumed to be of the Arrhenius form

$$D_{lm} = D_o \exp\left(-\frac{\Delta E_d}{RT}\right) \quad (17)$$

Thus, the model's prediction of  $D_{lm}$  shown in Figure 6 can be used to determine the mean value of the reaction coefficient  $\Delta E_d$ . The mean value obtained from the model is  $1.09 \times 10^5$  J/mole. An approximate expression for  $D_o$  as a function of initial liquid metal temperature is given by:

$$\ln(D_o) = -51.15 + 0.263T_{lm} - 3.13 \times 10^{-4} T_{lm}^2 \quad (18)$$

Finally, the dependence of  $D_{lm}$  on the time of reaction is depicted in Figure 5.

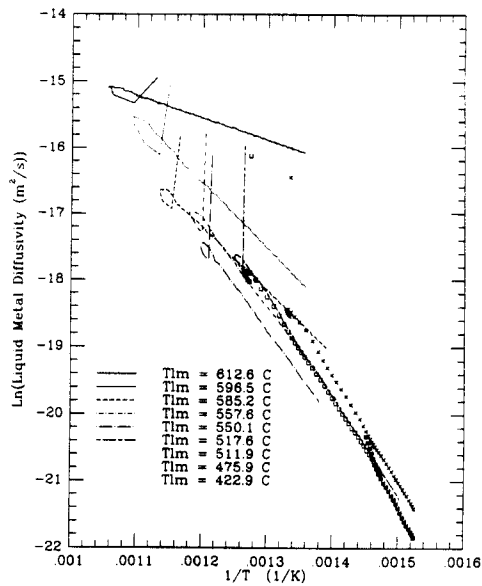


Figure 6. Liquid metal diffusivity as a function of temperature.

### Discussion of Results

Figures 2 and 3 indicate that the amount of hydrogen generated is a strong function of the initial liquid metal temperature. At lower initial metal temperatures, the reaction rate decreases rapidly with time. The rate equation for hydrogen generation is linear except in the beginning of the reaction when the rate drops rapidly. The increase in the surface temperature during this stage is the result of heat of reaction. Notice the initial shape of the curves for Figure 6. From the figure, it is apparent that the rate constant  $\Delta E_H$  is not a function of temperature. The behavior at the initial part of the reaction can be explained by the rapid reaction of the lithium atoms initially at the surface. Once the initial lithium is depleted, the subsequent reaction will depend on the diffusion of lithium atoms to the surface and of lithium hydroxide away from the surface. As a result, the initial part of the reaction is not described by the model. A much quicker rate of reaction initially occurs (quadratic or cubic). As the diffusion process continues the reaction rate becomes linear as expected from the model. Similar behavior is observed in Figures 4, 5 and 6. Figure 6 indicates that the constant  $D_o$  in the Arrhenius equation for the reaction is dependent on the initial liquid metal temperature. However, the constant  $\Delta E_d$  is independent of initial liquid metal temperature.

### Conclusions

Using the experimental data available for Li-Pb/water interaction, we have used a one-dimensional liquid metal diffusion model to estimate the values of the reaction constants for the Li-Pb/water interaction. The results from the model indicate that the reaction constants  $\Delta E_H$ ,  $\Delta E_d$  and  $D_H$  do not depend on the initial liquid metal temperature. However, the constant  $D_o$  in the Arrhenius equation shows a dependence on the initial liquid metal temperature.

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### Nomenclature

A	Surface area
C	Molar concentration
$c_p$	Constant pressure specific heat
D	Diffusion coefficient
$D_H$	Hydrogen generation rate proportionality constant
$D_{lm}$	Diffusion coefficient for liquid metal
$D_o$	Diffusion coefficient proportionality constant
H	Enthalpy
h	Molar enthalpy as used in Eq. 8; also as heat transfer coefficient as used in all other equations
$i_{fg}$	Specific enthalpy of vaporization
J	Molar flux
k	Thermal conductivity
$N_H$	Number of moles of hydrogen
n	Number of moles
P	Pressure
q	Heat flux
R	Universal gas constant
$R_{Li}$	Rate of reaction of lithium
s	Position of interaction surface from origin
T	Absolute temperature
t	Time
V	Velocity
z	Principal coordinate direction
$\delta$	Thickness of vapor film
$\lambda_c$	Taylor unstable wavelength
$\mu$	Dynamic viscosity
$\rho$	Density
$\sigma$	Surface tension
$\sigma_s$	Stefan-Boltzmann constant
$\Delta E_H$	Hydrogen generation rate activation energy
$\Delta E_d$	Activation energy in Arrhenius equation (Eq. 18)

### Subscripts

c	Convective
f	Property of a saturated liquid
$fg$	Difference in property between a saturated vapor and saturated liquid
g	Property of a saturated vapor
i	A component in a multicomponent system
Li	Lithium
pd	Products