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Lithium-Lead/Water Reaction Experiments and Analysis*

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J. P. Herzog and M. L. Corradini

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Argonne National Laboratory
Reactor Analysis and Safety Division
9700 South Cass Avenue
Argonne, IL 60439

M. L. Corradini
University of Wisconsin
Madison, Wisconsin 53706

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LITHIUM-LEAD/WATER REACTION EXPERIMENTS
AND ANALYSIS^a

J. P. Herzog
Argonne National Laboratory
Argonne, IL 60439
(312) 972-3439

M. L. Corradini
University of Wisconsin
Madison, WI 53706
(608) 263-2196

ABSTRACT

An experiment has been performed to investigate the chemical reaction between the liquid phases of the eutectic lithium-lead ($\text{Li}_{17}\text{Pb}_{83}$) and water. The reactants and products were constrained within a closed reaction vessel, allowing the extent of reaction to be determined from the partial pressure of the hydrogen reaction product. The data from the tests showed that the extent of reaction did not depend upon the water temperature. The data also indicated that the extent of reaction passed through a maximum as the initial liquid metal temperature was varied from 350 to 500 C, and a model was developed to explain this behavior.

INTRODUCTION

It is generally assumed that the first power reactors will use deuterium and tritium as their principal fuels, and that the tritium will have to be bred by capturing neutrons from the fusion reaction in a blanket containing lithium in some form.¹ Of the many lithium based materials being considered as a tritium breeder most have either a high lithium atom density, or require a neutron multiplier to insure adequate breeding. Lithium and lead based compounds and eutectics are an exception though, because they have the unique capability of being both low lithium atom density breeding materials and neutron multipliers at the same time.² From many standpoints the most attractive of these breeder-blanket materials is the eutectic lithium-lead ($\text{Li}_{17}\text{Pb}_{83}$). At operating temperatures of many proposed fusion reactor blankets, lithium-lead is highly fluid and thermally conductive, has high cross sections for fast and thermal neutrons, is inert to radiation, and provides an adequate breeding ratio.¹ Furthermore, a series of scoping compatibility tests indicates that lithium-lead possesses a much more benign chemical reaction potential with various reactor materials (e.g. water, air, and concrete) than other popular breeder material alternatives, such as lithium or Li_7Pb_2 .³ These favorable attributes of lithium-lead have caused it to become a prime candidate as the breeder-blanket material in current designs of conceptual fusion reactors.^{4,5,6} Because breeder-blanket coolant candidates include water,³ the possibility that liquid lithium-lead could contact water during postulated accident scenarios is a major safety concern in the design of these conceptual fusion reactors. Although the eutectic reacts mildly with water, the reaction does produce hydrogen.

The amount of hydrogen produced by the lithium-lead/water reaction will

^aWork performed at the University of Wisconsin-Madison.

depend upon the mechanics of the accident sequence and the chemical kinetics of the reaction. The mechanics of the accident sequence determine the amount of reactants available for the reaction and the area of contact between the reactants. For instance, a steam tube rupture accident in a liquid lithium-lead steam generator would lead to a particularly rapid and substantial production of hydrogen,^{7,8} because the initially enormous pressure difference between the two species would cause a considerable amount of steam injection and dispersal. In comparison, an accident scenario characterized by the pouring of liquid lithium-lead from a ruptured blanket module into a pool of water would lead to a much less substantial production of hydrogen, because the low pressure nature of the accident sequence would restrain bulk mixing of the reactants. For a given contact area, the rate of hydrogen production is dependant upon the chemical kinetics of the reaction. Therefore measurements of the rate of hydrogen production of the lithium-lead/water reaction for a known contact area can be used in conjunction with suitable dynamic mixing models to estimate the extent of hydrogen production for postulated accident scenarios.

DESCRIPTION OF THE EXPERIMENT

The experimental apparatus consisted of a closed vertical column which contained the reactants and products during the course of the reaction (figure 1). A closed system meant that the mass of hydrogen produced by the reaction could be determined from the system pressure, the gas and water temperatures, and the initial conditions of the experiment. During the initial phase of the experiment, the water (roughly 1 liter) was held in the upper section of the apparatus by a butterfly valve, while the lithium-lead ($20 \text{ gm} < \text{mass} < 65 \text{ gm}$) was held within a small cylindrical cavity in the lower section of the apparatus. The water was heated to an initial temperature which ranged from 60 to 90 C by the action of a water convection circuit, while the lithium-lead was heated to an initial temperature which ranged from 350 to 600 C by an annular, electrically heated furnace which enclosed the lower section of the apparatus. When the reactants were heated to desired initial temperatures, the butterfly valve was opened allowing the water to pour onto the surface of the liquid lithium-lead. The cross-sectional area of the cylindrical cavity was designed to be small enough to inhibit mixing of the reactants, which ensured that the contact area was constant during the experiment. The initial temperatures of the reactants were chosen such that the water at the interaction surfaced boiled in the film boiling regime, which meant that the liquid metal surface was covered by a thin film of steam and hydrogen. This condition was imposed in order to simplify subsequent diffusional modeling of the interaction. The experimental apparatus included four thermocouples and a pressure transducer with associated electrical circuitry which allowed for the automatic digital recording of system variables at a rate of once per second. The thermocouples were placed such that they registered the temperature of the gas above the water column, the temperature of the gas and later water above the liquid metal pool, the bulk temperature of the water, and the temperature of the bottom of the liquid metal pool.

As the reactants were being heated to desired initial temperatures, argon was fed through a connecting line into the gas region above the metal sample, from there it flowed through another connecting line to the gas region above the water column, and then out of the system through a third gas line. This system permitted equal pressures to be maintained in both sections of the apparatus, and ensured that the reactants were covered with an inert gas. A few minutes before the initiation of the interaction, valves on all three argon

feed lines were closed, which effectively closed the system and prevented water vapor from reaching the liquid metal surface via the connecting line between the two gas regions. At this time, the total mass of argon in the system could be determined from the gas temperature of both gas regions, the water temperature, and the system pressure. After the lithium-lead/water interaction was initiated, the hydrogen partial pressure could be evaluated by a process of elimination. At any time during the interaction, the system pressure had three components: the partial pressure of free hydrogen, the partial pressure of free argon, and the water vapor pressure. The argon partial pressure and the water vapor pressure could be determined from the mass of free argon, the water temperature, and the gas temperature. The hydrogen partial pressure was then evaluated by subtracting these calculated pressures from the measured system pressure. Finally, the extent of the reaction, as measured by the hydrogen mass, was determined from the hydrogen partial pressure and the gas temperature.

The indirect method of determining the hydrogen partial pressure was dependant upon the accurate evaluation of the water vapor pressure and the argon partial pressure. This presented a problem during the early phase of the interaction because the derivation of the water vapor pressure from standard steam tables was based on the assumption of liquid-vapor equilibrium. During the early phase of the interaction, rapid boiling of the water after it filled the lower section of the apparatus resulted in the accumulation of steam at the top of the apparatus. Because the bulk of the water remained subcooled by the continued action of the water convection circuit, equilibrium between boiling and condensation rates was eventually established. Liquid-vapor equilibrium, as evidenced by the leveling off of the gas and bulk water temperatures, was established 100-150 seconds into the interaction, which meant that the extent of reaction could only be effectively determined after this time. Therefore the hydrogen mass at 200 seconds into the interaction was chosen as the measure of the extent of the lithium-lead/water reaction.

RESULTS AND ANALYSIS OF THE EXPERIMENT

Analysis of the data from the experiment showed that the extent of reaction was not a function of the water temperature (figure 2). The extent of reaction was found to vary over the range of initial liquid lithium-lead temperatures investigated (figure 3). For tests with 350 C lithium-lead initial temperatures, the average mass of hydrogen produced during the first 200 seconds of the tests was 1.80 ± 1.61 mole/m² (moles of hydrogen per unit contact area). For tests with 400 C lithium-lead initial temperatures, the average mass of hydrogen produced during the first 200 seconds of the tests was 10.7 ± 1.05 mole/m². For tests with 500 C lithium-lead initial temperatures, the average mass of hydrogen produced during the first 200 seconds of the tests was 3.77 ± 1.01 mole/m². And for tests with 600 C lithium-lead initial temperatures, the average mass of hydrogen produced during the first 200 seconds of the tests was 13.4 ± 0.61 mole/m².

The discovery of a maximum in the extent of reaction as the initial liquid metal temperature was increased from 350 to 500 C was unexpected. An attempt to explain this behavior was made with the aid of a transport controlled reaction model for the liquid lithium-lead/water reaction. The model was based on the assumptions that the reaction occurred at the liquid metal surface and that the rate of diffusion in the liquid metal was the rate

controlling process. Because the reaction is highly exothermic,⁹ these assumptions implied that any unreacted lithium that diffused to the liquid metal surface found ample water with which to quickly react. Thus the reaction rate and hence the hydrogen production rate equaled the rate at which unreacted lithium diffused to the liquid metal surface.

The liquid metal was modeled as a solution with the liquid lead, which did not participate in the reaction, acting as a solvent. The solute consisted of unreacted lithium which diffused toward the liquid metal surface, and a liquid or solid reaction product (LiOH or Li₂O) which diffused away from the surface. By assuming that the liquid metal diffusion occurred only in the axial direction and that convective motion within the liquid metal was negligible, a mass balance on the liquid metal reduced to a simple counter-diffusion problem for the liquid lithium molar concentration (C_{Li}):

$$\frac{d C_{Li}}{d t} = D_{l m} \frac{d^2 C_{Li}}{d z^2} \quad (1)$$

Although the diffusion coefficient (D_{lm}) for this system has not been measured, application of a liquid metal diffusion theory developed by Pasternak and Olander¹⁰ provided an estimate of it based on the known self-diffusion coefficient of lead. Their theory, which predicts the diffusion coefficient of a dilute liquid metal in a liquid metal solvent, was used to estimate the temperature dependant diffusion coefficient for lithium atoms in a lithium-lead solution:

$$D_{l m} \left(\frac{m^2}{s} \right) = 5 * 10^{-7} \exp \left(- \frac{2.04 * 10^3}{T(K)} \right) \quad (2)$$

Completing the formulation with an energy balance for the liquid metal temperature, the model was used to solve for the rate of hydrogen production. The extent of reaction predicted by the transport controlled reaction model correlated well with the observed extent of reaction for the 500 and 600 C initial liquid metal temperature tests. But for the 350 and 400 C initial liquid metal temperature tests, the model underpredicted the extent of reaction.

The failure of the model to predict the extent of reaction for the low temperature tests and the transition in the observed extent of reaction between 400 and 500 C coincides with a change in phase of one of the metal reaction products (LiOH), which melts at 470 C. Lithium and water react to form Li₂O, H₂, and LiOH by two reaction paths:⁹

Because the reaction rate was controlled by the rate of diffusion of lithium towards the liquid metal surface, the reaction can be considered to be lithium

starved. This meant that at the interaction surface, there was an abundance of water vapor, but a deficiency of lithium. Therefore the reaction proceeded more readily by the second reaction path (equation 4), because it only takes one mole of lithium to react with one mole of water to form LiOH , while the first reaction path (equation 3) requires that two moles of lithium be present to react with one mole of water to form Li_2O . Thus the predominant metal reaction product was lithium hydroxide.

It is likely that the transition in the extent of reaction was due to the change in phase of the metal reaction product lithium hydroxide. Because the melting point of lithium hydroxide is 470 C and because it is less dense than the surrounding liquid metal, it is possible that the reaction product formed a solid precipitate at temperatures below 470 C, which accumulated at the top of the liquid metal layer. Because lithium hydroxide is soluble in water,¹¹ a portion of this solid product layer may have sufficiently mixed with the overlying water to have dissolved into it. This would have tended to enhance the rate of diffusion by removing a portion of the overall mass transfer resistance. At temperatures above the melting point of lithium hydroxide, the reaction was dominated by the process of liquid metal diffusion. In this case, the rate determining process was the counter-diffusion of liquid lithium and liquid lithium hydroxide in a liquid lead solution. Much of the lithium hydroxide likely remained in the liquid metal solution and provided a resistance to mass transfer in the liquid metal solution.

CONCLUSIONS

A series of small scale liquid lithium-lead/water reaction tests were performed. The data from the tests showed that the extent of reaction did not depend upon the water temperature. The data also indicated that the extent of reaction passed through a maximum as the initial liquid metal temperature was varied from 350 to 500 C. The reason for this appears to be due to the phase transition of the lithium hydroxide reaction product. A model, based on a transport controlled reaction, demonstrated that the reaction rate was controlled by the counter-diffusion of liquid lithium and the lithium hydroxide reaction product through a lead solution at temperatures above the lithium hydroxide melting point. The model also showed that the rate of diffusion, and hence the reaction rate, are strong functions of the local liquid metal temperature.

REFERENCES

1. R. BUXBAUM, "A Chemical Theory Analysis of the Solution Thermodynamics of Oxygen, Nitrogen, and Hydrogen in Lead-Rich Li-Pb Mixtures," Journal of the Less-Common Metals, 97, 27 (1984).
2. D. K. SZE, R. CLEMMER, and E. T. CHENG, "LiPb, A Novel Material for Fusion Applications," UWEDM-378, University of Wisconsin Fusion Technology Institute (1980).
3. D. W. JEPPSON, L. D. MUHLSTEIN, and S. COHEN, "Fusion Reactor Breeder Safety Compatibility Studies," Nuclear Technology/Fusion, 4, 278 (1983).
4. B. G. LOGAN, "The Mirror Advanced Reactor Study," Nuclear Technology/Fusion, 4, 563 (1983).

5. B. BADGER, et.al., "WITAMIR-I, A Tandem Mirror Reactor Study," UWFDM-400, University of Wisconsin Fusion Technology Institute (1980).
6. B. BADGER, et. al., "NUWMAK - A Tokamak Reactor Design Study," UWFDM-330, University of Wisconsin Fusion Technology Institute (1979).
7. J. P. HERZOG and M. L. CORRADINI, "Modeling of Lithium-Lead/Water Interactions in a Fusion Reactor Design," UWFDM-559, University of Wisconsin Fusion Technology Institute (1984).
8. D. W. JEPPSON and L. D. MUHLSTEIN, "Safety Considerations of Lithium Lead Alloy as a Fusion Reactor Breeding Material," HEDL-SA 3223-FP, Hanford Engineering Development Laboratory (1985).
9. D. W. JEPPSON, J. L. BALIFF, W. W. YUAN, and B. E. CHOU, "Lithium Literature Review," HEDL-TME 78-15, Hanford Engineering Development Laboratory (1978).
10. A. D. PASTERNAK and D. R. OLANDER, "Diffusion in Liquid Metals," AIChE Journal, 13, 1052 (1967).
11. N. A. LANGE, Lange's Handbook of Chemistry, McGraw-Hill, New York (1979).

Figure 1. Closed Vessel Experiment

1. Data Acquisition Computer
 2. Analog to Digital Converter
 3. Amplifier
 4. Pressure Equalization Line
 5. Resistance Heaters

6. Liquid Metal Well T.C.
 7. Liquid Metal Pool
 8. Butterfly Valve
 9. Convection Coil
 10. Water Region T.C.

11. Gas Layer Thermocouple
 12. Upper Plate
 13. Pressure Transducer
 14. Argon Supply
 15. Temperature Controller

Figure 2.

Figure 3.