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LITHIUM MASS TRANSPORT IN CERAMIC BREEDER MATERIALS

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OBJECTIVE

The objective of this activity is to measure the lithium vaporization from lithium oxide breeder material under differing temperature and moisture partial pressure conditions.

SUMMARY

The transport of lithium by vaporization of LiOH(g) from lithium ceramics, particularly $\text{Li}_2\text{O(s)}$, poses a constraint on the maximum operating temperature of the breeder blanket. Experimental measurements have shown that, depending on temperature, moisture partial pressure, and proximity of structural steels, the lithium transport process is complex. For conditions wherein the $\text{Li}_2\text{O(s)}$ is "free standing," the lithium vaporization is controlled by the $\text{Li}_2\text{O/H}_2\text{O}$ system thermodynamics that are already well established. That is lithium transport, as LiOH(g) , increases with increasing temperature and higher partial pressures of moisture. In the proximity of stainless steel there is an added chemical potential driving force due to formation of Li_2CrO_2 , LiFeO_2 , and LiNiO_2 . The transport of LiOH(g) to the stainless steel is driven by the concentration gradient of LiOH(g) from that at the $\text{Li}_2\text{O(s)}$ surface and that at the steel surface. This gas-solid reaction may become important for blanket designs where the structural steel is very close to the $\text{Li}_2\text{O(s)}$ ceramic.

PROGRESS AND STATUS

Lithium ceramics are being investigated for use as tritium breeding materials. The lithium is readily converted to tritium after reacting with a neutron. With the addition of 1000 ppm H_2 to the He purge gas, the bred tritium is readily recovered from the blanket as HT and HTO above 400°C. Within the solid,

tritium may also be found as LiOT which may transport lithium to cooler parts of the blanket. This process may cause loss of lithium from the blanket, blocking of flow paths, and increase of the tritium inventory. Laboratory studies⁽¹⁾ have established the pressure of LiOH(g) for reaction of $\text{Li}_2\text{O(s)}$ with water vapor,

The pressure of LiOT(g) , HTO(g) , or $\text{T}_2\text{O(g)}$ above $\text{Li}_2\text{O(s)}$ is the same as that for reactions involving hydrogen. In our experiments we were limited to the use of hydrogen. The purpose of this work is to investigate the transport of LiOH(g) from the blanket material.

Experimental

A fixed bed system was assembled that enabled good contact between the purge gas and the lithium oxide at high gas velocities. In this fixed bed arrangement, a silver lined quartz tube was used to hold seven (8mm long by 5.3 mm diameter) cylindrical Li_2O pellets arranged in a close-packed configuration. A platinum sieve was located at the downstream end to hold the pellets in place. The space through which the gas flows is divided into three different regions; a single region bounded by two concentric silver cylinders, six triangular regions bounded on two sides by Li_2O and on a third side by silver, and six small triangular regions bounded by Li_2O on all three sides. The quartz tube assembly was heated in a clam shell furnace. Chromel-alumel thermocouples provided temperature measurement and temperature control. Helium flowed through two rotometers, one line through a water saturator and the other line

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directly from the high purity tank helium. Needle valves on the rotometers were adjusted to reduce the water content to 5×10^{-4} atm. Total flow rates as high as 7000 cc/min (STP) permitted gas velocities as high as 2600 cm/sec at 850°C.

The furnace was heated to 850°C and held for experimental times ranging from 40 to 300 minutes followed by cooling to room temperature. After cooling, the silver tube was soaked in water to dissolve the condensed LiOH. The LiOH solution was added to a 100 mL volumetric flask along with 20 mL of 1-N HCl to produce the 0.2-N HCl solution required for lithium analysis.

The pressure of LiOH(g) was calculated from the lithium analysis and the ideal gas law,

$$P(\text{LiOH}, g) = nRT/V \quad (2)$$

where n is the number of moles of lithium transported per minute, R is the gas constant, T is the absolute room temperature, and V is the volume flow of helium per minute (STP) corrected for the fraction of helium gas (55.9%) flowing over the $\text{Li}_2\text{O}(s)$.

The gas velocity was calculated from the total volume and the total effective areas of the three regions. For this calculation the effective diameters were computed from,

$$d_{\text{eff}} = 4A/P_w \quad (3)$$

where d_{eff} is the effective diameter, A the geometric area, and P_w the length of the perimeter. The effective area is 0.1655 cm^2 as calculated from equation (4).

$$A_{\text{eff}} = \pi d_{\text{eff}}^2/4 \quad (4)$$

The decrease in the pressure of LiOH(g) was correlated with increase in flow velocity assuming that the process is diffusion controlled. The formation of LiOH(g) from reaction of $\text{H}_2\text{O}(g)$ with $\text{Li}_2\text{O}(s)$ is a two-step process: first, water vapor diffuses from the flowing helium to the lithium oxide surface, and second, the reaction of $\text{H}_2\text{O}(g)$ with $\text{Li}_2\text{O}(s)$ produces LiOH(g) which diffuses into the flowing helium. The two simultaneously occurring processes can be calculated from the product of the fractional saturation of each process. The fractional saturation of each process may be calculated from tables and equations of L. S. Darken² where the fractional saturation is given as a function of Dt/L^2 . D is the diffusivity of LiOH(g) or $\text{H}_2\text{O}(g)$ in helium, t is the time in seconds, and L is the half-thickness of the gas volume flowing past the lithium oxide. LiOH(g) originates primarily from the six triangular regions bounded by silver on one side and $\text{Li}_2\text{O}(s)$ on the two other sides and these

regions were treated as six slabs. Since one side of each of these six regions is silver, the value for L is the full thickness. L was estimated from the root of the product of the diameter of the geometric area and the effective diameter. L is equal to $0.191 + .077 \text{ cm}$. The diffusivities of LiOH(g) and $\text{H}_2\text{O}(g)$ gas in helium were estimated using equation (5), below, from R. E. Treybal,³

$$D_{AB} = \frac{(0.00107 - 0.000246 \sqrt{1/M_A + 1/M_B}) T^{1.5} \sqrt{1/M_A + 1/M_B}}{P_t (r_{AB})^2 [f(kt/e_{AB})]}$$

where D_{AB} is the diffusivity of LiOH(g) (or $\text{H}_2\text{O}(g)$) in He, M_A and M_B are the molecular weights of LiOH (or H_2O) and He, T is the absolute temperature, P_t is the total pressure, r_{AB} is the molecular separation at collision, and $f(kt/e_{AB})$ is the collision function given graphically in R. E. Treybal.

The time for the reaction was calculated from the gas velocity and the length of the Li_2O cylinders (8 mm). The fractional saturation equation for short times is given by equation (6).

$$F = 1.128 \sqrt{\frac{Dt}{L}}$$

The fractional saturation equation for long times is given by equation (7).

$$F = 1 - \exp\left\{-\frac{\left(\frac{Dt}{L^2} + 0.0851\right)}{0.4052}\right\}$$

At 1123 K, the diffusivities, (D) , calculated with equation (5) are 6.22 and 6.98 cm^2/sec for LiOH(g) and $\text{H}_2\text{O}(g)$ respectively. Fractional saturations for LiOH(g) and $\text{H}_2\text{O}(g)$ were calculated with equations (6) or (7).

These fractional saturations apply to a single step process. The two-step process is assumed to be the product of

$$F_{\text{H}_2\text{O}} \text{ and } F_{\text{LiOH}}$$

$$F_{\text{prod}} = F_{\text{H}_2\text{O}} \cdot F_{\text{LiOH}} \quad (8)$$

Values for the product are given in column 6 of Table 1. The calculated fractional saturation may be compared to the measured saturation in column 5 of Table 1. Figure 1 shows a plot of the log of the measured saturation against the log of the calculated saturation.

Table 1. Calculation of LiOH Fractional Saturation^a

P _{LiOH} atm x10 ⁶	Vol cc/sec at Temp	Velocity cm/sec	Residence Time sec	P _{LiOH} /P ⁰	Frctnl Saturtn	Log10 P/P ⁰	Log10 Frctnl Saturtn
32.3	8.3	50.2	0.016	1.90	0.999	0.278	-0.0006
12.9	8.7	52.7	0.0152	0.75	0.998	-0.123	-0.0009
16.2	15.8	95.7	0.0084	1.05	0.961	0.020	-0.017
3.39	297	1794	0.00045	0.20	0.103	-0.706	-0.987
20.9	12.3	74.4	0.0107	1.24	0.986	0.092	-0.006
12.6	11.2	67.9	0.0118	0.74	0.991	-0.131	-0.004
6.92	49.8	301	0.0027	0.41	0.612	-0.390	-0.213
4.90	98.6	596	0.0013	0.29	0.309	-0.542	-0.510
2.19	220	1332	0.00060	0.13	0.138	-0.887	-0.859
1.26	433	2618	0.00031	0.074	0.070	-1.128	-1.154

(a) The temperature was 1123 K, D_{LiOH} was 6.22 cm²/sec, D_{H₂O} was 6.98 cm²/sec, and L was assumed to be 0.19 cm. P⁰_{LiOH} is 1.70E-5 atm.¹

Data were derived from Noda's paper⁴ to calculate the degree of LiOH(g) saturation when helium and 500 ppm water were flowed through a cylinder packed with 5 mm spheres of Li₂O. The cylinder was 2 cm in diameter and 10 cm high. The log of the pressure of LiOH(g) measured by Noda divided by that calculated from Tetenbaum and Johnson⁽¹⁾ is plotted against the log of the calculated fractional saturation in Fig. 1. Noda's residence time was over 10 times greater than ours for the same gas velocity. Noda's measurements and our calculation of his data, plotted in Fig. 1, agree that the helium in his experiment was fully saturated with LiOH(g).

This work established conditions for calculating LiOH(g) undersaturation in helium as a function of the velocity of the purge gas. It has been assumed that fractional saturation of two-step interdependent reactions can be treated as the product of each fractional saturation. The measured and calculated fractional saturation agree within experimental uncertainties.

Measurements of the Effect of Stainless Steel on LiOH(g) Transport

Preliminary experiments were carried out to determine what effects the placement of structural stainless steel near the Li₂O(s) could have on the transport of LiOH(g) from the Li₂O(s) blanket material. In this study, a silver boat was used to hold Li₂O(s) with a stainless steel sheet placed at desired distances above the Li₂O(s). The boat and plate were placed inside a silver lined quartz

tube and the quartz tube assembly was heated in a clam shell furnace. Helium flowed through two rotometers, one line through a water saturator and the other line directly from the 61h purity helium tank. In some measurements the helium contained about 1% hydrogen. The two helium streams were mixed and flowed into the silver lined quartz tube containing the boat and lithium oxide. Needle valves were adjusted to reduce the water content within the range 0.001 to 0.01 atm. The furnace was heated to 750 °C for this set of measurements. Most of the LiOH(g) produced from the reaction of water vapor with Li₂O(s) deposited on the stainless steel plate. The remaining LiOH(g) condensed in cooler downstream regions of the silver tube.

After each experiment, the boat was removed and the silver tube was soaked in water to remove the condensed LiOH for chemical analysis. The deposit on the stainless steel was dissolved in nitric acid for lithium chemical analysis. The pressure of LiOH(g) was calculated from the lithium analysis of the condensed LiOH in the silver tube and the ideal gas law.

Six experiments were carried out at 750°C. In experiments 21, 22, and 26 He flow was 10 cc/min and water pressure was about 9000 ppm; in experiments 23-25 He flow was 100 cc/min and water pressure was about 1200 ppm. With the exception of experiment 21 all measurements were made with 303 stainless steel plates above the Li₂O(s) fixed bed. The results of experiments are summarized in Table 2. In column 6 of Table 2, the measured

Table 2. Diffusion driven LiOH(g) reaction with stainless steel

Run No	He Flow cc/min	Ratio meas/Tet	P(H ₂) atm	P(H ₂ O) atm	P(LiOH) atm meas	P(LiOH) atm* Tet
21	10	9.02	.0000	.00875	1.14E-4	1.26E-5
22	10	13.3	.0000	.00799	1.59E-4	1.20E-5
23	100	2.14	.0097	.00120	9.93E-6	4.44E-6
24	100	1.64	.0097	.00125	7.77E-6	4.75E-6
25	100	1.85	.0097	.00120	8.64E-6	4.67E-6
26	10	5.00	.0097	.00986	6.66E-5	1.33E-5

*Calculated from ref. 1.

LiOH(g) pressure was determined, assuming all the lithium condensed in the silver tube came from entrained LiOH(g) in the flowing helium. This was not the case in experiments 21, 22 and 26 where the apparent pressures were an average of nine times greater than those calculated from Tetenbaum¹. This was verified when the flow rate was increased to 100 cc/min and apparent LiOH(g) pressures decreased to within a factor of two of that calculated from Tetenbaum's work. The LiOH(g) condensed in the silver tube by two mechanisms: 1) transport by entrainment in flowing helium; 2) thermal migration from the flowing helium in the hot zone to cooler regions of the silver tube, driven by the temperature gradient. As the velocity of the helium flow decreases, transport of LiOH(g) by thermal migration is favored over transport of LiOH(g) by entrainment. increases toward infinity.

Steady State Diffusion

In our experiments the Li₂O(s) and the stainless steel sheet are separated by distances of five millimeters to less than a millimeter. During the experiment the LiOH(g) transports to the stainless steel surface, driven by the diffusivity of LiOH(g) in helium and the LiOH(g) pressure gradient, and deposits on the stainless steel.

The LiOH(g) pressure decrease may be caused by reaction of LiOH(g) with the steel to form Li₂CrO₂, or Li₂FeO₂, or Li₂NiO₂. For example, the chromate may be produced by the reactions,

and,

Fig. 1. Calculated versus Measured LiOH Saturation

The LiOH(g) pressure at the lithium oxide interface with water concentration of 93 ppm at the three temperatures used in the compatibility studies by Chopra et al.^{6,7} and the temperature of our experiments are given in Table 3 for reactions (10 and 11),

The LiOH(g) pressure at the stainless steel interface for reaction (11) in equilibrium with Cr₂O₃, LiCrO₂, and 93 ppm H₂O(g) are also given in Table 3. The LiOH pressure at the stainless steel interface will

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Table 3. Equilibrium LiOH(g) pressures (atm) as a function of the temperature (K) at the surfaces of $\text{Li}_2\text{O(s)}$ and stainless steel where $\text{Cr}_2\text{O}_3/\text{LiCrO}_2$ and 93ppm H_2O control the LiOH(g) pressure.

	723	823	923	1023
Li_2O	4.08E-10	1.16E-8	1.59E-7	1.31E-6
Stainless steel	7.90E-17	1.25E-14	5.45E-13	1.24E-11

depend on the composition of the corrosion layer on the steel surface. The composition depends on time, temperature, and gas composition. In all cases, this pressure will be substantially lower than that at the $\text{Li}_2\text{O(s)}$ surface.

The LiOH(g) pressures in Table 3 are based on Tetenbaum's¹ pressures in equilibrium with $\text{Li}_2\text{O(s)}$ and water vapor. The LiOH(g) pressures at the steel surface are $2\text{E}-7$ to $9\text{E}-6$ times lower than the pressures at the $\text{Li}_2\text{O(g)}$ surface. The LiOH(g) formed at the $\text{Li}_2\text{O(s)}$ surface is influenced by the pressure gradient and diffusivity of LiOH(g) in the gap between $\text{Li}_2\text{O(s)}$ and the stainless steel. In this steady state diffusion process, the flux of LiOH(g) is given by,

$$N_A = \frac{D_{AB} P_t}{RTz} [P_{A1} - P_{A2}] \quad (13)$$

where N_A is the flux of LiOH(g) in He in g mol/sec/cm², D_{AB} is the diffusivity in cm²/sec of LiOH(g) in He, P_t is the total pressure in atm, P_{A1} and P_{A2} are the LiOH(g) pressures at the $\text{Li}_2\text{O(s)}$ and stainless steel surfaces respectively, R is the gas constant (cc-atm/deg/mol), T is the absolute temperature, and z is the distance, in cm, between the $\text{Li}_2\text{O(s)}$ and the stainless steel. The flux of LiOH(g) varies inversely with the separation distance z , rising rapidly as z decreases.

CONCLUSIONS

These studies have shown that the transport of LiOH(g) can be strongly influenced by the proximity of a stainless steel surface to the $\text{Li}_2\text{O(s)}$. The pressure of LiOH(g) , in equilibrium with $\text{Li}_2\text{O(s)}$, is proportional to the square root of the $\text{H}_2\text{O(g)}$ pressure and increases exponentially with temperature. The transport of LiOH(g) to the stainless steel is driven by the concentration gradient of LiOH(g) from that at the $\text{Li}_2\text{O(s)}$ surface and that at the steel surface. At the stainless surface the LiOH(g) pressure is likely to be in

equilibrium with either LiCrO_2 , or LiFeO_2 , or LiNiO_2 . Experiments of this type must be run for extended periods to assess the importance of this interface complexity.

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