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EXTRACTION OF TRITIUM FROM LIQUID LITHIUM BY PERMEATION

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EXTRACTION OF TRITIUM FROM LIQUID LITHIUM BY PERMEATION

ABSTRACT

This paper assesses a method for extracting tritium from liquid lithium for specific application to the conceptual laser fusion reactor that uses a continuous lithium "waterfall." The tritium diffuses through a refractory metal that contains a getter and is then stored in a hydride-forming alloy. There are various uncertainties with this method including helium-4 extraction, unknown impurities that may accumulate in liquid lithium, the effects of these impurities on tritium separation, and the maintenance of tritium-contaminated equipment. Our study indicates that major tritium losses will occur during equipment maintenance rather than as a result of permeation losses through the primary vessel.

INTRODUCTION

There are several possible methods of extracting tritium from liquid lithium. Some promising ones are:

- The use of permeable metal windows^{1,2} e.g., refractory metal base alloys that contain getters such as zirconium or yttrium.

- Liquid eutectics that consist of a rare earth metal (Ce, La, Y) and a transition metal (Co, Ni, Fe, Mn).³

- The use of molten salts such as LiCl-KCl, LiF-LiCl, or LiF-LiCl-LiBr to extract hydrogen isotopes from liquid.⁴

- Coldtrapping in lithium or in the secondary loops to reduce tritium concentrations in the primary loops.

There are certain problems with these methods. For example, coldtrapping in the primary loops that contain liquid lithium is probably not a suitable procedure because the tritium concentrations achieved are not low enough.⁵ If tritium permeates the secondary loops containing liquid Na, K, or NaK and is then coldtrapped, lower tritium concentrations could be achieved. The biggest disadvantage of this method is that its feasibility cannot be evaluated because there are not enough experimental data.

Molten salt extraction methods could maintain tritium levels as low as 1 wt ppm in liquid lithium. However, a suitable means for recovering tritium from the molten salt has not been demonstrated.

The importance of other potential problems has not been established, that is, effects of mutual solubility of salt with lithium, neutronic effects, and materials compatibility problems.

In principle, liquid alloy getters could maintain tritium concentrations in lithium below 1 wt ppm. However, the difficulty of recovering tritium as well as the possibility of chemical reaction between lithium and the alloy could discourage their use. The magnitude of these problems should be established before the various methods are further considered or discarded.

The most studied method of separating hydrogen isotopes from lithium uses permeation of hydrogen through metals or alloys as the means of separation. These metals or alloys must have high permeability at temperatures greater than 850°C. To be effective, this method should be coupled with a hydride-forming alloy that absorbs and stores the separated tritium. Calculations using hydrogen permeability data indicate that suitable tritium concentrations of 1 to 10 wt ppm in lithium are possible.

This procedure, although attractive, has uncertainties. For example, we have not yet determined either the effect of accumulated impurities in lithium on its chemical compatibility with a permeable alloy, or the surface effects that could decrease permeabilities. In addition, temperature cycling of the permeable windows in the presence of tritium may cause hydrogen embrittlement.

However, the investigation of these uncertainties does not appear to be as formidable as an investigation of other separation processes.

For our study we chose to assess this method for specific application to the laser fusion reactor con-

cept that uses liquid lithium in a continuous waterfall-like motion. Therefore, conditions were chosen to simulate those expected in the conceptual reactor.^{6,7,8} Also included are the equations required to evaluate other reactors that have different dimensions, breeding rates, and temperatures.

TRITIUM PERMEATION THROUGH PRIMARY CONTAINER

In the one-dimensional case, the flow rate of hydrogen through metals can be expressed as⁹

$$J \text{ (A/}\ell\text{)(P}_1\text{/}^2 - \text{P}_2\text{/}^2\text{)} \phi_0 \exp(-\Delta H_\phi/\text{RT}), \quad (1)$$

where J is flow rate in quantity of H_2/s , A is the area, ℓ is the thickness, P_1 is the pressure on the inlet, P_2 is the pressure on the exit, and ϕ_0 equals $C_0 D$, (in units of $\ell^{-1} \text{P}^{-1/2} \text{s}^{-1}$) the product of the pre-exponential terms of diffusivity and solubility for dilute solutions. That is,

$$D = D_0 \exp(-\Delta E/\text{RT}) \text{ and } C = C_0 \exp(-\Delta H/\text{RT}).$$

It follows that ΔH_ϕ equals the sum of the activation energy for diffusion ΔE and the heat of solution ΔH .

Equation (1) shows that the driving force for hydrogen flow through metals is the difference of the square roots of pressure on the inlet and exit. If the conditions are such that $P_1 - P_2 \cong P_1$, then the flow is proportional to $P_1^{1/2}$.

It is possible to estimate the tritium loss rate, under steady-state operation, to the immediate area surrounding the primary vessel by choosing an appropriate container material with suitable dimensions. It is also necessary to assume a reasonable breeding rate and D/T ratio. A stainless-steel cylindrical vessel 10 m high, 5 m in diam, and 51 mm thick should hold 10^6 kg of liquid lithium at 500°C . To maintain a low tritium inventory and yet be practical, it is assumed that the hydrogen isotope partial pressure is limited to $\sim 10^{-3}$ Pa with a T/D ratio of 2. We used the following values for the adjustable parameters:

$$\Delta H_\phi = 65.78 \text{ kJ/mol,}$$

and

$$\phi_0 = 3.1 \times 10^{-1} \text{ mm}^{-1} \text{ s}^{-1} (\text{Pa})^{-1/2}.$$

These values were obtained from tritium permeability measurements made with 21Cr-6Ni-9Mn samples that were sputter-cleaned with argon then sputter-coated with 200 nm of palladium.¹⁰ These experimental conditions more realistically represent those conditions expected in the laser fusion waterfall reactor. It is assumed that the stainless steel surface in contact with liquid lithium would be the same as one coated with palladium. The expression chosen for the diffusion constant is that reported for H_2 in 304 austenitic stainless steel,¹¹ i.e.,

$$D[(\text{mm})^2/\text{s}] = 2.1 \times 10^{-1} \text{ p}(-46.09 \text{ kJ/RT}).$$

The classical correction was not applied; that is

$$D_{T_2} = \left[\left(\frac{m_{\text{H}_2}}{m_{T_2}} \right)^{1/2} \right] \left(D_{\text{H}_2} \right),$$

because it would not greatly affect the outcome. This calculation will be further refined when the necessary values are experimentally determined using tritium and the appropriate stainless steel.

The time-to-steady-state flow—the time beyond which Eq. (1) applies—can be calculated from the expression $t = 0.45\ell^2/D$. For the conditions discussed above, this time is 79.4 days, assuming that steady-state flow starts instantaneously. This assumption leads to an overestimate of the amounts that permeate; fortunately, these larger quantities can still be safely processed.

The loss rate of tritium from the primary container, as calculated by use of Eq. (1), can be maintained at 3 Ci/d by limiting the partial pressure of tritium and deuterium to 10^{-3} Pa at 500°C in the primary vessel. This loss rate can be further reduced to 1 Ci/d by surrounding the first container with a second stainless steel shell 6.5 mm thick, as well as by continuously removing tritium in the annular volume. A partial pressure of 10^{-7} Pa of hydrogen isotopes must be maintained in the annular volume throughout the pumping process.

CONCEPT OF TRITIUM EXTRACTION

In the primary container, the continuous, waterfall-like motion of lithium containing dissolved tritium and deuterium ensures rapid desorption of ^4He and the hydrogen isotopes. It is reasonable to expect that the desorption rate of ^4He and T_2 dissolved in liquid tritium will eventually equal the breeding rate. A constant partial pressure of DT , T_2 , D_2 and ^4He is maintained by continuously removing these gases at a rate equal to their generation rate. They can be removed by diverting a fraction of the lithium at equilibrium with the hydrogen isotopes in the primary container to a separate loop for extraction. This second loop must be made of a material like the alloy Nb-1wt%-Zr; it is chemically compatible with lithium at 900°C , and has a high permeability for hydrogen isotopes.

The helium-4 should be extracted prior to extracting hydrogen isotopes. Helium-4 can be removed by coldtrapping the lithium and leaving

helium-4 mixed with hydrogen isotopes in the gas phase. This initial separation could be followed by preferential diffusion of helium-4 through fused silica to separate it from the hydrogen isotopes.

Because hydrogen in liquid lithium is about 17 times more soluble at 500°C than at 900°C (at the same pressure), 94% of the hydrogen dissolved in lithium at 500°C can be extracted by raising the temperature to 900°C . Thus, the hydrogen desorbs and diffuses through thin-wall tubes of the second loop. This process separates DT , D_2 , and T_2 (H_2 impurities) from Li and ^4He . The separated hydrogen isotope mixture can be absorbed and stored in another material like the alloy Al-84wt%-Zr. This alloy can rapidly absorb hydrogen isotopes at 450°C and thus offers a convenient method for the alloy and hydrogen isotopes to be recycled. That is, the hydrogen isotopes can be removed for reuse by heating to 750°C leaving the reactivated alloy behind.

TRITIUM-LITHIUM PROCESSING

A tritium breeding rate of 10 mg/s with T/D ratio of 2 produces a hydrogen isotope generation rate of 15 mg/s, equivalent to 1.3 kg of $\text{T}_2 + \text{D}_2$ /day. For dilute solutions, the solubility of H_2 in lithium can be expressed as an atom ratio by the relationship¹

$$\text{NH} = 7.16 \times 10^{-5} P^{1/2} (\text{Pa})^{1/2}$$

$$\exp(6460/T(K)), \quad (2)$$

where NH is the weight ratio H/Li, T is temperature, and P is the hydrogen partial pressure.

Details of tritium processing were evaluated without correcting the values of the two adjustable parameters in Eqs. (1) and (2) to correspond to T_2 . These calculations, although not strictly correct, suffice for this assessment. More accurate values will not be needed until a functional engineering design is to be done.

To establish the A/l ratio of Nb-1 wt%-Zr necessary to process the amount of tritium and deuterium generated per day, the values¹² of ϕ_0 $3.6 \times 10^{-2} [\text{g}/(\text{Pa})^{1/2} (\text{mm}) \text{ s}]$ and $\Delta H_0 = 63 \text{ kJ/mol}$ are used in Eq. (1). To further investigate some of the practical limitations of this tritium-processing con-

cept, we evaluated a scheme that uses clusters of tubes 10 m high by 25.4 mm in diam with a wall thickness of $2.54 \times 10^{-1} \text{ mm}$. The A/l ratio per tube for this example is $6.3 \times 10^6 \text{ mm}$. These tube dimensions were chosen to ensure that the diffusion rate through the container walls was rate determining rather than the desorption rate from liquid lithium.¹³ Lithium density can be calculated from the expression¹

$$[\rho(\text{g}/(\text{mm})^3)] = 0.5368 - 1.0208 \times 10^{-1} t(^{\circ}\text{C}). \quad (3)$$

Because lithium density decreases with temperature, the amount needed for processing should be established by weight rather than volume. Thus, to process 1300 g of $\text{T}_2 + \text{D}_2$ per day with $\text{T}_2/\text{D}_2 = 2$, 1.6% of the lithium inventory needs to be processed—about $8.4 \times 10^4 \text{ g}$. Because steady-state flow is reached in about 46 s at 900°C , the minimum flow-through per tube is $3.3 \times 10^{-3} \text{ mg}$ of H_2/s for these conditions. It follows that 706 mg of $\text{D}_2 + \text{T}_2$ can be separated from lithium and helium-4 in $2.1 \times 10^4 \text{ s}$ in every tube by diverting lithium saturated with $\text{D}_2 + \text{T}_2$ at $1.33 \times 10^{-3} \text{ Pa}$ into these tubes at 500°C . The tubes are then heated to 900°C

to desorb hydrogen isotopes from lithium and to diffuse them through the walls until their partial pressure inside the tubes equals 1.33×10^{-3} Pa.

Thus, hydrogen isotopes are separated from lithium and absorbed for temporary storage by an appropriate metal. Then, to reduce the temperature back to 500°C, lithium that contains about 6% of its

original $D_2 + T_2$ at 1.33×10^{-3} Pa and 900°C can be cycled back into the primary vessel through a heat exchanger. This cycle can be repeated 41 times per day; thus, 0.3 g of $D_2 + T_2$ can be extracted from each tube daily. To extract $D_2 + T_2$ at a rate equal to the generation rate requires 4,333 tubes of the above dimensions.

TRITIUM ABSORPTION AND STORAGE

As previously suggested, hydrogen isotopes can be absorbed by an alloy such as Al-84-wt%-Zr. Because this alloy is commercially available as hydrogen getter pumps, we can evaluate its feasibility using reported pumping rates and capacities. The largest storage capacity pump (8000 torr litre) has a pumping rate of 500 litre/s at

450°C. Because storage capacity is the limiting property, 1380 pumps will be needed to store the amount of $D_2 + T_2$ generated daily. Both the alloy and the hydrogen isotopes can be recycled by simply raising the temperature to 750°C to desorb the hydrogen isotopes, thus leaving the reactivated alloy behind.

LIMITATIONS OF PERMEATION METHOD

The initial and boundary conditions of our study were chosen to represent those of a laser fusion reactor with a continuous lithium "waterfall." As previously stated, these conditions cause an overestimate of the tritium amounts that permeate the primary container. A more accurate estimate could be made by considering the startup process as a separate problem.

It is unrealistic to assess problems of extracting tritium from liquid lithium without also considering the related problems of separating helium-4 from lithium. Both problems are equally important because neutron-induced lithium reactions generate equal quantities of tritium and helium-4.¹⁴ We are not discussing detailed methods for extracting helium-4 from lithium or from tritium. Nevertheless, we suggest that helium-4 could be separated from lithium and from hydrogen isotopes

by first coldtrapping lithium, thus leaving tritium and helium-4 in the gas phase. Another permeation method would allow the gas mixture to flow through a material like vitreous silica. At room temperature, a $^4\text{He}/T_2$ ratio as high as 500 is possible. A safe method for handling the resulting large quantities of helium-4 slightly contaminated with tritium is still needed to complete the process.

Maintenance problems could be minimized by only processing tritium with equipment having no moving parts. The major amounts of tritium should be extracted near the source, assuming that keeping large quantities of T_2 near the source requires less maintenance.

This report does not address the details of maintenance problems. By not considering them, we do not infer that there are no maintenance problems, but rather that they need to be better defined.

CONCLUSIONS AND RECOMMENDATIONS

Our study has shown that hydrogen isotopes can probably be separated from lithium and helium-4 by diffusing hydrogen isotopes through thin-wall containers of a refractory metal that contains a getter. The suggested alloy for the container is Nb-1wt%-Zr. The diffusion process requires that hydrogen isotopes be absorbed by a suitable alloy

such as Al-84wt%-Zr, which absorbs and desorbs hydrogen isotopes reversibly.

This study has also focused attention on areas that need further research and development. Following is a series of suggestions of some technical information required for a more accurate assessment:

- Devise a procedure for separating helium-4 from lithium and hydrogen isotopes.
- Experimentally demonstrate the permeation method of separating hydrogen isotopes from lithium.
- Determine suitable methods for maintaining all tritium-contaminated equipment.
- Establish undesirable impurities in lithium, i.e., those elements that result in a high specific activity caused by neutron-induced reactions.
- Establish methods for removing impurities from lithium.
- Determine how refractory metals are affected by hydrogen embrittlement caused by cooling and heating cycles.
- Establish the chemical compatibility of refractory metals with lithium that contains impurities removed from stainless steel.

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