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ABSTRACT

Various techniques for tritium removal from the liquid eutectic $Li_{17}Pb_{83}$ under vacuum are considered as candidates for the tritium removal system (TRS) for the Mirror Advanced Reactor Study (MARS). The TRS baseline parameters require the removal of 60% of the tritium contained in the liquid metal at a tritium partial pressure of 1.0×10^{-4} torr (0.013 Pa). Degassing from a droplet spray was chosen as the preferred design option, although removal from thin films is a feasible alternative. Vacuum removal from a stirred pool was rejected because of the size and relatively poor transport conditions. The use of an inert purge gas was also rejected due to the large purge gas flow rate and the problem of separating tritium from a large quantity of inert gas.

INTRODUCTION

Vacuum degassing as a method of tritium recovery from a liquid lithium-lead breeding blanket has been proposed in previous reactor studies.[1,2] In this paper various techniques for vacuum removal of tritium are reviewed and analyzed for the purpose of identifying a suitable tritium removal system (TRS) for the Mirror Advanced Reactor Study (MARS).

Selection of the most suitable tritium recovery process from among the available candidates requires a set of baseline parameters for the process. The establishment of these parameters involves a tradeoff between reasonable operating conditions for recovery and the constraints on operating conditions set by tritium loss limits. The processes considered are vacuum degassing of a stream of droplets, thin film, stirred pool and gas sparging.

Presently there are no experimental data for the vacuum removal of tritium from lithium-lead alloys and data are also lacking for many of the transport calculations. In the absence of such data, data for the removal of hydrogen from liquid steel and aluminum[4,5] have been used as models for the tritium removal systems considered.

BASELINE PARAMETERS

The selection of an appropriate operational partial pressure involves a compromise between a pressure high enough for tritium recovery and yet low enough to minimize tritium losses due to permeation. The low value of Sievert's constant for tritium in lithium-lead in the temperature range 400-600°C[3] of 0.051 wppm/torr$^{0.5}$ establishes that a reasonably high partial pressure of tritium exists at low tritium solution concentrations. At 1×10^{-6} torr the TRS must handle the entire lithium-lead coolant stream and continuously remove ~ 96% of the tritium. To accomplish this an average pumping speed of 1.7×10^{10} 1/s is required at a temperature of 500°C. These requirements are unacceptable for a realistic recovery system, although the tritium containment problem would be eased. By operating at a tritium partial pressure of 1.0×10^{-4} torr, a lithium-lead side stream of 16% and a pumping speed at 500°C of 2.0×10^{6} 1/s would be needed. Under these conditions 60% of the tritium of the side stream has to be recovered. From the point of view of the TRS these conditions seem to be acceptable and therefore have been established as the baseline parameters (Table I) for the systems being compared.

However, at a tritium partial pressure of 1.0×10^{-4} a tritium barrier of 2.0×10^{4} is required in the power cycle to limit losses to water to less than 10 C_i/d by permeation. To accomplish this, a double-walled heat exchanger[1,6] is to be used and piping and valves will require some form of auxilliary secondary containment.

The TRS will be interconnected to various subsystems. A combination of turbomolecular pumps and cryopumps is used to supply the pumping capacity. Traps or baffles are necessary to condense lithium and lead vapors before reaching

TABLE I. Baseline Parameters for MARS Tritium
Recovery System

Reactor Parameters

LiPb flow rate in reactor (kg/s)	1.4×10^5
Tritium removal rate (mol T_2/s)	1.1×10^{-3}
Tritium partial pressure above LiPb (torr)	1.0×10^{-4}
Tritium concentration in LiPb (wppm)	5.1×10^{-4}

Tritium Parameters

LiPb flow rate into TRS (kg/s)	2.2×10^4
TRS outlet tritium concentration (wppm)	2.0×10^{-4}
TRS outlet tritium pressure (torr)	1.5×10^{-5}
Average pumping rate required to reduce pressure from P_{inlet} to P_{outlet} at 500°C (1/s)	2.0×10^6

the cryopanels. At 500°C, the lithium and lead vapor pressures above the eutectic are 1.4×10^{-5} and 3.7×10^{-7} torr and the vapor condensation rates are 0.032 g/s and 2.8×10^{-4} g/s, respectively. Impure tritium gases will then pass through a purification system similar to the reactor fuel cleanup unit.[7]

VACUUM DEGASSING OF LIQUID METALS

The kinetics of gas transport through a liquid metal involve three steps.[8,9]

1. Transport from the metal interior to the liquid-gas interface by convective transport in the interior and by diffusion through the boundary layer of the melt.
2. A phase transition region where gas atoms in the dissolved state at the surface combine to form molecules which are desorbed from the surface.
3. Diffusion of gas molecules into the gas space and removal by the pumping system.

As long as there is a sufficiently large mean free path for molecules leaving the surface, step 3 is rapid compared to steps 1 and 2. Active pumping on exposed surfaces and limited impedence to gas flow should be incorporated into the design. The phase transition step can become dominating if the concentration in the surface boundary layer is very small ($C_{ms} \to 0$). This can be minimized by agitation to equalize the concentration in the melt. Also, step 2 was not found to be rate controlling for hydrogen gas in liquid steel. Step 1, the transport in the liquid phase, is usually the slow process. Therefore, the liquid phase transport is assumed to be rate determining in the vacuum degassing of lithium-lead.

The transport of gas through the liquid metal boundary layer is described[8] by Eq. (1),

$$\ln \frac{C_m}{C_{mo}} = - \beta_m \frac{A}{V} t \qquad (1)$$

where C_m and C_{mo} are the concentrations of gas in the melt originally and at time t, A is the surface area, V is the metal volume and β_m is the mass transfer coefficient, which is the rate of transport across the diffusion boundary layer in cm/s. The value of β is unknown for hydrogen in lithium-lead. It is known that the average value of β_m is proportional to the square root of the diffusion coefficient, D, and is related to the degree of agitation of the melt. For hydrogen in liquid steel at 1500°C, the diffusion coefficient is 1.5×10^{-3} cm²/s.[8] For bubble free degassing and steel melts stirred by convection β_m is 10^{-1} to 10^{-2} cm/s and for induction stirred and gas agitated steels β_m is 10^{-1} - 1 cm/s.[8,9] The diffusion coefficient for tritium in lithium-lead has not been determined experimentally, but it is approximated as 10^{-3} cm²/s based on diffusion data on other liquid metals.[1] Therefore, the average mass transfer coefficient is estimated as 10^{-1} cm/s for tritium in a stirred or agitated lithium-lead melt.

The surface area required for a typical range of β_m values as a function of the percent tritium removed in the extraction unit is plotted in Fig. 1. The figure is derived from Eq. (1) using a liquid metal flow rate of 2.2×10^4 kg/s corresponding to a side stream of 16% of the total lithium-lead flow. It can be seen that the surface area requirement for systems constrained by our baseline parameters may vary by several orders of magnitude depending on the value of β_m. It is possible therefore that one controlling factor in the selection of a process may be the ability to produce the size of surface area necessary to successfully remove tritium by vacuum pumping.

DROPLET SPRAY

One method of providing a large surface area is to produce a droplet spray. This process, called stream degassing, is accomplished by forcing a liquid metal through a nozzle to form a stream of droplets which fall through a vacuum chamber. The degassing is improved and the vacuum requirements are lowered if bubbles form within the droplets. For bubble

Figure 1 (left column):

SURFACE AREA OF LIQUID METAL (m^2)

10^5
10^4
10^3
10^2
10^1

$\beta_m = 10^{-2}$ cm/s

$\beta_m = 10^{-1}$ cm/s

$\beta_m = 10^{0}$ cm/s

LiPb flow rate into extracter 2.2×10^4 kg/s

0   20   40   60   80   100

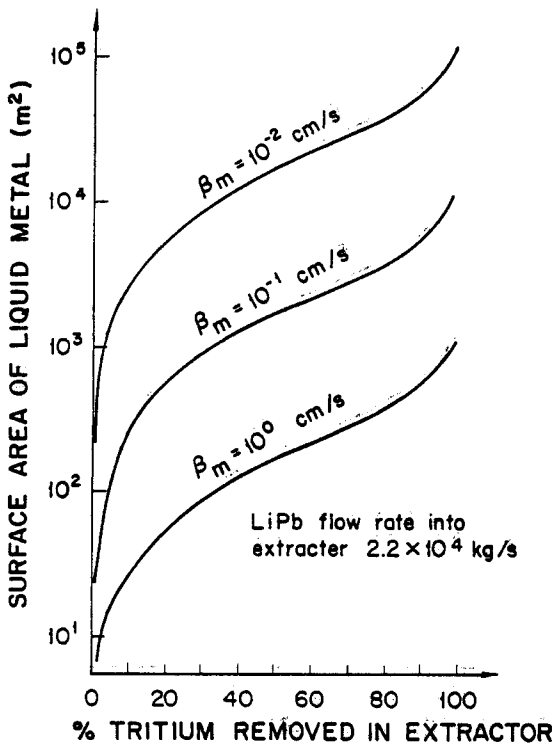% TRITIUM REMOVED IN EXTRACTOR

FIGURE 1

formation the equilibrium pressure in the drop must exceed the vacuum chamber pressure and the surface tension pressure. The surface tension pressure is $2\sigma/r$, where σ is the surface tension (estimated from the pure components as 430 dyne/cm for $Li_{17}Pb_{83}$) and r is the drop radius. The pressure on a drop of 1mm radius is ~ 6 torr which greatly exceeds the 10^{-4} torr pressure in the droplet. Therefore, bubbles will not form and the transport is dependent on diffusion of tritium from the droplet.

The rate of diffusion from a spherical droplet in a vacuum is given by the rapidly converging series[10]

$$U = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp - \left(\frac{n^2 \pi^2 Dt}{r^2}\right) \qquad (2)$$

where U is the fraction of initial hydrogen remaining, t is the time of fall, r is the droplet radius and D is the diffusion coefficient (10^{-3}

cm^2/s). The amount of gas liberated from drops 1-3 mm in diameter for times of fall of 0.5 - 1 s is shown in Table II. The required 60% gas removal is achieved for droplets 1 mm in radius falling for 0.5 s. If we assume a height of fall of 550 cm, a total residence time of 5 s for lithium-lead in the TRS and a distance of 1.0 cm between dispersed droplets we can estimate the size and other system parameters for a MARS TRS using stream degassing. These parameters (Table III) suggest that this technique for tritium removal should meet the MARS requirements.

THIN FILMS

A large surface area and favorable transport conditions can be created if liquid metal flows over a series of metal vanes in a "waterfall" type cascade (Fig. 2). The vanes are de-

TABLE II. Gas Removal From a Droplet Spray

Drop Radius (mm)	Time of Fall (s)	% Gas Removal
1	0.5	60
	1.0	77
3	0.5	24
	1.0	32

TABLE III. Stream Degassing TRS for MARS

A. Droplet Spray

time of fall (s)	0.5
height of fall (cm)	550
velocity (cm/s)	850
total mass of droplets (kg)	1.1×10^4
radius of droplets (mm)	1
surface area of droplets (cm^2)	3.5×10^7
number of droplets	2.8×10^8
volume of dispersed droplets (cm^3)	2.5×10^8

B. Pool

mass (kg)	9.9×10^4
volume (m^3)	10.5
surface area (m^2)	46
depth (m)	0.23
residence time (s)	4.5

C. Extraction Unit

volume (m^3)	2.7×10^2
radius (m)	3.8
height (m)	6

3

signed with the appropriate angle to form the desired film thickness and the size and number of vanes correspond to the required surface area.

The transport from the films is calculated by applying Eq. (1). The ratio of area to volume is 1/d where d is the film thickness and the overall mass transport coefficient β is assumed to equal 10^{-3} m/s. Making the above substitutions in Eq. (1) and assuming 60% tritium removal, the expression below is obtained:

$$0.92 = 10^{-3} \text{ m/s } \frac{t}{d} \tag{3}$$

If a 0.01 m thick film is used, the residence time is 10 s and the surface area is 2.2×10^3 m^2. If the metal film flows at the rate of 0.1 m/s and the vanes have an individual surface area of 11 m^2, 200 vanes occupying a volume of approximately 132 m^3 will be required. It appears that this technique could be used.

STIRRED POOLS

Favorable transport of tritium from a liquid metal pool requires agitation of the pool to equalize the concentration within the melt and to create a narrow diffusion boundary layer near the surface where the rate determining transport step occurs. It can be seen from Fig. 1 that for 60% tritium removal and $\beta = 0.1$, the surface area of the pool must be 2.2×10^3 m^2. This is a circular pool 26 m in radius. If the residence time is 100 s, the pool depth is 0.11 m. The large pool size and relatively poor transport conditions constitute an inferior design by comparison to the droplet spray and flowing thin films.

GAS SPARGING

The formation of gas bubbles in the melt has two important effects on the mass transfer. It causes agitation and it creates a surface area for diffusion in the interior of the melt. Bubbles form spontaneously if the equilibrium pressure in the melt is greater than the sum of the ambient pressure on the liquid, the hydrostatic pressure on the bubble and the capillary pressure caused by surface tension. The minimum pressure[8] for bubbles to form spontaneously directly under the surface is

$$P_{min} \geqslant 2 \sqrt{2\sigma\rho g} \text{ torr} \tag{4}$$

where σ is the surface tension, ρ the density and g the gravitational constant. For lithium-lead P_{min} is approximately 2.1 torr. Therefore, a pool containing 1.0×10^{-4} torr tritium will
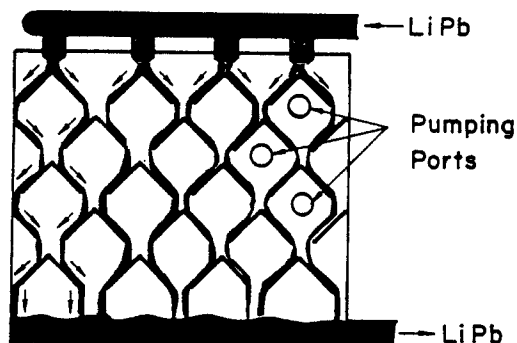

FIGURE 2

not spontaneously form bubbles when exposed to a vacuum and a purge gas must be injected at pressures much greater than 2.1 torr to create boiling throughout the melt.

The change in bubble size with pool depth due to the changing hydrostatic pressure on the bubble is shown in Fig. 3. A 0.1 cm bubble formed in a 200 cm deep pool with an external helium pressure of 1 torr on the pool is assumed in this case. The bubble size remains fairly constant for the first 150 cm of its rise. The bubble radius begins to increase and expands very rapidly in the last 5 cm. An estimate of the required purge gas flow can be made from this diagram. The maximum radius the bubble attains near the surface is 0.60 cm. If tritium saturates the bubble at this volume the bubble will contain 1.9×10^{-12} moles of T_2. Helium bubbles of 0.1 cm radii injected at the bottom of the melt at a pressure of 1388 torr contain 1.2×10^{-7} mol He. The helium:tritium ratio in a saturated bubble immediately before it is lost from the surface is 6.3×10^4. Since the tritium in the bulk must be removed at a rate of 1.1×10^{-3} mol T_2/s, the required purge gas rate is 70 mol He/s or 3.4×10^6 l/s at 1.0 torr and 500°C. This calculation estimates the minimum flow rate because it assumes that the bubble is always saturated with the equilibrium amount of tritium. This is particularly unlikely for the last 5 cm near the surface where the bubble volume is expanding too rapidly for equilibrium to be established. If the bubble radius at a depth of 5 cm is chosen as the final equilibrium point, the resulting purge gas flow rate is 2.0×10^7 l/s at 500°C and 1 torr. These excessive purge gas flow rates and subsequent separation
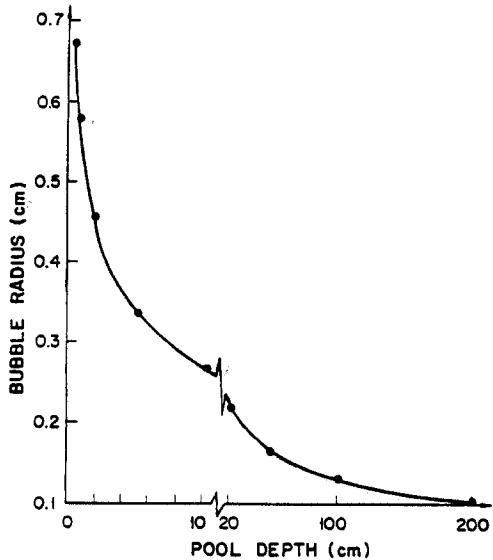
FIGURE 3

at large $He:T_2$ ratios make this degassing option unfavorable.

CONCLUSIONS

From our analysis of various vacuum degassing options for a MARS TRS the droplet spray and the flowing thin films are superior to stirred pools and gas sparging. The droplet spray is chosen as the main design option primarily due to its simplicity. The short time of fall of droplets results in short residence times and a low instantaneous lithium lead inventory in the TRS. In addition, the design of the vacuum parts and chamber is simple and the overall volume is smaller. There is experience with stream degassing of steels to remove hydrogen and predicted removal rates are in fair agreement with what is obtained in practice.[4] There are presently no systems analogous to the thin film design in operation.

Future work on the stream degassing TRS should include design of the vacuum system, analysis of heat loss from the liquid metal, the design of the trapping systems to collect particulates and metal vapors, the nozzle design and the overall cost analysis.

REFERENCES

1. B. BADGER et al., "WITAMIR-I - A Tandem Mirror Reactor Study," UWFDM-400, University of Wisconsin (1977), Chapter XI.

2. B. BADGER et al., "NUWMAK - A Tokamak Reactor Design Study," UWFDM-330, University of Wisconsin (1979), Chapter X.

3. E. VELECKIS, Argonne National Laboratory, Private Communication (1981). (A $\sqrt{3}$ isotope effect is assumed in converting hydrogen data to tritium data).

4. K. RUTTIGER, "Vacuum Degassing in the Liquid State," *Vacuum Metallurgy*, Elsevier Publishing Co., New York (1971), 337-463.

5. J.H. FLUX, "Vacuum Degassing 1955-1965: A Survey of Processes and Plants for Bulk Steel Production," *Proceedings of the Iron and Steel Institute Annual General Meeting*, London, England, May 5-6, 1965, Special Report-92, Percy Lund, Humphries and Co. Ltd., London, 1-23.

6. D.K. SZE, *Proc. 5th ANS Top. Mtg. on Tech. of Fusion Energy*.

7. E.C. KERR, J.R. BARTLIT and R.H. SHERMAN, "Fuel Cleanup System for the Tritium Systems Test Assembly: Design and Experiments," *Proc. Tritium Technology in Fission, Fusion and Isotopic Applications*, Dayton, Ohio, April 29-May 1, 1980, CONF-800427, ANS (1980) 115-118.

8. O. WINKLER, "Thermodynamics and Kinetics in Vacuum Metallurgy," *Vacuum Metallurgy*, Elsevier Pub. Co., New York (1971) 30-74.

9. A.V. BRADSHAW and F.D. RICHARDSON, "Thermodynamic and Kinetic Aspects of Vacuum Degassing," *Proc. of the Iron and Steel Institute Annual General Mtg*, London, England, May 5-6, 1965, Special Report-92, Percy Lund, Humphries and Co. Ltd., London, 24-44.

10. J.D. SHARP and A.T. SHERIDAN, "Physical Considerations in the Stream Degassing of Steels," Ibid 50-54.

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