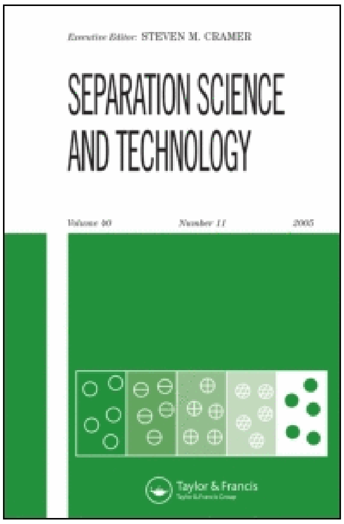

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The Use of Zirconium-Palladium Windows for the Separation of Tritium from the Liquid Metal Breeder-Blanket of a Fusion Reactor

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ABSTRACT

Any first generation fusion power reactor must be surrounded by a heat tranfer medium and a tritium breeder-blanket containing lithium in some form. Liquid lithium and liquid lithium alloys are considered to be particularly attractive choices for both purposes; the main disadvantage of these materials is the difficulty of tritium separation. The use of zirconium-palladium windows for tritium separation is shown to have many advantages over the best alternative devices. This is based on the materials properties and costs as they stand in 1983.

The design of a typical permeation window resembles that of a shell and tube heat exchanger; liquid lithium or lithium alloy loaded with tritium from the reactor, flows through on the zirconium side of the window, while a purge stream of argon and oxygen flows through on the side with the palladium coating. Oxygen is present so that sufficiently low tritium pressures may be maintained on the downstream side of the window. Tritium is recovered as T_2O.

Data are presented regarding the thermodynamics and the transport properties of tritium in lithium, in lithium-lead alloy, and in zirconium. Data are also presented for the reaction rate on a palladium surface. A permeation window is described; its cost is estimated to be $9,300,000 for use on a liquid lithium breeder-blanket or $1,100,000 for use on a lithium-lead alloy breeder-blanket.

Some remaining problems are outlined.

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INCENTIVE FOR THIS STUDY

1. Importance of this Separation

It is generally assumed that the first fusion 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.

From many standpoints the simplest and most attractive breeding media are lithium metal and molten alloys containing lithium (e.g. Li-Pb and Li-Pb-Bi). At typical temperatures proposed for fusion blankets, these metals are highly fluid and thermally conductive. In addition to their high cross-sections for fast and slow neutrons, they are non-corrosive to refractory metals, inert to radiation, and have high breeding ratios. Li-Pb alloys are of particular interest because they are relatively unreactive when exposed to water or air.

Among the disadvantages of molten lithium and its alloys is the fact that they are corrosive when contaminated and, also, since they are good conductors of electricity, some magnetohydrodynmaic energy degradations necessarily occur when they are pumped across magnetic flux lines. More importantly, lithium has an unusually high affinity for hydrogen and its isotopes, and consequently the recovery of tritium from lithium and lithium alloys is difficult, especially at the low tritium concentrations required for fusion blankets.

A number of workers in the past have examined the problem of recovering tritium form lithium at low concentration levels (1,2,3,4) and summaries of the problem have been presented by Watson (5) and by Johnson (6). As described below, some specific recovery processes have been recommended as practicable possibilities. In this section, I review briefly the full range of recovery processes and, on the basis of recent data, present a critical appraisal of what appears to be a particularly attractive recovery process.

For first generation fusion power machines, the principal constraint on the concentration of tritium in the reactor blanket is the total allowable tritium inventory. This inventory typically is taken to be of the order of a few kilograms (7), and since the mass of lithium in the blanket may exceed a million kilograms (8), the tolerable tritium concentration in the lithium must be around one weight part per million or less. By comparison, the tritium inventory in lithium-lead alloys, probably, will be maintained at about one weight part per billion; this is a consequence of the greater density of lithium-lead and of the lesser tritium affinity of these alloys when compared to lithium metal. The bulk of the tritium inventory, most probably, will have to be in reserve storage for the reactor fuel injection system and not in the blanket or tritium recovery system.

One reason for desiring a low tritium inventory is the expense of tritium, currently about twenty million dollars per kilogram (9). Even at minimal concentrations, the cost of tritium is expected to be a significant fraction of the start-up cost for the first fusion reactor. Another advantage of running at the minimum tritium concentration is safety. Tritium in reserve storage presents much less potential safety hazard than the same amount of tritium within the breeder material. Even if tritium prices fall drastically, the safety incentive will probably require that future generation fusion reactors are run at very low tritium concentrations.

For a more detailed description of reactor neutronics and the choice of liquid metals as optimal breeder blankets, see reference 10.

2. Possible Separation Processes

At concentration levels in the parts per million range, few separation processes offer any promise of success in recovering tritium from lithium or lithium-lead under conditions permitting easy concentration and regeneration of the tritium in pure form.

Most of the research cited below was preformed for tritium in liquid lithium metal however, except as mentioned separately, the results should be applicable to liquid lithium-lead eutectic as well.

Separation processes may be classified in ascending order of cost as:

1. mechanical separations,
2. phase-change separations, and finally
3. chemical processes.

Mechanical processes are not applicable because the tritium at all practical blanket temperatures, is present primarily as lithium tritides dissolved in the metal, hence it is not recoverable either by filtration or by sedimentation.

Most of the phase-change separations are in principle appliable, but in practice, uneconomic. Simple cold trapping is not possible becasue the solubility of lithium tritide at the eutectic lithium tritide system is too high (11). Also at the low tritide concentrations, and at temperatures near the melting point of pure lithium, the rates of crystallization would be so low that very large equipment would be required. This factor alone would also rule out the possiblity of adding a solvent to the lithium to salt out the tritide, i.e., to depress the solubility of the tritide below the desired concentration levels for the blanket.

Fractional distillation, or indeed any vaporization process, will not be practicable beause an azeotrope exists for the the lithium--lithium tritide system at excessively high concentrations for likely distillation temperatures. While this azeotrope is believed to form at low enough concentrations to make Li-Pb-T distillation possible, the vapor rates at the necessarily low pressures for distillation would lead to prohibitively large processing equipment. This factor also would preclude the use of solvent distillation (either azeotropic or extractive distillation) to break the azeotrope and effect Li-T separation.

Liquid-liquid solvent extraction employing molten halide mixtures as solvent has been shown to be a practicable possibility by Maroni, Wolson, and Staahl (12). The distribution coefficient for lithium tritide between the salt melt and liquid lithium is around 2.0, and an electrolytic process for recovering the tritium from the salt has been demonstrated by Calaway (13). Unfortunately, although the equilibrium characteristics are favorable by normal standards, the very low concentrations dictate that the amounts of solvent and the electrode size be very large. Furthermore, the salt mixtures tested have been observed to contaminate lithium to approximately 0.2 weight percent (14). If recirculated into the fusion reactor, these contaminates produce long-lived radioactive by-products, they adversely affect breeder neutronics, and they corrode materials proposed for fusion reactor construction (15,16). Even so, this technique is probably the best of the phase-change separations. The author is unaware of any attempt to estimate its cost (17).

The only important remaining phase-change separation process is adsorption (chemisorption or physisorption) which takes advantage of a favorable distribution of the solute between the fluid phase and a concentrated phase that is physically adsorbed on the surface on an appropriate solid adsorbent. There are no obvious candidate adsorbents.

3. Chemical Separation Processes

Only three chemical separation processes have been suggested or studied for the recovery of tritium from lithium:

1. absorption by liquid hydride formers,
2. absorption by solid hydride formers,
3. permeation through metal membranes.

I classify absorption by hydride formers as a chemical process because the tritium must dissociate from the lithium tritide in order for it to be absorbed. Studies on liquid-metal hydrogen getters comprising eutectic mixtures of selected rare earth metals (lanthanum-nickel and cerium mixed with iron, cobalt, or nickel) have been undertaken by Carstens (18,19). Sorption with these liquid getters can not be carried out at temperatures below about 450°C, the melting point of the getters. As a consequence, the thermodynamics of exothermic tritium sorption with liquids tends to be less favorable than that with membranes or with exothermic solid-phase sorbers: membranes and solid sorbers can be used at temperatures as low as 235° C with lithium-lead alloys or 200° C with lithium, (the melting points of the breeders.) A further difficulty with liquid-metal tritium-getters is that it is not clear how the tritium would be recovered from the resulting tritides, nor how the contamination of the lithium by the liquid getters could be avoided or controlled easily.

Hydride-forming solids offer another chemical means for extracting tritium from lithium. As early as 1954, Salmon (20) suggested the possibility of using titanium or zirconium to perform this extraction. However, these particular getters are at best marginal when compared to yttrium. As described by Buxbaum (10), a plant scale tritium recovery system using yttrium could comprise not fewer than three identical absorber vessels, one onstream removing tritium from the lithium, one offstream being regenerated, and the third on standby. Among the main costs for a tritium recovery system of this sort are yttrium (880 kg at $290,000) and tritium holdup (1.2 kg at $24,000,000). Even with such large costs, tritium sorption into yttrium metal is probably the most attractive separation system to have been evaluated to date.

One last suggested chemical process for the separation of tritium from lithium at low concentrations is permeation through a metal window. This method offers, in principle, an attractive alternative to sorption, because there is little chance of contamination, operations are continuous as opposed to semi-batch, and tritium holdup costs should be negligible. The rest of this paper will examine this separation technique.

A typical permeation window design resembles a series of heat exchangers with a slipstream of lithium or lithium-lead flowing through the metal shells and an argon-oxygen mixture flowing through the tubes. The presence of the oxygen on the downstream side of the window helps to maintain very low tritium pressures on this side by reacting with the tritium to form T_2O.

Watson (5), in his early and detailed appraisal of possible means of tritium recovery from fusion blanket systems, suggested that a particularly attractive window composition would be niobium coated with palladium. Both of these metals have relatively high hydrogen permeabilities; niobium is compatible with lithium; and palladium, while not compatible with lithium, would forstall the oxidation of the niobium while providing a highly effective catalytic surface for tritium oxidation. Unfortunately, the materials cost for such a system is high. Furthermore, the interdiffusion of palladium and niobium would subvert the protective features over a relatively short time. Badger (21), has suggested the use of a protective intermediate layer of yttrium to lessen this problem, however, a more attractive option remains open.

As indicated by Fraas (22), zirconium's hydrogen-permeability is considerably greater than niobium's at all likely temperatures of operation. Zirconium is cheaper per pound than niobium, zirconium is compatible with lithium at temperatures up to 1000°C (23), and the fabrication of zirconium tubes is a well known process. Even with all these advantages, the author is unaware of any research into the separation of tritium by permeation through zirconium-palladium, or other zirconium-composite windows.

DESIGN CONSIDERATIONS FOR ZIRCONIUM-PALLADIUM WINDOWS

1. Zirconium-Palladium Interdiffusion

The growth of an intermetallic Zr-Pd layer is important because this layer might be expected to affect the tube's hydrogen permeability and because the thickness of this layer is likely to determine the thickness of the palladium coating. Also, the feasability of annealing as a method for removing oxides and nitrides from the zirconium surfaces (heating would cause the oxygen and nitrogen atoms to be absorbed into the zirconium bulk) requires that intermetallic formation will not be excessive at practical annealing temperatures. Stokes and Buxbaum (24) have presented an analysis of the effects of zirconium-palladium intermetallic formation based on data in the literature and on best available estimation techniques. Their results are as follows. 1) The only intermetallic alloy to form to an appreciable extent will be Zr_2Pd, where Table I shows the intermetallic's estimated diffusivity and estimated thickness after 30 years of operation. 2) The experiments of Sawatsky and Ledoux (25) can be interpreted as demonstrations that relatively thick layers of Zr_2Pd have no appreciable effect on hydrogen permeability 3) Annealing is practical because, at conditions which have proven effective (26) -one hour at 500°C- diffusion coefficients for oxygen and nitrogen are much greater than those for inter-

TABLE I. Self-diffusion coefficients for Zr_2Pd and projected intermetallic thicknesses after 30 years operation

Temp (°C)	$\tilde{D}$ (cm^2/s)	λ 30 yrs (cm)
200	1.55×10^{-23}	4.9×10^{-8}
250	2.85×10^{-21}	6.7×10^{-7}
300	2.10×10^{-19}	5.8×10^{-6}
350	7.76×10^{-18}	3.5×10^{-5}
400	1.68×10^{-16}	1.6×10^{-4}
450	2.37×10^{-15}	6.1×10^{-4}
500	2.38×10^{-14}	1.9×10^{-3}
550	1.80×10^{-13}	5.3×10^{-3}
600	1.08×10^{-12}	1.3×10^{-2}

metallic formation 4) A preliminary model for radiation-activated diffusion suggests that radioactive-tritium decay will have no appreciable effect on intermetallic formation. From Table I, it is seen that a palladium coating of 7 x 10^{-4} cm thickness should give a safety factor of three times for thirty years' operation at 450°C.

One may now inquire about zirconium interdiffusion with other possible catalytic coatings. Preliminary calculations suggest that interdiffusion of palladium-gold alloys with zirconium will be about as fast as with pure palladium and that interdiffusion of platinum with zirconium will be considerably slower. These coatings are subtantially more active catalysts than pure palladium and, for operation with liquid lithium, either one might reduce the cost of a zirconium-composit window by a factor of ten or more. By contrast, the separation of tritium from lithium-lead is not expected to be reaction controlled, and palladium is an entirely suitable coating for this application. One last result of Table I is that it suggests that interdiffusion can always be controlled by a reduction in operating temperature. In the region of 450°C, a temperature reduction of 50°C decreases the interdiffusion-zone thickness by a factor of four.

2. Thermodynamic and Diffusion Effects in the Separation of Tritium from Liquid Lithium

Diffusion of tritium through zirconium, palladium, and lithium is so rapid that, at the low tritium pressures found within liquid lithium breeder-blankets, diffusion is not the rate-limiting step. Instead, the separation of tritium from liquid lithium is limited by reaction rates at the palladium surface. Diffusion in the zirconium will be shown to produce about a 5% effect and all other effects are negligable (although a 5% correction factor will be included for design purposes). Reaction-limited transport in the solid state has been observed by Zarchy (27) in his experiments on tritium permeation through stainless steel.

The thermodynamic relationship between hydrogen pressure and tritium concentration in liquid lithium has been studied by Smith and Co-workers (28)

$$K_{Li-T} = 42.8\ e^{(10{,}104/RT)} \tag{1}$$

where R is the gas constant, 1.987; and K_{Li-T} is the Sieverts constant for the system, wppm/torr$^{1/2}$. Similarly, the solubility of hydrogen in zirconium has been studied by Gulbransen and Andrew (29); their data may be expressed as

$$P_{H_2} = \left(\frac{M_H}{2-M_H}\right)^2 [1939 \exp(-14{,}270/RT)] \tag{2}$$

where P_{H_2} is the hydrogen pressure, torr; M_H is the mole ratio of hydrogen to zirconium; and R is the gas constant, 1.987 cal/°Kmole.

Gulbransen and Andrew (29) have also measured the diffusivity of hydrogen in zirconium. If the diffusion coefficient for tritium in zirconium is equal to $1/\sqrt{3}$ times the diffusion coefficient for hydrogen in zirconium (30), then

$$\begin{aligned} D_{Zr-T} &= (1/\sqrt{3})\ 4.7 \times 10^{-4} \exp(-5940/RT) \\ &= 7.18 \times 10^{-6}\ \text{cm}^2/\text{s at } 450°\text{C}. \end{aligned} \tag{3}$$

The surface area for a permeation window of shell-and-tube design is calculated below; the design parameters are considered conservative and there has been no attempt at optimization. Assume that the zirconium tubes are 0.5 inches in diameter and 0.061 inches (1.5 mm) in wall thickness; this is twice the ASTM standard for low pressure operation. Assume that the window operates at 450°C, that the upstream bulk concentration is 0.8 wppm T in lithium metal, and that the effect of mass-tranfer resistance in the liquid and in the palladium is to reduce the effective upstream tritium pressure by 5%. This estimation is considered conservative in light of the permeability data presented by Fraas (22) and by Buxbaum and Johnson (31). (Because liquid-phase mass transfer resistances are expected to be much more important for reactors which use lithium-lead breeders, a separate section is devoted to these calculations.)

The bulk vapor pressure of tritium in liquid lithium at 450°C, is calculated to be 2.72×10^{-10} torr. Because of liquid phase mass transfer resistance, the effective pressure at the zirconium surface will be 2.58×10^{-10} torr. If the tritium pressure in equilibrium with the adsorbed hydrogen on the palladium surface is $P_{(dn)}$, torr, then the concentration gradient in the zirconium is

$$\Delta M_H/Z = (\sqrt{2.58 \times 10^{-10}} - \sqrt{P_{(dn)}})\ (6.52)/(.15) \text{ mole ratio/cm}^3 \quad (4)$$

or

$$\Delta C/Z = 4.74 \times 10^{-5} - 2.95\sqrt{P_{(dn)}} \quad \text{g-atoms T/cm}^3\text{ cm.} \quad (5)$$

It is now possible to calculate $P_{(dn)}$ and, in that way, to size the window, by matching the diffusion flux to the reaction rate at the palladium surface. In the above calculation, no isotope effect on solubility was assumed, this is in agreement with the majority of the literature (32).

3. Reaction Effects in the Separation of Tritium from Liquid Lithium

Low vacuum and ultra-high vacuum experiments on the palldium-catalyzed, hydrogen-oxidation reaction have been preformed by Engel and Kuipers (33), by Lam et al. (34) and by Young (35). Efforts are currently underway in the author's laboratory to explain some anomalies which are seen in this system, especially at moderate pressures. However, for the separation of tritium from lithium, the reaction analysis is simplified considerably: the low tritium pressure eliminates nearly all trimolecular reactions and nearly all reactions which involve H_2 molecules. Reaction kinetics are expected to follow the dominent mechanism observed by

Engel and Kuipers (35) for pressures around 5 x 10^{-7} torr and temperatures in the range 250 to 600 K.

$$H_{ADS} + O_{ADS} \xrightarrow[\text{slow}]{} (OH)_{ADS} \xrightarrow[\text{FAST}]{H_{ADS}} H_2O\ (g)$$

The rate constant for the slow step was found to be

$$K\left(\frac{cm^2}{atom\ s}\right) = 4 \times 10^{-8} \exp\left(\frac{-7000}{RT}\right) \qquad (6)$$
$$= 3.1 \times 10^{-10}\ cm^2/atom\ s \text{ at } 450°C.$$

Here, R is the gas constant, 1.987 cal/g mol°K; and T is temperature in degrees kelvin.

For oxygen adsorption on paladium at 450°C, oxygen partial pressures in the range 10^{-4} to 10^{-7} atmospheres are high enough that the palladium surface becomes saturated with oxygen atoms; there are essentially 0.25 oxygen atoms per surface palladium atom, or approximately 1 x 10^{14} oxygen atoms/cm^2. The maximum oxygen pressure in this range is still low enough that bulk palladium oxide will not form.

For hydrogen adsorption on palladium, the experimental data of Engel and Kuipers (36) can be used tó determine the following equilibrium relation for the fractional coverage at hydrogen pressures below 10^{-7} torr.

$$\Theta = 3.22 \times 10^{-5} \sqrt{P} \exp(5006/T) \qquad (7)$$
$$= 3.27 \times 10^{-2} \sqrt{P} \quad \text{at } 450°C.$$

Here, Θ is fractional coverage, atoms of surface hydrogen per atom of surface palladium; and P is the hydrogen pressure in equilibrium with the surface, torr. Clearly, P in the above expression is the same as $P_{(dn)}$ in equations 4 and 5.

The value of $P_{(dn)}$ is calculated by equating the diffusion flux with the reaction rate; there are about 4 x 10^{14} palladium atoms per cm^2 on a palldium surface.

$$\frac{(2x(3.27x10^{-2})\sqrt{P_{(dn)}})(4x10^{14})(1x10^{14})(3.1x10^{-10})}{(6.02 \times 10^{23})}$$

$$= (4.74x10^{-5} - 2.95\sqrt{P_{(dn)}})(7.18x10^{-6})$$

$$\sqrt{P_{(dn)}} = 1.51x10^{-5} \text{ torr}$$

$$P_{(dn)} = 2.28x10^{-10} \text{ torr}$$

This is seen to be fractionaly-lower than the $2.58x10^{-10}$ torr pressure on the upstream side. The diffusive flux is calculated to be $2.00x10^{-11}$ g-atoms/cm^2s.

4. The Separation of Tritium from Lithium-Lead Alloys

Of the liquid alloys of lithium and lead which are being considered for fusion reactor applications, the most attractive are those near the eutectic composition, $Li_{17}Pb_{83}$. At this composition, the breeding ratios are acceptably high (although lithium-6 enrichment may be needed) and, because of low lithium activities, the fire/explosion hazard is low. Furthermore, the low melting point is a considerable advantage for startup operation and for blanket purification.

The thermodynamic relationship between deuterium pressure and deuterium concentration in lithium-lead eutectic has been studied by Ihle et al. (37) by Valeckis (38), and by Buxbaum (39). While an Arrhenius type relationship does not hold well over the entire temperature range, the following equation is acceptable for temperatures between the melting point and about 650°C.

$$\ln K_D = -8.53 - 6050/T \qquad (8)$$

Here, K_D is the Sieverts constant, mole-fraction T/torr $^{1/2}$; and T is the temperature, Kelvin. In standard international units, mole fraction T/(pascal)$^{1/2}$, this becomes

$$\ln K_D^* = -10.98 - 6050/T \qquad (9)$$

If the isotope effect is nil, equations 8 and 9 would hold for tritium pressures and concentrations as well. At 450°C, the tritium pressure above a 0.8 wppb solution of tritium in lithium-lead eutectic will be 1.2×10^{-2} torr. This is almost eight orders of magnitude greater than the tritium pressure above a 0.8 wppb solution of tritium in lithium.

The rate of tritium flux through a zirconium-palladium window is calculated for cases of 1) No major liquid-phase mass-transfer resistance and 2) liquid-phase mass-transfer resistance alone. The second case is shown to dominate.

If diffusion in the liquid-phase is unimportant, then the flux calculations would be very similar to those for separation from liquid lithium. Since all the terms in that calculation were proportional to the square root of pressure, the flux from a lithium-lead solution would be

$$(2.00 \times 10^{-11} \text{ g-atoms/cm}^2 \text{ s}) \left(\frac{\sqrt{1.2 \times 10^{-2} \text{ torr}}}{\sqrt{2.58 \times 10^{-10} \text{ torr}}} \right) = 1.36 \times 10^{-7} \text{g atoms/cm}^2 \text{ s.}$$

The flux will now be calculated based on diffusion in the liquid alone. Lacking transport data for the lithium-lead alloys, these properties will be estimated from the properties of lead, and from the properties of liquid lithium where data are unavailable for lead. The visosity of lead is .0021 poise at 450°C and its density is 10.0 gm/cm^3; from this, the kinematic viscosity of lithium-lead is estimated to be 2.1×10^{-4} cm^2/s. The diffusivity of tritium in lithium at 450° is 6×10^{-5} cm^2/s (31), and since the viscosity of liquid lead is about 1/4 the viscosity of liquid lithium, the diffusivity of tritum in lithium-lead is estimated to be 2×10^{-4} cm^2/s. The Schmidt number of lithium-lead is thus about 1.05. The mass-transfer coefficient can now be estimated from a Nusselt number correlation for flow through a channel.

$$N_{Nu} = 0.023 \, N_{Re}^{0.8} N_{Sc}^{0.33} \tag{10}$$

$$N_{Nu} = k \, d/D \tag{11}$$

Here N_{Nu}, N_{Re}, and N_{Sc} are the Nusselt number, the Reynold's number, and the Schmidt number, respectively; d is the diameter of the channel, cm; D is the diffusivity, cm^2/s; and k is the mass transfer coefficient, $(mole/cm^2 s)/(mole/cm^3)$. If the effective diameter of the channel (between the tubes) is one inch and, if the superficial velocity of the alloy is 3 ft/s, (900 cm/s), the Nusselt number equals $1.7x10^3$, and k equals 0.13 cm/s. The flux rate is calcualted from

$$N_T = k \Delta C \qquad (12)$$

where

$$\Delta C = \frac{(0.8x10^{-9}\ g\ T/g\ alloy)\ (10\ g\ alloy/cm^3)}{(3\ g\ T/g\text{-}atom)}$$

$$= 2.7x10^{-9}\ g\text{-}atom/cm^3.$$

The flux rate is thus $3.5x10^{-10}$ g-atoms/cm^2s. This value is considerably lower than that calculated by assuming no mass transfer resistance in the liquid-phase; but it is considerably greater than the value for tritium separation from liquid lithium. It is verified that liquid-phase diffusion dominates the separation of tritium from lithium-lead eutectic, but is relatively unimportant for the separation of tritium from lithium metal.

A question which I have considered at this point is: Can the zirconium-palladium window be replaced by a stainless-steel window considering that liquid-diffusion dominates and considering how high the tritium pressure is. Calculations based on the most accurate data available for the transport of tritium in steel (40), argue convincingly that this could not be done.

5. The Cost of Zirconium-Palladium Windows for Use with Liquid Lithium and with Lithium-Lead Breeder-Blankets

A zirconium-palladium window for fusion reactor use is expected to resemble a shell and tube heat exchanger. Floating head design is probably advantageous in order to reduce stresses which would result from thermal gradients within the window. The design and construction of these exchangers (with zirconium tube) is a standard practice in the chemical industry.

At this point, there appear a variety of good reasons for coating the inside surfaces of the tubes with palladium rather than the outside surfaces. For one, the insides are protected from scratches. Also, flowing the breeder material through the outside shell should reduce pressure drops and should enhance turbulent transport. Finally, the cost of palladium is a substantial part of the total cost, and it is thought that electroless plateing on the inside of the tube would be a simple way to minimize palladium waste and process cost.

The window surface areas required for the separation of the entire tritium production of a 5000 MW fusion reactor (167 g-atoms per day) are calculated below from the tritium flux rate. For a liquid-lithium breeder-blanket the surface area is:

$$A = \frac{167 \text{ g-atoms T/day}}{(2.00\text{x}10^{-11} \text{ g-atoms T/cm}^2\text{s})(8.64\text{x}10^{4} \text{ s/day})}$$

$$= 9.66 \text{ x } 10^{7} \text{ cm}^{2}$$

$$= 1.04\text{x}10^{5} \text{ ft}^{2}.$$

The window area for use with liquid lithium-lead eutectic mixture is calculated similarly.

$$A = \frac{167 \text{ g-atoms T/day}}{(3.5\text{x}10^{-10} \text{ g-atoms T/cm}^2 \text{ s})(8.64\text{x}10^{4} \text{ s/day})}$$

$$= 5.5 \text{ x } 10^{6} \text{ cm}^{2}$$

$$= 5.9 \text{ x } 10^{3} \text{ ft}^{2}.$$

The standard method for estimating the costs for zirconium shells and tubes is to use charts and tables in the most recent edition of "Plant Design and Economics for Chemical Engineers" by Peters and Timmerhaus (41). A factor of 1.5 is added to correct these data for infaltion since 1979. For a window designed for operation with a liquid-lithium breeder-blanket, the

1983 price for the tubes and shell is estimated to be \$5,300,000; this price could be reduced by about 10% by using a stainless steel shell instead of zirconium. To the above must be added the price of palladium, 28,000 oz at \$120/oz (April 1983), and tritium hold-up, 32 g at \$20,000/g. The total cost for this window is estimated to be 9,300,000 which, while not cheap, is still below the cost of any other system which has so far been proposed. However, even if a cheaper system were designed, the advantages of continuous operation, simplicity of design, and minimum impurities, might cause permeation windows to remain attractive. It should be possible to reduce this price significantly by improvements in design.

Breeder-blankets which use liquid lithium-lead eutectic require a lower surface area window than those for liquid lithium use. Consequently, the window cost is lower: \$600,000 for the zirconium tubes and shell, \$170,000 for palladium, and \$300,000 for tritium holdup. The total cost, \$1,100,000, is well below the cost of any other tritium separation technique which is currently being considered for fusion reactor use.

PROBLEM AREAS FOR FUTURE RESEARCH

1. Back Permeation of Oxygen

Although analysis of this phenominon is far from complete, permeation of oxygen, from the argon-oxygen sweep-gas, through the palladium metal does not appear to be a major problem. The solubility of oxygen is palladium can be estimated from experimental data at 1200°C (23). The temperature dependence of solubility is calculated from the enthalpy of reaction via á standard approximation to the Gibbs-Duhem equation. The diffusivity of oxygen in palladium at 450°C is estimated to be $1x10^{-10}$ cm^2/s, and the flux of oxygen is estimated to be

$$(1x10^{-4}\ \text{g-atoms/cm}^3\text{-cm})(1x10^{-10}\ \text{cm}^2/\text{s}) = 1x10^{-14}\ \text{g-atoms/cm}^2\text{s}.$$

This flux rate would not cause any significant changes in the transport properties of a 1.5 mm zirconium tube during thirty years of operation at 450°C; however, it might affect tritium transport through the zirconium-palladium intermetallic zone.

2. Catalytic Reactions

For operation with a liquid-lithium breeder-blanket, the palladium cost is the largest component of the window cost, the palladium-calalyzed oxadation-reaction effectively determines the window surface area, and diffusion effects within the palladium determine the palladium thickness. A better catalyst choice, for example platinum, could reduce the total window cost by a factor of ten or more.

3. Corrosion

Corrosion presents a critical problem for this fusion reactor component, and for many other components which come into contact with the metallic breeder-fluid. Substantial quantities of metal can dissolve in the fluid at high temperatures and can precipitate at lower temperatures. This process has been reviewed by Stewart and Sze (42). For a reactor constructed of stainless steel, 2500 kg/yr of corrosion products (mostly nickel) are expected. While the main targets for this corrosion are manifolds and heat exchangers, the zirconium window could also participate--especially if it is not insulated. This problem is not as severe as it could have been because, as mentioned above, diffusion in the window does not limit the transport rate.

Non-metallic impurity elements within the breeder fluid present another corrosion problem for zirconium based permeation windows. For example, nitrogen impurities within a liquid-lithium breeder-blanket could react with the zirconium tube surfaces, reducing their structural strengh and permeability. Thermodynamic aspects of this problem are treated in references 43 and

39 for liquid lithium and lithium-lead respectivly. Rates and impurity levels for commercial fusion-power reactors are hard to estimate, especially since, as mentioned above, the zirconium tubes may be continuously coated with nickel precipitating from the breeder-fluid.

CONCLUSION

Zirconium based windows have been shown to be an attractive means for separating tritium from liquid lithium and from lithium-lead for fusion reactor use. It was shown that reaction at the palladium surface limited mass transport from a liquid lithium breeder-blanket, and that diffusion in the liquid phase limited transport from a lithium-lead breeder-blanket. Of the remaining problems, corrosion deserves special attention. Work is proceeding on this problem and on methods for reducing the cost per window.

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REFERENCES

1. E. F. Johnson, "Recovery of Tritium from Dilute Solutions of Lithium Tritide in Lithium," U.S. Atomic Energy Report NYO-6371 (1956).

2. A. P. Fraas, "A Diffusion Process for Removing Tritium from the Blanket of a Thermonuclear Reactor," Oak Ridge National Laboratory Report ORNL-TM-2358 (1968).

3. A. P. Fraas, "Comparison of Two Tritium Removal Systems Designed to Minimize Contamination of Steam Systems in Full-Scale Thermonuclear Power Plants," Oak Ridge National Laboratory Report ORNL-TM-2932 (1970).

4. S. D. Clinton and J. S. Watson, "Tritium Removal from Liquid Metals by Sorption on Yttrium," Proceedings of the 7th Symposium on Engineering Problems of Fusion Research (Institute of Electrical and Electronics Engineers, New York, 1977) IEEE Pub. No. 77CH1267-4-NPS, Vol. II, pp. 1647-1649.

5. J. S. Watson, "An Evaluation of the Methods for Recovering Tritium from the Blankets or Cooling Systems of Fusion Reactors," Oak Ridge National Laboratory Report ORNL-TM-3794 (1972).

6. E. F. Johnson, "The Chemical Engineering Side of Nuclear Fusion Power," AIChE Journal 23, 617 (1977).

7. J. Darvas, "Tritium Technology in Fusion Devices," Proceedings of the International Conference on Radiation Effects and Tritium Technology for Fusion Reactors, J. S. Watson and J. W. Wiffen, eds. (National Technical Information Service, Springfield, Virginia, 1976) Conf-750989, Vol. III, pp. 1-31.

8. A. P. Fraas, "Comparative Study of the More Promising Conditions of Blanket Materials, Power Conversion Systems, and Tritium Recovery and Containment Systems for Fusion Reactors," Oak Ridge National Laboratory Report ORNL-TM-4999 (1975).

9. Robert C. Weast, ed., "Hydrogen," CRC Handbook of Chemistry and Physics, CRC Press, 60th Ed., Boca Raton, Fla. (1980) pp. B11-12.

10. R. E. Buxbaum, "The Separation of Tritium from the Liquid Lithium Breeder-Blanket of a Fusion Reactor: The Use of Yttrium Metal as a Getter," Ph.D. Thesis Dissertation (Princeton University, Ch.E. Dept. October 1981).

11. P. Hubberstey, P. F. Adams, and R. J. Pulham, "Hydrogen Removal from Liquid Lithium; Use of Yttrium Sponge as Getter," Proceedings of the International Conference on Radiation Effects and Tritium Technology for Fusion Reactors, op. cit., pp. 270-288.

12. V. A. Maroni, R. D. Wolson, and G. E. Staahl, "Some Preliminary Considerations of a Molten Salt Extraction Process to Remove Tritium from Liquid Fusion Reactor Blankets," Nucl. Technol. 25, 83 (1976).

13. W. F. Calaway, "Electrochemical Extraction of Hydrogen from Molten LiF-LiCl-LiBr and Its Applications to Liquid-Lithium

Fusion Reactor Blanket Processing," Nucl. Technol. 39, 63 (1978).

14. J. R. Weston, W. F. Calaway, R. M. Yonco, J. B. Hines, and V. A. Maroni, "Chemical Processing of Liquid Lithium Fusion Reactor Blankets," Proceedings of the 14th IECEC, ACS Pub IBSN-8412-0513-2, pp. 1572-76 (1979).

15. J. L. Anderson, "Tritium Handling Requirements and Development for Fusion," Proc. IEEE., 69, pp. 1069-1080 (1981).

16. J. H. Devan, "Compatibility of Structural Materials with Fusion Reactor Coolant and Breeder Fluids," J. Nucl. Matter, 87, p. 249 (1979).

17. J. R. Weston, W. F. Calaway, and V. A. Maroni, "Liquid Lithium Processing Studies," Argonne National Laboratory Report ANL/FFP 79-3, pp. 81-82 (1980).

18. D. H. W. Carstens, "The Absorption of Deuterium by Binary Alloys of Lanthanum and Nickel," J. Less Comm. Met., 61, pp. 253-259 (1978).

19. D. H. W. Carstens, "The Absorption of Deuterium by Cerium--Containing Binary Alloys," J. Nucl. Mat., 73, pp. 50-57 (1978).

20. O. N. Salmon, cited in letter from J. F. Flagg to L. Tonks (March 4, 1954).

21. B. Badger, "UWMAK-III, A Noncircular Tokamak Power Reactor Design," The University of Wisconsin Fusion Feasibility Study Group, UWFDM-150, pp. VII-D-1 - VII-E-1, July 1976.

22. A. P. Fraas, "Comparative Study of the More Promising Conditions of Blanket Materials, Power Conversion Systems, and Tritium Recovery and Containment Systems for Fusion Reactors," ORNL-TM-4999, Oak Ridge National Laboratory (1975).

23. W. G. Moffatt, The Handbook of Binary Phase Diagrams (General Electric Company, Schenectady, NY, 1978).

24. C. Stokes and R. E. Buxbaum, "The Use of the Palladium-Catalyzed Water-Formation Reaction for the Removal of Hydrogen Isotopes from the Zirconium Structure of a CANDU Reactor" In Preparation.

25. A. Sawatzky and G. A. Ledoux, "The Use of Palladium to Remove Hydrogen from Zirconium," Hydrogen in Metals, Proceedings of the 2nd International Congress, Paris, France, June 6-10, 1977.

26. E. A. Gulbransen and K. F. Andres "Mechanism of the Reaction of Hydrogen with Zirconium: Role of Oxide Films, Pretreatments, and Occluded Gases" J. Electrochem. Soc., 101, pp. 348-353.

27. A. Zarchy, Limitations on Hydrogenic Gas Transport at Ultra Low Pressures, Ph.D. Dissertation (Princeton University, Ch.E. Dept., June 1978).

28. F. J. Smith, A. M. La Gamma de Bashstoni, G.M. Begun, and F. L. Land, "The Solubility of Hydrogen Isotopes in Lithium," Proceedings of the 9th Symposium on Fusion Technology (Pergamon Press, Oxford, England, 1976) pp. 325-328.

29. E. A. Gilbransen and K. F. Andres, "The Solubility and Decomposition Pressures of Hydrogen in Zirconium," Westinghouse Research Laboratory Sci. Paper 1818 (1954).

30. C. M. Schwartz and M. W. Mallett, "Observations on the Behavior of Hydrogen in Zirconium," Report AECD-3510 (1954).

31. R. E. Buxbaum and E. F. Johnson, "The Diffusivity of Hydrogen Isotopes in Liquid Lithium and in Solid Yttrium" PPPL-1960 (1982).

32. R. L. Beck and W. M. Mueller, "Zirconium Hydrides and Hofnium Hydrides" in Metal Hydrides by W. Mueller, J. Blackledge, and G. G. Libowitz, Academic Press, (1968) pp. 241-286.

33. T. Engel and H. Kuipers, "A Molecular Beam Investigation of the Reaction $H_2 + 1/2\ O_2 \rightarrow H_2O$ on Pd(111)," Surface Science 90 (1979) pp. 181-196.

34. Y.L. Lam, J. Criado, and M. Boudart, "Enhancement by Inactive Gold of the Rate of the $H_2 - O_2$ Reaction on Active Palladium: A Ligand Effect," Nouveau Journal de Chimie 1 (1977) pp. 461-466.

35. J. R. Young, "Palladium-Diaphram Hydrogen Pump," Rev. Sci. Inst. 34 (1963) pp. 374-377.

36. T. Engel and H. Kuipers, "A Molecular-Beam Investigation of the Scattering, Adsorption, and Absorption of H_2 and D_2 from/on in Pd(111)," Surface Science 90 (1979) pp. 162-180.

37. H. R. Ihle, A. Neubert, and C. H. Wu, "The Activity of Lithium and the Solubility of Deuterium in Lithium-Lead Alloys," Fusion Technology (1979), pp. 639-644.

38. E. Valekis, Private Communication, March 1983.

39. R. E. Buxbaum, "A Chemical-Theory Analysis of The Solution Thermodynamics of Oxygen, Nitrogen, and Hydrogen in Lead-Rich Lithium-Lead Mixtures," J. Less Common Met., accepted for publication.

40. E. H. VanDeventer and V.A. Maroni, "Hydrogen Permeation Characteristics of Some Austinitic and Nickel-Base Alloys," J. Nucl. Mat. 92 (1980) pp. 103-111.

41. M. S. Peters and K. D. Timmerhaus, Chap. 14, "Heat Transfer Equipment-Design and Costs" in Plant Design and Economics for Chemical Engineers, third edition, McGraw Hill (1980) pp. 632-711.

42. W. E. Stewart and D. K. Sze, "Transport Problems in Lithium Cooling of Tokamak Reactors" AICHE Symp. Series., 128, (1977) pp. 56-62.

43. K. Natesian and D. L. Smith, "Influence of Nonmetallic Impurity Elements on the Compatability of Liquid Lithium with Potential CTR Containment Materials," Nucl. Tech., 22, (1974) pp. 392-404.