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SOME PROBLEMS ASSOCIATED WITH TRITIUM IN FUSION REACTORS

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SOME PROBLEMS ASSOCIATED WITH TRITIUM IN FUSION REACTORS^{*}

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ABSTRACT. A number of problems associated with the use of tritium in fusion reactors are yet to be considered. Some are peculiar to mirror machines and attempts at direct conversion of plasma energy to electricity, while others are of general concern. Several of these are considered from the point of view of one who has worked with tritium for several years. Specific areas mentioned include liquid-phase mass transfer of tritium in liquid lithium, isotopic separation, preliminary calculations on permeation barriers, isotopic swamping, and some thoughts on maintenance.

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1. INTRODUCTION

In the past three or four years, several papers have been presented on those aspects of the fusion reactor program which involve tritium. They generally have dealt with recovery schemes, inventories, and estimates of releases to the environment. In this presentation, some of these problems are considered, and some additional factors which will require very extensive study are mentioned.

2. MAINTENANCE

Everyone who has estimated environmental impact from fusion reactors has been concerned with releases during on-line operating conditions. The principal release mechanisms are permeation through high-temperature metal walls, mechanical leaks at shaft seals, and residual tritium in final effluent streams.

The problem of maintenance on tritium-contaminated equipment deserves some mention. This problem has not been previously considered, and some may feel it is premature to begin thinking about such matters. In fact, it is only in the last two years that maintenance on the Liquid Metal Fast Breeder Reactor (LMFBR) has received any serious consideration[1]. Remote maintenance operations on all the contaminated components in a fusion power plant will prove to be prohibitively expensive. Unlike a fission plant (LMFBR) where the radioactivity is restricted to the fuel, reactor vessel and coolant, a fusion reactor will have more widely spread tritium contamination. Furthermore, the tritium will have a much greater tendency to become airborne.

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Tritium-contaminated metals very often cannot be decontaminated well enough to allow their being shipped to commercial vendors for service. Contaminated equipment which is likely to deteriorate and require repair should, if possible, be cheap enough so it can be scrapped for safe burial, thus partially avoiding the maintenance problem.

In our tritium-handling building at LLL, we have a low level tritium background which is from inevitable small leaks, permeation and the like. This is the result of over ten years of operation in which fairly large (at least by most standards) inventories have been handled and stored. The actual inventories and release rates have been deliberately omitted because these are still classified figures. Most of our releases to the environment, however, result not from the background, but rather from operations which one could generally describe as maintenance. Such operations as changing pump oil, opening vacuum lines to the atmosphere, and decontaminating equipment so it can be repaired are responsible for most of our releases. These are tabulated on a percentage basis in Table I. The two years shown reflect a slight difference in research projects and the result of a successful effort to decrease our total releases by 90%. Other installations will show a different profile because their functions and operating procedures are not the same as ours. The fact remains that required maintenance operations may produce the largest releases from a fusion power plant, particularly when one considers the size of the equipment that will have to be exposed to air. Many releases associated with maintenance cannot generally be contained without endangering the maintenance workers, even though they may be wearing plastic suits with piped-in fresh air. It behooves us,

therefore, in our conceptual designs to restrict the spread of tritium to an absolute minimum, and to be aware of maintenance-associated problems when judging environmental impact of fusion reactors.

3. ISOTOPIC SEPARATION

In all proposed fusion reactor fuel cycles, a small fraction of the burned deuterium can be expected to react to form protium and tritium. Outgassing of metal components after startup will also add some protium to the fuel stream. It will not be possible to allow this inert isotope to accumulate indefinitely, and it is unlikely that replacement of the fuel will be economically attractive. This surely will be the case for a D-T reactor. The alternative is to provide an isotopic separation process, probably as an integral part of the power plant. The required capacity of the process equipment is not expected to exceed several grams of protium per day, which is within the scope of present technology.

On the other hand, some reactors would use neutral beam injection to establish and maintain the plasma. It has been suggested by workers at the Culham Laboratory that neutral beams might be used to start toroidal reactors[2]. For open-ended systems, which receive emphasis at LLL, continuous operation of neutral beam injectors is required. Control of the ion beams may require the use of magnetic optics, which in turn would require a preliminary isotopic separation.

In addition, neutralization efficiencies of positively charged ions are known to be rather low at the injection energies (several hundred keV) required for reactors. On the other hand, it is expected that D^+ ion beams may be converted to a neutral beam with fairly good

efficiency, as shown in Fig. 1. Unfortunately, existing ion sources do not produce an abundance of negatively charged ions. To solve this problem, Osher [3] has suggested that a series of Cs vapor cells be placed between the source and accelerator, converting the positively charged ion beam to a negatively charged one. At present this seems to be a viable approach, but it does have one minor drawback. The efficiency of charge exchange is a strongly peaked function of ion velocity. A mixed beam of T^+ and D^+ being extracted from a source will have the same energy but different velocities, so only one of the ions can be made to undergo charge exchange in a given cell. The implication is obvious. Tritium and deuterium must be injected separately, and this requires an isotopic separation process.

For a large mirror fusion reactor, the injection rate of fuel is expected to be about 2 kg/hr. Because of efficiencies less than 100% for several components, circulation rates within the injection system may be several times this high. Developing processes to produce deuterium and tritium at these rates would be a very challenging task. Although the tritium inventory required in a plant of sufficient capacity to supply these isotopes at the anticipated injection rates has not been estimated, it would be large.

At our Savannah River plant, Li is bombarded with neutrons to form tritium and helium which are extracted and separated. The tritium is contaminated with deuterium, so an isotopic separation is performed. Processes used for the isotopic separation include cryogenic distillation, thermal diffusion, and chromatographic columns. This separation plant was designed to complement fission-reactor, tritium production technology. The cost of building this plant was 100 million dollars.

Alternate approaches should be considered. Because we are already committed to developing ion sources and beam optics to handle very large and intense beams, a possible extension of this new technology might be in the area of electromagnetic separation. This is not a new concept, but its use has previously been restricted to beams of a few milliamperes because of space charge effects[4].

There are some interesting points in favor of electromagnetic separation. If resolution is good, complete separation is possible in a single "stage." This is particularly attractive when one tries to remove a small contaminant from the main stream (such as H from D-T). The equipment which becomes contaminated with tritium can be very simple, i.e., a big stainless steel box under vacuum. The magnet is outside the box, and we are already committed to providing the ion source and enormous vacuum pumping capacity. Additionally, the tritium inventory is negligible compared to other traditional schemes for isotopic separation. Power requirements for the magnet would be low because of the modest field required.

In practice, the magnetic sector has proven to be as good or better than the other electromagnetic devices, and an advanced technology for performing isotopic separations of the heavier elements has been developed with this technique. Everything else being equal, separating the light isotopes is easier than separating the heavy ones by this approach.

A possible arrangement is shown in Fig. 2. As the 10-cm-wide beam leaves the source, it is bent such that the 1, 2, 3 and 4-6 mass beams may be handled separately. Mass 1 beam is H^+ , and it is

titanium-pumped for eventual burial as radioactive waste. Beam 2 is D^+ , which is sent directly to the Cs vapor charge-exchange cells. Beyond that it goes through the d.c. accelerator, the low-temperature plasma neutralizer, and then into the reactor. Beam 3 is T^+ and HD^+ . Only a trace of HD^+ is present, and it will be recycled after the charge-exchange cell because it will be permanently neutralized before acceleration. After separation the T^+ ions are boosted to the optimum velocity for efficient charge exchange, and beyond that they follow a process identical to that for D^+ . Beams 4-6 contain the diatomic ions D_2^+ , HT^+ (trace), DT^+ and T_2^+ , none of which can be handled efficiently so they are recycled. Each of the components operates at less than 100% efficiency, so each has its own recycle stream. A range of efficiencies, depending on the state of the art when it is built, might be realized, but typical values might be as follows[5]: source, 30% (70% of the gas injected is not ionized); and again source, 80% (20% of the ions produced which account for about a third of the mass are diatomic and must be recycled); charge-exchange cell series, 60%; accelerator, 99.5%; and neutralizers, 85%.

The beam exiting from the source is so broad that a wide separation of adjacent mass peaks is required to resolve them. Let the largest radius of travel be 1 m. One then inquires about the spacing of the other beams. These are calculated from the following equation which assumes such parameters as the absence of external electric fields, perfect homogeneity of the B field, uniform direction and velocity through the cross section of the ion beam as it leaves the source, no collisions with residual gas and no space charge effects[6]:

$$\frac{Vm_i}{e_i} = \frac{r_i^2 B^2}{2} \quad (1)$$

This shows the radii of curvature to be proportional to the square root of the ion mass, provided they all have the same energy V and the same ionic charge e_i . The value of V is fixed at 1500 V because this is the optimum for deuteron charge exchange. For $m=6$ which is the heaviest ion, r is chosen to be a convenient 100 cm. For these circumstances, a magnetic field strength of around 90 G is all that is required to bend the beam. Such a magnet should be very cheap, even if it is quite large. The separation between adjacent peaks at the exit of the magnet are shown in Table II. As may be seen, the spacings expected on this basis are larger than the beam width, so it looks favorable.

Now let us consider the problem of space charge. This is a very serious problem indeed. One can make an approximate calculation on how much the beam will diverge in a 3-m traverse, given an initial energy of 1500 eV. Consider a 10-A beam of circular cross section with a diameter of 10 cm. Using classical theory, assuming uniformity of the beam and field free space, and neglecting the mutual inductance the beam has on itself which is said to be negligible[7], one can obtain the approximate expression:

$$2.09 \left(\frac{r}{r_m} - 1 \right)^{1/2} \approx \frac{t}{r} \left(\frac{eI}{\pi E_0 m^2} \right) \quad (2)$$

where

r = radius of the beam at time t ,

r_m = radius leaving the source, its minimum value,

t^* = time elapsed since leaving the position of r_m ,

e = charge of the particle,

I = beam current,

E_0 = permittivity of free space,

m = mass of the particle, and

z_0 = initial axial velocity, obtained from $eV = 1/2 m z_0^2$

where V is accelerating potential.

Inserting appropriate numerical values,

$$z_0 = 9.3 \times 10^4 \text{ m/sec,}$$

$$t^* = 3.21 \times 10^{-5} \text{ sec, and}$$

$$r = 12.9 \text{ m.}$$

That is to say, the original beam of 0.10-m cross section diverged to the extent that it would fill the entire chamber between the pole faces of the magnet. Whether it will be possible to overcome this problem is yet to be seen. We are, however, committed to the goal of greatly improving our ability to produce and manipulate very large and intense ion beams for use in neutral injection.

Another approach we might consider makes use of electrostatic deflection rather than magnetic. The sharply peaked velocity dependence of charge-exchange efficiency could form the basis for the required separation, as shown in Fig. 3. Two schematic diagrams of how this might be used are given in Fig. 4. In Fig. 4(a), the recycled stream from the reactor is split in half and fed directly to two beam

machines. The recycle stream from each beam is enriched in the other species so it is fed to the source of the other beam. In Fig. 4(b), the two beam machines are in series. A small accelerator is placed between Cs cell trains to boost the velocity of the tritons to their optimum charge-change velocity. One ion source is eliminated, but the one that remains must be of higher capacity. The beam length is larger so optics and spatial arrangement around the reactor may be a greater problem. Neither arrangement provides for the removal of protium, but this could be done separately using conventional techniques or this proposed technique. This second approach has the following advantages:

1. No additional equipment (cost),
2. No additional spread of radioactivity,
3. Minimum power cost,
4. No additional tritium inventory, and
5. No additional radioactive maintenance.

4. PERMEATION BARRIERS

Design and use of CTR reactors will be made more difficult because of the unavoidable contamination of major portions of the system by tritium. Widespread though this contamination will be, it will still be desirable to not contaminate the entire plant. Because high-temperature contaminated fluids (breeder-coolants, fuel) must be handled, there will be a pronounced tendency for tritium to permeate through hot walls and extend the contamination to other parts of the system.

It should be noted, however, that some materials are far more permeable to tritium than others. At temperatures in the range of 1000°K , it should

be possible to virtually stop tritium permeation by suitable choices of materials and development of technologies to take advantage of the properties of these materials. Coatings of relatively impermeable materials on metal surfaces or sandwiched between metals could be used. Oxides might be successfully used for the barrier materials.

While thousands of papers have been published regarding hydrogen solubility, diffusion and permeation through metals, only a handful are available on inorganic nonmetallic substances. Of those available some deal with hydrated salts, and the remainder are mostly on oxides. Little or nothing is published on other large classes of compounds such as nitrides, carbides and halides. Of the papers available on the oxides, all but one restrict their attention to diffusion coefficients of hydrogen in the host lattice, with no attention being paid to either the temperature or pressure dependence of solubility or overall permeability.

In Fig. 5, the results available on hydrogen diffusion in oxides are presented[8]-[13]. From measurements of the changes of the spectroscopic and electronic properties of the solids, it is established that the hydrogen dissolves in the atomic form, forming hydrogen bonds with the oxygen. The solubility should therefore be dependent on the square root of pressure, just as it does for metals. In the one case where solubility has been carefully measured (ZnO), it shows the square-root dependence.

As will be seen in Fig. 6 the reported solubility of H_2 in ZnO has been plotted, and the calculation of permeability has been performed. It is less permeable than austenitic stainless steel[14], but more permeable than tungsten at very high temperatures[15]. From Fig. 5, it is immediately apparent that ZnO is far from the most effective barrier material to employ. A more appropriate choice would be alumina. Beryllia seems to be even better, but it would have to be given mechanical protection to prevent abrasion and dusting because of its toxicity.

The solubility of hydrogen in alumina is probably less than in ZnO, based on the known solubility mode in these two materials combined with our knowledge of the oxygen-metal diatomic bond strengths. The Al-O bond is substantially stronger than the Zn-O bond, but the H-O is stronger than Zn-O so the ZnO is more likely to be a receptive host than alumina. One reaches the same general conclusion upon considering the heats of formation of the crystalline oxides and their respective hydroxides. Examination of the free energy of the systems at the temperature of use would be the most definitive approach, but the prevailing gas pressures for various applications have not been defined. Assuming a somewhat lower value of solubility of H_2 in Al_2O_3 than in ZnO and diffusion coefficients intermediate between those previously reported[11][12], I have estimated the permeability of alumina as shown in Fig. 6.

At $1000^\circ K$, the estimated permeability is 2.5×10^{-7} times less than that of stainless steel. If a 1-mm-thick wall of stainless steel were used, the permeation rate could then be reduced by 10^3 by applying a 10- μ m. layer of alumina. However, the technology for application of sufficiently dense and adherent coatings of these oxides needs to be developed. Permeation barriers developed by other workers have not been this successful[16].

Differences in thermal expansion coefficient between oxides and metals may cause cracking or spalling of the oxide during heat-up and cool-down, but one could probably arrange to minimize or even eliminate the tensile stress in the oxide by controlling the substrate temperature during deposition.

5. PERMEATION THROUGH TRITIUM WINDOWS

The Present Permeation Equation

Preliminary design studies have already been made for some processing equipment for extracting tritium from molten lithium breeder blankets. This equipment relies upon the fact that hydrogen isotopes dissolve and diffuse in niobium very readily, but I believe the permeation equation currently being used is subject to question. It may be faulted on two counts. The form may be incorrect because it assumes a diffusion-limited flow when in fact a surface process may very well determine the permeation rate. This is fairly general behavior when diffusion is rapid and pressures are low. This aspect of the problem is the more difficult, and will be dealt with later. The second defect is that the numerical constants in the equation are probably wrong. It is this that will be considered first.

The present equation is taken from a report by Webb[17]:

$$P = K_H \exp(-E_H/RT), \quad (3)$$

where

$$P = \text{permeability (stdcc-cm)/(hr-cm}^2\text{-atm}^{1/2}\text{)},$$

$$K_H = 1040 \text{ with units of } P,$$

$$E_H = 3.43 \text{ kcal/mole.}$$

The permeation flux of molecular hydrogen is obtained by multiplying the permeability and driving force, $(p_1^{1/2} - p_2^{1/2})/t$, where p is partial pressure of hydrogen, t is wall thickness, and the subscripts refer to the two gas-metal interfaces. The graphical representation of this equation[17]

is shown as Fig. 7. Even the most casual observer will note that there is something a little peculiar about the behavior of Nb. The discontinuous change in slope at about 950°F is unexpected. Furthermore, in the right-hand portion of the curve the continuously changing slope varies in an almost incomprehensible fashion, with a stronger temperature dependence being shown at high temperatures than at low ones.

These are the only permeability data for H in Nb that I have found. An alternate route to permeability is available, however, and this consists of combining data on solubility constant S and diffusion coefficient D . Then $P = SD$, and this equation is strictly valid so long as the activity coefficient of the migrating species is unity and the diffusion coefficient is independent of composition. Solubility constants are available, and several investigators show good agreement with one another. These papers have been summarized[18] and can be represented by the equation of Edwards and Veleckis

$$\ln \left(p_{\text{mm}}^{1/2} \right) = 10.212 + 0.984 \ln \left(\frac{r}{0.89-r} \right) + \frac{1}{T} (-4244.7 - 4000.4 r + \dots) \quad (4)$$

where r is the H/Nb atomic ratio. When r is very small, this reduces approximately to

$$S = 1.13 \exp \left(\frac{4244.7}{T} \right) \frac{\text{stdcc}}{\text{cm}^3 \text{-atm}^{1/2}} \quad (5)$$

after changing units.

Diffusion coefficients have been measured by a number of different techniques, and the variation between investigators is greater. Albrecht et al. [19] found

$$D = 0.0215 \exp (-9370 \pm 600/RT) \text{ cm}^2/\text{sec}, \quad (6)$$

using a classical transient absorption approach. Their desorption results were anomalously low. This activation energy was roughly corroborated by Wilcox [20]. Other authors, using Gorsky-effect measurements where no surface processes are involved, find values of

$$D = 5.4 \times 10^{-4} \exp \left(\frac{-2510}{RT} \right) \text{ cm}^2/\text{sec}, \quad (\text{Cantelli}[21]) \quad (7)$$

$$D = 5.4 \times 10^{-4} \exp \frac{-2540}{RT} \text{ cm}^2/\text{sec}, \quad (\text{Schaumann}[22]) \quad (8)$$

$$D = 5.0 \times 10^{-4} \exp \frac{-2440}{RT} \text{ cm}^2/\text{sec}, \quad (\text{Schaumann}[23]) \quad (9)$$

$$D = 1.2 \times 10^{-3} \exp \left(\frac{-2710}{RT} \right) \text{ cm}^2/\text{sec}, \quad (\text{Doremus}[24]) \quad (10)$$

Doremus refit the earlier data to a new model. During the restructuring of a metastable phase of Nb-H, Samsonov [25] found an activation energy of 3400 cal/mole, and Gissler [26], using neutron scattering, finds

$$D = 4.06 \times 10^{-4} \exp \frac{-2360}{RT} . \quad (11)$$

The nuclear magnetic resonance studies of Zamir [27] yield an activation energy of 3700 cal/g-atom. These latter measurements have been made from below room temperature up to about 500°C.

On the basis of all these measurements, we can guess that in the work of Albrecht, a surface process interfered with the measurements (slow surface processes tend to increase the observed activation energy) and the correct expression for D might be

$$D = 1 \times 10^{-3} \exp \left(\frac{-3000}{RT} \right) \text{ cm}^2/\text{sec.} \quad (12)$$

Combining this with Eq. (5), we find

$$P = DS = 1 \times 10^{-3} \exp \left(-\frac{3000}{RT} \right) 1.13 \exp \left(\frac{4244.7}{RT} \right) \frac{\text{cm}^2}{\text{sec}} \times (\text{stdcc}/\text{cm}^3 \cdot \text{atm}^{1/2}) \quad (13)$$

$$P = 1.13 \times 10^{-3} \exp \left(\frac{5404}{RT} \right) \frac{\text{stdcc}/\text{cm}^2 \cdot \text{sec}}{\text{atm}^{1/2}/\text{cm}}, \quad (14)$$

which brings one to a rather startling conclusion. For a diffusion-limited permeation process, the permeability is predicted to decrease with increasing temperature because the gain in diffusion coefficient is more than offset by the decrease in solubility.

Isotopic Swamping - Diffusion Limited Flow

The idea of using isotopic swamping to remove the maximum of a particular isotope from a very dilute stream by adding an excess of another isotope of the same element before the extraction process is not new. In some instances this approach is very attractive because the extraction process may be performed in a single equilibrium step and the

need for a cascaded process may be eliminated. It becomes particularly appealing when the two mixed isotopes need not be separated after the extraction process is completed (not the case in CTR). The application I had hoped this approach would fill was the removal of tritium from a molten Li stream which would be functioning as both a reactor coolant and tritium breeding blanket.

It would consist of two steps. In the first, protium would be injected through a small window using a fairly high gas pressure. In the second step, the protium and tritium would be extracted by simultaneous permeation through a large window.

For the injection step, the permeation rate equation is

$$R_H = \frac{A}{t} K_H \exp(-E_H/RT) \left(p_{H_1}^{1/2} - p_{H_2}^{1/2} \right) \quad (15)$$

where

R_H = permeation rate for hydrogen

A = equivalent wall area = $2\pi mL(r_2 - r_1)/\ln(r_2/r_1)$,

t = wall thickness = 0.05 cm,

p_{H_1} = molecular hydrogen pressure outside the tubes,

p_{H_2} = molecular hydrogen pressure inside the tubes,

K_H = permeation constant for Nb = $1,040 \frac{\text{stdcc/cm}^2 \text{ sec}}{\text{atm}^{1/2} \text{ mm}}$,

E_H = 3.43 kcal/mole,

T = 1100°K.

Simple calculations using Eq. (15) showed that the injection of protium is easily done in a tube bundle 1 m^3 in volume if a small side stream is treated.

For the extractor window, it is known that the hydrogen and tritium permeation rates are not independent. This results from the fact that both isotopes interact with the electrons of the metal in much the same fashion[28]. The rates of permeation of the two isotopes are given by[29]:

$$R_H = \frac{A}{t} K_H \exp(-E_H/RT) \left(X_{H_1} (p_H + p_T)_1^{1/2} - X_{H_2} (p_H + p_T)_2^{1/2} \right),$$

$$R_T = \frac{A}{t} K_T \exp(-E_T/RT) \left(X_{T_1} (p_H + p_T)_1^{1/2} - X_{T_2} (p_H + p_T)_2^{1/2} \right),$$
(16)

where X refers to mole fractions and p in the liquid metal refers to the equivalent vapor pressure of the hydrogen isotopes over the Li. Thus,

$X_H = p_H/(p_H + p_T)$ and $X_T = p_T/(p_H + p_T)$ and since $p_H \gg p_T$, $p_H + p_T \approx p_H$ Eq. (16) can be written

$$R_H = \frac{A}{t} K_H \exp(-E_H/RT) \left(p_{H_1}^{1/2} - p_{H_2}^{1/2} \right),$$

$$R_T = \frac{A}{t} K_T \exp(-E_T/RT) \left[\left(p_T/p_H^{1/2} \right)_1 - \left(p_T/p_H^{1/2} \right)_2 \right].$$
(17)

In Eq. (17), it is seen that the rate of permeation of hydrogen is unaffected (almost) by the presence of the tritium. On the other hand, the permeation of tritium is strongly affected. In the pure component case (if pressures on the vacuum side are neglected), its permeation is proportional to $p_T^{1/2}$, whereas in the mixed isotope case it is proportional to $p_T/p_H^{1/2}$.

Consider a numerical example. Suppose on the Li side of the window we could maintain tritium at a partial pressure of 10^{-5} torr by permeating to the vacuum side at 10^{-6} torr. Then

$$R_T \approx (10^{-5})^{1/2} - (10^{-6})^{1/2} = 2.1 \times 10^{-3}. \quad (18)$$

In the swamped case, we add a 100-fold excess of protium pressure on the Li side, but assume we could maintain the same total pressure on the vacuum side. Then $p_{T_1} = 10^{-5}$, $p_{H_1} = 10^{-3}$, and $p_{T_2} = 10^{-8}$ and $p_{H_2} = 10^{-6}$, so

$$R_T \approx \frac{10^{-5}}{(10^{-3})^{1/2}} - \frac{10^{-8}}{(10^{-6})^{1/2}} = 0.3 \times 10^{-3}. \quad (19)$$

We have succeeded in reducing to a negligible level the partial pressure of tritium on the vacuum side, but the tritium permeation has also been cut because of the nature of the interaction of the hydrogen with the metal.

Isotopic Swamping — Surface Limited Flow

If the permeation process is limited by a slow surface process such as atomic recombination to form molecular gas, a different rate dependence on pressure is found. The tritium removal rate by recombination is probably described by [30]

$$R_T = k_r \theta_T^2 \quad (20)$$

for the pure component case and

$$R_T = \frac{1}{2} k_r \theta_H \theta_T \quad (21)$$

for the isotopically swamped case. Isotopic dependence on k_r has been ignored, and θ refers to the fractional surface coverage of the hydrogen species.

Neglecting bulk diffusive effects, these rates can be related to the partial pressures contacting the surface. Since high surface coverages are obviously preferred, the Langmuir isotherm is selected. For the pure component case, we have

$$\theta_T = \frac{[(k_a/k_r)p]^{1/2}}{1 + [(k_a/k_r)p]^{1/2}} \quad (22)$$

where k_a and k_r are rate constants for adsorption and recombination, and p is tritium pressure. Then

$$\text{Rate} = k_r \theta_T^2 = k_r \left\{ \frac{[(k_a/k_r)]^{1/2}}{1 + [(k_a/k_r)p]^{1/2}} \right\}^2 \quad (23)$$

At low pressures this reduces to a linear dependence of rate on pressure, and at high pressures (high surface coverage),

$$\text{Rate} = k_r. \quad (24)$$

In the swamped case, the rate is given by

$$\text{Rate} = \frac{1}{2} k_r \theta_H \theta_T = \frac{1}{2} \frac{k_a p_{HT}}{\left\{ 1 + [(k_a/k_r)p_H]^{1/2} \right\}^2} \quad (25)$$

If we assume θ_H is much larger than θ_T . Details of this calculation are given in the appendix. At high hydrogen pressures, this reduces to

$$\text{Rate} = \frac{k_r}{2} \frac{p_{HT}}{p_H} \quad (26)$$

which always gives a rate less than that for the pure component case under conditions of the same total pressure. Therefore, isotopic swamping is expected to decrease tritium recovery efficiencies regardless of the dominant permeation process.

LIQUID PHASE MASS TRANSFER RATE IN TRITIUM EXTRACTION FROM LITHIUM BLANKETS FOR CTR

One of the major tritium inventory problems in the development of CTR involves the Li-containing blanket used for breeding tritium and the method used to remove this tritium. The process used to remove the tritium is of central importance because an efficient process will keep the total inventory lower. Development of a suitable process may be difficult.

Certainly one of the most innovative schemes proposed to date is the one by Werner[31] which involves using heat pipes to perform the dual functions of spreading the heat load through the depth of the blanket and removing the tritium by a two-step permeation process, as shown in Fig. 8. It is my purpose to examine the possibility of liquid-phase mass transfer limitation for this proposal, and to suggest some basic experiments and calculations which should be done in support of it. In some nuclear reactor discussions, mass transfer refers to corrosion problems in a closed loop where material is dissolved at one location at high temperature

and precipitated from solution at another location at a lower temperature. However, mass transfer in the present context refers to material transport by mechanisms quite analogous to convective heat transfer. Werner proposed that Li be used as coolant and breeder. The Li was pumped through the blanket in slightly flattened tubes, as shown in Fig. 9.

Normally, with liquid flowing at such high velocity in a tube, a fully developed turbulent velocity profile exists with the attendant contribution of eddy diffusivity to the overall mass transfer process in the liquid phase. With the imposition of strong magnetic fields, however, the flow in liquid metals remains laminar, so the assumption that there is negligible resistance to the transfer of tritium to the Nb tube wall may be too optimistic. Because of the very high thermal conductivity of liquid Li, this same limitation is not expected to seriously hinder the concurrent heat transfer process[32].

The calculations which follow have several limitations, and these will be noted. One of the physical properties required to do even simple calculations is the value of the diffusion coefficient of tritium in Li as a function of temperature when the tritium is present at low concentration. These data are not available. Therefore, only a very gross calculation is justified. First assume that the tubes through which the Li flows are not flattened. In the real case, heat and mass transfer do not occur through the flattened surfaces because they butt against each other. By assuming the tubes to be circular in cross section with uniform flux in the radial direction, it is more legitimate to use the existing mass transfer correlations. The alternative is to numerically solve the coupled equations of motion and mass transfer in three dimensions with discontinuous boundary conditions around the

perimeter of the tube. This is a calculation which should be performed if this method is ever considered very seriously. Then we neglect the resistance to diffusion that the Nb tube wall presents, and assume the tube wall acts as a perfect sink for all the tritium which reaches it. Put another way, we assume a homogenous boundary condition around the perimeter and down the length of the tube. After further assuming that the velocity profile is fully developed before entering the heat transfer zone in the blanket and that the temperature gradients which exist in the Li do not seriously change the physical properties, we can proceed with the calculations.

We address the question: What is the concentration of tritium in the bulk that will deliver a sufficient flow of tritium to the Nb to just equal the breeding rate? The required data on the reactor parameters are taken from Ref. [1] and are tabulated in Table III.

Viscosity μ , density ρ and heat capacity C_p of Li at 1100°K are taken from the report of Cowles and Pasternak[33] and are found to be 0.21×10^{-2} g/cm-sec, 0.451 g/cm^3 , and $1.0 \text{ cal/g}^\circ\text{K}$ respectively. The inside diameter, d , of the tube in which the Li flows is 1.8 cm. To calculate the Li average velocity v , it is necessary to know the desired average temperature rise, ΔT , as it passes through the blanket. The usual assumption is 200°K. The velocity is calculated as follows:

$$v = \frac{Q}{A \rho C_p \Delta T} \quad (27)$$

$$v = \frac{0.2866 \times 10^{10} \text{ cal/sec}}{8 \times 10^4 \text{ cm}^2 \cdot 0.451 \frac{\text{g}}{\text{cm}^3} \cdot 1.0 \frac{\text{cal}}{\text{g}^\circ\text{K}} \cdot 200^\circ\text{K}}$$

$$= 3.97 \times 10^2 \frac{\text{cm}}{\text{sec}}. \quad (28)$$

The Reynolds number, $Re = dvp/\mu$, is calculated to be 1.54×10^5 which normally would induce full turbulence, but because of the magnetic field does not. Now it is required that the mass transfer Graetz number, $Gz = ReSc \, d/L$, be calculated, where $Sc = \mu/\rho D$ is the Schmidt number and D is the diffusion coefficient of tritium in the Li. The value of D is not known, nor is there a reliable way to calculate it. Experimental values have been obtained for hydrogen dissolved in molten Al, Fe, Ni, Cu, and Ag in the desired temperature range. None of these metals form a stable hydride, so they are not likely to give reliable insight into the behavior of Li. Nevertheless, a value must be chosen to complete the calculation, so let it be $6.75 \times 10^{-4} \text{ cm}^2/\text{sec}$ at 1100°K , which is the value for hydrogen in Fe.

Schmidt and Graetz numbers may now be calculated directly:

$$Sc = \frac{\mu}{\rho D} = \frac{0.21 \times 10^{-2} \text{ g/cm-sec}}{0.451 \frac{\text{g}}{\text{cm}^3} \cdot 6.75 \times 10^{-4} \text{ cm}^2/\text{sec}} = 6.9, \quad (29)$$

$$Gz = Re \, Sc \, \frac{d}{L} = (1.54 \times 10^5) (6.9) \frac{1.8}{1000} = 1.94 \times 10^3. \quad (30)$$

The mass transfer situation is best described by the Leveque approximation, and from Fig. 10[34], one obtains a mass transfer Nusselt number of about 22.5. The mass transfer Nusselt number is defined as $Nu' = Kd/D$

where K is the average mass transfer coefficient for the entire length of tubing. Note that it is legitimate to invoke the heat-mass transfer analogy due to the low interfacial velocity which does not perturb the velocity field.

Knowledge of the Nusselt number permits the calculation of the bulk concentration of tritium,

$$Nu' = \frac{Kd}{D} = 22.5 \quad (31)$$

$$K = \frac{22.5 (6.75 \times 10^{-4}) \text{ cm}^2/\text{sec}}{1.8 \text{ cm}} = 0.85 \times 10^{-2} \text{ cm/sec.} \quad (32)$$

Then finally,

$$\begin{aligned} \text{Total flow} &= OP(BR) \\ &= 12,000 \text{ MW} \left(1.70 \times 10^{-6} \frac{\text{gT}}{\text{MW-sec}} \right) \\ &= 20.4 \times 10^{-3} \text{ g/sec,} \end{aligned}$$

and total flow also equals $A'K (C_b - C_i)$ where C_b = the bulk concentration and C_i = the interface concentration which is assumed to be zero. Equating the flows gives

$$20.4 \times 10^{-3} \text{ g/sec} = A'K C_b, \quad (33)$$

or

$$\begin{aligned} C_b &= \frac{20.4 \times 10^{-3} \text{ g/sec}}{4 \times 10^7 \text{ cm}^2 (0.85 \times 10^{-2} \text{ cm/sec})} \\ &= 0.06 \times 10^{-6} \text{ g/cm}^3. \end{aligned} \quad (34)$$

Converting to parts per million by weight,

$$\frac{0.06 \times 10^{-6} \text{ gT/cm}^3}{0.451 \text{ gLi/cm}^3} = 0.13 \text{ ppm.} \quad (35)$$

This number is encouragingly low, indicating mass transfer in the magnetic field will not have a significant impact on the tritium inventory. The steady-state concentration of tritium in the blanket is indeed dominated by the permeation rate through the Nb tube wall if the assumption of a value for the diffusion coefficient is correct. With slightly different assumptions, similar conclusions for turbulent flow conditions have been reached[35]. Noting in Fig. 9 that the slope of the line is about 1/3, one can manipulate the various parameters used here and show that

$$C_b = aD^{-2/3}, \quad (36)$$

where "a" is a constant. Thus C_b can be significantly influenced if the assumed value of D is grossly in error.

In conclusion, the suggested use of heat pipes continues to look encouraging. It would be most desirable, however, to obtain an experimental value for D because it is a parameter of central importance, regardless of the final scheme chosen to extract tritium from the blanket.

CONCLUSION

Demonstration of feasibility (from the point of view of plasma physics) for a thermonuclear fusion power reactor is anticipated by

many in the scientific community. If this should come to pass, the ability of fusion power to meet the energy needs of our people will depend on major advances in other scientific fields. It is not too soon to begin to explore these fields. I personally feel it is past time, for the confidence shared by those studying the physics of plasmas is generally not shared by those who study the physics of materials in the condensed state.

APPENDIX

Consider the problem of relating gas phase composition to reaction rates on a solid surface. Restricting ourselves to the simplest pure component case, suppose the recombination rate is given by

$$\text{Rate} = k_r \theta^2 \tag{A-1}$$

which is known to be the case for desorption of hydrogen from tungsten. In Eq. (A-1), k_r is a rate constant dependent on the solid surface, the gas, and the temperature. We will ignore these factors. This is justified since we are interested in finding what effect isotopic swamping might have. The factor θ^2 is proportional to the probability that two adsorbed atoms will find themselves adjacent to allow reaction. There will be an isotope effect on k_r , but it will be of second order as compared with pressure dependence of the rate.

We assume that after recombination has occurred, the molecular hydrogen desorbs very rapidly so that a negligible fraction of the surface is covered by it. This is a requirement for a good catalyst. It is also possible that some atoms could desorb at a rate equal to $k_d \theta$ without recombining. This is something I will ignore in spite of the fact that we know very hot filaments will partially atomize a gas. The rate of arrival of hydrogen at the surface to replenish that which is escaping is $k_a (1-\theta)^2 p$. The term $(1-\theta)^2$ is proportional to the probability that an approaching molecule will find two vacant sites adjacent, thus allowing dissociative chemisorption. Equating the rates of arrival and departure, we find at steady state

$$k_a (1-\theta)^2 p = k_r \theta^2 + k_d \theta^0 \quad (A-2)$$

which leads directly to the Langmuir isotherm when the square root of both sides is taken.

If two gases, H and T, are present, the recombination rate to form HT is $k_r \theta_H \theta_T$. The total removal rate of tritium from the surface is $(1/2 k_r \theta_H \theta_T + k_r \theta_T^2)$. We assume that θ_T is small so the second term can be ignored.

The equations analogous to Eq. (A-2) are:

$$k_a (1 - \theta_H - \theta_T)^2 p_H = k_r \theta_H^2 \quad (A-3a)$$

$$k_a (1 - \theta_H - \theta_T)^2 p_{HT} = k_r \theta_H \theta_T \quad (A-3b)$$

Neglecting θ_T because it is much smaller than θ_H gives

$$k_a (1 - \theta_H)^2 p_H = k_r \theta_H^2 \quad (A-4a)$$

$$k_a (1 - \theta_H)^2 p_{HT} = k_r \theta_H \theta_T \quad (A-4b)$$

From Eq. (A-4a),

$$(1 - \theta_H)^2 = \frac{k_r \theta_H^2}{k_a p_{H_2}} \quad (A-5)$$

which is inserted into Eq. (A-4b),

$$k_a \frac{k_r \theta_H^2}{k_a p_{H_2}} p_{HT} = k_r \theta_H \theta_T \quad (A-6)$$

By taking the square root of both sides of Eq. (A-4a) and rearranging,

$$\theta_H = \frac{\left(\frac{k_a}{k_r} p_{H_2}\right)^{1/2}}{1 + \left(\frac{k_a}{k_r} p_{H_2}\right)^{1/2}} \quad (A-7)$$

which can be squared to give

$$\theta_H^2 = \frac{\frac{k_a}{k_r} p_{H_2}}{\left[1 + \left(\frac{k_a}{k_r} p_{H_2}\right)^{1/2}\right]^2} \quad (A-8)$$

Eq. (A-8) may be inserted into Eq. (A-6):

$$\frac{k_r \frac{k_a}{k_r} p_{H_2} p_{HT}}{p_{H_2} \left[1 + \left(\frac{k_a}{k_r} p_{H_2}\right)^{1/2}\right]^2} = k_r \theta_H \theta_T \quad (A-9)$$

or

$$\frac{k_a p_{HT}}{\left[1 + \left(\frac{k_a}{k_r} p_{H_2}\right)^{1/2}\right]^2} = k_r \theta_H \theta_T. \quad (A-10)$$

If we let p_H become large to be sure $\theta_H \gg \theta_T$ (which is the object in isotopic swamping), Eq. (A-10) reduces to

$$\frac{k_r p_{HT}}{p_{H_2}} = k_r \theta_H \theta_T \quad (A-11)$$

and the tritium removal rate is just half this,

$$\text{Rate} = 1/2 k_r \theta_H \theta_T = \frac{k_r p_{HT}}{2 p_{H_2}}. \quad (A-12)$$

REFERENCES

- [1] NECHAN, W. J., MILLER, W. E., Radionactive Repair Engineering, ANL Chemical Engineering Division Annual Report, 1970, ANL-7775.
- [2] SWEETMAN, D. R. et al., Neutral Injection Heating of Toroidal Reactors, UKAEA Rep. CLM-R 112 (1971).
- [3] OSHER, J. E., Formation of A D^+ Beam for Efficient Production of A D^0 at High Energies, Lawrence Livermore Laboratory, Rep. UCID-15893 (1971).
- [4] LONDON, H., Separation of Isotopes, George Newnes Ltd., London (1961).
- [5] OSHER, J., Personal communication (1972).
- [6] ROBINSON, N. W. Physical Principles of Ultra High Vacuum, Chapman and Hall Ltd., London (1968).
- [7] SEPTIER, A. Focusing of Charged Particles, Vol. II, Academic Press, New York (1967).
- [8] WHEELER, V. J. J. Nucl. Mat'l. 40 (1971) 189.
- [9] THOMAS, D. G., LANDER, J. J., J. Chem. Phys. 25 (1956) 1136.
- [10] HILL, G. J., Brit. J. Appl. Phys. 1 (1968) 1151.
- [11] HAUFFE, K., HOEFFGEN, D., Ber. Bunsenges. Phys. Chem. 74 (1970) 537.
- [12] ROBERTS, E. W., ROBERTS, J. P., Bull. Soc. Fr. Ceram. 77 (1967) 3.
- [13] SCOTT, K. T., WASSELL, L. L., Proc. Brit. Ceram. Soc., 7 (1967) 375.
- [14] COLLINS, J. C. TURNBULL, J. C., Vacuum 11 (1961) 114.
- [15] FRAUENFELDER, R., J. Vac. Sci. Tech. 6 (1969) 388.
- [16] STEIGERWALD, E. A., "The Permeation of Hydrogen through Constructional Materials," TRW Inc., Rep. ER-4776 (1961).
- [17] WEBB, R. W., Permeation of Hydrogen through Metals, Atomics International, Rep. NAA-SR-10462 (1965).

- [18] MUELLER, W., et al., eds., Metal Hydrides, Academic Press, New York (1968).
- [19] ALBRECHT, W. M., GOODE, W. D., MALLETT, M. W., J. Electrochem. Soc. 106 (1959) 981.
- [20] WILCOX, B. A., BRISBANE, A. W., KLINGER, R. F., Trans. Am. Soc. Metals, 55 (1962) 179.
- [21] CANTELLI, R., MAZZOLAI, F. M., NUOVO, M., Phys. Stat. Sol. 34 (1969) 597.
- [22] SCHAUHANN, G., VOLKL, J., ALEFELD, G., Phys. Rev. Lett. 21 (1968) 891.
- [23] SCHAUHANN, G., VOLKL, J., ALEFELD, G., Phys. Stat. Sol. 42 (1970) 401.
- [24] DOREMUS, R. H., J. Phys. Chem. Solids 32 (1971) 2211.
- [25] SAMSONOV, G. M. ANTONOVA, M. M., Russ. J. Phys. Chem. 34 441 (1961).
- [26] GISSLER, W., ALEFELD, G., SPRINGER, T., J. Phys. Chem. Solids 31 (1970) 2361.
- [27] ZAMIR, D., COTTS, R. M., Phys. Rev. 134 (1964) 666.
- [28] HICKMAN, R. G., J. Less Common Metals 19 (1969) 369.
- [29] ACKERMAN, F. J. KOSKINAS, G. J., Ind. Eng. Chem. Fund. 11 (1972) 3328.
- [30] ERLICH, G., "Modern Methods in Surface Kinetics," in Advances in Catalysis, Vol. 14, Academic Press, New York (1963).
- [31] WERNER, R., Heat Pipes for Recovery of Tritium in Thermonuclear Reactor Blankets, Lawrence Livermore Laboratory, Rep. UCRL-72329 (1970).
- [32] HOFFMAN, M. A., Magnetic Field Effects on the Heat Transfer of Potential Fusion Reactor Coolants, Lawrence Livermore Laboratory, Rep. UCRL-73993 (1972).
- [33] CONLES, J. O., PASTERNAK, A. D., Lithium Properties related to use as a Nuclear Reactor Coolant, Lawrence Livermore Laboratory, Rep. UCRL-50647 (1970).

- [34] KREITH, F., Principles of Heat Transfer, International Text Book Company, Scranton, Pa. (1958).
- [35] WATSON, J. S., An Evaluation of Methods for Recovering Tritium from the Blankets or Coolant Systems of Fusion Reactors, Oak Ridge National Laboratory, Rep. ORNL-TM-3794 (1972).

TABLE I. ATMOSPHERIC RELEASE PROFILE FOR LLL TRITIUM FACILITY

Type of Release	Magnitude (% of Annual Total)	
	1968	1971
Background	2	15
Open vacuum lines	30	20
Decontaminate	15	20
Analytical services	30	10
Pump oil change	10	10
Drybox flushing	5	15
Miscellaneous	8	20

TABLE II. SEPARATION FOR HYDROGEN ISOTOPES IN 180° MAGNETIC SECTOR

Mass	Radius (cm)	Diameter (cm)	Separation (cm)
6	100	200	17
5	91.5	183	20
4	81.5	163	22
3	70.5	141	27
2	57	114	32
1	41	82	

TABLE III. REACTOR PARAMETERS

Reactor output, OP	12,000 MW
Total flow area, A	$8 \times 10^4 \text{ cm}^2$
Total heat and mass transfer area, A'	$4 \times 10^7 \text{ cm}^2$
Tube wall thickness	0.1 cm
Tube outside diameter	2 cm
Tube length, L	1000 cm
Average temperature, T	1000°K
Tritium burn rate	$1.55 \times 10^{-6} \text{ g/MW-sec}$
Tritium breeding rate, BR	$1.70 \times 10^{-6} \text{ g/MW-sec}$

FIGURE CAPTIONS

- Fig. 1. Efficiency of conversion of an ion beam to a neutral beam.
- Fig. 2. Schematic diagram suggesting use of a magnetic separator in the injection system of a fusion reactor.
- Fig. 3. Charge change cell and electrostatic deflector optics to provide negative ions for acceleration.
- Fig. 4. Injection cycles for a D-T reactor using charge exchange cells as the basis for isotopic separation.
- Fig. 5. Diffusion coefficients of hydrogen in various oxides.
- Fig. 6. Solubility of hydrogen in zinc oxide and various hydrogen permeabilities.
- Fig. 7. Permeability of hydrogen through niobium, from Webb[17].
- Fig. 8. Schematic diagram of the use of heat pipes in a lithium blanket.
- Fig. 9. Tube configurations used for liquid-phase mass transfer coefficient.
- Fig. 10. Curves illustrating solutions for laminar flow heat transfer at constant wall temperature.

Hickman - Fig. 1

Hickman - Fig. 2

Hickman - Fig. 3

Reactor exhaust recycle

(a)

(b)

Hickman - Fig. 5

Hickman - Fig. 6

Hickman - Fig. 7

Hickman - Fig. 8

Actual tube
configuration

Hickman - Fig. 9

Hickman - Fig. 10