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RADIATION EFFECTS *and* TRITIUM TECHNOLOGY
for
FUSION REACTORS

Editors

J.S. WATSON
F.W. WIFFEN

Compiling Editors

JULIA L. BISHOP
BRENDA K. BREEDEN
OAK RIDGE NATIONAL LABORATORY

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PREFACE

Encouraging results during the past few years from both magnetic and inertial confinement experiments have shown the need for larger-scale and more realistic experiments which "burn" deuterium and tritium and produce significant quantities of neutrons and activation products. Some such experiments have been approved and are in advanced stages of design (the Tokamak Fusion Test Reactor, the Joint European Tokamak, and the USSR T-20); other more advanced experiments are in early stages of conceptual design (Tokamak Experimental Power Reactor and Fusion Demonstration Reactor). As fusion research moves into these large, complex experiments, increased attention is required to develop the technology to build and operate the reactor systems. If fusion power becomes a commercial reality and follows patterns set by other advanced technologies (such as nuclear fission), development of the supporting technologies may prove to be more difficult, time-consuming, and expensive than demonstration and evaluation of the fundamental concepts.

A growing interest in fusion technology has been evident in the greater number of national and international meetings that include sessions on fusion technology, the increased attendance at such sessions, and recently the organization of meetings devoted solely to the discussion of technological problems.

As the logical outgrowth of these developments and as a means of fulfilling major current needs of the fusion program, the International Conference on Radiation Effects and Tritium Technology for Fusion Reactors was held in Gatlinburg, Tennessee, on October 1-3, 1975. This conference, which was sponsored by Oak Ridge National Laboratory, the Energy Research and Development Administration, the American Nuclear Society, and the Nuclear Metallurgy Committee of AIME, brought together scientists and engineers to discuss two elements of fusion technology: bulk radiation effects and tritium technology. In many ways, the presentation of papers on the two subjects in parallel sessions gave the effect of two separate conferences; however, several individuals attended sessions on both subjects. The conference was particularly timely because current conceptual design studies of Experimental Power Reactors have shown the immediate need for data on both subjects. In addition, it provided an excellent opportunity for workers from throughout the world to present their most recent results and to share insight into the remaining research needs. Judging from the quality of the papers, the number of attendees, and the interest and enthusiasm generated, the conference was eminently successful. We hope that publication of the proceedings will further enhance the benefits of the conference to all participants and also extend these benefits to others who were not able to attend.

The papers in these proceedings, which were published directly from copy supplied by the authors, are arranged in four volumes. The keynote address, delivered by E. E. Kintner of the Energy Research and Development Administration, is the first paper in Volume I. Papers concerned with radiation effects are included in Volumes I and II, while the tritium technology papers are collected in Volumes III and IV. The arrangement of the papers with regard to subject subdivision and order is the same as that used for presentation at the conference. Each of the four volumes contains a complete table of contents and author index for the entire proceedings.

The editors wish to express their gratitude to everyone who contributed to the success of the conference by assisting in the organization, chairing sessions, presenting papers, or participating in discussions throughout the conference. Special thanks are extended to J. L. Scott for conference arrangements and to D. Steiner, C. J. McHargue, and W. R. Grimes for their assistance with the organization.

J. S. Watson
F. W. Wiffen
Program Chairmen and Editors

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TRITIUM TECHNOLOGY IN FUSION DEVICES

J. Darvas

Kernforschungsanlage Jülich, Federal Republic of Germany

ABSTRACT

Tritium containment and tritium recovery from the plasma exhaust and from the blanket are the main tritium technology problems in fusion devices. The containment problem is discussed for a fusion power station in the frame of a model allowing for the release of 20 Ci/day of tritium in normal operation. Under reasonable assumptions for the overall design features of the power station, the model is shown to lead to design limitations for the reactor and for the energy conversion system. Assuming an inward gradient for the tritium pressure from the power station building to the blanket and to the coolant of the reactor, the choice for these and for the applicable schemes of tritium recovery from the blanket are also severely limited. Reprocessing of spent D-T fuel in experiments and in the reactor is also shortly discussed from the containment point of view. The author's primary intention is to exemplify the strong impact of tritium technology on the design of fusion devices.

INTRODUCTION

Present ideas on the development of fusion power are based on the fusion reaction between deuterium and tritium, because this is energetically the most favorable among all possible reactions between light nuclei. Moreover, it is hardly conceivable that any other fusion reaction could lead to a positive energy balance in a reactor operating with the existing methods for producing and confining a thermonuclear plasma. Consequently we are faced with a tritium problem deriving from the radioactive nature of this hydrogen isotope, both in the future reactor and in the tritium burning experiments of plasma physics.

To generate 5 GW of thermal power in a fusion reactor, we have to burn tritium at a rate of about 8 mg/s (675 g/d) and to breed the same amount in the lithium blanket. The burnup in most of the proposed reactor schemes is a few percent, hence the tritium will circulate at a rate 20 - 30 times the consumption. The total tritium inventory of a fusion power station is difficult to estimate, but it will probably be larger than 10^7 Ci distributed to a number of reactor components, as shown schematically in fig. 1. The main tritium loop of the reactor consists of some injector or fuelling device, the reaction vessel, the exhaust system, and the exhaust processing plant which closes the loop. This will be also the scheme to follow in tritium burning experiments, unless external tritium supplies are available so that we can afford to waste the tritium in the exhaust. The tritium produced in the blanket of a reactor by nuclear processes in lithium will be recovered from the breeding material and fed into the main fuel loop. In general we are aiming at a breeding ratio larger than 1 in order to provide the startup

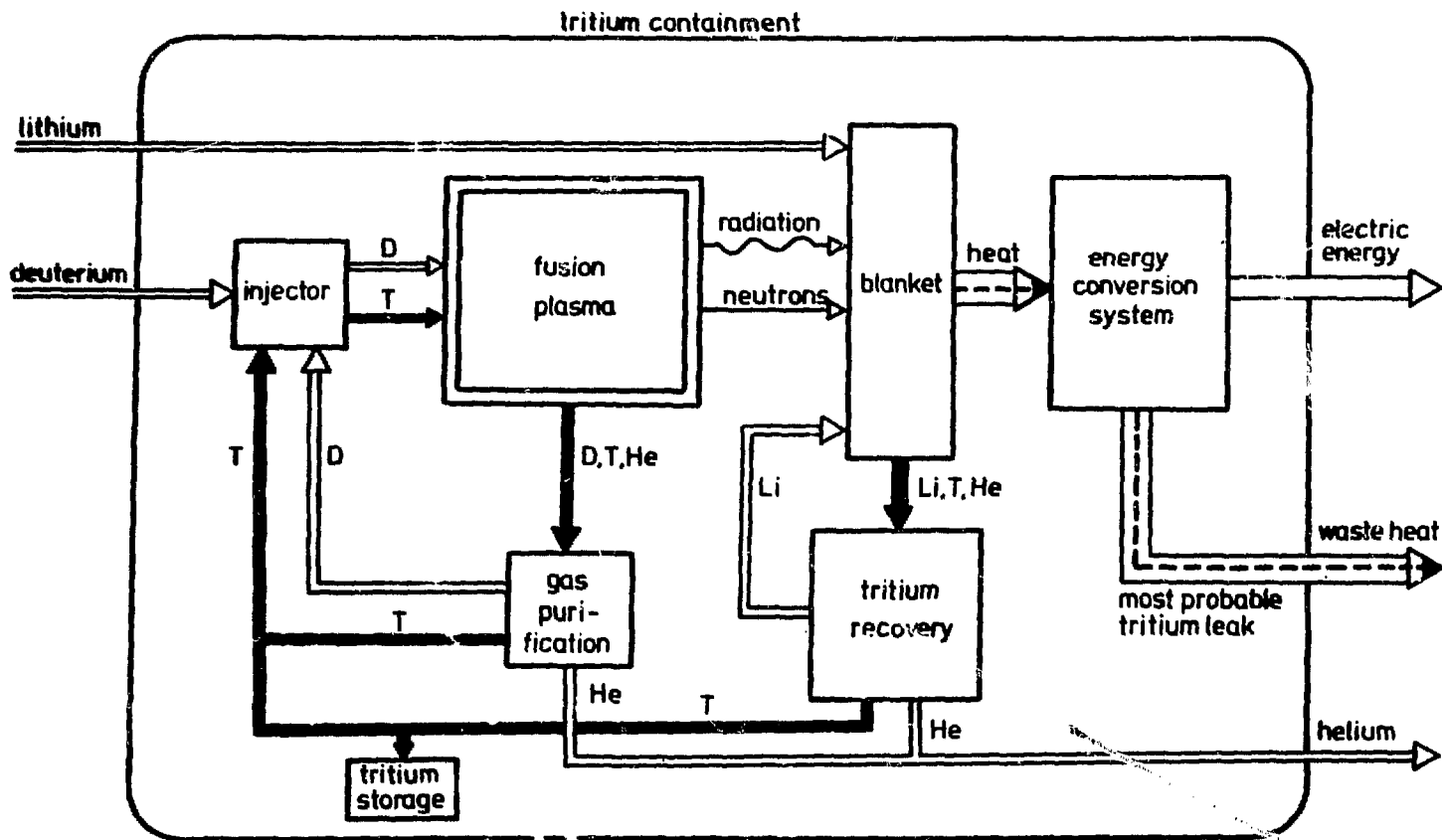


Fig. 1 Schematic View of a Fusion Reactor and of the Flow of Tritium Fuel.

inventory for another power station. This surplus is collected in some tritium storage for later shipping.

In an ideal system we would have a closed tritium cycle and no tritium would leave the power station, except - in a perfectly controllable way - the surplus production. In a real system however, leaks are unavoidable, especially when large boundary surfaces at temperatures considerably above ambient are involved. Such is certainly the case for most of the main components of the fusion reactor, especially for the energy conversion equipment. Hence we are faced with tritium losses to the environment which could affect to some extent the fuel balance, but, above all, will have to be minimized by safety reasons.

With this oversimplified scheme of the reactor we can already outline the main aspects of tritium technology: recovery from the exhaust and from the blanket, and tritium containment. By looking more deeply into the system, it will become clear that recovery and containment are strongly interdependent tasks which in addition have also quite close cross-connections to the design and performance of virtually all main reactor components, to the extent that some of these will probably have to be designed according to boundary conditions dictated by the tritium problem. This will be exemplified in the following, by adopting a certain containment philosophy, deriving some model and discussing the implications. We do not claim by any means that the underlying containment philosophy is the right one and that the basic figures are all correct. The boundary conditions imposed by environmental considerations will be discussed more competently in the first session of the tritium technology program of this conference. But we want to demonstrate and to strongly emphasize that the experimental studies related to

the tritium problem will have a deep influence on the design of the fusion reactor and, viceversa, the work in the tritium field should be guided by overall design considerations.

Table 1 summarizes the tritium technology problems of fusion and anticipates some details of the following discussion. In addition to the containment and recovery problems, a few other topics are listed at the bottom, which, albeit important, are in a first approximation independent of the reactor as a system and hence will not be discussed here. Tritium technology in D-T burning experiments will gradually approach the technology required for the reactor, including in a first stage containment under relaxed conditions, in the next stage recovery from the exhaust, and finally recovery from the blanket of an experimental power reactor. Hence only brief consideration will be given to tritium problems in experiments, also because the topic will be discussed at this conference for specific projects.

The starting point for the analysis of tritium technology problems in the reactor will be the tritium release rate under normal operation. No attempt will be made at this stage to include accidental release, because we feel that we have not enough data for such a task. However, we want to recall that the public acceptance of fusion power will largely depend on convincing proofs that the release of tritium from fusion power stations, both normal and accidental, can be kept under control.

Table 1 Tritium Technology Problems

CONTAINMENT	Inner Containment Outer Containment Release to Environment

RECOVERY	from the Blanket from the Exhaust from Other Components

OTHER	e.g.:	Storage and Shipping Commercial Availability Health Physics Aspects Safety Regulations

TRITIUM CONTAINMENT

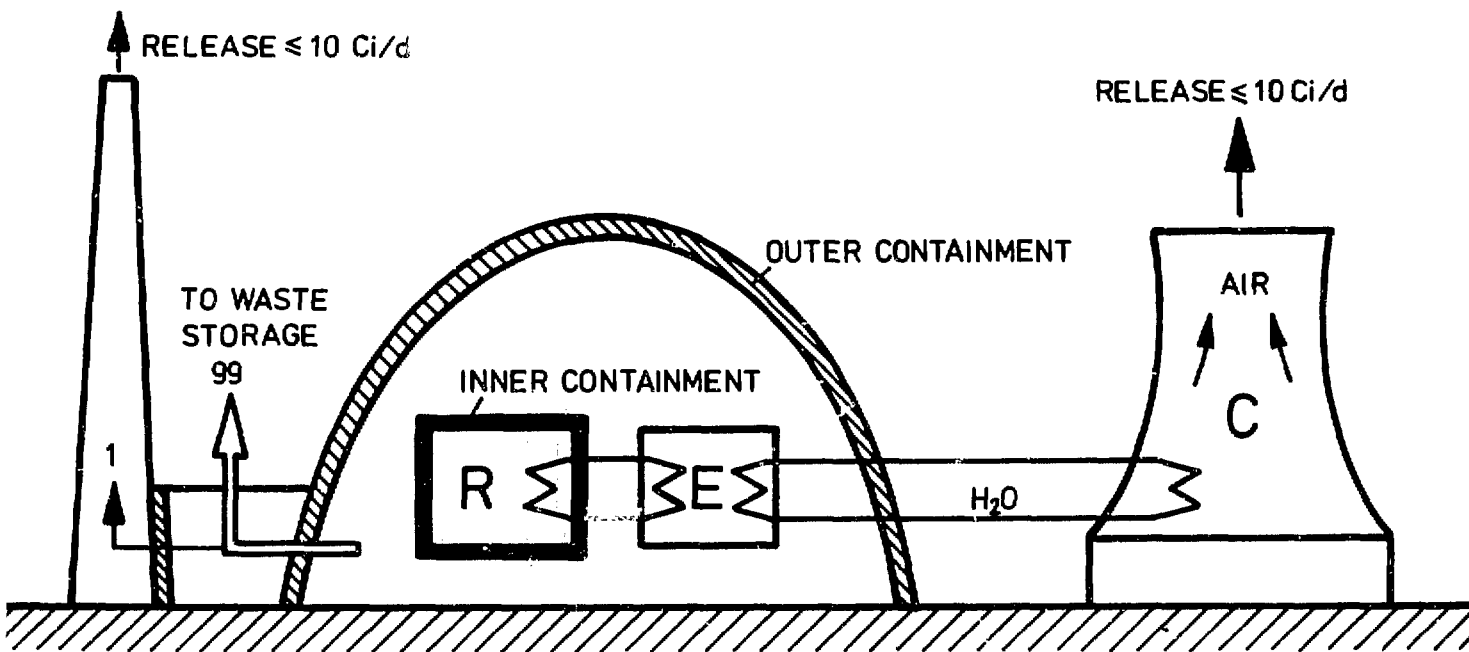
The Basic Philosophy

To begin with, we make an ansatz for the containment philosophy as shown in fig. 2. We consider the reactor (R), the energy conversion equipment (E) and the plant cooling (C) as subsystems of the power station, linked by the loops for the reactor coolant and for the waste heat transport respectively.

The reactor includes the reaction chamber, all devices to heat, to confine, and to maintain the thermonuclear plasma, the blanket, and the equipment required to recover tritium from the exhaust and from the blanket. Most of the tritium inventory will be located in these components, hence the reactor should be as tritium-tight as possible by virtue of an inner containment. We cannot expect, of course, a 100% efficiency for this containment, hence by necessity there will be a second or outer containment at the confines of the power station building.

The energy conversion system is located inside the outer containment, because we have good reasons to suspect that tritium will leak from the reactor through the coolant. No inner containment is assumed for E, because the technological and economic implication would be extremely severe.

As indicated in fig. 2, there is a potential tritium leak path to the environment through C, regardless of the effectiveness of the tritium barrier in the outer containment. It is also clear that we need a tritium sink within the outer containment, in order to keep the reactor building at a



(R = REACTOR, E = ENERGY CONVERSION SYSTEM, C = COOLING TOWER)

Fig. 2 Ansatz for the Containment Philosophy in a Fusion Power Station.

radiologically acceptable activity level. In view of the large volume involved (a few 100.000 m³), it seems reasonable to assume that we remove the tritium from that space, but do not recover it for use in the reactor. The removed tritium is not released to the environment, but we rather consider here the possibility of using the techniques anticipated for fission-fuel reprocessing plants, where only 1 % of the tritium is released, and 99 % is retained and concentrated to give storable waste.

The tritium source for the outer containment is the release from the reactor through the inner containment, and from the energy conversion system. Both R and E are critical; R because many components of complicated shape are involved, with quite different temperatures and tritium pressures, E because of very large potential permeation surfaces at high temperatures.

The effectiveness of the containment depends on the permeability of the barrier (depending strongly on the temperature), on the effectiveness of the tritium sinks - pumps, getters - and, of course, on the surface areas involved. It becomes then clear, that in order to estimate the release rates from the power station, we need at least a first design of R, E and C, detailed enough to give a picture of tritium sources and sinks, to localize the tritium (in terms of pressure) within the system, to estimate the permeation area between regions at different tritium pressure and hence to specify the dynamic behaviour of the tritium-map. On the grounds of published reactor designs it seems not unrealistic to do such a release-rate calculation, provided the implications of the different conceptual tritium recovery methods and of the possible energy conversion schemes (the most important pieces in this game) are carefully analyzed. This has been done for two

reference reactor designs in a remarkable analysis by Maroni.¹

What certainly should be attempted is to reverse the analysis, i.e., starting from target release figures, to find the allowable tritium pressure in the outer containment (assuming reasonable removal techniques for this few 100.000 m^3 volume), as well as to find the concentration and pressure data at the head end of the cooling loop - and with this to define the requirements on the inner containment of R and on E. Such boundary conditions will eventually reduce the alternatives for the tritium recovery and for the energy conversion schemes and even lead to restrictive conditions for other reactor components like the blanket, where there seems to be still ample freedom for design variations. To give an example, we shall construct a model by introducing numerical data in our ansatz for the containment, and see where the conclusions will lead us.

Target Release Rates for Normal Operation

Several criteria can be adopted to fix the target release rates from a fusion power station. We could try to deduce these from present or anticipated future regulations, or alternatively from the requirement that the global release in a fusion-powered world should not affect significantly the natural tritium equilibrium of our earth (about $30 \times 10^6 \text{ Ci}$ equilibrium inventory, with a birth rate of about $1.6 \times 10^6 \text{ Ci/year}$). For our analysis we adopt the view that the anticipated release rates from fusion and from fission power (fuel reprocessing plants) should be comparable in magnitude, i.e. about $10 - 20 \text{ Ci/day}$ according to table 1 (compiled from reference ²). We assume that this is released through the stack, symbolic for release either into the atmosphere or into the

ambient water.

Table 2 Tritium Release from Fission Power (Ci/d)
Compiled from ref.².

	Power Station (1 GW-el.)	Repro-Plant ^a (50 GW-el.)
BWR	0.5	27
PWR	2.5	27
HTR	2.5	17
FBR	0.3	16

^a Assuming 1% release fraction

The Outer Containment

A release rate of 10 Ci/day through the stack has some interesting implications for the outer containment. We can reasonably assume, that techniques will be available to retain 99% of the tritium collected from the space enclosed by the outer containment, and to compact this for waste storage. The total tritium throughput would then be about 1000 Ci/day. In terms of fuel losses this is only a very small fraction (about 1.5×10^{-4}) of the tritium produced in a 5 GW-thermal reactor. However, to dilute 1000 Ci/day of tritium in water to a concentration level of 10^{-3} Ci/m³ (the limit for the similar situation in a fission fuel reprocessing plant), we would need water supplies of about 10⁶ m³/day. This is

about the order of magnitude of the water supplies required for the cooling of the power station. Hence there is a strong incentive to reduce the tritium flow rate through the outer containment, say to about 10 Ci/day. Another limitation which could help to define the level of performance of the "sink"-whatever this may be - arises from the requirement that the space between the inner and outer containment should be radiologically accessible. According to present regulations,^x the maximum permissible tritium concentration is 2×10^{-6} Ci/ m^3 -air, corresponding to a partial pressure in this area of 5×10^{-10} torr. Assuming $250,000 \text{ m}^3$ as a representative order of magnitude for the volume involved, the tritium inventory should not exceed 0.5 Ci.

The power station cooling system C can be considered as part of the outer containment. We assume dry air cooling, both because we believe that in 30 years from now this will be by necessity the universal power station cooling system in most countries, and also because a closed water cooling loop between E and C is beneficial to the purpose of containment. The characteristics of this loop depend on the energy conversion scheme E. In the case of a steam turbine, the water temperature will be about 30°C upstream and 15°C downstream. At such low temperature there is virtually no tritium leakage to C in normal operating conditions. The situation is about the same for a gas turbine, where the upstream temperature will be about 80°C . Consequently, if any tritium is present in E, this will eventually leak only into the space enclosed by the outer containment. From this, the tritium discharge from the reactor to E should be limited to less than the total release rate from the power station (e.g. $\lesssim 10 \text{ Ci/day}$).

^x in the Federal Republic of Germany

The results of these findings are summarized in table 3. We are now in the position to analyze the implications on the inner containment and on the reactor cooling system.

The Inner Containment

By the inner containment we want to prevent tritium leaks from a number of reactor components of different shape, in some of which, like e.g. in the plasma reaction chamber, physics will require a certain tritium pressure. All these components are potential "sources" of tritium and ought to have a tritium-tight jacket, in which the pressure can be controlled. Fig. 3 is a very schematic picture of the situation: the "source" stands for all tritium-bearing components, the circle "inner containment" is the sum of all jackets, p_i are the tritium pressures in the space between jackets and components. ^{Leakage rate} Outside the inner containment we assume a pressure of 5×10^{-10} torr, according to our previous deductions.

In principle, several models are possible for the control of the pressure in each section. For instance, each section could have its own sink from which the tritium is recovered, i.e. the pressures p_i are controlled separately and low permeation walls between sections would possibly be beneficial. Another option is to have a single but "deep" sink, characterized by p_0 , controlling the pressures in all sections, or at least in the sections associated with the blanket and the coolant. These are indeed very important, because the interface between these two will necessarily exhibit high temperatures and hence the most probable leak from the reactor.

We shall examine the model, using a single sink, again for the sake of an example, and see the implications on the choice of the coolant, and on the blanket design. By "deep sink" we understand keeping p_0 at a level lower than the pressure in

Table 3 Summary of Findings for the
Outer Containment

T - release to environment	20	Ci/day
T- inventory in the outer containment ^a	0.5	Ci
T - pressure in the outer containment ^a	5×10^{-10}	torr
T - discharge from R through inner Containment	10	Ci/day
T - discharge from R through E	10	Ci/day

^a in a volume of 250.000 m³

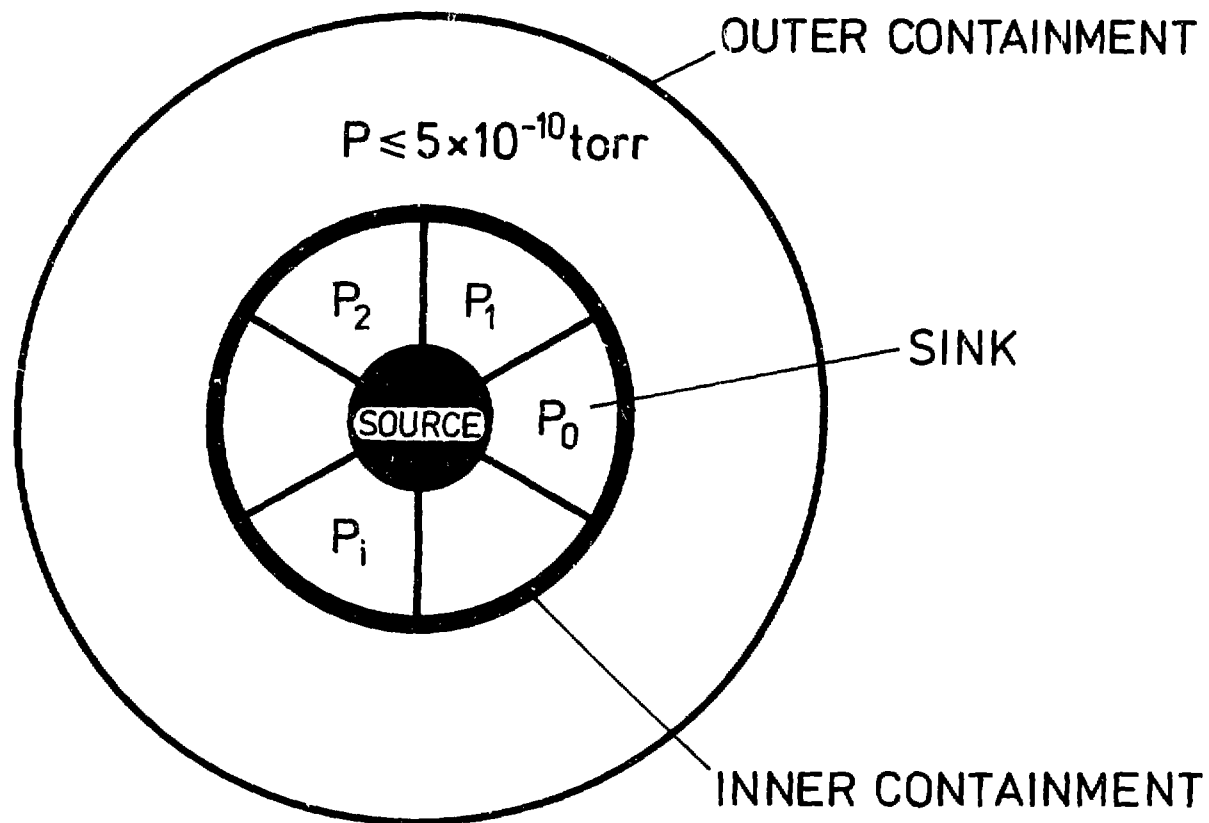


Fig. 3 Model for the Inner Containment

the outer containment, e.g. $p_0 \lesssim 10^{-10}$ torr.

We consider first the case of a tritium sink connected with the coolant. Lithium cooling of the blanket will be ideal for this purpose, if the tritium pressure over Li can be kept at 10^{-10} torr. In a blanket using natural lithium for breeding, we shall have to remove tritium from lithium at a rate of about 675 g/day in a 5 GW-thermal power station. For the recovery we need a bypass to the main coolant stream which in principle should be located at the high-temperature portion of the coolant loop in order to reduce tritium leaks through the heat exchanger, (see fig. 4). From Sieverts' law, $p^{1/2} = K_s C$, with K_s depending on the temperature, we can easily find the tritium concentration C which corresponds to the above pressure at a certain lithium temperature. From recent measurements by Ihle and Wu³ on D_2 in Li in the 1 - 100 ppm range, and corrected to T_2 by $K_s(T_2) = 1.16 K_s(D_2)$ as proposed by Maroni⁴, we have

$$\ln K_s = - \frac{6381.17}{T} + 9.981$$

(T in degrees in Kelvin, K_s in $\text{torr}^{1/2}/\text{atom-fraction}$).

Results from a few example calculations are shown in table 4. Assuming 900°C for the working temperature of the lithium, the concentration corresponding to 10^{-10} torr is about 0.1 ppm. It is difficult to believe that any of the proposed recovery schemes will work on a technical scale at this concentration level. The level of 10 ppm seems to be a more credible figure, but the corresponding pressure is too high by 4 orders of magnitude. If we want to keep the pressure at 10^{-10} torr, the lithium temperature should not exceed 366°C , which is too low for efficient heat conversion. An acceptable temperature of $500 - 550^\circ\text{C}$ would require efficient recovery at a concentration level of about 1 ppm. Even admitting that

EXAMPLE FOR RECOVERY FROM COOLANT: Li

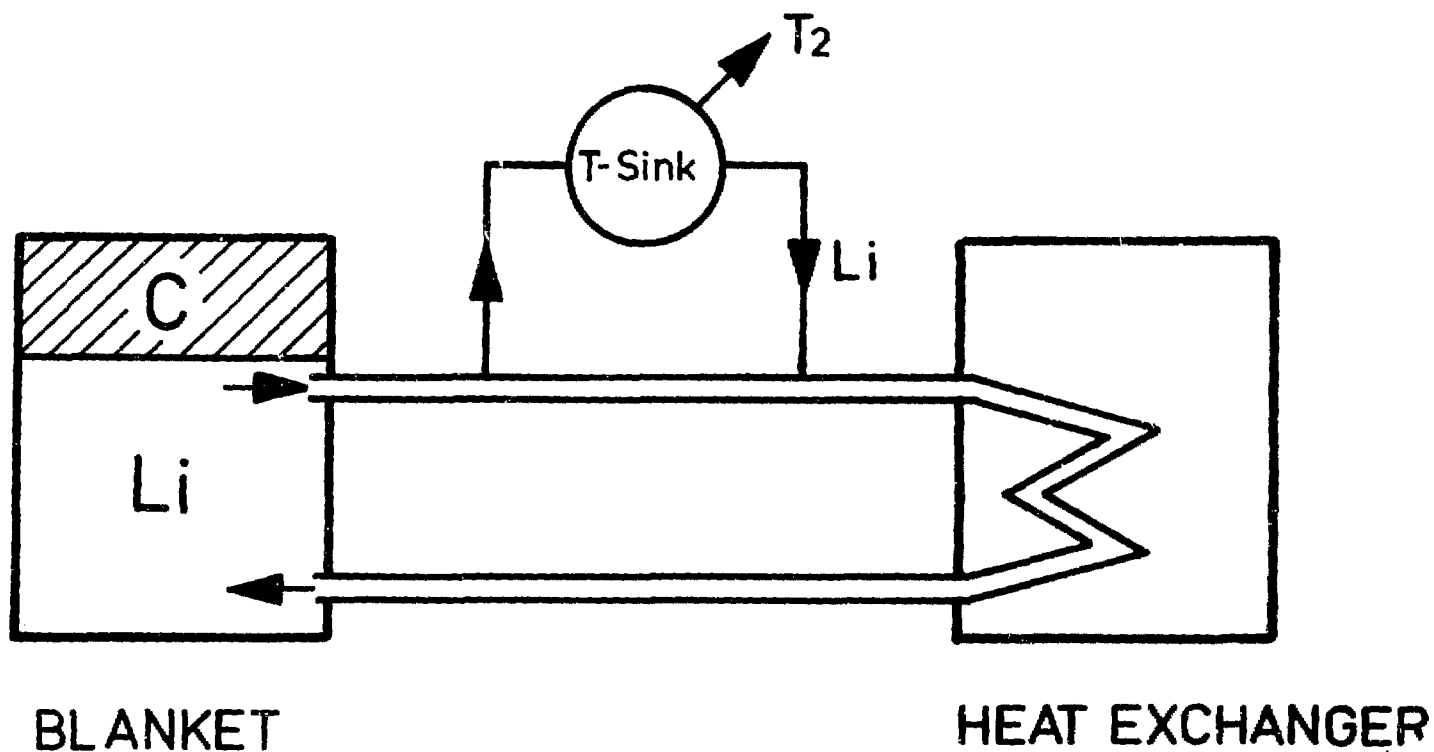


Fig. 4 Tritium Recovery from the Coolant:Li

recovery at 1 ppm is perhaps possible, it should be kept in mind that the bypass will be of the order of 1% from energy balance considerations, and that the equilibration of concentrations and pressures between the bypass and the main coolant stream requires careful consideration.

Table 4. Results from Sieverts' Law

Li-temperature (°C)	T-concentration (ppm)	T-pressure (torr)
900	0.1	10^{-10}
900	10	10^{-6}
366	10	10^{-10}
558	1	10^{-10}

Consider next the case of helium cooling and, for example, solid lithium compounds for breeding. The hydrogen solubility of most solid lithium compounds being low, the tritium produced in the blanket will permeate to the He-coolant (assuming high-permeation walls for the ducts). The He-pressure will be of the order of 40 atmospheres, hence a tritium partial pressure of 10^{-10} torr corresponds to 4×10^{-8} wpm T_2 in He. With a bypass of the order of 1% the case becomes nearly hopeless. However, an interesting possibility is to burn the tritium with small amounts of oxygen (~ 0.1 ppm) in the helium^{1,5}. This is represented schematically in fig. 5. It remains to see whether such an amount of O_2 is tolerable from the corrosion point of view, and also what the implications of hydrogen impurities are, which are always pre-

EXAMPLE FOR RECOVERY FROM COOLANT: He

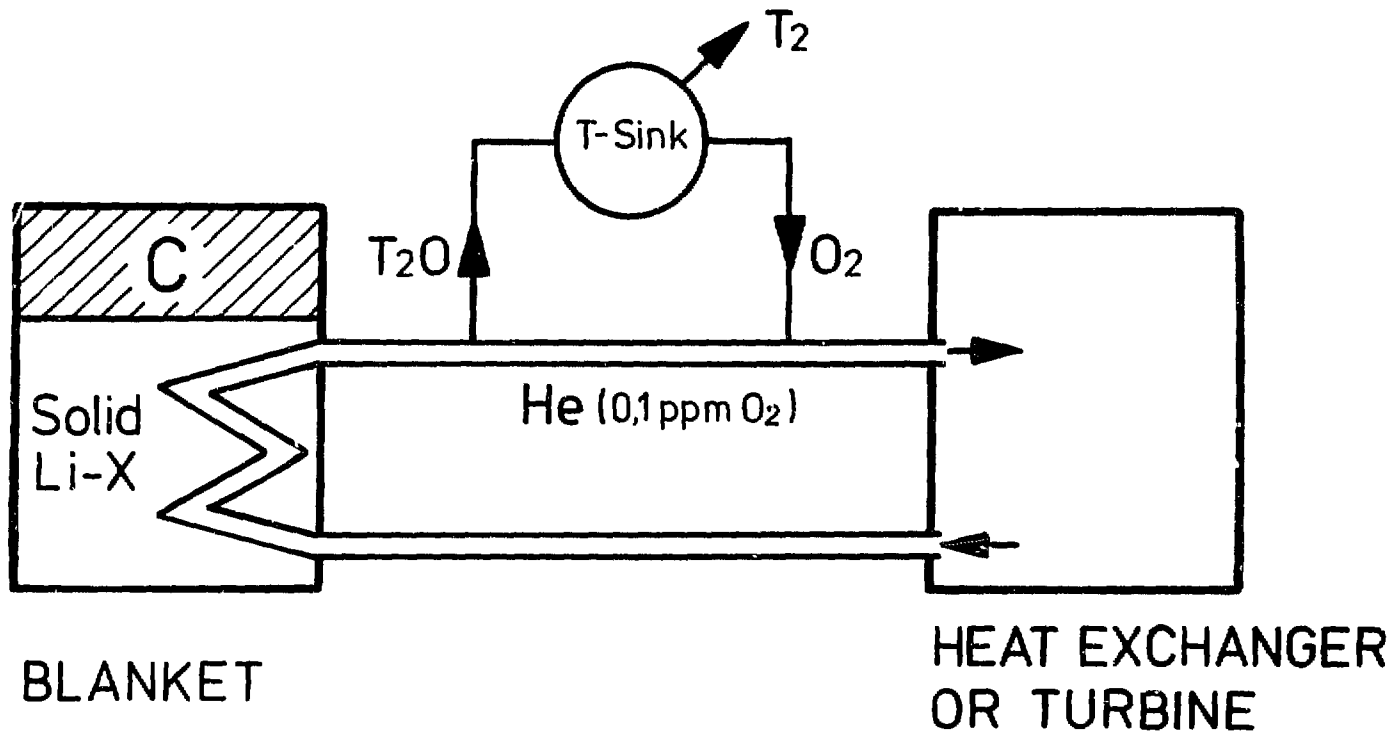


Fig. 5 Tritium Recovery from the Coolant:He

sent in He (~ 0.1 wpm) ^x.

Instead of connecting the sink with the coolant, we can also consider the breeding fluid as a universal sink for the blanket. In the example given by fig. 6, the breeding fluid is enriched lithium, Be is used for neutron multiplication and the coolant is again He. The bulk of the heat is generated in the Be and in the graphite reflector regions, hence we can afford to operate the lithium at temperatures below 400°C (corresponding roughly to a He-inlet temperature of 350°C). According to table 4, it should be possible to keep the required pressure of 10^{-10} torr with tritium recovery at a concentration level approaching 10 ppm. The amount of lithium involved being relatively small, recovery e.g. by distillation as proposed by Ihle and Wu³ seems appropriate. Some amount of tritium will be also produced in Be, hence we need again highly permeating structures in the blanket in order to pump effectively with the lithium.

In conclusion, an inward gradient for the tritium pressure from the outer containment to the blanket and to the blanket coolant will impose quite severe conditions on the tritium recovery scheme. This rough analysis also shows, that the design of the blanket and of the coolant ought to be consistent with the requirements on the outer and on the inner containment.

We still have to consider the containment problem for the main fuel loop including the plasma, the fuelling and exhaust system, and the impurity and ash removal from the

^x Coolant losses of about 0.1 - 1% He per day have to be compensated for by fresh supplies.

EXAMPLE FOR RECOVERY FROM BREEDING FLUID

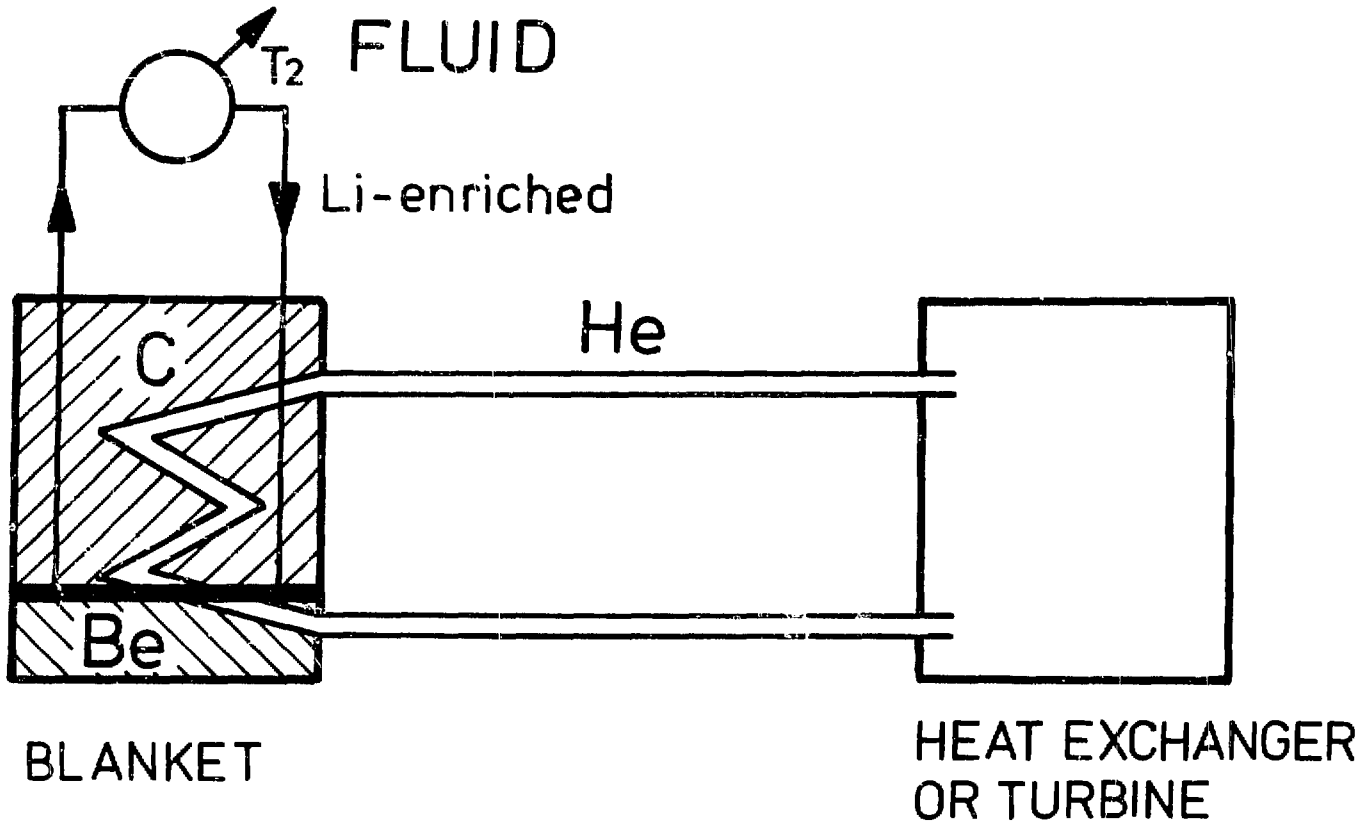


Fig. 6 Tritium Recovery from the Breeding Fluid

exhaust. The performance of these depends on the confinement scheme for the plasma. For instance, the relevant tritium pressure in the reaction vessel depends in the case of the Tokamak on the boundary layer of the plasma- which is difficult to specify at this stage - and in the case of laser fusion on the vacuum requirements for the focusing of the laser beams. The Tokamak will eventually require injection heating, while the Theta Pinch will not. The total amount of tritium involved varies by perhaps about a factor of 10 from burnup considerations (about 5 % in the Tokamak, perhaps 50 % in laser fusion). Hence in order to think about the containment problem of the main fuel loop those reactor components have to be specified for each confinement scheme. The same is true with respect to advanced confinement experiments burning tritium.

Common to all confinement schemes is the need for processing the plasma exhaust, removing He and heavy impurities, and in most cases separating hydrogen isotopes. It is often argued that such techniques are available in several countries. We want to recall that the tritium losses reported from the tritium factory at Marcoule, France, using Pd-diffusion techniques and double jackets for all components, are about 4×10^{-6} . Such losses clearly cannot be afforded in a fusion reactor. We would like to suggest that the problem be given careful consideration, especially in view of the fact that large tritium burning devices will be built in a close future.

TRITIUM RECOVERY

It is not our purpose to review extensively the proposed schemes for the recovery of tritium from the blanket, from the

exhaust or from other spaces with tritium pressure control in the inner containment. This has been done by more competent authors (see e.g. ref.⁵). We only want to make a few comments on some of the proposed schemes from the point of view of tritium containment.

Recovery from Lithium

One promising method to remove tritium from lithium is by diffusion through a permeating surface to vacuum. Because the affinity of lithium for hydrogen is among the highest known, pumping on the vacuum side is far from trivial, especially if (sticking to our containment model) we want to keep the tritium pressure on the lithium side at 10^{-10} torr. The problem has been discussed and tentative solutions offered by several authors. Hickmann⁷ proposed cold Li to getter tritium from the hot Li-stream. In his calculation example, the tritium pressure over the Li in the blanket is about 10^{-7} torr at 800°C , corresponding to about 5 ppm T/Li. The scheme is applicable to a blanket where the Li is "stagnant", i.e. the blanket is cooled by a second fluid, e.g. helium. The method should also work at a tritium pressure of 10^{-10} torr at the above concentration, provided the Li-temperature can be kept lower.

In the Wisconsin Tokamak Reactor Design⁸, Wittenberg et al. proposed yttrium for pumping at the vacuum side. They calculated an equilibrium tritium pressure of about 10^{-11} torr at 285°C , corresponding to 10 ppm T/Li. From the containment point of view, the method is again promising, provided the extraction can be operated at low Li-temperature.

Cold trapping by e.g. NaK has been discussed by Natesan and Smith⁹. Applied to the low temperature end of the lithium

coolant loop, cold trapping should lead to a tritium pressure of 5×10^{-6} torr at 700°C average Li-temperature. This would be too high for our containment philosophy, however, according to the calculations in ref.⁹, a pressure of 4×10^{-10} torr could be achieved in an intermediate NaK loop to the steam generator, provided cold trapping is again applied to the intermediate loop and the walls of the heat exchanger are clad with tungsten.

Pumping by small amounts of oxygen in a sweep gas has been recommended by Watson⁵, provided the permeation wall material (perhaps Pd) is resistant enough against corrosion. The method should be suited to give the low pressure of interest for the containment.

A quite different approach to the problem has been suggested by Ihle and Wu^{3,10}. They have shown experimentally, that in Li-D above 1000°C the deuterium concentration in the gas phase is higher than in the liquid phase, due to the predominant presence of Li_2D molecules in the gas phase. The separation factor in a distillation process is >1 for the above temperature and is (below ~ 100 ppm) independent of the concentration in the liquid phase. The latter makes the procedure really interesting, because it opens the possibility of keeping the tritium pressure low, even at lithium temperatures above 500°C .

Finally, Maroni¹¹ proposed to contact a portion of the lithium flowing back from the heat exchanger with a molten salt (e.g. LiCl-KCl or LiF-LiCl), estimating that about 50% of tritium present in Li can be removed on each pass. The tritium is extracted from the salt by electrolysis. It is anticipated that 10^{-10} torr can be maintained at 500°C Li-temperature, with less than 1 MW electrical power required for the extractor units.

Recovery from the Helium Coolant

In all high-temperature gas-cooled fission reactors (HTR) provision is made for the purification of the He-coolant in a bypass (of the order of 1%) to the main coolant loop. To maintain a tritium pressure of 10^{-10} torr in the coolant of a fusion reactor by similar techniques, seems beyond the technology available at present. However, as was mentioned in the discussion of the inner containment, catalytic burning of the tritium with a small amount of oxygen present in the helium is at least a possibility worth further exploration. The removal of tritium from the helium coolant will certainly be of necessity for helium-cooled reactor designs, regardless of the "deep sink" philosophy.

A General Comment

From the point of view of reactor design it is desirable to maintain a very low tritium pressure ($\sim 10^{-10}$ torr) in the blanket and in the coolant. If such a pressure can be derived from thermodynamic equilibria for some recovery scheme, this can be quite useful as a first approach. However, for a thorough analysis we need to consider the kinetics of the reactions involved in order to study the dynamic process of pressure equilibration in different parts of the system. This is especially important for removal schemes operating at the downstream side of the heat exchanger, because there are hundreds or even thousands of meters of ducting between the blanket, where the tritium is produced, and the tritium trap. In addition, it is fundamental to know the permeation properties of many kinds of metallic surfaces at realistic surface conditions, in order to complete the dynamic analysis of the tritium flow in this part of the system.

Recovery from the Exhaust

Reprocessing the exhaust fuel involves in most cases two different steps (Fig. 7). The first is to separate He and heavy impurities from the hydrogen isotopes (D, T, and probably small amounts of H.) The required purity of the hydrogen isotopic mixture will be determined by plasma physics and is not accurately known at the present. However, the purity obtainable by diffusion through Pd (leaving a few hundred ppm of impurities⁶) is probably sufficient. The optimum temperature for this process is in the range where the diffusion velocities of the hydrogen isotopes are nearly equal, i.e. $T \geq 350^{\circ}\text{C}$ ¹². The amount of D-T gas to be processed in a reactor of 5 GW thermal power at 5% burnup is about 9000 mol/day and the dimensions of Pd-surfaces have to be chosen accordingly.

Cryogenic distillation is another attractive possibility for purification of the fuel, and from the point of view of containment it has the obvious advantage of operating at low temperature. Other advantages over Pd diffusion, like small tritium holdup, have been discussed by Johnson in the conceptual design of a Tokamak power station by the Princeton Plasma Physics Laboratory¹³. On the laboratory scale, Pd-diffusion looks simpler and hence will be eventually the preferred method for plasma physics experiments where relatively small quantities of tritium are involved.

It is not yet clear whether separation of the hydrogen isotopes - the second step in reprocessing the exhaust - is really necessary in fusion devices. For refuelling, the D:T ratio can be adjusted by simpler means and the only remaining question is the amount of protium which can be tolerated in the plasma. For neutral beam heating (e.g. in the case of the Tokamak), it is usually assumed that injection techniques

CLOSED TRITIUM-CYCLE

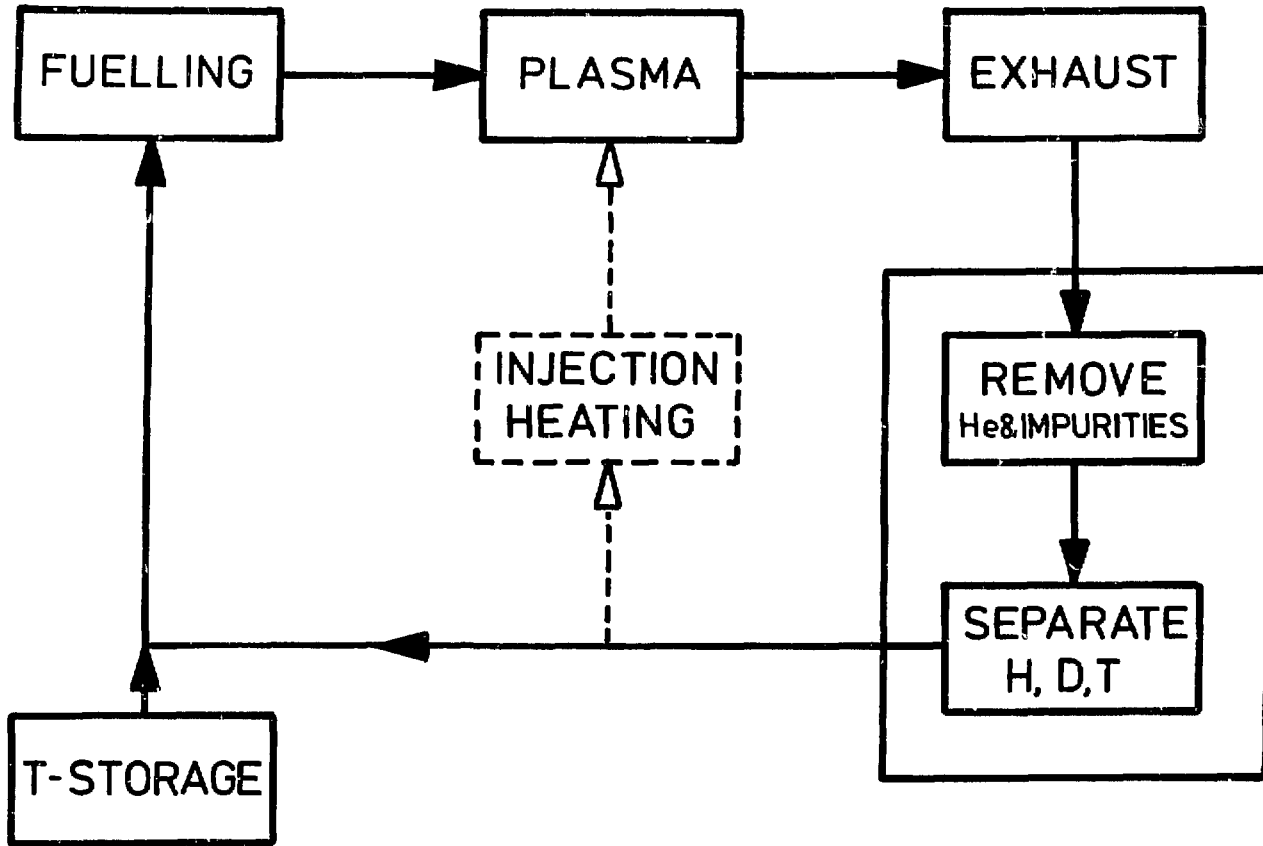


Fig. 7 Fuel Reprocessing in a Closed Tritium Cycle

will require separate beam lines for deuterium and for tritium. Here again cryogenic distillation would be the preferred method from the containment point of view, against irreversible processes like thermal diffusion, used in some of the large tritium production plants⁶.

In most of the early tritium burning experiments there will be an open tritium cycle, and the exhaust will be processed only for the sake of controlled release or, eventually, for storage of the tritium waste (Fig. 8). The stage at which one has to switch to a closed tritium cycle is dictated by economics and by the availability of tritium supplies. The situation is different for the US and for Europe; a preliminary assessment for European experiments has shown that recovery from the exhaust is worthwhile if the total amount of tritium involved exceeds 50 g¹⁴.

Recovery from Other Components

In the main fuel loop there are further components, like e.g. neutral beam injectors or vacuum pumps, where large tritium quantities will be handled and where the tritium pressure and the temperatures of confining walls cannot be chosen in accordance with the needs of tritium containment. For these we need a cold jacket, a venting system to remove the tritium from the space between the component and its jacket and, if the leaks are important, we also have to recover the tritium. There are current technologies to do this in principle, like catalytic burning on CuO. Experience in such techniques will hopefully be gained in tritium burning experiments.

OPEN TRITIUM CYCLE FOR EXPERIMENTS

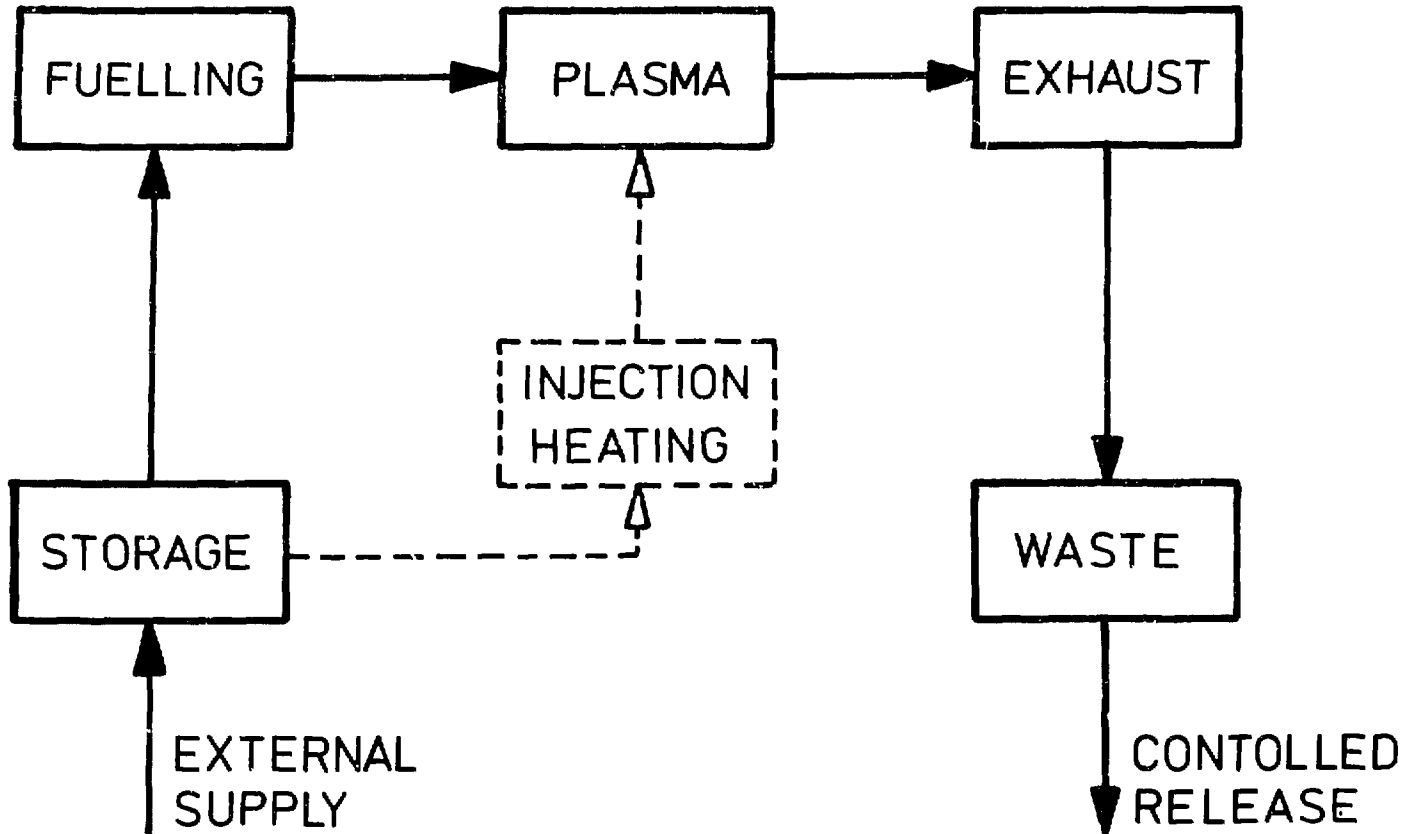


Fig. 8 Open Tritium Cycle for Experiments

SUMMARY AND FINAL REMARKS

The basic problems of tritium technology in fusion are containment, and recovery from the blanket and from the exhaust. In a reactor, the two problems are strongly interdependent and also closely related to the design of some of the important sub-systems and components of the power station. Therefore, research in the field of tritium technology for fusion should be guided by reactor design, and the design of the reactor should account for the problems of tritium containment. The requirements for the containment will largely govern the choice of particular recovery techniques as well as the design of the blanket and of the reactor cooling system. For the evaluation of different concepts, it is indispensable to adopt a containment model (but not necessarily the model chosen in this work) and to work back from release figures to a tritium pressure and flow pattern for the power station and its components. This has been done already by several workers in the field, and should be done in the future.

Careful consideration should be given to minimize tritium losses from the main fuel loop and tritium discharge from the blanket to the energy conversion system. Plasma experiments burning tritium will provide valuable experience in tritium handling problems, but the techniques to be applied in reactors will eventually be different.

The ultimate success of fusion power will largely depend on our ability for reliable and safe handling of tritium.

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DEFINITION OF SOURCE TERMS FOR TRITIUM
EVOLUTION FROM CTR SYSTEMS

T. J. Kabele
A. B. Johnson
L. K. Mudge

Battelle Pacific Northwest Laboratories

ABSTRACT

Tritium containment is one of the major environmental challenges in the development of fusion reactors. The objective of this work is to identify and begin to quantify the source terms for tritium release from fusion reactors under normal operation. Realistic estimates of tritium releases require access to detailed reactor designs. While none of the fusion reactor conceptual designs provide complete reactor component descriptions, selected designs provide a basis for realistic estimates of tritium releases. In line with the current emphasis on the Tokamak concept, four reference designs were reviewed in this study: a lithium-cooled, stainless steel system (UWMAK-I); a helium-cooled, stainless steel system (UWMAK-II); a nimonic steel, helium-cooled system (Princeton Fusion Reactor Reference Design); and a helium-cooled, aluminum system (Brookhaven Low Radioactivity Blanket Design). The general approach was to derive solid, liquid and gaseous source terms for each major reactor component for the UWMAK-I design. Impacts of temperature, material and design differences were then compared for the other reactor designs.

INTRODUCTION

Deuterium-tritium fueled fusion power reactors offer the promise of substantial energy supplies for the future. However, the environmental compatibility of such plants depends on the control of tritium releases to the off-site environment. Thus, careful control and handling of tritium within the plants will be prime requirements for fusion reactor design and operation.

Tritium control is an existing requirement for the fission reactor industry. The extension of that technology, therefore, is a logical first step in the development of tritium control technology for fusion reactors. However, fusion power plants will differ significantly from fission plants, and will pose additional tritium control problems over those already encountered in the nuclear industry. Factors such as the greater size and larger tritium inventories (3 to 23 kg for 5000 MWth plants)^{1,2a} in fusion reactors compared to fission reactors, will require further development of existing tritium control procedures. Lastly, the trend is toward more stringent limits on radioactive releases from nuclear facilities, suggesting that existing technology may not be adequate to meet release standards required by the year 2000, when fusion plants are expected to begin coming on line. Early recognition of the potential problem areas in fusion reactor tritium control will provide a basis for timely advances in control technology.

This paper presents the results of a study with the objective to quantify the tritium source terms for several fusion power reactor reference designs. These reference or conceptual designs have been analyzed to determine, where possible, the amounts and locations of tritium sources within the plants, and the pathways for tritium escape to the environment. Only steady-state operation of the plants was addressed in this study. Accidental tritium releases are being addressed as part of a PNL environmental study, but the results are not complete. Major maintenance also is a potential source of tritium release which eventually will need to factor into a comprehensive assessment.

Regarding terminology, tritium loss mechanism means the pathway by which tritium escapes from plant components. The loss mechanisms result in tritium releases, for example

by permeation through a pipe into a controlled area. The released tritium is either collected and stored as waste or it escapes to the environment. The amounts of tritium released to the off-site environment will be referred to as source terms in this treatment.

METHODOLOGY

Four Tokamak fusion reactor reference designs were analyzed to estimate the magnitudes of the tritium releases and source terms for this type of power plant. The reference designs reviewed in this study were UWMAK-I, UWMAK-II, the Princeton Fusion Power Plant, and the Brookhaven minimum activation fusion reactor.¹⁻⁴ These plants were chosen because (a) the Tokamak design is currently favored to be the most likely first generation fusion power reactor, and (b) the materials proposed for these plants are within the realm of current technology.

The methodology followed in this study to determine the tritium sources and releases from large fusion power plants has three major components: calculation, substitution, and estimation. Where sufficient details were present in the design of a plant, a calculational approach was taken. This generally involved calculation of a tritium permeation rate through the walls of a given component, or calculation of a fluid leak rate from hardware which contained a tritium contaminated fluid.

Where a process or piece of equipment was identified but not described in sufficient detail to permit calculations, a substitutional approach was used. Since several fusion reactor designs of nearly the same power rating were reviewed, it was occasionally possible to substitute calculational results from a component or process in one plant design for a similar, but less well defined one, in another plant design. This was particularly true of the power systems and the divertors.

When design details were undefined or simply lacking, source term estimates were based on experience in the existing installations which handle tritium. These estimates were based on comparisons with similar processes or equipment in light water power reactors and/or ERDA tritium production facilities.

The tritium loss mechanisms considered in this study included the following:

- Permeation
- Leakage from fluid system connections
- Leakage from valves, pumps, blowers, etc.
- Losses of tritiated water from the power system
- Maintenance on fluid piping systems
- Maintenance on power system components
- Contamination of work areas and personnel during maintenance
- Losses associated with handling and disposal of tritium contaminated wastes.

These mechanisms and their applications are described below.

Tritium Containment Boundaries

The general method used to arrive at the estimated tritium source terms or releases for each reference design involved considering the plant and its components to be within a series of tritium containment boundaries. This is represented graphically in Figure 1.

First, the tritium releases and source terms from individual components were determined. Next, this information was used as input to determine the source terms and releases for the reactor containment buildings and/or major subdivisions of those buildings. Finally, the calculations for releases from building containments were used to

TRITIUM CONTAINMENT BOUNDARIES

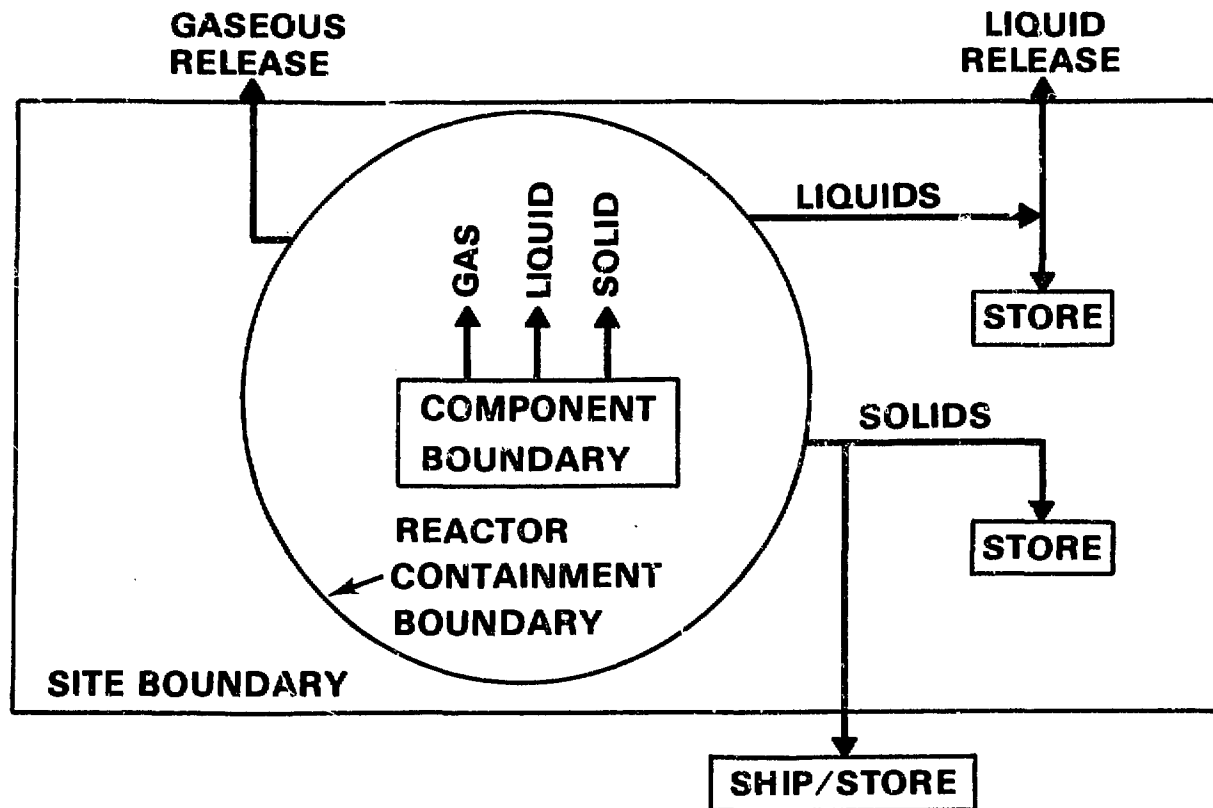


Figure 1. Tritium Containment Boundaries

determine the magnitudes of tritiated waste accumulation and the corresponding source terms.

This general approach identifies those areas where significant tritium losses originate within the plant, where it is usually easier to apply tritium control than just prior to release at the stack or waste water stream where the tritium has been diluted with large volumes of air or water. This method also permits the differences among the various reference designs to become more visible.

Tritium Permeation

Tritium permeation of structural and containment materials accounted for a substantial fraction of the tritium releases estimated for the reference plant designs. To determine the magnitude of permeation in the designs under consideration, the calculational method and data of Webb⁵ were used.

With this method, one must have a detailed description of a component, including the dimensions, temperatures and chemical compositions of the environment that the component is part of. This in turn requires a relatively complete understanding of the processes taking place in or around the component. Detailed information was not always available. Fortunately, however, since tritium permeation of containment materials is such an important tritium loss mechanism, sufficient details usually were given to permit evaluation of the major tritium permeation losses in most of the reference designs.

Tritium Loss Mechanisms

As previously defined, loss mechanism does not necessarily denote a loss to the environment because the major fraction of tritium "lost" from plant components would be recovered and stored as waste.

Several tritium loss mechanisms other than permeation were included in this study. However, most other loss mechanisms were less tractable to quantitative evaluation than the permeation losses. In the following sections, the other loss mechanisms and the methods to evaluate them are described.

Losses During Normal Operation

The major thrust of this study was to evaluate tritium source terms and releases during the normal operation of fusion power plants. The following tritium loss mechanisms (in addition to permeation), which resulted in tritium releases to building containments and the environment, were evaluated for routine plant operations:

- Leakage from fluid system connections and penetrations in the blanket and shield regions of the plants
- Leakage from valves, blowers, pumps, etc.
- Losses of tritiated water from the power systems via spills, leaks, etc.

Losses During Maintenance

Tritium losses during maintenance of fusion power reactors are functions not only of the reactor design, but also of the operating philosophy of plant management. Put simply, a certain amount of tritium control can be designed into a plant to limit releases during maintenance. However, careful and clean work habits, and procedures are also an integral part of tritium control during maintenance operations. Maintenance losses addressed in this study included:

- General maintenance on fluid piping systems
- Maintenance on power system components
- Contamination of work areas and personnel during maintenance operations

Tritium Contaminated Wastes

Tritium contaminated wastes are a by-product of normal operation and maintenance of a fusion power plant. These wastes may be stored on site, representing potential for accidental releases. Or they may be shipped to off-site storage. Tritium contaminated wastes considered in this study include:

- Clothing
- Vacuum pump oil
- Vacuum pump mercury
- Sorbates for tritium cleanup systems
- Ion exchange resins from the power system
- Discarded equipment

Not included in this study were the wastes generated during replacement of first wall components. These highly radioactive and massive components are a special case, and their replacement was not considered a routine or normal operation.

The quantity of tritiated wastes from the reference fusion plants was estimated both by calculation and by comparisons with existing nuclear facilities. Details for each reference design are presented later.

General Assumptions

A number of general assumptions or guidelines were made for this analysis; some of them significantly influence the final results. In all cases, these assumptions are conservative, i.e., they lead to predictions of higher tritium releases rather than lower ones. They were:

- The reference designs were evaluated as presented. No effort was made to "improve" a design even when changes which would reduce tritium losses were obvious.

- No credit was taken for permeation barriers such as oxide films or special materials except as specified in the reference design.
- Tritium permeation rates in metals were assumed to be proportional to the square root of the tritium partial pressure. Although the assumption is used in all of the reference designs, there is doubt about its validity at low tritium pressures (<1 torr). Recent evidence^{6,7} suggests that tritium permeation at low pressures may be directly proportional to the tritium partial pressure. This would substantially reduce our calculated tritium permeation rates, rendering tritium losses via the permeation mechanism insignificant. With no tritium permeation into the power systems, releases of tritium contaminated liquids to the environment would be eliminated for the four reference plants studied.
- All tritium released to the containment building atmosphere(s) was assumed to be oxidized to water and processed in a tritium recovery system. The oxidation of the tritium and its subsequent recovery were assumed to be accomplished with an overall efficiency of at least 90 percent. This assumption is the exception to the first item listed above. Most of the reference designs indicated some type of containment atmosphere cleanup process but did not provide specifics.

In laboratory tritium removal systems, tritium concentrations of less than one part per billion in the effluent gas have been reported,⁸ and other systems are under development.⁹ In principal, it appears possible to achieve substantial scaleup of these systems. Whether they can operate in a favorable economic regime on the scale required for large fusion reactor containment volumes is not clear.

RESULTS

For each reference reactor design a detailed tabulation of tritium releases and source terms was prepared. Each "release" was identified as to form (gas, liquid, solid, adsorbed on solid) and disposition (released to containment atmosphere, to the environment, or recovered and stored on-site). As noted previously, ninety percent of the tritium released to containment was assumed to be adsorbed on molecular sieves, with the remaining ten percent released to the environment.

Tritium Transport in UWMAK-I

UWMAK-I is a Tokamak-type fusion power reactor with a thermal power rating of about 5000 MW. Its heat transport system consists of a liquid lithium primary system, a sodium secondary system, and a steam-turbine power system with wet cooling towers. Tritium is bred in a blanket region, with the lithium serving as both primary coolant and fertile material. From a tritium control viewpoint, lithium is an excellent coolant because of the low tritium partial pressure due to the relatively stable Li-T bond.

There are two published versions of UWMAK-I. The first version^{2a} had the following temperatures in the lithium primary system: 483°C(max); 283°C(min). The second version^{2b} addressed effects of mildly higher coolant temperatures on increased thermal efficiency; the maximum lithium temperature was 489°C and the minimum was 359°C. The second version also had a helium-gap barrier in the steam generator to reduce tritium permeation. Tritium source terms and releases presented in Table 1 relate to the original UWMAK-I design. However, we analyzed impacts of the higher system temperature in the second version on tritium losses. This is discussed later in this section.

It is instructive to note in Table 1 that more tritium accumulates as wastes than is routinely released to the environment. Obviously, careful attention must be paid to the generation and disposal of tritiated wastes from fusion reactors. The current reference design for UWMAK-I provides much detail on the permeation of tritium through the power system into the environment, but much less detail on tritiated waste handling. Advances in future reference designs should include more detailed consideration of tritium control technology.

The matter of tritium fuel storage also has a significant impact on the overall tritium distribution in a fusion reactor. Table 1 does not include a figure for tritium leakage from a fuel storage system. The form of the stored tritium in UWMAK-I was not specified. Tritium losses are approximately 9000 curies per year from an existing gas phase storage system at the Savannah River Plant¹⁰. Better tritium storage technology appears to be available, using solid tritides, allowing lower storage pressures; but it is not clear how effectively losses can be reduced in systems having large inventories, numerous valves, and frequent need to revert to the gas phase for tritium transport to fueling facilities.

The effect of raising coolant temperatures to increase thermal efficiency on tritium control is demonstrated in a comparison of the two versions of UWMAK-I. For example, in the second version both the hot and cold leg temperatures of the lithium system were raised. So was the temperature of the yttrium hot trap, which is in thermal equilibrium with the cold leg. The temperature increase had a dual effect on tritium losses: a) it raised the partial pressure of tritium over the lithium coolant, and b) it increased tritium permeation through the lithium system piping. These effects caused a two-to four-fold (depending on location) increase in the tritium permeation rate through the primary system containment.

Table 1. Tritium Releases: UWMAK-I

Tritium Source	Release to Containment	Stored On-Site	Release to * Environment
(all in curies/year)			
1. Blanket and Shield	400	4060	40
2. Shield Cooling System	400	360	40
3. Piping Systems (Li + Na)	2800	2500	300
4. Heat Exchangers	20	18	2
5. Power Systems (Steam)	730	660	3770
6. ³ H Extraction System	6400	5760	640
7. Diverter System	570	880	60
8. Fuel Handling Systems	1100?	1000?	100?
9. Waste Handling Systems	--	1840	--
Totals	12,400	17,100	5,000

* Environmental Source Terms

Note 1: Assumes Operation 100% of the Year

Note 2: Question Mark Denotes Substantial Uncertainty

The penalty of increased tritium release must be weighed against the small increase in the plant thermal efficiency. This illustrates the complex interties of tritium control with nearly all of the thermal aspects of fusion power plants. It produces some difficult design challenges and trade-offs for the fusion plant designer.

Princeton Fusion Reactor

The fusion power reactor designed by the Princeton Plasma Physics Laboratory is a Tokamak with a thermal power rating of about 5300 MW¹. The maximum primary system temperature is $\sim 660^{\circ}\text{C}$. Tritium is bred in a molten salt blanket (flibe, a mixture of LiF and Be F_2) and heat is removed from the blanket by pressurized helium flowing through a complex array of coolant piping. The helium coolant transfers the reactor heat to steam generators which produce steam for a conventional steam-turbine electrical generating plant. This design involves a high tritium partial pressure over the flibe. The higher tritium partial pressure, however, makes tritium control more difficult. Tritium releases and source terms for this reactor are presented in Table 2.

Tritium releases are minimized in this design by using double-walled pipe and vessels in all systems containing tritium and operating at elevated temperatures. The only significant tritium source term identified is a 2200 curies per year loss from the steam system. Tritium reaches the steam system by diffusion from the molten salt to the helium coolant and then by diffusion through the steam generators.

In general, the Princeton design has treated the problems and hazards associated with tritium in a reasonably thorough manner. However, there are some areas where the existing design may prove impractical and thus different methods of tritium control might have to be addressed.

Table 2. Tritium Releases: Princeton Reactor

Tritium Source	Release to Containment	Stored On-Site	Release to * Environment
		(all in curies/year)	
1. Blanket and Shield	400	360	40
2. Helium Coolant System	1100	990	110
3. Piping Systems (He + Flibe)	400	360	40
4. Heat Exchangers	--	Included in 3	--
5. Power Systems (Steam)	730	660	2270
6. ³ H Extraction System	?	?	?
7. Diverter System	360	3230	40
8. Fuel Handling Systems	1100	1000	100
9. Waste Handling Systems	--	1840	--
Totals	4,100	8,400	2,600

III-15

* Environmental Source Terms

Note 1: Assumes Operation 100% of the Year

Note 2: Question Mark Denotes Substantial Uncertainty

In this reactor, control of tritium releases to plant atmospheres and ultimately to the environment is primarily dependent on a system of double-walled pipe and components in the molten salt and helium coolant systems. This double-walled system is necessary to prevent the release of about 20,000 curies per day of tritium which otherwise would diffuse into the plant atmospheres, where it would be an intolerable burden. Whether or not such a double-walled system is a practical design solution to the control of tritium in this reference design is a critical question. The answer affects nearly every aspect of tritium control and release in the plant, with the possible exception of the steam system. With the double-walled systems the tritium releases are very small; without them whole areas of the plant must be isolated and large volumes of containment atmosphere must be processed to keep tritium losses at acceptable levels.

Another area where tritium source terms and releases are difficult to assess for this plant is maintenance. Tritium control and releases during maintenance depend upon whether or not the double-walled piping systems prove to be practical. If they are, then the maintenance problems associated with tritium are primarily those associated with disposing of tritium saturated components and piping. If double-walled systems prove difficult to use in practice, then the maintenance problems involve access to contaminated atmospheres as well as tritium saturated equipment.

In the Princeton reactor, tritium fuel would be stored as a metal hydride. Tritium leakage from such a system may be considerably less than losses from a gas storage system. However, no firm estimates were possible because no design details were given for the fuel storage system. Thus Table 2 includes no estimate for tritium leakage from fuel storage system components.

A brief word is in order here with regard to the relative completeness of each of these four reactor designs. In general, the UWMAK-I and PPPL designs were more complete than the UWMAK-II and BNL designs. The major difficulty that this caused was to prevent identification of some tritium losses that might be associated with the UWMAK-II and BNL designs. Thus those designs will generally appear to have smaller tritium source terms than the other plants. Recognizing the preliminary nature of all of these designs, the lower tritium source terms should be attributed more to lack of design details than to any inherent feature of those plants.

UWMAK-II

UWMAK-II is a Tokamak-type fusion power reactor with a thermal power rating of 5000 MW.³ A helium coolant transfers heat from a blanket region to a conventional steam-turbine power system with wet cooling towers. The maximum primary system temperature is $\sim 650^{\circ}\text{C}$. Tritium is bred in a solid lithium blanket (LiAlO_2) where it is collected in a manifold system. Some tritium diffuses into the helium coolant, where it is recovered. Tritium source terms for UWMAK-II are given in Table 3.

Many of the comments appropriate to UWMAK-I are also appropriate here, particularly regarding losses from tritium storage systems. As in UWMAK-I, the actual form of the stored tritium fuel was not specified. Thus Table 3 includes no estimates for tritium leakage from a fuel storage facility.

Several systems in UWMAK-II were not described as completely as were similar systems in the UWMAK-I and Princeton designs. Thus, the numbers quoted in Table 3 should be regarded as minimums.

Table 3. Tritium Releases: UWMAK-II

Tritium Source	Release to Containment	Stored On-Site	Release to * Environment
		(all in curies/year)	
1. Blanket and Shield	400	3960	40
2. Shield Cooling System	400	360	40
3. Piping Systems (He + Na)	2570?	2300?	260?
4. Heat Exchangers	70?	63?	7?
5. Power Systems (Steam)	730	660	370
6. ³ H Extraction System	440?	400?	40?
7. Diverter System	1100	1360	110
8. Fuel Handling Systems	1100?	1000?	100?
9. Waste Handling Systems	--	1840?	--
Totals	6,800	12,000	1,000

* Environmental Source Terms

Note 1: Assumes Operation 100% of the Year

Note 2: Question Mark Denotes Substantial Uncertainty

Brookhaven Fusion Reactor

The BNL fusion reactor design is a Tokamak with a thermal power rating of about 5000 MW.⁴ It is cooled with a combination of water and helium heat transfer systems which transfer energy to a standard steam-turbine power system. The maximum primary system temperature is $\sim 760^{\circ}\text{C}$. Tritium is bred in solid lithium-aluminum or lithium-aluminate regions. Tritium releases and source terms for this design are listed in Table 4.

The major portion of the BNL fusion reactor study dealt with the design of a low activation blanket for a Tokamak similar to UWMAK-I. Thus, tritium source terms for this reactor were estimated using information from both the UWMAK-I and BNL design reports.

As in the cases of the other three reactors, no figure for tritium leakage from a fuel storage facility was included in Table 4. No description of the fuel storage system was given for this plant.

A summary of the tritium source terms for all four designs is presented in Table 5. Note that in all cases the accumulation of tritium as solid or liquid wastes far exceeds estimated releases to the environment, pointing up the requirement for suitable waste handling facilities.

Non-Tokamak CTR's

At the writing of this paper, analyses of several non-Tokamak fusion power plants are underway. Mirror and theta-pinch plants will be evaluated for tritium releases and source terms.

Comparisons Among Fusion Reactors and Existing Nuclear Facilities

To place the results of this study in better perspective, the estimated tritium releases from the fusion power plants were compared with tritium releases from existing light water

Table 4. Tritium Releases: Brookhaven Reactor

Tritium Source	Release to Containment	Stored On-Site (all in curies/year)	Release to * Environment
1. Blanket and Shield	400	360	40
2. Helium Coolant System	--	Included in 3	--
3. Piping Systems (He + H ₂ O)	1200?	1080?	120?
4. Heat Exchangers	?	?	?
5. Power Systems (Steam)	730	840	80
6. ³ H Extraction System	400?	360?	40?
7. Diverter System	?	~	?
8. Fuel Handling Systems	730?	660?	70?
9. Waste Handling Systems	--	1840	--
Totals	3,500	5,100	350

* Environmental Source Terms

Note 1: Assumes Operation 100% of the Year

Note 2: Question Mark Denotes Substantial Uncertainty

Table 5. Tritium Source Terms for Tokamak Fusion Reactors

<u>Plant:</u>	<u>UWMAK-I</u>	<u>PPPL</u>	<u>UWMAK-II</u>	<u>BNL</u>
Power Level				
Thermal:	5000 MW	5305 MW	5000 MW	5000 MW
Electrical:	1500 MW	2030 MW	1716 MW	1605 MW
Gaseous Releases (Curies/Year)				
From Stack or Vent:	1250*	2600**	700*	350*
Cooling Towers:	2500	-- **	200	--***
Liquid Releases (Curies/Year)				
Power System Blowdown:	1200	---**	90	---***
Waste Accumulations in Containment (Curies/Year)				
Liquids:	2200	4700	2200	2000***
Solids:	15000*	3700	10000*	3100*

* Does not include estimates for releases from tritium storage systems

** 2200 ci/yr of tritiated water from power system is released up stack

*** 183 ci/yr of tritiated water from power system is recovered and assumed stored as a liquid

Note: Assumes operation 100% of the year

reactors. One must bear in mind, however, that a long time span (30 years?) separates the large fusion plants from current facilities. The technology of tritium control will likely improve significantly in that period. What the future tritium release limits will be is not presently clear. The trend, however, is definitely towards a reduction in radioactive releases of all kinds. The data used in the comparisons is presented in Table 6.

Table 6. Comparisons of Tritium Releases

<u>Plant</u>	<u>Gaseous Releases</u> (All in curies/yr)	<u>Liquid Releases</u>
Fusion Reactors:		
UWMAK-I (1500 MWe)	3750	1200
PPPL (2030 MWe)	2600	Small
Light Water Reactors: * (1972 averages)		
BWR (Zircaloy-2 clad, 550 MWe)	0.5-5	24
PWR (Zircaloy-4 clad, 530 MWe)	<100	280

* Source: Reference 11, p. 361.

The differences between the fusion reactors and the LWR's are quite apparent. The fusion plants, even on a "curies/MW(e)" basis release much more tritium than the fission plants. The liquid releases from the fusion plants appear to be generally higher than those from the LWR's.

One must add several qualifying observations to the above comparisons, however, to get a complete picture of the relative radioactive releases from these power plants. The LWR's also

release noble fission gases at rates substantially above the rates for emission of tritium vapor. Thus the above comparisons are valid only for tritium and should not be taken as a relative measure of the environmental desirability of fission vs. fusion. The light water reactor industry is, however, actively pursuing a goal of reducing all radioactive emissions to "as low as practicable" levels. At least one reactor, Monticello, reports a nearly zero release of tritium (8×10^{-5} curies over one six-month period in 1972).¹¹ This was accomplished by an ambitious program of waste water recycle, treatment, and on-site storage.

A second major qualifying observation is that both fusion and fission reactor tritium releases are expected to be far less than those from modern fuel reprocessing plants.

A third observation is that major advances in tritium control technology have been made at U. S. weapon sites over the past five years.⁹ Some of the control procedures are still in developmental stages and their potential value is not fully evaluated.

Thus, fusion reactors will benefit from tritium control procedures developed for existing nuclear facilities. However, they will be subject to the same pressures to reduce radioactive emissions which now and in the future will apply to other nuclear facilities. Therefore, fusion technology will need to generate additional momentum for improved tritium control technology, aimed particularly at the tritium loss mechanisms and storage of tritium wastes.

RECOMMENDATIONS AND CONCLUSIONS

Much remains to be done in the broad area of tritium control and handling technology before large or even medium-sized tritium-burning fusion reactors can be adequately designed. Efforts must be concentrated in two general areas:

(1) improvement of basic tritium technology and (2) development of improved or innovative tritium control and processing technology. Progress in these areas should permit more complete designs for tritium control in fusion power plants than is currently possible.

Basic Tritium Technology

Certain improvements in our understanding of basic tritium chemistry, physical properties, and interactions with candidate structural materials are necessary to compliment programs for the development of tritium control processes and hardware. An underlying problem with much of our understanding of the basic chemical and physical behavior of tritium is that it was obtained from extrapolation of measurements of hydrogen or deuterium behavior. While this information is certainly useful, better information, obtained directly from tritium measurements, is required for accurate design of process and control hardware. Areas where basic tritium technology improvements are critical to fusion are:

- Tritium permeation at low pressures (<1 mm Hg)
- Tritium permeation of composites and potential barrier materials
- Tritium permeation enhancement by corrosion
- Tritium separations chemistry, including complete chemical and physical equilibrium relationships with candidate coolants, sorbates, etc.

Tritium Control and Handling Technology

The development of improved processes, techniques, and hardware for the control of large quantities of tritium will be critical to the safety, operability, maintainability, and public acceptance of fusion power plants.

Listed below are some areas where significant efforts could result in reduced tritium emissions from fusion reactor power plants:

- Development of efficient tritium removal systems for cover gas treatment.
- Development of a strong data base for the interaction of tritium with advanced materials (niobium, composites, etc.).
- Development of optimum tritium storage processes, hardware, and materials.
- Optimization and development of tritium waste storage methods, both interim and final.
- Development of barrier materials or coatings to reduce tritium permeation.
- Development of innovative tritium processing schemes with low tritium evolution potential as a major goal.

Use of Existing Technology

A last area of potentially large improvements in the control of tritium in fusion reactors lies in the innovative use of current technology as it is applied to this new power source. Some of the practices and technology applied to fission reactors and fuel reprocessing plants are obviously candidates for application to fusion reactors. Among the more important areas for consideration are:

- The use of limited volumes or inerted cells within containment buildings to reduce the volume of tritium contaminated atmosphere that must be processed.
- The use of greenhouses or other temporary enclosures to limit the release of tritium and the spread of contaminated materials during maintenance.
- Leak-proof construction as a major design criterion for all fluid systems containing tritium; LMFBR and HTGR technology have many applications.

- Fusion reactor designs with maintenance and tritium control as major design criteria.

IMPROVEMENT OF FUSION REACTOR DESIGNS

The current group of fusion power plant reference designs has served to focus attention on the need for improved tritium control. Evolutionary developments in fusion technology will automatically produce additional generations of reference designs for large electrical generating plants. The following suggestions should be factored into these future design efforts:

- Designs should incorporate only realistic tritium control features, having plausible technical/economic bases.
- Much greater design detail than is present in the current designs is required to assess the adequacy of tritium control in fusion power plants. Details such as pipe and component dimensions, temperatures, numbers and types of valves, flanges, and fluid connections, fluid stream compositions, temperatures, and flow rates, and internal and external containment building design are needed to quantify tritium losses.
- Efforts should be made to permit easier comparison of point designs. Too often one reference design differs sufficiently from other designs that meaningful comparisons are difficult. It would aid the whole CTR effort if reference design efforts were more carefully coordinated among design teams.
- Additional effort is needed to incorporate existing tritium control measures into the designs and to assess the impacts of building and component designs on tritium control.

ACKNOWLEDGEMENTS

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TRITIUM RELEASE STRATEGY FOR A GLOBAL SYSTEM*

C. E. Easterly
D. G. Jacobs

Health Physics Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

A multi-compartment model of global hydrologic cycling is used as a basis for determining the relative effects of alternative modes of tritium discharge on the collective dose to the world population. Consideration of the various modes of discharge indicates that tritium releases to the atmosphere may give rise to as much as an order of magnitude less collective dose on a global basis than releases to surface waters. Other modes of discharge are compared. The influence on the comparative analysis of the assumptions and imprecisely known variables, such as the rate of conversion of tritiated hydrogen gas to tritiated water are discussed.

Considerable efforts are being devoted to the development of fusion as a source of power and we foresee that within a relatively short period of time mankind will be producing large quantities of tritium. Although advances in tritium control technology will undoubtedly occur, total containment may still be technologically unachievable and/or accompanied by severe economic penalties. It would appear prudent to begin exploring the potential health effects of alternative tritium release strategies so that planned or unplanned releases of tritium would give rise to a minimum of deleterious effects on human life within an economically acceptable cost.

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Three human receptor groups must be considered for potential deleterious effects. They are (1) the occupational worker, (2) the sensitive or critical individuals or population groups within the public, and (3) the population as a whole. Ultimately it will be necessary to understand the interplay of costs and benefits for the three groups relative to the alternate release strategies, but this can be done only after understanding the potential impacts on each group separately.

It is the purpose of this paper to sketch our current understanding, as quantitatively as possible, of the effect of alternative tritium discharge modes on the collective dose to the world population. Jacobs¹ has reviewed the movement of tritium in the various compartments of the environment and has concluded that, in general, the movement of tritiated water would follow rather closely the movement of ordinary water. Thus, for this initial study, a generalized global hydrologic cycle is used as a model to determine the fate of tritium introduced into the environment. Tritium releases are divided into two classes: (1) those released as tritiated hydrogen gas, HT or T_2 , and (2) those released as tritiated water, HTO. The quantities of HT and HTO relative to the volumes of the atmosphere and circulating water are quite small and the assumption is made that the introduction of HT and/or HTO into the system has no effect on the system.

A block diagram of the generalized global hydrologic cycle used in this study is seen in Fig. 1. The model is described by a set of linear, homogeneous, differential equations. The water compartments are assumed to mix uniformly and instantaneously and to interact with

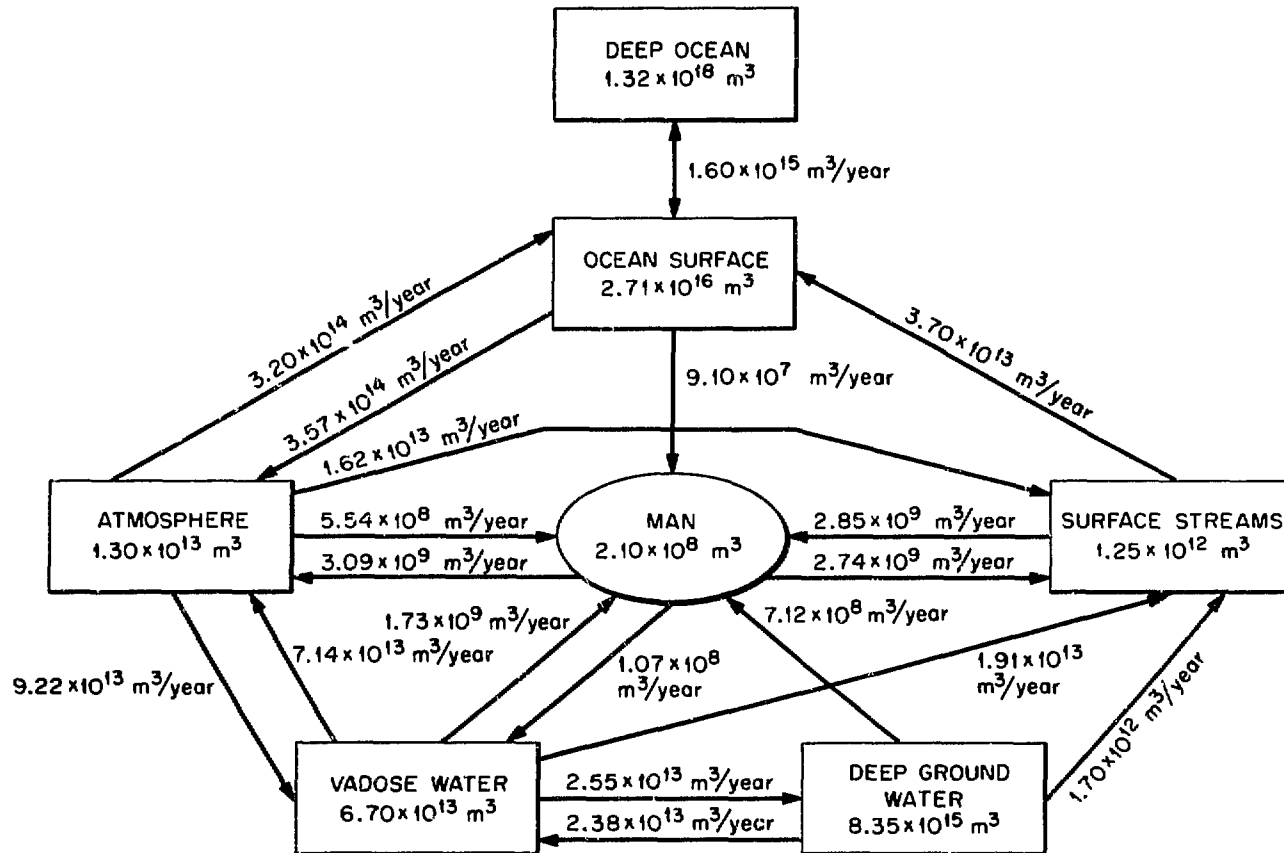


Fig. 1. Global Hydrologic Cycle with Respect to Man.

each other in a linear manner (only first order transfer rate constants are used). For a set of initial conditions (for example, a globally uniform input of tritiated water into a compartment or compartments), the equations are solved and evaluated for the relative compartmental distributions at subsequent times. Solutions can also be evaluated for the case of a continuous discharge of tritium into the environment.

The volumes of the hydrologic compartments are taken from Todd², and for man a population of 5×10^9 people is used as representing the year 2000. Most of the transfer coefficients are also taken from Todd². However, the surface to deep ocean exchange rate is based on the advection rate for noble gases into the deep ocean of 1.4×10^{-5} cm/sec, as determined by Bieri et al.,³ and the ground water exchange rate is based on a diffusion rate of 5×10^{-6} cm²/sec. Transfer coefficients to and from man are based on water balance data taken from the *Reference Man* report⁴. The ingestion rates for the base case were taken as follows: 5% of the food intake is from the ocean and 95% is in equilibrium with the vadose water; the water supply is assumed to be 80% from surface waters (rivers, lakes and reservoirs), and 20% from wells (deep ground). In order to have well behaved solutions to the differential equations, it is necessary to make minor adjustments to the rates so that no water is gained or lost in any compartment.

The solution to the base case (actually six separate cases) is presented in Table 1. Conditions for this case are the numerical values of Fig. 1 and continuous injection of tritiated water into each compartment separately. The equations were solved to determine the

TABLE 1. RELATIVE CONTRIBUTION TO GLOBAL COLLECTIVE DOSE AS A
FUNCTION OF DISCHARGE MODE FOR TRITIATED WATER RELEASES.

COMPARTMENT OF TRITIUM DISCHARGE	RELATIVE COLLECTIVE GLOBAL DOSE TO MAN AFTER CONTINUOUS DISCHARGE FOR:			
	1 YEAR	25 YEARS	50 YEARS	100 YEARS
Atmosphere	0.1	0.2	0.2	0.2
Vadose water	0.3	0.4	0.4	0.4
Deep groundwater	0.002	0.03	0.03	0.04
Surface waters	1.0	1.0	1.0	1.0
Ocean surface (75m)	0.001	0.01	0.02	0.02
Deep ocean	5×10^{-7}	0.0002	0.0003	0.0003

relative fraction of tritiated water present in man's compartment at the end of 1, 25, 50 and 100 years as a function of the compartment of injection. It is seen that by the end of 25 years equilibrium is essentially attained in man's compartment regardless of the compartment of injection. Additionally, the potential dose to man varies substantially depending on the compartment into which the tritiated water is released.

In order to determine the sensitivity of the results to those transfer rates which are known with the least precision, a set of cases was run for two likely compartments of release, atmospheric and surface water. The results are listed in Table 2. Upon changing the exchange rate between vadose and deep ground water by an order of magnitude, the resultant fraction of tritium in man registers only a small change for releases to the atmosphere and none for releases to surface waters. Eriksson⁵ suggests that the total transfer of tritium from the atmosphere to the ocean is 2.5 times the actual rainfall due to vapor exchange; considering this in the model changes the fraction in man by a factor of two for atmospheric releases but for surface water releases the fraction is unchanged.

For the case of gaseous tritium releases, the principal uncertainty is the rate of conversion to tritiated water vapor. Doury⁶, using the laboratory data of Yang and Gevantman⁷, has suggested an isotopic exchange rate half-time of between 3 weeks and one year. This data, however, was taken at high tritium concentrations for environmental considerations (0.05 to 0.7 curies/liter); the isotopic exchange rate measured in inert atmospheres is considered to be a second order rate.

TABLE 2. RELATIVE FRACTION OF TRITIUM IN MAN'S COMPARTMENT AFTER 25 YEARS OF CONTINUOUS TRITIUM INJECTION INTO THE ATMOSPHERE AND SURFACE WATERS.

CONDITIONS	ATMOSPHERE	SURFACE WATERS
	($\times 10^{-8}$)	($\times 10^{-8}$)
	Tritiated Water Vapor	Tritiated Water
1. Base Case	3.4	21.
2. Vadose $\rightarrow$ Deep Ground, Rate Increased $\times 10$	2.1	20.
3. Vadose $\rightarrow$ Deep Ground, Rate Decreased $\times 10$	3.9	21.
4. Total Ocean Vapor Exchange = Base Case Rainfall Increased $\times 2.5$	1.7	20.
	Tritium Gas	
5a. Half-Life HT $\rightarrow$ HTO 1 yr	3.0	
5b. Half-Life HT $\rightarrow$ HTO 10 yr	1.4	
5c. Half-Life HT $\rightarrow$ HTO 100 yr	0.21	
6. 4 + 5a	1.5	

Eakins and Hutchinson⁸ have made laboratory measurements of conversion half-times on the order of 4.2×10^5 days. Once again the reaction was second order and was determined in moist air with an initial tritium concentration of 3.4×10^{-5} curies/liter. Data collected over a period of 10 hours after the tritium gas release from the Savannah River Plant on May 2, 1974⁹ indicate that, for some parts of the plume, a possible lower limit for the tritium conversion half-time may be less than one day. The concentrations of tritiated gas at sample points ranged from 8.0×10^{-15} to 3.9×10^{-10} curies/liter. However, for much of the data presented, the tritium concentrations appear to be within the normal range of monitoring point values, hence the data must be used with caution.

Four cases were run for uniform releases of tritium gas into the atmosphere. There is only a factor of two difference in dose to man for conversion half-times of one or ten years. From case 6, inclusion of atmosphere-ocean vapor exchange only affects the resultant dose commitment to man by a factor of two.

From the data presented, several observations may be made:

- (1) The potential dose to man resulting from releases of tritium to surface waters is not significantly affected by small errors in compartment sizes or transfer rates.
- (2) For the most likely situation, that of case 4, releases of tritiated water to the atmosphere give rise to a factor of 10 less dose to man than releases into surface waters.
- (3) For tritium gas conversion half-times of up to 10 years, there is little difference in potential dose to man for atmospheric releases of tritiated gas or tritiated water.

In conclusion, it must be noted that the results presented are based on a simple global model assuming uniform and continuous discharges of tritium into the environment; the real situation is, of course, much more complex. However, the results based on the model appear to warrant that more sophisticated analyses be performed in order to properly substantiate a sound tritium release strategy.

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TRITIUM IN SURFACE WATER AFFECTED BY NUCLEAR FACILITIES

JULY 1973 - JULY 1975

Ann B. Strong, Imogene G. Brooks

Eastern Environmental Radiation Facility, EPA

ABSTRACT

Surface waters at 55 locations in the United States are currently being monitored for tritium as part of EPA's Environmental Radiation Ambient Monitoring System (ERAMS). The program is operated by the Office of Radiation Program's Eastern Environmental Radiation Facility (EERF) in Montgomery, Alabama. Sites covered include downstream locations from all of the nuclear power plants scheduled to become operational by 1978 as well as various AEC-ERDA facilities and national laboratories. The network has expanded from 10 sites in 1964 when it was operated by the U. S. Public Health Service to the present number in 1973. Grab samples are collected quarterly and sent to the EERF for analysis. This program was designed to provide ambient tritium concentrations as affected by various nuclear facilities. Without the contribution from these sources, activity levels resulting from fallout and cosmic radiation would probably be below normal detection limits of 0.2 nCi/l in most cases. Approximately 70% of the stations have detectable activity concentrations. The most significant influences noted by this monitoring system have been in samples collected from (1) the Clinch River in Kingston, Tennessee, attributed to the Oak Ridge National Laboratory, (2) the Savannah River in Allendale, South Carolina, attributed to the Savannah River Plant, (3) Lake Robinson at Hartsville, South Carolina attributed to the H. B. Robinson Nuclear Power Plant, and (4) Humboldt Bay in Eureka, California, attributed to the Humboldt Bay Power Plant. Even at these locations estimated dose equivalents to the population have not exceeded one percent of the Radiation Protection Guide of 170 mrem/year for an average population dose. Data collected from these stations from July 1973 to July 1975 are summarized.

INTRODUCTION

As early as 1964, a tritium sampling network was established by the Public Health Service to measure the levels of tritium in surface waters of the United States that were influenced by nuclear facilities.¹ Eight of the nine rivers being sampled at that time are continuing to be sampled today by the Environmental Protection Agency's radiation monitoring system. ERAMS, as the agency's Environmental Radiation Ambient Monitoring System is called, currently monitors the nation's surface waters at 55 locations. Downstream locations from all nuclear power reactors scheduled for operation by 1978 are covered.² AEC-ERDA-NRC facilities such as Oak Ridge, the Savannah River Plant, and Hanford are also monitored.

ERAMS is operated by the EPA at the Office of Radiation Program's Eastern Environmental Radiation Facility in Montgomery, Alabama.

TRITIUM SAMPLING

The program has been operating on its current status since July 1973. Figure 1 shows the sampling locations with respect to the nuclear facilities under surveillance. Note that this is an ambient monitoring system whose purpose is to denote changes with respect to the environment and the population affected rather than a specific source monitoring program. Drinking water samples from 77 sites and precipitation samples from 21 sites are also monitored for tritium as part of the comprehensive ERAMS program.

TRITIUM ANALYSIS

Grab samples are collected quarterly and shipped in disposable polyethylene cubitainers to the EERF for analysis. All samples are distilled and counted by liquid scintillation using an emulsion cocktail.³ Ten ml of water are mixed with 15 ml of cocktail for counting at room temperature. The background count of our instruments is usually 8-10 cpm with a 23% efficiency. Thus our minimum detectable concentration using this procedure is slightly less than 0.2 nCi/l for 100 minute counting times. Data from this program were presented in

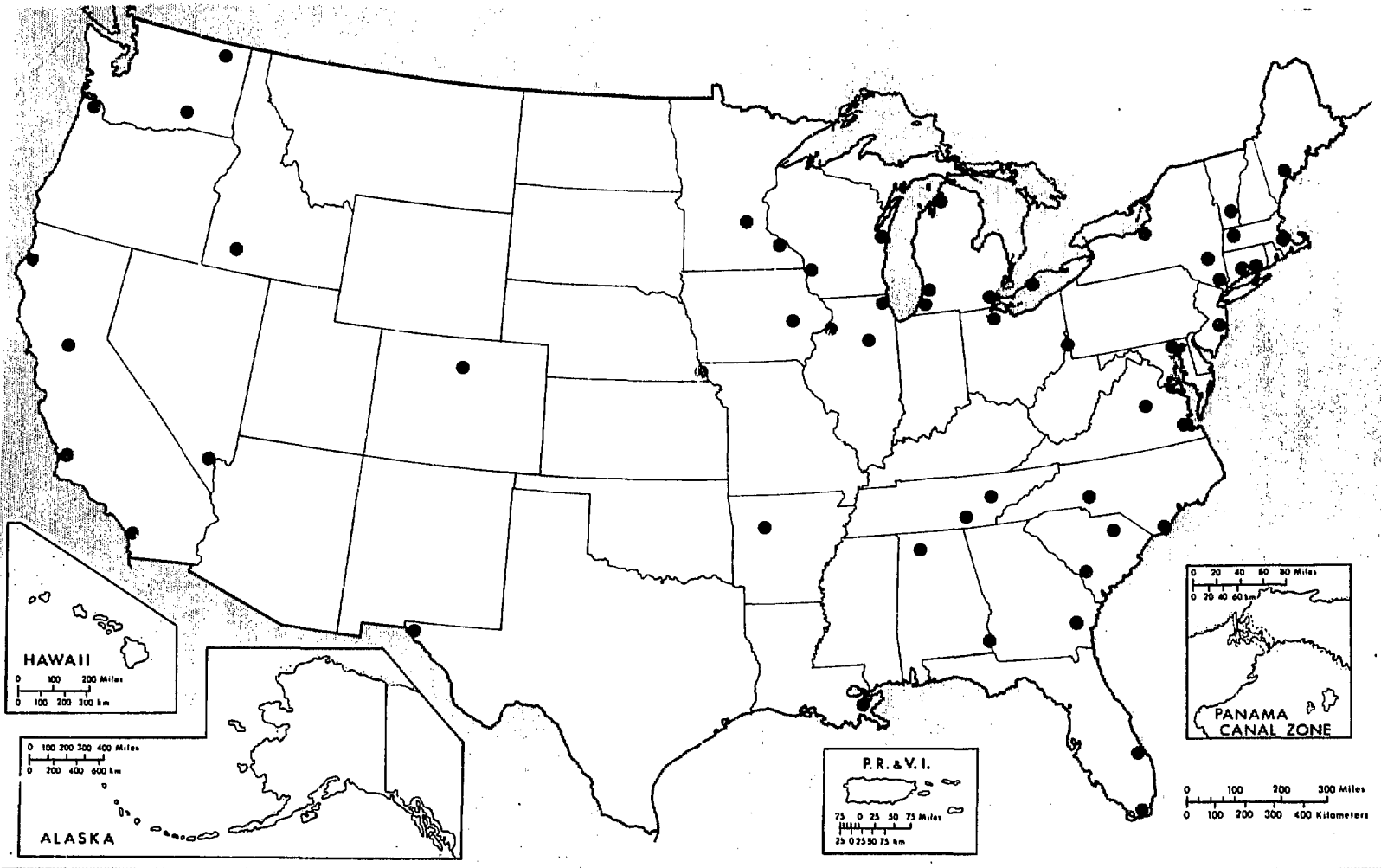


Fig. 1. ERAMS Surface Water Sampling Sites

Radiation Data and Reports until publication was discontinued in December 1974. Currently results are being made available in a report series from the EERF entitled Environmental Radiation Data.

RESULTS

A summary of the tritium data from July 1973 through July 1975 is presented in Table 1. Since the ultimate purpose of most all monitoring programs is to evaluate the effect of contaminants on man, dose estimates were made as follows:

DE (mrem/yr) = 0.1 QC (nCi/l) when Q is 1.0 as recommended by ICRP⁴.

Thus the DE value in mrem/yr may be represented as 0.1 of the concentration in nCi/l. Based on this calculation, the average DE did not exceed 0.04% of the Radiation Protection guide value of 170-mrem/yr for the time period covered.

Table 2 shows how the values for the highest level stations and background locations compared to the average. Note the large fluctuations in the elevated locations indicating discharges from the nuclear facilities in the area.

Without the influence of these facilities it is probable that all or nearly all of these samples would be at or below our minimum detectable concentration of 0.2 nCi/l.

As might be expected, the highest concentrations were most consistently noted downstream from the large ERDA National Laboratory Facilities where experimental work is being performed. The exception to this is the sampling location at Eureka, California, near Humboldt Bay Nuclear Power Reactor. In contrast to the others, samples from this site are usually collected only when waste is being released into the Bay.

Activity levels near Oak Ridge and the Savannah River Plant are generally decreased since the inception of the sampling program in 1964 when levels frequently exceeded 30 nCi/l.

Table 1. Tritium in Surface Water Averages and Dose Estimates

	7-9 1973	10-12 1973	1-3 1974	4-6 1974	7-9 1974	10-12 1974	1-3 1975	4-6 1975	7-9 1975
Network Average nCi/l (# samples)	0.45 (43)	0.68 (44)	0.48 (50)	0.63 (52)	0.48 (51)	0.40 (53)	0.38 (50)	0.36 (53)	0.31 (47)
Percentages Containing Detectable Levels of Activity ≥ 0.2 nCi/l	81%	73%	62%	71%	65%	68%	64%	64%	68%
DE (mrem/yr)	0.045	0.068	0.048	0.063	0.048	0.040	0.038	0.036	0.031

Table 2. Tritium in Surface Water Selected Stations (nCi/l)

River Location Nuclear Facility	7-12 1973	10-12 1973	1-3 1974	4-6 1974	7-9 1974	10-12 1974	1-3 1975	4-6 1975	7-9 1975
Clinch River Kingston, TN Oak Ridge	1.0 ± 0.2	2.4 ± 0.3	1.1 ± 0.2	2.6 ± 0.3	0.4 ± 0.2	0.5 ± 0.2	2.6 ± 0.2	0.3 ± 0.2	0.3 ± 0.2
Savannah River Allendale, SC Savannah River Plant	4.8 ± 0.3	9.4 ± 0.4	4.0 ± 0.2	5.2 ± 0.3	5.9 ± 0.3	4.2 ± 0.3	2.6 ± 0.2	2.2 ± 0.2	2.6 ± 0.2
Lake Robinson Hartsville, SC H. B. Robinson Nuclear Power Plant	0.7 ± 0.2	< 0.2	3.2 ± 0.3	2.5 ± 0.2	< 0.2	2.7 ± 0.2	3.3 ± 0.2	2.2 ± 0.2	1.4 ± 0.2
Humboldt Bay Eureka, CA Humboldt Bay Power Plant	No sample	No sample	4.9 ± 0.3	7.5 ± 0.3	5.0 ± 0.2	No sample	No sample	No sample	0.3 ± 0.2
Deerfield River Rowe, MA Yankee Nuclear Power	0.3 ± 0.2	4.7 ± 0.3	< 0.2	1.7 ± 0.2	< 0.2	0.2 ± 0.2	0.3 ± 0.2	< 0.2	No sample
Hudson River Poughkeepsie, NY Background	0.3 ± 0.2	< 0.2	< 0.2	< 0.2	0.3 ± 0.2	0.2 ± 0.2	0.2 ± 0.2	0.2 ± 0.2	0.2 ± 0.2

Table 3 summarizes the average tritium concentrations for each of the sampling stations for the time period covered in this report. Probability plots of these data show that the distribution is best described as log-normal distribution.

SUMMARY

Although this program is operated on a grab sample basis, general trends are observed, fluctuations are noted, and estimates can be made of the effect of nuclear facilities on the ambient radiation environment. This independent evaluation of tritium levels allows dose estimates to be calculated for general population exposure and provides a wide data base for environmental comparisons.

Table 3. . ERAMS Average Tritium Concentrations (Surface Water)

July 1973 - July 1975

Station Location	Water Source	Facility	Station Avg. T ₃ (nCi/l)
AL:Decatur	Tennessee River	Browns Ferry	0.3
Gordon	Chattahoochee River	Joseph M. Farley	0.2
AR:Little Rock	Arkansas River	Arkansas Nuclear	< 0.2
CA:Clay Station	Folsom S. Canal	Rancho Seco	< 0.2
Diablo Canyon	Pacific Ocean	Diablo Canyon	< 0.2
Eureka	Humboldt Bay	Humboldt Bay	4.4
San Onofre	Pacific Ocean	San Onofre	< 0.2
CO:Greeley	South Platte River	Fort St. Vrain	0.6
CT:East Haddam	Connecticut River	Connecticut Yankee & Vermont Yankee	0.4
Waterford	Long Island Sound	Millstone	< 0.2
FL:Crystal River	Gulf of Mexico	Crystal River	< 0.2
Ft. Pierce	Atlantic Ocean	Hutchinson Island	< 0.2
Homestead	Biscayne Bay	Turkey Point	0.5
GA:Baxley	Altamaha River	Edwin I. Hatch	0.4
ID:Buhl	Snake River	National Reactor Testing Station	0.3
IL:Moline	Mississippi River	Quad-Cities	0.3
Morris	Illinois River	Dresden & Argonne	0.3
Zion	Lake Michigan	Zion	0.3
IA:Cedar Rapids	Cedar River	Duane Arnold	0.4
LA:New Orleans	Mississippi River	(Several)	0.2
ME:Wiscasset	Montseway Bay	Maine Yankee	0.2
MD:Conowingo	Susquehanna River	Peach Bottom & Three Mile Island	0.3
Lusby	Chesapeake Bay	Calvert Cliffs	< 0.2
MA:Plymouth	Cape Cod Bay	Pilgrim	0.2
Rowe	Deerfield River	Yankee	0.9
MI:Bridgman	Lake Michigan	Donald C. Cook	0.3
Charlevoix	Lake Michigan	Big Rock Point	0.3
Monroe	Lake Erie	Enrico Fermi	0.4
South Haven	Lake Michigan	Palidades	0.3
MN:Monticello	Mississippi River	Monticello	0.5
Red Wing	Mississippi River	Prairie Island	0.3
NE:Rulo	Missouri River	Fort Calhoun & Cooper	0.0
NV:Boulder City	Colorado River	Background	0.6

Table 3. (Continued)

Station Location	Water Source	Facility	Station Avg. ³ H (nCi/l)
NJ:Dayside	Delaware River	Salem	< 0.2
Oyster Creek	Toms River	Oyster Creek	< 0.2
NY:Ossining	Hudson River	Indian Point	< 0.2
Oswego	Lake Ontario	Nine Mile Point & R. E. Ginna	0.4
Poughkeepsie	Hudson River	Background	< 0.2
NC:Charlotte	Catawba River	Wm. B. McGuire	0.3
Southport	Atlantic Ocean	Brunswick	< 0.2
OH:Toledo	Lake Erie	David-Besse	No sample
OR:Westport	Columbia River	Trojan & Hanford	0.2
SC:Allendale	Savannah River	Savannah River Plant & Oconee	4.5
Hartsville	Lake Robinson	H. B. Robinson	2.4
TN:Daisy	Tennessee River	Sequoyah	0.3
Kingston	Clinch River	Oak Ridge	1.2
TX:El Paso	Rio Grande	Los Alamos	0.2
VT:Vernon	Connecticut River	Vermont Yankee	0.2
VA:Mineral	North Anna River	North Anna	0.2
Newport News	James River	Surry	0.2
WA:Northport	Columbia River	Background	0.4
Richland	Columbia River	Hanford	0.5
WV:Wheeling	Ohio River	Shippingport	0.2
WI:Two Creeks	Lake Michigan	Point Beach & Kewaunee	0.4
Victory	Mississippi River	Genoa & Prairie	0.3

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FIXATION AND LONG-TERM ACCUMULATION OF
TRITIUM FROM TRITIATED WATER IN AN
EXPERIMENTAL AQUATIC ENVIRONMENT

J. A. Strand

W. L. Templeton

P. A. Olson*

Battelle, Pacific Northwest Laboratories
Richland, Washington 99352

ABSTRACT

The accumulation of tritium in selected freshwater biota was studied in a 10 m diameter concrete-lined pond at the U.S. E.R.D.A. Hanford Project. Tritium as tritiated water was introduced for 8 months continuously in the replacement water at a concentration of 1 μCi per liter; and water, biota (carp, clams, crayfish, periphyton, pondweed), and sediments were sampled on a predetermined schedule. The pond was maintained on uncontaminated replacement waters for an additional eight months to determine the rate of elimination from the ecosystem.

After the first day, tissue-free-water tritium in all biota approached an equilibrium with pond water. Final concentration factors of 0.89, 0.87, 0.82, 0.92, 0.77, and 0.32 were calculated for carp, clam, crayfish, snail, periphyton, and pondweed. Although highly variable, analyses of pond sediments suggested an initial rapid uptake by the loose water fraction, attaining 0.30 of the pond equilibrium level in three days. There was evidence to suggest a secondary slower rate of uptake that accounted for 0.65 of the pond equilibrium level as determined at seven months.

Tissue-bound tritium initially increased rapidly in all biota sampled but slowed with time. Equilibrium conditions were not reached. Final concentration factors for carp, clam, crayfish, snail, periphyton, and pondweed were calculated to be 0.49, 0.10, 0.53, 0.54, 0.15, and 0.62. Analyses of sediments after removal of the loose water fraction revealed little or no organically bound tritium.

Loss of tritium from pond waters occurred exponentially with time with less than 10% of the final equilibrium concentration remaining after the first month. Rate of loss of tritium from both animal and plant species was also rapid, with animal forms generally eliminating their respective tritium burdens more rapidly than plant forms. Sediments tended to lose tritium more slowly.

*Deceased

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After the first day, tissue-free-water tritium in all biota approached an equilibrium with pond water. Final concentration factors of 0.89, 0.87, 0.82, 0.92, 0.77, and 0.88 were calculated for carp, clam, crayfish, snail, periphyton, and pondweed. Although highly variable, analyses of pond sediments suggested an initial rapid uptake by the loose water fraction, attaining 0.30 of the pond equilibrium level in three days. There was evidence to suggest a secondary slower rate of uptake that accounted for 0.65 of the pond equilibrium level as determined at seven months.

Tissue-bound tritium initially increased rapidly in all biota sampled but slowed with time. Equilibrium conditions were not reached. Final concentration factors for carp, clam, crayfish, snail, periphyton, and pondweed were calculated to be 0.49, 0.10, 0.53, 0.54, 0.15, and 0.62. Analyses of sediments after removal of the loose water fraction revealed little or no organically bound tritium.

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*Deceased

INTRODUCTION

The accumulation of tritium as tritiated water into mammalian tissues has been well studied. The subject has recently been reviewed by Woodward¹ and Bond². However, relatively little information is available with respect to accumulation of tritium in aquatic organisms. The data are limited to those of Foster³, Skauen⁴, Koranda⁵, Elwood⁶, Harrison and Koranda⁷, Rosenthal and Stewart⁸, Stewart et al.⁹, Strand et al.¹⁰, and Harrison et al.¹¹.

Most such investigations have embraced acute exposures conducted over relatively short time periods. Other studies have followed a single injection of tritium which has served to simulate an accidental release from a nuclear reactor or other nuclear facility. However, in no known situation have similar studies been conducted under conditions of protracted exposure, thus, simulating the routine releases of tritium from a nuclear reactor or other nuclear installation.

It is generally agreed that incorporation of tritium into the tissue-free-water of aquatic organisms occurs at a rate corresponding to a half-time of less than 1 hour. After several hours exposure, the tritium concentration of the tissue-free water amounts to 90% of that of environmental water. However, it is known from studies of mammalian systems, slower turnover components are characteristic of tritium elimination (Thompson, 12,13). Certain tissue components have demonstrated half-times to 100 of 300 days. As well, under chronic conditions, there may occur greater organic binding which could result in overall slower turnover rates. Under sustained equilibrium conditions, this could result in higher concentrations and hence, higher radiation exposures than would be predicted from water concentrations alone.

Information pertaining to this subject is desired in light of current practices and future intent to utilize more extensively water-borne animals and plants as food resources. With increasing application of nuclear energy, there exists a distinct possibility that contamination of surface waters by radioactive materials will increase with clear potential for harmful interactions with inherent biological systems. This may be parti-

cularly true for advanced reactor designs such as CTR (Controlled Thermonuclear Reactor), where there is opportunity for escapement of tritium in both gaseous and liquid effluents in quantities significantly greater than for PWR (Pressurized Water Reactor) or BWR (Boiling Water Reactor) designs.

Accordingly, it was the objective of this investigation to follow the uptake of tritium in the tissue-free-water and tissue-bound fractions of aquatic organisms in a simulated freshwater ecosystem. Tritium as tritiated water was introduced continuously for eight months in replacement waters at a concentration of 1 $\mu\text{Ci/liter}$. At termination of the uptake phase of the experiment, additional data were sought on elimination of tritium from the ecosystem. Freshwater fish, clams, and crayfish served as principal test organisms as they represent sources of food utilized by man.

MATERIALS AND METHODS

A 10 m diameter concrete-lined pond located at the U.S.E.R.D.A. Hanford Project, Richland, Washington was used in the present study. A standpipe outlet located centrally maintained a constant depth of 0.6 m, and a constant volume of 3.0×10^4 liters. Columbia River water entered the pond peripherally at a rate of 8 liters/min.

Approximately 6 m³ of Columbia River sand, gravel, and rocks were introduced four weeks prior to beginning the experiment. At two weeks before the scheduled start-up, the pond was stocked with 60 carp, Cyprinus carpio, 60 crayfish, Pacifastacus trowbridgi, 60 clams, Anodonta californiensis, and an undetermined quantity of pondweed, Potamogeton spp. Snails, Lymnaea spp. and periphyton were recruited naturally from Columbia River waters.

Initially, 30 mCi of tritium as tritiated water were dispersed over the surface of the pond, the surface agitated to insure complete mixing. Thereafter, tritium was introduced continuously for a period of eight months in the replacement water at a concentration of 1.0 $\mu\text{Ci/liter}$. On a predetermined schedule (0, 1, 2, 3 days; 1 week; 1, 3, 5, and 7 months)

samples of water, biota, and sediments were analyzed for tritium.

Three 1 liter water samples were collected from the periphery of the pond at each sampling interval. Three 10 g sediment samples were also collected at the same location. Each replicate of water and sediment samples provided 5 subsamples for analysis.

The fish (mean weight 8.2 g) were prepared for analysis by dissecting-out samples (< 0.5 g) of their lateral muscle masses. Crayfish (average weight 5.4 g) were prepared by first removing the shell and then dissecting-out samples (< 0.5 g) of their abdominal muscles. Clams (mean weight 128 g) were prepared by first removing the shell and then dissecting-out samples (< 0.5 g) of their adductor muscles. No less than three replicates of each species were collected at each sampling interval, each replicate providing five subsamples for analysis.

The samples of pond water were analyzed for tritium by adding 0.1 ml of the aqueous sample to 19.9 ml of a liquid scintillation solution.

Tissue-free-water tritium was extracted in a model 300 Tri-Carb Sample Oxidizer (Packard Instrument Corp., Inc., Downers Groves, Illinois). Each tissue sample was placed within the oxidizer unit and subjected to an instrument heat of 200°C. A low flow of H_2 gas was used to sweep the evolved volatile tritium fraction into a liquid scintillation solution. This procedure was carried out for a period of 45 minutes. The loose water of sediment samples was determined similarly.

At the end of 45 min, a fresh scintillation vial was emplaced in the oxidizer unit and the residue of the tissue was combusted in an oxygen stream to obtain the tissue-bound tritium fraction. The water of combustion was trapped directly by the liquid scintillation solution. The same procedure was conducted for determination of organically bound tritium of sediments.

A liquid scintillation solution prepared by dissolving 100 g of Naphthalene, 5 g PPO, 0.2 g POPOP in a mixture of 720 ml of dioxane, 135 ml toluene, and 45 ml methanol was used for all analyses. Counting of samples was conducted on a Mark II liquid scintillation system (Nuclear-

Chicago Corp., Des Plaines, Illinois).

The pond was maintained on uncontaminated Columbia River water for an additional eight months to determine the rate of elimination of tritium from the ecosystem. On a predetermined schedule (1, 3, 4, and 8 months) water, biota and sediments were sampled and analyzed as before.

RESULTS

As shown in Figure 1, after the first day, tissue-free-water tritium in all biota approached an equilibrium with pond water.

Although highly variable, analyses of pond sediments in Table 1 revealed an initial rapid uptake by the loose water fraction, attaining 0.30 of the pond equilibrium level in three days. There was also observed evidence to suggest a secondary slower rate of uptake that accounted for 0.05 of the pond equilibrium level as determined at seven months.

As shown in Figures 2 and 3, tissue-bound tritium increased rapidly in all biota sampled, but slowed with time. Of the animal forms, highest values were found in crayfish and snail. Pondweed consistently demonstrated higher values than periphyton.

Analyses of sediments after removal of the loose water fraction revealed little or no organically bound tritium.

Upon termination of the uptake experiment, loss of tritium from pond water occurred exponentially with less than ten percent of the initial concentration remaining after the first month. As shown in Figures 4 and 5, rate of loss of tritium from both animal and plant species was also rapid, with animal forms generally eliminating their respective tritium burdens more rapidly than the plant forms. As shown in Table 1, sediments tended to eliminate tritium more slowly.

DISCUSSION AND CONCLUSIONS

The concentration of the tissue-free-water tritium rapidly approached that of the pond indicating a rapid exchange between tissue and pond water. Final concentration factors of 0.89, 0.87, 0.82, 0.92, 0.77 and 0.88 were

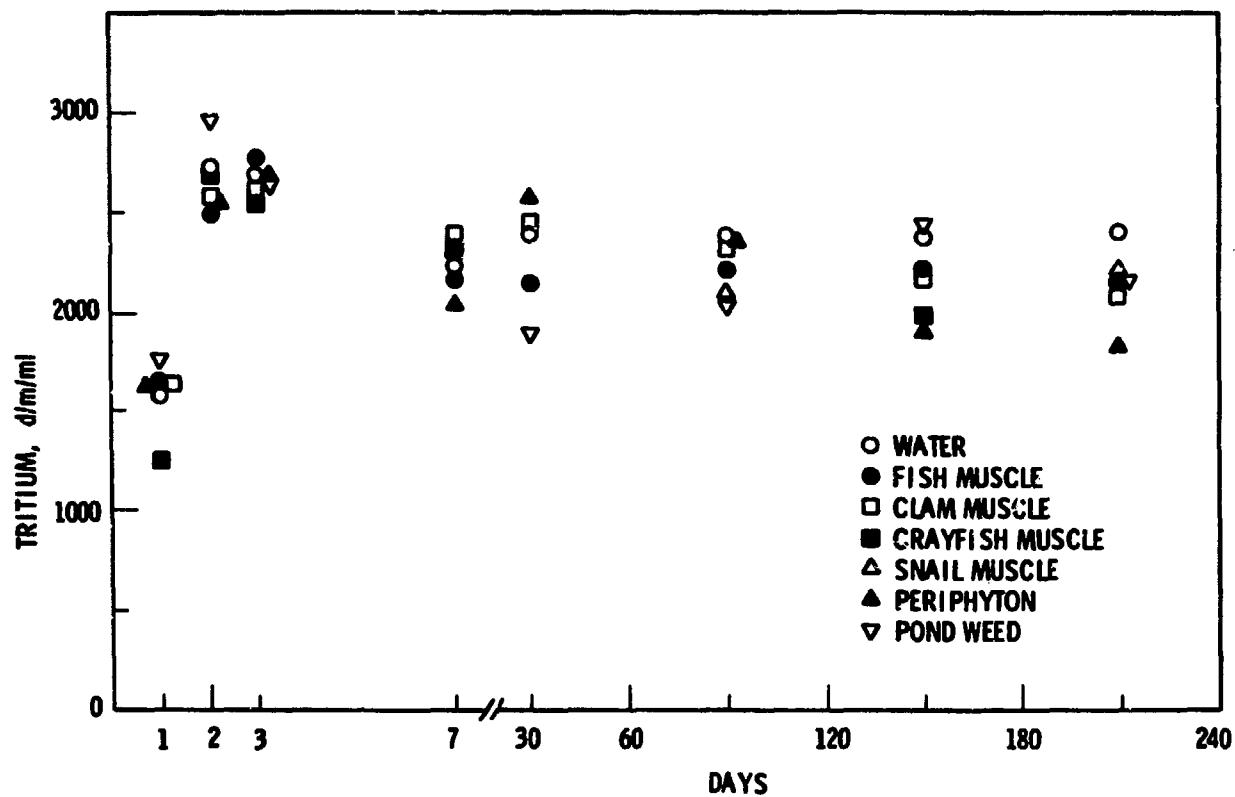


Fig. 1. Mean Tritium Concentrations in the Tissue-Free Water Fraction of Test Organisms.

Table 1. Tritium Concentrations in Pond Sediments

Time in Days	Ambient Water d/min/ml $\pm$ S.D.	Loose Water d/min/ml $\pm$ S.D.
1	1600 $\pm$ 168	442 $\pm$ 142
2	2719 $\pm$ 770	809 $\pm$ 144
3	2713 $\pm$ 718	792 $\pm$ 151
7	2326 $\pm$ 97	477 $\pm$ 169
30	2405 $\pm$ 39	479 $\pm$ 198
210	2425 $\pm$ 54	1568 $\pm$ 524
120 ^a	13 $\pm$ 1	678 $\pm$ 325
240 ^a	18 $\pm$ 5	21 $\pm$ 3

^aElimination phase.

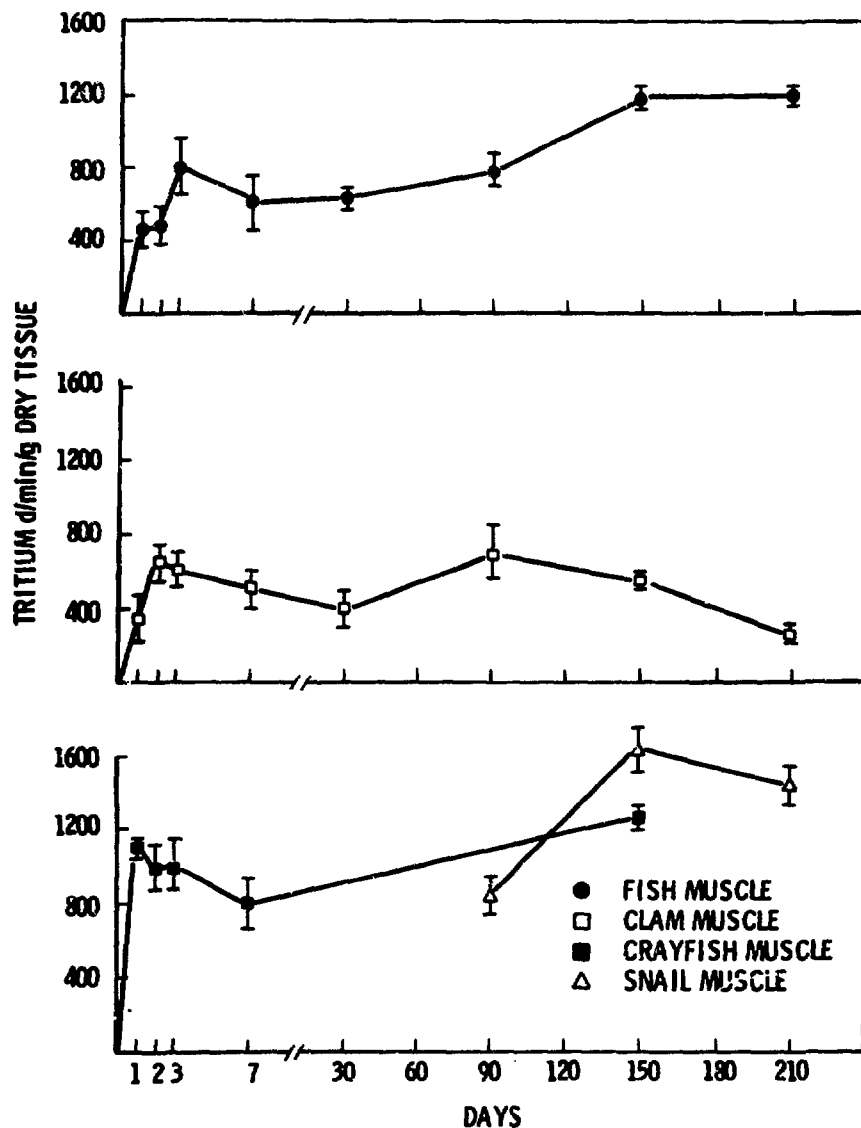


Fig. 2. Mean Tritium Concentrations in the Tissue-Bound Fraction (± 1 standard deviation) of Fish, Clam, Crayfish, and Snail.

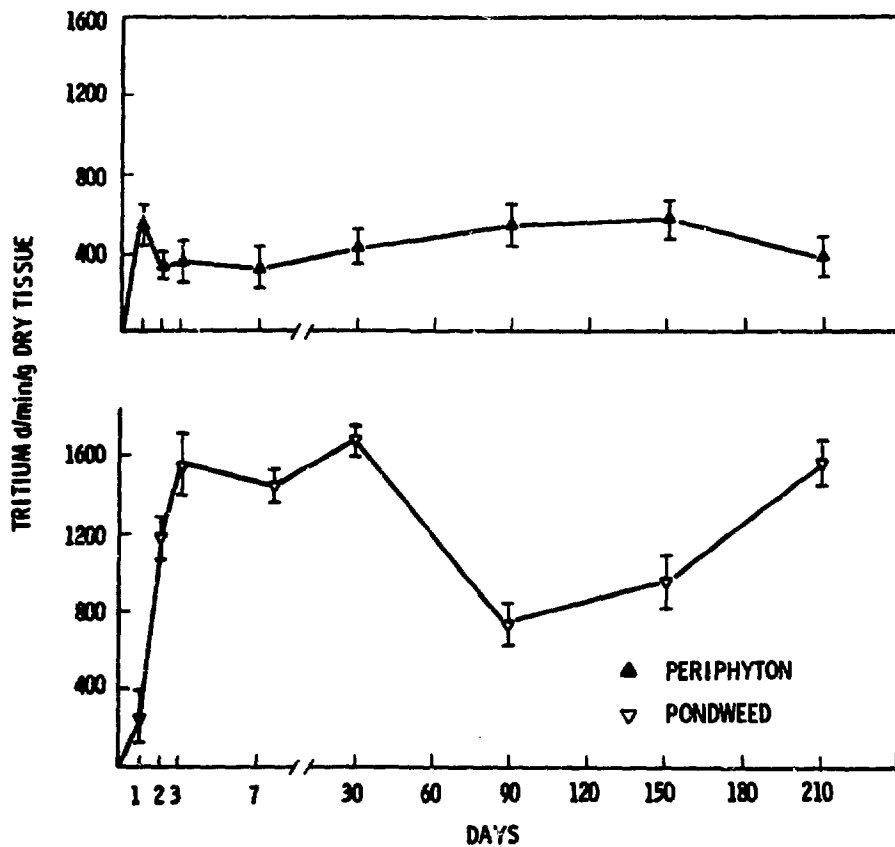


Fig. 3. Mean Tritium Concentrations in the Tissue-Bound Fraction (± 1 standard deviation) of Periphyton and Pondweed.

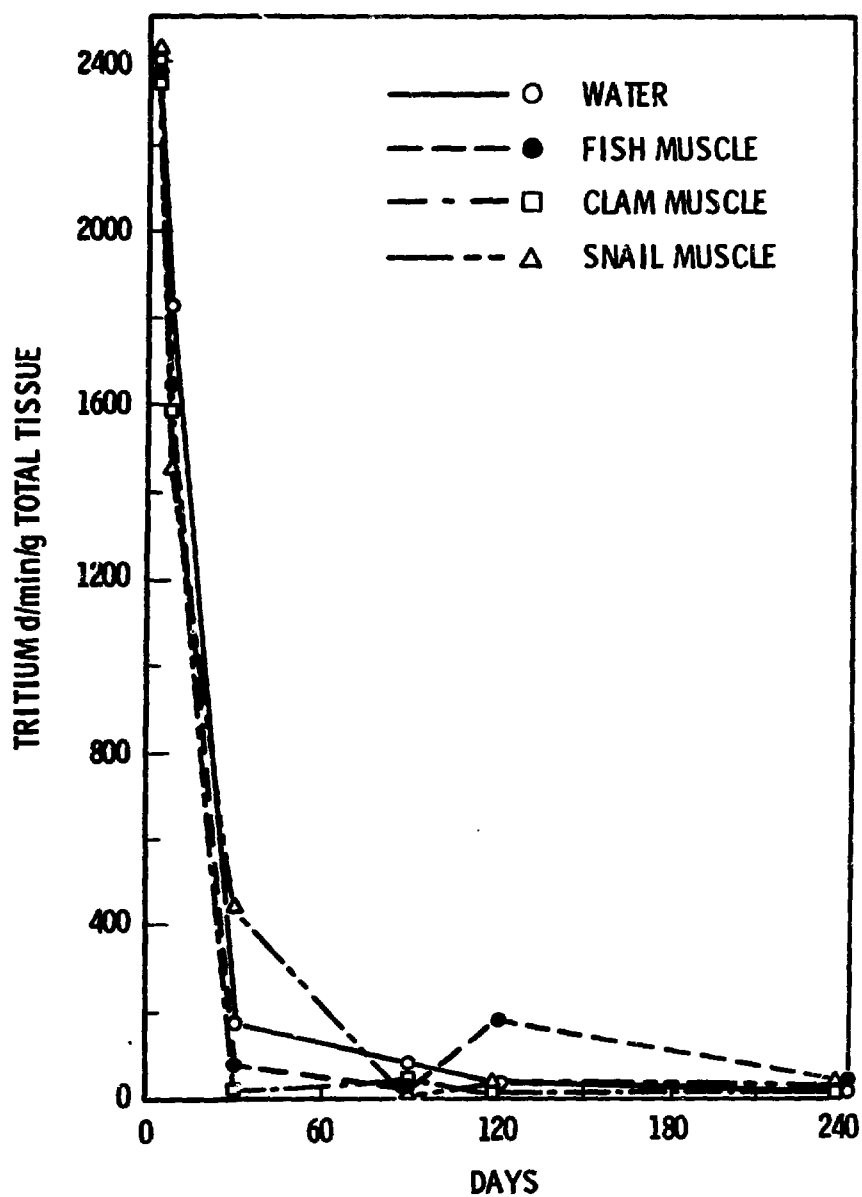


Fig. 4. Elimination of Tritium from Fish, Clam, and Snail.

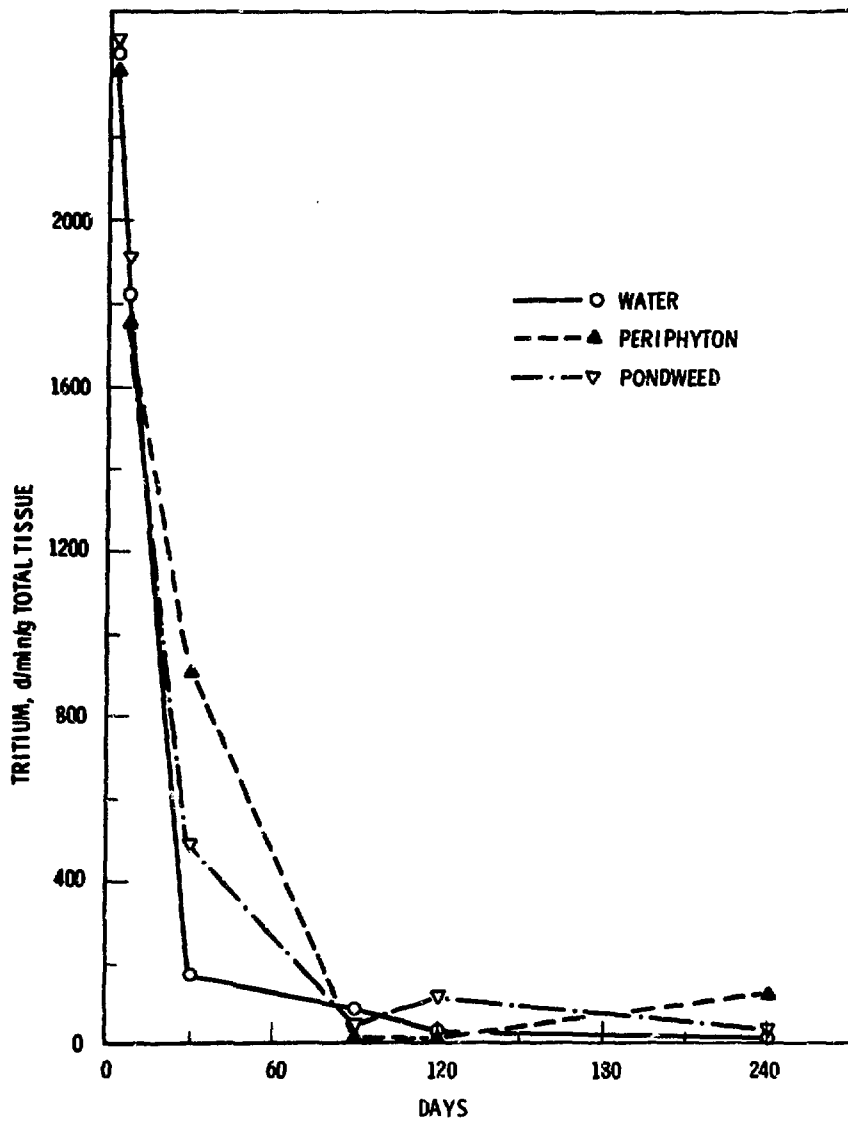


Fig. 5. Elimination of Tritium from Periphyton and Pondweed.

calculated for carp, clam, crayfish, snail, periphyton, and pondweed respectively; and are in good agreement with the results of Elwood⁶, Harrison and Koranda⁷, Rosenthal and Stewart⁸, Stewart et al.⁹, and Harrison et al.¹¹.

The concentration of tissue-bound tritium was initially observed to increase rapidly, but slowed with time. Equilibrium conditions were not reached. Final concentration factors for carp, clam, crayfish, snail, periphyton, and pondweed were calculated to be 0.49, 0.10, 0.53, 0.54, 0.15, and 0.62. Elwood⁶, Rosenthal and Stewart⁸, Harrison and Koranda⁹, and Harrison et al.¹¹ also found a marked discrimination against incorporation of tritium into organic molecules and attributed their findings to the availability of less hydrogen per unit weight of tissue as compared to an equal weight of water, and there occurred less sites in the tissue-bound fraction for exchange. Additionally, Thompson^{12,13} reported exchange rates to be significantly slower for tissue-bound hydrogen than for tissue-free-water hydrogen.

With certain assumptions, specific activity is a true indication of an organism's demand from the environment and is a useful index in predicting the accumulation of an element by an organism. In the present context, specific activity is a convenient measure of the degree of tritiation of organisms in the pond. For this exercise, values of hydrogen content for carp, clam, crayfish, snail, periphyton, and pondweed were obtained from the literature (Vinogradov¹⁴, Spector¹⁵, Harrison and Koranda⁹ and are shown in Table 2.

As in Table 3 in all biota sampled, the specific activities of the tissue-free-water tritium rapidly approached that of the pond and essentially remained at that level. Specific activities of the tissue-bound fractions, however, never reached that of the water with the exception of pondweed.

The ratio of the specific activities (tissue-bound tritium/tissue-free-water tritium) is another useful index in predicting the accumulation of an element by an organism, and here may serve to determine whether steady-state conditions of uptake and loss were reached. Results of this

Table 2. Percentage of Hydrogen in Dry Tissues of Aquatic Organisms

Tissue	Percent Hydrogen
Carp muscle	7.6
Clam muscle	6.8
Crayfish muscle	7.4
Snail muscle	6.3
Periphyton	3.8
Pondweed	5.2

Table 3. Specific Activities as d/min/g H for Carp, Clam, Crayfish, Snail, Periphyton and Pondweed Exposed to THO for Seven Months.

Tissue-Free-Water Tritium

	1 Day	2 Day	3 Day	1 Week	1 Month	3 Months	5 Months	7 Months
Carp	1.4×10^4	2.2×10^4	2.0×10^4	1.9×10^4	1.9×10^4	2.0×10^4	2.0×10^4	1.9×10^4
Clam	1.4×10^4	2.3×10^4	2.4×10^4	2.1×10^4	2.1×10^4	2.1×10^4	2.0×10^4	1.8×10^4
Crayfish	1.4×10^4	2.4×10^4	2.3×10^4	2.1×10^4	-	-	1.8×10^4	-
Snail	-	-	-	-	-	1.9×10^4	2.2×10^4	2.0×10^4
Periphyton	1.4×10^4	2.2×10^4	2.4×10^4	1.8×10^4	2.3×10^4	2.1×10^4	2.0×10^4	1.5×10^4
Pondweed	1.5×10^4	2.7×10^4	2.4×10^4	1.7×10^4	1.7×10^4	1.8×10^4	2.1×10^4	1.9×10^4
Pond Water	1.4×10^4	2.4×10^4	2.4×10^4	2.1×10^4	2.1×10^4	2.1×10^4	2.1×10^4	2.2×10^4

Tissue-Bound Tritium

Carp	6.2×10^3	6.4×10^3	1.0×10^4	7.7×10^3	8.2×10^3	1.0×10^4	1.6×10^4	1.5×10^4
Clam	5.6×10^3	1.0×10^4	1.0×10^4	7.0×10^3	5.8×10^3	1.0×10^4	6.7×10^3	3.7×10^3
Crayfish	1.4×10^4	1.3×10^4	1.3×10^4	1.0×10^4	-	-	1.7×10^4	-
Snail	-	-	-	-	-	1.3×10^4	2.7×10^4	2.0×10^4
Periphyton	1.4×10^4	8.3×10^3	8.8×10^3	8.1×10^3	1.0×10^4	1.4×10^4	1.5×10^4	9.8×10^3
Pondweed	4.7×10^3	2.2×10^4	2.9×10^4	2.6×10^4	3.2×10^4	1.3×10^4	1.8×10^4	2.8×10^4

exercise are shown in Table 4.

These results indicate a relatively slow rate of incorporation for clam as compared with carp, crayfish and snail; and a relatively slow rate of incorporation for periphyton as compared with pondweed.

The relatively high ratios for carp, crayfish, and snail may reflect an enhanced rate of accumulation attributable to intake of tritiated food-stuffs. Carp, crayfish and snail were observed to feed on periphyton and/or the detrital material associated with the decay of pondweed which had become tritiated during the course of the present exposure. Clams, however, derived their forage from relatively sparse planktonic constituents entering the pond in replacement waters. Koranda and Martin¹⁶, Evans¹⁷, and Rosenthal and Stewart⁸ have all suggested that exposure to organically bound tritium resulted in higher concentrations of tissue-bound tritium than if exposure occurs by water or tissue-free-water alone. The implication is made that tritium may increase above the second trophic level of food chains in a classical manner.

Pondweed increased in biomass significantly during the course of the experiment. Since the source of hydrogen for this organism was the pond water, it may be expected that the newly synthesized organic fractions would demonstrate a higher degree of tritiation. Harrison and Koranda⁷ recorded similar results and offered a similar explanation.

Sediment analyses, although highly variable, suggested a relatively slow rate of turnover between loose water and the overlaying pond water. The finding of low or negligible values for the bound fraction was likely attributable to the low organic content (< 2%) of the sediments employed.

Elimination of tritium burdens were the reverse of the rapid phase of uptake for organisms studied, which is in good agreement with results reported by Elwood⁶, Stewart et al.⁹, Strand et al.¹⁰, and Harrison and Koranda⁷. Generally animals demonstrated faster rates of elimination than plants. Tritium in sediments, however, appeared to turnover more slowly.

Table 4. The Ratio of TBT/TFWT for Carp, Clam, Crayfish, Snail, Periphyton and Pondweed Exposed to THO for Seven Months.

<u>Organism</u>	<u>TBT</u> <u>TFWT</u>
Carp	0.71
Clam	0.17
Crayfish	0.79
Snail	0.94
Periphyton	0.44
Pondweed	1.31

In summary, the experimental results reported herein are in good agreement with present understanding of the behavior of heavy hydrogen isotopes, and may be interpreted as indicating living organisms discriminate against tritium, as opposed to protium in biosynthetic reactions. Early accumulation of tritium is largely attributed to the more mobile HTO form, while final accumulation may be influenced by the intake of tritiated compounds as in the diet. Such results suggest that tritium may increase above the second trophic level of food chains in the classical way; however, because of demonstrated continued isotopic discrimination and rapid turnover rates, this response should not be significant.

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INCORPORATION OF TRITIUM FROM TRITIUM GAS INTO NUCLEOSIDES IN AQUEOUS SOLUTIONS

G. Stöcklin and F. Cacace

Institut für Chemie der Kernforschungsanlage Jülich GmbH
Institut 1: Nuklearchemie
D-5170 Jülich, FRG

ABSTRACT

In view of environmental and biological implications the decay induced incorporation of tritium from T_2 into nucleosides in aqueous solutions has been studied by means of chromatographic methods. It could be shown that at a tritium level of about 1 to 2 mCi/ml labelling of thymidine or deoxyuridine mainly occurs via the $^3\text{HeT}^+$ decay ion and not via β^- -radiolysis. In a saturated solution of thymidine only $8 \cdot 10^{-4}$ thymidine molecules are labelled per tritium decay (L-value), concomitantly 0.6 HTO molecules are also formed together with CH_3T ($L = 0.2$) and an unidentified organic product ($L = 10^{-3}$). Compared to identical tritium concentrations of HT and HTO in aqueous deoxyuridine solutions the labelling efficiency of T_2 is an order of magnitude higher.

INTRODUCTION

Tritium release from different types of nuclear activities is steadily increasing. At present the major sources are fission reactors in which the production occurs via (n,t) reactions on light nuclei as well as fission of heavier nuclei. Only a small fraction of the tritium produced is released during operation, the major part eventually during fuel reprocessing^{1,4}. Production in heavy water reactors currently creates the most serious operational problems. Future large

scale DT-thermonuclear fusion experiments will further increase the steady state concentration, and due to the high permeation rate of tritium through most materials, designers of fusion reactor plants will be confronted with a variety of problems associated with confinement of tritium. Attempts have been made²⁻⁴ to evaluate the relative environmental consequences of accidents associated with fission reactors vs. fusion reactors. Even though on a global scale this does not represent a serious problem, it is necessary from the safety point of view to restrict the total tritium inventory to specified levels since the principle radioactivity hazard of an accident would arise from volatile tritium.

Very little is known about the distribution of tritium in various chemical forms (HT, T₂, HTO) immediately after release from the different sources of tritium. The major fraction of tritium produced as HT or T₂ will eventually appear as HTO either via oxidation in air or by isotopic exchange. These processes, however, are very slow for molecular hydrogen unless they are catalyzed. This may in fact occur in the natural environment by surface reactions or by ionizing radiation. Tritium migrates through wall materials in atomic form, and it will depend on a variety of conditions, whether it recombines with another tritium atom when emerging on the other side of the wall or whether it will be picked up by an O₂ or H₂O molecule, in which case it will eventually end up as HTO. It has also been shown that β -radiation from tritium decay will initiate a reaction between tritium and oxygen⁵ or between hydrogen gas and water⁶. Ionizing radiation also promotes the exchange between isotopic hydrogen^{7,8}.

In any case, in a possible accident in DT-fusion experiments a large fraction of tritium will first appear as DT and T₂. It is interesting to note that this is also true for a DT-neutron generator⁹. Table 1 shows the distribution of tritium species released from a tritium target of a 14 MeV neutron generator during bombardment with 280 keV deuterons.

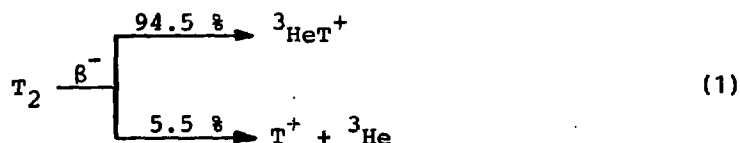
Table 1. Distribution of Tritium Species
Released from a Tritium Target of
a 14 MeV Neutron Generator^a

Product	Abundance (%)
HT	13.7
DT	17.0
T ₂	68.0
CH ₃ T	1.3

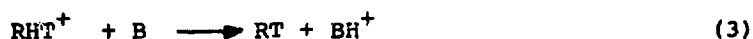
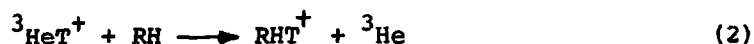
^a 900 μ A of 280 keV deuterons on a tritium target containing 85 Ci of tritium on titanium (H₂O cooled)

It can be seen that the major fraction (68 %) appears as T₂.

From these gaseous species, the T₂ is the most dangerous one, because its decay leads in about 95 % to the highly reactive ³HeT⁺ ion¹⁰:



The ³HeT⁺-ion is highly reactive ($\Delta H^\circ = 320$ kcal/mol) and it easily substitutes hydrogen in organic molecules RH¹¹:



Proton transfer (eq. 3) is carried out by any Lewis base (B)

or by the substrate itself or even the wall. Once the tritium atom has entered a biologically significant molecule such as the DNA or a precursor like thymidine it can cause damage when it decays, not only by β^- -radiolysis but also by the so called transmutation effects (for a review cf. citation ¹²). The β^- -decay gives rise to 3 major sources of excitation (for a review cf. citation ¹³):

1. β^- -Recoil
2. Shaking (electronic excitation)
3. Change of identity (cf. eq. 4).

If the tritium is bound to a carbon atom, the C- $^3\text{He}^+$ bond is almost invariably (70 - 90 %) ¹³ ruptured leaving a carbonium ion behind:



Transmutation effects and local β -radiolysis cause damage with functional implications. It is especially the genetic material, the DNA which is particularly sensitive, and the damage to this critical molecule essentially determines the biological effects. One of these effects is the breakage of DNA strand. Table 2 shows the probability for a strand breakage from ^3H -decay in a mammalian cell nucleus resulting from the β^- -radiolysis on the one hand and the transmutation effects on the other hand.

Table 2. Strand Breakage from ^3H -Decay
in Mammalian Cell Nucleus
(after L.E. Feinendegen ¹⁴)

	ssb	dsb
β^- -Radiation	0.8	< 0.08
Transmutation	0.3	< 0.01

It is evident that the major damage is caused by the β^- -radiation, namely 0.8 single strand breaks (ssb) per decay as compared to 0.3 from transmutation. The more dangerous double strand breaks (dsb) are a relatively rare event in the case of tritium. These calculated probabilities agree well with the total experimentally observed strand breaks in tritium labelled pneumococcal DNA¹⁵.

Tritium can be incorporated into biomolecules via isotopic exchange between HTO and "labile" hydrogen. Due to the excess of water this can only be a relatively small fraction. Tritium can also be incorporated via decay induced reactions (cf. eq. 2,3). In order to obtain more information on the extent of decay-induced labelling in the presence of dissolved tritium gas we have carried out model experiments using aqueous solutions of deoxyuridine and thymidine in which T_2 and for comparison HT were dissolved.

EXPERIMENTAL

4.5 % (w/w) of thymidine (TdR) and 16 % (w/w) deoxyuridine (UdR), respectively, were dissolved in deairedated water, which was redistilled twice. About 20 mCi (12 mCi in the case of UdR) of T_2 or HT diluted with H_2 [$T_2:H_2 = 1:16$, total volume: 143 μ l (spt)] was then pressed into 9.5 ml of the above solution by means of mercury which then also served as a seal (the solubility of hydrogen is 0.19 ml in 10 ml H_2O at 760 torr and 25 °C). This sampling and storing device is shown in fig. 1. The aqueous solution of tritium gas and the organic substrate was then stored for various decay periods. After storage the samples were degassed by multiple freezing and melting cycles. The hydrogen (HT, T_2 , H_2) was transferred into a separate bulb and an aliquot was submitted to gas chromatographic separation of HT, T_2 and CH_3T . A 120 cm column (2 mm i.d.) of 100 - 150 mesh alumina I (neutral) from Woelm was used. The column was

aqueous solution of T_2 and substrate

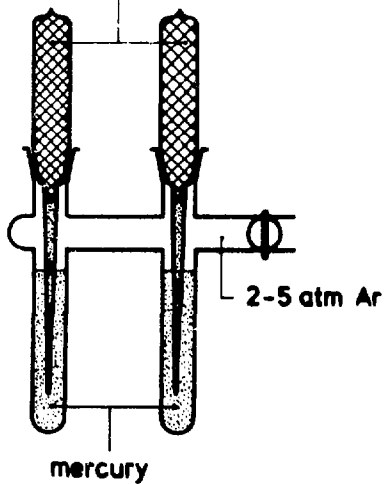


Fig. 1 Device for dissolving and storing the tritium in aqueous solutions of nucleosides.

kept at liquid nitrogen temperature, and the flow rate of the He carrier gas was 50 ml/min. An internal gas flow proportional counter was used as detector. The total gaseous activity was determined separately after drying by means of a liquid nitrogen trap in an internal proportional gas counter. It should be mentioned that during the time of sample preparation some exchange between H_2 and T_2 is observed, which is probably radiation induced. Blank experiments indicate that under our experimental conditions about 10 % of the total tritium is converted to HT (for 20 mCi of a T_2/H_2 mixture 1:16) before the end of the sample preparation.

In order to remove "labile" tritium the degassed aqueous solution was purified by means of repeated evaporation and dilution cycles at $-0^\circ C$ and 2 torr until the specific activity remained constant. The total activity of the solution was measured by liquid scintillation counting. The solution was then submitted to high pressure liquid chromatography in conjunction with tritium radioactivity determination of the individual fractions. A 50 cm silica gel column (1.8 mm i.d., Merckosorb Si 60, 10 μm) was used at a pressure of 78 atmospheres at $23^\circ C$. The eluent was diethyl ether-acidic acid (98:2) at a flow rate of 1.5 ml/min.

Fig. 2 shows the chromatogram of authentic compounds (lower part of the figure), as detected with an UV-detector at 254 nm except for the sugar 2-deoxy-D-ribose, which does not absorb and the retention time of which was determined via radioactivity using a ^{14}C -labelled sugar) together with the tritium radioactivity histogram of the individual fractions from a typical sample containing a solution of T_2 and TdR. It can be seen that HTO is still observed with the inert peak and that only a relatively small tritium activity is present in T-labelled thymidine. In addition, an unidentified T-labelled organic product appears.

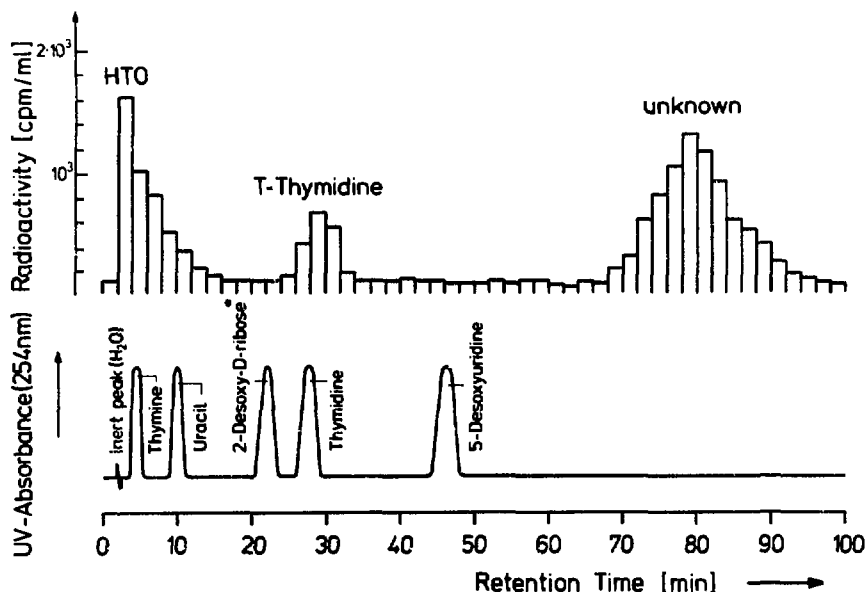


Fig. 2 Radio-chromatogram of nucleosides and constituents

Lower part: UV-absorbance at 254 nm of authentic inactive compounds (except for 2-deoxy-D-ribose, the retention time of which was determined via the ^{14}C -labelled product).

Upper part: Tritium radioactivity histogram of the individual fractions from a sample containing a solution of T_2 and TdR.

Conditions: Merckosorb Si 60, 10 μm , 50 cm long, 1.8 mm i.d.; 78 atm, 23 $^{\circ}\text{C}$, 1.5 ml/min.

Eluent: Diethyl ether - H_3COOH (98:2).

RESULTS AND DISCUSSION

The T-labelled products appearing in aqueous solutions of T_2 (or HT) and thymidine (TdR) after a storage of several days are HT, HTO, CH_3T and TdR-T (stable C-T bond, but position unknown) and an unidentified T-labelled organic product. The increase of the specific tritium activity in these four products with increasing storage time is shown in fig. 3. Several features can be observed:

1. As expected, the increase in the specific activity of the individual products is proportional to the exposure time (decay period) in the case of T_2 exposure.
2. Qualitatively the highest tritium activity appears in the form of HT (several mCi under our experimental conditions) while that of HTO is two orders of magnitude and that of the T-labelled organic products four orders of magnitude smaller.
3. In the case of HT exposure only a comparatively small almost time independent T-labelling of the organic product is observed.
4. The HT as well as the HTO yield show an intersect with the ordinate at zero decay time.

The results clearly indicate that labelling via T_2 is much more effective than that via HT under identical conditions. In the case of thymidine there is obviously a small zero exchange fraction, which is formed during sample preparation, even in the case of HT. At this T-activity level the time dependent T-labelling of thymidine obviously proceeds only via a decay induced reaction and not via radiation induced processes. The high HT yield, on the other hand, can only be explained by a radiation induced exchange between T_2 and the H_2 -carrier. The zero fraction of HTO probably also arises from a wall catalyzed exchange between T_2 (HT) and H_2O .

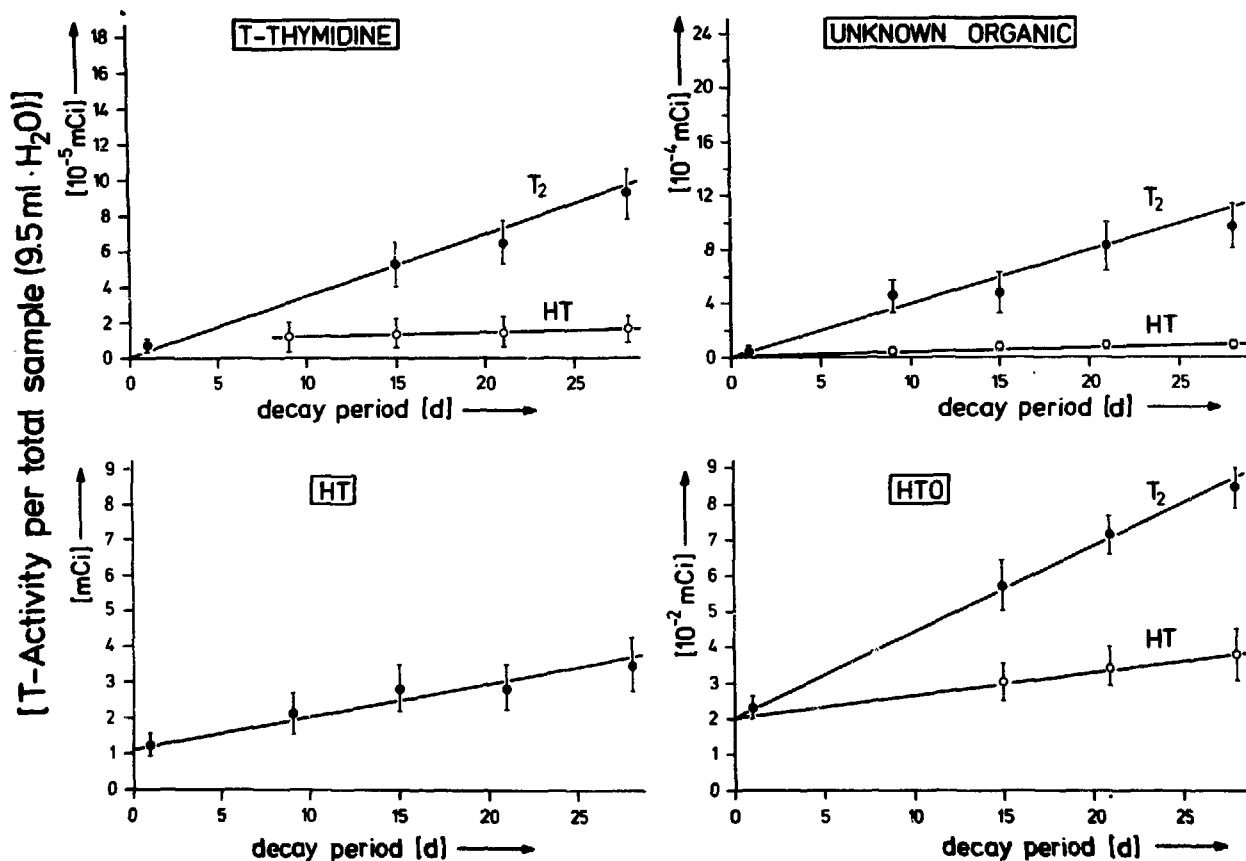


Fig. 3 Exposure-time dependence of specific tritium activity of the individual labelled products arising from the decay of T_2 and HT, respectively, in aqueous solutions (9.5 ml) containing $3.14 \cdot 10^{-3}$ mol/fraction of TdR and 20 mCi of T_2 or HT.

It is interesting to calculate the number of molecules labelled per decay of tritium (L-value). If the labelling occurs via a decay induced reaction of the $^3\text{HeT}^+$ ion the L-value cannot be greater than 1. The L-values have been calculated using the numbers presented in fig. 1 for the T_2 exposure after subtracting the corresponding value for HT-exposure (blank). Except for the product HT, all L-values are < 1 , as can be seen from table 3.

Table 3. L-Values for the Formation of T-Labelled Products from the Decay of T_2 in an Aqueous Solution of Thymidine^a

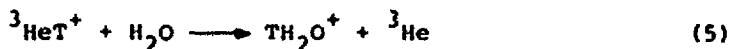
	L-Value ^b
HT	25
CH_3T	0.2
HTO	0.6
TdR-T ^c	0.0008
Unidentified	0.01

^a 4.5 % (w/w) TdR and 20 mCi T_2 dissolved in 9.5 ml of de-aired water

^b number of T-labelled molecules per T-decay

^c "stable" C-T bonds

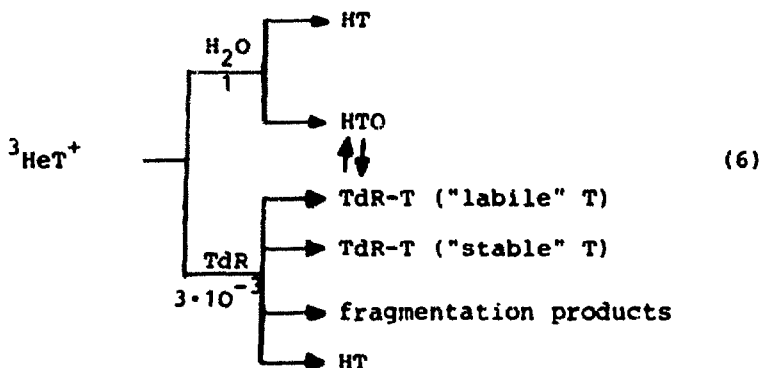
If we neglect the high L-value for HT, which can only be due to radiation induced exchange, the largest L-value is obtained for HTO. This is to be expected, since the aqueous solution contains only $3.14 \cdot 10^{-3}$ mole fraction of TdR and the highly reactive decay ion $^3\text{HeT}^+$ will mainly encounter H_2O molecules. Neutralization is an endothermic process and unlikely to occur. The main reaction to be expected is the formation of the hydronium ion:



This reaction is strongly exothermic with $\Delta H = -120 \pm 5$ kcal/mol. Those tritiated hydronium ions, which survive excitation decomposition will enter the proton exchange equilibrium of the water molecules. Excitation decomposition of the first formed TH_2O^+ may also lead to HT.

The fact, that the L-value for TdR is a factor of 750 smaller than that for H_2O simply reflects the small concentration of TdR ($3.14 \cdot 10^{-3}$ TdR molecules per 1 H_2O molecule), when taking into account that each TdR has several reactive centers while each H_2O has only one. This also demonstrates the rather indiscriminate attack of the ${}^3\text{HeT}^+$ -ion and the random nature of decay induced labelling.

The overall reaction scheme can then be outlined as follows:



The reaction of ${}^3\text{HeT}^+$ with water leads predominantly to HTO, some HT may also be formed. The reaction of ${}^3\text{HeT}^+$ with TdR leads to the substitution of hydrogen in stable as well as in labile positions. The labile tritium (e.g. on oxygen and nitrogen atoms) will rapidly exchange with the excess of water and thus will end up as HTO. Some HT and other labelled fragmentation products may also be formed in the reaction of ${}^3\text{HeT}^+$ with TdR.

We have already seen from fig. 3 that HT at an identical radioactivity level is much less effective in labelling than T_2 . A similar blank experiment has also been carried out using HTO as a tritium source at the same activity level. The labelling efficiencies of T_2 , HT and HTO for the H_2O -deoxyuridine (UdR) system are shown in table 4, where the L-values are given with respect to the labelling of the biomolecule UdR.

Table 4. Tritium Incorporation into Deoxyuridine (UdR) from T_2 , HT and HTO in an Aqueous Solution of Deoxyuridine^a

T-Source	L-Value for UdR- T^b
T_2	$1 \cdot 10^{-3}$
HT	$8 \cdot 10^{-5}$
HTO	$9 \cdot 10^{-5}$

^a 12 mCi T_2 , HT and HTO, respectively, dissolved in 9.5 ml H_2O containing 16 % (w/w) UdR
Storage: 93 days at 8 °C

^b T-labelled UdR-molecules ("stable" C-T bonds) formed per tritium decay

It can be seen that T_2 is more effective than an identical activity of HT and HTO by a factor of 12.5 and 11.1, respectively.

CONCLUSION

The results indicate that in a closed homogeneous system T_2 is considerably more dangerous than an identical activity of HT or HTO. This is, however, only true for the relatively low activity range ($\lesssim 1 - 2$ mCi per ml aqueous solution) where tritium incorporation from T_2 almost exclusively proceeds via the ${}^3\text{HeT}^+$ decay ion and not via radiation induced processes. While T_2 contributes to possible biological damage via labelling, i.e. hydrogen substitution in biomolecules, HT can mainly contribute via radiolytic effects, which lead only to a minor extent to labelling. It should be pointed out, however, that the resulting inactive ${}^3\text{HeH}^+$ decay ion can also cause damage by fragmentation after attacking the nucleoside, e.g. the attack at an oxygen atom (protonation) can be followed by the cleavage of the glycosidic bond¹⁶. This part of the damage cannot be observed with our radioanalytical techniques.

In general, hydrogen gas (HT, T_2) should only impose a minor safety problem in case of accidents, since only a small fraction will be dissolved in body fluids after inhalation and then rapidly attain equilibrium with the environment. In addition, due to the unselective high reactivity of the ${}^3\text{HeT}^+$ or ${}^3\text{HeH}^+$ decay ions, the major part of the reactions will occur with the excess of water giving rise to labelled HTO.

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CONTAINMENT AND DECONTAMINATION SYSTEMS PLANNED
FOR THE TRITIUM RESEARCH LABORATORY BUILDING AT
SANDIA LABORATORIES, LIVERMORE

P. D. Gildea

Sandia Laboratories, Livermore, California

ABSTRACT

Sandia Laboratories, Livermore, is constructing a new facility, the Tritium Research Laboratory, that incorporates containment and cleanup facilities which hold any tritium that is accidentally released rather than allow the material to be vented to the atmosphere. This containment is achieved with hermetically sealed glove boxes that are connected on demand by manifolds to two central decontamination systems called the Gas Purification System (GPS) and the Vacuum Effluent Recovery System (VERS). The primary function of the GPS is to remove tritium and tritiated water vapor from the glove box atmosphere. The primary function of the VERS is to decontaminate the gas exhausted from the vacuum pumps in the building before venting this gas to the stack.

FACILITY DESCRIPTION

The Tritium Research Laboratory was proposed by Sandia Laboratories, Livermore, in 1969. Funding for the project became available in July, 1972, and construction was begun in August, 1973. The laboratory was designed as a research facility to be used for a diverse range of experimentation using gram amounts of tritium. It is a 24 x 55 m single story structure that contains approximately 1068 m² of laboratory floor space. As is normal for this type of facility, ventilation is provided by a once-through system exhausting to a 30 m stack. Pressure zoning is used to control ventilation air flow through the building.

The building construction phase of the Tritium Research Laboratory project has just been completed, and the equipment installation process is beginning. It is expected that the laboratory will be operational in late calendar year 1976.

Since no operational experience has been accrued, this paper presents the proposed operational mode of the facility and describes the design capabilities of the containment and decontamination systems.

This laboratory contains the capabilities required to support tritium related fusion research. It is important to realize that personnel and environmental safeguards at least as stringent as those described in this paper will almost certainly be required for future tritium handling facilities. Thus the operational experience to be gained using this concept for providing environmental protection should be very important to those who may require an equivalent laboratory capability.

CONTAINMENT AND DECONTAMINATION SYSTEMS

This is the first major tritium laboratory to depart from the established concept of protecting personnel from tritium release by using high velocity air hoods that exhaust to a stack. AEC guidelines issued during the time the Sandia Livermore facility was being planned required adoption of a design philosophy which would limit tritium release to "as low a level as practicable". The system proposed to achieve this requirement is conceptually illustrated in Figure 1. The Tritium Research Laboratory employs a secondary containment system connected to two central decontamination systems called the Gas Purification System (GPS) and the Vacuum Effluent Recovery System (VERS). Both decontamination systems are being manufactured to a Sandia performance specification by Engelhard Industries Systems Department, East Newark, New Jersey.

The first of these systems, the GPS, is used to remove tritium and tritiated water from the sealed glove box atmosphere. The second system, the VERS, is used to remove tritium, tritiated water, and tritiated hydrocarbons from the gases exhausted from the vacuum systems in the laboratory before venting them to the stack. Both systems are capable of reducing tritium concentration to the low ppb level. Thus instead of allowing released material to be vented directly to the atmosphere through the laboratory stack it is contained for proper disposal. The distribution of glove boxes throughout the laboratory is shown in Figure 2. The

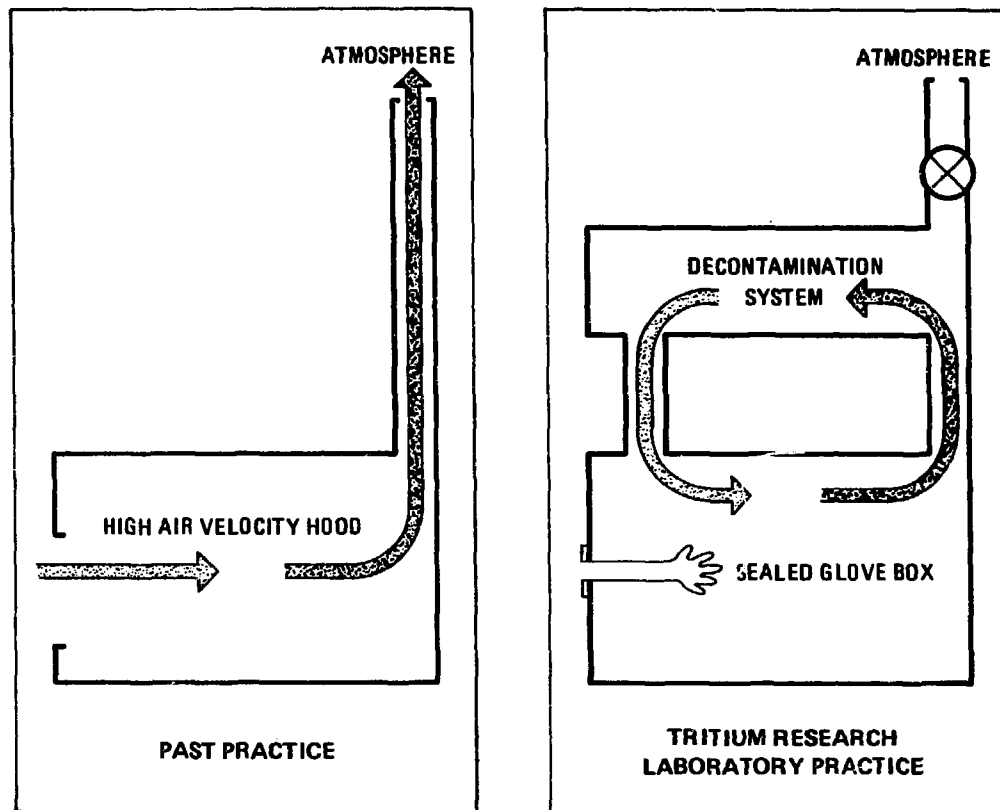


Figure 1. Tritium Research Laboratory Containment Concept.

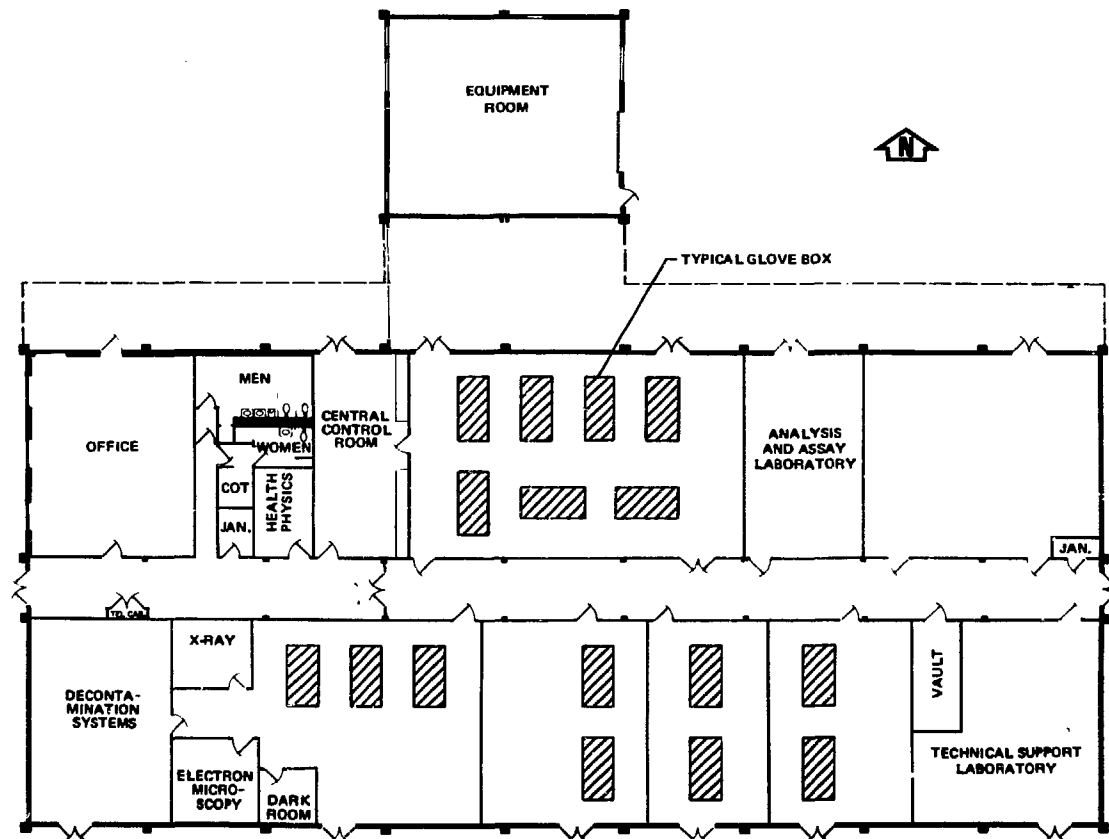


Figure 2. Tritium Research Laboratory Floor Plan.

manifolds connecting the glove boxes to the decontamination systems run down the corridor and stub-out into the laboratories.

The glove box tritium concentrations are scanned by a computerized control system which will automatically connect the box to the gas purification system in the event a tritium release occurs.

Conventional high velocity air hoods will be used for operations in which the chance of a tritium release is negligible, but where tritium contamination may be a problem. An evacuable box line with its own purification system will be used for those experiments requiring an inert, highly pure atmosphere. Since these are standard laboratory use items, they will not be discussed further in this paper.

Experiment Containment

Sealed Glove Boxes

Box Description.--All experimentation is secondarily contained in 1.2 x 2.4 x 2.4 m sealed glove boxes as depicted in Figure 3. The boxes are of welded construction of 2.0 millimeter thick Type 304 stainless steel. Each box is equipped with 34 glove ports, 14 safety glass viewing windows and one 0.3 m diameter by 0.46 m long air lock passthrough. The box contains both 0.8 x 0.8 m and 1.1 x 1.1 m removable panels, one on each end for installation of large items. The windows, glove ports and access doors are gasket sealed.

Both regular utility and emergency electrical power is provided within the box. Feedthrough provision is made for instrumentation and inert gas pressure connections. A cooling system is provided to remove the heat load generated by the experimental apparatus within the box.

A housing attached to the end of the box encloses two vacuum pumps used for evacuating the glove ports and passthrough, the box pressure control system and the tritium monitor.

Each box is connected to the two central decontamination systems as well as the building ventilation system. Both humidity and tritium

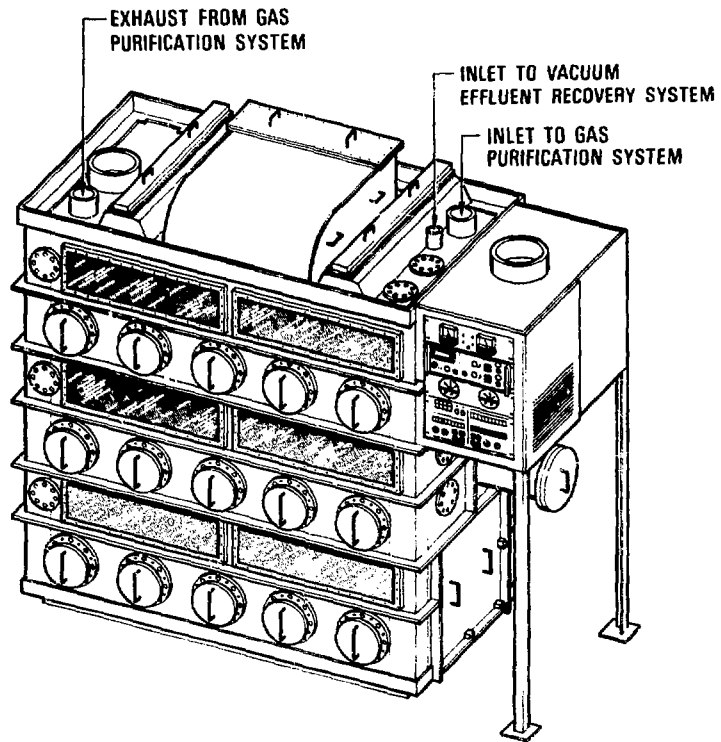


Figure 3. Sealed Glove Box.

concentration control are achieved by the connection of the boxes to the gas purification system. A backup to the pressure control system on the glove box is provided by a bubbler system which is set to relieve the glove box pressure when the differential with respect to the room exceeds ± 1.5 KPa.

Major system performance criteria are summarized in Table 1.

Table 1. Sealed Glove Box Performance Criteria

Volume	8.84 m ³ (1.2 x 2.4 x 2.4 m)
Atmosphere	Air, Nitrogen, Argon
Pressure Limits	
Operating	-0.25 to -1.0 KPa relative to the laboratory
Maximum	± 1.5 KPa relative to the laboratory
Humidity	Down to 1 ppm water
Cooling Load	10.8 megajoule
Electrical Power	18.0 megajoule

Box Operation.--The glove boxes are operated in a stagnant mode with dry ambient air maintained at a pressure of -0.25 to -1.0 KPa, with respect to the room, by the box pressure control system. The capability also exists to operate the box with an inert (argon or nitrogen) atmosphere if desired.

The box pressure differential is achieved by the use of two Dwyer photohelic controllers. One of the units operates a valve to either the laboratory vacuum manifold or a makeup source. The second unit protects the system by isolating the box from vacuum pumps and pressure sources in the event the normal pressure limits are exceeded. The pressure control system may be operated by a remote foot switch or by push buttons on the control panel.

The glove box is normally valved off from the gas purification system, and the box tritium monitor continuously measures the tritium concentration of the glove box atmosphere. In the event the tritium concentration exceeds a set level, the tritium monitor

provides a signal for the facility control computer to send a command to start the gas purification system and reduce the tritium concentration to the ppb level in a matter of minutes.

When conditions permit, the glove box may be operated as a high velocity air hood by opening either of the large end panels and manually opening a valve to the building ventilation exhaust system.

Decontamination Systems

s Purification System (GPS)

GPS Description.--The Gas Purification System (GPS) will decontaminate the glove box atmosphere in the event of either an accidental release or a slow buildup of background. Since this system is in the fabrication stage, this section describes the system requirements as stated in the specifications and the system configuration as defined by the manufacturer. Although performance data are not available, it is felt that the specification generally defines a system whose various components are commercially available. When the specification was written the possible singular exception was catalyst performance. This was the requirement that the tritiated species concentration be reduced by a factor of 1000 in a single pass from inlet concentrations as low as 1 ppm. Catalyst performance tests using a prototype reactor were run at Monsanto Research Corporation, Mound Laboratory¹, and verified the catalyst's ability to more than meet this requirement, i.e., a reduction factor of approximately 10^5 from inlet concentrations of approximately 1 ppm.

The GPS, conceptually illustrated in Figure 4, consists of the following major elements:

1. A closed loop manifold with glove box bypass capability extending throughout the laboratory.
2. A blower section for circulating the box atmosphere through the system.

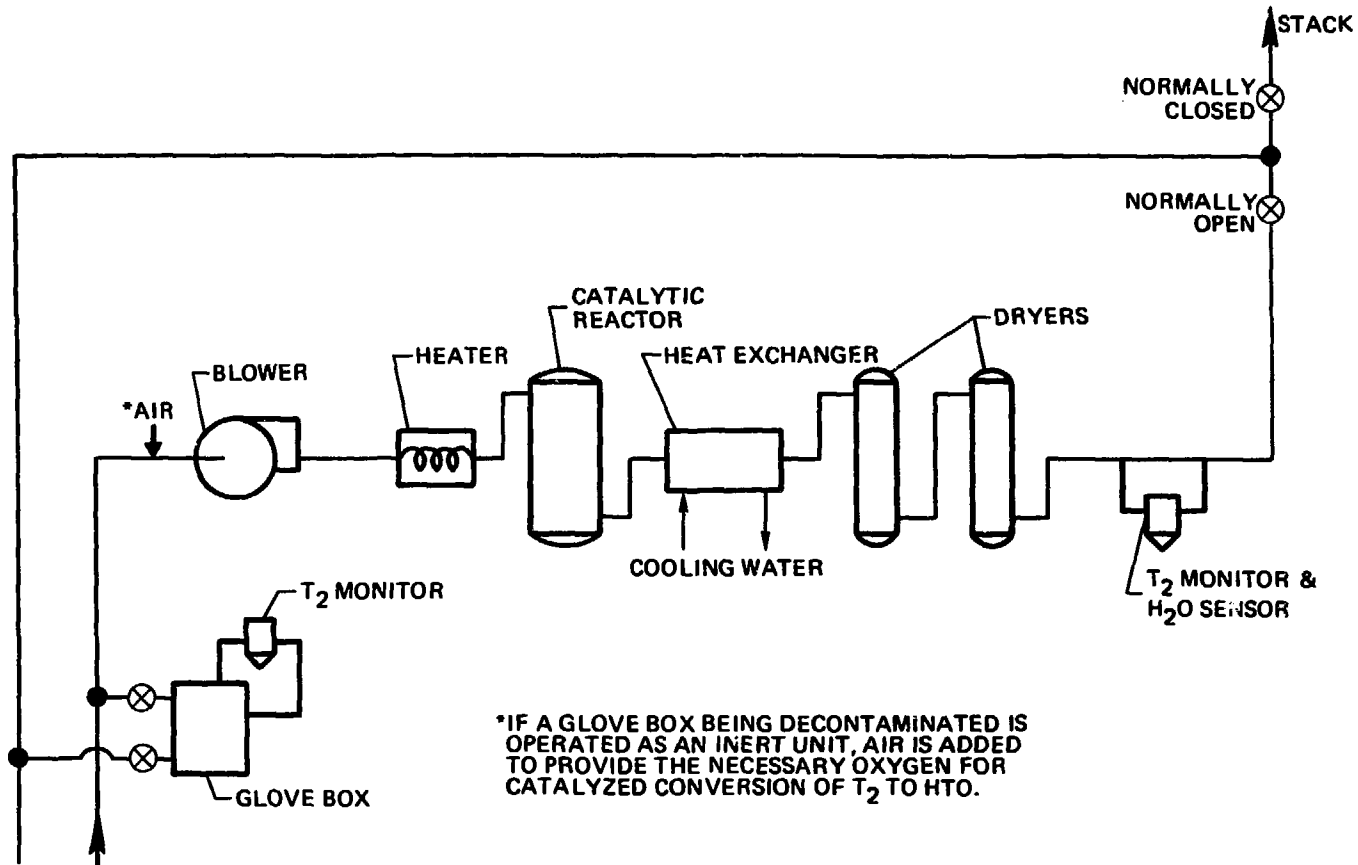


Figure 4. Gas Purification System Schematic.

3. A catalyst section for conversion of the hydrogen isotopes to water.
4. A dryer section which performs three functions:
 - a. Collect the oxidized hydrogen isotopes.
 - b. Regenerate the dryers for continued usage and collect the tritiated water for subsequent safe disposal.
 - c. Dehumidify glove boxes as required.
5. A control and diagnostics system for providing both remote and local control and for assessment of the operational status. This system includes tritium and humidity sensors for assessment of system efficiency.

Redundant prime function components, i.e., blowers, heating elements, catalysts and dryer beds are provided for reliability.

Major system performance criteria are summarized in Table 2.

GPS Operation.--Upon receipt of a signal from the glove box tritium monitor, the laboratory control computer selects the flow path for the glove box and signals the GPS to start. The GPS operates the valves to program the selected flow path. Standby heaters maintain the catalyst at approximately 561°K to ensure catalytic conversion at startup.

The GPS blower starts recirculating the gas in the manifold through the bypass valve. The pressure control system adjusts the pressure of the manifold between the limits of -0.25 to -1.0 KPa relative to the laboratory. Pressure control is necessary to prevent damage to the glove box when the box valves are opened. Within 30 seconds the manifold pressure is controlled within the specified limits and the flow established at 0.08 m³/sec.

The valves connecting the box to the manifold are opened and the bypass valve closed. The control system then introduces combustion air into the manifold. An equal volume of gas is vented to the VERS so that pressure control is maintained.

Table 2. GPS Performance Criteria

Processing Capacity	0.08 m ³ /sec minimum air and argon
Catalytic Reactor	
Operating Temperature	672°K
Standby Temperature	561°K
Catalyst	Engelhard Minerals & Chemicals No. A-16648
Tritium Concentration Reduction Factor	1000 per pass for concentrations from 20,000 ppm to 1 ppm
Molecular Sieve Dryer	
Capacity	37 moles of water while maintaining less than 1 ppm water at exit
Regeneration Time	6 hours
Regeneration Temperature	561°K
Molecular Sieve	Type 4A
Start Up Operating Time	30 seconds
Glove Box Pressure Control	-0.25 to -1.0 KPa relative to the laboratory
System Leak Rate	1 x 10 ⁻¹⁰ m ³ (STP)/sec maximum helium at 98 KPa differential.

The flow of gas through the GPS is approximately as follows:

The gas leaves the box through the remotely actuated valve, travels down the intake manifold and through the blower. Downstream of the blower the gas is heated to approximately 672°K. This gas temperature is sufficiently high to crack any hydrocarbons contained in the gas stream. The gas then enters the catalytic reactor where the tritium is oxidized to tritiated water.

The tritiated water/gas stream is then cooled to 294°K and passes into the first molecular sieve dryer. The dryer section is capable of removing moisture from the gas stream to the 1 ppm level or less. Water in excess of 1 ppm is adsorbed onto the molecular sieve. The gas stream exits the first dryer at no more than 1 ppm tritiated water concentration, and 1000 ppm H₂O is added to it before it enters the second dryer. Exiting the second dryer the moisture content of the gas stream will again be 1 ppm; however, only 1/1000 of this or 1 ppb will be tritiated water. The gas stream exiting the second dryer enters the exhaust manifold and is returned to the glove box. The glove box atmosphere is recirculated until the tritium concentration has been reduced to an acceptable level at which time the laboratory control computer sends a shut down command to the GPS.

The GPS can also be operated manually by Tritium Research Laboratory personnel to perform routine testing and dehumidification of glove boxes. The manual mode will also be used when computer or interface maintenance is required. The control system has been designed to operate unattended on a 24-hour basis.

The tritiated water collected in the dryer will be removed and held in a trap during regeneration. The tritiated water collected in the trap will be transferred to a DOT/ERDA approved sieve vessel and shipping container for later recovery or disposal. The sieve vessel and shipping container planned for this use have been designed by Monsanto Research Corporation, Mound Laboratory².

Vacuum Effluent Recovery System (VERS)

VERS Description.--The VERS is used to decontaminate the exhaust gases from the laboratory vacuum systems before venting these gases to the stack. Because the system is also in the fabrication stage and performance data are not available, this section describes the specification requirements and the system configuration as defined by the manufacturer. The VERS is a system similar to the GPS and uses the same precious metal catalyst.

The VERS, as conceptually illustrated in Figure 5, consists of the following major elements:

1. A vacuum manifold extending throughout the facility for connection to all sources of tritiated effluent.
2. An effluent separation section to divide effluent into two contamination level categories; one for venting up the stack and one for decontamination.
3. A storage section consisting of two 5.7 m^3 tanks for effluent collection.
4. A decontamination section consisting of a catalytic reactor for conversion of hydrogen isotopes to water and molecular sieve beds for collection of the tritiated water.
5. A control and diagnostics section for providing both automatic and manual operation and for assessment of the operational status. This system includes tritium and humidity sensors for assessment of effluent contamination and system efficiency.

The VERS does not have as many redundancies built into it as the GPS because the holding tank storage time is sufficient to permit any part of the system to be replaced or repaired. Similarly the catalytic reactor will not be maintained at an elevated temperature standby condition but will be ready to begin processing within 30 minutes of a start signal.

Major system performance criteria are summarized in Table 3.

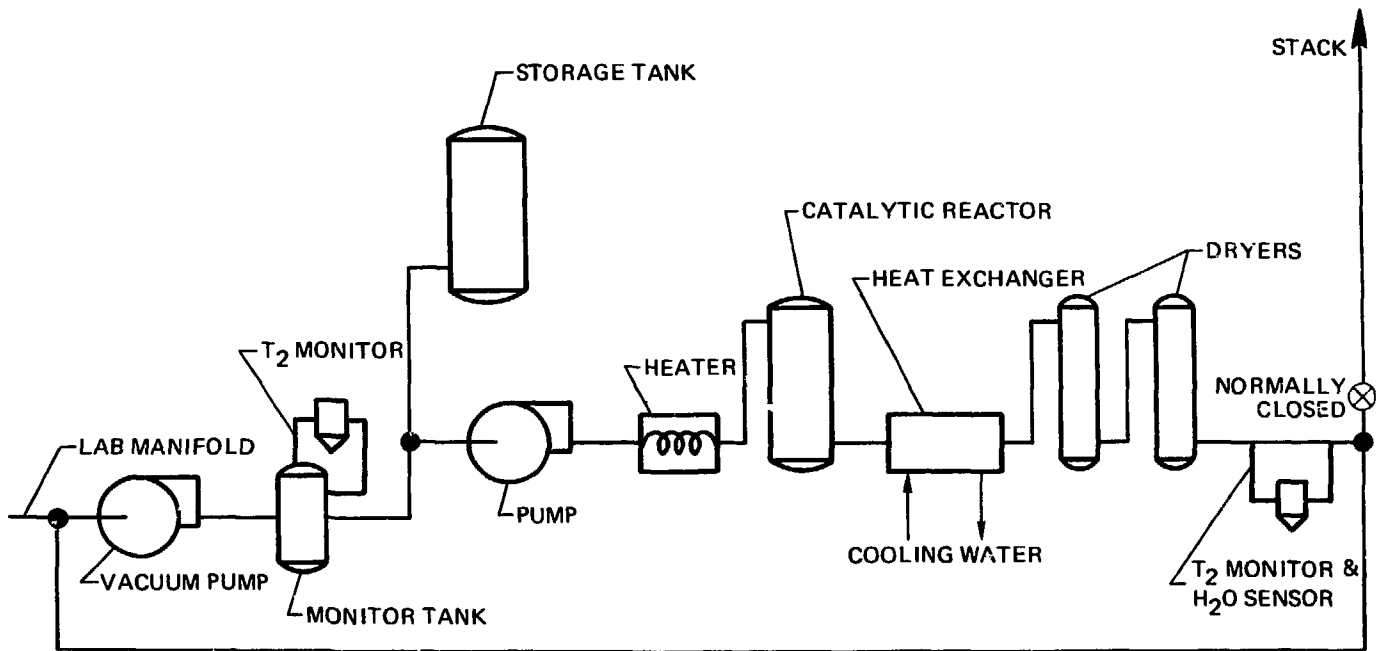


Figure 5. Vacuum Effluent Recovery System Schematic.

Table 3. VERS Performance Criteria

Processing Capacity	5.7 m ³ /hr.
Holding Capacity	11.4 m ³ at 93 KPa
Catalytic Reactor	
Operating Temperature	672°K
Catalyst	Engelhard Minerals & Chemicals No. A-16648
Tritium Concentration Reduction Factor	1000 per pass for concentration from 20,000 ppm to 1 ppm
Molecular Sieve Dryer	
Capacity	3 moles of water while maintaining less than 1 ppm water at exit
Molecular Sieve	Type 4A
Start Up Operating Time	30 minutes
System Operating Pressure	0.13 to 103 KPa
System Leak Rate	1 x 10 ⁻¹⁰ m ³ (STP)/sec maximum helium at 98 KPa differential.

VERS Operation.--The laboratory vacuum manifold is expected to be maintained at an average pressure of approximately 3.3 KPa. The effluent exhausted to the manifold is pumped into a 0.3 m³ tank where its contamination level is monitored. To minimize VERS operating time the effluent of the 0.3 m³ tank is divided into two levels of tritium concentration which are collected in separate 5.7 m³ holding tanks. The lower concentration will be selected such that the effluent can be vented directly to the stack while the effluent with the higher tritium concentration will be decontaminated before stacking.

Effluent is collected until the holding tank pressure reaches 93 KPa. The decision to stack the holding tank contents will be made by control room personnel and will be initiated manually. The decision to process the holding tank contents through the decontamination section will be automatically made by the VERS control system.

The tritium monitor at the exit of the decontamination system will, depending upon the tritium concentration, generate a signal to either recirculate the effluent through the VERS or direct it to the stack.

When a holding tank is to be processed through the decontamination section, the VERS control system will alert the control room by means of an alarm light and turn on the catalyst bed heater. When the catalyst bed reaches operating temperature, the system will begin circulation of the hold tank contents through the decontamination system. When the hold tank pressure is reduced below 1.3 KPa the system will shut down.

The VERS has the capability for being operated in a continuous stacking and processing mode. However, the decision to use this mode will not be made until a later time as a result of operational experience.

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THE FIXATION OF AQUEOUS TRITIATED WASTE IN
POLYMER IMPREGNATED CONCRETE AND IN POLYACETYLENE

P. Colombo
R. Neilson, Jr.
M. Steinberg

ABSTRACT

Tritiated aqueous waste can be used to hydrate hydraulic cement producing a concrete that contains a network of interconnected porosity and as such is subject to water intrusion and subsequent tritium loss by leaching and exchange. Techniques have been developed to impregnate this porosity with styrene monomer, which is then polymerized *in situ*, resulting in a concrete that is essentially impermeable while its strength, durability, and resistance to chemical attack are significantly improved. An adsorbent additive can be incorporated to increase the tritiated waste loading of the concrete. Tritiated aqueous waste can also be fixated in polymeric form through reaction with calcium carbide to form tritiated acetylene and calcium hydroxide. Polymerization of the acetylene is accomplished by either ^{60}Co γ -irradiation or thermal catalysis over cupric oxide. The tritiated polyacetylene produced can contain up to 50 atomic percent tritium and is essentially non-leachable, insoluble, thermally stable up to 325°C, and chemically inert. Tritiated polyacetylene can be incorporated as an aggregate in concrete, polymer concrete (PC) or polymer impregnated concrete (PIC) to form a monolithic solid. The tritiated calcium hydroxide formed in the calcium carbide-water reaction may be calcined, with the recovered tritiated water recycled, or incorporated directly into PC or PIC to impede tritium release.

THE FIXATION OF AQUEOUS TRITIATED WASTE IN
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P. Colombo
R. Neilson, Jr.
M. Steinberg

Brookhaven National Laboratory
Upton, New York

POLYMER IMPREGNATED TRITIATED CONCRETE (PITC)

Aqueous tritium waste reacts with hydraulic cement to form hydrated silicate and aluminate compounds. Theoretically, portland cement can bind 28% water by weight and high alumina cement (Lumnite) 57 wt. %.¹ The actual water that hydrates the cement is probably somewhat lower due to cement impurities. The hydration reaction is rapid at early ages but continues more slowly for an indefinite period, thus, not all of the tritiated water is bound as hydrate but is present as residual or unreacted water.

Since cement concrete is an open cell type structure as a result of the interconnected porosity formed during the cure stage, it is permeable to water and corrosive fluids and thereby susceptible to tritium loss by leaching and exchange. A method for minimizing or preventing tritium or HTO loss from cement paste blocks by the use of surface coatings has been described by Emelity et al.² More recently, techniques have been developed to impregnate the porosity, voids and capillaries throughout the entire monolith by styrene monomer which is subsequently polymerized in situ.^{1,3-5} This results in a concrete that is essentially impermeable while its strength, durability and resistance to chemical attack are significantly improved.

Process Description

Figure 1 schematically illustrates the process for producing polymer impregnated tritiated concrete. Hydraulic cement, tritiated aqueous waste and an adsorber, if desired, are added in the proper proportions prior to

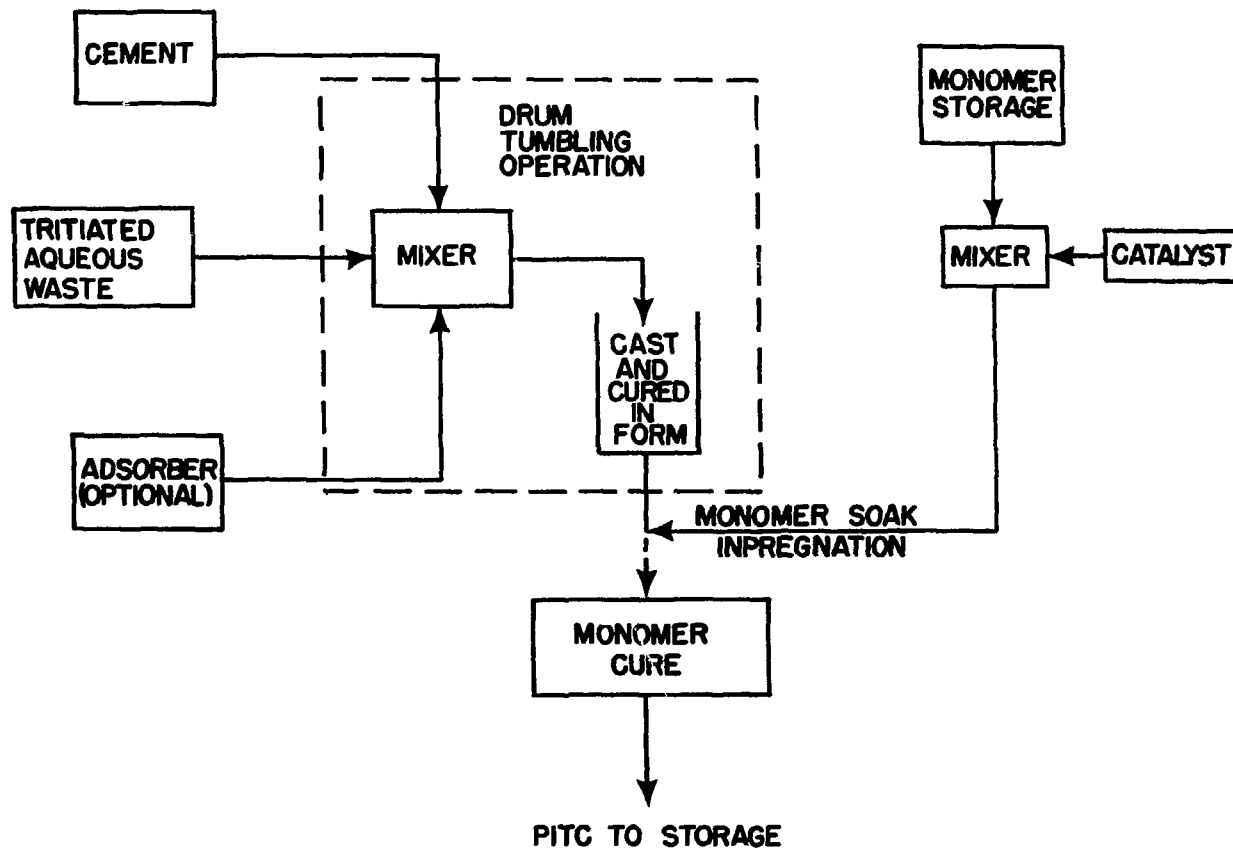


Fig. 1. Fixation of tritiated aqueous waste in polymer impregnated tritiated concrete (PITC).

mixing. The water to cement (w/c) ratio (and water to adsorber ratio) must be carefully determined, as excess tritiated water in an unbound state may be more easily leached or evaporated. A dry cement mix with a w/c ratio of ~ 0.20 minimizes the amount of unbound water and also enhances the ease of monomer impregnation. The use of adsorber, such as silica gel, allows a larger tritiated water content in the composite than is possible with the use of cement alone. Other materials, such as perlite, vermiculite and diatomaceous earth are also attractive based on their low cost and increased tritium loadings in such composites.

Alternatives for the cement mixing and casting operation have been considered. While there are several techniques for achieving a good mix, the method chosen must minimize the possibility of contamination of the process equipment and the operations area. Required cleaning of the process equipment could generate larger volumes of tritiated waste, although of a lower level, than the process disposes. Such considerations obviously rule out conventional concrete processing equipment. In-drum mixing provided by an end-over-end drum tumbler provides the most viable alternative. In this operation dry cement and adsorber are added to the mixing drum (which also becomes the casting and storage container) in a "cold" area of the disposal facility and stored until needed. Monitoring of this drum filling step would be done on a weight rather than volumetric basis to ensure proper formulation. A mixing weight, if necessary to assure adequate mixing, may also be added to the drum at this time. The mixing and casting operations simply consist of adding the required amount of tritiated aqueous waste to the drum, closing the bung-hole, transference to the drum tumbler as shown in Figure 2 and tumbling the mix. Experiments indicate that a casting which occupies in excess of $2/3$ of the volume of a 30 gallon drum can be thoroughly mixed by tumbling at 20 rpm for 10 minutes without a mixing weight.

Standard 30 gallon DOT 17C mild steel drums were selected for maximum volume based on consideration of exotherm temperature resulting from the heat of hydration of a water-cement mix. The dimensions of such a drum are approximately $18\frac{1}{4}$ in. I.D. by $27\frac{3}{8}$ in. high. A composite occupying 80% of the nominal volume of this container will have a volume

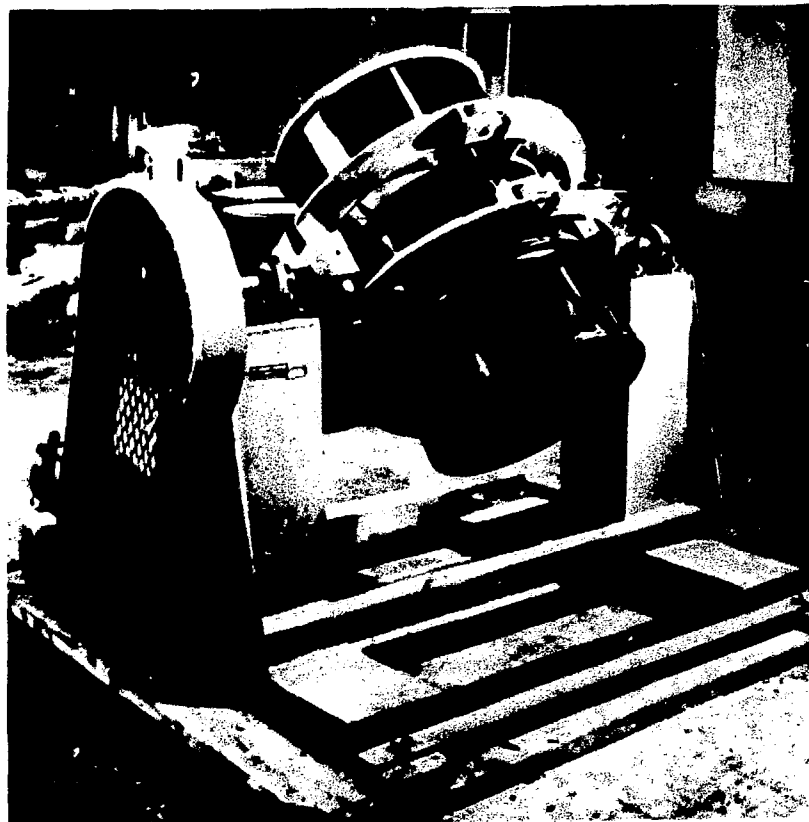


Fig. 2. Drum tumbler used for making large-scale cement mixes.

of 3.2 cubic feet. This composite incorporates 5.8-8.3 liters HTO per cubic feet. Such a 30 gallon drum may also be inserted into a standard 55 gallon drum in the event of contamination, leakage or the desire to provide an additional containment barrier.

After curing, which requires approximately 24 hours with portland type III or with high alumina cement, the composite is impregnated with styrene monomer by a soak technique. Styrene monomer was chosen because of its low viscosity, excellent radiation stability and ease of polymerization. The monomer containing approximately 0.5 wt. % benzoyl peroxide, used as a low temperature polymerization initiator, is introduced in the prescribed amount through an opening in the drum cover. There is sufficient free volume in the drum to accommodate the total monomer required for impregnation. Monomer loadings of approximately 15% by weight are typical. By such a soak technique, an 18 inch diameter concrete casting with a low w/c ratio is completely impregnated in 3-4 hours. A clamshell drum heater shown in Figure 3 is then placed around the casting and maintained at 50°C. Complete polymerization results within 24 hours. Higher temperatures, to 80°C, appreciably decrease the polymerization time. Preliminary formulations for PITC production using the above described process are given in Table 1.

Property Evaluation

The properties which have been considered of primary importance to the safety of PITC are leachability, radiation stability, thermal stability, mechanical strength and resistance to chemical attack.

Leachability of PITC was measured by a modification of the IAEA standardized leach test.⁶ Composites of the preliminary formulations shown in Table 1 have been prepared for leach testing. In this procedure, the test specimen is submerged in distilled water in a covered polymethylpentene container such that all surfaces of the composite are exposed. The leachant solution is changed daily and analyzed for tritium content using a Packard Model 3000 Tri-Carb liquid scintillation counter. The tritium content of the leachant is used to determine the fraction

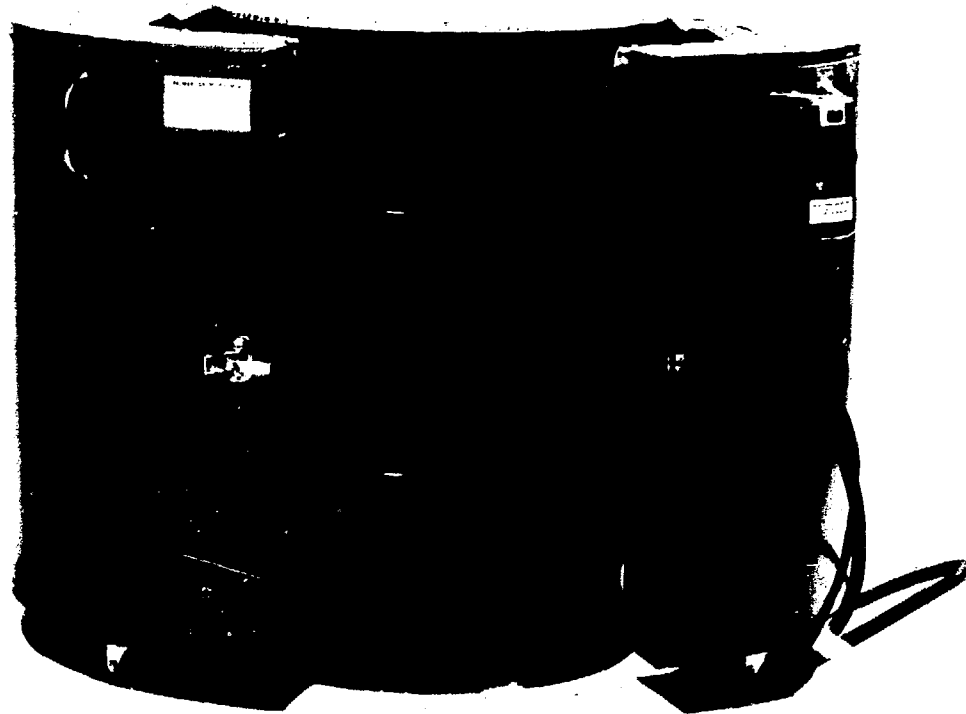


Fig. 3. Clamshell resistance drum heater.

Table 1. Preliminary Formulations for Polymer Impregnated Tritiated Concrete Composites

Specimen	Composition, wt. %			Polymer loading wt. %	Water/cement ratio	Water/adsorber ratio
	Cement	Silica Gel ^a	Water			
1. Lumnite ^b tritiated concrete	84.7	--	15.3	--	0.18	--
2. Lumnite PITC	84.7	--	15.3	12.4	0.18	--
3. Portland type III PITC	84.7	--	15.3	16.5	0.18	--
4. Lumnite-silica gel PITC	40.4	36.8	22.8	16.0	0.18	0.40
5. Portland type III silica gel PITC	40.4	36.8	22.8	15.8	0.18	0.40

^aGrade 42, 6-16 mesh Davison Chemical Company, Baltimore, Maryland 21226

^bLumnite, trademark for the high alumina cement produced by the Universal Atlas Cement Co., Pittsburgh, PA. 15230

release and hence the bulk leach rate, L_B , of the composite where,

$$L_B = F_i \times \frac{d \times v}{s \times t}$$

and

F_i = fraction release of the i^{th} species

d = composite density, g/cm^3

v = composite volume, cm^3

s = surface area, cm^2

t = leach time, days

Table 2 presents the leach data for these preliminary formulations. As indicated in Table 2, impregnation results in bulk leach rates of several orders of magnitude lower than those for tritiated concrete.

The use of silica gel as an adsorbent to increase the specific water content of the formulations did not affect bulk leach rates. Incorporation of absorbent additives such as perlite, diatomaceous earth, and vermiculite resulted in PITC composites with leach rates approaching those of unimpregnated concretes.

The bulk leach rates of these cement and cement-adsorber PITC formulations were lower than those reported by Emelity² for concretes with one inch thick asphalt coatings. Such coatings are also susceptible to coating failures by cracking, spallation, and delamination.

The extensive use of concrete for reactor shielding applications has shown excellent radiation stability.⁷ Polystyrene, used for impregnating tritiated concrete has been irradiated at BNL, by ^{60}Co gamma-rays for a total integrated dose of 10^{10} rads at a radiation intensity of 1.2×10^7 rads/hr. The radiolysis products consisting almost entirely of hydrogen gas resulted in $G(\text{H}_2) = 0.02$ molecules/100eV.

When cement is heated, the primary factor influencing changes in the structural properties is the loss of water. Above a temperature of

Table 2. Tritium Leach Test Data for Preliminary Formulations

<u>Specimen</u>	<u>Tritium content μCi</u>	<u>Mass, g</u>	<u>Surface area cm²</u>	<u>Leach time days</u>	<u>Fraction release per day</u>	<u>Bulk leach rate g/(cm²-day)</u>
1. Lummite tritiated concrete	100	650.0	248.8	10	3.59×10^{-2}	9.33×10^{-2}
2. Portland type III tritiated concrete	100	456.7	336.5	10	6.56×10^{-2}	1.11×10^{-1}
3. Lummite PITC	100	693.0	298.6	10	7.25×10^{-5}	1.68×10^{-4}
4. Portland type III PITC	100	673.4	282.2	10	1.01×10^{-4}	2.41×10^{-4}

$\approx 120^{\circ}\text{C}$ loss of chemically combined water begins (dehydration of hydrated cement phases). The water loss from this process is extremely low and changes in mechanical properties are not easily detectable below 538°C .⁸ DTA-TGA analysis has indicated that at temperatures above 538°C for long periods of time considerable strength losses and failure by cracking or spallation may occur. It has also been determined calorimetrically that polystyrene is thermally stable to a temperature of $\sim 250^{\circ}\text{C}$.

Normally cement paste as conventionally made ($w/c = 0.5$) exhibits a compressive strength of 8,000-12,000 psi. In this process, however, the compression strength is compromised as a result of a low w/c ratio. Impregnation of this cement paste having an initial strength of several hundred psi results in compressive strength values of 16,000 to 20,000 psi. The high durability of PITC has been demonstrated by subjecting specimens to 3,650 freeze-thaw cycles with a weight loss of $< 0.5\%$, whereas normal concrete loses 25% of its weight after 500 cycles.

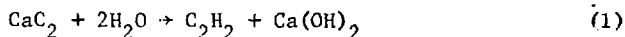
PITC specimens have also shown resistance to chemical attack by 15% hydrochloric acid. The unimpregnated concrete specimen lost 25 wt. % in 105 days whereas the PITC lost < 1 wt. % in 497 days. The polymer serves to protect the alkaline phase from attack by acid.

POLYACETYLENE

Low tritium exchange rates are expected to occur for organic compounds where hydrogen is attached to carbon by a strong nonlabile covalent bond. Polymeric compounds that are hydrophobic and non-volatile are of particular interest.

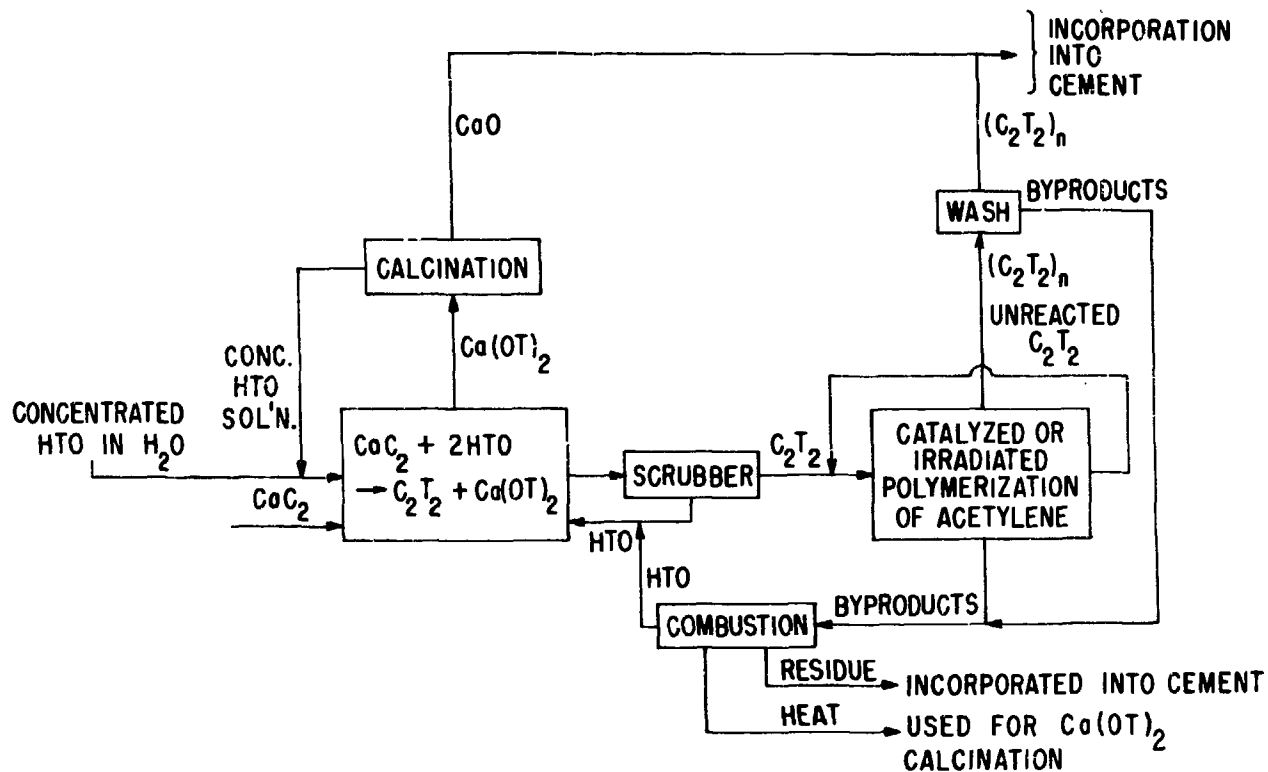
Process Description

The most direct approach to the preparation of such polymers using tritiated water as a starting material is by the reaction with calcium carbide to form tritiated acetylene Eq. (1) which is then polymerized to produce tritiated polyacetylene Eq. (2).



The tritiated calcium hydroxide formed during the acetylene generation step can be calcined to form calcium oxide while the tritiated water liberated is recycled. Tritiated acetylene is scrubbed prior to polymerization to remove entrained water which is returned to the acetylene generator. Polymerization by ^{60}Co gamma irradiation and thermal catalysis over cupric oxide have been studied.^{1,3,9} Unreacted acetylene is recycled through the polymerization reactor. The polyacetylene produced is washed to remove organic by-products which are combusted, while the tritiated water produced is returned to the acetylene generator. Cement or a polymer could be used as a solidification agent both to form a monolithic mass and decrease the surface area susceptible to leaching. A schematic flow diagram for tritium fixation in tritiated polyacetylene is shown in Figure 4. By this technique, 50 atomic percent of the hydrogen from 0.68 grams of tritiated water can be incorporated into 1.0 gram of polyacetylene.

The radiation polymerization of acetylene has been studied by many workers, although it is not well understood.¹⁰ The apparatus shown in Figure 5 was used for the static polymerization of acetylene gas by ^{60}Co gamma irradiation. The polymerization was also performed with liquid water present in the reactor vessel. A $G(-\text{C}_2\text{H}_2)$ value of 140 molecules/100eV was obtained with a dose rate of 1.8×10^6 rad/hr for a total integrated dose of 18×10^6 rad in the presence of water, while without water the $G(-\text{C}_2\text{H}_2)$ value was 111. A decrease in the G value for acetylene polymerization was observed above this dose. The decrease is presumed to be due to the decrease in acetylene gas density and benzene formation which poisons the acetylene polymerization reaction. Figure 6 shows an SEM micrograph of the spherical polyacetylene formed by heterogeneous polymerization and precipitation from the gas phase. The polyacetylene sphere diameter varies from 1.0-2.0 μ with an average of approximately 1.5 μ .



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Fig. 4. Tritium fixation by the polymerization of tritiated acetylene and its incorporation into cement concrete.

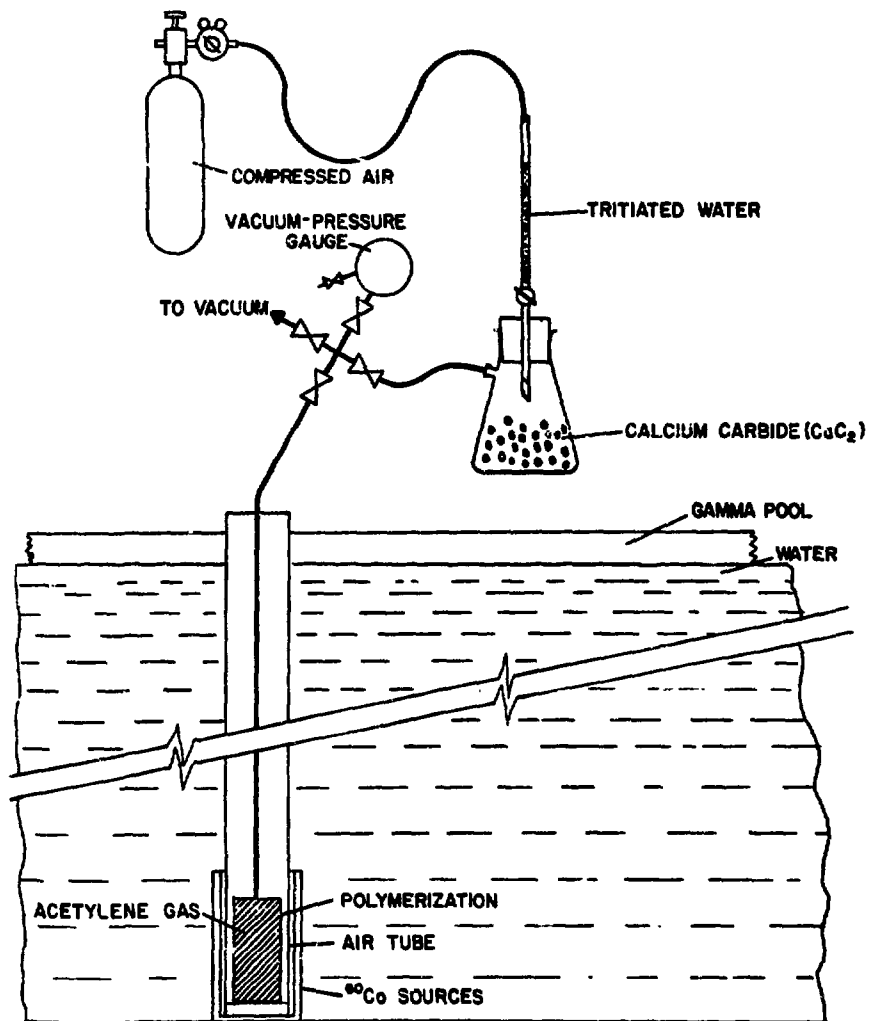


Fig. 5. Experimental apparatus for the static polymerization of acetylene by ^{60}Co gamma irradiation.

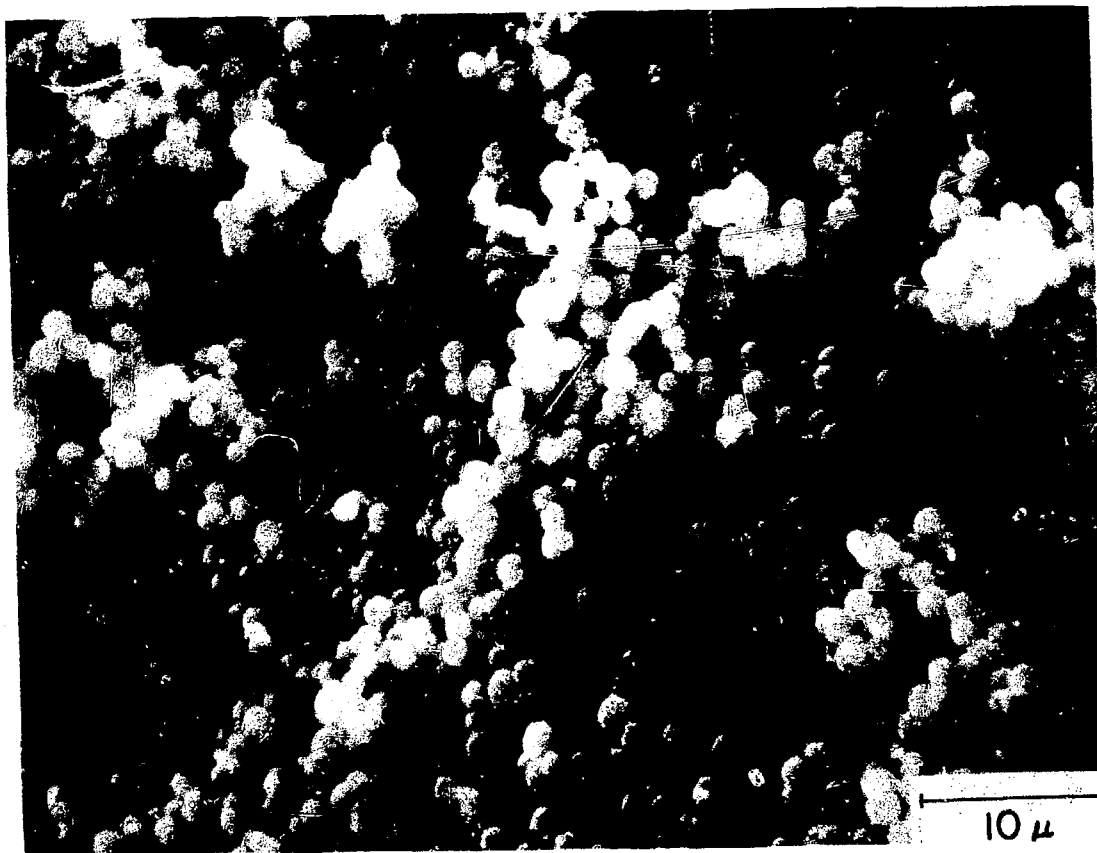


Fig. 6. Polyacetylene produced by the ^{60}Co gamma irradiation of acetylene gas.

Acetylene gas is polymerized while flowing over heated cupric oxide wire catalyst. Flow rates of 10-80cm³/min through a catalyst bed volume of 11cm³ were utilized for polyacetylene production while a clamshell furnace was used to heat the reaction vessel. Acetylene polymerization was observed at 215°C with the rate increasing with temperature to 280°C. The major by-products of this reaction are unreacted acetylene, water, carbon dioxide and ethylene. The presence and relative amounts of by-products are dictated by the reaction temperature. At low reaction temperatures (230°C or below), the by-product is essentially unreacted acetylene. Increasing the reaction temperature to 240°C greatly increases the polyacetylene yield with water being the principal by-product. At 280°C, the by-products are largely ethylene, carbon dioxide and water, with a large number of other constituents also formed. Oxygen products in the off-gas result from reduction of the cupric oxide catalyst. A SEM microphotograph of the polyacetylene produced is shown in Figure 7. An empirical formula of (C₆H₅)_n was derived from carbon-hydrogen analysis. An entrained copper content is evident.

Property Evaluation

The polyacetylene formed by both polymerization techniques can be described as inert, non-volatile, completely insoluble, and of unknown molecular weight. The polymer does not melt, but begins to decompose at approximately 325°C. The polymer will burn when exposed to a flame.

Leachability of tritiated polyacetylene produced by ⁶⁰Co gamma irradiation was measured by a modification of the IAEA standardized leach test.³ In this procedure, 2.95 grams of polyacetylene with a specific activity of 0.332μCi/g was immersed in one liter of distilled water. Periodically this leachant was replaced, distilled to remove any contained polyacetylene and analyzed by liquid scintillation counting to determine its tritium content. A rapid release of 3.8% of the contained tritium was noted within several hours, however, little further activity release was noted over a period of 28 days. The initial release is probably due to surface contamination of reaction by-products. The subsequent tritium release corresponds to a bulk leach rate of

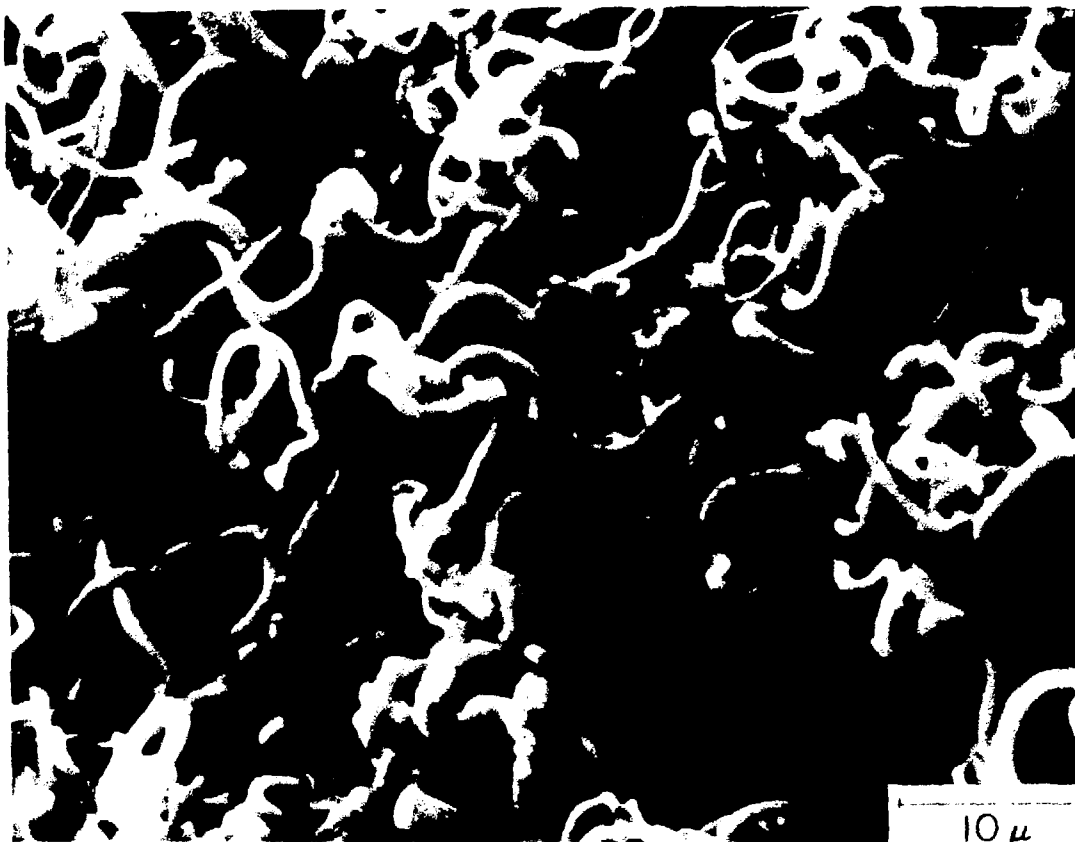


Fig. 7. Polyacetylene produced by the polymerization of acetylene gas over a heated cupric oxide wire catalyst bed.

approximately $1.8 \times 10^{-8} \text{ g}/(\text{cm}^2\text{-day})$.

The hydrogen gas evolution from the radiolysis of polyacetylene subjected to ^{60}Co gamma irradiation was measured as an index for determining tritium activity losses for long term storage. Polyacetylene was irradiated to a total dose of 1.22×10^8 rad at an intensity of 6.3×10^6 rad/hr. The yield of evolved hydrogen gave $G(\text{H}_2) = 0.15$ molecules/100eV. This corresponded to a loss of 0.022% of the initial hydrogen present.

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STEPPING INTO TROUBLE
(A Video Training Film)

G. L. Phillabaum
C. W. Taylor

Monsanto Research Corporation, Mound Laboratory

ABSTRACT

Video films are effective training tools in radiological safety. This film portrays one way in which a personnel exposure to tritium can occur and the emergency actions to be taken to limit the exposure.

INTRODUCTION

Training is a key part of the radiological safety program at Mound Laboratory. The Health Physics Group offers a wide variety of training programs in the effective control of personnel radiation exposures, contamination control, and protection of the environment. One training method is the use of video films. A demonstration of an on-the-job event is taped, edited, and then shown as a training film.

This video training film portrays one way in which a personnel exposure to tritium can occur and the emergency actions to be taken to limit the exposure. The film also demonstrates the tracking of contamination and the actions involved in controlling the tracking.

THE OIL LEAK

The film shows an employe entering a laboratory and being sprayed on the leg with tritium-contaminated oil from a leaking vacuum pump. Unaware of the oil leak, the employe leaves the room and becomes "the tracker."

Momentarily, the room alarm sounds, indicating a release of contamination. Laboratory personnel spot the oil leak, shut off the vacuum pump, and evacuate the room. The Health Physics Surveyor responds to the alarm, monitors the area, and alerts appropriate personnel of the problem. He then sets off on the trail of the tracker.

OVERTAKING THE TRACKER

The next sequence of events shows the tracker being overtaken. His contaminated clothing is immediately removed, and decontamination steps then follow. The tracker is monitored, and bioassay samples are counted.

SUMMARY

Although the above situation is overly dramatized, the actions shown would take place in the event of such an incident.

BREACHING A TRITIUM CONTAMINATED SYSTEM
(A Video Training Film)

P. C. Adams
G. L. Phillabaum
C. W. Taylor

Monsanto Research Corporation, Mound Laboratory

ABSTRACT

This video training film portrays the procedures required whenever a tritium contaminated system is breached.

INTRODUCTION

Training is a key part of the radiological safety program at Mound Laboratory. The Health Physics Group offers a wide variety of training programs in the effective control of personnel radiation exposures, contamination control, and protection of the environment. One training method used is video films.

This video training film depicts the procedures required whenever a tritium contaminated system is breached. This particular job involves replacing a defective valve in a tritium contaminated line. The film portrays the prejob conference - its purpose, how it functions, and its importance when a tritium contaminated system is breached. Shown are the preparation of the job site and assembly of the monitoring equipment and protective clothing, namely the supplied-air bubble suit and rubber glove combinations. Finally, the results of these procedures, which are reduced personnel radiation exposures, are illustrated.

THE PREJOB CONFERENCE

Many systems that are part of a tritium processing facility have some probability of being contaminated with tritium oxide and tritiated organics. The exposure potential of the oxide and the organics require that special precautions be taken prior to opening a tritium processing system.

The prejob conference is required before breaching any system where there exists a realistic probability that tritium oxide or tritiated organics are present. During the prejob conference, personnel involved discuss, evaluate, plan, and coordinate the proposed job before the work is started. All reviewing parties must reach agreement on how the job is to be performed.

PREPARATION OF THE JOB SITE

Adequate preparations of the work area are made to prevent personnel exposures and release to the environment.

An attempt is made to reduce the level of any tritium in the system while it is still intact. Various techniques have proven effective, such as isolating, purging, and evacuating.

The determination of the presence of liquids in the system is very important. All systems where this evaluation cannot be made visually must be tested using the best method available. For this job, the line is ultrasonically tested to determine the presence and approximate quantity of liquid.

In all cases where liquids are suspected or known to be present, preparations must be made to contain any liquid that may be released. The concept of complete containment is important during this operation. The defective valve and adjacent line are enclosed in a double plastic bag. Inside

the bag are the new valve, the tools for doing the job, and absorbent cloths for any liquid. The removal and replacement of the defective valve are done completely inside the plastic bag.

PROTECTIVE CLOTHING

Personnel performing the breaching operation on a tritium system must wear proper protective clothing. The Mound Laboratory supplied-air bubble suit and a specific combination of rubber gloves are used for tritium operations where any contaminated liquid is suspected or at any time tritium is likely to be inhaled or absorbed through the skin.

The supplied-air bubble suit is a two-piece, full-body, vinyl protection suit with a transparent headpiece. Forced breathing air enters the suit through an air hose and exits around the waist. This forced air atmosphere creates a positive pressure, or "bubble effect," inside the suit and helps prevent contamination from entering the suit and coming in contact with the wearer.

Four pairs of rubber gloves in combination are used with the bubble suit to provide the ultimate personnel hand protection for tritium operations. The combination is based on evaluations made for resistance to tritium permeation, toughness, feel, and contrasting color.

RESULTS

When these procedures are used (the prejob conference, containment techniques, bubble suit, glove combinations, etc.), highly satisfactory results are achieved in personnel protection. Personnel dosimetry has shown a significant reduction in tritium exposures to personnel.

TRITIUM ECONOMY OF FUSION POWER PLANTS
WITH LIQUID LITHIUM BLANKETS

W. Dänner

Max-Planck-Institut für Plasmaphysik, Garching
Fed. Rep. of Germany

ABSTRACT

As being one of the key problems in fusion reactor development, tritium economy is strongly influenced by the reactor design, the power conversion system applied, and the method of tritium recovery. Some inter-relationships between economic quantities are outlined, yielding the initial tritium inventory as the most important unknown. An optimization method for quantifying this figure is described and applied to a number of different thermal power cycles: an ordinary steam cycle, a binary potassium/steam cycle, and a direct helium cycle. Either case refers to a fixed reactor size with a "standard blanket". For tritium recovery a permeation process is assumed which makes use of the fluidized bed technology, the equipment being located in a bypass to the main coolant loop. Results for the optimum tritium concentration, the initial inventory, and the doubling time are presented. A short safety consideration is included.

INTRODUCTION

Tritium economy is one of the most crucial problems in fusion reactor development. This problem area is not only determined by the size of the tritium breeding ratio of the blanket; this information has to be supplemented especially by a knowledge of the tritium inventory of the entire reactor.

At least for a first generation of fusion reactors, this may as initial inventory be a decisive cost factor which is closely connected with the question of tritium availability.

As total inventory, it is the basis for estimating the tritium safety both during reactor operation and in the event of accidents. The initial inventory and breeding ratio, finally, determine the size of the doubling time, which is an important economic quantity for any long-term fusion reactor strategy.

QUANTITIES OF TRITIUM ECONOMY

D. Steiner¹ and W.F. Vogelsang² have established the relationships between the tritium inventory I , the breeding ratio B , and the doubling time t_2 . In both cases one parameter had to be chosen more or less arbitrarily to arrive at a quantitative statement. In this paper we use the mean tritium concentration in lithium, C_{Li} , as the free parameter since this quantity represents a direct link between the economic considerations and technical implications of the tritium recovery method applied.

According to Fig. 1 we define the following quantities:

The tritium capacity K_T of the entire reactor is defined as the product of the mean tritium concentration in lithium, C_{Li} , and the total lithium mass G_{Li} being loaded with tritium:

$$K_T = C_{Li} \cdot G_{Li} \quad (1)$$

This definition neglects those amounts present, for example, in the fuel cycle or solved in the blanket structure. In the case of liquid lithium blankets, which are exclusively considered here, this should, however, be a sufficient approximation. G_{Li} comprises all lithium of the primary system, which includes the blanket, any existing external heat transfer loop, and the recovery facility.

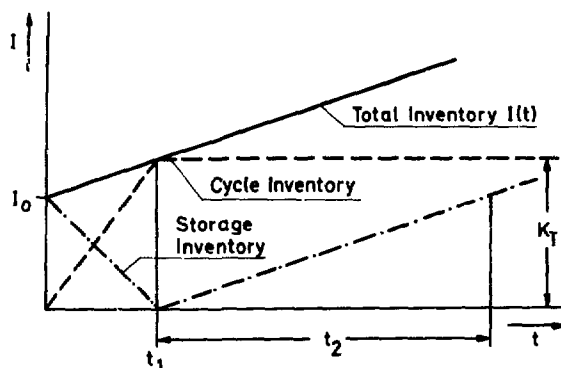


Fig. 1. Definition of Tritium Inventory and Doubling Time.

The tritium capacity K_T has to be built up during a time t_1 to reach a concentration level high enough to force the recovery process. With the tritium production rate P_T this time can be expressed by

$$t_1 = \frac{K_T}{P_T} \quad (2)$$

During this time the reactor must be supplied by a storage which contains at start-up the initial inventory I_0 defined by

$$I_0 = t_1 \cdot V_T = \frac{K_T}{P_T/V_T} = \frac{K_T}{B} \quad (3)$$

V_T being the tritium consumption rate. By definition the ratio of P_T and V_T is the tritium breeding ratio B .

Beginning at t_1 , the reactor can be supplied by the recovery facility. If the breeding ratio B exceeds unity an excess inventory is produced and fed to the storage, which will have reached the size of the initial inventory I_0 just after the doubling time t_2 :

$$t_2 = \frac{I_0}{V_T (B-1)} = \frac{K_T}{P_T (B-1)} \quad (4)$$

All quantities of interest, I_0 , t_1 , and t_2 are dependent on the tritium capacity K_T . It is therefore necessary to quantify C_{Li} and G_{Li} of Eq. (1) if statements about the tritium economy are to be derived.

THE SYSTEMS INVESTIGATED

The purpose of this investigation was to identify characteristic differences in the quantities indicated above when different power conversion cycles were applied to a fixed toroidal reactor.

Reactor and Blanket

The characteristic reactor parameters chosen were a thermal power of 5000 MW, an overall wall loading of 5 MW/m^2 , an aspect ratio of 4, and a ratio of plasma to wall radius of 0.8. Assuming a "standard type" blanket as proposed by D. Steiner¹, we arrive at a fixed lithium volume of about 750 m^3 . Depending on the temperature level dictated by the thermal power cycle, the lithium mass inside this blanket volume is somewhat different.

More significant differences, however, become apparent for the lithium masses present in the external heat transfer loop.

Ordinary Steam Power Cycle

The first power conversion system investigated is an ordinary steam power cycle, as shown in Fig. 2, with an intermediate liquid metal loop between the primary lithium loop and steam cycle. It was assumed that the most essential part of the lithium mass is concentrated in the liquid metal heat exchangers. The requirements for the heat transfer surface area and the primary coolant mass were derived from typical figures for the heat exchanger design published by K. Gast et al.³.

Binary Potassium/Steam Cycle

The same was done for a binary potassium/steam power cycle (see Fig. 3) with the heat exchange external to the blanket. Representative figures for the heat transfer surface area required have been published by A.P. Fraas⁴ and have been used for estimating the external lithium mass.

Direct Helium Cycle

The direct helium cycle (see Fig. 4) dispenses with an external lithium loop for heat transfer. Therefore, the total lithium mass is - at first - restricted to the inventory inside the blanket.

The most important figures for these three power cycles are again summarized in Table 1.

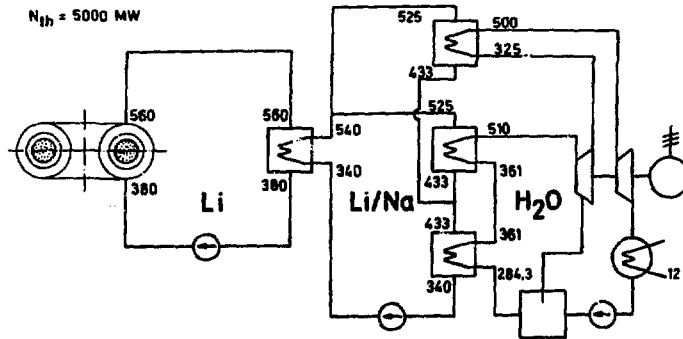


Fig. 2. Heat Flow Diagram for an Ordinary Steam Power Cycle ($\text{Li} \rightarrow \text{Li-H}_2\text{O}$).

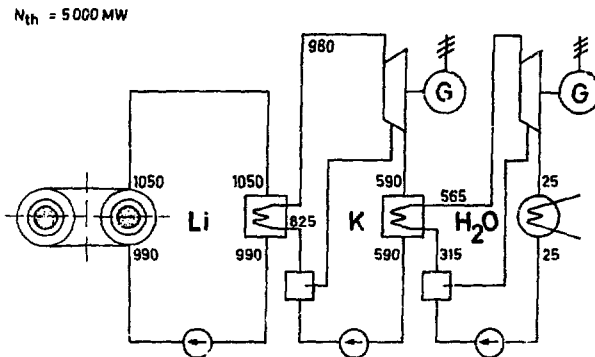


Fig. 3. Heat Flow Diagram for a Binary Potassium/Steam Power Cycle ($\text{Li} \rightarrow \text{K-H}_2\text{O}$).

Table 1. Characteristic Data of Different Power Conversion Systems

$$N_{th} = 5000 \text{ MW}; A = 4.0; y = 0.8; P_w = 5 \text{ MW/m}^2$$

Power Conversion System	Li $\rightarrow$ Li-H ₂ O	Li $\rightarrow$ K-H ₂ O	Li $\leftarrow$ He
Lithium Weight in Blanket [t]	365	326	306
External Lithium Weight [t]	440	109	-
Total Lithium Weight [t]	805	435	306
Heat Transfer Surface Area [m ²]	25500	7000	1600
Coolant Inlet Temperature [C]	380	990	518
Coolant Outlet Temperature [C]	560	1050	950
Max. Lithium Temperature [C]	560	1050	1300
Net Efficiency [%]	41.1	55÷60	46

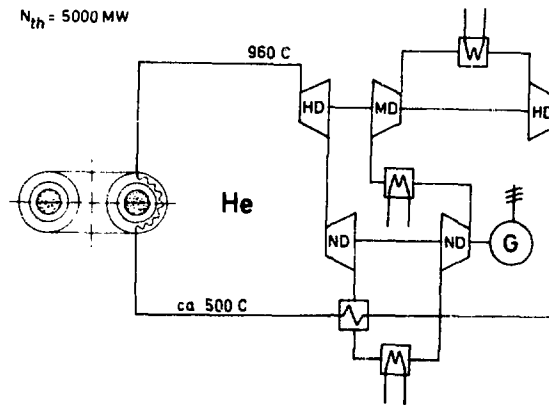


Fig. 4. Heat Flow Diagram for a Direct Helium Cycle ($\text{Li} \leftarrow \text{He}$).

Tritium Recovery Facility

So far a fixed lithium mass for each of the three power conversion systems has been identified. An increase of these figures has, however, to be expected owing to those amounts present in the tritium recovery facility.

In our study we assumed utilizing the method proposed by H. Weichselgartner⁵. The scheme of this method is shown in Fig. 5. In principle, this method relies on a permeation process coupled to a fluidized bed for tritium uptake, the equipment being located in a bypass to the main coolant string.

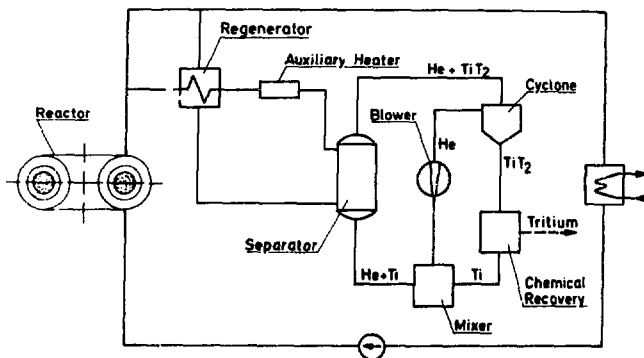


Fig. 5. Bypass Tritium Removal Facility.

A small amount of the coolant mass flow - of the order 0.1 to 1 % - is heated to a certain separator temperature ϑ_s . The separator itself consists of a vessel containing a large number of niobium tubes. On the secondary side of these tubes a fluidized bed is maintained using, for example, helium as the carrier gas for any suitable gettering substance.

The amount of lithium present in this facility depends primarily on the size of the permeation surface needed. It has been assumed that the necessary lithium mass per unit permeation surface area is equal to that per unit heat transfer surface area.

Compared with other recovery schemes utilizing tritium permeation through highly permeable metals, e.g. that proposed by A.P. Fraas^{6,7}, we see two main advantages of the bypass arrangement:

- there is no limitation of the permeation surface area by heat transfer requirements
- there is - within certain limits, of course - a free choice of the temperature level governing the permeation process.

OPTIMIZATION PROCEDURE

This freedom in designing the tritium recovery facility offers the possibility of optimizing the entire primary lithium loop with respect to costs.

For: Increasing the permeation surface area entails increasing the material costs and additionally increasing the lithium and tritium inventories and hence their costs owing to those amounts present in the bypass equipment.

On the other hand, an increase of the permeation area causes a decrease of the tritium concentration necessary to force permeation and hence a decrease of the tritium inventory and its costs.

At the same instant this optimization procedure yields the criterion for fixing the tritium concentration in the course of the economic considerations described in Sec. 2.

In a first approximation the costs can be expressed by the following equation:

$$K = \alpha + \frac{\beta}{C_{Li}^2} + \frac{\gamma}{C_{Li}} + \delta C_{Li} \quad (5)$$

with the coefficients

$$\alpha = \sigma_{Li} [G_{LB} + G_{LC}] \quad (6)$$

$$\beta = 2 \cdot 10^6 \frac{E_T \cdot s}{f (2s)} [s \cdot \sigma_{Nb} \cdot \rho_{Nb} + v' \cdot \sigma_{Li} \cdot \rho_{Li}] \quad (7)$$

$$\gamma = \frac{2 \sigma_T V_T \cdot s \cdot v' \cdot \rho_{Li}}{f (2s)} \quad (8)$$

$$\delta = \frac{10^{-6} \cdot \sigma_T [G_{LB} + G_{LC}] \cdot V_T}{E_T} \quad (9)$$

In these equations G_{LB} and G_{LC} denote the lithium masses inside the blanket and the external part of the primary circuit respectively; V_T is the tritium consumption rate of the reactor; E_T is the tritium extraction rate in the separator, which equals the tritium production rate P_T if tritium losses are neglected; s is the thickness of the separator tubes; v' is the specific lithium volume of the separator related to the unit surface area of the permeation wall; ρ_{Nb} and ρ_{Li} are the densities of niobium and lithium respectively; σ_{Nb} , σ_{Li} , and σ_T are the specific costs of niobium, lithium, and tritium per unit weight.

The first term of Eq. (5) stands for the costs of the fixed lithium inventory.

The second term is the costs for the niobium of the separator tubes and the additional lithium inventory in the

bypass. Both expressions inside the brackets of Eq. (7) denote the costs per unit area of the permeation surface. The factor in front of the brackets is, together with the square of the concentration in the denominator of Eq. (5), the permeation surface area itself. This factor was gained by using the permeation equation and data published by R.W. Webb⁸ and A.P. Fraas⁶. The dependence of the tritium partial pressure on the temperature and concentration was arrived at from publications of A.P. Fraas⁶ and C.E. Messer⁹. A more detailed description of this procedure can be found in a report of W. Dänner¹⁰.

The last term in Eq. (5) describes the costs for the tritium inventory in the fixed lithium mass, while the term before stands for those of the additional tritium inventory in the bypass which again depends on the size of the permeation surface area.

If Eq. (5) is now used to find a cost minimum with respect to the tritium concentration:

$$\frac{\partial K}{\partial C_{Li}} = 0 \quad (10)$$

the optimum concentration C_{opt} has to obey the equation

$$C_{opt}^3 = \frac{2\beta}{\delta} + \frac{\gamma}{\delta} C_{opt} \quad (11)$$

RESULTS

Table 2 summarizes the assumptions involved, which are common to all three cases of power conversion cycles investigated. Some of these assumptions, especially those

Table 2. Assumptions for Model Calculations

Lithium Density	0.5 g/cm ³
Niobium Density	8.55 g/cm ³
Tritium Consumption Rate	25 g/h
Tritium Extraction Rate	30 g/h
Tritium Loss Rate	0
Thickness of Separator Tubes	0.1 cm
Specific Lithium Volume	3.6 m ³ /m ²
Tritium Partial Pressure on Secondary Side	0
Tritium Costs	8000 DM/g
Lithium Costs	0.03 DM/g
Niobium Costs	0.6 DM/g

concerning the separator layout, must be qualified as arbitrary to a certain degree because no work has been performed up to now on a more detailed consideration of this component. Furthermore, the specific material costs reflect the situation of the year 1969 and have only been updated in the case of niobium. So all results should be considered as an intercomparison rather than be quoted as absolute figures.

Table 3 presents the results for the optimum tritium concentration for three different levels of the separator temperature ϑ_s . A noticeable difference between the three types of power conversion systems can be detected, although the influence of the separator temperature is more pronounced.

Table 3. Optimum Tritium Concentration in Lithium [ppm]

Separator Temp. [C]	1000	1100	1200
Li $\rightarrow$ Li-H ₂ O	35.3	22.9	15.8
Li $\rightarrow$ K-H ₂ O	39.6	28.2	19.5
Li $\leftarrow$ He	48.3	31.3	21.6

As far as the ordinary steam cycle is concerned, it should be mentioned that a significant temperature increase above the maximum coolant temperature is absolutely necessary. This condition, however, can only be met by the proposed bypass arrangement of the recovery facility.

The significance of having a free choice for the separator temperature level even in the case of low temperature thermal power cycles is underlined by the results for the initial tritium inventory shown in Table 4. The value of 30 kg at a separator temperature of 1000 C in the case of the ordinary steam cycle appears almost marginal if not impossible. This table also shows the great influence of the total lithium mass in the different systems: In spite of the higher concentration levels in high temperature thermal power cycles the tritium inventory is lower.

Whereas the results for the tritium inventory reveal a rather crucial situation of the tritium economy problem, this is not true of the doubling time and the time t_1 necessary to reach the optimum tritium concentration. These are shown in Table 5 and Table 6 respectively. These figures look very reasonable from the point of view of reactor operation. They also meet very well the requirements which might be set by the growth of a fusion reactor economy.

The increase of the optimum concentration with increasing temperature level of the power conversion system has, as indicated above, an advantageous effect on the initial inventory. With respect to tritium safety, however, it is most disadvantageous because an increase in both concentration and temperature level imposes more stringent safety requirements. This is most impressively demonstrated by the figures in Table 7.

Table 4. Tritium Initial Inventory [kg]

Separator Temp. [C]	1000	1100	1200
Li $\rightarrow$ Li-H ₂ O	30.0	18.3	12.1
Li $\rightarrow$ K-H ₂ O	18.2	12.3	8.2
Li $\leftarrow$ He	16.2	9.8	6.4

Table 5. Tritium Doubling Time [days]

Separator Temp. [C]	1000	1100	1200
Li $\rightarrow$ Li-H ₂ O	250	150	100
Li $\rightarrow$ K-H ₂ O	150	105	70
Li $\leftarrow$ He	135	80	55

Table 6. Time Necessary to Reach Optimum Tritium
Concentration [days]

Separator Temp. [C]	1000	1100	1200
Li $\rightarrow$ Li-H ₂ O	50	30	20
Li $\rightarrow$ K-H ₂ O	30	20	14
Li $\leftarrow$ He	27	16	11

Table 7. Tritium Amount Accumulated in the Secondary Loop
after 20 years of Reactor Operation [g]

Separator Temp. [C]	1000	1100	1200
Li $\rightarrow$ Li-H ₂ O	$9 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$2 \cdot 10^{-3}$
Li $\rightarrow$ K-H ₂ O	$7 \cdot 10^3$	$4 \cdot 10^3$	$2 \cdot 10^3$
Li $\leftarrow$ He	$7 \cdot 10^4$	$3 \cdot 10^4$	$1 \cdot 10^4$

Here the total tritium losses through the heat exchanger surfaces, accumulated in the secondary loop over 20 years of reactor operation, are summarized. Highly tritium-tight materials have been assumed in calculating these losses: stainless steel in the case of low temperature power cycles, molybdenum in the case of high temperature power cycles. In either case these figures do not affect the tritium economy. They tell us, however, that a low temperature thermal power cycle is superior to a high temperature cycle by at least six orders of magnitude from the safety point of view.

SUMMARY AND CONCLUSIONS

Assuming a fixed reactor and a fixed tritium recovery method, quantities describing the field of tritium economy have been investigated as a function of the type of thermal power cycle coupled to the reactor. Two free parameters in the layout of the recovery facility - the permeation surface area and temperature level - permit the essential parameters of tritium economy to be quantified by a cost optimization procedure.

The results of the numerical examples are based partly on arbitrary assumptions, thus restricting the value of this investigation mainly to the method, but also to a most valuable intercomparison between the power conversion systems considered.

It turns out that the most crucial quantity of tritium economy is the initial inventory. High temperature power cycles are favoured over low temperature power cycles from this point of view. The same holds for the tritium doubling time, the absolute size of which does not impose any obstacles, however, in either case.

The very opposite conclusion must be drawn, however, with regard to the safety problem. Here low temperature power cycles offer striking advantages over their competitors.

It must therefore be concluded that the problem of tritium economy cannot be treated without taking safety considerations into account. If it is possible to quantify the costs connected with the tritium safeguards, the method described should be suitable for answering more far-reaching questions as well.

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TRITIUM PROBLEMS IN A HELIUM COOLED THERMAL BLANKET

F. K. Altenhein, H. Andresen, J. Gruber, H. Migge, W. Lutze,
Hahn-Meitner-Institut für Kernforschung Berlin GmbH., Berlin-W.

ABSTRACT

*A helium cooled low lithium inventory blanket has been analyzed in terms of tritium sources and tritium distribution among the blanket materials. The $^9\text{Be}(n,t)$ reaction is the mayor source of tritium production outside the breeding zone and is responsible for considerable tritium storage in beryllia, on graphite, in the structural material, and for accumulation of tritium in the gas purification plant. HTR coolant chemistry was applied to the helium coolant cycle of a CTR. As in HTR's ratios $\text{H}_2/\text{H}_2\text{O}$ of 20:1 to 40:1 and CO/CO_2 of 5:1 to 50:1 are expected. The ratio H/T will be about 5:1.

The consequences of high permeable first wall and lithium canning were investigated. It was found that considerable gettering of hydrogen in liquid lithium may take place, due to the extremely low hydrogen vapor pressure over lithium. This inherent gettering, therefore, is proposed as an alternative possibility to keep the tritium partial pressure low in the coolant. Various parameters of the gettering capability are discussed qualitatively and in part quantitatively in order to evaluate the potential feasibility of the new concept.

INTRODUCTION

This paper refers to a modular thermal blanket proposed by J. Darvas^{1,2}, by which a drastic reduction of the lithium inventory is achieved and breeding remains sufficiently high. Since the neutron spectrum is thermalized by using large quantities of graphite and beryllium, tritium production is based on the $\text{Li-6}(n,\alpha)\text{T}$ -reaction. Beryllium is also used to produce excess neutrons necessary for breeding. Lithium is placed between the beryllium and graphite zones. Heat removal from the module is achieved by helium, this being in direct contact with beryllium and graphite. Three different versions of the blanket design are being discussed in this context and are referred to as CTRD I - III (Fig. 1).

Though the major fraction of tritium is bred in the lithium zones, considerable amounts of tritium are produced outside these zones. Listed in Tab. 1 are the corresponding nuclear reactions. Among these the reactions starting with beryllium have the highest yields. Since all the tritium produced outside the breeding zone has direct access to the cooling cycle, the contamination of the coolant becomes an important point.

The objective of this paper is to estimate the sources of protium, deuterium, and tritium outside the breeding zones, and the distribution of hydrogen among beryllia, graphite, and the coolant. In section I the blanket structural material and the canning of the breeding zones are considered to be impermeable for hydrogen. In section II the changes in hydrogen distribution are discussed resulting from the introduction of high permeable walls.

I		II		III	
PLASMA		PLASMA		PLASMA	
	[cm]		[cm]		[cm]
first wall (V)	0.5	first wall (V)	0.5	first wall (V)	0.5
Be zone +6%V	7.0	Be zone +6%V	3.0	Be zone +6%V	2.0
Mo	0.1	Mo	0.1	Mo	0.1
Li 90% enriched	1.0	Li 28% enriched	1.0	Li 90% enriched	1.0
Mo	0.1	Mo	0.1	Mo	0.1
Be zone +6%V	13.0	Be zone +6%V	6.0	Be zone +6%V	4.0
		Mo	0.1	Mo	0.1
		Li 28% enriched	1.0	Li 90% enriched	1.0
		Mo	0.1	Mo	0.1
Carbon +6%V	80	Be zone +6%V	3.0	Be zone +6%V	2.0
		Carbon +6%V	80	Carbon +6%V	80
Vanadium	0.5	Vanadium	0.5	Vanadium	0.5

Fig. 1

The schematic CTRD I - III blanket.

The design parameters used in addition are:

Reactor output 5GW_{th}
Major radius 16,73m
First wall radius 5,79m
First wall power loading 1,31 MW_{th}/m²

Table 1

Tritium generating nuclear reactions outside the breeding zones

No.	Reaction	Source	Neutron Group
1	${}^9\text{Be}(n, \alpha){}^6\text{Li}$	Beryllium	fast
2	${}^9\text{Be}(n, t){}^7\text{Li}$	Beryllium	fast
3	${}^3\text{He}(n, p)\text{T}$	Coolant	slow
4	${}^{12}\text{C}(n, \alpha){}^9\text{Be}$	Graphite	fast
5	${}^{10}\text{B}(n, \alpha){}^7\text{Li}$	Impurity	slow
6	${}^{10}\text{B}(n, 2\alpha)\text{T}$	Impurity	fast
7	${}^7\text{Li}(n, n' \alpha)\text{T}$	Impurity	fast
8	${}^6\text{Li}(n, \alpha)\text{T}$	Impurity	slow

SECTION 1: TRITIUM GENERATION AND DISTRIBUTION

In this section the generation and distribution of tritium from the main sources 1 and 2 (Tab. 1) is estimated. The influence of the breeding zone will not be considered and the blanket structural material is thought to be impermeable.

The calculations are based on a model consisting of four reservoirs (Fig. 2). As shown there tritium is produced from beryllium via the reaction chain ${}^9\text{Be}(n, \alpha){}^6\text{Li}(n, \alpha){}^3\text{H}$ and by the ${}^9\text{Be}(n, t){}^7\text{Li}$ -reaction. It can then enter the coolant where a fraction of tritium is removed by gas purification. As the diffusion of lithium in beryllia is very slow³, it was assumed that lithium is not released into the coolant under reactor operating conditions.

Build-up curves and the stationary state quantities for tritium in the beryllia zones and in the helium coolant can be calculated using the following equations:

$$\frac{dN^{\text{Be}}}{dt} = - (R_{n, \alpha}^{\text{Be}} + R_{n, t}^{\text{Be}}) N^{\text{Be}} \quad (1)$$

$$\frac{dN^{\text{Li}}}{dt} = R_{n, \alpha}^{\text{Be}} N^{\text{Be}} - R_{n, \alpha}^{\text{Li}} N^{\text{Li}} \quad (2)$$

$$\frac{dN_{\text{BeO}}^{\text{H3}}}{dt} = R_{n, t}^{\text{Be}} N^{\text{Be}} + R_{n, \alpha}^{\text{Li}} N^{\text{Li}} - (\beta + \lambda) N_{\text{BeO}}^{\text{H3}} \quad (3)$$

$$\frac{dN_{\text{He}}^{\text{H3}}}{dt} = \beta \cdot N_{\text{BeO}}^{\text{H3}} - (\gamma + \lambda) N_{\text{He}}^{\text{H3}} \quad (4)$$

$$R_{n, x}^k \text{ (unit: per atom per year)} = \sum_i \bar{\sigma}_{n, x}^k(E_i) \Phi_{\text{INT}}(E_i)$$

$\bar{\sigma}_{n, x}^k(E_i)$ = group averaged (n, x) -cross section for isotope k

$\Phi_{\text{INT}}(E_i)$ = neutron flux in energy group about E_i in blanket interval INT

λ = decay constant for tritium

$N^k(t)$ = number of atoms k in interval INT as a function of time t

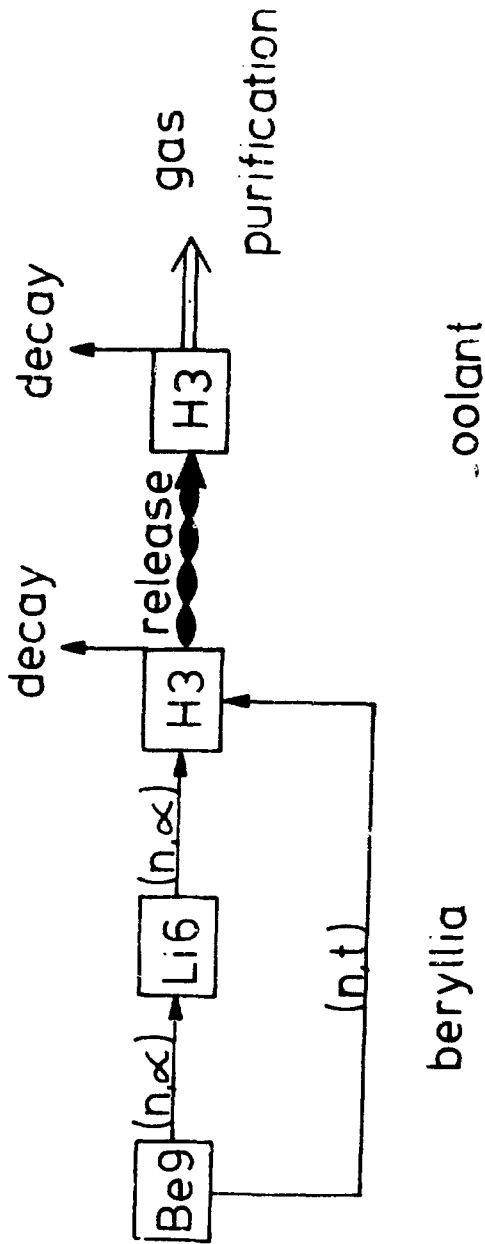


Fig. 2 Tritium generation and distribution

β = time constant for tritium release into the coolant

γ = time constant for tritium removal from the coolant by the gas purification plant ($\gamma = K \frac{f}{G}$)

f = purification flow (kg/h)

G = total weight of He (kg)

K = correction factor

Equations (1) to (4) were solved for each blanket interval separately because of the spatial variation of the neutron fluxes. Because of $(R_{n,a}^{Be} + R_{n,t}^{Be}) < 10^{-4} \gamma^{-1}$ and for $\gamma, \beta \geq 10 R_{n,x}^k$ ^{4,5} the solution can be approximated by

$$N^{Be}(t) = N^{Be}(t=0) = N^{Be} \text{ for } 0 \leq t \leq 20 \quad (5)$$

(t = operation time of CTR in years)

$$N^{Li}(t) = \frac{R_{n,a}^{Be}}{R_{n,a}^{Li}} N^{Be} (1 - \exp(-R_{n,a}^{Li} t)) \quad (6)$$

$$N_{BeO}^{H3}(t) = \frac{1}{\beta} (R_{n,a}^{Li} N^{Li} + R_{n,t}^{Be} N^{Be}) \quad (7)$$

$$N_{He}^{H3}(t) = \frac{1}{\gamma} (R_{n,a}^{Li} N^{Li} + R_{n,t}^{Be} N^{Be}) \quad (8)$$

where N_b^a is again the number of atoms of species a in material b .

For the whole blanket the number of atoms will be:

$$M^k(t) = \sum_{INT} N^k(t) \quad (9)$$

Estimates of the tritium amounts to be expected in the beryllia zones and in the helium coolant were performed with MATEXP⁶ and based on:

- a) neutron fluxes from ANISN-calculations for the blanket containing 94% beryllium (aside from 6% structural material) in the beryllia zones instead of BeO.

- b) Tritium release data from reference 4,7. In order to simplify the calculation tritium release is set proportional to the tritium content (Eq. 3). The proportionality constant $\beta(T)$ is a function of temperature T . Taking $\beta \approx \frac{\pi^2 D}{r^2}$, (D = diffusion coefficient, r = grain radius) the experimental values from Stöver⁴ yield $D' = \beta/\pi^2 = 2,3 \cdot 10^{-2} \text{ h}^{-1}$ for $T = 690^\circ \text{C}$.
- c) Tritium removal similar to protium removal tested in DRAGON injection experiments⁵. The protium content for constant protium injection w was found to be

$$N^{\text{H1}}(t) = \frac{w}{\gamma} (1 - \exp(-\gamma t)), \text{ where } 1,1 \geq \gamma \geq 0,7 [\text{h}^{-1}].$$

Appropriate values for K , f , and G (constituents of γ , see above) are $f/G = 0,6 \text{ h}^{-1}$, $1,1 \leq K \leq 1,7$. (For comparison: $f/G = 0,3 \text{ h}^{-1}$ for the 300 MW_e THTR⁸ and $f/G = 0,14 \text{ h}^{-1}$ for the 3GW_{th} high temperature breeder design⁹.)

Computational results for the content of tritium in BeO and in the primary coolant as function of operation time are shown in Fig. 3 for $\gamma = 0,7 \text{ h}^{-1}$. With the above value of $D' = \beta/\pi^2$ one obtains the two curves designated by (1). As long as the time constants β and γ are greater than the tritium production rate via the $\text{Li-6}(n,\alpha)\text{H-3}$ reaction the latter determines the tritium build-up in BeO and in the coolant. If the BeO retains tritium considerably better than assumed, a reduction of the tritium content in the primary coolant occurs at the expense of a drastic increase of the tritium content in the BeO. Decreasing D' by up to a factor of 10^3 increases the amount of tritium in BeO by about this factor but has still little effect on the amount of tritium in the coolant (see curves 2 in Fig. 3). If D' is a factor of 10^4 to 10^5 smaller - as observed by Scott and Wassell⁷ - the amount of tritium in BeO will be increased by a factor of 4 to 5 orders of magnitude, whereas the amount of tritium in the coolant will only be reduced by 50 to 90 % (Fig. 3, curves 3 and 4). For design II and III the computational results are mainly the same as far as the variation of D' is concerned.

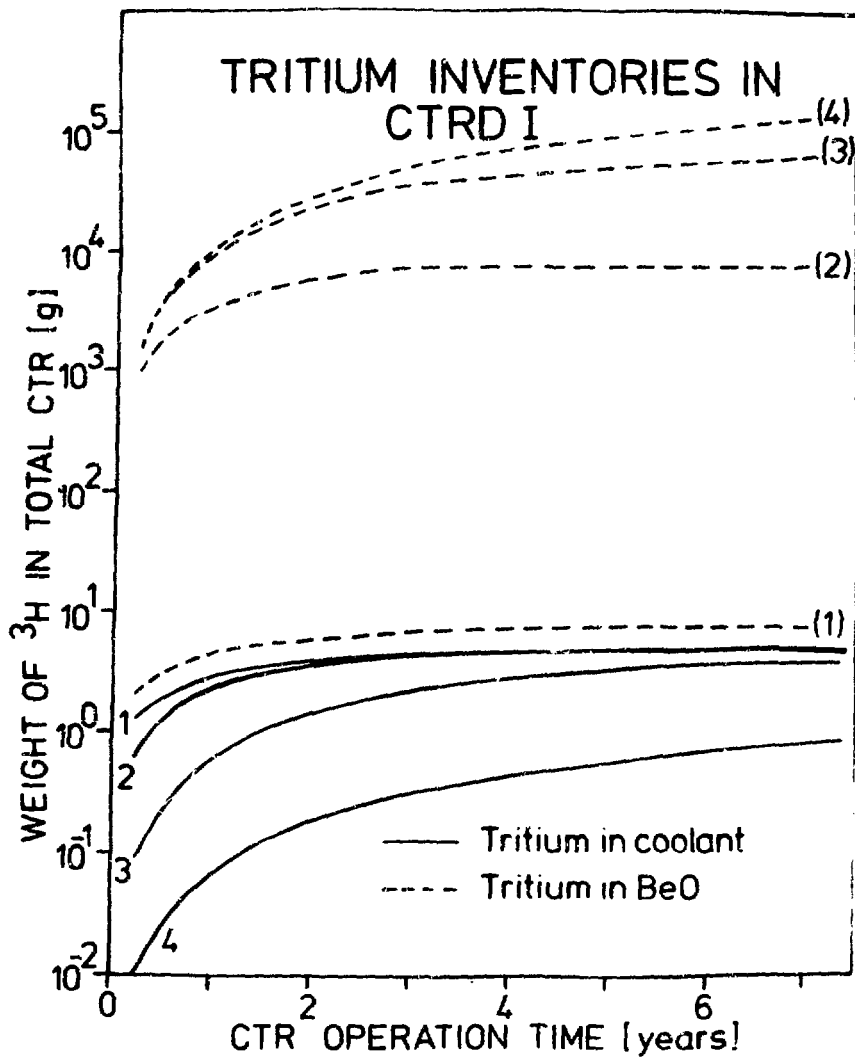


Fig. 3

Total tritium inventory for CTRD I in the coolant (M_{He}^{T}) and in BeO ($M_{\text{BeO}}^{\text{T}}$) for various effective diffusion constants $D' = D/r^2$

- (1) $D' = 2,3 \cdot 10^{-2} \text{ h}^{-1}$
- (2) $D' = 2,3 \cdot 10^{-5} \text{ h}^{-1}$
- (3) $D' = 2,3 \cdot 10^{-6} \text{ h}^{-1}$
- (4) $D' = 2,3 \cdot 10^{-7} \text{ h}^{-1}$

Fig. 4 compares the tritium content in the coolant for the three blanket designs as a function of operation time ($\beta/\eta^2 = 2,3 \cdot 10^{-2} \text{ h}^{-1}$, $\gamma = 0,7 \text{ h}^{-1}$). It can be seen that in CTRD I after about 5 years the equilibrium is reached and the primary coolant contains 4,5g tritium. This steady state value is maintained when about 75g/d of tritium enter the coolant and become removed by gas purification. Smaller beryllia zones (design II, III) reduce the thermal and epithermal neutron fluxes and tritium production via the $\text{Li-6}(n,\alpha)\text{H-3}$ reaction is slower. A reduction of the tritium content by a factor of about 2 to 4 after 5 years is the result (Fig. 4).

Tritium Implantation

From a rather thin zone of liquid lithium a considerable amount of tritium becomes implanted by recoil into the canning material. Taking the Culham reference design the implanted amount is 10kg tritium per day (about 1 % of the daily tritium production). In case of implantation even permeation barriers may fail in retaining tritium: Once tritium has entered the lithium canning, it diffuses through the metal. Its escape into the coolant is promoted if the outer surface of the canning facing the helium does not contain a protective oxide film. The reducing gas atmosphere of this CTRD hinders the formation of an intact film. However, compared with the release of tritium from BeO the release by implantation may be ignored in this special design.

Chemical Behaviour of Tritium in the Coolant

In the designed blanket the helium coolant is in direct contact with large amounts of hot graphite, as it is the case in HTR's. For this reason we transfer the coolant chemistry experience from existing helium cooled graphite moderated reactors to our CTR design. The graphite is involved in the chemical reactions and one has to expect a reducing atmosphere in the coolant. Its oxidation potential is determined by the ratios of $\text{H}_2/\text{H}_2\text{O}$ and CO/CO_2 . Taking data from the DRAGON reactor⁵, these ratios are ranging from 50:1 to 10:1 and stationary state concentrations [vpm] of impurities in helium are

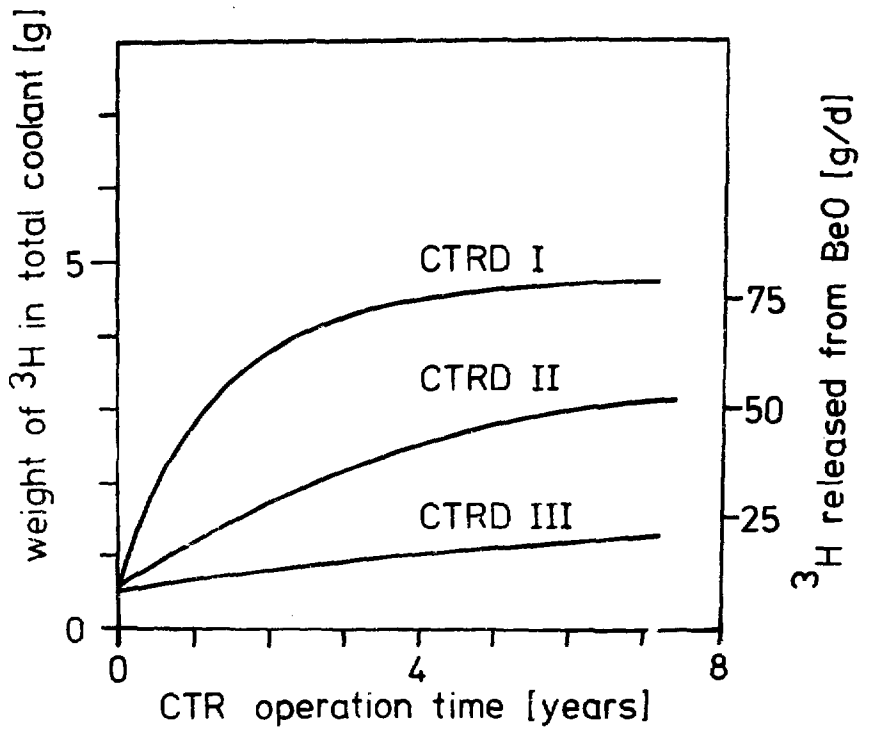


Fig. 4

Tritium inventory in the coolant due to release from BeO for the various designs

H ₂ O	H ₂	CO ₂	CO	CH ₄	N ₂	O ₂
0,05-0,10	0,8-2,0	≤0,02	0,1-1,0	0,15	0,15	0,02

It is assumed that a similar composition of impurities is present in our cooling circuit. Especially we expect a protium concentration of about 1 vpm. This value seems to be independent of the coolant volume and was a design value in a HTGR project with 10^5 Nm^3 of helium⁹. The same holds for our CTR design. Therefore we expect a protium content of 9g in our coolant, which results in a relation of 1:6 between tritium and protium. The almost complete absence of oxygen makes the situation different as compared to other CTR designs.

Tritium Inventories

Liquid Lithium.-- The total lithium inventory is 7 tons¹. With a stationary state tritium concentration of 1 - 10 ppm the tritium inventory amounts to 1 - 10 mol.

Vanadium blanket structural material.-- The steady state tritium content of the vanadium structural material was estimated assuming a linear temperature profile from 400°C to 730°C, 10^{-2} torr hydrogen pressure in the coolant, and using solubility data given in¹¹. The 2000 tons vanadium were found to dissolve 7 kg hydrogen corresponding to (T/H = 0,2) about 230 moles tritium.

Graphite.-- Graphite is known to absorb hydrogen tenaciously. Strehlow¹⁰ discussed that a few milligrams of hydrogen per kilogram graphite could be absorbed under CTR conditions. The 10^6 kg graphite in the blanket then represent a potential reservoir in the order of one kg of hydrogen (500 moles) or with the above T/H ratio about 100 moles tritium.

Helium.-- The coolant contains about 1 mole tritium in case of design 1.

Beryllia.-- BeO might accumulate considerable quantities of tritium (Fig. 3). (After 5 years 1, 10^3 , $8 \cdot 10^3$, $1 \cdot 10^4$ moles, curve (1), (2), (3), and (4) respectively.) As reasonable design data only values in the range be-

tween curve (1) and curve (2) can be accepted for the present blanket. It must be pointed out that these values are considerably lower than those based on experimental data from Scott and Wassell⁷, curves (3) and (4), Fig. 3.

The inventories are summarized in table 2.

Table 2 Tritium inventory of the CTRD I blanket

Reservoir	T-inventory T_2 [mole]
Helium coolant (20 tons)	1
Lithium (7 tons)	1 - 10
Graphite (6000 tons)	600
Vanadium structure (2000 tons)	230
Beryllia (2000 tons)	1 - 1000

It can be seen from the table that the tritium inventory of the design I will be determined mainly by graphite, vanadium, and beryllia, not by the lithium as is the case in other designs. The exact values depend very much on the material data (see the wide range for beryllia; the chemisorbed quantity on graphite is also rather uncertain).

Even, if the stationary tritium concentration in the coolant does not add much to the inventory, it must be kept as low as possible because the inventory in graphite and structural material are dependent on this equilibrium pressure, and because leakage and tritium transfer to the gas purification plant should be low. The higher inventory given in the table for BeO seems to be prohibitive compared to the other tritium reservoirs. The results of the parametric study, shown in Fig. 3 indicate strongly that quick release of tritium from BeO is necessary and must be guaranteed by appropriate grain sizes.

SECTION II: HYDROGEN GETTERING BY THE BREEDING ZONE

High quantities of tritium in the coolant loop and in the gas purification plant increase the hazard potential of a CTR. Leakage of tritium to the secondary coolant may cause contamination problems. Several alternatives have been proposed in the literature to reduce both, the tritium and leakage of tritium containing chemical species from the coolant loop: a) addition of oxygen to the coolant to reduce the HT and T₂ partial pressure by water formation¹², b) permeation barriers which are impermeable for hydrogen/tritium¹¹, c) gettering of tritium by hydride forming metals (Zr, Y)¹³.

Solution a) causes new corrosion problems and seems not to be applicable when the coolant is in contact with graphite, b) needs development of new materials and techniques, c) requires an additional facility.

There seems to be, however, a possibility to decrease the tritium partial pressure without any need for additional devices or processes, which we would like to discuss in this section.

The liquid lithium being present in big quantities as breeding material is a potential hydrogen getter, if the hydrogen content in the liquid can be kept as low as several authors deem necessary in terms of low lithium inventory.

As has been shown in the first part of this paper, the partial pressure of the hydrogen isotopes in the coolant is expected to be about 10^{-2} torr corresponding to 1 vpm. If the canning of the lithium is permeable to hydrogen, the liquid lithium will getter hydrogen from the coolant. Since the area of the lithium canning facing the coolant is huge ($8 \cdot 10^7 \text{ cm}^2$ for design I) and the wall is thin (0,1 cm), the gettering should be considerable, if the hydrogen transfer at the phase boundary canning-material/lithium is not too slow. To our knowledge, nothing is known about this transfer, but several authors discuss the possibility of direct tritium diffusion from liquid lithium through thin metal walls¹⁴ (in connection with tritium separation). This is only a possible concept, if the tritium transfer between the phases is rapid enough. The estimates to follow are all based on this assumption.

The permeation rates and directions of net transport may be calculated if a complete set of data for the respective hydrogen partial pressure, interface area, wall thickness, and temperatures, and permeation constants is available. According to the present design the lowest pressure is expected to exist above the liquid lithium (10^{-10} - 10^{-8} torr at 600°C and for hydrogen concentration of 1 - 10 ppm). These pressures have been taken from Ihle¹⁵, who investigated the lithium/deuterium equilibrium. The D_2 and T_2 pressures in the diverter region are still questionable, but design values in the order of 10^{-5} torr¹⁶ have been reported. A calculation of net hydrogen isotope transport is based on our blanket design data and Eq. (10) was used.

$$\sqrt{p_{\text{H}_2}(T)} = \frac{d}{A} \cdot \frac{1}{K_{\text{H}}} \exp(\Delta H/RT) \cdot \sum_i S_i^{\text{Li}} + \sqrt{p_{\text{H}_2}^{\text{Li}}(T)} \quad (10)$$

where

A = surface of the liquid lithium zone

d = wall thickness

K_{H} = permeation constant = $2,1 \text{ mol cm}^{-1} \text{ d}^{-1} \text{ torr}^{-1/2}$ ¹⁷

ΔH = activation energy = 14200 cal/mol ¹⁷

$\sum_i S_i^{\text{Li}}$ = sum of all H, D, T sources (in moles/d) outside the lithium zone which contribute to the hydrogen pressure in the coolant. Isotopic effects have been neglected.

$p_{\text{H}_2}^{\text{Li}}$ = hydrogen pressure over lithium for the designed stationary state H, D, T concentration at a given temperature. ($p_{\text{H}_2}^{\text{Li}} = 10^{-9}$ torr for xHDT = 3ppm atomic at 600°C .)

In Fig. 5 the hydrogen pressure in helium is shown as a function of $\sum_i S_i^{\text{Li}}$ for various lithium temperatures. For blanket design I we have one lithium zone, its temperature is chosen here to be 600°C . The hydrogen sources are: $S_{\text{T}_2}^1 = 13 \text{ moles/d}$ release from BeO, $S_{\text{H}_2}^2 = 75 \text{ moles/d}$ due to water leakage from the helium steam heat exchanger (the value was extrapolated from the $20 \text{ MW}_{\text{th}}$ DRAGON reactor value to the 5 GW_{th} of the present design). $S_{\text{D}_2\text{T}_2}^3$, the deuterium and tritium permeation rate via the plasma blanket interface amounts to about 60 moles/d if the wall temperature is held at 400°C and when the surface is $1 \cdot 10^8 \text{ cm}^2$ and the wall thickness is 0,5cm. The sum of $S^1 + S^2 + S^3$

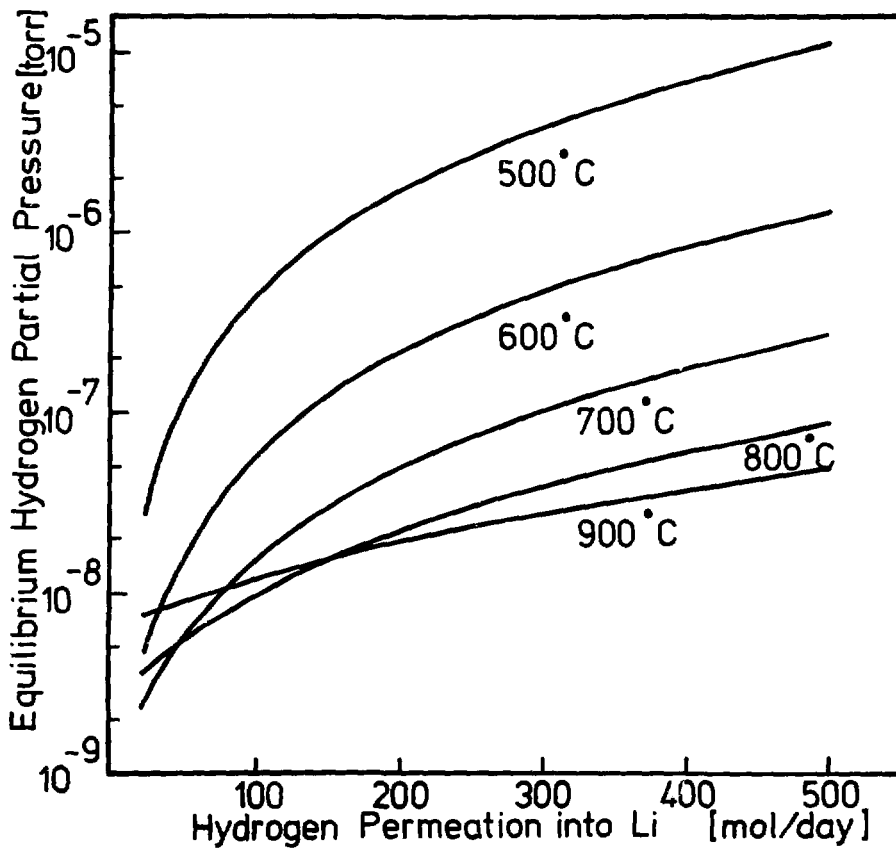


Fig. 5

Hydrogen sources (S) and equilibrium pressures for CTRD I

then gives 148 moles/d (Tab. 3) and Fig. 5 yields a hydrogen pressure in the blanket of about 10^{-7} torr. The ratio of H:D:T is 2,5:1,0:1,4. It follows from these atomic ratios that the tritium pressure is also of this order of magnitude and that it is maintained without any additional hydrogen removal facility.

Table 3 Protium, deuterium, and tritium leakage into the helium coolant.

Source	Species	moles/d
BeO plasma/blanket interface	T ₂	13
	D ₂	30
heat exchanger	T ₂	30
	H ₂ (from H ₂ O)	75

It can be seen from table 3 that considerable quantities of tritium have to be gettered by the liquid lithium. The total of 148 moles hydrogen per day is comparable to the quantity of tritium within the lithium being bred per day (some 140 moles/d). It must, therefore, be recalled that a lot of speculation remains as to the feasibility of the gettering concept. The problem of the above mentioned phase - transfer step for tritium from the metal into the liquid lithium should be clarified. Permeability data are poor. The quantities of hydrogen permeating through the first wall into the blanket may be subject to changes by at least an order of magnitude. The latter, however, does not have too much influence on the steady state hydrogen pressure. It increases by a factor of three when the permeating quantity is raised by a factor of ten (see Fig. 5). It can further be shown that the relatively slow diffusion of tritium in lithium as well as the implantation of recoil tritium from the nuclear reaction ${}^6\text{Li}(n,\alpha)\text{T}$ need not to be considered in the above calculations. McCracken et al.¹⁸ discussed the consequences of slow tritium diffusion in lithium for tritium separation via permeation. They presented experimental evidence for a concentration dependent diffu-

sion coefficient of deuterium in lithium and for the D-value determining the permeation rate through niobium into static lithium. However, for the blanket concept of this paper we must consider circulating lithium as it will be pumped through a separation plant. The possibility of diffusion controlled permeation was checked. An estimation for laminar flow yields a static lithium layer adjacent to the wall of 10^{-4} cm thickness and a minimum concentration gradient of only 10^{-4} moles/cm⁴ across this layer to getter 148 moles hydrogen per day (Tab. 3). (Fick's first law was used with $D = 10^{-7}$ cm²/s¹⁸.) The increase of the stationary tritium concentration in lithium from 3ppm to 3,2ppm maximum in the boundary layer is so small that an influence on permeation flow is negligible.

Next the implantation of tritium into vanadium was considered. The maximum increase of the concentration in vanadium due to implantation was calculated by Eq. (11) to $5 \cdot 10^{-2}$ % of the concentration equilibrium with the P_{HDT} value over lithium (10^{-9} torr). The increased concentration corresponds to an apparent increase of P_{HDT} of 10^{-12} torr and has, therefore, no influence on the permeation flow.

$$c = \frac{q \cdot r}{3D} \quad (11)$$

q = implantation rate, r = range, and D = diffusion coefficient of tritium in vanadium

Independent of the possible use of permeable walls it seems that it is not easy to avoid transfer of hydrogen isotopes into the lithium zone even when using less permeable materials. The permeability of steel is three orders of magnitude lower than that of vanadium¹¹, however, the hydrogen permeation still amounts to 40 moles/day (600°C, hydrogen pressure in helium 10^{-2} torr). Such a high permeation causes a dilution of the bred tritium (1:4) and calls for effective hydrogen isotope separation. Only tungsten may be impermeable enough to avoid remarkable permeation of hydrogen into lithium.

The calculations of hydrogen permeation through vanadium walls led to an

equilibrium pressure by gettering of about 10^{-7} torr. This low pressure has appreciable influence on the blanket tritium inventories as can be seen from Tab. 4.

Table 4 Tritium inventory in CTRD I blanket at $p_{\text{HDT}} = 10^{-7}$ torr

Reservoir	T-inventory T_2 [moles]
Helium coolant (20 tons)	$1 \cdot 10^{-5}$
Lithium (7 tons)	1 - 10
Graphite (6000 tons)	100 ^a
Vanadium structure (2000 tons)	4
Beryllia (2000 tons)	1 - 800

^a exact values not known

CONCLUSIONS

Section I

- The tritium production from beryllium via n, t and n, α reactions leads to considerable contamination of the helium coolant.
- BeO will retain tritium and thereby increase the tritium inventory of the reactor.
- It has been shown that a lot of information about the chemical nature of tritium in helium can be obtained from existing HTGR's.
- The gas purification plant accumulates considerable quantities of tritium which must be recovered.
- The tritium inventories in the blanket designs I - III are most likely determined by tritium chemisorption on graphite and storage in BeO.

Section II

There are good reasons to regard hydrogen gettering by the lithium zone as a possible concept to keep the lithium pressure low in the helium coolant. Thus, hydrogen-permeable walls should be considered as an alternative design component; the main consequences being:

- The hydrogen gettering capability of the breeding zone is high, provided that the hydrogen content in the liquid lithium can be kept as low as some authors consider necessary. It can be shown that in this case no precautions are necessary to prevent leakage of H, D, and T from the plasma into the blanket.

- All tritium and deuterium which enters the coolant is gettered by the breeding material and thus rejoins directly the fuel cycle in the tritium separation plant.

- It is expected that all possible hydrogen molecules (H_2 , HD, D_2 , HT, DT, T_2) are present in the separation plant in considerable quantities, if not very low permeability of the casing can be guaranteed.

- Considerable decrease of tritium content in the gas purification plant and possibly a simpler construction results because hydrogen need not be handled.

- The tritium inventory in the coolant, wall material, and graphite is decreased.

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I: DESIGN AND MINIMIZATION OF TRITIUM INVENTORY

J.R. Powell

Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

ABSTRACT

Tritium blanket inventories of 100 curies/MW(e) are readily achievable, and inventories as low as 10 curies/MW(e) are possible for blankets with small lithium compound particulates ($\leq 50\mu$) at $T \geq 800^\circ\text{C}$. Of the three release modes [A - to the main coolant (e.g., He) stream; B - to a separate processing circuit; and C - to the plasma region], mode A appears optimum for blankets using gas-cooled metallic structures (e.g., Al, stainless), while mode C appears optimum for high temperature refractory (e.g., C, SiC) structures. The greater structural complexity of mode B makes it less attractive than modes A and C. No recovery method is required for mode C release. With mode A release, tritium inventory in the coolant circuits ranges from 1 to 10 curies/MW(e), depending on processing parameters. Tritium leak rates to the environment during normal operation can be kept to $\leq 10^{-3}$ curies/MW(e) per day with low permeability barriers. In general, a mixture of T_2 and T_2O is present in the coolant stream. Three methods of tritium recovery are examined: (1) Conversion to T_2 followed by absorption in a metal hydride bed. (2) Conversion to T_2 followed by condensation at $\approx 6^\circ\text{K}$. (3) Conversion to T_2O followed by condensation at $\approx 100^\circ\text{K}$.

INTRODUCTION - MATERIALS AND BLANKET CHOICES

The use of solid lithium compounds to breed tritium in fusion reactor blankets was proposed at BNL several years ago¹ and has been examined in more detail since then.^{2,3,4} Solid lithium compounds have three important advantages for fusion blankets:

1. Elimination of the corrosion of structural materials by blanket coolants.
2. Reduction of the tritium inventory in the blanket by an order of magnitude or more.
3. Reduction of the residual long term blanket activation by many orders of magnitude.

The first advantage results from using solid lithium compounds with gaseous blanket coolants, i.e., helium. If liquid lithium or lithium salts are used for breeding, the structural materials might seriously corrode, even in stagnant or near-stagnant systems. With an all solid blanket and gas coolant, the possibility of corrosion can be virtually eliminated (except perhaps for corrosion of refractory metal structures by impurities in the coolant gas).

The second advantage results if the solid lithium compound is selected to have very low retentivity for tritium. For example, compounds can be selected to give mean holding times of only a few minutes for the bred tritium. Total blanket tritium inventories for a 1000 MW(e) reactor can then be kept at $\sim 10^4$ curies, or almost two orders of magnitude less than possible with liquid lithium metal or salts.

The third advantage results from selection of blanket structural materials, e.g., Al, C, or SiC, with very low residual activation. These materials do not appear compatible with liquid lithium metal or salts. Residual activations of ≤ 1 curie/MW(e) are possible, compared to $\sim 10^6$ curies/MW(e) with structural materials like stainless steel or niobium.

There are dozens of solid lithium alloys (binary and ternary) and compounds with melting points high enough to be suitable for fusion reactor blankets. Selection of an optimum alloy or compound will depend on many factors besides the physical properties of the solid, so it is not possible at this time to definitely pick a best choice. However, the relative advantages and disadvantages of 10 of the most promising candidates are summarized in Table 1. These are not listed in any order of potential promise. Of the 10 alloys or compounds, all those that have been tested for tritium retentivity appear to have very low mean hold up times, i.e., less than one hour, at the conditions they would operate in a blanket. It is likely that all those listed in Table 1

Table 1. Characteristics of Solid Lithium Compounds for Tritium Breeding

<u>LITHIUM ALLOY OR COMPOUND</u>	<u>M.P. °C</u>	<u>TRITIUM RETENTIVITY AT OPERATING CONDITIONS</u>	<u>NEUTRON MULTIPLIER NEEDED FOR BR>1</u>	<u>LOW RESIDUAL RADIOACTIVITY</u>	<u>REACTS WITH AIR</u>	<u>SINTERING PROBLEMS</u>	<u>CHEMICALLY STABLE</u>	<u>RESOURCE LIMITATIONS</u>
LiAl ⁽⁵⁾	718	VERY LOW	YES	YES	SLOWLY	MAYBE	YES	NO
LiAlO ₂ ⁽⁶⁾	1900-2000	VERY LOW	YES	YES	NO	PROBABLY NOT	YES	NO
Li ₂ SiO ₃ ⁽⁶⁾	1204	VERY LOW	YES	YES	NO	PROBABLY NOT	YES	NO
Li ₂ Be ₂ O ₃ ⁽⁷⁾	1150	UNKNOWN	NO	YES	NO	UNKNOWN	YES	Be (7)
Li ₇ Pb ₂ ^(5,8)	726	VERY LOW	NO	YES	SLOWLY	UNKNOWN	YES	NO
Li ₃ Bi ⁽⁵⁾	1145	UNKNOWN	NO	SOME Po ²¹⁰	PROBABLY SLOWLY	UNKNOWN	YES	Bi
Li ₄ Si ⁽⁸⁾	635	UNKNOWN	NO	YES	PROBABLY SLOWLY	UNKNOWN	PROBABLY	NO
Li ₃ N ⁽⁹⁾	~800	UNKNOWN	NO	YES	PROBABLY SLOWLY	UNKNOWN	PROBABLY REQUIRES N ₂ GAS	NO
Li ₄ Sn ⁽⁵⁾	765	UNKNOWN	NO	NO	PROBABLY SLOWLY	UNKNOWN	PROBABLY	NO
Li ₂ B ₄ O ₇ ⁽⁶⁾	930	UNKNOWN	YES	YES	PROBABLY NOT	UNKNOWN	YES	REQUIRES SEPARATED B ¹¹

will have very low tritium retentivity, since all exhibit a strongly exothermic reaction upon formation, and the lithium is tightly bound chemically in the alloy or compound. All appear chemically stable, with the exception of Li_3N , which will require some low partial pressure of N_2 gas in the coolant to prevent decomposition. Li_2O has been suggested¹⁰ as a possible solid breeding compound since it has a high lithium content and a high melting point (1700°C). However, it has a relatively high vapor pressure and probably would have to be enclosed in some type of container to be acceptable.

Of the 10 choices in Table 1, the ceramic compounds (LiAlO_2 , Li_2SiO_3 , $\text{Li}_2\text{Be}_2\text{O}_3$, and $\text{Li}_2\text{B}_4\text{O}_7$) do not react with air, other than to absorb moisture, while the alloys (LiAl , Li_7Pb_2 , Li_4Si , Li_4Sn) and Li_3N react slowly at room temperature. These materials can be formed and stored in an inert atmosphere. Assembly into blanket modules or structure may involve exposure to air, but the short exposure should not cause deterioration. LiAl and Li_7Pb_2 have been exposed to air in BNL experiments without affecting their ability to release tritium.

Sintering behavior is not well known. There appears to be some indication that LiAl may have some problems. Experiments with LiAlO_2 indicate that for times of a month at 1000°C , particles do not sinter. In fact, tritium release rates increase if LiAlO_2 is held at high temperatures for long periods. At the lower temperature characteristic of most blanket designs, i.e. $\sim 700^\circ\text{C}$, it seems unlikely that there will be a sintering problem for LiAlO_2 , and probably also for most of the other compounds, during the several year life of the blanket.

For these blankets using a lithium alloy or compound that is strongly enriched in Li^6 , it is likely that the solid lithium alloy or compound will be diluted with some inert material for acceptable volumetric power densities. The diluent, e.g., graphite, alumina, etc., will be the major part of the mixture, so that possible reactions of the lithium alloy or compound with the diluent will be governing, not sintering reactions of the solid lithium material.

Most of the materials listed in Table 1, if sufficiently purified, will have very low long term residual radioactivity (other than tritium) in a fusion reactor. The actual activity level will depend on details

of design, but will generally be on the order of 10^3 curies or less for a 1000 MW(e) reactor. Impurities (i.e., Fe, Mn, Zn, etc.) which result in radiologically objectionable isotopes will have to be kept at the ppm level or below to achieve these levels of activity, however. The principal exception to the low activity characteristic is Li_4Sn , which will have a number of long lived tin daughters. Some Po^{210} will be produced by (n, γ) absorptions in Bi. Since this is a particularly objectionable radio-isotope, detailed examination would have to be made of blanket designs with this material to see if undue hazards were involved.

Most of the materials in Table 1 are not resource limited (other than the possible limitations on lithium, which is a common consideration for all DT fusion reactors). Be is limited, but present resources appear ample for a large fusion economy, i.e., 10^6 MW(e)¹¹, and future discoveries, together with exploration of low grade deposits not now counted as reserves, should permit much larger fusion economies. Bismuth appears to be much more limited in resources,¹² and it may not be possible to sustain a large fusion economy. Lithium compounds with boron, e.g., $\text{Li}_2\text{B}_4\text{O}_7$, will not be resource limited, but would require that the boron principally be B^{11} , obtained by isotope separation, to achieve good neutron economy.

In order to have net tritium breeding, i.e., a breeding ratio (BR) greater than one, the solid lithium alloy or compound must either be principally lithium, or a neutron multiplier must be present in the blanket. Materials such as Li_3N and Li_4Si have enough lithium content to breed without a neutron multiplier and the lithium would be natural, i.e., not enriched in Li^6 (natural Li^6 content is 7.5%). Materials such as Li_7Pb_2 , Li_3Bi and $\text{Li}_2\text{Be}_2\text{O}_3$ have a neutron multiplying element as part of the material and would have higher breeding ratios than Li_3N or Li_4Si . These materials would also be used without enrichment.

The remaining materials - LiAl , LiAlO_2 , Li_2SiO_3 , and $\text{Li}_2\text{B}_4\text{O}_7$, do not have a high enough Li content to breed without incorporating some type of neutron multiplier in the blanket. These could be: Be or Be compounds (BeO , Be_2C), Pb or Pb compounds (PbO , PbS); Bi or Bi compounds (Bi_2O_3 , BiS). It is more efficient to minimize parasitic neutron reactions in the companion elements of the lithium compound by enriching the lithium in Li^6 . This then allows the amount of lithium

compound in the blanket to be reduced, ensuring that most of the 14 mev source neutrons interact with the neutron multiplier. Almost all of the breeding is then by neutron absorptions in Li^6 . The optimum Li^6 enrichment must be determined by detailed design; in general, however, it will probably be 50% or greater. Enrichment also minimizes tritium blanket inventory if the tritium release rate from the solid lithium compound is controlled by equilibrium between T_2 gas and the solid and not by diffusion in the solid.

Table 2 shows some of the breeding blankets possible with solid lithium compounds. These have been grouped into three categories: sub-breeders, sustainer-breeders, and super-breeders. Sustainer-breeders have breeding ratios greater than one, but cannot breed enough surplus tritium for other reactors to be significant. Sub-breeders must be supplied with makeup tritium from other reactors, while super-breeders can supply significant amounts of surplus tritium to other reactors. Table 3 lists some of the relative advantages and disadvantages of the various breeding blanket choices. Depending on design, one super-breeder could supply one to four sub-breeders. There is also the possibility that sub-breeders could obtain surplus tritium from other sources than a super-breeder with a solid lithium compound blanket. Reactors with liquid Li metal blankets, such as INWAK-1, or DD reactors, or fusion-fission reactors, could supply surplus tritium to sub-breeders. Such sources would require development of additional technologies and in general would not seem as attractive as a solid blanket super-breeder, unless Be resources were so limited as to not be significant for CTR purposes, which seems unlikely, and in addition, the alternate super-breeder choices had very low temperature capability.

With the wide variety of choices available and the many uncertainties about properties, resources, etc., it is not possible to make a definitive assessment of the optimum type of solid breeding blanket. Some rough judgments can be made, however, and these are summarized in Table 4. One of the most important determinants for choosing blanket type is the availability of Be. Present Be reserves seem ample for a large fusion economy [10^6 MW(e)] provided Al is used as the structural material and blankets operate at first wall loads of several MW(th)/m².

Table 2. Breeding Characteristics
of Blankets Using Solid Lithium Compounds

BREEDER TYPE	SOLID LITHIUM COMPOUND	ENRICHMENT STATE	STRUCTURAL MATERIAL	MODERATOR	NEUTRON MULTIPLIER	NOTES
<u>SUB-BREEDERS</u> (BR-1)						
I	LiAlO_2	ENRICHED	C WITH INNER BLANKET	C	NONE	HIGH TEMP GRAPHITE BLANKET, BR ~ 0.7
II	LiAl	NATURAL	Al	C, SiC (SECONDARY)	NONE	BR ~ 0.9
III	$\text{LiAl}, \text{LiAlO}_2$ Li_2SiO_3	ENRICHED	Al, SS, Nb, V, Mo	C, SiC, Al_2O_3	NONE	BR ~ 0.8
<u>SUSTAINER-BREEDERS</u> (1-CR61.3)						
I	$\text{LiAl}, \text{LiAlO}_2$, Li_2SiO_3	ENRICHED	Al, SS, Nb, V, Mo	C, SiC, Be BeO, Be_2C	Be, Be, C, BeO, PbO, PbS	
II	Li_7Pb_2 , Li_3Bi	NATURAL	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	NONE	Pb or Bi ARE NEUTRON MULTIPLIERS
III	$\text{Li}_2\text{Be}_2\text{O}_3$	NATURAL	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	NONE	Be IS NEUTRON MULTIPLIER
IV	Li_3Si , Li_3Sn , Li_4Sn	NATURAL	Al, SS, Nb V, Mo	C, SiC (SECONDARY)	NONE	SOME COMBINATIONS MAY HAVE BR > 1
<u>SUPER-BREEDERS</u> (BR-1.3)						
I	$\text{LiAl}, \text{LiAlO}_2$, Li_2SiO_3	ENRICHED	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	Be, Pb, Bi	MAX BR ~ 1.5
II	Li_7Pb_2 , Li_3Bi	NATURAL	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	NONE	Pb AND Bi ARE NEUTRON MULTI- PLIERS

Table 3. Advantages and Disadvantages of Alternate Solid Blanket Choices

BREEDER TYPE	ADVANTAGES	DISADVANTAGES
<u>SUB-BREEDER</u>		
I	HIGH TEMPERATURE GRAPHITE (~2000°C), MINIMUM RADIATION DAMAGE	LOW BR
II	BR CLOSE TO ONE	MAXIMUM TEMPERATURE LIMITED (~500°C)
III	HIGH TEMPERATURE CAPABILITY (~900-1000°C) WITH Li_2SiO_3 OR LiAlO_2	LOW BR
<u>SUSTAINER-BREEDER</u>		
Ia	HIGH TEMPERATURE CAPABILITY (~900-1000°C) WITH Li_7SiO_3 OR LiAlO_2 AND BERYLLIUM (Be, BeO, Be ₂ C) OR PbS AS MULTIPLIER	Be (RESOURCE LIMITED?) OR S ACTIVATION
Ib	NO Be, NO S ACTIVATION	MEDIUM TEMPERATURE CAPABILITY (~700°C) WITH PbO
IIa	NO RESOURCE LIMITATION	MAXIMUM TEMPERATURE LIMITED (~500°C) WITH Li_7Pb_2
IIb	GOOD TEMPERATURE CAPABILITY (~800°C)	Bi RESOURCE LIMITATION
III	GOOD TEMPERATURE CAPABILITY (~800°C)	Be (RESOURCE LIMITED?)
IV	NO RESOURCE LIMITATION	MAXIMUM TEMPERATURE LIMITED (~500°C). Sn ACTIVATES IF Li_4Sn USED.
<u>SUPER-BREEDER</u>		
Ia	HIGH TEMPERATURE CAPABILITY (~900-1000°C) WITH Li_2SiO_3 OR LiAlO_2 AND Be AS NEUTRON MULTIPLIER	Be (RESOURCE LIMITATION)
Ib	NO RESOURCE LIMITATION WITH Pb AS MULTIPLIER	LOW TEMPERATURE CAPABILITY (~300°C)
IIa	NO RESOURCE LIMITATION WITH Li_7Pb_2	MAXIMUM TEMPERATURE LIMITED (~500°C) WITH Li_7Pb_2
IIb	GOOD TEMPERATURE CAPABILITY (~800°C) WITH Li_3Bi	Bi RESOURCE LIMITATION

Table 4. Assessment of Favored Alternate Solid Blankets

AMPLE BERYLLIUMDESIRED CHOICE

1. SUSTAINER-BREEDER-I WITH Be
OR Be_2C AND LiAlO_2

OR

2. SUB-BREEDER-I (HIGH TEMPERATURE
C AND LiAlO_2)

AND

SUPER-BREEDER-I WITH Be AND LiAlO_2 NOTESMINIMUM Be REQUIREMENTS - HIGH
TEMPERATURE CAPABILITYHIGH TEMPERATURE CAPABILITY -
SUB-BREEDER HAS MINIMUM RADI-
ATION DAMAGE - REQUIRES DEVEL-
OPMENT OF 2 BLANKET TYPESSECOND CHOICE

3. SUB-BREEDER-III WITH LiAlO_2

AND

SUPER-BREEDER-I WITH Be AND LiAlO_2 HIGH TEMPERATURE CAPABILITY -
REQUIRES 2 BLANKET TYPES -
SOME REACTORS OPERATE WITHOUT BeINSUFFICIENT BERYLLIUMDESIRED CHOICE

4. SUSTAINER-BREEDER-I WITH PbO AS
NEUTRON MULTIPLIER AND LiAlO_2

GOOD TEMPERATURE CAPABILITY

SECOND CHOICE

5. SUPER-BREEDER-II WITH Li_7Pb_2

AND

SUB-BREEDER-I OR SUB-BREEDER-III
WITH LiAlO_2 SUB-BREEDER HAS HIGH TEMPERATURE
CAPABILITY - SUPER-BREEDER
TEMPERATURE CAPABILITY IS
LIMITED - 2 BLANKET TYPES

If blankets are suitably designed, further low grade Be resources that are presently uneconomic can be exploited for CTR blankets without appreciably increasing blanket cost. Increases in Be mining costs of a factor of 10 can be tolerated without serious economic penalty. It thus appears likely that ample Be will be available for CTR's. The best choice from the 3 options shown will depend on factors such as benefits from minimizing radiation damage (Sub-Breeder-I), acceptability of Be in reactors sited near population centers, and acceptability of tritium shipments between reactors.

If Be resources are insufficient for a large fusion economy, sustainer-breeders with PbO neutron multipliers and LiAlO_2 would appear to be the most desirable choice, since they would have a fairly good temperature capability. Second choice would appear to be a sub and super-breeder combination with the super-breeder using Li_7Pb_2 , and the sub-breeder being of either the I or III type with LiAlO_2 as the breeding material.

In general, LiAlO_2 seems to be a very attractive choice for the solid breeding compound, since it should permit high temperature operating of the blanket, and appears to be quite inert. If the initial favorable results are confirmed by further work, then it would be the best choice for the blanket, with other Li alloys or compounds only being used in the event that Be or other neutron multipliers, e.g., Pb, were not feasible.

MODES OF TRITIUM RELEASE IN SOLID LITHIUM BLANKETS

There are 3 possible release modes for the tritium that is bred in the solid lithium alloy or compound:

- A. Diffusion from the solid into the main He coolant stream.
- B. Diffusion from the solid into a separate He processing stream, which is essentially isolated from the main He coolant stream (a small amount of mixing would probably be tolerated).
- C. Diffusion from the solid into the vacuum region between the first wall and the plasma.

In modes A and B, the bred tritium would be recovered from the He streams by some form of trapping. The various alternative trapping methods are discussed in a later section. In mode C the bred tritium would mix with the escaping plasma, and would be recovered either from the divertor exhaust or from the reactor diameter vacuum pumps.

Figure 1 shows these different release modes for a modular blanket concept. All 3 release modes are feasible with enriched lithium alloy or compound modular blankets. However, with aluminum modular shells (shown in Figure 1), the module diameter must be reasonably large, e.g., 0.3-0.6 meter, to effectively thermally insulate the cool aluminum structure from the hot interior. This is necessary to achieve good overall power cycle efficiency, since the hot interior receives ~70% of the fusion energy. If the entire blanket had to operate at the temperature allowed for the aluminum shell, the resultant overall cycle efficiency would be unacceptably low. The minimum module diameter restriction for aluminum makes modes B and C, in which the lithium compound must be localized, unattractive.

The large module diameter results in relatively high flux disadvantage factors and inefficient use of neutrons. A further drawback of mode C for aluminum structures is that the 4.8 Mev neutron absorption energy in Li^6 is deposited in the cool aluminum shell instead of the hot interior, as in mode A. This substantially reduces the overall power cycle efficiency.

With structures other than Al, i.e., SS, Nb, V, Mo, the blanket modules can be operated with a much hotter structure. Thermal insulation is not required, and modes B and C are as neutronicallly and energy efficient as mode A. Mode B remains more mechanically complex than the other two modes, however. The choice between mode A and C for these blankets must depend on more detailed design considerations.

With natural enrichment solid Li alloys or compounds, (e.g., LiAl , Li_4Si , etc.), the solid Li must fill virtually the entire module shell, since Li^7 reactions are very important to obtain good breeding ratios. Almost all of the fusion energy is then deposited in the solid Li compound, and modes B and C do not appear to be feasible. This holds for

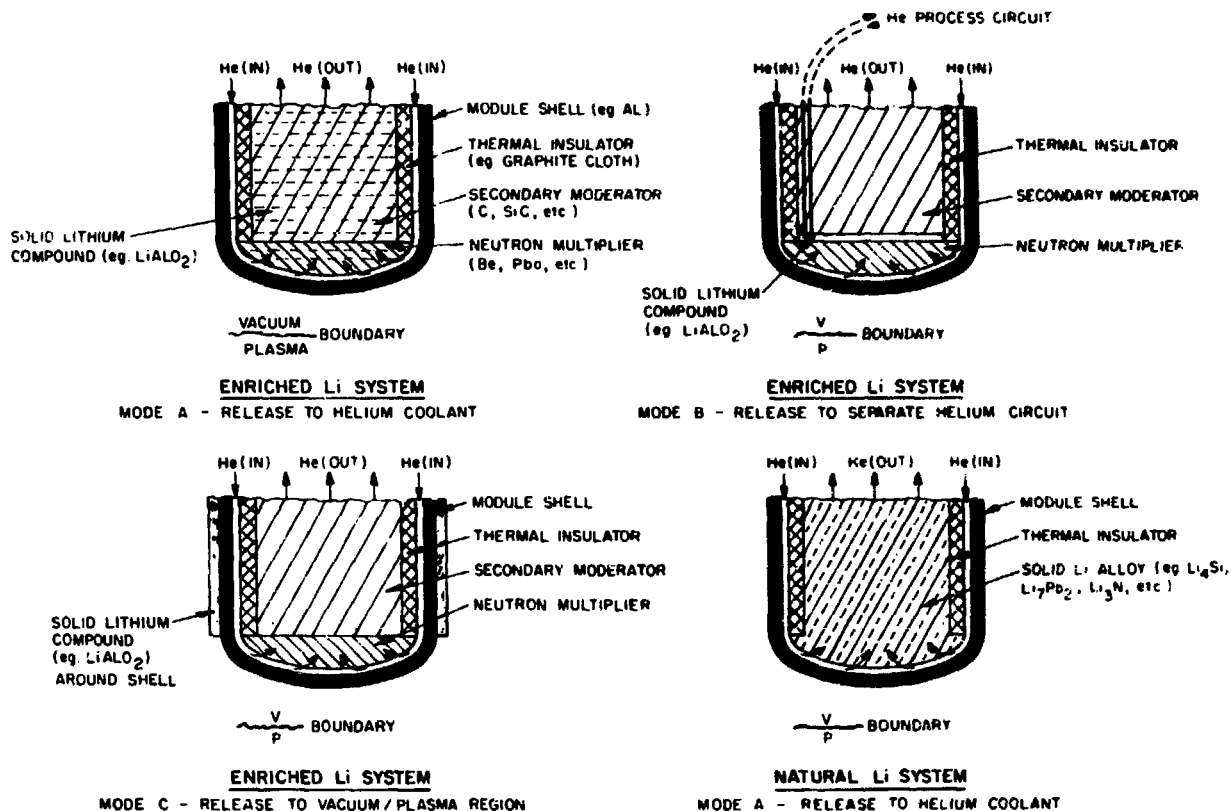


Fig. 1 Modes of Tritium Release for Modular CTR Blankets Using Solid Lithium Alloys or Compounds

all choices of blanket structure, including Al, SS, Mo, V, and Nb. Mode A release is quite acceptable, however.

With high temperature graphite blankets [Figure 2] all 3 release modes appear feasible, with the preferred mode being either C or A. The graphite blanket is essentially a thick (30-50 cm) structure of graphite with internal slots to permit radiant heat transfer to readily spread thermal energy deposited by neutrons and gammas through the blanket. Internal coolant tubes receive this energy by thermal radiation from the hot graphite. These coolant tubes are protected against radiation damage by the graphite structure. In mode C release, solid LiAlO_2 pellets can be incorporated into holes in the cooler graphite regions. The bred tritium will then flow out into the vacuum region by way of small spaces between the graphite blocks. In modes A and B release, the solid Li compound would be placed into some or all of the coolant tubes, and the bred tritium would enter the helium streams. Mode C would appear to be optimum for this type of blanket. In a variant of this blanket, the pulsed graphite blanket¹³, there are no coolant tubes incorporated in the graphite structure. The reactor is operated in the pulsed mode with no cooling while the plasma burns. After an extended burn, typically 10 minutes in length, the graphite blanket temperature has increased by $\sim 500^\circ\text{C}$, and the blanket is quickly cooled (typically 2 minutes) by direct contact with helium coolant at ~ 2 atm. The plasma volume is then quickly pumped down from 2 atm to a few microns in a short time (typically 2 minutes) and a new burn is started. Here mode C release is the only possible mode. A small fraction of the bred enters the pulsed He coolant flow, and can be recovered by a small process side stream.

The various possible release modes are summarized for the different blanket materials and breeder types in Table 5. Since mode A is the mode most likely to be chosen, the remainder of this paper concentrates on blanket inventories and trapping methods associated with this mode.

Actual blanket designs would be more complex than the idealized versions shown in Figure 1 and 2. Figure 3 shows an aluminum modular blanket design¹⁴ containing both LiAl and LiAlO_2 with a Be neutron

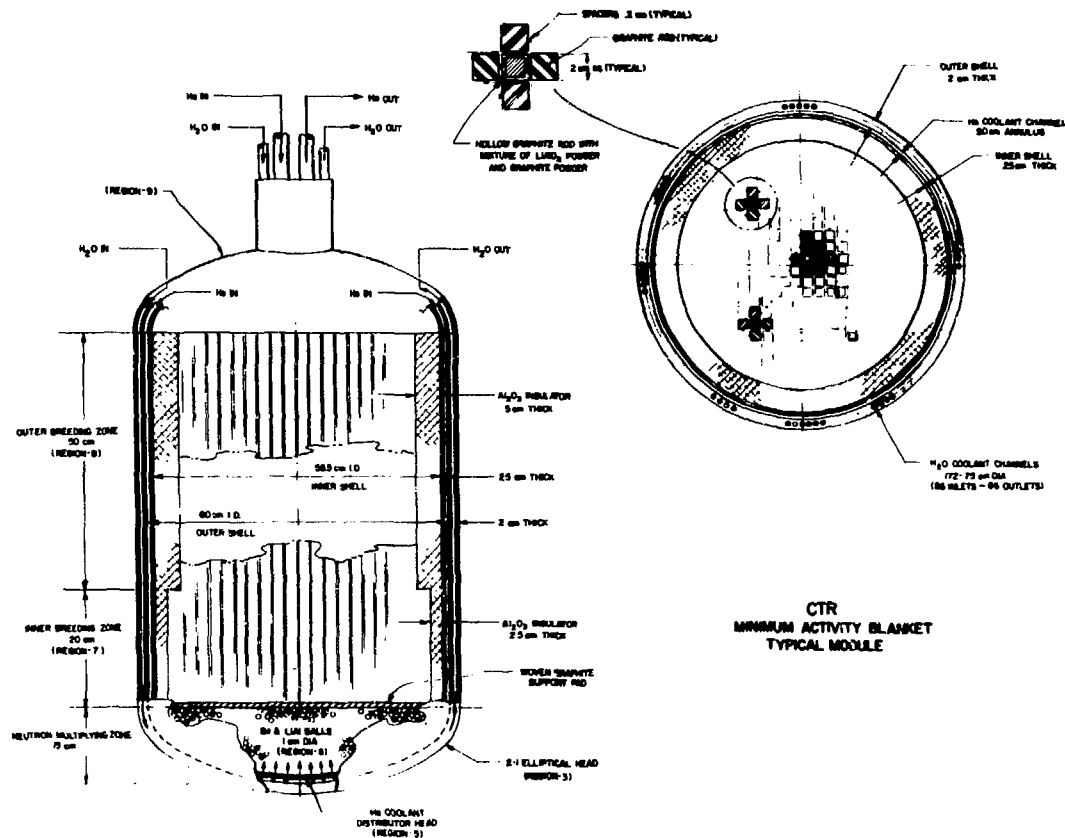
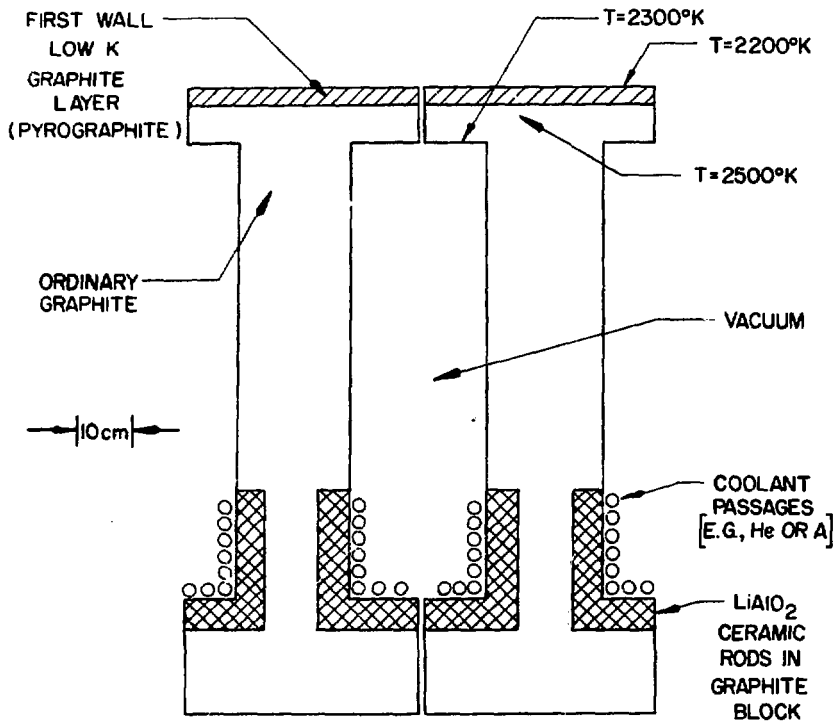


Fig. 2 High Temperature Graphite Blanket Structures

Table 5. Feasibility of Release Modes for Solid Blanket Options

<u>BLANKET MATERIALS</u>	<u>BREEDER CLASSIFICATION</u>	<u>MODE A RELEASE [To He Coolant]</u>	<u>MODE B RELEASE [To Separate He Circuit]</u>	<u>MODE C RELEASE [To Vacuum Region]</u>
1. HIGH TEMPERATURE GRAPHITE WITH ENRICHED LiAlO_2	SUB-BREEDER I	FEASIBLE	FEASIBLE BUT COMPLEX	OPTIMUM
2. ENRICHED LITHIUM (LiAlO_2 , etc.) WITH ALUMINUM STRUCTURE	SUB-BREEDER III SUSTAINER- BREEDER I SUPER-BREEDER I	OPTIMUM	FEASIBLE - COMPLEX AND NEUTRONICALLY INEFFICIENT	FEASIBLE - NEUTRONICALLY AND ENERGY INEFFICIENT
3. ENRICHED LITHIUM (LiAlO_2 , etc.) WITH SS , Nb, Mo, OR V STRUCTURE	SAME	FEASIBLE	FEASIBLE - COMPLEX	FEASIBLE
4. NATURAL LITHIUM (LiAl , Li_2Pb_2 , Li_2Si , etc.) ² WITH ALUMINUM STRUCTURE	SUB-BREEDER II SUSTAINER- BREEDER II, III, IV SUPER-BREEDER II	ONLY MODE FEASIBLE	NOT FEASIBLE	NOT FEASIBLE
5. NATURAL LITHIUM (LiAl , Li_2Pb_2 , Li_2Si , etc.) ² WITH SS , Mo, V, OR Nb STRUCTURE	SAME	ONLY MODE FEASIBLE	NOT FEASIBLE	NOT FEASIBLE

TYPE B-1 BLANKETS



ALTERNATIVE FIRST WALLS

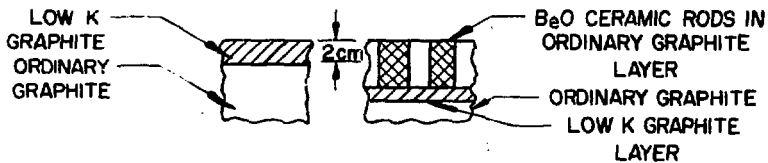


Fig. 3 Aluminum Blanket Module Design Incorporating Solid LiAl and LiAlO_2

multiplier and graphite moderator. The non-uniform temperature distribution in the module requires both a high temperature lithium compound (LiAlO_2) for the hotter regions, and a lithium material (LiAl) that releases tritium readily at lower temperatures ($\sim 400^\circ\text{C}$).

TRITIUM BLANKET INVENTORY

A number of factors can affect the tritium blanket inventory in a solid lithium blanket with mode A release. These include:

1. Type of solid lithium material
2. Total amount of solid lithium material
3. Particle size
4. Particle temperature
5. Coolant parameters [pressure, ΔT , reactor power]
6. Coolant impurities [O_2 , H_2]
7. Absorption in other blanket materials

For this paper, it is assumed that other blanket materials play no important role in determining tritium blanket inventory. It is further assumed that no significant diffusion barrier exists between the particles of solid lithium material and the He coolant. In general, the Li material will exist in a loose powder or lightly compacted state, and will probably be contained in some metallic or ceramic container, which will in turn be porous enough to permit rapid diffusion of the released tritium into the He coolant.

The tritium blanket inventory is then only a function of the release rate from the solid particles. At steady state, it is further assumed that either the diffusion rate of T in the solid particles is controlling, or that equilibrium between the partial pressure of T in the He coolant and T in the solid is controlling. For equilibrium, the atomic concentration of T is assumed constant throughout the particle. In practice, of course, sometimes both may be important.

If diffusion in the particle is controlling, the tritium inventory in the blanket is

$$I_T = 3 \times 10^4 \tau_T \dot{N}_T = 3 \times 10^4 \tau_T \frac{P_O (BR)}{Q N_O} \text{ curies} \quad (1)$$

where

τ_T = mean holdup time of T in particles, sec

$\dot{N}_T$ = g atoms T bred in blanket per sec

P_O = reactor power, watts

BR = breeding ratio, atoms T found in blanket per atom T burnt in plasma

Q = total energy per DT fusion, joules

N_O = Avogadro's Number

The mean holdup time must be averaged over the varying distribution of particle sizes, shapes, and temperatures. As a rough guide, assuming spherical particles of uniform diameter at uniform temperature ¹⁴, the mean holdup time for a continuously extracted system is

$$\tau_T = \frac{r_p^2}{15D} \text{ sec} \quad (2)$$

where

r_p = particle radius, cm

D = diffusion coefficient of T in solid, cm²/sec

The diffusion coefficient, D rapidly increases with increasing temperature. At any given temperature, τ_T can always be decreased by using smaller particles. Experiments described elsewhere ¹⁴ and in Part II of this paper indicate that tritium release from LiAlO₂ and Li₂SiO₃ is controlled by diffusion. Most of the released tritium comes off as T₂O. It appears very likely that compounds such as Li₂BeO₃ will also be diffusion limited.

Figure 4 shows the blanket tritium inventory in a 1000 MW(e) [2500 MW(th)] reactor as a function of mean holdup time. Holdup times of 10 minutes result in blanket inventories of $\sim 2 \times 10^4$ curies. Also shown are mean holdup times measured in 4 sets of experiments at BNL. In the experiments, the tritium is produced uniformly throughout the particle by neutron irradiation, and the tritium is then batch extracted by flowing He. The experiment is isothermal, but the particles have a

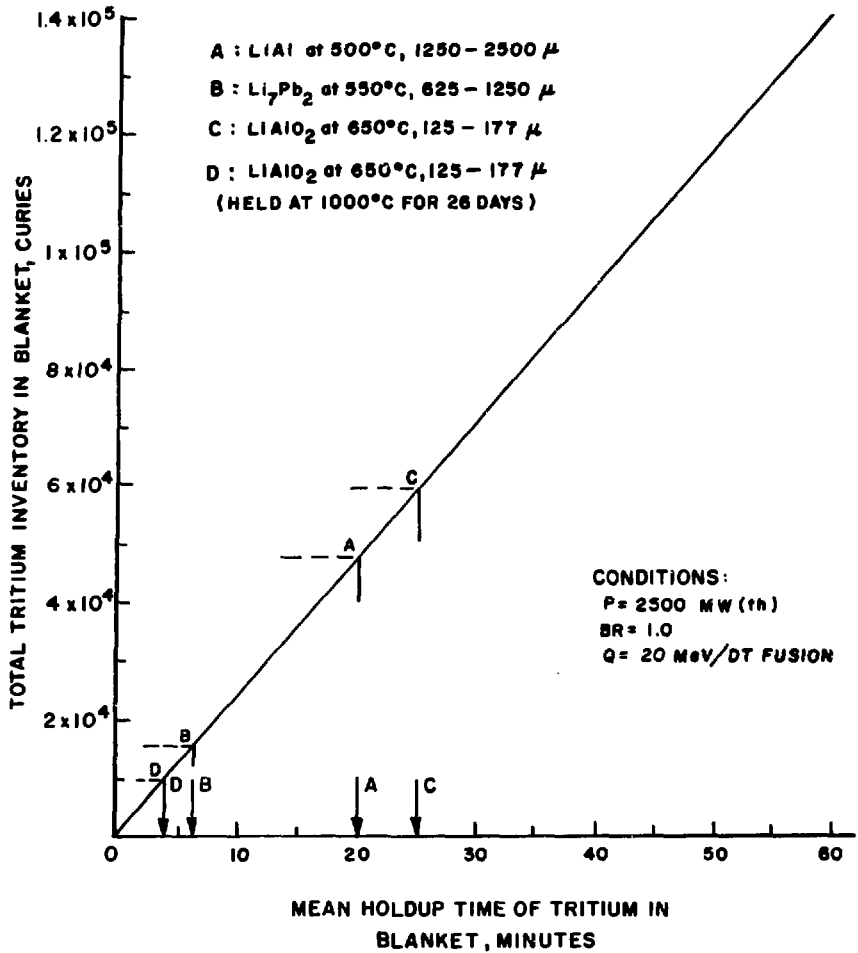


Fig. 4 Tritium Inventory in CTR Blankets As a Function of Mean Tritium Holdup Time

range of sizes and shapes. For purposes of this graph, the mean holdup time is taken as the time corresponding to 75% extraction of the bred tritium. Points C and D are different samples of the same material, with different holding times at 1000°C before irradiation and extraction. Interestingly, the tritium holdup time is much shorter for D, held at 1000°C for 28 days, than for C, which was not held at 1000°C . This indicates that extraction rates in a reactor may increase with time.

The material used was relatively coarse. Finer material would probably have shown considerably faster release rates. It appears from these experiments that if release is diffusion controlled, there should be no difficulty in maintaining tritium blanket inventory at $\sim 10^4$ curies.

With diffusion controlled release, the tritium blanket inventory is not affected by either the amount of Li compound, the coolant flow parameters, or impurities in the coolant.

With the other possible release controlling mechanism, equilibrium between the particles and tritium in the coolant, the release rate is not determined by particle size, but is affected by the other parameters—temperature, type and amount of solid material, and coolant parameters and impurities.

At equilibrium, the partial pressure of tritium, P_{T_2} , in the He coolant is related to the atomic concentration of tritium in the solid particles by

$$P_{T_2} = K_s^2 X_T^2 \text{ torr} \quad (3)$$

where

X_T = atom fraction of T in solid

K_s = Sieverts' constant, $\text{torr}^{\frac{1}{2}} [\text{atom fraction}]^{-1}$

with

$$X_T = 3.3 \times 10^{-5} \frac{I_T}{N_{SL}} = 3.3 \times 10^{-5} \frac{I_T A_{SL}}{\bar{f}_{SL} V_B \rho_{SL}} \quad (4)$$

where

I_T = tritium blanket inventory, curies

N_{SL} = amount of Li alloy or compound in blanket, g moles

A_{SL} = molecular weight of Li alloy or compound

f_{SL} = volume fraction of solid lithium material in blanket

V_B = blanket volume, cm^3

ρ_{SL} = density of solid lithium material, g cm^{-3}

A side stream of the He coolant is passed through a trap to remove tritium gas. Assuming the trap removes all of the tritium passing through it,

$$\dot{N}_{T_2} = f_p \dot{N}_{He} \frac{P_{T_2}}{P_{He}} = f_p \frac{P_o}{C_p \Delta T} \frac{P_{T_2}}{P_{He}} = \frac{\dot{N}_T}{2} = \frac{P_o (BR)}{2QN_o} \quad (5)$$

where

$\dot{N}_{T_2}$ = g moles T_2 removed by trap sec^{-1}

f_p = fraction of He coolant passing through trap

P_{He} = helium coolant pressure, torr

P_o = reactor power, watts

C_p = heat capacity of helium at constant pressure, J g mole^{-1}

ΔT = temperature rise of coolant across blanket, $^{\circ}\text{C}$

$\dot{N}_T$ = breeding rate of tritium in blanket, g atoms sec^{-1}

Solving the above equations, the K_s necessary to achieve a given tritium inventory is given by

$$K_s = 3 \times 10^4 (I_T)^{-1} (N_{SL}) \frac{(P_{He})^{\frac{1}{2}}}{(2f_p)^{\frac{1}{2}}} \frac{(C_p \Delta T)^{\frac{1}{2}}}{Q^{\frac{1}{2}} N_o^{\frac{1}{2}}} (BR)^{\frac{1}{2}} \quad (6)$$

Taking typical blanket values ($\Delta T=500^{\circ}\text{C}$, $BR=1.0$, $P_{He}=30 \text{ atm}$, $Q=20 \text{ mev/fusion}$, $V_B=1000 \text{ m}^3$) curves (Figure 5) relating K_s to I_T , N_{SL} , and f_p are obtained. The optimum processing fraction will probably lie somewhere between 1 to 10%. A higher processing fraction than 10% would probably result in excessively large and costly systems. The amount of solid lithium material depends on whether natural or enriched lithium is used. Representative values for natural enrichment blankets are on the order of $f_{SL} \sim 0.50$, while enriched (90% Li^6) are on the order of $f_{SL} \sim 0.01$. The curves in Figure 5 show that a K_s of $\sim 5 \times 10^4 \text{ torr}^{\frac{1}{2}} [\text{atom fraction}]^{-1}$ is required to achieve a blanket inventory of 10^4

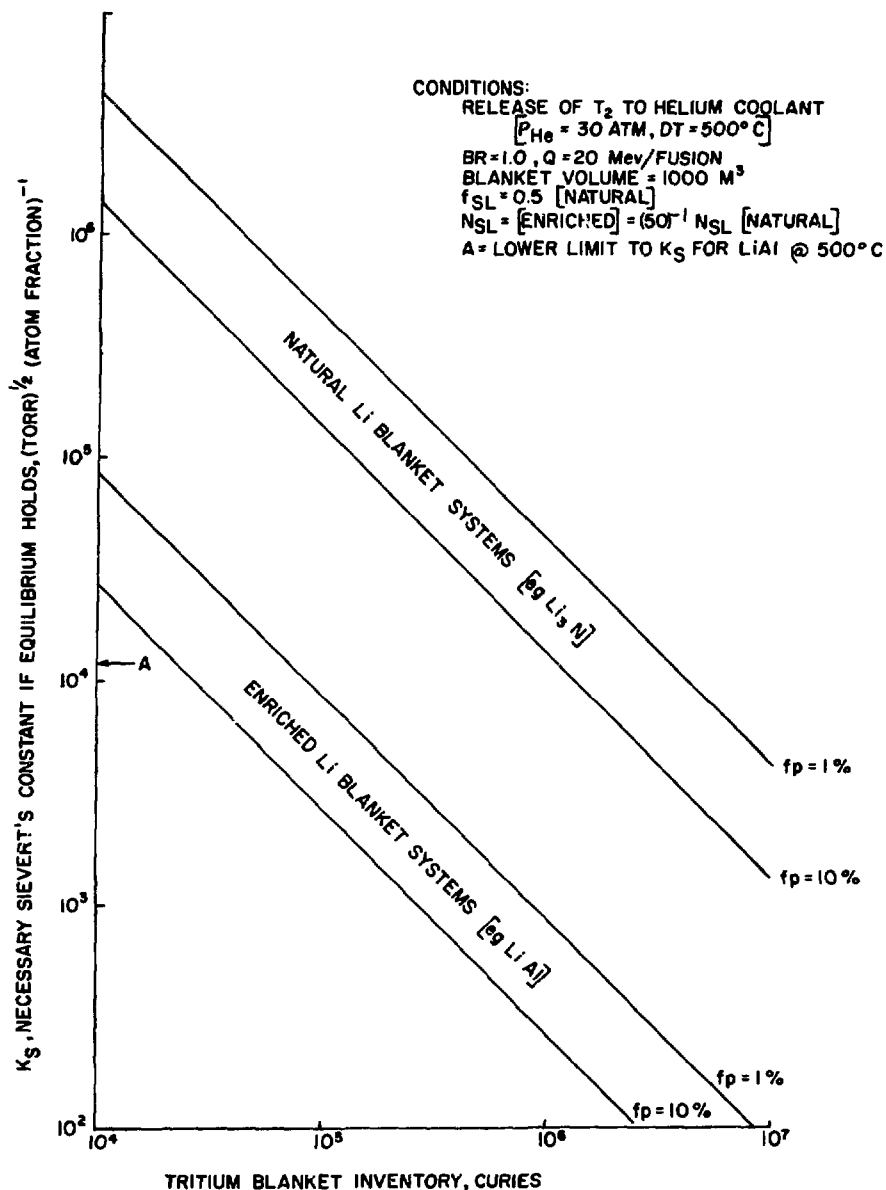


Fig. 5 Sieverts' Constant Required to Achieve Given Tritium Blanket Inventory if Tritium Release is Controlled by Equilibrium

curies with enriched Li and a value of $K_s \sim 2 \times 10^6$ for natural Li blanket systems. Point A corresponds to the lower limit to K_s for LiAl, determined by experiments at 500°C with 10-20 mesh particles. Experiments with 5-10 mesh particles show considerably slower release rates, indicating that diffusion is controlling. If further experiments with LiAl particles smaller than 10-20 mesh show still faster release rates, then the lower limit for K_s can be raised. There is no method for predicting K_s values; the experiments with LiAl and Li_7Pb_2 show K_s for these materials to be at least three orders of magnitude greater than that for pure Li at the same temperature. Qualitatively, K_s should be much higher for solid Li materials than for pure Li, since the chemical affinity of Li for T is greatly reduced in a stable compound.

The enriched lithium blanket systems give low tritium blanket inventories even if K_s is no greater than the presently established lower limit. Natural lithium blankets result in high tritium inventories ($\sim 2 \times 10^6$ curies), however, if the K_s is actually on the order of this lower limit. In order to confirm that low blanket inventories are possible with natural Li systems, it will be necessary to more accurately determine K_s values for the various possible alloys (LiAl, Li_7Pb_2 , Li_3N , Li_4Si , etc.). The compounds (LiAlO_2 , Li_2SiO_3 , etc.) do not seem to have any chance of being controlled by equilibrium.

In an equilibrium controlled situation where it is desired to further reduce tritium blanket inventory, scavenging hydrogen (protium or deuterium) can be added to the helium coolant stream. This effectively raises the partial pressure of T in the coolant, though the primary species will now be HT instead of T_2 . Assuming that the Sieverts' constants are the same for all hydrogen isotopes,

$$I_T(S) = 2S^{-\frac{1}{2}} I_T(S=0) \quad (7)$$

where the scavenging parameter is given by the ratio of the addition rate of H or D to the tritium breeding rate

$$S = \dot{N}_{\text{H or D}} / \dot{N}_T \quad (8)$$

at a S of 400, tritium blanket inventory is reduced by a factor of 10.

Additions of O_2 to the coolant stream would lower the tritium partial pressure and thus decrease blanket inventory. Unfortunately, all the lithium materials (e.g., LiAl) to which this method might be applied are likely to be oxidized by the free O_2 in the coolant, while the oxidized forms, e.g., $LiAlO_2$, probably are diffusion controlled and would not be benefited by lowering of the T tritium partial pressure in the coolant.

In general, there seems to be no problems in reaching tritium blanket inventories of $\sim 10^5$ curies for most solid blanket systems, and it appears quite feasible to reduce the inventory to $\sim 10^4$ curies.

RECOVERY OF TRITIUM FROM HELIUM COOLANT

Several methods can be used to recover tritium from the helium coolant. In all methods, a portion of the main helium stream will be diverted into a process train where most of the tritium in the processed helium can be removed. The processing stream flow rate can be up to $\sim 10\%$ of the main coolant flow. Any higher fraction would probably be unduly expensive and/or degrade power cycle efficiency. In general, unless relatively large amounts of O_2 or H_2 are added to the coolant, the tritium will be contained in a number of species, i.e., T_2 , HT, T_2O , HTO, etc. H and D will be formed in the blanket by (n,p) and (n,d) reactions; O_2 will probably be present as a coolant impurity. With solid lithium materials like LiAl, the tritium will probably be present principally as T_2 and HT, while with materials like $LiAlO_2$, it will probably be present principally as T_2O and HTO. The three principal methods for receiving tritium from the process stream would then be:

1. Reduce the T_2O and HTO present in the stream to T_2 and HT and absorb all T_2 and HT in a metal hydride bed.
2. Oxidize the T_2 and HT present in the stream to T_2O and HTO and freeze out all T_2O and HTO on a cold surface or absorb it a suitable dessicant.

3. Convert none of the species in the process stream. The T_2O and HTO would then be trapped on a cold surface or in a dessicant, followed by freezing out of the T_2 and HT at cryogenic temperatures ($\sim 6^\circ K$).

The first two methods are shown schematically in Figure 6. The third method avoids the converter beds or the equivalent processes, the controlled addition of O_2 or H_2 gas, but has the disadvantage of incorporating a very low temperature region as part of the process train. In practice, the large irreversibilities associated with this step, even with good heat recovery, would probably severely limit the fraction of helium coolant that could be processed to $\leq 1\%$. The other two methods should allow for much larger processing fractions, i.e., up to $\sim 10\%$.

The second method requires a thermal regenerator as part of the process train, since the trapping of T_2O and HTO must be done at temperatures well below the blanket operating temperature. In the first method, metal hydrides can be chosen that will trap efficiently at blanket operating temperatures, so little or no thermal regeneration need be carried out. In Figure 6, the process stream is diverted from the main helium coolant stream at its highest temperature before it enters the power conversion system. The process stream can also be withdrawn after the main coolant stream leaves the power conversion system at a lower temperature. This would reduce the amount of thermal regeneration required for the second method.

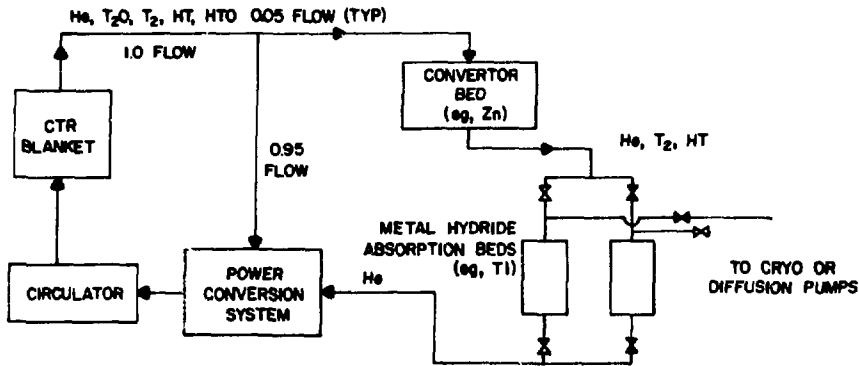
Eq. (5) can be rearranged to yield

$$P_{\Sigma T_2} = \frac{P_{He} (BR) (C_p \Delta T)}{2 f_p Q N_o} \quad (9)$$

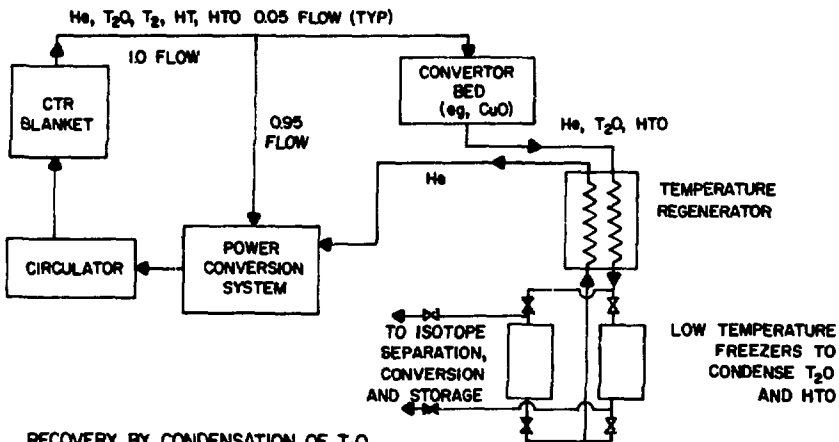
where ΣT_2 refers to all tritium in the gas, expressed as T_2 . For typical blanket conditions ($P_{He} = 30$ atm, $BR = 1.0$, $\Delta T = 500^\circ C$, $Q = 20$ mev/fusion),

$$P_{\Sigma T_2} = \frac{6.2 \times 10^{-5}}{f_p} \text{ torr} \quad (10)$$

so that $P_{\Sigma T_2}$ ranges between 6.2×10^{-4} and 6.2×10^{-3} torr for processing fractions between 0.10 and 0.01.



RECOVERY BY ABSORPTION
IN METAL HYDRIDE BED



RECOVERY BY CONDENSATION OF T_2O

Fig. 6 Methods for Recovering Tritium from Helium Coolant Stream

Assuming the second method of recovery with freezing out of T_2O on cold surfaces, and all tritium present as T_2O or HTO , the frost point ranges between $-78^{\circ}C$ and $-62^{\circ}C$ for f_p 's between 0.10 and 0.01. To remove essentially all (e.g. $\sim 98\%$) of the contained T_2O and HTO , the gas must be cooled an additional $\sim 20^{\circ}C$. If we assume a very non-optimized system with regenerative heat exchange to the frost point, with $\Delta T = 20^{\circ}C$ across the regenerator, and further cooling in a separate refrigerated vessel to freeze out the T_2O , the necessary input power to the refrigerator that cools the helium (the heat released by the freezing T_2O is negligible) varies between $\sim 1\%$ and $\sim 0.1\%$ of the reactor electrical output for f_p between 0.10 and 0.1. This power could probably be reduced by a factor of ~ 3 in an optimized system.

The refrigerated vessels would have to be thermally cycled periodically to recover the trapped T_2O and HTO . The vessels could be brought up to a few degrees above $0^{\circ}C$ and the liquid T_2O collected. Alternatively, the vessel could be raised to an intermediate temperature and the subliming T_2O collected at a higher pressure. The refrigeration load associated with the thermal cycling of the vessels depends on the mass of the thermally cycled collecting surfaces, the ΔT during the cycle, and the cycle time. The tritium inventory in the trap is proportional to the cycle time. As an example, for a trapping period of 4 minutes (tritium trap inventory of 10^4 curies), thermally cycled mass of 1000 kg of aluminum (which is excessive), and a ΔT cycle = $100^{\circ}C$, the refrigerator input power for thermal cycling is less than 0.05% of the reactor electrical power.

Thus the second recovery method can be readily carried out by freezing out T_2O and HTO . The energy costs are very small in terms of plant output, and equipment costs should also be quite small compared to overall plant costs. Tritium trap inventories can be very low, on the order of 10^4 curies.

If a dessicant is used with an asorption/desorption process to recover T_2O , energy requirements and equipment costs would be even smaller than those for the freezing process.

We now consider the first recovery method, absorption of T_2 and HT in metal hydride beds. Figure 7 shows a conceptual view of a

ABSORBING-DESORBING BEDS FOR T_2 RECOVERY
FROM HELIUM COOLANT

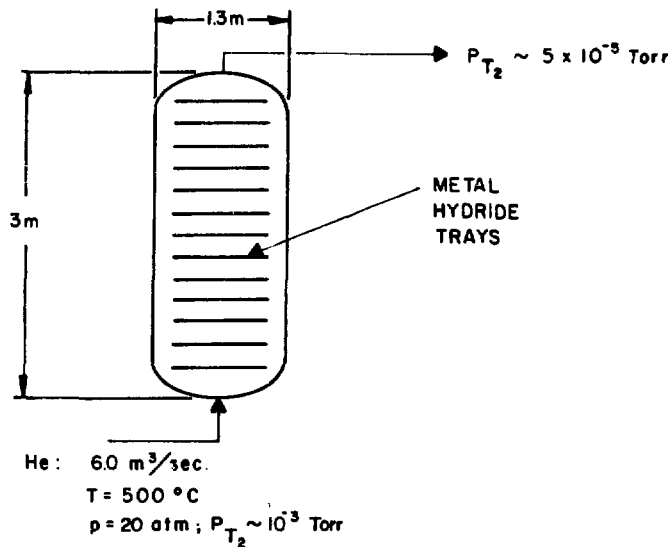
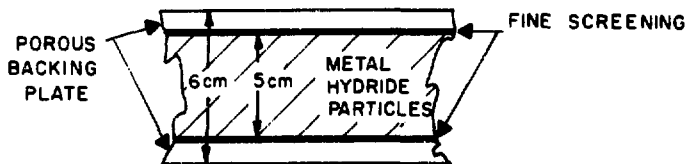


Fig. 7 Conceptual Design of Metal Hydride Absorber Beds for Tritium

hydride absorbing bed. The helium process stream flows in parallel through a set of trays holding the metal hydride particles. The rate controlling step is probably diffusion of 1_2 through a laminar ($N_{Re} \sim 0.1$) He gas film to the solid particles, rather than the reaction at the surface of the metal particles. Data of Gulbransen and Andrew¹⁵ for hydriding of thin Ti sheets indicate that the absorbing rate, even with relatively low temperatures (300°C) and very low fractions of Ti particles in the bed (1% Ti, 99% inert solids) is much faster than needed.

The total volume of the absorbing bed (metal hydride particles, inert particles, and voids) is given by

$$V_A = [\dot{V}_{He}]_A \tau_c = \dot{V}_{He} f_p \tau_c = \dot{V}_{He} f_p \frac{\tau^*}{f_v} \quad (11)$$

where

- V_A = volume of absorbing bed, m^3
- $[\dot{V}_{He}]_A$ = volumetric flow rate of process helium through absorption bed, $m^3 \text{ sec}^{-1}$
- $\dot{V}_{He}$ = volumetric flow rate of helium cocurrent through blanket, $m^3 \text{ sec}^{-1}$
- τ_c = superficial contact time for process stream in bed, sec (assumes no particles in bed)
- τ^* = actual contact time for process stream in bed, sec ($\sim 40\%$ of τ_c)
- f_v = fraction of bed occupied by solid particles (metal hydride plus inerts)

Specification of one other variable (flow area, flow velocity, bed thickness) is sufficient to fix the other bed variables through the relations

$$v = [\dot{V}_{He}]_A / A_f = \frac{\Delta Z}{\tau_c} \quad (12)$$

where

- v = superficial contact velocity, m/sec
- A_f = superficial flow area, m^2
- ΔZ = bed thickness, m

The next step is to select the metal hydride for the absorbing bed. Figure 8 shows how some of the possible choices meet the requirements. The entering process stream is assumed to have a partial pressure of 10^{-3} torr. Cerium and yttrium hydride are too stable to be suitable, while Ti and Zr appear to be feasible choices. The metal hydride must not only absorb T_2 but must release it when the bed is pumped out, at a pressure not too much lower than the partial pressure at which it is absorbed. For simplicity, the bed has no internal cooling or heating surfaces and is assumed not to be heated or cooled by an auxiliary helium stream. The temperature of the bed is then isothermal, changing only by a negligible amount (10^{-2} °K) during an absorption - desorption cycle.

In order that the tritium discharge pressure should not vary too greatly during the desorption phase of the cycle, it is necessary to keep the swing in concentration of T in the metal hydride relatively small, e.g., $\Delta C/C \sim 0.2$ to 0.3. The advantage of keeping variations in tritium discharge pressure small must be traded off against the increase in the average tritium inventory in the bed. The inventory for the case of partial desorption of tritium is essentially the inventory for complete desorption multiplied by the factor $\bar{C}/\Delta C$.

Figure 8 further shows that not all of the bed can be metal hydride, since if even 10% of the solids are titanium, the tritium discharge pressure would be several orders of magnitude below the absorption pressure. The bed thickness is fixed by the contact time, 0.5 sec, necessary to permit effective diffusion of tritium through the He gas film to the particles. Under these conditions, it is better to keep the Ti content at $\sim 1\%$ of the solids, to keep discharge pressure relatively high.

For reasonable cycle times, e.g., 10 minutes, the tritium trap inventory will be on the order of 10^5 curies for 1000 (MW(e)). Reduction of trap inventories to $\sim 10^4$ curies would require unreasonable short cycle times. If it is desired to reduce inventories to this level, it probably would be necessary to thermally cycle the hydride bed, so as to get a large tritium concentration swing in the metal hydride. This would make the bed somewhat more complex, but it appears feasible if desired.

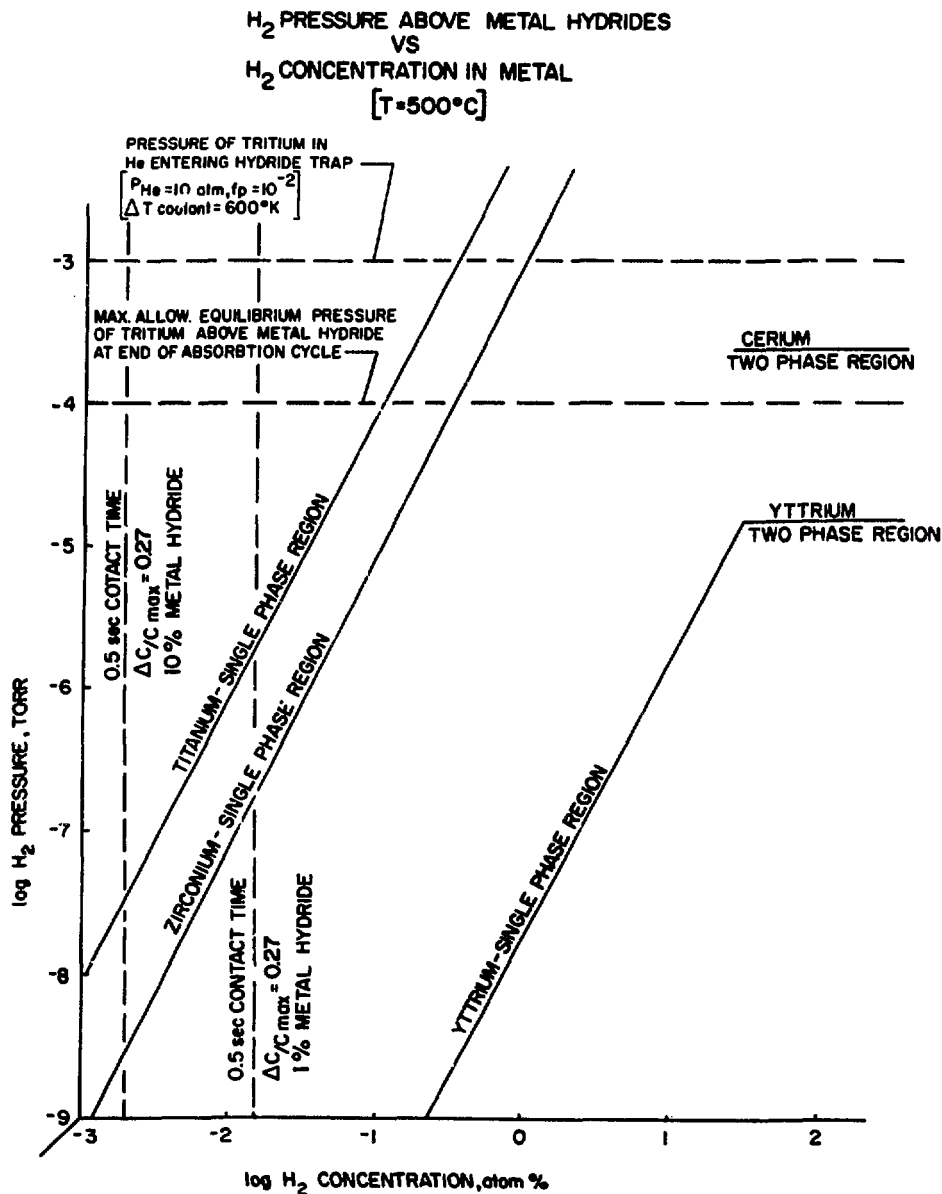


Fig. 8 Trapping Characteristics of Metal Hydride Absorbers for Tritium Trapping

The other tritium inventory of interest, if tritium is recovered from the helium coolant, is the inventory in the coolant circuit. This inventory is given by

$$(I_T)_{He} = 3 \times 10^4 \frac{N_T \tau_{He}}{f} \text{ curies} \quad (13)$$

where

τ_{He} = circulation time for helium through blanket circuit, sec

for a typical circulation time of 5 seconds the coolant inventory in the tritium circuit will range from 2000 to 20,000 curies for processing fractions of 0.10 to 0.01.

CONCLUSIONS

More experiments and designs must be made for definitive assessments about which of the different solid lithium compounds are optimum for fusion blankets. Some preliminary conclusions can be drawn, however.

1. There are many solid lithium alloys or compounds that should be suitable for fusion blankets operating at temperatures of 500°C or above.
2. Most of the promising solid lithium materials inherently will have very low residual activations in fusion blankets.
3. The materials tested to date ($LiAl$, $LiAlO_2$, Li_2SiO_3 , Li_7Pb_2) will have very low tritium retentivities under operating conditions projected for fusion blankets.
4. Beryllium or beryllium compounds are not necessary for net breeding if solid lithium compounds are used. Lead compounds (PbO , PbS) can be used as neutron multipliers, or natural lithium alloys with a high lithium content (e.g. Li_7Pb_2 , Li_4Si , Li_3N) can be used without neutron multipliers.
5. A large number of blanket design options exist comprising various combinations of solid lithium compounds, structural materials, and neutron multipliers (if used). Blankets can be sub-breeders, sustainer-breeders, or super-breeders, and CTR economies can be

developed that use different combinations of the various blanket options.

6. If neutron multipliers are used, LiAlO_2 appears a very promising solid lithium material. It has a very high melting point (1900°C), very low tritium retentivity and residual activations, and is stable and inert.
7. With suitable design, tritium blanket inventories of $\sim 10^4$ curies/1000 MW(e) are readily achievable. This is two orders of magnitude less than inventories for liquid Li metal or flibe blankets.
8. Of the 3 possible tritium release modes (to helium coolant, to separate helium processing circuit, and to vacuum region around plasma), the optimum release mode for most blanket options appears to be release to the helium coolant.
9. If released to the helium coolant, tritium will generally be present as a mixture of species, e.g., T_2O , T_2 , HT and HTO. Optimum processing fractions (fraction of helium coolant stream withdrawn for processing to remove tritium) will be in the range of 0.01 to 0.10.
10. Tritium species in the process stream can be converted to the reduced form (T_2 , HT) or the oxidized form (T_2O , HTO). The former species can be removed by cyclical absorption/desorption in a metal hydride particulate bed (e.g., Ti), with subsequent recovery into a fuel fabrication system. The latter species can be removed by cyclical condensation/vaporization on cold surfaces with subsequent recovery into a fuel fabrication system (the oxidized species can be electrolyzed).
11. Tritium trap inventories are on the order of 10^4 curies if recovered as T_2O and on the order of 10^5 curies if recovered as T_2 . The latter inventory can be reduced if the metal hydride bed is thermally cycled.

ACKNOWLEDGEMENTS

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TRITIUM RECOVERY FROM FUSION BLANKETS USING SOLID LITHIUM
COMPOUNDS-II: EXPERIMENTS ON TRITIUM REMOVAL AND ABSORPTION

R. H. Wiswall and E. Wirsing

Department of Applied Science
Brookhaven National Laboratory
Upton, N. Y. 11973

ABSTRACT

It has been shown experimentally that tritium can be easily removed from certain solid lithium compounds that have been proposed as components of CTR breeder blankets. The compounds tested were LiAl , Li_7Pb_2 , LiAlO_2 and Li_2SiO_3 in granular or powder form; the procedure was to pass a stream of helium through a bed of material maintained at a temperature in the range 400-600°C. As the tritium, which had been previously generated in the materials by exposure to thermal neutrons, diffused out and was carried away, its concentration was continuously monitored by radioactive assay of the gas stream. From the data, it was possible to calculate average lifetimes of tritium in a continuously extracted breeder blanket. Lifetimes of a few hours were found for LiAl and Li_7Pb_2 at 400-500°, LiAlO_2 at 600° and Li_2SiO_3 at 500-600°. The extraction kinetics of LiAlO_2 were consistent with a diffusion-controlled process, and it was possible to calculate diffusion coefficients from the data. A series of hydride-forming metals were tested for their ability to trap out tritium from dilute helium streams and later release it on heating. Vanadium appears to be satisfactory.

INTRODUCTION

It has recently been proposed by J. R. Powell¹ et al. that blankets in which lithium is present in a solid form offer certain advantages over systems containing it in the form of the liquid metal or in a fused salt mixture. Possible solid vehicles for lithium are LiAl , Li_7Pb_2 , LiAlO_2 and Li_2SiO_3 . The first criterion in the selection of candidate solids is that they do not acquire long-lived induced radioactivity under blanket conditions since a primary goal of the solid-blanket concept is to achieve a system with a low inventory of radioactive, and therefore hazardous, material. This goal also requires, and the concept postulates, that bred tritium will be removed from the

blanket after a very short average residence time. The purpose of the research described below was to find out whether tritium could indeed be moved from a lithium-bearing solid of suitable nuclear properties at reasonable rates under practically attainable conditions. An affirmative answer having been obtained early on, a more detailed study of the removal kinetics was undertaken, and is continuing. In this, we determine the effect on tritium removal rates of changes in a number of variables, such as chemical composition of the solid, particle size, high-temperature pre-treatment (to accelerate any possible sintering), temperature of extraction, helium flow rate, presence of normal hydrogen in the helium, etc.

Once the bred tritium has been extracted into helium and conveyed outside the blanket, it must be removed from the carrier gas and concentrated to essentially pure T_2 before its introduction into the plasma. The use of a hydride-forming metal for this purpose appeared promising and was chosen for testing. It is of course well known that hydrogen and its isotopes can be absorbed very strongly by some metals. Such a reaction is used at the Fort St. Vrain gas-cooled reactor when titanium sponge scavenges tritium from the helium coolant. The absorbed tritium can in principle be recovered by heating the solid at an elevated temperature under reduced pressure. A series of experiments was carried out for the purpose of defining the exact conditions required for absorption and recovery, both for titanium and a number of other metals and alloys which hold hydrogen less tenaciously.

TRITIUM EXTRACTION

Experimental Procedure

Experimental procedure parallels the processes that are postulated for the solid blanket concept as closely as possible. Small concentrations of tritium are generated uniformly throughout small (ca. 0.5g) samples of a solid compound or alloy of lithium by exposure to thermal neutrons in the Brookhaven Medical Reactor. A typical exposure is one hour at a flux of 10^{13} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. This results in the formation of about ten millicuries of tritium per gram of lithium, or an atom

fraction of tritium, relative to lithium, of 2.4×10^{-6} . For comparison, an atom fraction of not more than 1.0×10^{-6} is desired as the steady-state concentration in an actual blanket; this would give a tritium holdup of 160g in a 1000 MWe reactor. In some respects (temperature, radiation flux) the irradiation conditions are very different from those of a blanket, and in-pile experiments must eventually be resorted to in order to confirm present results.

Material is customarily crushed, if necessary, and screened to approximately uniform particle size before exposure in the reactor. In some cases, samples are given a sintering pre-treatment that consists of exposure, under vacuum, to a temperature several hundred degrees higher than that of subsequent tritium extraction runs. After irradiation, a sample of about 250 mg is transferred to the extraction tube, which is simply an 11 mm OD tube of Pyrex, Vycor or stainless steel provided with a frit of the same material to support the sample. This is connected into the extraction and analysis train, a schematic diagram of which is given in Figure 1. Helium flows up through the frit and carries away whatever tritium is released by the sample. Except where otherwise noted, a flow of 60 cc/min, or 1.4 lb/hr-ft^2 , was used. A tube furnace and its associated controller can maintain the reaction zone at any temperature up to 850° . The tritium content of the helium leaving the extraction tube is determined from radioactivity measurements by means of an internal proportional counter². For this purpose, the helium first goes to a mixing device where one part of helium is mixed with ten parts of P-10 counting gas (90% argon, 10% methane). In runs on the oxygen-containing compounds Li_2SiO_3 and LiAlO_2 , the tritium is at least partly in the form T_2O or HTO. A unit was therefore inserted into the reaction train for the purpose of reducing oxygen-containing species. It consists of a 3/16" ID stainless steel tube filled for about 6" of its length with 30-mesh zinc powder, which has first been cleaned with dilute HNO_3 . A furnace maintains it at a temperature of 400° during a run.

Tritium disintegrations are registered and recorded on standard counting equipment. It can measure either "instantaneous" count rates (with a variable time constant) or it can integrate the total number of

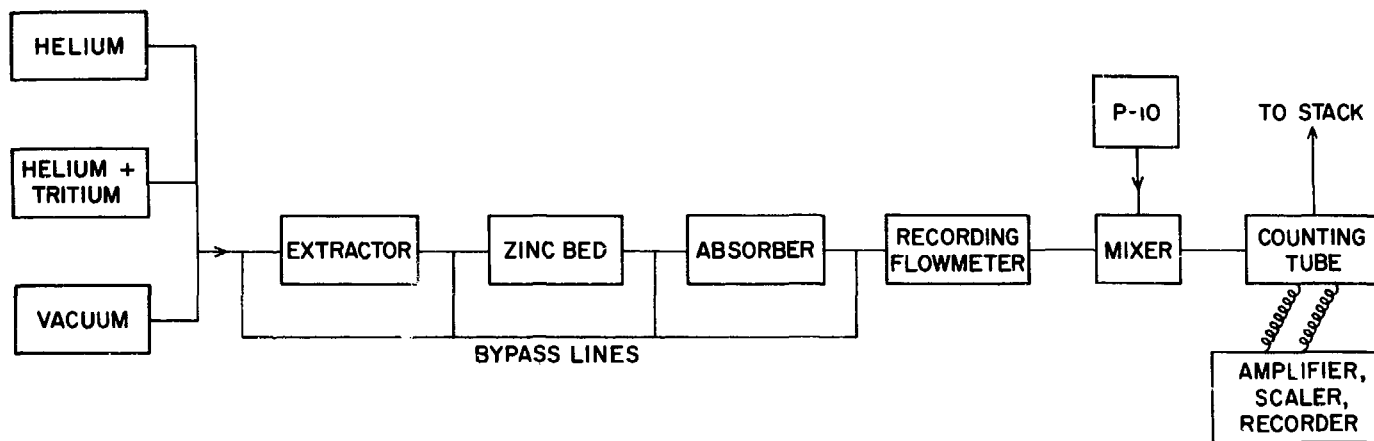


Fig. 1. Flowsheet for tritium extraction and absorption. Not shown are the numerous valves that permit one or more units to be by-passed; nor the furnaces, together with their associated control and recording equipment, that are provided for the extractor, zinc bed, and absorber.

counts recorded over a period. The latter mode has been the more usual in our work. The number obtained does not have an absolute significance, but relative counts provide all the needed information in these runs. It is only necessary to make sure that the helium and P-10 flow rates are constant throughout a run. Results are analyzed more easily if the total tritium activity that has been removed at any point can be expressed as a fraction of the total activity in the sample at the beginning of the run. Whenever possible, this quantity is obtained by driving the entire tritium charge into the helium stream. In low-temperature runs, where only a fraction of the tritium is extracted in a reasonable time, the temperature is raised at the end to a point where removal is essentially complete in an hour or two. Completeness of removal is usually verified by dissolving part of the material at the end and analyzing the aqueous solution by scintillation counting.

Results

LiAl

This is the highest-melting (718°) intermediate phase in the Li-Al system, and would be suitable for blanket temperatures up to about 650° . Samples were made by melting Li and Al together under an inert atmosphere in a stainless steel crucible heated by an induction furnace. The cooled product was transferred to an argon-filled glove box for grinding, screening and encapsulating prior to irradiation.

The removal of tritium from coarsely granular LiAl proved relatively easy. Even as low as 400° , half of the tritium was carried away by helium in five hours. The initial removal rate was always fast, but decreased rapidly, so that the results are most conveniently plotted on log-log paper. Figures 2 and 3 show several graphs of this sort. These illustrate the effect on the extraction kinetics of changes in the principal variables of the present series, namely particle size and temperature. Figure 4 repeats selected curves from Figures 2 and 3 for cross-comparison purposes.

The helium flow is another variable quantity, one which could be important if transfer of tritium across the solid-gas interface were

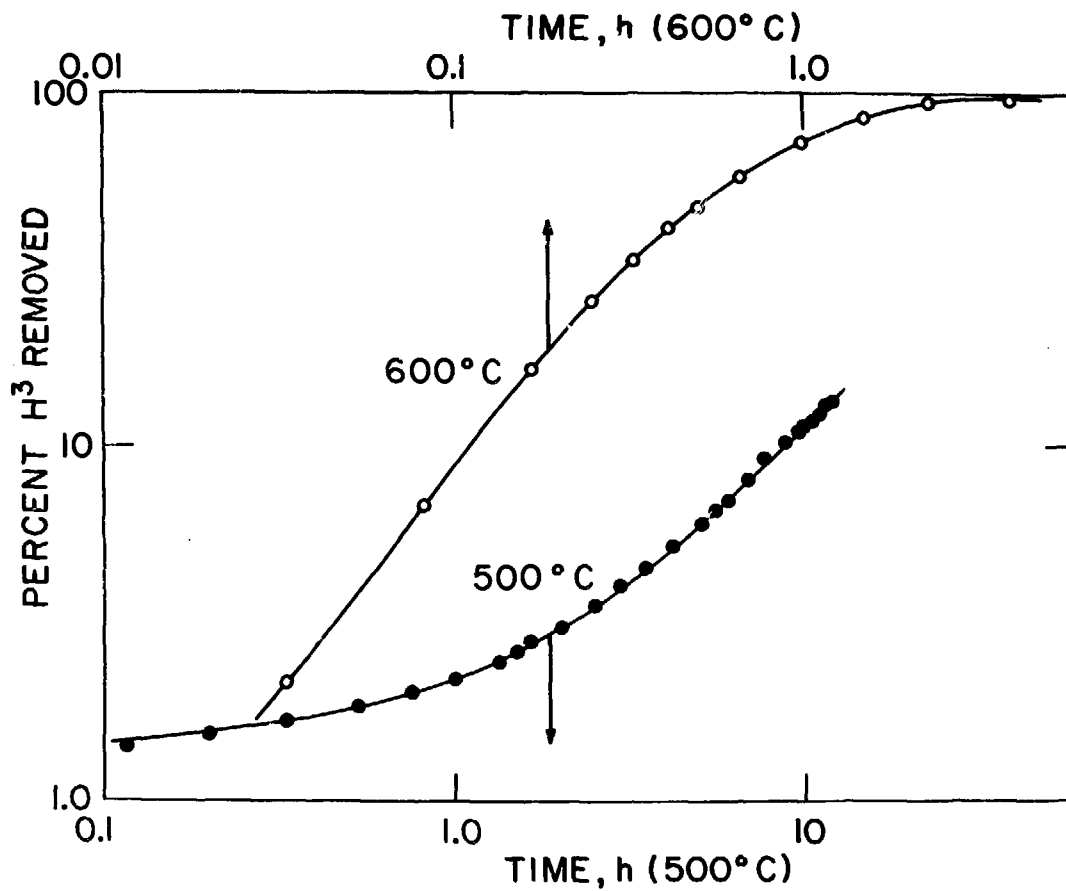


Fig. 2. Removal of tritium from LiAl of 5-10 mesh.

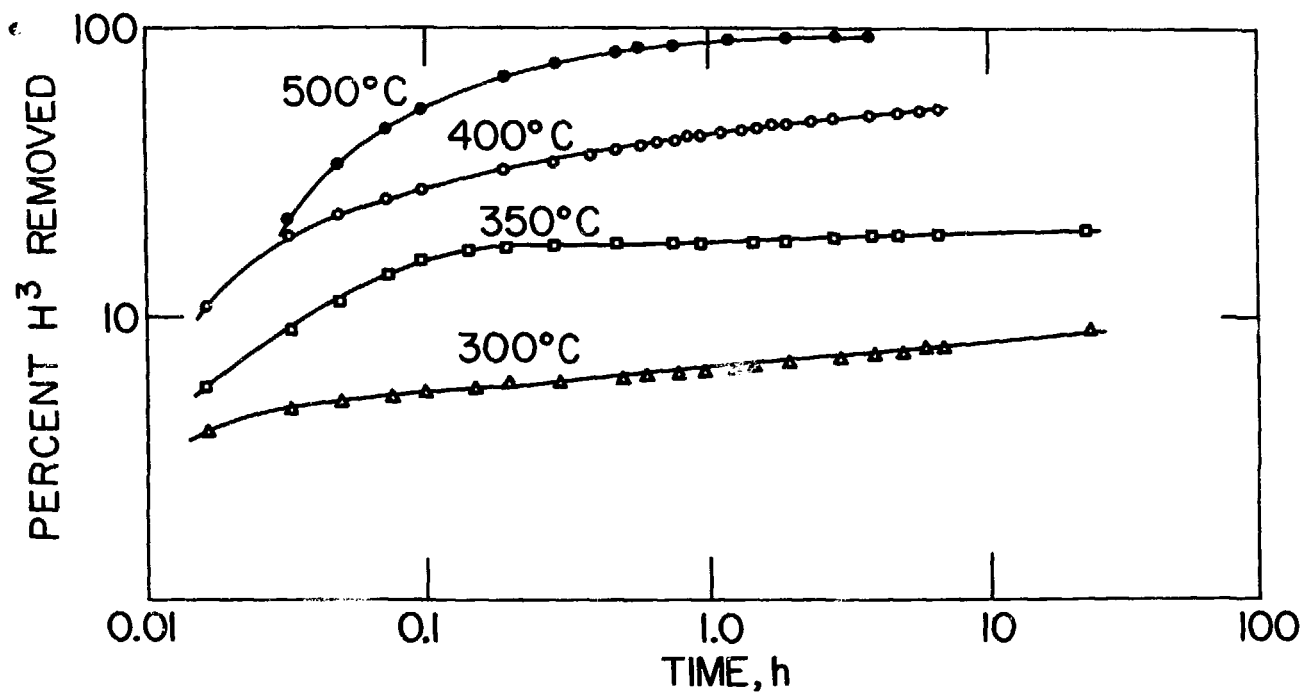


Fig. 3. Removal of tritium from LiAl of 10-20 mesh.

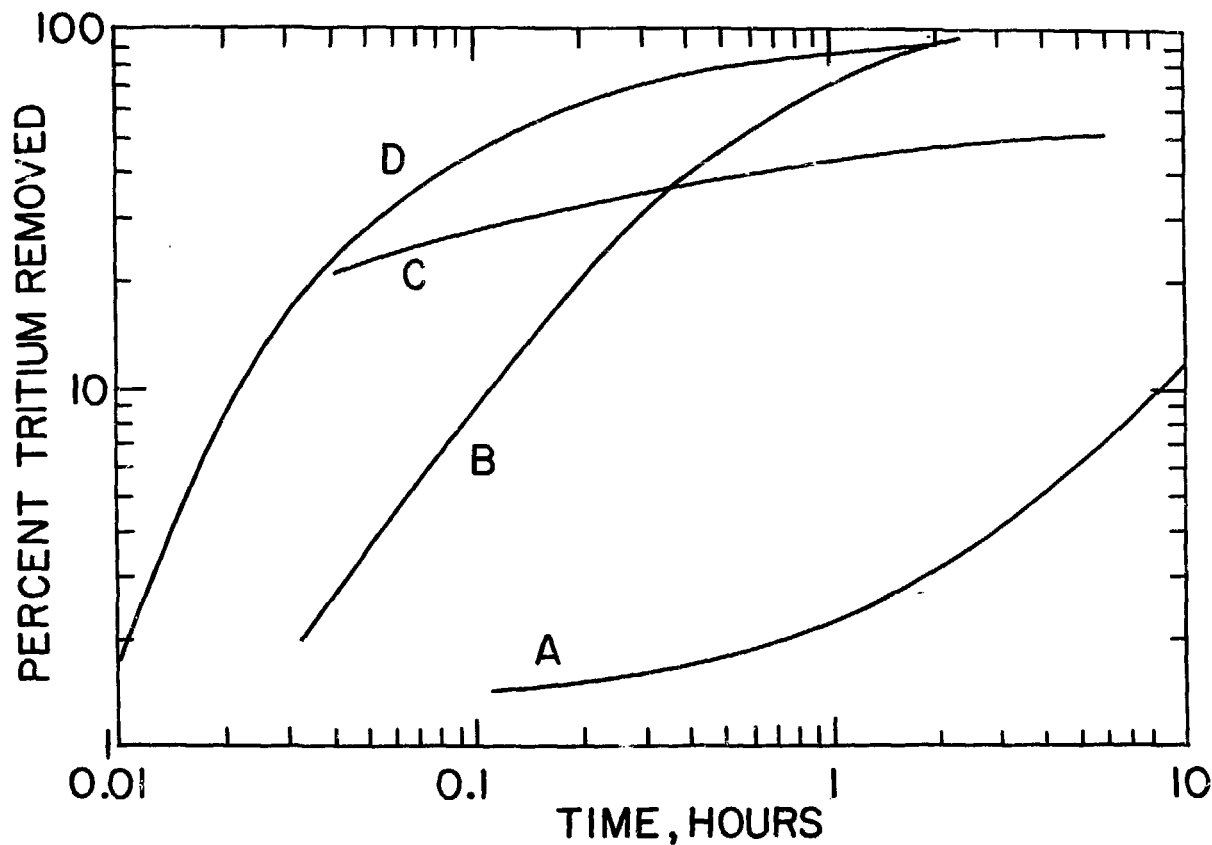


Fig. 4. Removal of tritium from LiAl; effect of temperature and particle size.

A. 5-10 mesh, 500°	C. 10-20 mesh, 400°
B. 5-10 mesh, 600°	D. 10-20 mesh, 500°

rate-limiting. A tendency for tritium in the gas phase to be redeposited on to the alloy would be lessened by increased flow. In Figure 5, two runs are shown in which everything was kept constant except the helium flows, which differed by a factor of five. The difference is probably significant, although it must be admitted that "identical" pairs of runs have differed nearly as much. Further experiments are needed on the effect of flow rate.

Another test of the role of surface reactions in the overall extraction process was obtained by comparing runs with and without added hydrogen. If the combination of tritium atoms to form T_2 at the solid-gas interface were rate-limiting, the addition of hydrogen to the helium should hasten the removal by permitting the formation of HT molecules. Figure 6 shows the course of tritium removal in four runs. In two, the usual tank helium was used; in the other two, 1000 ppm H_2 was added to the helium. It is clear that the tritium was removed faster by the H_2 -He mixture, especially in the early stages of the runs. The difference is much larger than the difference between the members of either pair of similar runs.

Li_7Pb_2

Less complete data have been obtained on another intermetallic compound of lithium, Li_7Pb_2 , m.p. 726° . The method of preparation was like that of $LiAl$, except that a graphite crucible was used. Figure 7 shows the course of tritium removal from 20-40 mesh material at two temperatures.

$LiAlO_2$

Lithium aluminate (m.p. $> 1625^\circ$) was obtained from Alfa Products as a white powder stated to contain 21.4% Li_2O (theoretical for $LiAlO_2$, 22.7%). After size classification by wire sieves, the material was dried by heating under vacuum overnight at 500° . Samples were then irradiated, and extracted by the same procedures as before. Somewhat higher temperatures and smaller particle sizes were required than with the alloys, but good rates were still obtained under practically attainable conditions.

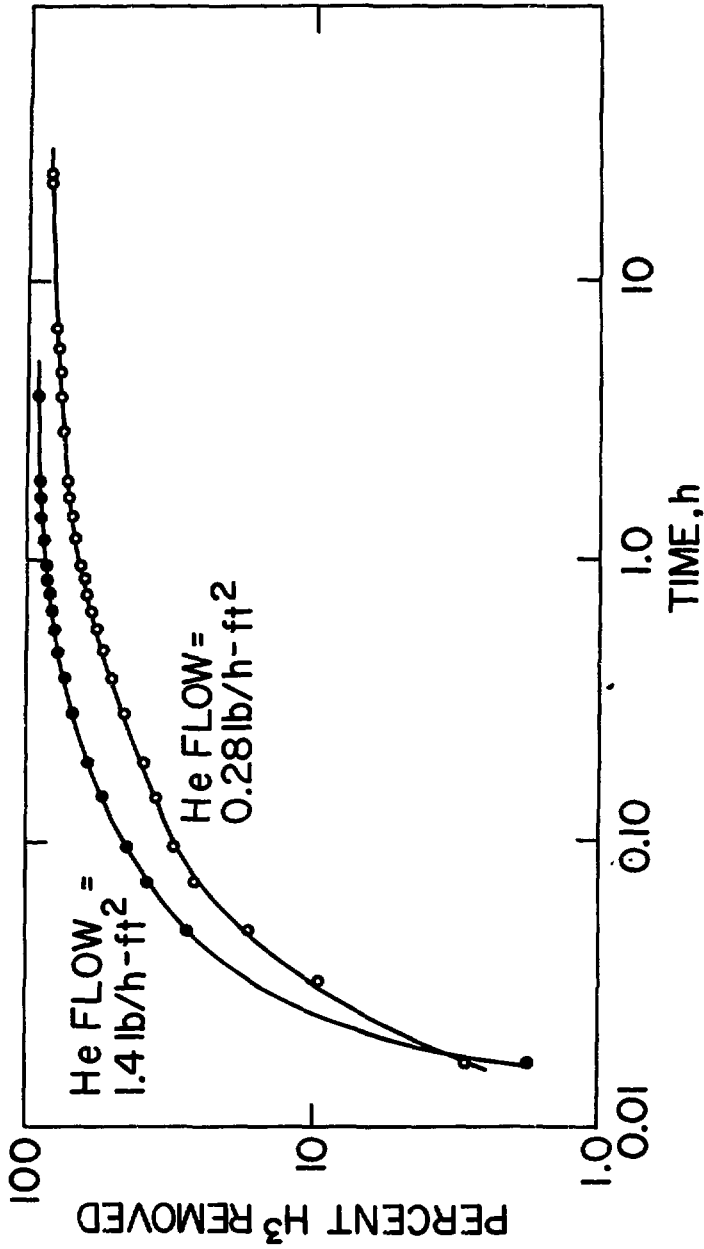


Fig. 5. Removal of tritium from LiAl of 10-20 mesh at 500° ; effect of helium flow rate.

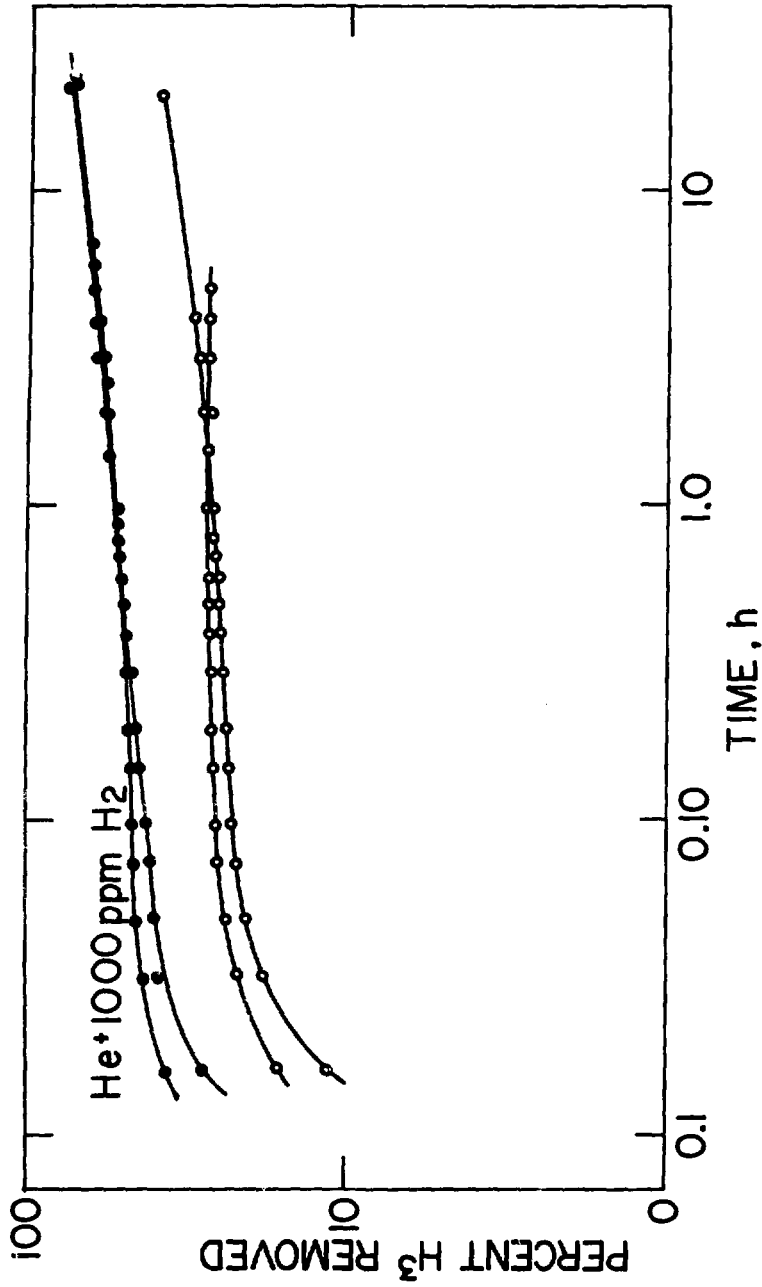


Fig. 6. Removal of tritium from LiAl of 10-20 mesh at 400°C; effect of added H₂.

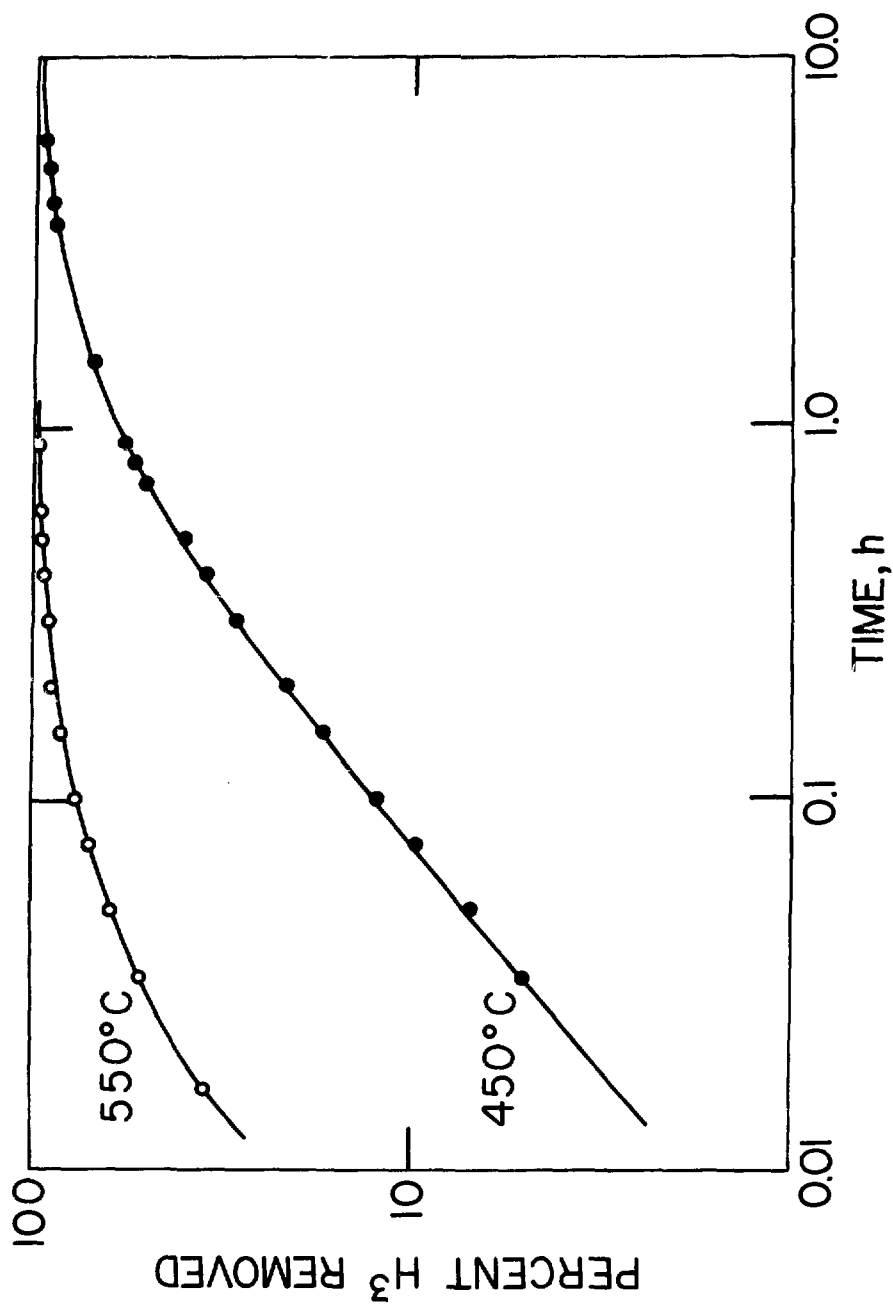


Fig. 7. Removal of tritium from Li_7Pb_2 .

Figure 8 illustrates the performance of 70-100 mesh (150-210 μ) material at 500° and 600°.

It was thought possible that long exposure to such temperatures might cause a slowing down of extraction rates because of sintering. Accelerated sintering tests were therefore carried out by exposing samples of LiAlO_2 to temperatures of 1000°, in air, for periods of up to a month before irradiation and extraction. Figure 9 shows the results for such a series.

Li_2SiO_3

Lithium silicate (m.p. 1200°) was also obtained from Alfa, as a fine powder of "+98%" purity. It was handled in the same way as the aluminate, except that no sintering tests have yet been done. Its extraction performance is shown in Figure 10.

Discussion

It is clear that low tritium inventories can be attained by the continuous extraction of LiAl or Li_7Pb_2 blankets about 500°, and of LiAlO_2 or Li_2SiO_3 blankets about 600°. An exact determination of the holdup times to be expected requires an analysis of the kinetic behavior illustrated in Figures 2 through 10 and the development of a physical model of what is happening. It is reasonable to expect the removal rate to be limited by slow diffusion of tritium from the interior of a particle to the surface; although a slow transfer of tritium from the surface to the gas phase may also play a role. A rigorous analysis of diffusion-controlled extraction yields a rather complex function relating fraction removed to time, but certain approximations are permissible and useful³. At relatively short time,

$$f \approx \frac{6}{r \sqrt{\pi}} \sqrt{Dt} \quad (1)$$

where f is the fraction removed, r is the particle radius, D the diffusion coefficient and t the time. In a regime where this equation held, our log-log removal plots should be linear, with a slope of 1/2. It would then be possible to calculate D if r were known. Even if r is unknown, the data can be used to calculate mean holdup times, τ , in a continuously irradiated,

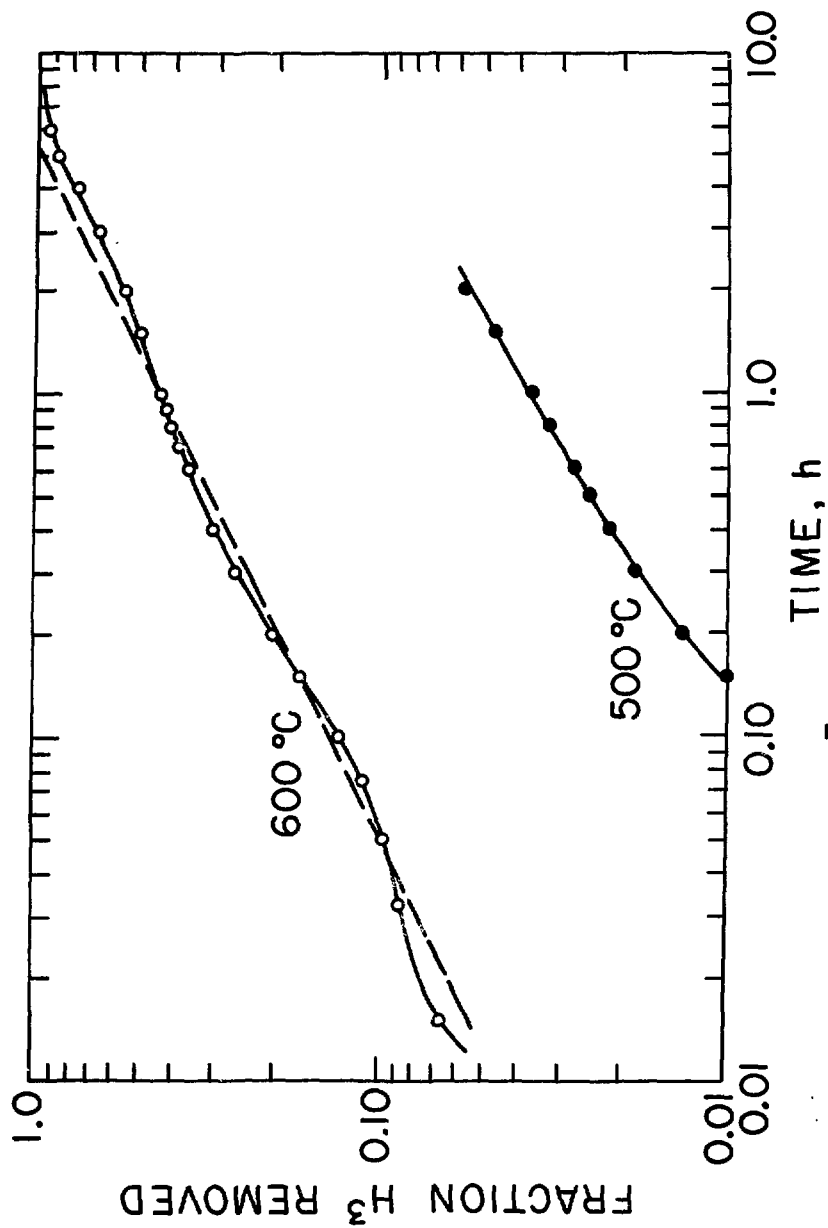


Fig. 8. Removal of tritium from LiAlO_2 of 70-100 mesh. Dashed line has slope of 1/2.

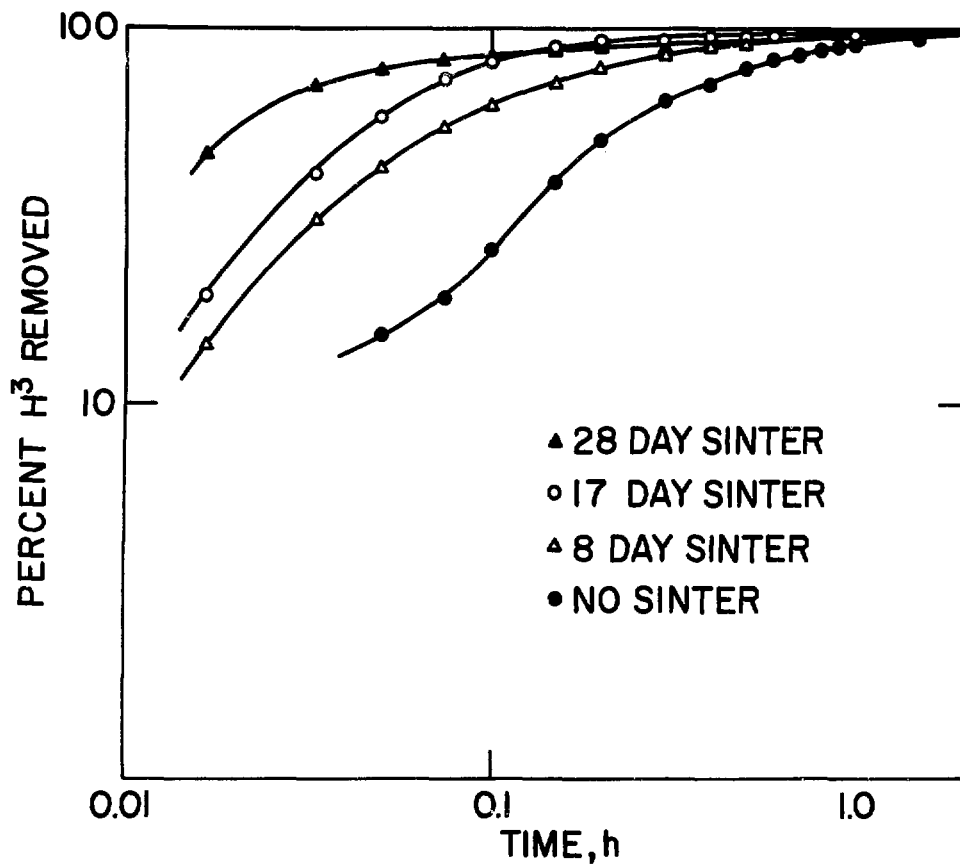


Fig. 9. Removal of tritium from sintered $LiAlO_2$ at 650° .

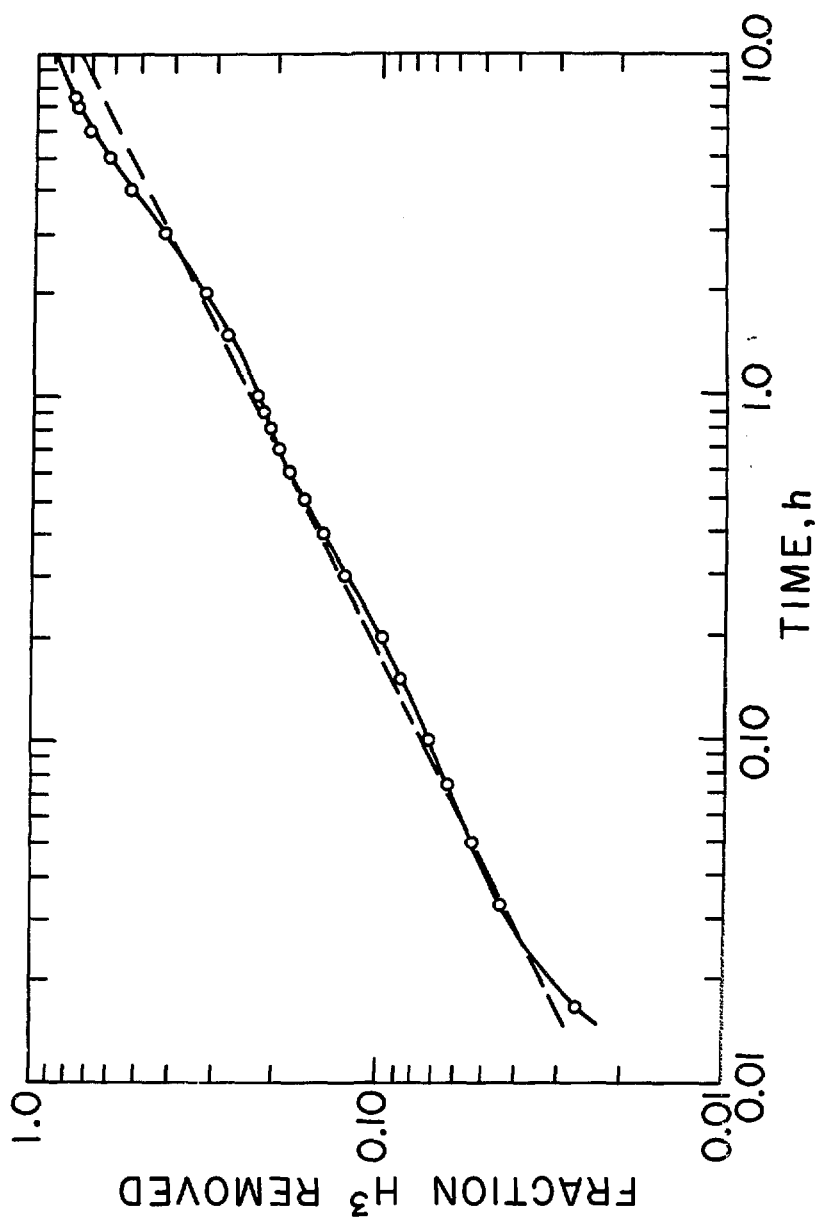


Fig. 10. Removal of tritium from Li_2SiO_3 of 70-100 mesh at 500°.

continuously extracted material. Since

$$\tau = \frac{r^2}{15 D} \quad (2)$$

D and r can be eliminated from Eq. (1) to give

$$f = \frac{6}{\sqrt{15} \pi} \sqrt{\frac{t}{\tau}} \quad (3)$$

In practice, linear plots with the right slope were obtained with some of the runs on LiAlO_2 and Li_2SiO_3 . With LiAl and Li_7Pb_2 , no such linear regions were observed. Nevertheless, holdup times calculated by Eq. (3) from the data in those parts of the curve closest to a slope of 1/2 may have some significance. Table 1 summarizes the τ values thus calculated from the data of Figures 1-10. The numbers, which are doubtless correct as to order of magnitude for the alloys, and considerably closer for the aluminate and silicate, are quite encouraging from a practical point of view. It is noteworthy that "sintering" the LiAlO_2 apparently improved its extraction properties. This effect may be due to a phase transition which has been reported⁵ to take place at 900° , from a rhombohedral to a tetragonal structure.

Table 1. Holdup Times for Tritium in Solids

Material	T, °C	τ , hours
LiAl, 5-10 mesh	500	1500
LiAl, 5-10 mesh	600	14
LiAl, 10-20 mesh	400	6
LiAl, 10-20 mesh	500	0.3
LiAl, 10-20 mesh H ₂ added to He	400	1
Li ₇ Pb ₂ , 20-40 mesh	450	3.3
Li ₇ Pb ₂ , 20-40 mesh	550	0.13
LiAlO ₂ , 70-100 mesh	500	500
LiAlO ₂ , 70-100 mesh	600	3.9
LiAlO ₂ , 80-120 mesh	650	1
LiAlO ₂ , 80-120 mesh, sintered 17 days at 1000°	650	0.2
Li ₂ SiO ₃ , 70-100 mesh	500	13.9

TRITIUM RECOVERY

Experimental Procedure

Tests were carried out on the same apparatus that was used for extraction runs, described above. Absorption test specimens were inserted into the gas train just downstream of the zinc bed. In each, about 10g of metal in the form of sponge, powder or granules was supported on a porous metal frit in a 1/4" OD stainless steel tube; the bed depth was about 6". This was enclosed in an automatically controlled furnace capable of maintaining the test material as high as 900°. The same unit was used both for tritium absorption and desorption runs. For absorption, helium-tritium mixture was generated in one of two ways. In early work, irradiated lithium compounds like those used in the extraction experiments were heated in a helium stream to a temperature high enough to give an adequate tritium activity in the downstream gas. Later, a large supply of gas of about the right activity was made up by mixing one curie of carrier-free T_2 with 1000 psi of helium in a No. 1A gas cylinder (volume ~, 1 1/2 ft²). One one-thousandth of this mixture was then mixed with 100 parts of helium in a second tank at 500 psi, to give a mixture containing about 3.5 nanocuries/ml. Whatever source was used, the stream was passed at 60 cc/min over the heated metal specimen, and was then conveyed to the usual flow meters, counting-gas admixer and counting tube. A shunt tube was also provided, in parallel with the specimen holder, so that the latter could be by-passed. Conditions of flow-rate, temperature, etc. were then sought under which no counts (above background) were registered when the stream passed over the metal being tested; but a high count resulted when the by-pass was used.

Results and Discussion

The first material tested was titanium, in the form of commercial sponge. The particle size was far from uniform, but it appeared to be a moderately high-area material, possibly equivalent to 1 mm particles. In an attempt to activate it for tritium absorption, it was heated to 700° in helium. This procedure was not very successful, since the

product turned out not to pick up tritium below about 700° ; well-activated titanium should react with hydrogen at much lower temperatures. Above 700° , our material did scavenge tritium quantitatively from a flowing helium-tritium stream. When an attempt was made to reverse the absorption by heating the solid in a stream of tritium-free helium, no tritium came off even at 1000° . It seemed likely that a metal forming a less stable hydride than that of titanium would serve better. Vanadium was therefore studied next. Metal of 99.9% purity was ground and sieved, fractions of 20-40 mesh and 45-80 mesh being chosen for testing. After a pre-treatment consisting of about one hour at 700° in flowing helium, samples of either size range absorbed tritium quantitatively at all temperatures between 300° and 500° . It was found possible to recover the tritium by desorption into helium at readily accessible temperatures, which were to some extent a function of particle size. With the 45-80 mesh vanadium, some release was observed at 600° ; at 700° , 95% was removed in 28 minutes. The coarser material required nearly 900° for removal at a good rate. It seems likely that the tritium diffuses into the bulk metal and that the recovery is limited by the rate of the reverse diffusion process, which will be slower for larger particles.

In a search for an absorber which would pick up and release tritium in a still lower temperature range, the alloys TiFe and TiCo were tested. These are known to form hydrides that are exothermic but of considerably smaller stability than vanadium hydride⁴. Apparently their affinity for hydrogen is too small for them to be useful as tritium absorbers; they did not remove tritium from a helium stream even at room temperature.

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TRITIUM RECOVERY OF THE FUSION REACTOR
OF LITHIUM OXIDE BLANKET

K. Tanaka H. Kudo H. Amano

Division of Radioisotope Production
Japan Atomic Energy Research Institute

ABSTRACT

An experiment on the tritium removal from neutron-irradiated lithium oxide was performed. The lithium oxide powder of several origins were subjected to neutron irradiation of up to 3×10^{16} neutrons cm^{-2} in a vertical hole of the JRR-4 in the Japan Atomic Energy Research Institute. By a radio-gaschromatographic analysis it was found that tritium was mostly removed by heating the irradiated salt and trapped in the cold trap as the fraction condensed at -72°C . As the gaseous fraction of minor component, $\text{H}_2\text{-T}$, $\text{CH}_4\text{-T}$, and $\text{C}_2\text{-hydrocarbons-T}$ were simultaneously removed. The residual fraction was always less than 0.5%, when the irradiated lithium oxide powder was heated to 600°C under vacuum. A maximum was observed around 370°C in the tritium release curve. Certain parameters relevant to the tritium release from lithium oxide were briefly studied. From the data obtained, the use of an additional equipment for the tritium recovery system was proposed.

INTRODUCTION

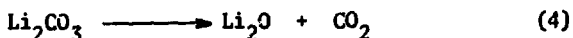
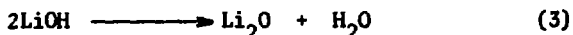
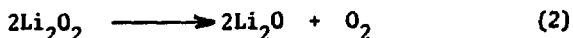
Solid blanket materials in a controlled thermonuclear reactor have recently been proposed, because they have certain advantages in comparison with liquid metal or fused salts. The merits can be summarized as follows; lowering the compatibility barriers, simplifying the cooling device, and the availability of safer operations. Sako et al.¹ proposed a concept using lithium oxide as a blanket material at the Culham Workshop. They predicted that high tritium breeding ratio was served in the lithium oxide system. The tritium breeding ratio being concerned, the lithium oxide system is placed in the second position next to a LiD system among several candidates of the ceramic lithium compounds as is shown by Seki et al.² Lithium oxide could be used as a natural substance without isotopic enrichment or the addition of beryllium.^{3,4} The following are other desirable characteristics of lithium oxide: It is one of the simple lithium compound which allows us to produce low radioactivity inventory, and its high density permits us to lessen the blanket thickness, however, there remains a typical problem that the behavior of tritium in this compound is entirely unknown.

Our purpose of this study is, therefore, focussed on finding out the evidence of the tritium removal from the thermal-neutron-irradiated lithium oxide. We studied the tritium release from lithium oxide by heating and measuring tritium by radiochemical techniques, and certain parameters, such as temperature, density of the target, and the effect of atmosphere during heating, relevant to the tritium release.

Our preliminary results on the tritium removal were applied to consider a tritium recovery system of the lithium oxide blanket, assuming that tritium was released from the lithium oxide pebble as T_2O .

MATERIAL CONSIDERATIONS AND RELATED PRELIMINARY EXPERIMENTS

Lithium oxide is obtained by following processes.



Among them the reactions (1) and (2) are proceeded at the lowest temperature and the reaction (1) is assured to give the highest purity of the product. Target materials of lithium oxide used here were commercial products, except one which was prepared by the reaction (1).

The physical and chemical properties of lithium oxide are summarized in Table I. Lithium oxide is a fcc crystal of antiferite type. The X-ray diffraction analysis of the products obtained by the reaction (1) and (3) were compared. The results closely coincided with those obtained by Swanson⁵, except for that in the pattern of the latter there were considerably many weak lines which could not be identified. Recently, Stecula⁶ reported the formation of Li_3O_2 by the dehydration of LiOH with Mo crucible in vacuo (10^{-5} torr). Our data did not agree with his results.

The density of the lithium oxide is known as 2.013 g cm^{-3} . The preparation of the lithium oxide pellet was started by Takahashi and Kikuchi⁷ in JAERI. The pellets having 71 - 92 % of the theoretical density were obtained.

The reported melting points of lithium oxide scatters widely in literatures.^{8,9,10} We expect that lithium oxide may react with materials, especially with crucibles, at a quite high temperature, and that this reaction is promoted in the presence of oxygen or water vapor or affected by the metallic impurities, contained in the sample, such as Si, Al and any other elements which is possible to form ceramics with lithium oxide.

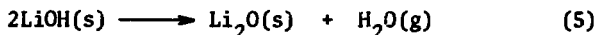
Although the thermal conductivity of the pebble is hardly known in

Table 1. Physical and Chemical Properties of Lithium Oxide and Lithium Hydroxide

Properties		Li ₂ O	LiOH
Molecular Weight		29.88	23.949
Density	(g cm ⁻³ , 298K)	2.013	1.46
Crystal Form		cubic antifluorite	tetragonal
Crystal Parameter	(Å)	a = 4.619	a = 3.55 c = 4.34
Atomic Distance	(Å)	Li-O 2.00 Li-Li 2.32 O-O 3.27	Li-OH 1.97 Li-Li 2.51 OH-OH 3.05
Ratio of Ionic Radii		0.52(Li ⁺ /O ⁻)	
Melting Point	(K)	1700 1773 2005	735
Boiling Point	(K)	2873	1197
Heat of Formation	(kcal mol ⁻¹)	-142.4	-116.6
Free Energy of Formation	(kcal mol ⁻¹)	-132.9	-106.1
Heat of Hydration	(kcal mol ⁻¹)	31.2	
Latent Heat of Fusion	(kcal mol ⁻¹)	14.0	5.01
Latent Heat of Vaporization	(kcal mol ⁻¹)	56.0	
Thermal Conductivity	(W cm ⁻¹ K ⁻¹ , 333K)	0.0173	
Electrical Conductivity	(Ω ⁻¹ cm ² , 1843K)	108	
Refractive Index		1.644	1.452

literature at the present time, the order of magnitude and its temperature dependence might be resembled with those of other ceramic materials such as UO_2 or MgO .

The equilibrium pressures of water vapor above LiOH and Li_2O have been measured by Gregory and Mohr¹¹ using transpiration and effusion methods. They demonstrated the temperature dependence of the vapor pressure of H_2O in the system



as

$$\log P(\text{atm}) = -7073/T + 2.102 \times \log T - 2.54 \times 10^{-3} \times T + 2.767. \quad (6)$$

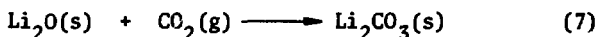
The heat of formation is

$$-\Delta H^\circ = 32.6 \text{ kcal mol}^{-1}$$

and the free energy of formation

$$-\Delta F^\circ = 22.5 \text{ kcal mol}^{-1}$$

Lithium oxide is an active material with CO_2 gas. This oxide react rapidly with CO_2 gas at the temperature around 200 - 300°C. The heat of formation for the reaction



is reported as

$$-\Delta H^\circ = 54.2 \text{ kcal mol}^{-1}$$

EXPERIMENTAL

Approximately 20 mg of the target material was sealed in a quartz ampoule under reduced pressure (9×10^{-4} torr) and put into a plastic capsule. The sample was subjected to neutron irradiation at the vertical hole of the Japan Research Reactor(JRR)-4 of the Japan Atomic Energy

Research Institute. A typical exposure was 20 min at a thermal neutron flux of 3×10^{13} neutrons $\text{cm}^{-2}\text{sec}^{-1}$. During the handling of lithium oxide, especially in the case of powder, the atmosphere was maintained in argon or in vacuo in order to reduce the reaction of lithium oxide with CO_2 or H_2O which was contained in air. About 100 mg of the sample sealed in a quartz ampoule was bombarded with 40 MeV bremsstrahlung radiation from an electron linear accelerator for 30 min, followed by the separation of silica. The carbon content was determined by the measurement of ^{11}C amount, formed by the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction, using gamma-ray spectrometry.

The method of chemical separation and analysis of tritium fraction were very similar to those of previous paper¹² except for small modifications; The irradiated target being stored for more than one week, the gaseous species of tritium having been present in the ampoule were introduced into a gas chromatograph(GC), the ampoule being broken at a room temperature. The GC consisted of a thermal conductivity detector and a stainless steel column(3 mm diameter and 2 m length) packed with activated carbons of which temperature was kept at 0°C . The out gas of the GC was mixed with propane(He : PR = 1 : 1.5) and passed through a proportional counter(PC, Aloka Ltd.). The calibration of this counter of tritium measurement was made by the known amount of methane-T which was used as the reference. After the gas was released over, the sample was transferred to the center of a quartz cylinder which was mounted in an electric furnace and connected with a vacuum line. The cylinder was evacuated and heated at a prescribed temperature for 30 min under vacuum less than 5×10^{-4} torr. The released fraction to be analyzed were fed to the GC with He carrier through the cold trap at -72°C . Tritiated species collected in the cold trap were repeatedly washed out with water and their radioactivities were measured by Beckman's LS-100 liquid scintillation counting system(LSC). Toluene-methanol (7 : 3) solution containing 4 g l^{-1} of diphenyloxazole(PPO) was used as a scintillator. In order to measure tritium remained in the residue, the solid was dissolved in water and counted by the LSC. Relative counting efficiency between the PC and the LSC was obtained beforehand. The experiments under the helium gas atmosphere was held in the same

apparatus as aforementioned one.

THE EVIDENCE OF TRITIUM REMOVAL FROM LITHIUM OXIDE

The percent distribution of tritiated species released from neutron-irradiated lithium oxide powder on heating up to 600 - 620°C under vacuum is listed in Table 2. For convenience, the species are divided into three fractions; the gaseous fraction for the species not trapped at -72°C, the condensed fraction for those collected in the cold trap, and the residual fraction for those remained in the target material. Although chemical forms have not been identified yet, the majority of tritium was found in the condensed fraction, independent of the kind of targets. Target A from Wako was subjected to neutron irradiation without any treatment. Target B was identical with Target A, except for being heated at 600°C for 90 min under vacuum before the irradiation. Target C was from Cerac/Pure and Target D from Mitsubishi Atomics Ind.

A few percent of tritium was found in the gaseous fraction, in which tritiated hydrogen(T_2 and/or HT) and methane(CH_4 -T) were observed. The isotope separation between hydrogen isotopes was not carried out. In addition, C_2 -hydrocarbons, such as ethane, ethylene, and acetylene, labeled with tritium were observed but minor amount in this fraction. The appearance of mass signals of H_2 , CH_4 and CO in the gaschromatogram of this fraction suggested the presence of hydrogen and carbon in the target material. The carbon contents were determined by means of photoactivation analysis using pure analytical grade Na_2CO_3 as a reference material. The results were 0.3 % for the lowest value in the sample from Mitsubishi Atomics as shown in Table 3, while there were no examination for hydrogen content at the present study.

In order to elucidate the feature of tritium removal from lithium oxide, the distribution of tritium fractions released was obtained as a function of the temperature with stepwise rise from 100 - 600°C. Figure 1 shows the tritium release curve obtained for Target D. When the ampoule

Table 2. Distribution of Tritium Activity from Neutron-Irradiated Li_2O , LiOH and Li_2CO_3 on Heating to 600°C under Vacuum

Targets		Distribution (%)				
		$\text{H}_2\text{-T}$	Gaseous Fraction $\text{CH}_4\text{-T}$	$\text{C}_2\text{-hydrocarbons}$	Condensed Fraction at -72°C	Residue
Li_2O	A(2) *	0.4	0.3	0.1	99.1	0.1
	B(3)	1.7	1.3	0.5	96.3	0.2
	C(5)	0.7	0.6	0.1	98.4	0.2
	D(2)	0.8	0.8	0.1	98.1	0.1
LiOH	(1)	0.3	0.1	0.2	99.4	0.01
Li_2CO_3	(2)	1.5	0.3	0.9	97.2	0.1

* The number of determination was quoted in parenthesis

Table 3. Estimated Carbon Content in Lithium Oxide Targets

Carbon Content (%)	B	Target C	D
as Carbon(C)	4.7	0.5	0.3
as Carbonate(Li ₂ CO ₃)	28.8	3.0	2.2

was broken, H₂-T was detected with 0.01 % of emergence, and its removal reached 0.8 % at 600°C. The release of CH₄-T began above 300°C, and reached the final value of 0.8 %.

For the condensed fraction with the highest emergence, we speculated that, if tritium produced by the ${}^6\text{Li}(n, \alpha){}^3\text{H}$ reaction was present in the form of LiOT in the target material, T₂O would predominate in the condensed fraction, released following by the dehydration of LiOT. The curve in Fig. 1, however, revealed that tritium of this fraction was released at the temperature around 370°C, which was lower by about 100°C than that of the dehydration of LiOH.^{13,14} The dehydration was reconfirmed by the thermogravimetric analysis using Mo crucible under vacuum, and we obtained a dehydration curve with a maximum at 480°C.

There was no apparent difference between the release curves of the gaseous fraction and of the condensed fraction, but in some cases there appeared rather slower release of CH₄-T than those of H₂-T.

The residual fraction was always kept at lower than 0.5 % and in a typical case the amount was around 0.1 %. The result suggested that tritium produced by a thermal neutron irradiation of lithium oxide had few probabilities to stabilize as a stable state which was hardly removed from the target.

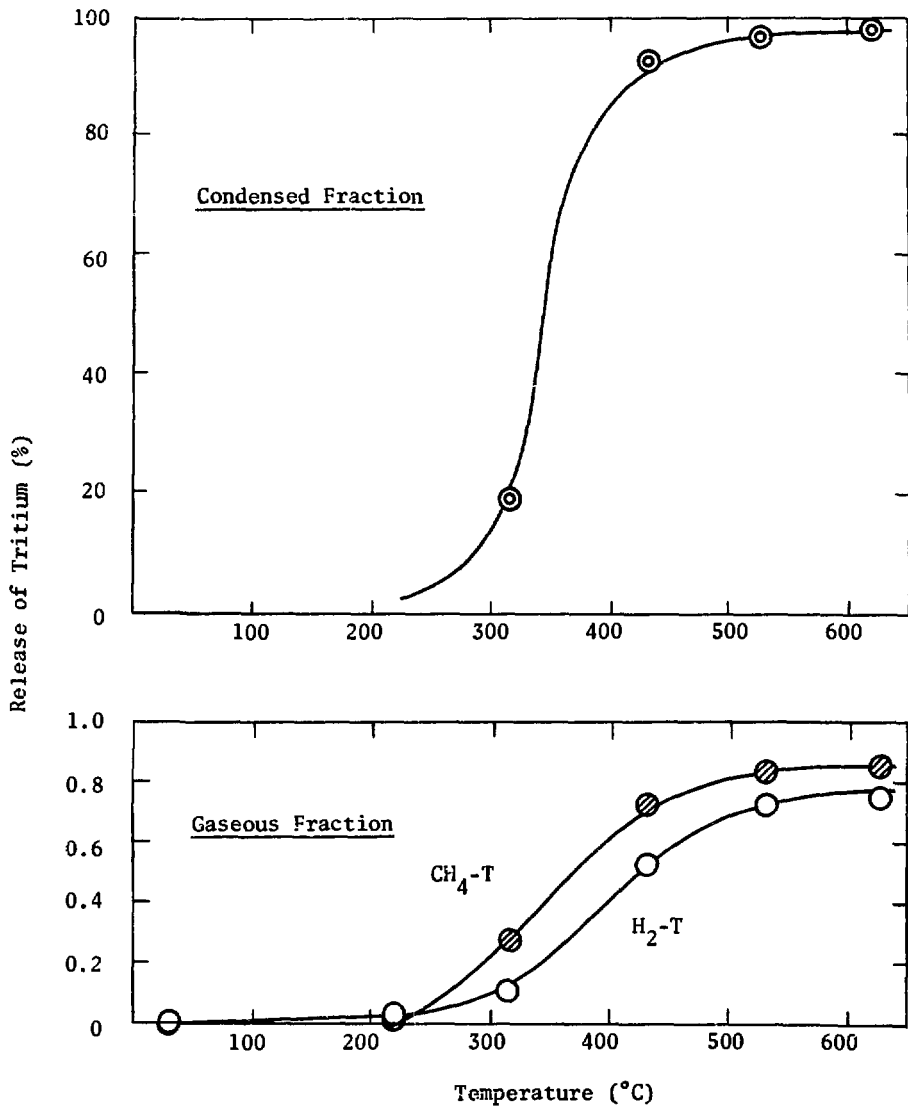


Fig. 1. Tritium Release Curve from Li_2O (Target D) Under Reduced Pressure

Tritium was released from the powders of neutron-irradiated Li_2CO_3 and LiOH , as shown in Fig. 2. On the tritium removal from Li_2O , Li_2CO_3 , and LiOH under reduced pressure, there was slight difference among them. In the case of Li_2CO_3 the amount of hydrocarbons slightly increased.

Preliminary data showed that the release of tritium from the pellet of lithium oxide under vacuum was similar to that obtained for the powder, except for that the release temperature seemed to shift to a little higher side. In Fig. 3., the release curve obtained for the pellets is shown in comparison with that of powder. The release of tritium was clearly affected with the pellet density. This was confirmed by the more precise experiment, as shown in Fig. 4. This result suggested

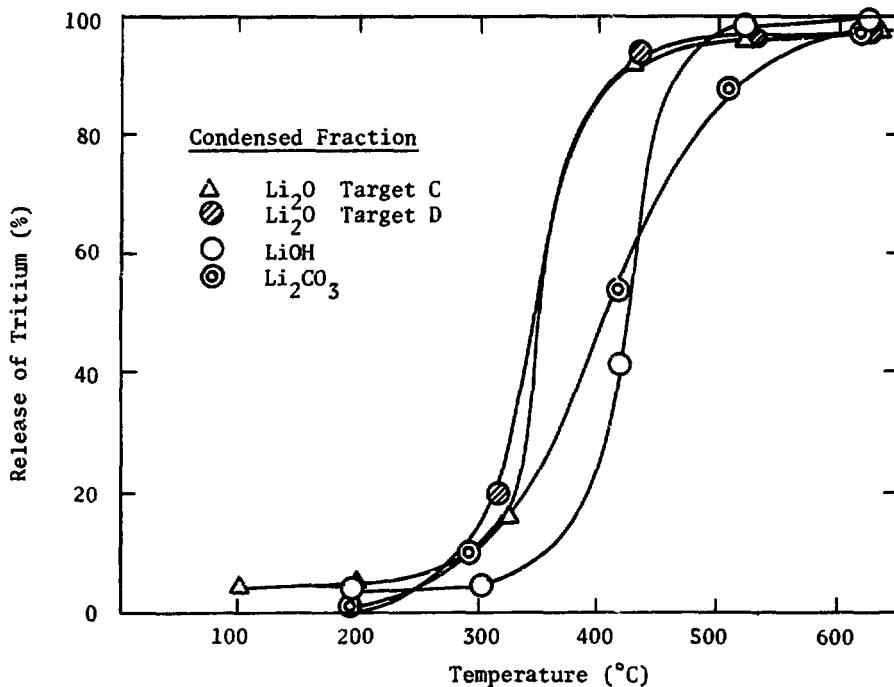


Fig. 2. Tritium Release Curves from Neutron-Irradiated Certain Lithium Compounds Under Reduced Pressure

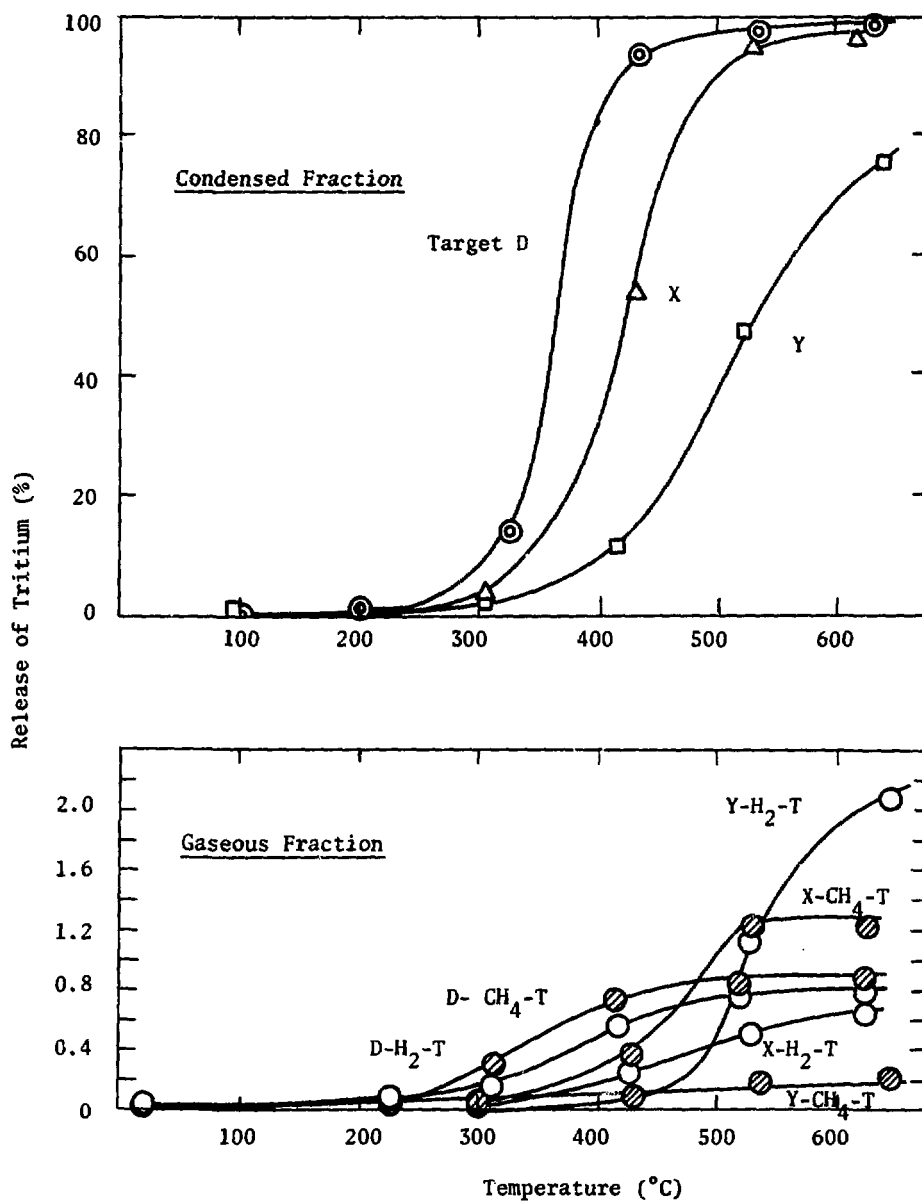


Fig. 3. Tritium Release Curves from Li₂O Powder and Pellets

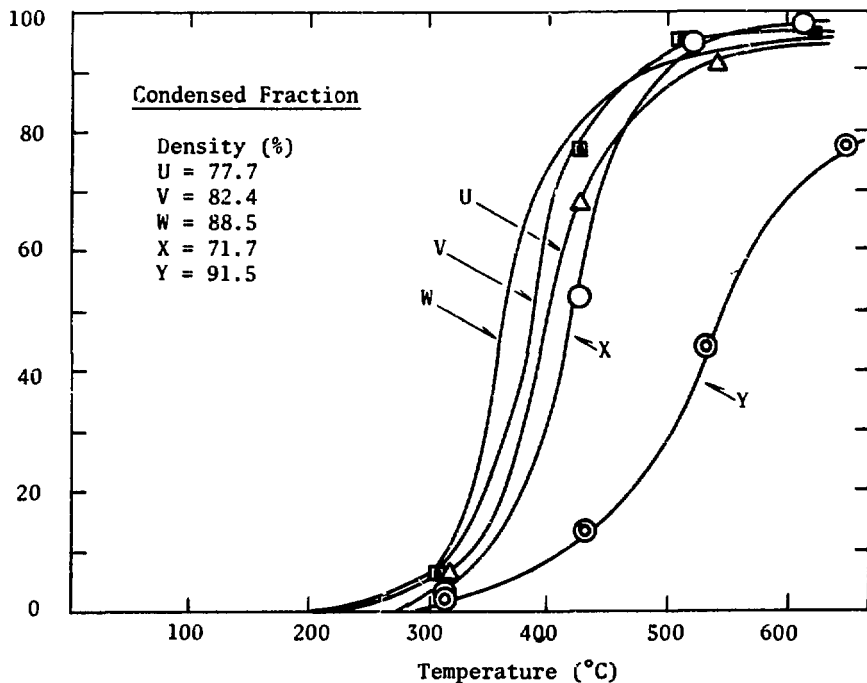


Fig. 4. Tritium Release Curves from Li_2O Pellets, dependence upon densities

that the abrupt change in the tritium release around 90 % of its theoretical density, but we need more efforts to confirm these results in future study. The details of the effect of density on the release of tritium from lithium oxide will be published elsewhere by Nasu et al.

We also observed the tritium removal from the neutron-irradiated lithium oxide powder on heating in the stationary helium gas atmosphere at the pressure of approximately 1.2 atm, as shown in Fig. 5. Even in this case, most of tritium were released from neutron-irradiated lithium oxide on heating to 600°C.

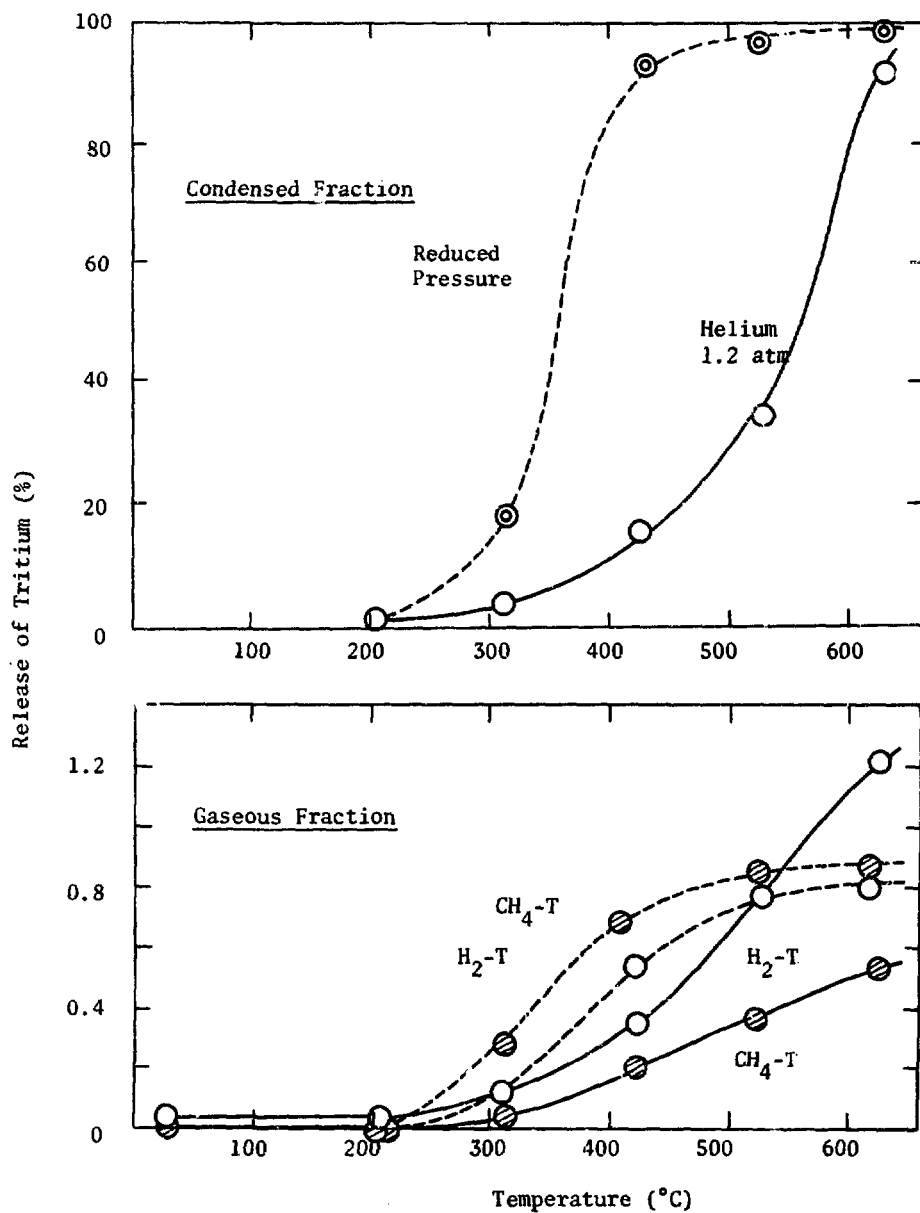


Fig. 5. Tritium Release Curves from Li_2O Powder (Target D), comparison with the release under reduced pressure and that under helium atmosphere at 1.2 atm.

We are continuing our study on the tritium removal experiment by introducing isothermal technique and mass spectrometry.

TRITIUM RECOVERY SYSTEM FOR THE LITHIUM OXIDE BLANKET

The tritium recovery system of the proposed fusion reactor with a lithium oxide blanket have been studied by Sako et al.¹⁵ The concept of the tritium removal from the helium coolant is based on the adsorption method of the reduced tritium gas: First, tritium species is reduced to tritium gas(T_2), secondly the tritium gas passes through palladium or palladium base alloy, and finally tritium is removed from the gas phase by the adsorption on the rare earth metal such as yttrium which is expected to have the lowest hydrogen partial pressure in gaseous phase.¹⁶ Our observation of the tritium removal from lithium oxide showed that the majority of the tritium species might be present as T_2O , and as for an effective trapping method of tritiated water, we could think of two types. The one is a recovery in that chemical form(T_2O), and the other is the introduction of the conversion technique as described above.

We propose an introduction of the additional cold trap filled with a dessicant such as molecular sieve or silica-gel into the previous system. By the additional use of the dessicant, we expect somewhat higher rate of tritium removal, because of rapid equilibrium between stationary dessicant and flowing helium coolant, than that of the adsorption method. We do not expect, however, the complete removal by the cold trap technique alone, because the equilibrium pressure of tritiated water will be considerable affected with the temperature of the coolant.

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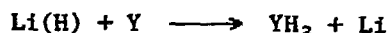
HYDROGEN ISOTOPE REMOVAL FROM LIQUID LITHIUM;
USE OF YTTRIUM SPONGE AS A GETTER

Peter Hubberstey
Paul F. Adams
Richard J. Pulham

Department of Inorganic Chemistry, University of Nottingham,
Nottingham, NG7 2RD, England.

ABSTRACT

The efficiency of hydrogen isotope removal from liquid lithium by filtration, cold trapping and chemical gettering is assessed from solubility and thermodynamic data. The Free Energy-Temperature diagram for metallic hydrides indicate that calcium, barium, scandium, yttrium and lanthanum should getter hydrogen from lithium, but isopleths for unsaturated solutions, derived from recent solubility results, indicate that gettering may not be complete. Thus, preliminary experiments, using resistivity techniques to monitor hydrogen isotope concentration in lithium, have been undertaken to assess the gettering efficiency of yttrium sponge for unsaturated Li-H and Li-D solutions (and by extrapolation Li-F solutions). The results show that hydrogen isotope removal occurs readily according to



and it is not restricted by formation of surface protective films. Large quantities of hydrogen can be removed from solution and gettering occurs to low levels. The gettering rate is exceptionally rapid even at relatively low temperatures (e.g. 400°C) and thermal cycling of the hydrided getter induces a marked increase in rate.

INTRODUCTION

A knowledge of the efficacy of techniques for hydrogen isotope removal from liquid lithium is a necessary prerequisite to fusion reactor design, since the production of tritium in, and its removal from, the reactor blanket is an essential part of the fuel cycle. The maximum tritium concentration which can be tolerated in a lithium blanket is thought to depend on both economic and safety criteria; various estimates have been proposed varying from 0.005^1 to $0.1 \text{ mol \% T}^2$

Four classical techniques, distillation, diffusion through transition metal membranes, filtration (cold trapping) and chemical gettering, have been developed recently for the removal of hydrogen, and other non-metals, from liquid alkali metals. Removal of hydrogen isotopes from lithium by distillation is impossible since lithium exerts an appreciable vapour pressure at distillation temperatures, giving rise to azeotropic conditions. In fact, at low hydrogen concentrations the vapour is depleted in hydrogen, constant boiling mixtures being formed at $0.024 \text{ mol \% H}$ (700°) and $0.174 \text{ mol \% H}$ (1000°C)¹. On the other hand, extraction through transition metal (e.g. niobium) membranes is the subject of a number of well established investigations and is considered an attractive possibility.¹

To facilitate the assessment of filtration and chemical gettering as purification techniques in the lithium-hydrogen isotope systems we have investigated the lithium-rich sections of the Li-H and Li-D phase diagrams.^{3,4} Impurity levels attained after filtration of a metal are related to impurity solubilities at the filtration temperature. The lithium-rich sections (0 - 0.07 mol % solute) of the Li-H and Li-D phase diagrams (Figure 1) indicate that the minimum hydrogen isotope concentrations attainable (by filtration at the melting point (180.49°C)) are $0.016 \text{ mol \% H}$ and $0.013 \text{ mol \% D}$. Filtration at a technologically more viable temperature (e.g. 200°C) will reduce concentrations to $0.027 \text{ mol \% H}$ and $0.021 \text{ mol \% D}$, (points C and C', respectively, Figure 1). A simple extension of the solubility data⁴ would suggest that the solubility of tritium in liquid lithium at these temperatures will be similar to and presumably not greater than that quoted for Li-D solutions. It can

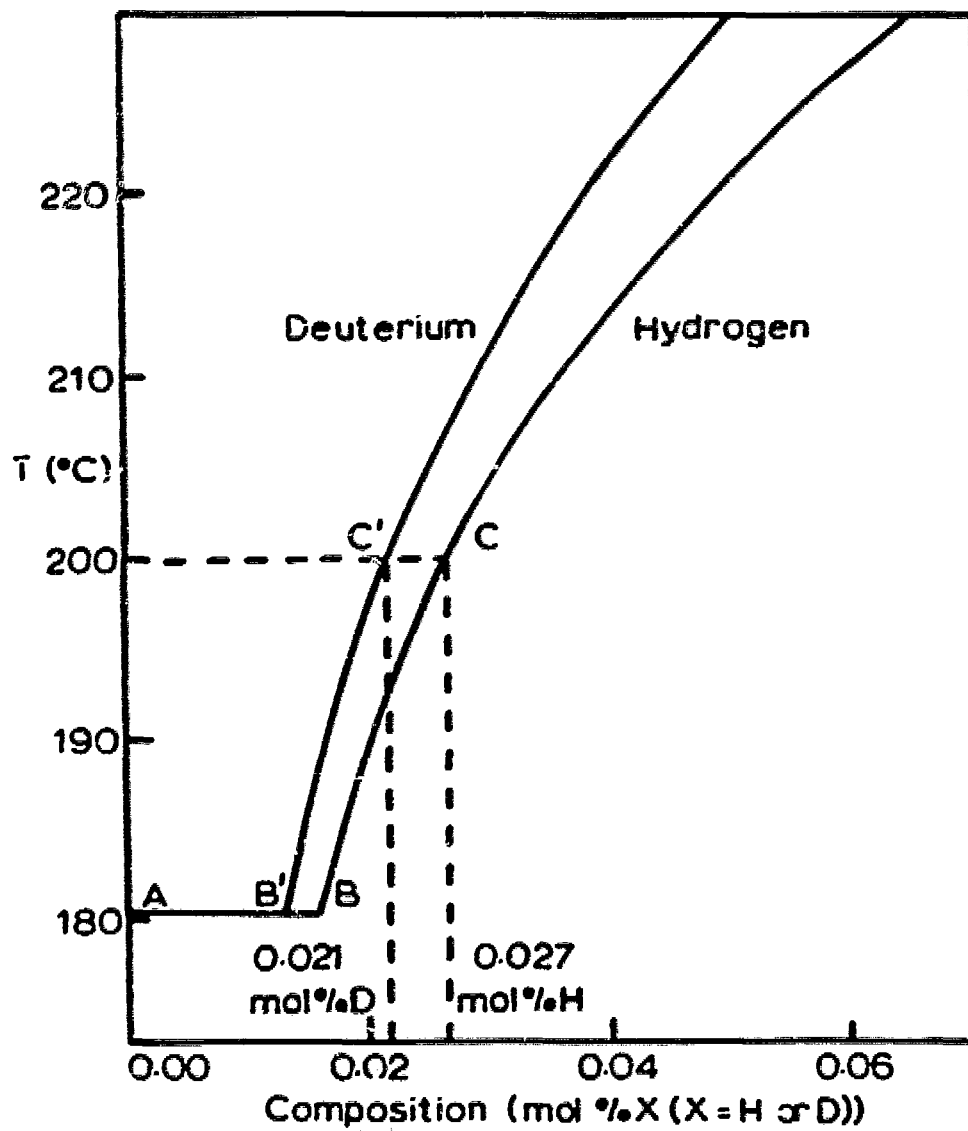


Fig.1. The lithium-rich sections of the Li-LiX (X=H or D) phase diagrams.

thus be inferred that tritium concentrations remaining after filtration of Li-T will not be greater than those quoted for Li-D solutions. These residual concentrations can be attributed to the presence of a detectable hypoeutectic liquidus in the Li-LiX (X = H,D) phase diagrams (A-B and A-B' respectively, Figure 1). With the exception of the Li-Li₃N and Cs-Cs₂O systems, these are the only alkali metal-non-metal systems for which the hypoeutectic liquidus has been established.⁵

Gettering may be represented by the chemical reaction



where X is a soluble non-metal impurity and M a suitable insoluble getter. The efficacy of the getter is determined by the free energy change associated with reaction 1: if negative, the non-metal will be removed from the liquid metal, if positive, it will remain in solution. A simple assessment of this energy change is based on the relative thermodynamic stabilities (free energies of formation, ΔG°) of the appropriate lithium compound and the corresponding getter compounds. This information is conveniently represented on a Free Energy-Temperature diagram; such a diagram for hydrides is shown in Figure 2. Since it is based on thermodynamic data of varying reliability, the diagram can only be used as a guide. Nevertheless, it does show that although the alkali metal hydrides (e.g. KH, NaH) are, in general, relatively unstable, lithium hydride has a stability similar to that of many of the transition metal and alkaline earth hydrides. Consequently, but a few metals (i.e. Sc, Y, La, Ca and Ba) may be used to remove hydrogen from liquid lithium.

Since, in reality, gettering is carried out on unsaturated solutions, this analysis can be extended by estimating the free energies of unsaturated solutions $(\Delta G^\circ)^1$ as a function of temperature and impurity concentration, x_{LiX} , using the derivation of Evans and Thorley,⁶ (eq.(2));

$$(\Delta G^\circ)^1 = \Delta G^\circ + RT \ln \left[(x_{\text{LiX}})/(x_{\text{LiX}})_S \right] \quad 2$$

and a knowledge of the temperature dependence of the solubility $(x_{\text{LiX}})_S$ of hydrogen in liquid lithium³ (eq.(3));

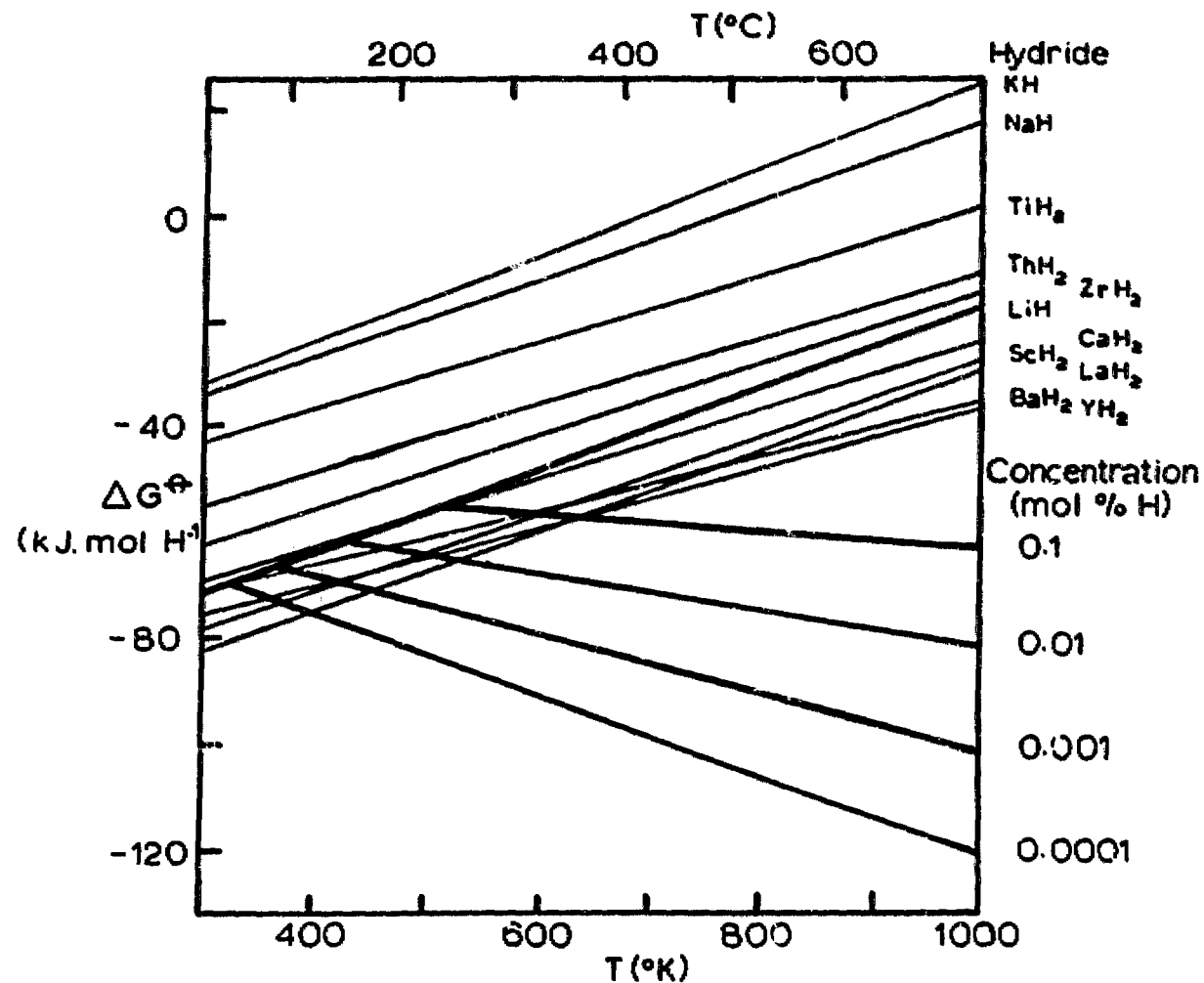


Fig.2. Free Energy-Temperature diagram for hydrides showing isopleths for unsaturated Li-H solutions.

$$\log_{10} S \text{ (mol \% H)} = 3.523 - 2308/T \text{ (K)} \quad 3$$

Isopleths, (i.e. free energies of unsaturated solutions of constant hydrogen concentration) have been calculated for 0.1, 0.01, 0.001 and 0.0001 mol % H solutions and are superimposed on Figure 2. Thus, the minimum hydrogen concentration attainable with yttrium or lanthanum at 400°C is predicted to be 0.10 mol % H. This is a relatively high value and it is clear that dilute unsaturated solutions of hydrogen in lithium are exceptionally stable. An improvement in gettering appears possible at lower temperatures and obviously a getter is required which rapidly absorbs hydrogen at low temperatures.

Residual hydrogen concentrations derived from this analysis are maximum values, since they are based on the assumption that there is little or no solid solubility of hydrogen in the getter (i.e. the getter hydride is in equilibrium with the liquid metal solution). For those metals which exhibit considerable hydrogen solid solubility (e.g. at 400°C the solubility of hydrogen in yttrium is ca. 28 mol % H⁷) isopleths can be constructed which show that the minimum concentrations attainable in the lithium can be lower and will depend on the partitioning of the hydrogen between the two metals. This refinement of the analysis, however, might not apply in real conditions since it assumes that equilibrium is maintained throughout the process and, in particular, within the getter. In reality, this might not be so since the surface of the getter might be richer in hydrogen than the interior and hence contain getter hydride.

The corresponding analysis for Li-D solutions is similar to that discussed above (the standard free energies of formation of LiH and LiD are -90.67 and -91.13 kJ mol⁻¹ respectively⁸) and by inference that for Li-T solutions should also be similar.

We have carried out several preliminary experiments to estimate the effectiveness of yttrium as a getter for hydrogen and deuterium in lithium at low temperatures (400°C) as part of a general study of the chemistry of liquid alkali metals as solvents and reaction media.

EXPERIMENTAL

Apparatus

The stainless steel (AISI 321) apparatus is shown in Figure 3. A cylindrical reservoir, A, (0.28m high, 0.05m diam.) which contained the bulk of the lithium (ca 40g) was provided with a glass-to-metal seal, M, (0.025m diam.) and a glass joint. The liquid metal was circulated independently through two loops using small electromagnetic pumps, P₁ and P₂, described previously.⁹ The main pump, P₁, was used to provide a continuously regenerated clean metal surface for (a) rapid reaction with the solute gas and (b) to ensure rapid mixing of the solution. The second pump, P₂, fed the solution into a capillary, R, (0.0015m i.d., 0.35m long) for continuous resistance measurement.

The apparatus was equipped with getter and valve assemblies (Figure 3) for the in situ addition of yttrium sponge (ca 4g, Koch-Light 99.99%) to and its removal from the liquid metal and gas reaction zones. Randomly shaped pieces of the metal (yttrium sponge is too hard to fabricate into rods) were threaded onto a stainless steel rod, G, and supported by a steel chain, C₁, which was wound round a glass spindle. This was rotated through a greased glass joint, W₁, to pass the getter through the open valve assembly and into the apparatus. The two sections, B and D, of the gas-tight valve assembly, which was attached to a vacuum frame at points F and H (for access to vacuum, purified argon, and reactant gases) could be isolated by lowering the ball joint, J, into the socket, K, using a winding device, C₂, W₂, similar to that of the getter assembly. With the valve closed, alternative getter assemblies could be attached to section D of the valve assembly without contamination of the liquid metal.

Procedure

The apparatus was cleaned and dried as described previously¹⁰. Its resistance, when both empty and charged with lithium (Koch-Light 9998%) which had been cleared of surface impurity, was measured by means

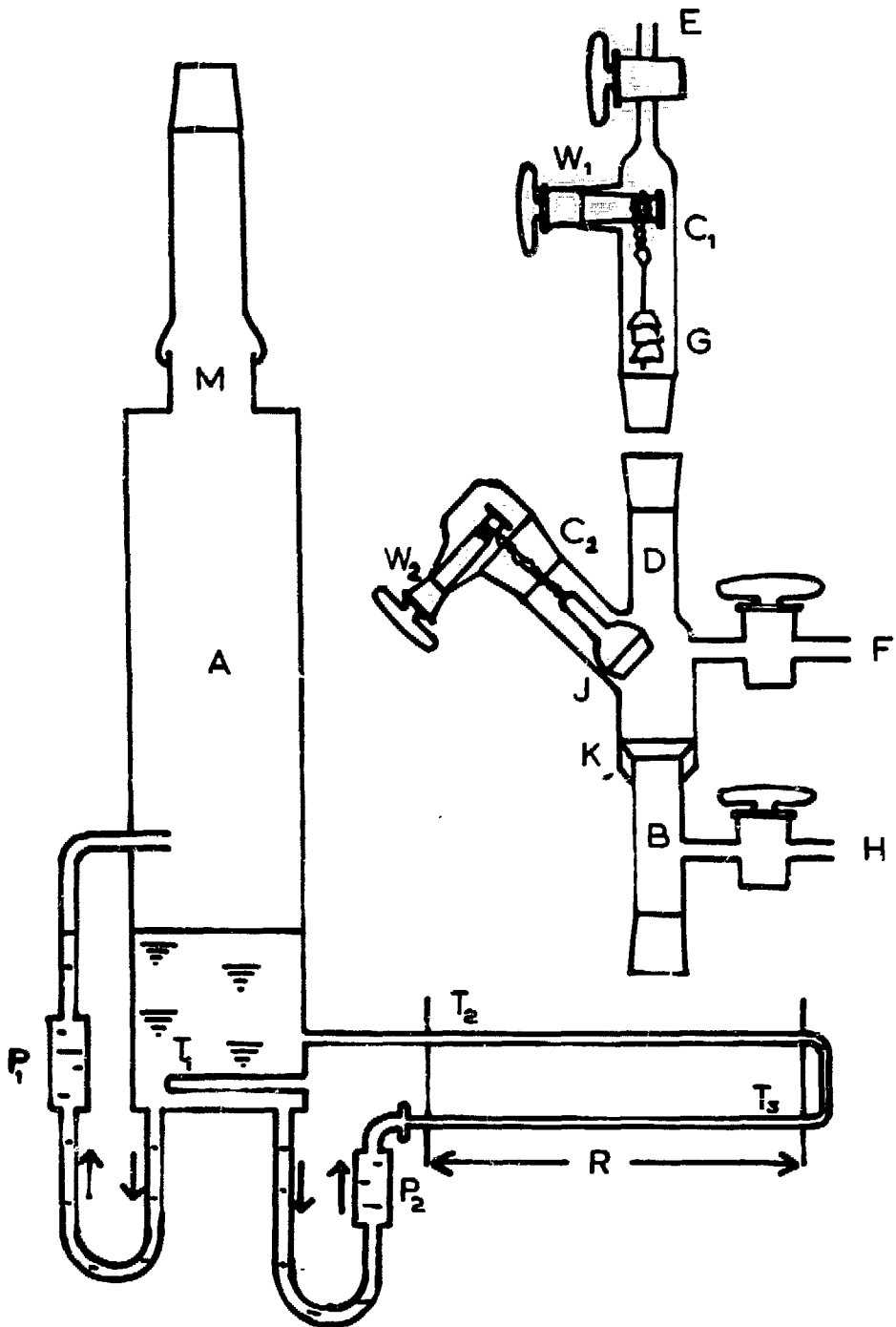


Fig.3. Apparatus.

of a Kelvin-Wheatstone bridge at selected constant temperatures (450 - 185°C) in an air oven, the temperature of which could be controlled to $\pm 0.5^\circ$ at 400°C. Temperatures were measured to $\pm 0.05^\circ\text{C}$, by means of thermocouples situated at T_1 (bulk temperature) and T_2, T_3 (capillary temperatures) as shown in Figure 3. The liquid was further purified by gettering with yttrium at 400°C, the process being monitored by resistance changes. When resistance remained constant for 72 hours, the getter was isolated and the resistance remeasured at selected temperatures. Hydrogen (Air Products, 99.98%) and deuterium (Matheson Gas Products, 99.9%) purified as reported previously,¹¹ were added to the metal in small volumes (ca 10^4 mm^3 at STP) at constant temperature. The resistance of the solution was determined under equilibrium conditions after each addition. The solute was then removed by lowering the getter into the liquid metal at 400°C and resistance changes determined as a function of time. Resistivities were calculated from the resistances and capillary dimensions as described previously¹⁰ using the formula for parallel conductors.

Determination of solute concentration during gettering

Determination of the resistivity of the solution during the gettering process provides a direct measure of the solute concentration since these two parameters are almost linearly interdependent. The resistivity-concentration (ρ -c) calibration graph for a lithium-hydrogen solution (maximum concentration 1.0 mol % H) at 400°C is shown in Figure 4(a) it exhibits a slightly increasing concentration dependence of resistivity with average gradient, $4.9 \times 10^{-8} \text{ } \Omega\text{m/mol \% H}$. Since resistivity can be determined to an accuracy of $\pm 0.05 \times 10^{-8} \text{ } \Omega\text{m}$, this relatively high gradient ensures the accuracy of the concentration analysis ($\pm 0.01 \text{ mol \% H}$) during gettering.

The derived concentration can be checked at any stage by the determination of the resistivity of the solution as a function of temperature at selected constant temperatures (450 - 185°C) whilst the getter is isolated from the liquid metal. Resistivity-temperature (ρ -T) graphs obtained for three lithium-deuterium solutions are

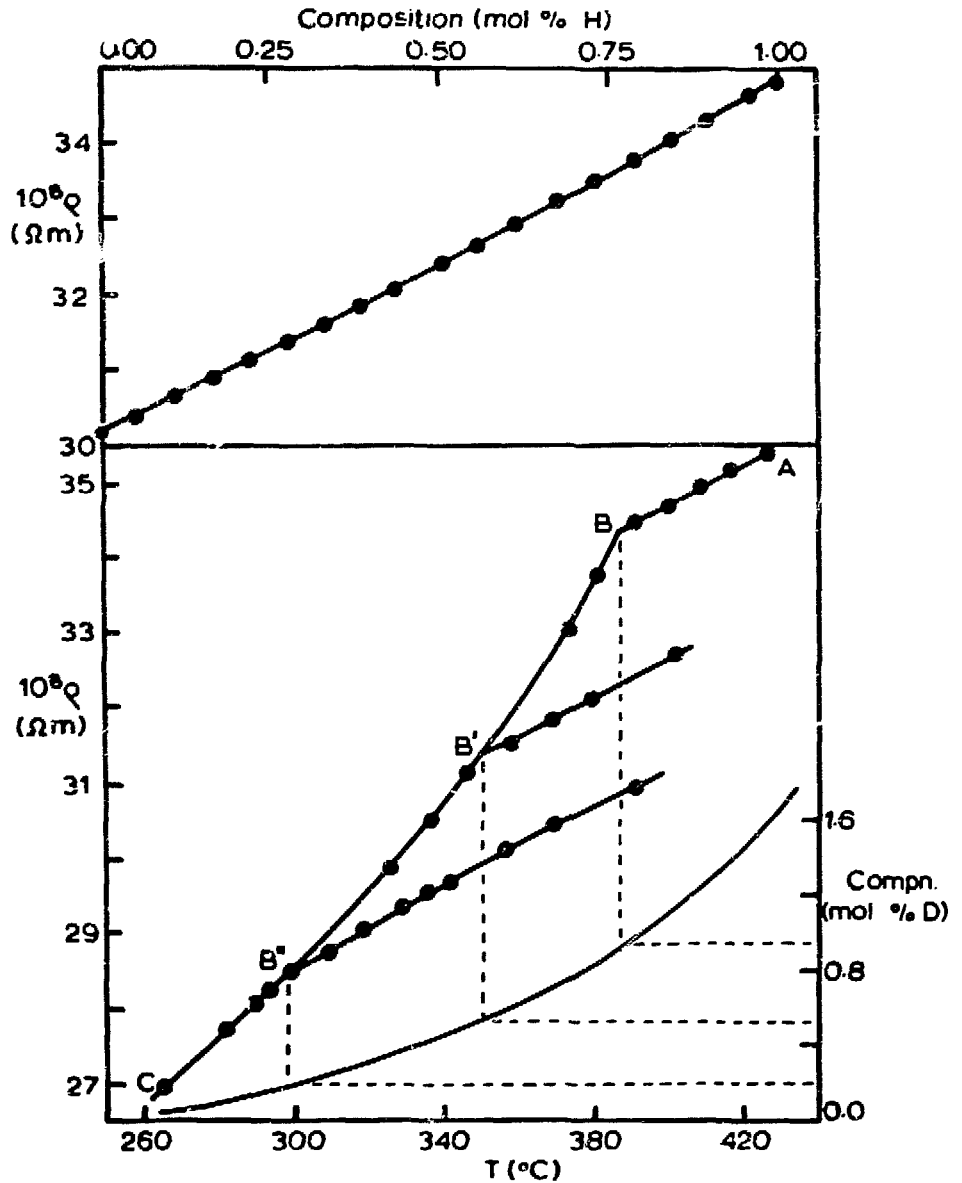


Fig. 4. (a) Resistivity-composition isotherm (400°C) for solutions of hydrogen in liquid lithium (0-1 mol % H).
(b) Resistivity of lithium-deuterium solutions as a function of temperature and the solubility of deuterium in liquid lithium.

illustrated in Figure 4(b). The solution at A, although of unknown composition, is unsaturated at this temperature (430°C). On cooling, resistivity falls smoothly until at B, the solution becomes saturated and precipitation of LiD occurs; from B to C the solution contains a diminishing quantity of deuterium and the resistivity falls much more steeply. More dilute solutions, investigated at later stages of the gettering process, have lower resistivities and precipitate at B' and B". The precipitation temperatures can be related to the solution concentration using the hypereutectic liquidus of the appropriate metal-salt phase diagram (Figure 4(b)) for which the corresponding solubility equations are

$$\text{Li} - \text{H} : \log_{10} S (\text{mol \% H}) = 3.523 - 2308/T(\text{K}) \quad 4$$

$$\text{Li} - \text{D} : \log_{10} S (\text{mol \% D}) = 4.321 - 2873/T(\text{K}) \quad 5$$

RESULTS AND DISCUSSION

The resistivity changes observed when solutions of hydrogen (1.00 mol % H) and deuterium (0.99 mol % D) in liquid lithium were gettered with yttrium sponge at 400°C are shown in Figure 5 as a function of time. Since resistivity can be converted directly to hydrogen or deuterium concentration using the appropriate ρ -c calibration (e.g. Figure 4(a)) ordinate axes corresponding to these concentrations are also included. When yttrium was added to the Li-H solution, hydrogen was steadily removed (section A-B) until a concentration of ca 0.5 mol % H was attained. The getter was then isolated from the liquid metal for two days (B-C) during which time the concentration did not change. It was then re-immersed and gettering monitored for a further 23 days (C-D) until no further change in concentration was detected.

Initially gettering of the Li-D solution was also effected until ca. 50% of the solute had been removed (E-F). The getter was then isolated for 24 hours (F-G) and after reimmersion, gettering was

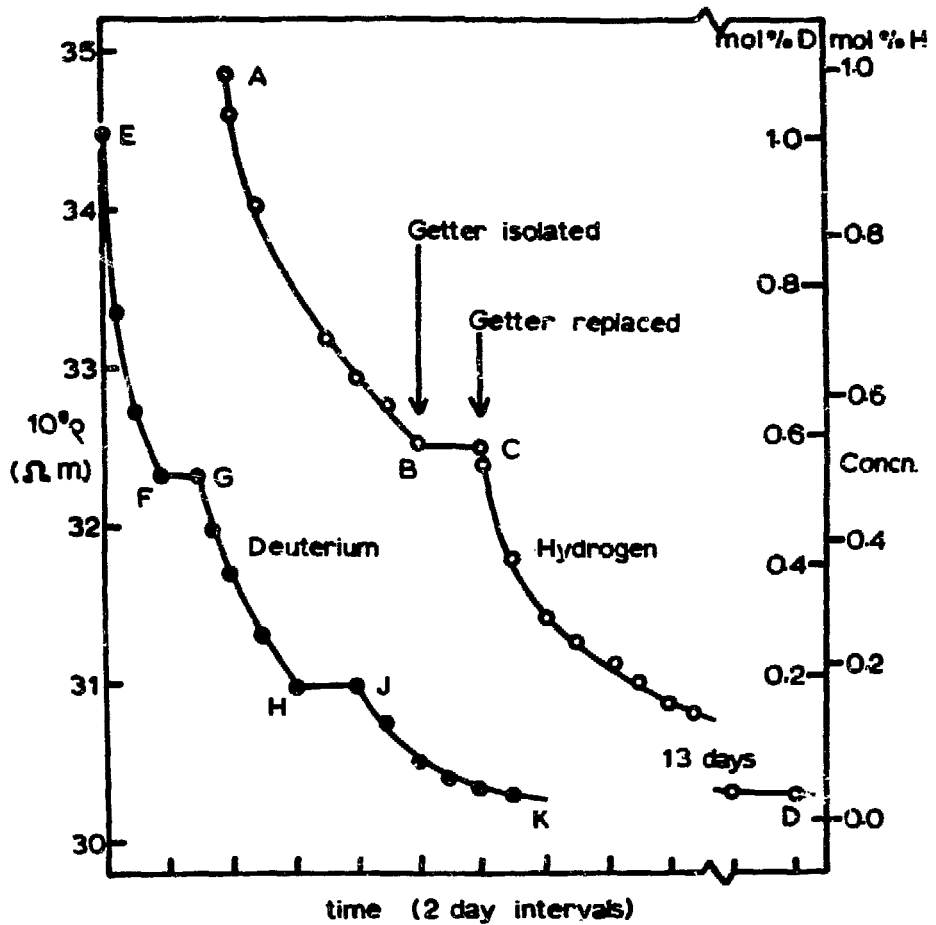


Fig.5. Resistivity of solutions of hydrogen and of deuterium in liquid lithium as a function of time during the gettering process.

Table 1. Experimental Details

	Li-H Solution	Li-D Solution	
Weight of lithium (g)	36.31	25.88	
Initial concentration (mol % X)	1.00	0.99	
		section E-H	section J-K
Weight of yttrium (g)	3.64	2.46	1.99
Apparent surface area of yttrium (m^2)	7.2×10^{-4}	10.1×10^{-4}	8.0×10^{-4}

continued until ca 75% complete (G-H). The getter was then replaced by a fresh sample of yttrium sponge (H-J) and gettering further monitored (J-K) until there was no observable change in concentration over a period of two days. On neither occasion when the getter was isolated from the solution (sections F-G, H-J) was a change in concentration observed.

The higher initial gettering rate observed for the Li-D solutions can be accounted for by the fact that the surface area of getter used in this experiment was markedly greater than that of the getter used for the Li-H solution despite the bulk of yttrium being smaller. Furthermore, the fact that gettering of the Li-D solution was complete in the shorter time can be attributed to the addition of fresh getter when 75% of the solute had been removed. All relevant experimental details are given in Table 1.

The solute concentration axes were checked at points A, B and D (Li-H solutions) and E, F, H and K (Li-D solutions) by the ρ -T method. Examples of ρ -T graphs for Li-D solutions are shown in Figure 4(b). The temperatures below which precipitation of LiD occurred and the derived solute concentrations are collected in Table 2 together with the resistivity of the solution immediately

Table 2. Concentration Analysis during Gettering.

Point	$10^8 \rho(400^\circ\text{C})$ ($\Omega\text{ m}$)	Concn. (ρ -c) (mol % X)	T ($^\circ\text{C}$)	Concn. (ρ -T) (mol % X)
Li-H Solution				
A	34.87	1.00	382	0.99
B	32.50	0.53	335	0.53
D	30.31	0.04	-	<0.04
Li-D Solution				
E	34.45	0.99	390	0.97
F	32.51	0.54	355	0.56
H	30.96	0.19	299	0.20
K	30.27	0.05	243	0.06

prior to isolation of the getter and the solute concentration derived from the ρ -c calibration. The concentration values are in excellent agreement for both the Li-H and Li-D solutions.

Gettering Efficiency; Extent of Hydrogen Isotope Removal.

The results (Figure 5) show that a small amount of yttrium will getter substantial quantities of both hydrogen and deuterium from liquid lithium. The resistivity decreases (A-D and E-K) are equivalent to the removal of ca. 1 mol % solute from the liquid. Moreover, the low resistivities at D and K are consistent with the removal of virtually all hydrogen (< 0.05 mol % solute). This is a slightly lower concentration than predicted by the thermodynamic analysis (0.10 mol % H at 400°C); the discrepancy may be due to either inaccuracies in the thermodynamic data or invalid assumptions used in the derivation of the isopleths.

Gettering Rates

Gettering rates, as determined at points A to D (Li-H solutions) and E to K (Li-D solutions) and corrected for the apparent surface area of getter are collected in Table 3. In general, the solute was removed at a slowly diminishing rate; this reduction may be caused by either the decreasing hydrogen concentration in the liquid or equally build-up of hydrogen at the getter surface. A remarkable increase in gettering rate was observed on those occasions (points C and G) when the getter was reimmersed in the liquid after a period of isolation at room temperature. For example, the rate at C was an order of magnitude greater than that at B and approached that at A. It thus appears that the hydrided yttrium was more effective after thermal cycling. Presumably during the cooling and heating cycle, fresh yttrium was exposed on the hydrided yttrium surface. This may be due to one of a number of factors including (a) the marked decrease in solubility of hydrogen in yttrium from 400°C to room temperature, (b) different coefficients of expansion of yttrium and

and yttrium dihydride, and (c) equilibration of hydrogen concentration through the yttrium sample.

An accurate comparison of the gettering rates between the two experiments is not possible, principally because of the difficulty in determining the surface area of a sponge. Accepting this limitation, however, an indication of the relative rates can be obtained by comparing the initial values (i.e. at points A and E); they are similar, that for the Li-H solution being slightly faster than that for the Li-D solution.

Table 3. Gettering Rates ($10^2 \text{ mol \% X.s}^{-1}.\text{m}^{-2}$ (X=H or D))

Li-H solution		Li-D solution	
Point	Rate	Point	Rate
A	1.78	E	1.42
B	0.05	F	0.09
C	0.57	G	0.25
D	0.00	H	0.08
		J	0.09
		K	0.01

Reaction Products and Stoichiometry.

The hydrided getters have been studied using X-ray powder diffraction techniques. Diffractometer traces (Figure 6) show that the surface layers contain face-centred cubic YH_2 (YD_2) only, whereas interior samples (at 2 and 4mm from the surface) contain increasing amounts of yttrium and decreasing amounts of YH_2 (YD_2). The unit cell dimensions of this yttrium ($a=3.652 \text{ \AA}$, $c=5.777 \text{ \AA}$) are slightly larger than those of pure yttrium¹² ($a=3.6474 \text{ \AA}$, $c=5.7306 \text{ \AA}$) showing it to be a saturated solid solution of hydrogen in yttrium. There

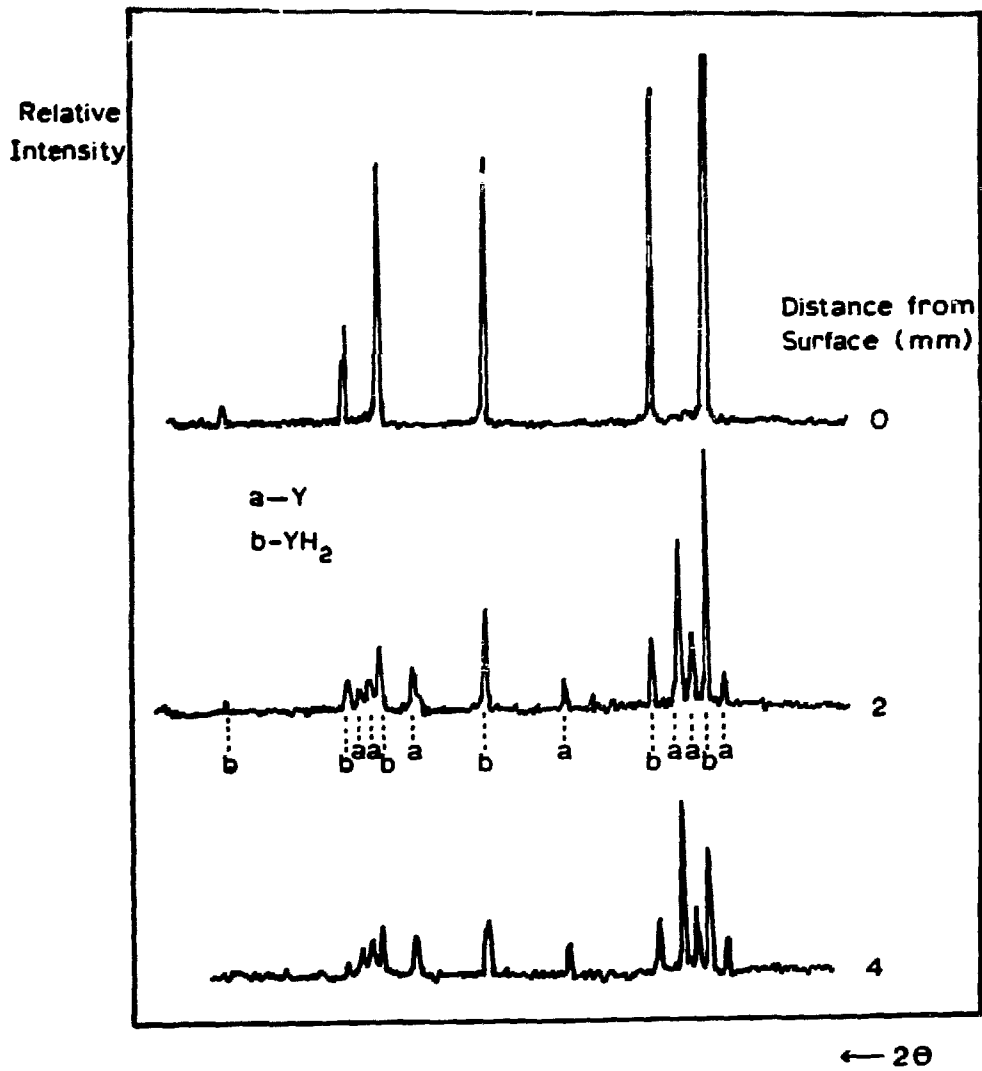
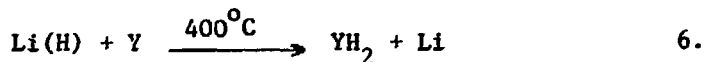


Fig.6. Diffractometer traces of samples of hydrided yttrium.

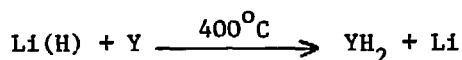
is no evidence for any other phases (e.g. YH_3) and so the reaction is probably



Final H:Y and D:Y ratios in the getters used in sections A-D and E-H respectively are 1.29:1 and 1.09:1, (i.e. 65% and 54% conversion of Y to YH_2 and YD_2 , respectively. The efficiency of the getter is clearly not restricted by the amount of hydrogen consumed nor is the reactivity reduced by a hydride surface coating. Although dihydride in the yttrium lattice had a deleterious effect on its mechanical properties the hydride did not spall off.

CONCLUSIONS

This investigation has shown that the gettering of hydrogen isotopes from liquid lithium using yttrium sponge can be satisfactorily monitored using simple resistance techniques. The reaction proceeds according to



The efficacy of the getter to absorb hydrogen is not restricted by high solute concentrations in either lithium or yttrium. The diffusion of hydrogen in the yttrium lattice is not hindered nor is the reactivity significantly reduced by a hydride surface coating, the rate of gettering being remarkably rapid at the low temperature (400°C) employed. Hydrogen isotope concentration in lithium can be reduced from 1.00 to less than 0.05 mol % X (X=H or D) which is slightly less than that predicted theoretically. These residual concentrations are similar to those obtainable by filtration of lithium-hydrogen isotope solutions at 200°C (0.027 and 0.021 mol % X for Li-H and Li-D solutions, respectively).

In extrapolating the data to Li-T solutions there is no reason to believe that tritium should be different to hydrogen and deuterium except in a kinetic sense. Consequently, it should be possible to

apply all conclusions derived in the discussion to Li-T solutions, the minimum tritium concentration attainable by filtration and gettering being less than 0.021 and 0.05 mol % T, respectively.

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EVALUATION OF SEVERAL LIQUID AND SOLID TRITIUM BREEDING BLANKETS

J. S. Watson
P. W. Fisher

S. D. Clintor
J. B. Talbot

Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37830

ABSTRACT

Tritium breeding blankets for controlled thermonuclear reactors are likely to contain liquid lithium, molten LiF-BeF₂ salt mixtures, or one of several solid lithium compounds. Recently, tritium recovery processes have been proposed for each of these breeding systems. The recovery processes are reviewed and evaluated. Attempts are made to determine which process steps are current or near-term technology and which steps involve significant uncertainties or require extensive development. Where appropriate, alternate process steps or conditions are recommended.

INTRODUCTION

During the past year, a new review and evaluation of proposed methods for recovering tritium from the blanket of fusion reactors has been completed. A continuous assessment of recovery processes has been made at ORNL for several years, but recent reference designs for fusion reactors have included tritium recovery systems which needed more thorough and independent evaluation. Space will not permit inclusion of all calculations and results in this paper, but more detail can be obtained from a forthcoming report.¹

No criticism of individuals is intended in these evaluations. All flowsheets considered come from highly regarded sources. They are evaluated here because they are considered to be significant proposals which are worthy of further evaluation. Also, we are fully aware that it

* Operated by Union Carbide Corporation for the Energy Research and Development Administration.

is far easier to criticize processes than to propose them. Where weaknesses are believed to exist in the reference processes, modifications or alternatives are suggested. There are, of course, potential faults remaining even in the new or modified processes suggested in this paper. Some potential problems are recognized and mentioned.

Recovery processes are considered for blankets of liquid lithium, molten fluoride salt, and solid lithium compounds. Principal attention is given to liquid lithium because at the present time this appears to be the most likely blanket material for experimental power reactors (EPR) and demonstration reactors, as well as eventual commercial reactors. In addition, the process options for lithium blankets are believed to be less understood than those for molten salt blankets. However, one must also investigate other materials since blanket designs are still in planning stages.

LITHIUM BLANKETS

Although reference designs²⁻⁵ currently include more lithium metal blankets than any other material, there are still several differences. Perhaps the most significant difference is the blanket temperature. High temperatures² are desired for thermal efficiency; temperatures up to 1000°C have been proposed. These require that the blanket be constructed of refractory metals such as niobium or vanadium. Other designs³⁻⁵ have stayed with more common structural materials such as stainless steels or other iron based alloys. This, however, restricts the maximum allowable lithium temperature to approximately 500°C.

The maximum lithium temperature greatly affects the tritium process requirements and options.⁶ Maximum allowable tritium concentrations or pressures in high-temperature systems (800 to 1000°C) are restricted by tritium release rates via permeation of the steam generator. This restricts the tritium concentrations to very low values (less than 1 ppm) and the tritium pressures to values probably between 10^{-4} and 10^{-8} torr, depending upon the allowed release rate and the permeability

of the steam generator. Maximum allowable tritium concentrations in low-temperature systems (500°C) are likely to be limited by inventory considerations, but there is at this time no way to know this limit. The limit will depend upon the volume of the lithium blanket, the cost of tritium [an unknown value for the quantities and time when tritium will be required for controlled thermonuclear reactors (CTRs)], and possibly the availability of tritium. Availability and initial costs will depend upon government policy and actions. The cost of tritium must decrease for later models; availability will increase as large fusion reactors go into operation; and thus inventory restrictions will be relaxed. This is a situation where a substantial subsidy appears sensible to provide significant quantities of tritium to the fusion program at prices no more than those expected in a fully developed fusion economy. The technology required for early reactors should not be made more difficult than that required in later and more advanced systems.

Metal Windows

One of the simplest tritium recovery techniques proposed uses a large permeable surface through which tritium can move into a recovery system, perhaps to a vacuum pump. Alternate chemical means have been considered for trapping tritium on the low pressure side of the window, but compatibility problems have usually dictated against this technique. Metal windows, as usually conceived, are constructed like a shell and tube bundle heat exchanger. Lithium flows through the tubes, and the required vacuum is pumped from the shell region. Such a system will obviously remove tritium from lithium, but the principal question is if the window area and costs are tolerable. As the required tritium concentration decreases, the tritium pressure also decreases, and larger windows with more surface area are needed to maintain the required concentrations. Thus metal window costs are closely coupled to allowable tritium inventories or perhaps to tritium costs.

Metal windows could prove uneconomical because of other technical problems. The most likely problem is a low effective permeability of

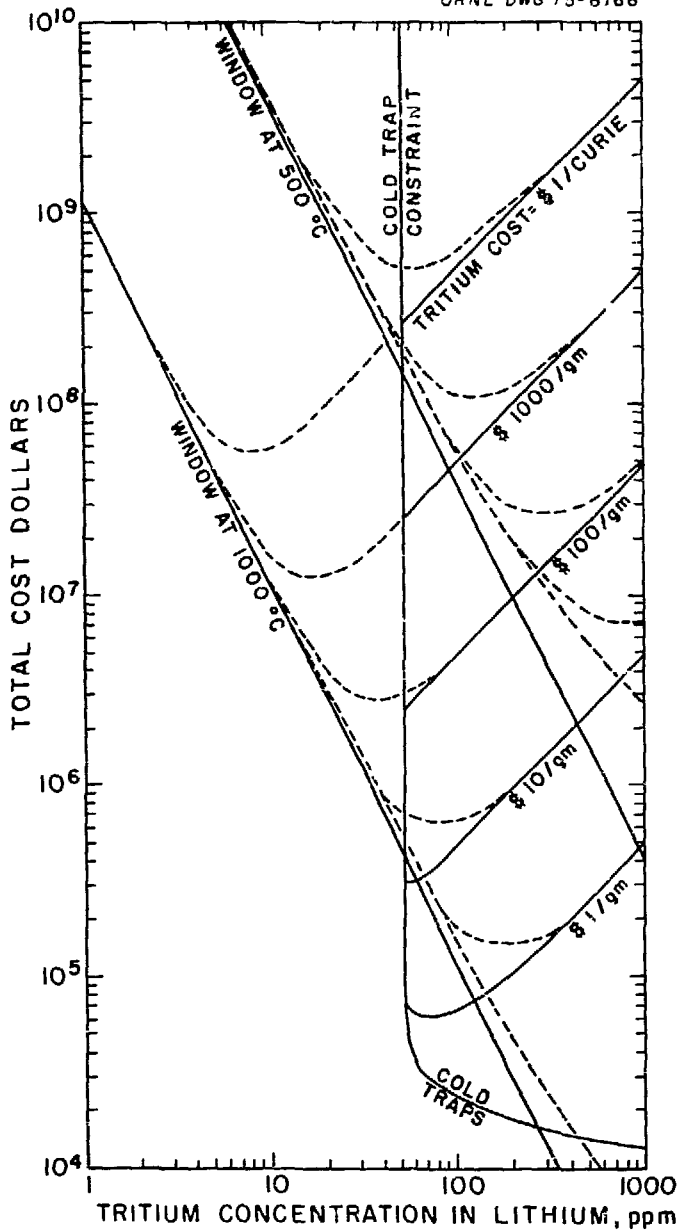
niobium. Although it has been extensively studied, the permeability of niobium under the conditions required for metal windows is still uncertain. Several studies made with thin niobium foils⁷ or with nonsteady-state techniques⁸ suggest a low "effective" permeability and surface effects. The surface effects could result from the presence of impurities such as oxygen on or near the surface. A steady-state study using relatively thick niobium specimens⁹ indicated higher "effective" permeability, and the pressure dependence of permeation rate suggests the absence of surface effects. No data are available for the temperature, pressure, and wall thickness required for a metal window recovery system. If the system was ideal, that is, obeyed Sieverts' law and displayed a constant activation energy, extrapolations to conditions of interest would be simple and reliable. Furthermore, the results from all investigators would agree; however, extrapolations of various results do not agree. Since practical metal window structures are likely to be approximately 1 mm thick, which is about the same as the thickness used by Rudd,⁹ his data are believed to be the most useful for our purposes. However, Rudd's data cover a narrow temperature range and higher pressures than those of interest. Since the permeation rate varies as the square root of pressure (Sieverts' law), at least some extrapolation in pressure is justified. Deviations from the square-root dependence could occur during extrapolation over the several orders of magnitude required.

Even if the permeability of a new niobium window is known, the window surface could change in use. Lithium will not transfer oxygen to the niobium; it is more likely to remove oxygen from the original surface. Other materials, however, may be transferred to the niobium surface. Lithium entering the low-temperature (500°C) metal window system will be in equilibrium with the stainless steel surfaces used in the blanket. In addition, nitrogen entering the lithium could transfer to the niobium window. Carbon and nitrogen have been suggested¹⁰ as potentially troublesome materials. If accumulation of impurities on the niobium surface impairs permeation, the rate of accumulation of impurities will be important.

Although the uncertainties just described indicate that metal windows are not simple well-understood devices which can be applied immediately to lithium blankets, they are considered among the more promising recovery systems for lithium blankets, especially for high temperature systems. Rough estimates of the cost of metal window systems are presented in Fig. 1. The estimates include the costs for the niobium taken at \$22 per pound, for the shell at \$38,500 per 6000 ft², and for vacuum pumps at \$0.65 per liter/sec pumping speed (based upon present commercial cryosorption pumps). Again, there is uncertainty about the major cost of the assembled shell and tube structure. The values are believed to be realistic within a factor of 2 and thus accurate enough to reach meaningful preliminary evaluations. The current ERDA selling price for small quantities of tritium (relative to CTR needs) is \$1/Ci. Actual production costs of tritium are not public information, but they are certainly less than the selling price. The capital costs of vacuum pumps were based upon current cryosorption pump models, and economies are expected to occur if the market expands and demand brings larger pumps into production.

The projected costs of a metal window system (excluding building, services, etc.) are shown in Fig. 1 as a function of the tritium concentration in a 1000-MWt reactor whose blanket contains 4.6×10^5 kg of lithium. At first, the costs decrease with increasing tritium concentration (on the left side of the figure). In this region, the costs of niobium windows and vacuum pumps are the important parameters. Costs pass through a minimum and then increase again (on the right side of the figure) as tritium inventory costs become important and eventually dominate the overall cost. Clearly, under these assumptions, there is an optimum tritium concentration to be maintained in the blanket.

The analysis ignores three factors which could prevent one from operating at the optimum concentration: (1) availability of tritium, (2) acceptable permeation losses to the steam system, and (3) hazards associated with a large tritium inventory. The first factor was discussed earlier in this paper. Although one must be aware of potential availability problems, the advantages of having large inventories of tritium on hand for the first reactors should be clearly



PERMEATION DATA FOR WINDOW:
 (—) RUDD, VOSS, AND JOHNSON
 (---) LEVIN AND STICKNEY
 WINDOW BACK PRESSURE: $P_{T_2}/10$

Fig. 1. Comparison of total cost for tritium windows and cold traps.

documented to aid in government (ERDA) decisions which will affect availability. The second factor, tritium release rates by permeation, will limit allowable tritium concentrations in high temperature systems¹¹ (about 1000°C) to values below the economic optimum. This, however, is not likely to be a limitation in stainless steel (about 500°C) systems. The permeation into a He coolant which does occur can be oxidized to a nonpermeable form before it reaches the steam generator.¹¹⁻¹³ The effects of the third factor, hazards from tritium inventory, can be minimized by a careful system design. Figure 1 is presented only to demonstrate that metal windows are economically feasible but are likely to be expensive. This is not an accurate cost estimate. Higher costs for Nb surface would raise the left side of the figure. Reducing the lithium inventory or lowering the cost of tritium could significantly lower the right side of the curve. Remember that tritium costs for later fusion reactors should be much lower than for the first reactor (unless government supplies the first tritium).

Solid Sorbents

Thermodynamic considerations suggest that tritium can be removed from lithium by sorption into yttrium.^{3,12,14,15} To be practical, however, the sorption process must proceed at an acceptable rate. It has been recognized that solid phase diffusion rates could be too slow, especially if impurities such as oxygen in the metal surface impedes diffusion.^{11,13} In another paper¹³ to be presented at this conference, tritium sorption into a particular yttrium specimen was shown to follow a first order process such as one might expect from diffusion through a resistance at the yttrium surface. The rate becomes greater with increasing temperature (the highest temperature tested was 400°C). Present data indicate that metal sorbents are likely to be even more expensive than metal windows.

Extraction Processes

Tritium recovery from lithium by extraction into a molten salt was first proposed by Maroni.^{16,17} The proposed flowsheet is shown in Fig. 2. The process involves two principal steps. First, the tritium

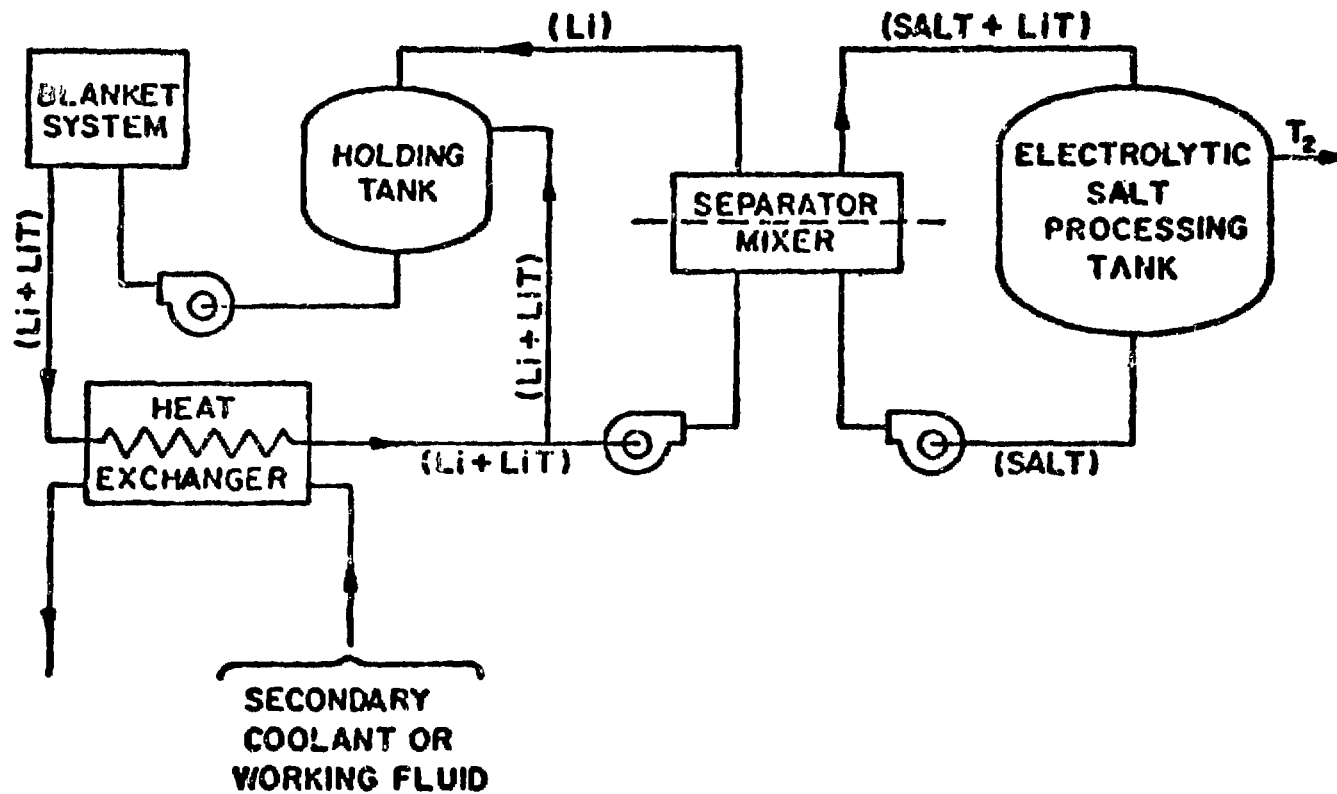


Fig. 2. Schematic of extraction process for recovering tritium from lithium.

is extracted into a molten salt; several salts have been studied - a LiCl-KCl eutectic appears attractive. Moderately favorable distribution coefficients have been measured, and a mechanically agitated contactor previously studied for pyrometallurgical processing of fission reactor fuels was suggested. There is, of course, little merit in extracting tritium from liquid lithium into a molten salt unless the tritium can be more easily removed from the salt; that is the second step of the process. Maroni suggests an electrolytic cell for recovering tritium from the salt. The electrolytic cell is similar to fuel cells under development at ANL, but the current flow is in the opposite direction, producing rather than consuming hydrogen (tritium).

Many of the potential problems of the system are discussed by Maroni, but some of the major questions can not be answered with current information. Perhaps the most serious question is the effect of the recovery process on the rest of the blanket system. Lithium metal leaving the extraction will contain K and Cl (in equilibrium with the salt). The concentrations of both components will be low, and should have little effect on blanket neutronics. Corrosion or compatibility effects, however, are more difficult to estimate. Although neither Maroni nor DeVan¹⁰ expect the trace of Cl and K to significantly affect corrosion rates in the blanket, stainless steel corrosion by lithium is complex, and "in loop" tests, perhaps with magnetic fields, are needed to demonstrate that an extraction process will not damage the blanket.

Contacting equipment for liquid metal-molten salt extraction processes have been studied both at ORNL¹⁸ (for molten salt reactor processing) and at ANL¹⁹ (for pyrometallurgical processing). The ORNL work is continuing and includes development of both mixer-settler and column devices. The study is concentrating on near zero entrainment devices which are required for the molten salt reactor systems and which are likely to be desired for CTR systems. Work at both laboratories indicates that contacting equipment can be developed for the proposed process.

The weakest part of the original flowsheet is believed to be the electrolytic cell. There are important differences between the hydrogen fuel cell and the proposed electrolytic cell which must be considered. First, the electrolytic cell operates at much lower tritium concentrations. This not only affects polarization of the electrodes (current densities are controlled by diffusion of reacting ions to the electrode surface), but it also affects diffusion through the electrode itself. At the pressures of interest, permeation through solid electrodes is undesirably slow. Two porous electrodes have been suggested. One would use controlled pore sizes to permit only partial penetration of the nonwetting salt at a carefully controlled pressure. The second concept would use a composite electrode with a wettable porous structure facing the salt; the salt would then only penetrate to the composite interface. This arrangement could further hinder diffusion to the active electrode surface and reduce current densities.

All aspects of electrode design are complicated by the presence of relatively large concentrations of free lithium (plus potassium) in the salt, estimated to be several times the concentration of tritium.²⁰ This results from equilibration with metallic lithium. High free lithium concentrations enhance the chance of tritium recombination at or near electrode surfaces and probably require tritium removal with low pressures at the electrode surface.

In summary, an extraction process does appear to be promising for recovery of tritium from lithium blankets, but a replacement for the electrolytic cell is needed to recover tritium from the salt. Several alternate approaches have been suggested, and ORNL plans to evaluate modified versions²⁰ of the extraction process experimentally.

MOLTEN SALT BLANKETS

Molten salts containing lithium and Be have long been considered for fusion reactors. The Princeton Reference Design¹² includes a molten fluoride salt blanket and proposes a recovery system. Molten salts have lower breeding ratios than lithium metal,²¹ but the Princeton design indicates that adequate breeding ratios are possible.¹² Although the

thermal conductivity of the molten fluoride salt is low, it is less affected by magnetic fields; it can be pumped more freely; and turbulence is not suppressed. Under turbulent flow, heat transfer capabilities of molten salts can equal or exceed those of lithium.²² Although magnetic fields do not affect pumping costs for molten salts, they can cause charge separation or induced voltages. The effects of induced voltages have not been fully evaluated; they could include enhanced corrosion.

Princeton Reference Design*

In the Princeton Reference Design fusion reactor,¹² tritium is generated in a molten fluoride salt (Li_2BeF_4) blanket. The practicality of the blanket processing scheme proposed by Johnson¹² was reviewed by studying each of the process steps and estimating the feasibility and equipment size involved.²³

Description of the Process. Figure 3 shows the proposed tritium recovery system for the molten salt loop. The flow rates and concentrations are listed in Table 1.

The breeder salt circulates constantly through eight disengagers arranged in parallel about the periphery of the reactor. The salt is sprayed into the disengagers as small droplets to provide an extended area for the dissolved helium and TF to diffuse from the liquid salt. Salt collects in the bottom of the disengager and flows back to the reactor blankets. An unspecified doctor system removes impurities from the tube and adds makeup agents to maintain the desired salt composition to a small drag stream of salt.

First, the gas effluent is drawn through a water-cooled trap and then through liquid nitrogen cooled cyclic condensers. The helium is discharged to a storage system for final control. Solid TF is melted out of the "off-stream" cyclic condenser and collected in a small receiver. The salt flows intermittently through a purification system and into an electrolysis cell, where a solution of KF and TF is electrolyzed to F_2 and T_2 . The gases emerging from the electrodes are

* This study was conducted in cooperation with the Oak Ridge Associated Universities program for Laboratory Graduate Participation.

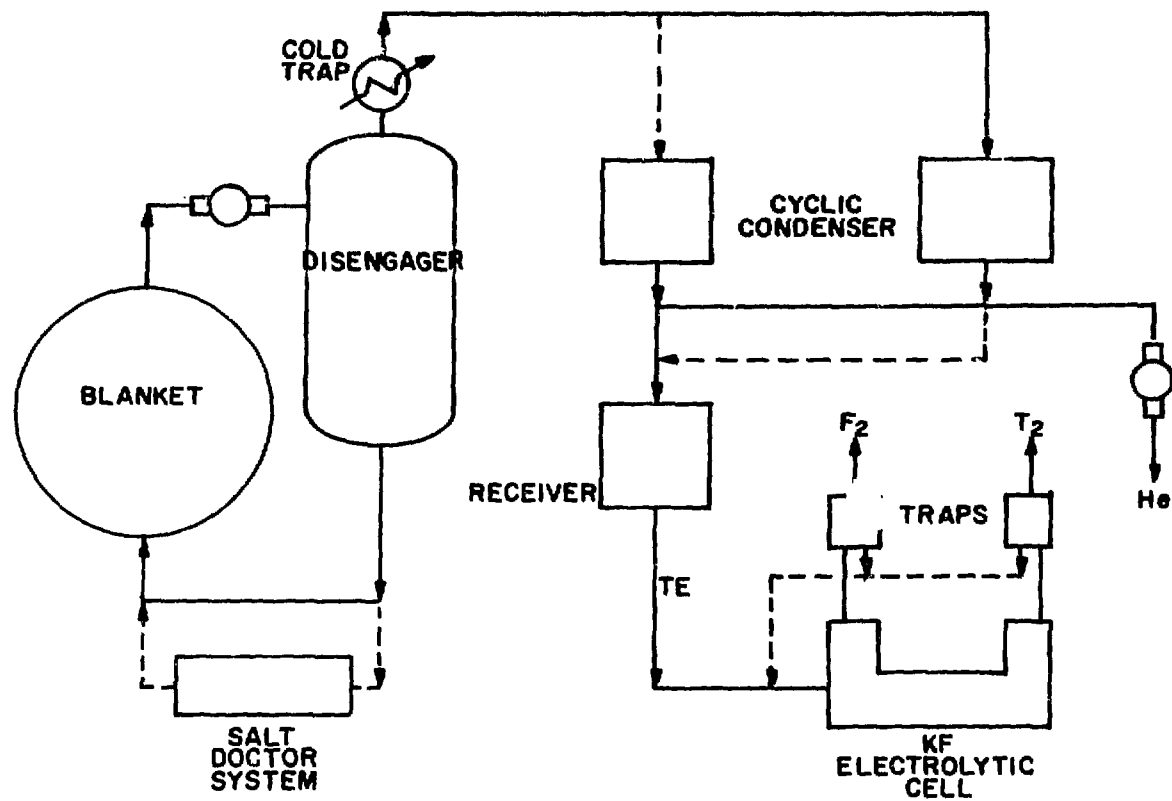


Fig. 3. Princeton Reference Design salt blanket processing system.

Table 1. Flow rates and concentrations for tritium recovery system for the Princeton Reference Reactor

Li_2BeF_4 salt flow through disengagers	4.0×10^5 kg/hr
TF concentration in salt:	
Entering disengagers	2.09×10^{-7} mole fraction
Exiting disengagers	1.29×10^{-8} mole fraction
Exhaust gas composition:	
TF	1.0×10^{-4} atm
Helium	1.53×10^{-4} atm
Salt	1.3×10^{-4} atm
Tritium recovery	543 g/day
Helium ash discharge	1120 g/day

saturated with TF and must pass through the liquid nitrogen cooled traps to remove the TF. The pure tritium gas is recycled to the primary fuel loop.

The main components of the processing scheme, the spray disengagers and cyclic condensers, were evaluated. Evaluations of the disengagers included studies of (1) the diameter and residence time of the droplets needed for adequate mass transfer of the dissolved TF and helium from the salt, (2) the ability to spray a molten salt in an evacuated vessel, and (3) spray nozzle designs for the disengager. Evaluations of the cyclic condensers considered (1) the effect of a non-condensable gas on the surface area needed for condensation and (2) TF flow in the condenser.

Disengager Analysis. Figure 4 shows a detailed schematic of the proposed disengagers. The eight disengagers are each equipped with spray nozzles near the top and a salt discharge line at the bottom. Baffles near the top of the vessel prevent salt entrainment into the vapors vented at the top.

To avoid wall embrittlement, the maximum tolerable tritium pressure in the salt was estimated¹² to be 10^{-2} torr or 1.32×10^{-5} atm, but the validity of this limit is questionable.²⁴ The corresponding TF concentration in the entering salt was calculated to be 2.09×10^{-7} mole fraction. The exit concentration corresponding to a TF pressure of 10^{-4} atm is 1.29×10^{-8} mole fraction.

A simplified picture of the mass transfer mechanism assumed for an individual salt droplet is as follows: (1) TF diffuses from within the drop to the surface of the drop, and (2) TF diffuses from the drop surface into the gas phase. For the first step involving liquid diffusion in a spherical drop, the rate equation is:²⁴

$$\frac{C}{C_0} = \frac{6}{\pi^2} (e^{-\pi^2 Dt/r^2} + 1/4 e^{-4\pi^2 Dt/r^2} + 1/9 e^{-9\pi^2 Dt/r^2} + \dots), \quad (1)$$

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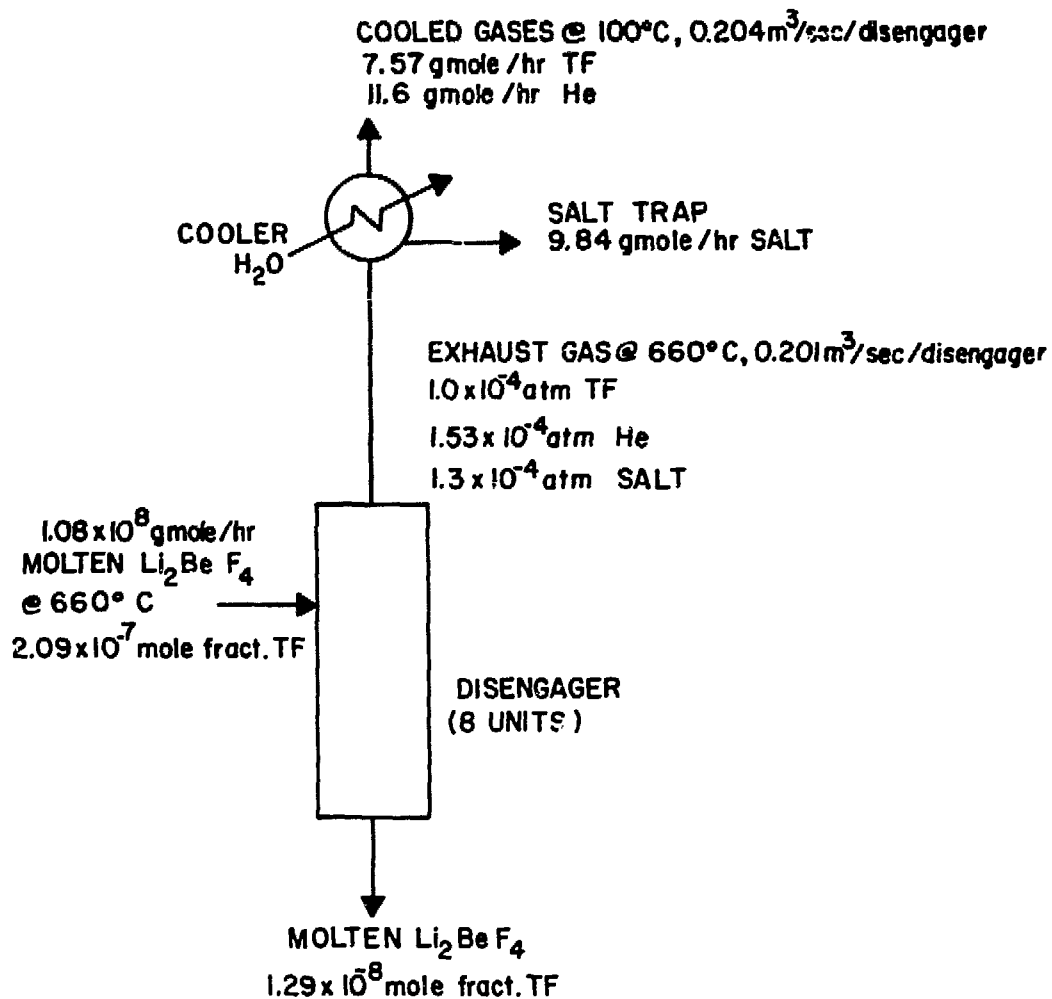


Fig. 4. Schematic of the salt disengager and salt trap.

where

C_0 = initial TF concentration, mole fraction

C = final average TF concentration, mole fraction

D = liquid diffusivity of TF in molten salt, cm^2/sec

r = radius of the droplet, cm

t = time, sec.

Using the values for the initial final average TF concentrations in the salt, C/C_0 equals 6.17×10^{-2} . The corresponding Dt/r^2 value is 0.232. The liquid diffusivity of TF in molten salt suggested by Cantor²⁵ is $10^{-5} \text{ cm}^2/\text{sec}$; therefore, t/r^2 equals $2.32 \times 10^4 \text{ sec}/\text{cm}^2$. The second step, gas film resistance, can be neglected since the salt is sprayed into a vacuum, and the gas film resistance is essentially zero.

Atomization of a fluid usually involves the application of an external force, such as a gas resistance. However, disintegration will occur in a vacuum if the liquid jet is turbulent throughout, and its surface tension is overcome.²⁶ The effects of liquid properties and jet velocity on the jet breakup has been studied for atomization without the influence of a surrounding medium. The mechanism can be predicted to be dependent on jet diameter, jet velocity, liquid density, surface tension, and viscosity. For this system, the jet velocity needed to achieve atomization must be greater than 488 fps, to obtain a droplet size of 150 μ . The residence time for mass transfer for a 150 μ drop is 1.3 sec; therefore, a column height over 637 ft is necessary. A smaller droplet size would decrease the height of a disengager. The tall column results because droplets injected into a vacuum at high velocities (488 fps) do not slow down, but accelerate slightly. Adding packing surface to the column would slow the salt particles and increase residence time, but it would also cause coalescence and conductance (pumping) problems.

The selection of the type of spray nozzle has a considerable bearing on the dimension of the spray tower. The characteristics, operating ranges, advantages, and disadvantages for hydraulic-pressure nozzle and spinning-disk atomizers are listed in Table 2. The maximum capacity through a single nozzle or the feed rate from a spinning disk is about

Table 2. Characteristics, advantages, and disadvantages of pressure nozzles and spinning-disk atomizers

Hydraulic-pressure nozzles	Spinning-disk atomizers
1. Pressure: up to 10,000 lb/in.² 2. Capacity: up to 10,000 lb of feed per hr per nozzle 3. Feed viscosity: up to several hundred centipoises depending on pressures, capacity, and orifice size	1. Disk speed: 500-30,000 Rcy/min 2. Disk diameter: 2-10 in. 3. Feed rate: 0.05-15,000 lb per hr per disk
<u>Advantages</u>	<u>Advantages</u>
1. Suited for multiple atomizers 2. Used for countercurrent spray drying 3. Nozzles generally inexpensive 4. Flexibility in designs and types 5. Better for viscous fluids than are spinning disks, since feed can be preheated under pressure	1. More flexible than nozzles; handle changes in feed rate since disk speed and feed rate vary independently 2. Multiple fluids easily handled and mixed 3. Liquid feed under low pressure 4. No small clearances or openings to plug or erode
<u>Disadvantages</u>	<u>Disadvantages</u>
1. Inflexible due to pressure, capacity, and orifice size variables being independent 2. Nozzle susceptible to erosion and plugging 3. Expensive high-pressure pumps 4. Limit to the fineness of atomization 5. Variations in feed rate not always feasible	1. Difficult counterflow 2. Expensive disk drive mechanisms 3. Not readily adapted to horizontal spray dryers 4. Not well suited to very viscous liquids

10,000 lb/hr. The salt rate through each disengager is 5.0×10^5 kg/hr or 1.1×10^6 lb/hr. Therefore, the minimum number of nozzles per disengager would be about 110.

A preliminary study of a dropwise liquid-gas contacting system was made by Gabor et al.²⁷ Fused NaF-ZrF₄ containing dissolved uranium tetrafluoride was sprayed into a fluorine atmosphere to recover uranium hexafluoride. Experimental equipment was developed to test heat and mass transfer rates. A Spraying Systems Company full-cone spray nozzle (1/8 G3001.4) constructed of Monel was used for the heat transfer tests. This nozzle had a 0.026-in. orifice. The salt was heated to 650°C and sprayed into air at 20°C. The average diameter for a droplet was determined to be 164 μ .

Several problems were encountered in spraying the fluoride salt. Plugging of the spray nozzle was a difficulty. This was solved by heating the nozzle for fully controlled operation. In other fused-salt process studies, autoresistive heated salt transfer lines have proved successful. The nozzles used were removed and inspected after 20 batch sprayings. The orifice had enlarged from 26 to 32 mils diam, increasing the area by approximately 50%. This experiment suggests that frequent nozzle replacement would be necessary.

The prospect for a spray process for the recovery of tritium from molten fluoride salt appears discouraging. The velocity of the jet must be large to overcome the surface tension of the salt for atomization to occur in a vacuum of 10^{-4} torr. The droplet diameter and residence time in the disengager needed for mass transfer, coupled with the drops accelerating as they fall, leads to a tower of considerable height. If the minimum number of nozzles is 110, the column diameter must also be large to decrease coalescence of the droplets. Corrosion within the spray nozzles would make frequent replacement necessary for full operation.

Cyclic Condenser Analysis. A schematic of the cyclic condensers is shown in Fig. 5. The cooled helium and TF leave the salt trap and are drawn through an onstream cyclic condenser. The gas is cooled further to the liquid nitrogen temperature of 77.4°K, and the TF is condensed out.

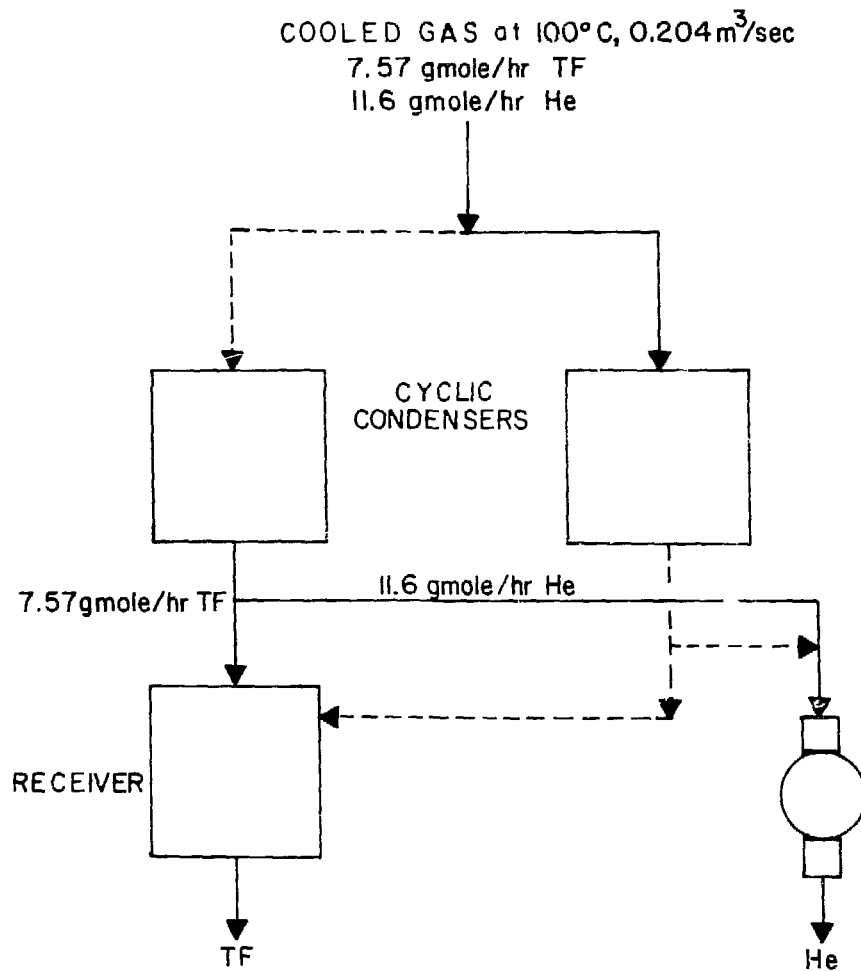


Fig. 5. Schematic of the cyclic condenser.

Ideally, the condenser walls must be kept cold enough to freeze out nearly all the TF to a negligibly low equilibrium pressure. This would expose the condensate surface to gas bombardment; so the pumping speed would be limited only by surface area and the sticking probability of the impinging molecules.²⁵ Non-condensables often influence the pumping speed and the condensate surface area. The condensing gas could sweep the uncondensable gas against the condenser surface, creating a blanket through which the condensing gas must diffuse to reach the cold wall. However, gas blankets are not formed when the mean feed paths are long or when the fraction of uncondensable gas is sufficiently low²⁸ as in this case.

The heat load of each condenser consists basically of the periodic heating and cooling of the mass of metal (equivalent to 500 kg of steel) constituting the condenser. The freezing out of TF is a minor part of the heat load. The heat flux to cool the TF gas from 373°K to 77.4°K can be approximated by summing the latent and sensible heat changes. The total enthalpy change was calculated to be approximately 132 kcal/hr, but assuming the energy loss equals the dropping of the condenser temperature itself from the melting point of TF (20°C) to 77.4°K, the total heat exchange duty per condenser is 1075 kcal/hr.

Hence, the cyclic condensers seem feasible as an integral part of the tritium recovery system. Helium will not increase the surface area required to freeze out the TF greatly.

Other Design Considerations. The salt traps above each spray tower and the vacuum pump system may be areas of additional design problems. The molten salt entering the spray disengagers at 660°C may be boiling; the uncertainty in the reported values of vapor pressures for molten salt is a factor of 10.²⁹ The vapor pressure of the molten salt at 660°C is approximately 1.3×10^{-4} atm, and the total pressure of the vessel is 3.83×10^{-4} atm. An increase in the quantity of vaporized salt in the gas effluent would increase the size of the salt trap needed. Salt captured in the cold traps may have to be reprocessed due to TF redissolving into the salt.

Tritium loss from the vacuum pump system will be inherent; therefore, a trapping system would be a requirement to prevent tritium escape. The Princeton design specifies that 2% of the tritium will be T_2 which will not be caught in the cold traps. In choosing the vacuum pumps, the TF compatibility with the pump components must be reviewed since traces of TF will inevitably reach the pumps.

Alternate Flowsheet. Although the flowsheet just described has some difficulties, slight modifications can be made which are expected to remove these difficulties. It will be necessary to go to much higher tritium pressures to simplify the process. The Princeton design selected the allowable tritium pressure as 10^{-2} torr due to embrittlement problems, but materials are available which are believed to be able to sustain considerably higher tritium pressures at approximately 500°C. High tritium pressures over the molten salt do not result in significant tritium inventory;³⁰ this is unlike lithium blankets. If the pressure is increased closer to atmospheric pressure, a very small disengager would be required. If the salt circulation pump is a long vertical shaft unit like those used in molten salt (fission) reactor tests, the pump bowl itself may be adequate for tritium removal. High tritium pressures will result in higher permeation rates to the helium coolant and through all other exposed piping. Tritium escaping in this matter must be contained, but secondary containment techniques are available or^{11,12} under development¹⁶ which should be able to handle this problem.

Thus, although we question the size of the disengagers in the proposed Princeton design, only slight modification would be required to make the system look more attractive. The ability of the proposed structural materials to avoid embrittlement at the required temperatures and pressures, however, may be questioned. If this is satisfactory, the recovery of tritium from molten salts does appear to be easier than recovery from lithium.

SOLID BREEDING MATERIALS

Solid breeding materials were first suggested for CTR blankets because they promised low activation blankets [with low temperature Al or "sintered aluminum products" (SAP) structure] and/or low tritium inventories.³¹ Some have also seen ease of tritium removal or simpler blanket designs with helium cooled solid blankets, but these advantages are nonexistent in many cases and highly questionable in others. There are many proposed solid blanket materials and many designs (sometimes even from the same laboratory), and it is difficult to make simple checks to verify or devise the feasibility of all of these systems. When one tabulates all of the requirements and needs of a CTR blanket, some blanket design can be found which meets any of these needs, but no solid blanket design, yet, meets all the needs. Some requirements on blanket systems involve considerations not usually counted under the heading - tritium handling. These considerations will be mentioned only briefly in this paper.

The first question to be asked of a solid blanket design is, "Will it breed?" With only one exception, Li_2O , the answer is neither a clear "yes" nor a clear "no". Without neutron multiplication, no other proposed solid "breeding blanket" can reach tritium breeding ratios greater than unity and thus, the qualified answer to the question. The qualification is the availability and performance of a neutron multiplier - Be. The availability of Be (world supply) has been estimated to be insufficient to support a substantial fusion power economy.³² Solid Be used as a neutron multiplier also would undergo considerable swelling and other forms of radiation damage.³³

Solid blankets with helium coolants present some heat removal difficulties. Low coolant gas pressures and low flow rate cause high thermal stresses; high gas pressures require thick walls; and high gas flow rates can take many large coolant ducts. Several designs, however, have been prepared which apparently can handle the heat load, but possible "hot spots" from local plasma discharges onto the wall have not been fully analyzed.³⁴ Liquid blankets place more heat capacity in

contact with the wall. Although solid breeding modules have been considered for three experimental fusion power reactor scoping studies,³⁵⁻³⁸ none chose solid materials for their reference designs.

Recently, data have been reported which permit some evaluations of tritium recovery from solid blankets. Tritium diffusion rates in such materials are generally low, and very small blanket particles are required if low inventories are to be achieved. Recent data from LiSiO_2 and LiAlO_2 ³⁹ indicate that with 2 μ particles, tritium removal rates are adequate. The data do not cover a range of particle size sufficient to confirm the proposed simple solid diffusion controlled process, but release vs time curves suggest the model. Available data on Li-Al, however, present an unclear picture. Release rates do not suggest the solid diffusion controlled model³⁹ and recent sorption studies²³ suggest surface resistance to diffusion and/or surface sorption.

A few words should be said about the difficulty of using fine powder blankets. The powders must be enclosed, perhaps in a tubular structure, and flushed with helium to remove the released tritium. Pressure drops through the powder can be large if substantial flow rates are required. One must avoid either sintering or further fragmenting the bed into even finer particles. Either change could cut-off or reduce helium flow, and forces will be at work which could do either. Sintering can also reduce tritium release rates. Fine powders sinter far below their melting point, and sintering temperatures may limit the operating temperatures of some solid blankets, especially Li-Al. On the other hand, under radiation, blanket powders may fragment even further if helium formed by lithium transmutation (or the T_2O product formed in some materials), can not diffuse out of the particles.

In summary, solid lithium-containing materials do show promise for CTR blankets, but problems still remain which could limit or prevent their use. Breeding ratio is perhaps the most serious problem, but neutron multiplication (another questioned technique) could solve this problem. Heat transfer and tritium recovery may be possible, but these are not simple processes which can be designed with current information.

CONCLUSIONS AND RECOMMENDED PROGRAM

The advantages of lithium blankets, particularly their breeding ratios and heat removal capabilities (even when stagnant), suggest that the major tritium recovery efforts be directed at these systems. If EPR and later reactor designs continue to choose lithium blankets (or test modules), a principal emphasis on lithium systems is essential to provide data to design the necessary test modules and blankets. The most promising recovery systems - extraction and permeation techniques - should be pressured vigorously. Although extraction processes (without electrolytic cells) currently appear to have less serious questions of feasibility, these are complex systems with still enough uncertainties that vigorous development of one alternate system is needed. One or two alternate techniques should be followed, but these should be low level efforts which do not consume significant fractions of the available funding.

Molten salt and solid blanket development should continue but remain a secondary effort (to lithium blankets) until EPR or other design studies show more favorable results for these systems. Tritium recovery from molten salts appears to be reasonably simple using a modification of the flowsheet proposed by Johnson.¹² Tritium recovery from some solid blankets appears to be feasible, but other serious problems accompany solid blanket materials.

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TRITIUM HANDLING SCHEME FOR THE J.E.T. EXPERIMENT

H. Clerc* and G. Venus**

J.E.T. Design Team,
UKAEA Culham Laboratory, Abingdon, Oxon (U.K.)

ABSTRACT

The J.E.T. (Joint European Torus) experiment is designed as a tokamak with plasma currents of 2.6 MA (standard performance) up to 4.8 MA (ultimate performance). If approved it will become operational in 1980. If plasma performance during the first stage of conventional performance proves successful, studies of nuclear heating will be performed with a mixture of tritium-deuterium as filling gas. Provisions for the future use of tritium will be made in two steps: those which will be incorporated in the design from the beginning, like a double-wall structure of the vacuum vessel, sufficient shielding of the "test-cell" to reduce the outside neutron fluxes etc., and those which could be installed before the tritium experiments, such as equipping a tritium-room and constructing a stack with adequate height, etc. The two stages have been investigated, and the results of these studies will be presented.

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- *) permanent address: C.E.A., BP 511-15 75015 Paris, France
- **) permanent address: Max-Planck-Institut für Plasmaphysik,
Garching, Germany

Introduction

The JET (Joint European Torus) experiment is designed as a tokamak with plasma currents of 2.6 MA (Standard performance) and up to 4.8 MA (ultimate performance). The construction of the machine is now being prepared by the JET Design Team working at Culham in the U.K. If approved, it will become operational in 1980.

A perspective view of the machine is shown in Figure 1. The main features are the toroidal vacuum chamber, the set of toroidal magnetic coils, the iron transformer with its eight limbs and the primary windings (poloidal windings) of this transformer.

The vacuum vessel is a completely welded, all metal structure. Figure 2 shows a cross section in a meridional plane of the torus. It consists of thirty-two so-called rigid sectors, wedged shaped parts constructed out of relatively thick (12 to 20mm) plates of Inconel 600. The rigid sectors are joined together by thirty-two bellows sections consisting each of two bellows in a concentric arrangement, each made from Inconel 625, of 1.7 to 2mm thickness. The rigid sectors as well as the bellows sections form a completely double-walled torus.

The torus has eight horizontal ports, four of which are used as pumping ports. The pump sets attached to them each consists of four cryo-pumps welded to the pump-port backed by four mechanical pump sets, consisting of a turbomolecular pump and a vane-type rotary pump each. We get an effective pumping speed to the torus of approximately 45000 l/sec from the cryo-pumps and approximately 6000 l/sec from the turbomolecular pumps

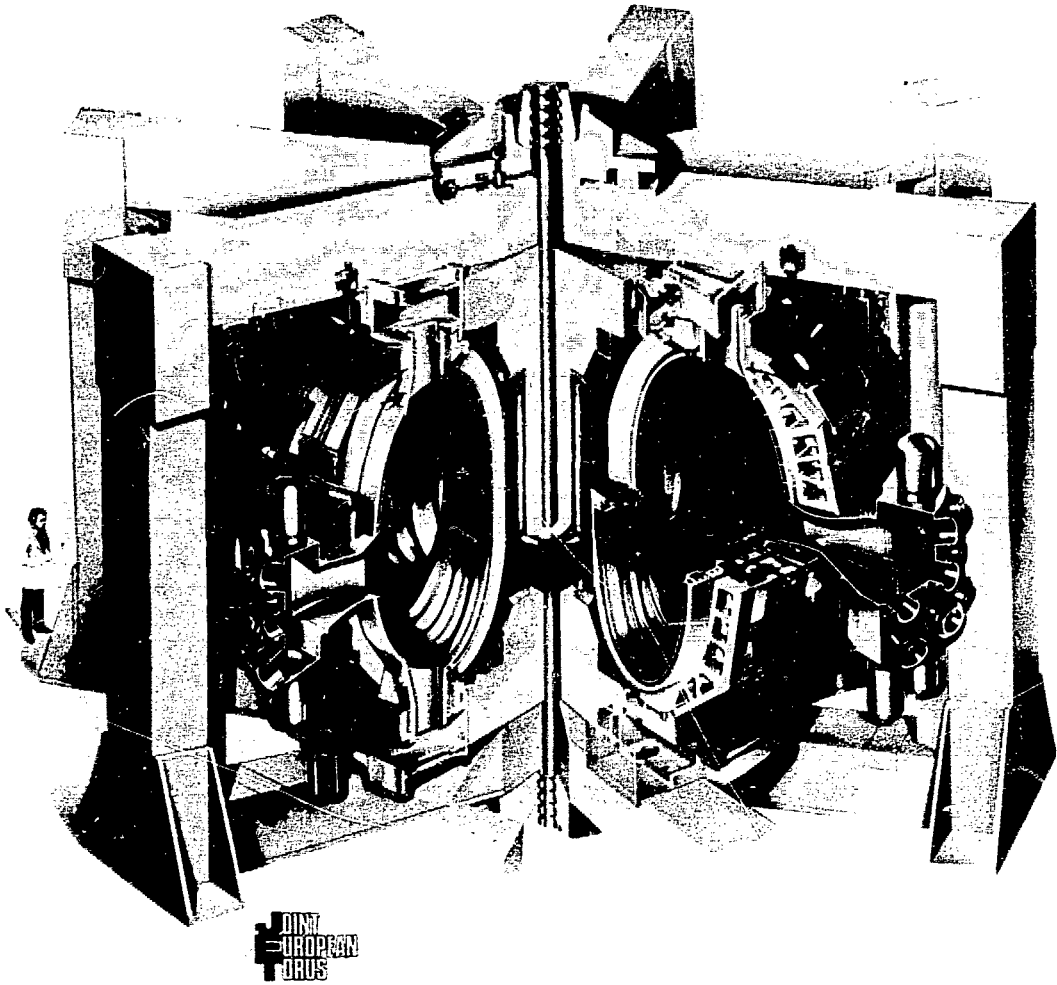


Figure 1. The JET Device. Artist's impression.

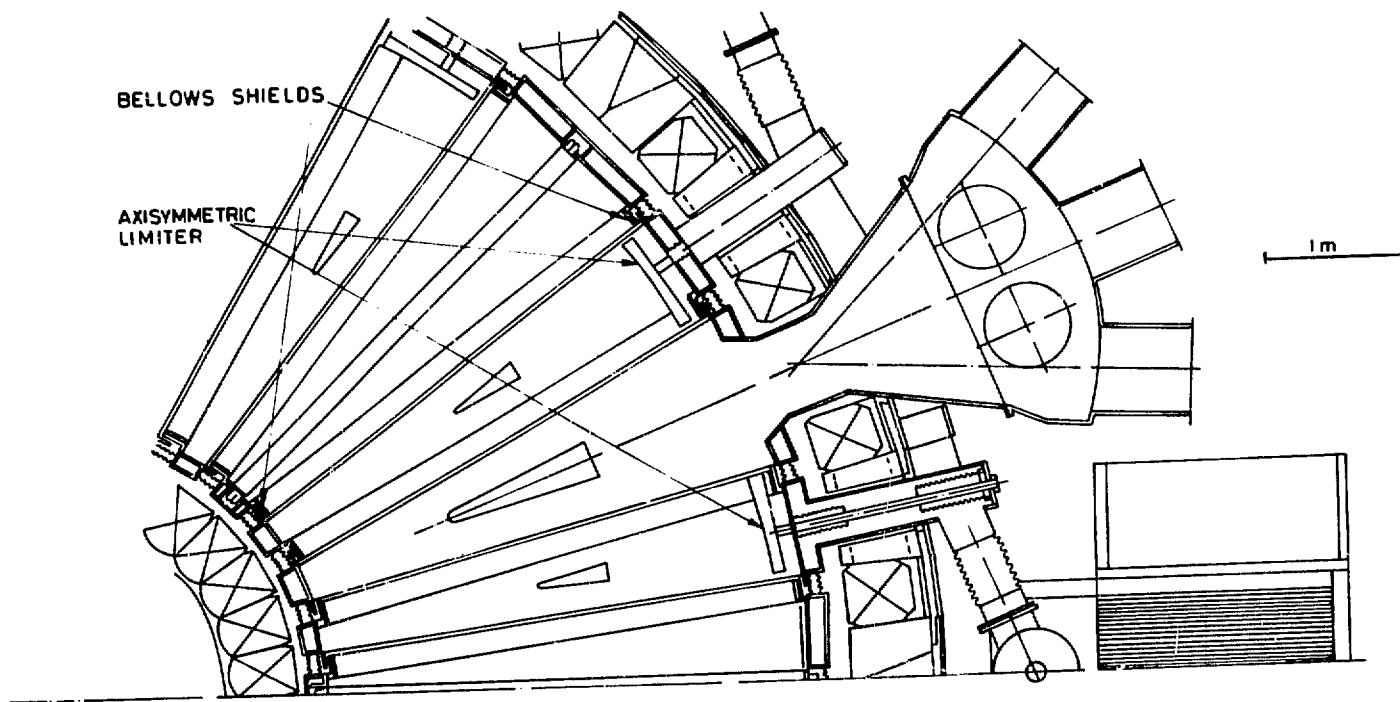


Figure 2. Section through Midplane of Torus

altogether. The envisaged base pressure will be in the order of 10^{-10} torr. Baking of the torus to 350°C - 500°C is foreseen. The interspace between the bellows and inside of the rigid sectors can be pumped out thus forming a shell vacuum.

The aim of the experiment is to get a plasma with characteristics as close as possible to those required for thermonuclear fusion processes. If the plasma performance during the first stage of the conventional operation proves successful, studies of nuclear heating will be performed with a mixture of deuterium-tritium as a filling gas, or by injecting beams of energetic tritons into a deuterium plasma. By the use of tritium, some restraints are imposed on the JET experiment.

Quantities of tritium involved in the JET experiment.

The filling pressure of tokamaks usually varies between 10^{-5} and 10^{-3} torr of hydrogen isotopes corresponding to a (dissociated) particle density of $7 \cdot 10^{11}$ to $7 \cdot 10^{13} \text{ cm}^{-3}$. If we introduce in JET a 1:1 D-T-mixture we will need between 1 and 100 torr·l of tritium, equivalent to 0.35 to 35mg of T_2 or 3.44 to 344 Ci. The volume of the vacuum vessel with pump ports, pump boxes and diagnostic ports, is assumed to be 200 m^3 .

For the injection of fast neutral tritium beams a tritium consumption of 5 torr·l/sec per megawatt is assumed [1]. At present an injection system of 20 MW during 1 second is planned so that we expect a tritium consumption of 100 torr·l, or 35mg for a discharge with tritium injection.

In order to be able to make some 100 discharges with the tritium inventory stored on site and taking into account that a certain amount of the tritium will stick in the tritium handling system, we propose to have a tritium inventory of approximately 10 gramms or 10^5 Curies on site.

General remarks on tritium handling in JET.

Although tritium will come into operation at a relatively late stage of the JET experiments we must, from the outset, consider the possible design of the tritium handling system and of the auxiliary systems which are necessary for the operation with tritium (tritium monitoring system, ventilation system and tritium recovery system - description see below), in order to:

- make the later transition to tritium operation as smooth as possible,
- to make a first assessment of the radiological risks connected with the tritium operation,
- to get an idea of the cost necessary for the tritium operation.

To comply with the first requirement we have to split the preparations for the tritium use into two steps: those measures which will be incorporated in the design from the beginning, and those which can be installed shortly before the tritium experiments begin. For the first step we will have to equip JET:

- with a double walled vacuum vessel, where the interspace is connected to the so-called shell vacuum system in order to reduce tritium losses from the vacuum vessel by permeation through the walls of the vessel (in particular through the relatively thin bellows), or through small leaks;
- with vacuum systems which are compatible with tritium use or which make conversion into ones compatible with tritium very easy;
- with a heating and cooling system for the torus and the limiters which is compatible with tritium use.

Furthermore, the buildings for JET have to be prepared for the tritium operation, which means, mainly:

- to build the test-cell* for JET so that it can act as an emergency container for accidentally released tritium and to equip it with concrete walls of sufficient thickness for neutron shielding;
- to provide for the installation of the tritium handling system and the auxiliary systems, especially the feed-throughs between the tritium room and the test cell;
- to prepare the ventilation so that it may easily be extended for the requirements imposed by the tritium use.

The tritium handling system

The installation of the tritium handling system can be delayed until shortly before the tritium experiments start.

The primary functions of this system are:

- to store the on-site tritium inventory in a safe way with a minimum probability of an accidental release of substantial quantities of tritium to the buildings and to the environment;
- to purify tritium from inert gas contaminations, especially from He^3 , and to provide this high purity tritium on demand for the introduction to the torus;
- to introduce measured and programmable quantities into the torus;
- to remove and store the spent tritium;
- to purify - if required - the spent tritium or the mixture between tritium and other hydrogen isotopes from other gases (isotropic separation is not taken into consideration) and to provide it for the reintroduction

* building in which JET is operated.

to the torus;

- to analyse the tritium in the different stages of the tritium handling system for the:
 - (a) content of other admixtures than hydrogen isotopes,
 - (b) content of different hydrogen isotopes.

A system which would fulfil these requirements was outlined schematically for JET. It is shown in Figures 3 and 4.

The tritium is supplied in gaseous form in two bottles B each containing approximately 5g of tritium. For the introduction into the torus the tritium is purified by means of a palladium diffusion cell DC through which the unpurified tritium is circulated by a dry pump DP 1. The purified tritium arrives in the reservoir R1 with a pressure of approximately 0.5 atm. Here we have the possibility of checking the purity of the tritium (An. 1). It is then transferred through a pipe of approximately 15m length to the reservoir R2 of the introduction system near the torus by means of a dry pump (e.g. an air pressure operated bellows pump). This transfer from the tritium room to the torus might present some difficulties as the transfer line because of its great length will have a relatively low conductance and a large surface and so the recovery of the tritium after the transfer might be incomplete. From the introduction system a well defined quantity of tritium (working range 0.3 to 300 torr.l), represented by the volume of the temperature-stabilised reservoirs R3 or R4, is introduced into the torus. From other introduction systems the required quantities of deuterium or other gases will be introduced. After each discharge the gas mixture will be pumped off by the cryo-pumps of the torus pumping system. It should be noted that no accumulation of tritium above approximately 500 - 1000 Ci should occur in the pump system. That means that after a certain number of shots (depending on

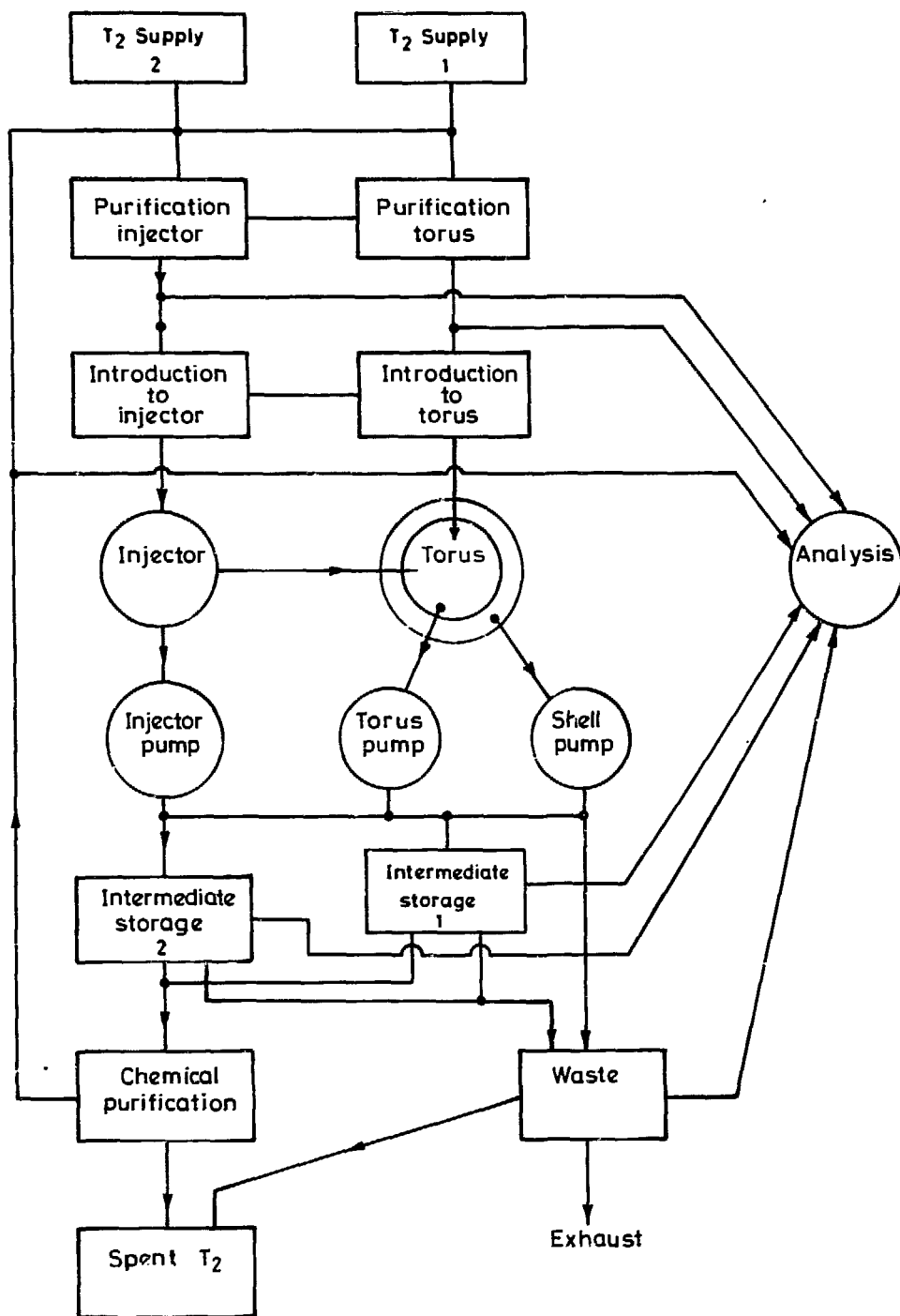


Figure 3. Proposed Tritium Handling System (schematic)

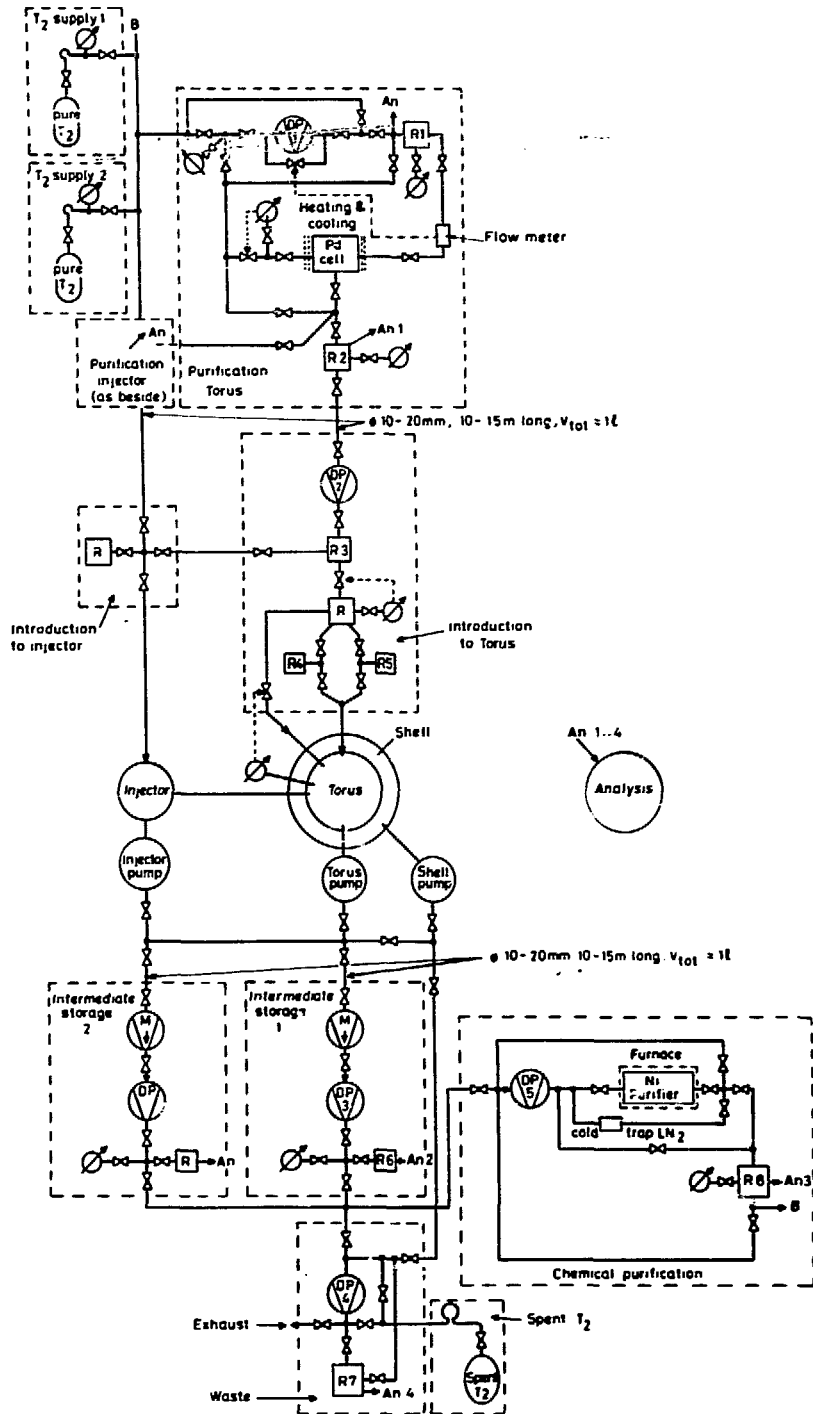


Figure 4. Proposed Tritium Handling System (Flow-Diagram)

the amount of tritium used per shot) the cryo-pumps have to be cleaned by the mechanical pump sets. In this procedure the spent tritium, together with the other gases of the mixture, is transferred to the intermediate storage system in the tritium room through an approximately 15m long pipe. Here the stored gas mixture can be analysed (An. 2). It can then either be exhausted or pumped to the spent tritium bottle SB, or brought to the chemical purification system where oxygen and hydrocarbons are separated off. Then the gas mixture containing mainly hydrogen isotopes and noble gases can be fed back to the purification system for the reintroduction to the torus. Perhaps the ratio between the hydrogen isotopes has to be readjusted.

The tritium analysis facility is equipped with a gaschromatograph for "non-isotopic" analysis (He , N_2 , O_2 , hydrocarbons etc), and "isotopic" analysis (H_2 , D_2) and a small mass spectrometer for covering the range up to mass 100, e.g.

The outlined tritium handling system was designed so that reprocessing of tritium is possible to a certain extent. Whether this is sensible or not will mainly depend on the experimental programme to be performed with tritium. Rough estimates of the costs of the purification installations have shown that a tritium quantity of the order of 50g (equivalent to the quantity necessary for approximately 1000 discharges at maximum tritium consumption) would be the limit beyond which reprocessing of the spent tritium would be more economic. If no reprocessing of the spent tritium is envisaged we can dispense with the chemical purification system. Also the analysis system can be simplified in this case e.g. by dropping the costly gaschromatograph for isotopic analysis.

The tritium handling system will be installed mainly in a tritium room inside "caissons" or "glove-boxes" in order to minimise the health hazard for the staff and to simplify counter measures in the case of an accidental release of tritium. Only the introduction systems and the transfer pipes to and from the experiment will be outside the tritium room. The idea is to have only that amount of tritium outside the tritium room which is indispensable. In our case this quantity will be up to approximately 1000 Ci at maximum.

Losses of tritium due to permeation from the torus and from the tritium handling system.

Tritium, like hydrogen and deuterium, diffuses more or less rapidly through all bodies. Thus we have to expect tritium losses from all tritium containers. We have tried to assess the tritium losses due to permeation by means of the formula for steady state permeation. (For more details see the Annex). These permeation losses are calculated for different tritium pressures inside the discharge vessel and for different wall temperatures taking into account the duty cycle of the machine i.e., the ratio between the time when the torus is filled with tritium and the pause time. Implantation of fast tritium ions into the walls of the discharge vessel during a plasma pulse and subsequent diffusion to the outside have not been regarded.

It was an aim in designing the vacuum vessel for JET to surround those parts of the vessel by a second wall which contain the thin bellows and which, during operation, would rise to higher temperatures. As one can see from the Annex, this double wall structure together with the pumping applied to its inter-space, can lower the tritium losses to the outside considerably. The exact assessment of the tritium escape is,

however, complicated by the lack of information on the probable temperature of the vessel wall during the experiments. But even at 400°C , which is certainly the highest temperature to which the vessel will be allowed to raise during operation, the losses with a maximum filling pressure of 10^{-3} torr are low. We can expect the losses through the double walled part, by permeation to be smaller than $3 \cdot 10^{-7}$ Ci/sec or approximately 10 Ci/year. Probably the losses will be in the order of $7 \cdot 10^{-10}$ Ci/sec or 0.02 Ci/year as the assumption of a vessel temperature of 200°C seems sensible.

The losses through the single wall parts of the vessel (pump ports, pump boxes, diagnostic ports), which can be assumed to stay at lower temperatures during operation since they are more remote from the plasma, will be below:

$$5 \cdot 10^{-9} \text{ Ci/sec or } 0.16 \text{ Ci/year. (Wall temperature } 100^{\circ}\text{C)}$$

or

$$2.7 \cdot 10^{-7} \text{ Ci/sec or } 8.6 \text{ Ci/year. (Wall temperature } 200^{\circ}\text{C)}$$

These losses were calculated for clean, unoxysided surfaces. Oxydised surfaces can reduce the permeation losses by the factor 10 to 100.

The losses through the walls of the tritium handling system are difficult to assess because they will strongly depend on the actual construction details (material, wall thickness, surfaces etc.,). In order to get a feeling for the order of magnitude, we quote here the losses of the 15m long tritium transfer pipe (diameter 2cm, wall thickness 1mm, material: Inconel) at a tritium pressure of 100 torr inside and a wall temperature of 50°C :

$$7.8 \cdot 10^{-8} \text{ Ci/sec or } 2.5 \text{ Ci/year.}$$

The tritium losses from hot parts of the tritium handling system (e.g. the palladium diffusion cell) could be much higher. But

it is known [2] that by coating with refractory metals, the permeation losses through hot walls can be lowered considerably.

Auxiliary Systems.

To enable a safe tritium operation in JET we need the following auxiliary systems:

- (a) an effective ventilation system connected to a stack of proper height;
- (b) a tritium monitoring system in all rooms where tritium is going to be handled, in the ventilation pipes and in the stack;
- (c) a tritium recovery system which is able to recover larger quantities of tritium which have escaped to the atmosphere.

As the ventilation-the monitoring-and the recovery system have important functions, in particular in the case of a tritium accident, they have to be provided with parallel drives for the fans, parallel catalytic burners and safety arrangements for all other important components, including an emergency power supply.

(a) Ventilation System.

One of the best protections against the build up of high tritium concentrations in buildings is an effective ventilation system. The envisaged ventilation system for JET is schematically shown in Figure 5. The ventilation system of the test cell - also foreseen for the basic performance of JET - has to be extended so that:

- a subatmospheric pressure of 5-7mbar is established in the test-cell;
- a flow speed in all pipes and orifices of greater than 1.5m/sec is maintained;

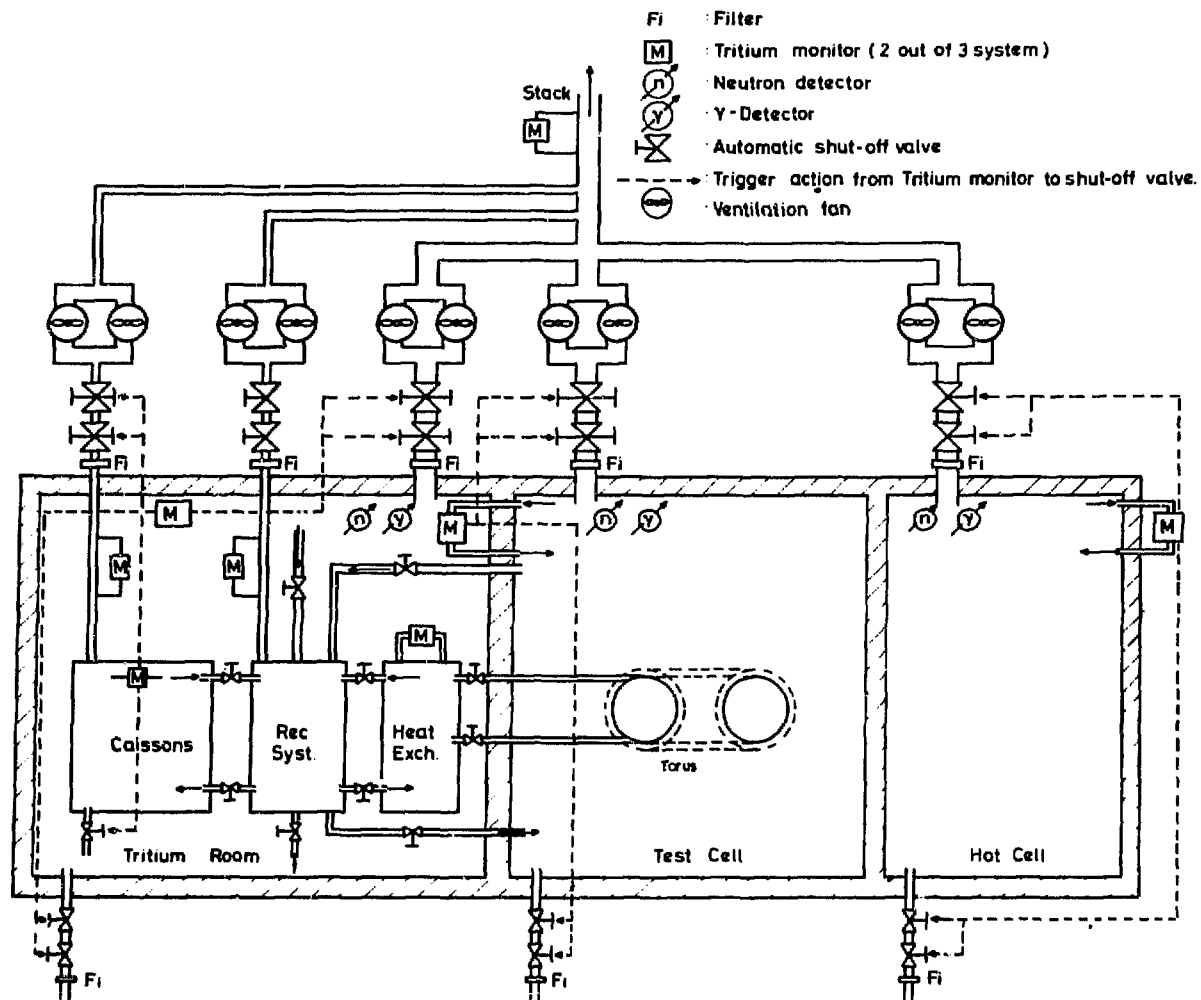


Figure 5. Ventilation and Monitoring System

- the relative air humidity in the test cell is controlled to 45% to 50%;
- the air is effectively filtered at the intake and outlet (use of 99.99% filters);
- the tritium concentration in the exhaust pipes is monitored;
- the exhaust is fed to a chimney of 60m height;
- the ventilation system can be shut off hermetically.

Quite similar ventilation systems will be installed to the tritium room, the caissons, the glove boxes and the hot cell. The Table 1, gives some details of the different ventilation systems.

	Change per hour	Volumetric flow rate	Ventilation speed	Subatmospheric pressure
Tritium room	10	4.5 m ³ /sec	1.5 m/sec	5 to 7m bar
Caissons, glove-boxes	20 to 40	Appr. 1m ³ /sec	1.5 m/sec	40 ± 10m bar
Test cell	2	11 m ³ /sec	1.5 m/sec	5 to 7m bar
Other rooms (hot cell, control room etc.)	2	Appr. 4m ³ /sec	1.5 m/sec	3 to 5m bar

Table 1. Specifications of the Ventilation Systems.

(b) Monitoring System.

The proposed tritium monitoring system is shown schematically in Figure 5. Each tritium monitor indicated in Figure 5, will be a two out of three system. The monitors themselves will be ionisation-chambers of a volume of some litres with a detection limit of approximately $1 \cdot 10^{-6}$ Ci/m³, equivalent to 0.2 MPC of tritiated water in air. The monitors will be inserted in an automatic alarm and control system, giving alarm at certain

preset tritium levels, e.g., at 2, 20 and 200 times MPC, and triggering the shut-off valves.

(c) Tritium Recovery System.

To remove those quantities of tritium which have escaped from the tritium handling system, tritium recovery systems are foreseen. They are composed of catalytic burners which oxydise hydrogen to water, and of subsequent desiccation stages. These systems should be able to de-contaminate the air in the room concerned within twenty-four hours to a tritium concentration so that the exhaust through the stack is possible without problems. As the systems are expected to remove the tritium nearly quantitatively they will also extract the water vapour from the atmosphere completely. In order to reduce the requirements to these systems the relative humidity in all rooms where tritium will be handled must be kept at low as tolerable. At present we envisage a relative humidity of 45%. But even in this case, the recovery system for the JET test-cell, for example, has to trap approximately 200kg of water. To trap this quantity of water we need 6 to 8m³ of molecular sieve at minimum. This example elucidates the size and the problems connected with the recovery systems. The recovery systems should be placed in the tritium room.

Safety and environmental impact

Considerable effort has been made to design the tritium handling system so that any accidental release to the rooms of the buildings is small, and, of course, even smaller to the environment. In the case of an accidental tritium release, the room concerned will be hermetically shut off and should act as a secondary container confining the tritium. The recovery system would be automatically triggered in order to extract the tritium. According to the design of the tritium handling system

the biggest quantities of tritium can be released inside the glove boxes or the caissons in the tritium room. Thus, for those parts of the apparatus where large quantities could be released, we have two additional safety containers.

As the worst case accidents, we assume that all tritium which is handled in the tritium room and in the test-cell is released into these rooms. We get contamination levels as they are shown in Table 2.

Table 2.

	Volume	approximate T_2 quantity	Tritium concentration arising	Times MPC HTO	Time of stay for ingestion of maximum permiss- ible single intake
Test cell	$20000m^3$	500 Ci	$2.5 \cdot 10^{-2} Ci/m^3$	$5 \cdot 10^3$	approx 30 mins
Tritium room	1600	10^5	62.5	$1.25 \cdot 10^7$	0.7 sec

In the case of a release of these tritium quantities through the chimney of 60m height to the environment according to [3] maximum doses of 2 mrem (500 Ci release) or $3.8 \cdot 10^2$ mrem (10^5 Ci release) will occur.* The second value represents, according to the JCRP-norms, approximatively the dose limits per year for members of the general public ($5 \cdot 10^2$ mrem/a). Hence the total loss of that quantity once a year will present no serious accident from the point of view of health physics.

* In the literature there is no good agreement on the dose rates in the environment resulting from the release of radioactive material to the atmosphere (see e.g. [4], [5] and [6]). We tend to follow reference [3] because it assumes rather hard meteorological conditions and leads to relatively pessimistic dose rates.

In Figure 6, the doses arising at ground level in the case of a tritium release of 500 and 10^5 Ci through the stacks of 60 and 80m height are shown as a function of the distance to the point of release. The maximum doses arise at a distance of approximately 1000 metres, i.e., probably outside the fenced-off JET site.

Reliability of the Tritium Handling System.*

It has been shown that an accidental release of the total amount of tritium stores on site once a year would not present a serious radiological problem as it leads to an off-site exposure smaller than 500 mrem (JCRP norm for the general public) at maximum. The JET tritium handling system was analysed to find out the probability of accidental tritium releases. The assessment has been based on generic failure data extracted mainly from the UKAEA Systems Reliability Service Data Bank. Both maloperations of components and human error have been taken into account. The result is presented in Figure 7 (in a way introduced in [7] for the siting of nuclear power reactors) where the probability of a release is shown as a function of the releasable activity. Lines with an angle of 135° with respect to the abscissa represent boundaries of equal risk. The line in Figure 7 is corresponding to the release of 10^5 Ci with a probability of 1 per year. It can be seen:

- that the level of the hazard which may arise is assessed to be several orders of magnitude below the maximum permissible as set by the JCRP, and represented by the boundary line in the diagram
- and that the risks are fairly equally distributed with respect to the different subsystems.

* Work done under a EUE-JET Study Contract by K. J. Williams, Systems Reliability Service, U.K.A.E.A. Harwell.

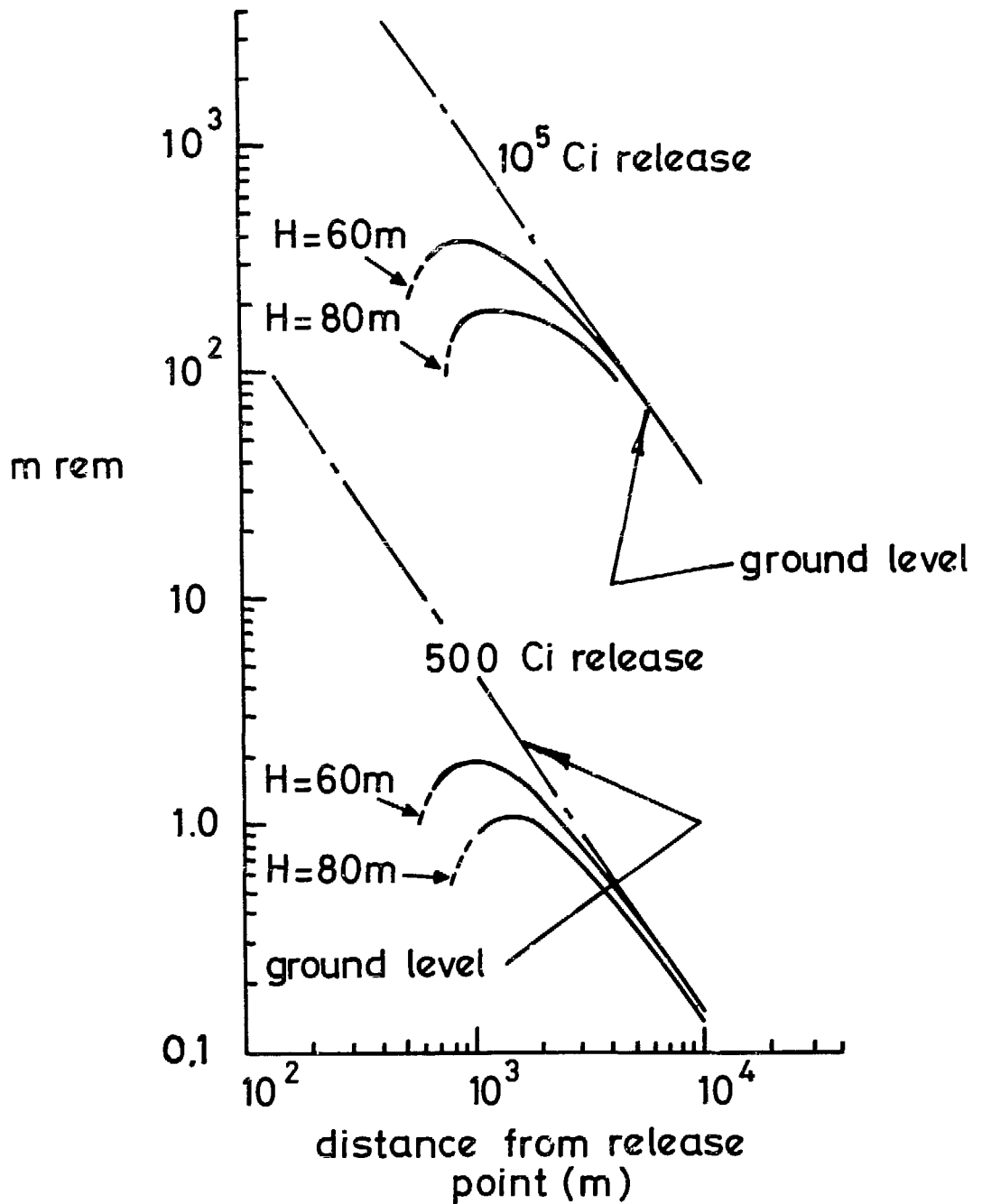


Figure 6. Calculated Dose-level down wind of Point of Release

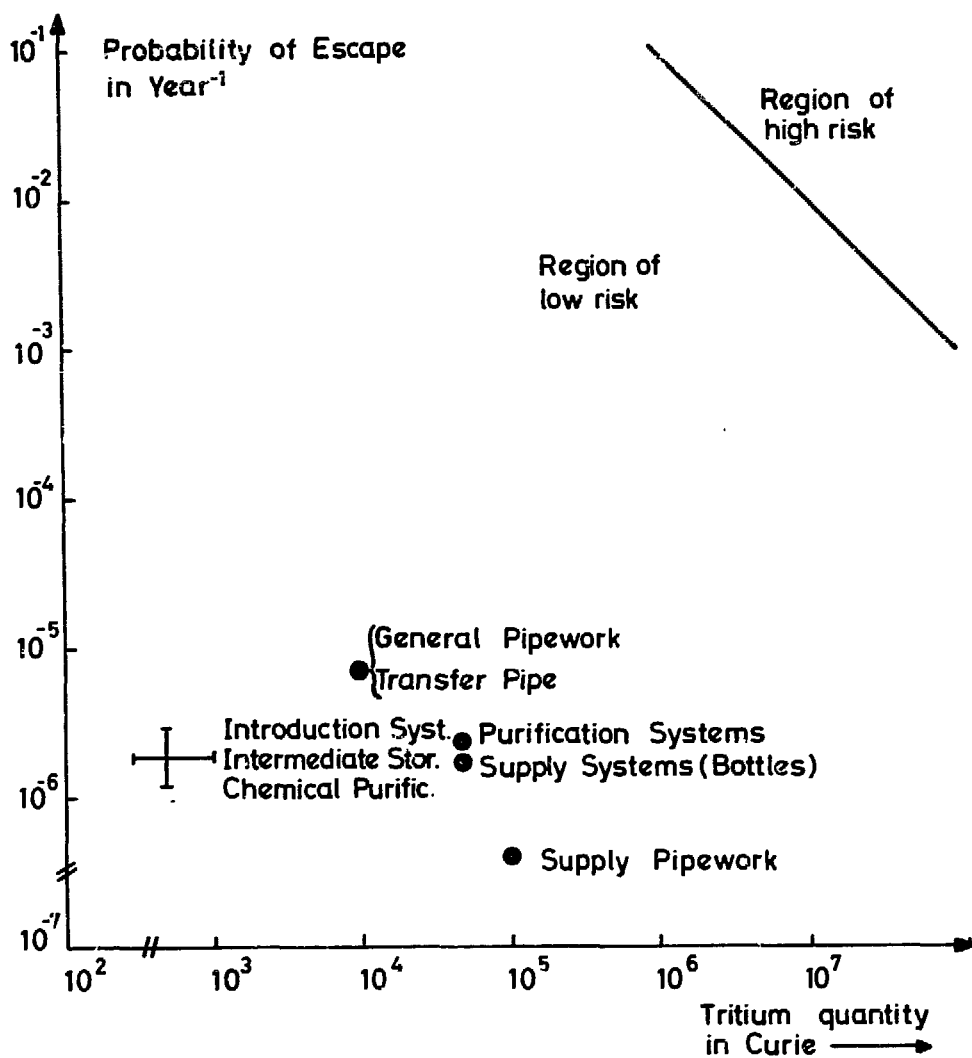


Figure 7. Incident Risk - Probability Diagram

Conclusion

It appears at present that the possible use of tritium in JET does not impose difficulties beyond the present technical know-how or involve fundamental changes in the basic design of JET. Although the total expenses connected with the use of tritium are considerable, that part which has to be incorporated in JET for its basic performance is comparatively low. If one accepts that the double walled structure of the vacuum vessel, apart from preventing tritium losses has other functions to fulfil as well, namely to present a safeguard against small leaks that might arise during operation in the torus and to enable heating and cooling of the vessel in an efficient and convenient way, the preparations for the use of tritium are very small. Hence it would seem unwise to drop these preparations and to lose, or at least, to complicate the option of using tritium in JET later on.

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IAEA Conf. Containment and Siting. Vienna Apr. 1967 SM-89134

ANNEX.Losses of tritium due to permeation through the wall of the torus.

The steady state tritium flux ϕ permeating through a layer of the thickness, d , is given by:

$$\phi = \frac{\phi_0}{d} \sqrt{P_T} e^{-\frac{Q_p}{RT}} \quad (A1)$$

where ϕ_0 is the permeability constant, P_T the partial pressure and Q_p the activation energy for permeation.

We have tried to estimate the tritium losses through the discharge vessel of JET using equation (A1). The permeability data of the system tritium-Inconel 600 or 625 have not been available at the moment. Thus we have used the data from the system hydrogen-Inconel 718 assuming that the results in this case could be similar and regarded as an upper limit because of the lower mass of the atom of hydrogen. As the full tritium pressure inside the vessel is only applied for a short time (approximately the time during the discharge) compared with the repetition time for discharges, and because the initial transient phase for diffusion is long or comparable, even at a wall temperature of 500°C, with repetition time of the experiment, we multiply the flux given by (A1) with the duty cycle η of the machine in order to get average values.

The losses from the vessel are split into two parts:

1. escape through the single walled parts of the torus (pump ports, pump boxes, diagnostic ports);
2. escape through the double walled parts where interspace pumping is applied.

Escape of tritium through the single walled parts

The total average amount of tritium $\bar{Q}_s$ which escapes through the single walled parts can be assessed as:

$$\bar{Q}_s = \eta \sum_i \phi_i \cdot S_i = \eta \cdot \phi_o \sqrt{P_T} e^{-\frac{Q_p}{RT}} \sum_i \frac{S_i}{d_i} \quad (A2)$$

where ϕ_i denotes the steady state flux through sheets of particular thicknesses d_i , and S_i the surface of the parts of the vessel which is made out of sheets of the thickness. The temperature of all walls is assumed to be uniform. Using the values:

$$\phi_o = 3.88 \cdot 10^6 \frac{\text{torr} \cdot \text{l}}{\text{m}^2 \text{sec}}$$

$$Q_p = 13.3 \frac{\text{kcal}}{\text{mol}}$$

$$\sum_i \frac{S_i}{d_i} = 163 \frac{\text{m}^2}{\text{cm}}$$

and

$$\eta = 8.3 \cdot 10^{-3}$$

we get values for $\bar{Q}_s$ as they are shown in Table A1, as a function of the wall temperature, T , and the tritium filling pressure P_T .

Escape of tritium through the double walled parts.

Interspace pumping is applied in the double walled parts of the torus. The path of tritium escaping in this case can be schematically described as shown in Figure A1.

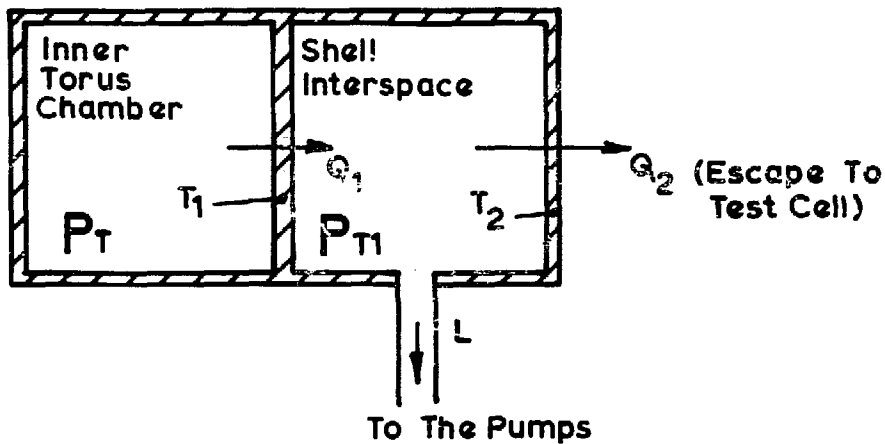


Figure A1. Escape path of tritium through the double walled part of the torus, schematically.

The torus wall consists of relatively thick plates ($d_{RS} = 12\text{mm}$) in the rigid sectors and of relatively thin plates ($d_B = 1.7\text{mm}$) in the bellows sections. So we describe the quantity Q_1 of tritium which permeates from the torus into the shell interspace using equation (A1) as:

$$Q_1 = 32 \cdot (\phi_{RS} \cdot S_{RS} + \phi_B \cdot S_B) = 32 \cdot \phi_0 \cdot P_T \cdot e^{-\frac{Q_P}{RT}} \left(\frac{S_{RS}}{d_{RS}} + \frac{S_B}{d_B} \right) \quad (A3)$$

where ϕ_{RS} is the flux through layers of the thickness d_{RS} of the rigid sector material, ϕ_B the flux through layers of the thickness d_B of the bellows material, S_{RS} the surface of a rigid sector and S_B the surface of a bellow. The average flux is:

$$\bar{Q}_1 = \eta Q_1 \quad (A3')$$

Using the values:

$$S_{RS} = 4.82\text{m}^2$$

$$S_B = 4.87\text{m}^2$$

$$d_{RS} = 1.2\text{cm}$$

and

$$d_E = 0.17 \text{ cm}$$

we get values for $\bar{Q}_1$ as they are listed in Table A2 for different wall temperatures T_1 and different tritium pressures P_T inside the torus. The main contribution to $\bar{Q}_1$ results from the diffusion through the relatively thin bellows; permeation through the rigid sectors contributes to $\bar{Q}_1$ only by approximately 15%.

Interspace pumping reduces the tritium pressure inside the shell and thus lowers the permeation losses through the outer wall to the JET test cell. The outer wall of the shell resembles very much the inner one. Therefore we can use the same values for the geometrical dimensions. Furthermore we assume that the temperature of the outer wall T_2 is equal to T_1 i.e. $T_1 = T_2 = T$. [The mechanical requirements to the shell are such that, in any way, only small temperature differences (in the order of 50°C) between the inner and the outer wall are tolerable]. Under these assumptions the average permeation flux $\bar{Q}_2$ can be written as:

$$\bar{Q}_2 = \bar{Q}_1 \cdot \sqrt{\frac{P_{T1}}{P_T}} \quad (\text{A4})$$

where P_{T1} denotes the tritium pressure in the interspace. If we apply a pumping speed L to the shell (L : pumping speed applied to all eight parts of the shell) the tritium pressure in the interspace is given by

$$P_{T1} = \frac{\bar{Q}_1 \left(1 - \sqrt{\frac{P_{T1}}{P_T}}\right)}{L} \quad (\text{A5})$$

P_{T1} is listed for $L = 3200$ l/sec, different temperatures T and different tritium pressures P_T in Table A3. P_{T1} was calculated from:

$$P_{T1} = \frac{\bar{Q}_1}{L}$$

neglecting $\sqrt{\frac{P_{T1}}{P_T}}$ against 1. Inserting P_{T1} in equation (A4) leads to the tritium losses $\bar{Q}_2$. They are listed in Table A4.

Finally we work out a figure of merit α for the double walled part of the vacuum vessel which gives the reduction of the tritium losses through the double walled part by interspace pumping. We want to refer to the same amount of material used for the wall of the torus and therefore we compare $\bar{Q}_2$ with $\frac{\bar{Q}_1}{2}$ (the loss through a single walled torus with a double wall thickness).

We define

$$\alpha = \frac{2\bar{Q}_2}{\bar{Q}_1} \tag{A6}$$

α is listed in Table A5 as a function of wall temperature and tritium filling pressure.

For the conversion of tritium-quantities in activities we use the conversion factor

$$f = 3.44 \frac{\text{Ci}}{\text{sec}} / \frac{\text{torr} \cdot \text{l}}{\text{sec}}$$

TABLE A1. $\bar{Q}_s$ in $\frac{\text{torr} \cdot \text{l}}{\text{sec}}$

P_T in torr T in $^{\circ}\text{C}$	10^{-3}	10^{-4}	10^{-5}	10^{-6}
50	$8.88 \cdot 10^{-11}$	$2.81 \cdot 10^{-11}$	$8.88 \cdot 10^{-12}$	$2.81 \cdot 10^{-12}$
100	$1.46 \cdot 10^{-9}$	$4.62 \cdot 10^{-10}$	$1.46 \cdot 10^{-10}$	$4.62 \cdot 10^{-11}$
200	$7.96 \cdot 10^{-8}$	$2.52 \cdot 10^{-8}$	$7.96 \cdot 10^{-9}$	$2.52 \cdot 10^{-9}$
300	$7.89 \cdot 10^{-7}$	$2.50 \cdot 10^{-7}$	$7.89 \cdot 10^{-8}$	$2.50 \cdot 10^{-8}$
400	$4.50 \cdot 10^{-6}$	$1.42 \cdot 10^{-6}$	$4.50 \cdot 10^{-7}$	$1.42 \cdot 10^{-7}$
500	$1.65 \cdot 10^{-5}$	$5.21 \cdot 10^{-6}$	$1.65 \cdot 10^{-6}$	$5.21 \cdot 10^{-7}$

TABLE A2. $\bar{Q}_1$ in $\frac{\text{torr} \cdot \text{l}}{\text{sec}}$

P_T in torr T in $^{\circ}\text{C}$	10^{-3}	10^{-4}	10^{-5}	10^{-6}
50	$5.69 \cdot 10^{-10}$	$1.80 \cdot 10^{-10}$	$5.69 \cdot 10^{-11}$	$1.80 \cdot 10^{-11}$
100	$9.33 \cdot 10^{-9}$	$2.95 \cdot 10^{-9}$	$9.33 \cdot 10^{-10}$	$2.95 \cdot 10^{-10}$
200	$5.10 \cdot 10^{-7}$	$1.61 \cdot 10^{-7}$	$5.10 \cdot 10^{-8}$	$1.61 \cdot 10^{-8}$
300	$5.06 \cdot 10^{-6}$	$1.60 \cdot 10^{-6}$	$5.06 \cdot 10^{-7}$	$1.60 \cdot 10^{-7}$
400	$2.89 \cdot 10^{-5}$	$9.14 \cdot 10^{-6}$	$2.89 \cdot 10^{-6}$	$9.14 \cdot 10^{-7}$
500	$1.05 \cdot 10^{-4}$	$3.32 \cdot 10^{-5}$	$1.05 \cdot 10^{-5}$	$3.32 \cdot 10^{-6}$

TABLE A3.

 P_{T1} in torr

P_T in torr T in $^{\circ}\text{C}$	10^{-3}	10^{-4}	10^{-5}	10^{-6}
50	$1.78 \cdot 10^{-13}$	$5.63 \cdot 10^{-14}$	$1.78 \cdot 10^{-14}$	$5.63 \cdot 10^{-15}$
100	$2.92 \cdot 10^{-12}$	$9.22 \cdot 10^{-13}$	$2.92 \cdot 10^{-13}$	$9.22 \cdot 10^{-14}$
200	$1.59 \cdot 10^{-10}$	$5.03 \cdot 10^{-11}$	$1.59 \cdot 10^{-11}$	$5.03 \cdot 10^{-12}$
300	$1.58 \cdot 10^{-9}$	$5.00 \cdot 10^{-10}$	$1.58 \cdot 10^{-10}$	$5.00 \cdot 10^{-11}$
400	$9.03 \cdot 10^{-9}$	$2.86 \cdot 10^{-9}$	$9.03 \cdot 10^{-10}$	$2.86 \cdot 10^{-10}$
500	$3.28 \cdot 10^{-8}$	$1.04 \cdot 10^{-8}$	$3.28 \cdot 10^{-9}$	$1.04 \cdot 10^{-9}$

TABLE A4.

 $\bar{Q}_2$ in $\frac{\text{torr} \cdot \text{l}}{\text{sec}}$

P_T in torr T in $^{\circ}\text{C}$	10^{-3}	10^{-4}	10^{-5}	10^{-6}
50	$7.59 \cdot 10^{-15}$	$4.27 \cdot 10^{-15}$	$2.40 \cdot 10^{-15}$	$1.35 \cdot 10^{-15}$
100	$5.04 \cdot 10^{-13}$	$2.83 \cdot 10^{-13}$	$1.59 \cdot 10^{-13}$	$8.96 \cdot 10^{-14}$
200	$2.03 \cdot 10^{-10}$	$1.14 \cdot 10^{-10}$	$6.43 \cdot 10^{-11}$	$3.61 \cdot 10^{-11}$
300	$6.36 \cdot 10^{-9}$	$3.58 \cdot 10^{-9}$	$2.01 \cdot 10^{-9}$	$1.13 \cdot 10^{-9}$
400	$8.68 \cdot 10^{-8}$	$4.89 \cdot 10^{-8}$	$2.56 \cdot 10^{-8}$	$1.55 \cdot 10^{-8}$
500	$6.01 \cdot 10^{-7}$	$3.39 \cdot 10^{-7}$	$1.90 \cdot 10^{-7}$	$1.07 \cdot 10^{-7}$

TABLE A5.

Reduction factor α

P_T in torr T in $^{\circ}\text{C}$	10^{-3}	10^{-4}	10^{-5}	10^{-6}
50	$2.67 \cdot 10^{-5}$	$4.74 \cdot 10^{-5}$	$8.44 \cdot 10^{-5}$	$1.50 \cdot 10^{-4}$
100	$1.08 \cdot 10^{-4}$	$1.92 \cdot 10^{-4}$	$3.41 \cdot 10^{-4}$	$6.07 \cdot 10^{-4}$
200	$7.96 \cdot 10^{-4}$	$1.42 \cdot 10^{-3}$	$2.52 \cdot 10^{-3}$	$4.48 \cdot 10^{-3}$
300	$2.51 \cdot 10^{-3}$	$4.48 \cdot 10^{-3}$	$7.94 \cdot 10^{-3}$	$1.42 \cdot 10^{-2}$
400	$6.01 \cdot 10^{-3}$	$1.07 \cdot 10^{-2}$	$1.77 \cdot 10^{-2}$	$3.39 \cdot 10^{-2}$
500	$1.14 \cdot 10^{-2}$	$2.04 \cdot 10^{-2}$	$3.62 \cdot 10^{-2}$	$6.45 \cdot 10^{-2}$

TFTR TRITIUM HANDLING CONCEPTS

Harold J. Garber

Westinghouse Electric Corporation
Fusion Power Systems

ABSTRACT

The Tokamak Fusion Test Reactor, to be located on the Princeton Forrestal Campus, is expected to operate with 1-2.5 MA tritium-deuterium plasmas, with the pulses involving injection of 50-150 Ci (5-16 mg) of tritium. Attainment of fusion conditions is based on generation of a ~ 1 keV tritium plasma by ohmic heating and conversion to a moderately hot tritium-deuterium ion plasma by injection of a "preheating" deuterium neutral beam (40-80 keV), followed by injection of a "reacting" beam of high energy neutral deuterium (120-150 keV). Additionally, compressions accompany the beam injections. Environmental, safety and cost considerations led to the decision to limit the amount of tritium gas on-site to that required for an experiment, maintaining all other tritium in "solidified" form. The form of the tritium supply is as uranium tritide, while the spent tritium and other hydrogen isotopes are getter-trapped by zirconium-aluminum alloy. The issues treated include: (1) design concepts for the tritium generator and its purification, dispensing, replenishment, containment, and containment-cleanup systems; (2) features of the spent plasma trapping system, particularly the regenerable absorption cartridges, their integration into the vacuum system, and the handling of non-getterables; (3) tritium permeation through the equipment and the anticipated releases to the environment; (4) overview of the tritium related ventilation systems; (5) design bases for the facility's tritium clean-up systems.

INTRODUCTION

The Tokamak Fusion Test Reactor (TFTR) will be the first U.S.A. fusion device built to obtain experimental data on the fusion of tritium and deuterium under or at near power reactor conditions. The TFTR is to provide design, construction, and operational experience with a prototypical T-D burning fusion power system. The main objectives of the TFTR program are:

- Demonstrate T-D fusion power at break-even conditions.
- Gain design, construction and operating experience with a prototypical fusion power system.
- Provide for a significant part of the engineering preparation to proceed to Experimental Power Reactor (EPR-1).

The TFTR plasma will be operated in the two-energy-component mode. Plasma heating is to be accomplished both by ohmic heating, adiabatic compression and neutral beam injection. Most of the fusion reactions will result from interaction between the relatively cold tritium ions in the bulk plasma and highly energetic deuterium ions introduced as neutral beams.

Sizing of the TFTR device is dictated by the dual requirements of confining 120-150 keV deuterons and attaining $n \cdot \tau_e \approx 10^{13} \text{ sec/cm}^3$ at $T_e \approx 5 \text{ keV}$. No electrical power will be generated. The fusion neutron yield will be measured. Attenuation of these neutrons within the biological and structural shielding will not generate significant quantities of thermal power in these components. Establishment of proximity to "scientific break-even" will be based on comparing the fusion energy yield to the energy input of the injected neutral beams.

Tables 1 and 2 list the key systems design criteria and some selected design features of TFTR. Figures 1, 2 and 3 illustrate some of the configuration concepts for the reactor torus and support systems, the vacuum vessel, and the bellows packages of the vacuum vessel. The main purpose of the bellows is to incorporate a high electrical resistance for the torus vacuum vessel.

Table 1. TFTR Systems General Design Criteria

- Components and Techniques to be as Close to State-of-the-Art as is Practical
- Minimize the Total Cost of the Program
- Minimize Component Activation to Promote Access and Maintainability
- Minimize Tritium Inventory - Use Simple, Reliable, Ultra-Safe Handling Systems
- Provide Experiments - Flexibility and Accessibility
- Maximize Relevance of Technology Approach to Future Devices - Within Cost and Risk-Level Constraints

Table 2. TFTR Selected Design Features

• Total Number of Pulsing Cycles	5×10^5
• Vacuum Vessel Inner Minor Radius, meters	1.1
• Vessel Major Radius, meters	2.65
• Vessel Material	AISI 305 SS
• Vessel Construction	Bellows, Ring-Stiffened Shells
• Vessel Protection	
Plates Over Bellows	AISI 305 SS
Beam Catchers	Tungsten-Molybdenum
• Diverter	None
• Plasma Cross-Section	Circular
• Flat-Top Time at Maximum TF, sec	1
• Peripheral Device Shielding	Borated, Lead Loaded Mortar, Metal Sheathed
• Test Cell Shielding	
Material	Ordinary Concrete
Wall Thickness, meters (ft)	1.8 (6)
Ceiling Thickness, meters (ft)	1.2 (4)
• Work Area Dimensions, meters (ft)	
TFTR Cell	36.6 x 33.5 x 15.8 (120 x 110 x 52)
Shielded Bay	36.0 x 18.3 x 7.3 (118 x 60 x 24)
Hot Cell	19.5 x 12.2 x 9.0 (64 x 40 x 29.5)
Warm Cell	18.3 x 15.8 x 9.0 (60 x 52 x 29.5)

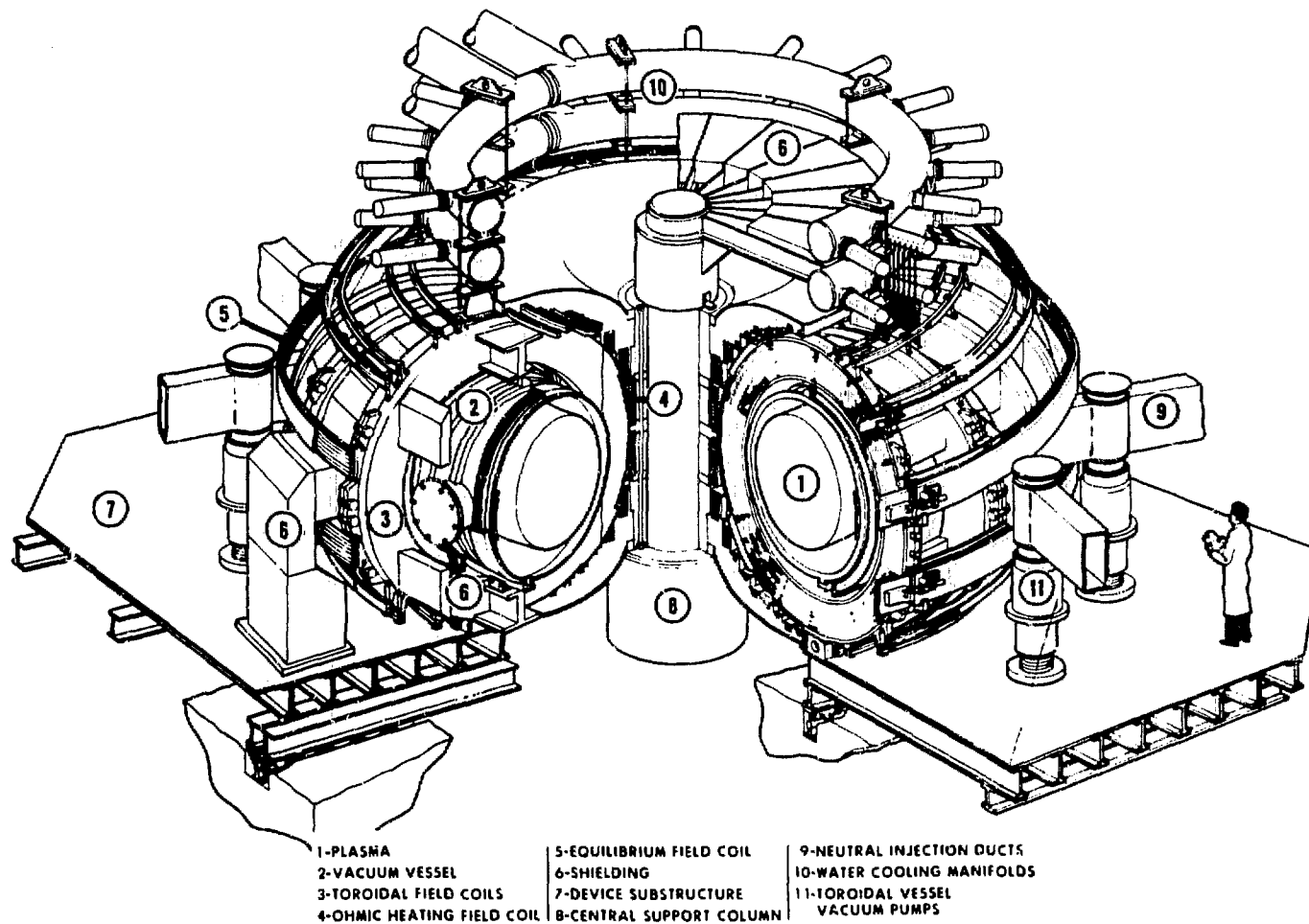


Fig. 1. Tokamak Fusion Test Reactor

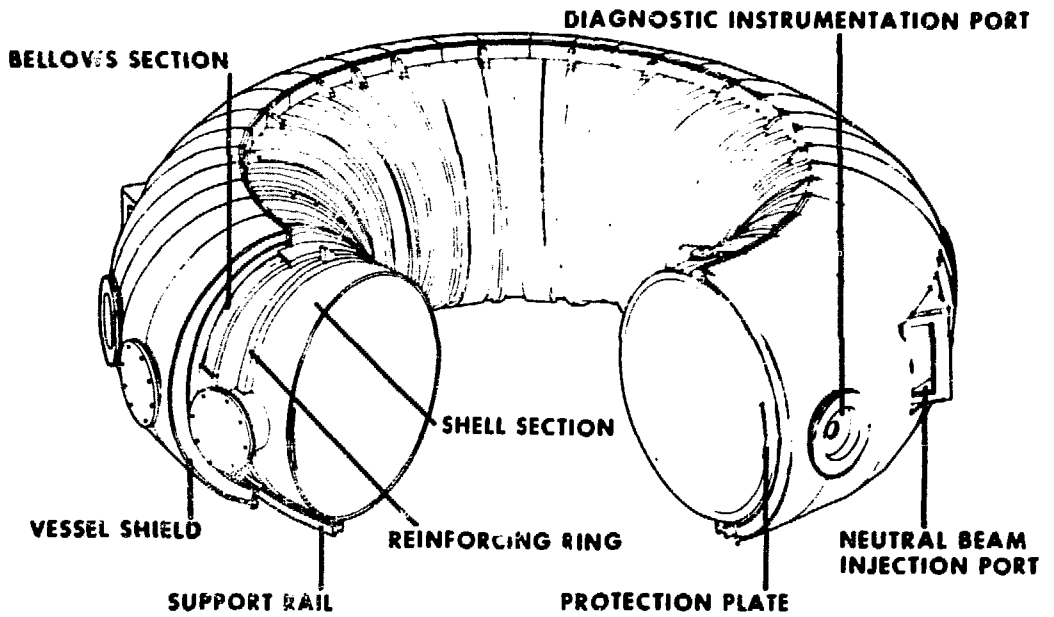


Fig. 2. Vacuum Vessel

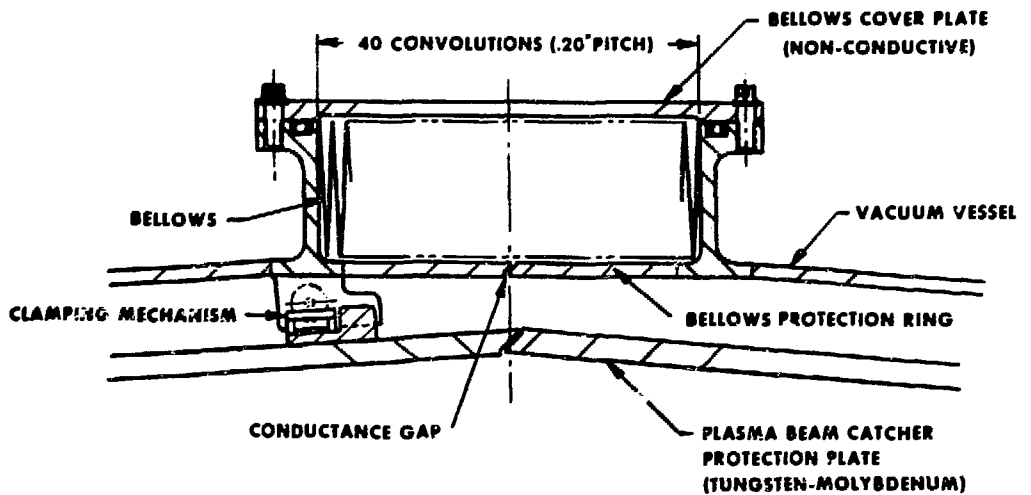


Fig. 3. Bellows Assembly

The TFTR Facility, comprising the tokamak devices and the support installations (electrical power generators and conditioners, experimental and laboratory facilities, conventional offices, etc.) is to be located on a controlled-site area of the James Forrestal Research Campus of Princeton University. This location for TFTR made strong impacts on the selection of tritium handling concepts under consideration for the facility design.

Conceptual design effort on TFTR by Princeton University Plasma Physics Laboratory and Westinghouse Fusion Power Systems Engineers-Scientists began in early-February 1974. This presentation describes the tritium handling concepts operative in mid-June 1975. Changes in modes of operation, program scenarios, and facility configuration have been many and additional changes incidental to the design maturity processes can be expected to have their effect on the tritium handling concepts and design features incorporated into the ultimate design.

ELEMENTS OF TRITIUM HANDLING AND VACUUM SYSTEMS

Because of the close intertwining of both the design and operations of the vacuum and tritium handling system, any description of one of these systems necessarily requires reference to the details of the other. For this reason, the basic features of the vacuum and tritium handling systems are treated here in tandem fashion. In subsequent sections, additional details regarding tritium handling are presented.

The primary functions of the vacuum pumping system are summarized in Table 3, in general terms.

The aforementioned functional requirements can be satisfied by a number of design approaches. However, for the TFTR located at Princeton, constraints are imposed by this location on workable design approaches for both the torus vacuum pumping and tritium handling systems. In this connection, very careful consideration of the safety issues involved virtually dictated the following tritium handling approaches:

- Minimize site constraints, with virtually zero release for credible accidents.

Table 3. Functions of the Torus Vacuum Pumping System

- Provide a low base pressure prior to initiation of a pulse in order to limit the impurity level during the pulse.
- Exhaust the fuel and plasma by-product gases after a pulse in preparation for reloading the torus with the desired high purity gas, in consideration of experimenting with a variety of plasma precursor gases (H, D, T, T-D, He, He-3).
- Remove the working gas and impurities liberated during contemplated discharge cleaning operations.
- Remove the T-D gas mixtures generated during the tritium buildup and tritium flushout campaigns associated with interspersed modes of operation in order to move from D-D plasma studies to T-D plasma testing, and then back to D-D plasma experiments.
- Exhaust the torus, initially and as required following shutdowns, from atmospheric pressure to the desired base pressure in a reasonable time.
- Provide the necessary capacity to permit continuous pulse operation, when handling tritium, for hundreds of pulses under closed system conditions to totally contain the tritium because of its radioactivity and biological effects. This function includes storage of tritium bearing non-trappable gases until appropriately decontaminated.

- Maximum potential release must be within regulatory limits.
- Maximize containment and minimize dilutions of releases, within constraints of accessibility and maintainability.
- Provide means for relatively rapid cleanup for both normal and emergency release conditions.

In connection with selecting the design approach to be followed for the torus vacuum pumping and tritium handling systems, the options indicated in Table 4 were considered. The options selected as best suited for TFTR are indicated by the Asterisked items in Table 4.

VACUUM PUMPING SYSTEM

For the vacuum system, to the extent possible, conventional ultra-high vacuum components and technology are to be employed. System subassemblies are to be vacuum pre-baked to reduce subsequent outgassing, mainly hydrogen. Assembly will be by tungsten-inert (TIG) welding and metal gaskets. In-situ bakeout of the totally assembled torus with its many diagnostic equipment appendages to an effectively high temperature ($\sim 400^{\circ}\text{C}$) has been under consideration. However, the efficacy and practicality of a 400°C in-situ total system bakeout is in doubt, and instead a lower bakeout temperature is under consideration. Final vacuum conditioning is to be effected using plasma discharge cleaning to obtain specific outgassing rates of $\leq 10^{-10}$ and $\leq 10^{-12}$ torr liter/sec cm^2 for hydrogen and other gases respectively and a system base pressure of $\sim 4 \times 10^{-8}$ torr.

The T-D operation of TFTR imposes a variety of design requirements not normally encountered for ultra-high vacuum systems. The presence of tritium dictates that the vacuum system be closed in regard to this gas, so that the pumps cannot discharge tritium to the atmosphere. Additionally, because of the possibility of hydrogen isotope exchange, for reasons of safety and materials integrity against radiation damage, hydrocarbons, elastomers and other organics must be avoided. Accordingly, the pumping system consists of cryogenically trapped mercury diffusion pumps which discharge

Table 4. Tritium Handling and Vacuum System Design Options

- Tritium Handling
 - Gaseous vs. solid tritide inventory*
 - One time use and trap* vs. recover-purify-recycle
- Vacuum Pumping
 - Mercury diffusion* vs. oil diffusion vs. cryogenic panels
- Torus and Vacuum Equipment
 - All welded* vs. joints for torus
 - Hard bakeable seals* vs. soft seals for vacuum system
- Containment
 - Complete equipment enclosure vs. selected equipment enclosure*
 - Facility sealed tritium boundary* vs. open construction
 - Closed cycle ventilation* vs. in-out ventilation during pulsing operations
- Emergency Cleanup of Accidental Releases
 - Trap and dispose* vs. recovery-recycle
 - General facility system vs. separate dedicated systems*

into a foreline volume where hydrogen isotopes are removed. The significant feature of the closed vacuum system is the use of non-sublimating Zr-Al getter pumps* in the foreline (getter cartridges housed within canisters) to convert the gaseous hydrogen isotopes to solids by solution (physi-sorption) in bulk metal or by hydriding. In this regard, the foreline volume is sized to accommodate accumulation of other gases (which may include non-getterables containing tritium) for extended times before the critical backing pressure of the diffusion pumps is reached. These gases are removed by mechanical vacuum pumps.

Other engineered safety features for the vacuum system design against releases of tritium to the atmosphere include catalytic crackers in the foreline to fragment gases such as tritiated hydrocarbons (non-getterables) and a tritium cleanup system which can be valved to the exhaust of the mechanical pumps to remove any residual tritium. Cleanup is to be accomplished by catalytic oxidation and desiccation of the tritiated water. Monitoring of the partial pressures and tritium containing gases in the foreline is to be accomplished through use of a differentially pumped residual gas analyzer. The aforementioned tritium cleanup system (torus cleanup system) is a dual-purpose device which can also be valved to detritiate the torus of both bulk gaseous residual tritium and adsorbed surface layer tritium prior to opening up the torus for maintenance.

The material of construction for the vacuum vessel and all associated components and ducts for the vacuum system is austenitic stainless steel. As used here, the "vacuum system" designation means the main vacuum vessel, the vacuum pumping system from the pumping ports on the main vessel through the pumping lines, valves and traps, the neutral beam injector lines back through the first "effective-trap", and all appendage arms to the main vacuum vessel such as diagnostic equipment arms and the like. This includes any volume that is in communication with the main vacuum vessel that can contribute impurities to the discharge.

*Sorb-AC Zr-Al getter pump cartridges are a product of SAES (Societa Apparecchi Elettricie Scientifici), described in several product brochures (e.g. AC69124).

In general, the demountable flange and joint seals for the vacuum system are to use flat copper gaskets of the Conflat type*. In particular situations, gold wire seals will be used. Additionally, in situations where joints cannot be made demountable by the gasket-flange method due to space and configuration limitations, welded joints will be used. This also applies to welded joints that are designed to be cut open and re-welded on infrequent occasions.

As shown in Figure 1, high vacuum pumping of the torus is provided by eight 16-inch diffusion pumps or their equivalent which are mounted on the neutral beam injector arms in order to conserve ports, in pairs. Each pump, in turn, is provided with two getter canister stations, one of which is on-line and the other in stand-by. Periodically, groups of eight getter canisters will have to be replaced with reactivated canisters. The frequency of regeneration-replacement of the canisters as well as the number of getter cartridges installed per canister depends both on the facility operations schedule and the sorption capability of the getters under the expected operating conditions. Figure 4 shows some of the construction features of representative getter cartridges. Not shown on the Figure 4 is an integrally mounted heater capable of raising the temperature of a cartridge to 700-850°C. These heaters come into action under different circumstances: 1) initial vacuum activation of the getter by elevation to ~750°C to diffuse thin surface layers of zirconium oxide and nitride into the metal interior matrix; 2) occasional heating the getters to ~200°C to restore pumping capability that may have been impaired by impurities generated by plasma discharges; 3) regenerating the cartridges by a 700-750°C vacuum treatment off-site at an ERDA-facility to drive off the reversibly sorbable-desorbable hydrogenous species.

Back-transport of mercury into the torus is prevented by the liquid nitrogen cooled cryogenic traps. Similarly, vapors from the mechanical pumps are prevented from contaminating the vacuum system by zeolite traps which are periodically reactivated by means of integral internal heaters. During such reactivation, a flow of metered

*"Conflat" is a registered trademark of Varian Associates, Palo Alto California. Similar and interchangeable flanges are available under other names from other U.S.A. manufacturers.

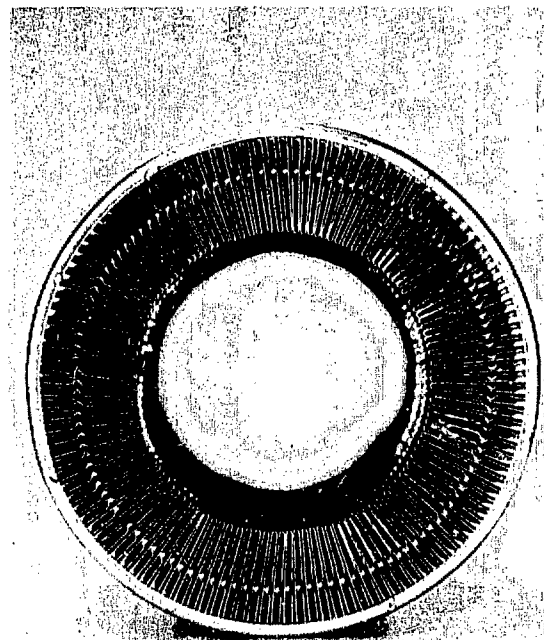


Fig. 4. SAES "SORB-AC" C-200 Zr-AL Getter Cartridge

dry nitrogen carries the vapors released from the traps to the mechanical pumps. Additionally, carry-over of oil mists and vapor from the mechanical pumps to the gas holding tanks is prevented by interposing pairs of oil traps between the mechanical pumps and the gas holding tanks. The main purpose of these is to guard against oil carry-over into the torus and vacuum system when the torus cleanup system is being used to detritiate the torus.

Table 5 summarizes the principal features of the design of the torus vacuum system. The schematic shown in Figure 5 gives more details of the overall vacuum system and the manner in which it interfaces with the torus, torus cleanup system and tritium storage and delivery system. Also shown are the piping arrangements that permit operation of the torus cleanup system in its dual-function role. With appropriate settings of the valving, either one of the cleanup operations - holdup tank or torus detritiation - can be readily accomplished.

The key dimensional characteristics of the torus and vacuum system that are relevant to expected chronic tritium releases during TFTR operations and standby at base pressure during non-operating periods are listed in Table 6.

TRITIUM STORAGE AND DELIVERY

This section deals with an overview of the features of the TFTR tritium storage and delivery system, whose functions are to store and deliver prescribed quantities of highly purified tritium to the torus on demand by remote operation from the facility control center. Table 4 lists the design options open for the tritium handling system, and indicates which options were selected. These options were selected on the basis that they best comply with the safety and operations guidelines set forth previously. Further details concerning the basis for these selections have been reported elsewhere.^{1,2}

Table 7 summarizes the ways, in general, in which the TFTR tritium handling concepts selected implement the safety and operations guidelines prescribed previously.

The basis for selection of depleted uranium metal as the working material for the tritium generator over other candidates (Ca, Cs, Gd, Hf, La, Li, Mg, Na, Nb, Pd,

Table 5. Torus Vacuum System Design Summary

- Eight 40.6 cm (16-Inch) Mercury Diffusion Pumps (or its equivalent) Coupled to Neutral Beam Ports
- Valve and Cryogenic (LN) Cold Trap for Each Diffusion Pump
- Hard Seals, TIG Welding, Metal Gaskets
- Pre-Bakeout at $> 400^{\circ}\text{C}$, Lower for Selected Parts
- Discharge Cleaning
- Outgassing Rates
 - Hydrogen $\leq 5.9 \times 10^{-15}$ g mole/sec cm^2 (10^{-10} torr liters/sec cm^2)
 - Other Gases $\leq 5.9 \times 10^{-19}$ g mole/sec cm^2 (10^{-12} torr liters/sec cm^2)
- Base Pressure $\sim 5.3 \times 10^{-6}$ Pa (4×10^{-8} torr)
- Pumping Capabilities
 - Achieve Base Pressure within 4 Hours Starting from Atmospheric
 - Achieve Base Pressure within 1 Minute after Each Pulse
 - Pump Out e-Fold Time of 4 Seconds for T-D Mixtures
 - 4.1×10^4 liters/sec for Hydrogen, 2.4×10^4 liters/sec for T:D = 1:0.214
- High Fore Pressure Tolerance, 1.3 - 67 Pa (0.01 - 0.5 torr)
- Closed Vacuum System During Pulse, Diffusion Pumps Discharge into Ballast Tank
- Zr-Al Getter Cartridge Canisters in Backing System, Two Canister Stations per Pump - One On-Line, One in Stand-By
- Mechanical Backing Pump via Zeolite (Oil) Trap for Removal of Non-Hydrogen Gases and Non-Getterables
- Residual Gas Analyzers and Monitors to Check Tritium Content and Other Gases
- Gas Holding Tanks for Interim Storage of Non-Hydrogens and Non-Getterables
- Oil Demisters and Traps in Feed Line to Gas Holding Tanks
- Tritium Cleanup System to Treat Holding Tank Gases, via Cracking, Catalytic Oxidation, Desiccation

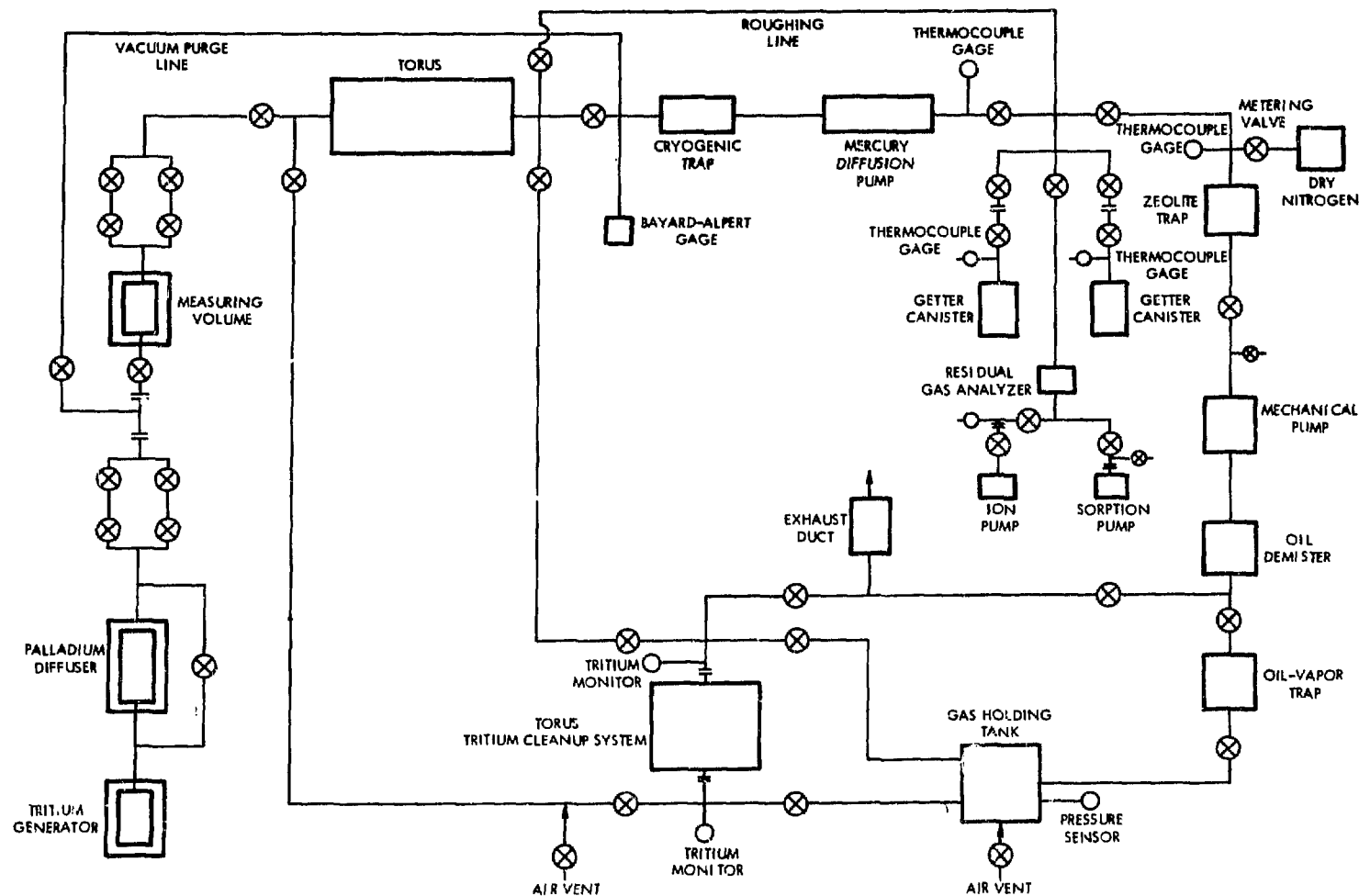


Fig. 5. Simplified Schematic of TFTR Tritium Handling - Vacuum System

Table 6. Torus and Vacuum System Dimensional Parameters

Item	Internal Surface cm^2	Thickness cm	Surface to Thickness Ratio cm	Internal Volume cm^3
Torus				
Bellows	6.41×10^6	0.102	6.31×10^7	
Body	8.28×10^5	0.675	1.23×10^6	
Reinforcing Rings	1.10×10^5	7.62	1.44×10^4	
Sub-Total	7.35×10^6		6.43×10^7	7.17×10^7
Diagnostics	1.35×10^6	0.388	3.48×10^6	6.75×10^6
Margin for Ducts, Ports, Etc.	1.74×10^6	0.388	4.48×10^6	1.04×10^7
Totals	1.04×10^7		7.22×10^7	8.89×10^7

Table 7. Tritium Handling Implementation

- Solid State Storage
 - Tritium Evolved from U-Tritide Dissociation
 - Spent Tritium Trapped on Zr-Al Getters
- Maximum Gas Inventory
 - One Pulse Worth ~ 70-100 Ci (< 10 mg)
- Reference Tritium Inventory
 - 25,000 Ci On-Line
 - 50,000 Ci On-Site ~ 5 g
- Containment
 - Tritium Generator in Sealed Inerted Steel Enclosure
 - Tritium Dispenser in Inerted Glove Box
 - Generator-Dispenser Housed in Sealed Fuel Vault
- Cleanup Systems
 - Cracking of Tritiated Hydrocarbons, Catalytic Oxidation, Desiccation
 - Five Systems: 2 Emergency, 3 On-Line
- Hazardous Operations Off-Site
 - Generator Charging
 - Getter Disposal or Regeneration

Sc, Ta, Th, Y, Zr) included many items such as: a) ready tritide formation at modest temperatures as 200-400°C; b) tritides are essentially non-dissociable at ~20°C; c) respectable, convenient dissociation pressure at ~300°C in the range 30-100 torr; d) essentially zero vapor pressure for the virgin metal up to ~500°C; e) acts as a vigorous and retentive getter for impurities as oxygen, carbon, and nitrogen; f) is non-reactive with other materials of construction for the generator as stainless steels, tungsten, nichrome, alumina. Despite the pyrophoricity of finely divided tritided uranium, which can be mitigated by a double-containment design of the tritium generator and additionally emplacement of the generator in an inerted gas enclosure, uranium is the preferred working material. The self-purification capability and favorable dissociation pressure are compelling attributes for its selection. This is exemplified by the dissociation pressure behavior shown in Table 8. The entries shown in Table 8 for tritided zirconium indicate why Zr Al alloy is a most desirable choice for the getters for the vacuum system - the tritium is very firmly trapped below temperatures of 250°C, leading to excellent getter pumping behavior.

Figure 5, presented previously, shows the interfacing between the vacuum system and the tritium handling system. Figure 6 is a schematic portrayal of the proposed TFTR tritium storage and delivery system. The more salient features of this system are: a) configuring the system in two packages, with the generator and palladium alloy diffuser housed in a sealed steel box, and the tritium dispenser located within a glove-box; b) providing two generator boxes, one of which is on-line, and the other on stand-by when it is not enroute to or at an ERDA facility for initial charging or re-charging with tritium; c) maintenance of an argon atmosphere within the two mated enclosures; d) providing a tritium cleanup subsystem within containment for the generating and dispensing system; e) providing a closed-cycle, sealed, dedicated cooling water package for this system so as to confine any tritium permeated to the small volume of coolant held up in this unit.

The foregoing exposition has outlined some of the general features of the hardware involved in the TFTR vacuum and tritium handling systems. In the ensuing section,

Table 8. Comparison of Tritide Dissociation Pressures (Torr)

Temperature, °C	UT _{2.8} ⁽³⁾	UT ₃ ⁽⁴⁾	ZrT ₂ ⁽⁵⁾
0	3.2×10^{-5}	1.3×10^{-7}	5.9×10^{-28}
50	2.6×10^{-3}	4.3×10^{-5}	7.4×10^{-22}
100	6.6×10^{-2}	3.1×10^{-3}	2.2×10^{-17}
150	7.7×10^{-1}	7.9×10^{-2}	5.6×10^{-14}
200	5.3	1.0	2.7×10^{-11}
250	2.6×10^1	8.3	4.1×10^{-9}
300	9.3×10^1	4.6×10^1	2.6×10^{-7}
400	7.0×10^2	6.6×10^2	1.6×10^{-4}
500	3.1×10^3	4.8×10^3	1.9×10^{-2}
600	9.8×10^3	2.2×10^4	7.3×10^{-1}
700	2.4×10^4	7.4×10^4	1.4×10^1

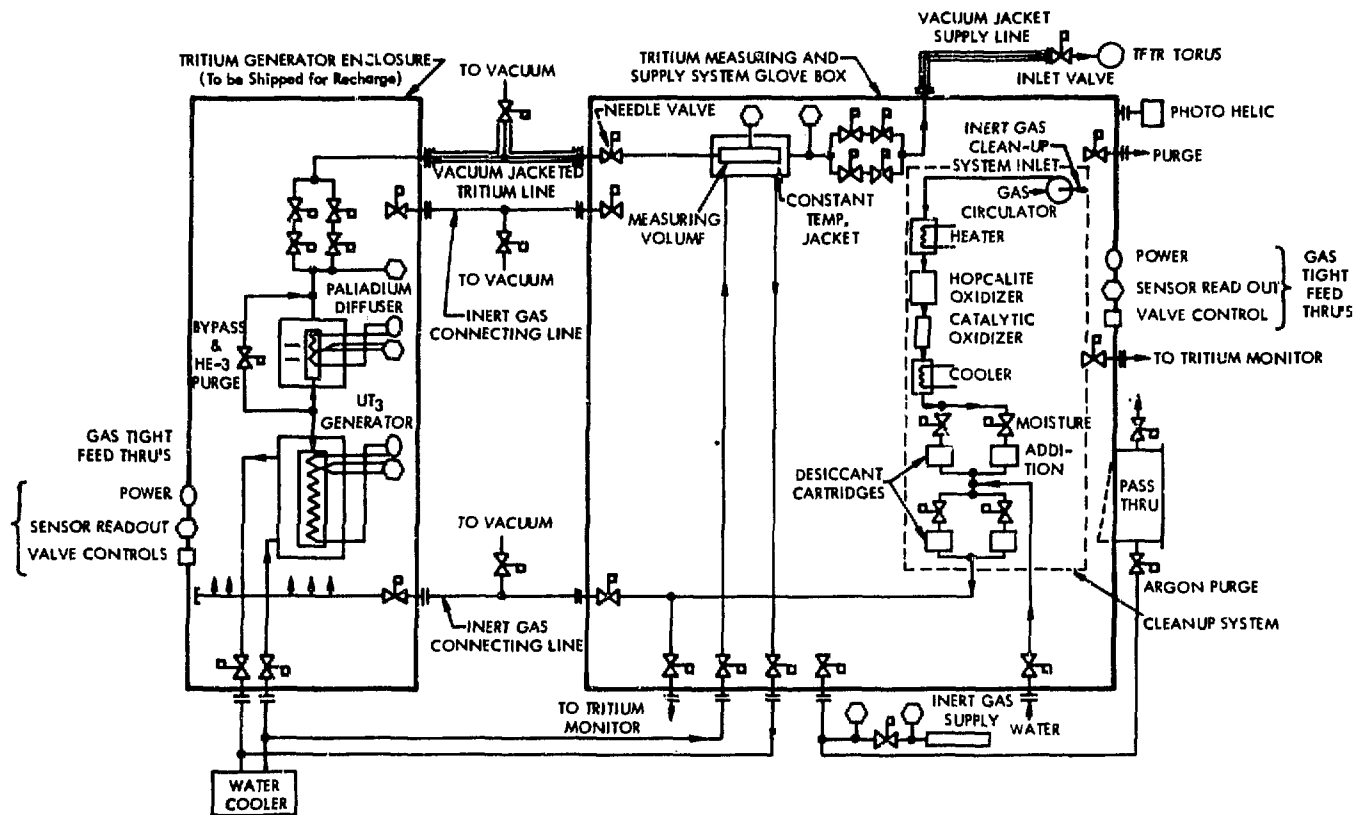


Fig. 6. Schematic of Tritium Storage and Delivery System

the attention is focused on the tritium containment issue and the approaches being followed in containment design.

TRITIUM CONTAINMENT DESIGN APPROACH

Because of the relatively high permeability of tritium, unavoidable small releases of tritium of a chronic nature occur from tritium containing equipment. In order to minimize these releases into the facility as well as prevent more than tolerable releases of tritium to the environment under normal operating conditions or in the event of failures, the facility design and prescribed mode of operation has been guided by a number of safety oriented requirements and policy. Some of these have already been considered in the preceding exposition.

The approaches taken to prevent tritium releases to the environment in general have proceeded along the lines of: a) providing the susceptible areas with single or multiple enclosures and equipping these enclosures with appropriately sized detritiating systems; b) providing engineered safeguards which prevent release even in the case of single fault failures; c) designing the ventilation systems with flexibility, permitting operation in a number of modes and adequate to cope with all foreseeable failures.

Regarding the issue of providing enclosures for tritium containing equipment and building-in engineering safeguards, the following exemplify the approaches taken:

1. The policy followed is to contain and detritiate in the smallest possible volume of equipment enclosure, with adherence to the practice of avoiding dilution to the extent possible.
2. The tritium generator housing is a double-wall thick steel shell, providing the first level of containment, and the two wall temperatures are maintained low so as to minimize permeation.
3. The gaseous tritium supply and measuring-injection systems are contained in an 80 ft³ inerted (argon) atmosphere enclosure both to minimize escape of permeated tritium into the facility and to prevent uranium tritide

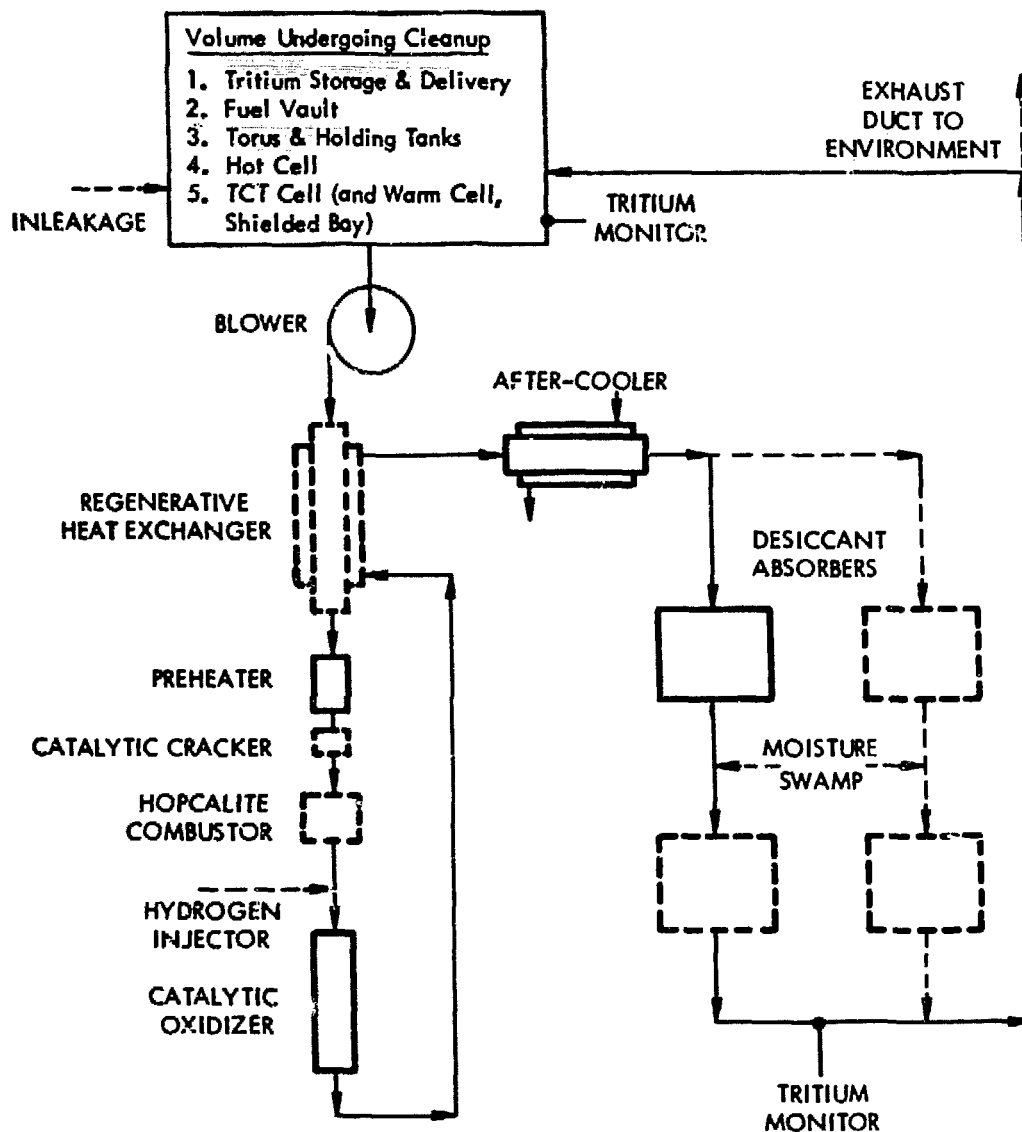
oxidation-nitriding in event of rupture. As shown in Figure 6, these enclosures are equipped with a continuously operating self contained oxidant (Hopcalite) and noble metal catalytic oxidizer detritiation system, wherein the tritium is trapped in desiccant (disposable cartridge design) as firmly bound tritiated water. This system circulates the box gas through the system continuously at a rate of 1.5 cfm and has a design capability to reduce the box gas level to $5 \times 10^{-6} \mu\text{Ci}/\text{cm}^3$ (mpc for controlled areas) within 24 hours following a release as large as 25,000 Ci. This provides the second level of containment.

4. The cooling water system for the tritium generator, measuring volume, and cleanup system gas after-cooler is a closed-cycle 30 gallon package type sealed unit, thereby confining the tritium permeated through the equipment walls of the units cooled to this small volume of water. Eventually, this water will have to be removed, solidified (as concrete), and disposed of by off-site burial.
5. The gaseous tritium supply and measuring-injection system enclosures are contained in a doubly sealed 1,200 ft^3 fuel vault. This vault, which provides a third level of containment, is maintained at 1 inch of water negative with respect to ambient, is located within the sealed "tritium boundary" of the facility, and is supplied with a closed-cycle 7 cfm detritiating system and monitors. This cleanup system, which can be operated continuously or intermittently, has a design capability to reduce the vault air activity to $5 \times 10^{-6} \mu\text{Ci}/\text{cm}^2$ or lower within 72 hours subsequent to a release of as much as 50,000 Ci.
6. The stand-by tritium generator box, which is also stored in the fuel vault, but not connected in-line, is contained in a sealed all-steel enclosure.
7. As indicated in Figure 6, the tritium bearing lines interconnecting the two enclosures in the fuel vault and the supply line to the torus are vacuum jacketed. The vacuum space is monitored.

8. As described previously and shown on Figure 5, a torus cleanup system is provided to detritiate the torus prior to opening up the torus in preparation for disassembly-modification operations. This involves closed-cycle circulation of air at ambient pressure at a rate of 40 cfm through the torus and cleanup system. Provided with both a hydrocarbon catalytic cracker and a catalytic oxidizer, this unit has a design capability to trap 2000 Ci within a 24 hour cleanup period. As indicated previously, this unit serves in a dual capacity. It operates on the gases of the gas holding tank, and may also come into service in the event of a burn-through of the torus wall.
9. A facility recovery system is provided to detritiate the TFTR cell air. Employing closed-cycle operation on the cell air at 4,000 cfm, and based on catalytic oxidation with desiccation of the tritiated water, this unit has a design capability to reduce the air activity to $5 \times 10^{-6} \mu\text{Ci}/\text{cm}^3$ or lower within 48 hours following a release of 2000 Ci. Operation of the detritiator is activated by detection of a pre-set activity level of the cell air or rate of vacuum loss in the torus. This system can also be used for clean-up campaigns necessitated by releases originating in the facility warm cell or transfer bay.
10. A facility recovery system similar to that for the TFTR cell is provided for the hot cell.

Tritium Cleanup Systems

Figure 7 illustrates the general make-up of a detritiation system in schematic fashion, based on catalytic oxidation of gaseous tritium followed by trapping the tritiated water on either a chemical reacting or physi-sorbing type or desiccant. For the TFTR application, the current preference is for a chemical reacting type of desiccant for safety reasons in that such materials do not release the trapped tritiated water unless heated to relatively high temperatures ($\sim 200^\circ\text{C}$). This is in contrast to physi-sorbing desiccants which are already releasing at $\sim 60^\circ\text{C}$.



- NOTES:**
1. Valves not shown.
 2. Dotted items optional, depending on specific cleanup system.
 3. All systems operate in "closed cycle mode," except for inleakage and compensating purge at detritiated stream.

Fig. 7. Simplified Schematic, Tritium Cleanup Systems

For physi-sorbing desiccants, which are mainly used with regenerative-duty cycles, it is usually necessary to use a "moisture swamping" technique and several stages of absorption to achieve high overall system decontamination factors on the order of 10^6 or more. In the case of very low concentrations of tritium in gases fed to the oxidation catalyst, it is advantageous to utilize the "carrier technique" of injecting a small flow of hydrogen upstream of the catalyst. This situation applies to the cleanup systems for the TFTR cell and the hot cell. For gases to be treated that are very oxygen deficient, as is the case for the inert atmosphere within the tritium storage and delivery system enclosures, Hopcalite can be used to supply the oxygen. Hopcalite is a proprietary solid regenerable preparation (50 w/o MnO_2 , 30 w/o CuO , 15 w/o CoO , 5 w/o Ag_2O) which is a vigorous oxidant at modest temperatures.

Table 9 lists the principal features of the five aforementioned tritium cleanup systems. When designed in accordance with the requirements set forth in Table 9 for the design basis tritium releases listed, the five cleanup systems will yield the decontaminations shown in Figures 8 and 9. The dropoff of the tritium concentration in the atmosphere within the containment being treated with time elapsed since actuating the system is shown in Figure 8. Figure 9 is a companion plot which shows the course of dropoff of residual activity with time of operation of the systems, in terms of percent of the initial total release not yet removed from the containment atmosphere. In connection with the emergency cleanup campaigns, a small amount of tritium release to the environment will occur from the TFTR cell and the hot cell. This stems from the need to discharge a small stream of partially decontaminated air to the environment equivalent to the air inleakage rate in order to maintain a negative pressure in the cell being treated. Figure 10 shows the progression of the cumulative activity releases, and indicates that these releases are essentially negligible.

TFTR CELL VENTILATION

Properly speaking, ventilation of the TFTR cell is an intimate part of the containment operations. However, the ventilation approach selected is treated here as a separate item.

Table 9. Cleanup System Principal Features and Design Parameters

ITEM	Tritium Storage & Delivery	Fuel Vol., ft	Torus	Hot Cell	TFTR Cell
Treated System Gas Volume, m ³	2.27	36.8	88.9	2140	19,440
Design Basis Tritium Release, Ci	25,000	50,000	2,000	2,000	2,000
Gas Medium	Argon	Air	Air	Air	Air
Estimated Air Inleakage Rate, m ³ /min	0	0	0	0.37	3.40
Nominal Gas Medium Inlet Conditions					
Temperatures, °C	25	25	22	22	22
Absolute Humidity, %	<1	40	40	40	40
Operation Mode	Continuous	Continuous	Intermittent	Emergency	Emergency
Maximum Initial Tritium Concentration, $\mu\text{Ci}/\text{cm}^3$	1.1×10^4	1.5×10^3	2.3×10^1	9.4×10^{-1}	1.0×10^{-1}
Design Basis Final Tritium Concentration, $\mu\text{Ci}/\text{cm}^3$	1×10^{-8}	1×10^{-8}	1×10^{-8}	1×10^{-8}	1×10^{-8}
Operations Goal Final Tritium Concentration, $\mu\text{Ci}/\text{cm}^3$	5×10^{-6}	5×10^{-6}	5×10^{-6}	5×10^{-6}	5×10^{-6}
Desired Cleanup Operation Period, hr	24	72	24	48	48
Design Basis Flow Rate, m ³ /min	0.042	0.20	1.13	15.6	110
Hermetic Type Gas Compressor-Circulator	No	Yes	Yes	Yes	Yes
Capability for Cracking-Oxidizing Hydrocarbons	No	No	Yes	No	No
Hopcalite Oxidizer	Yes	No	No	No	No
Capability for Hydrogen Carrier Addition	No	No	No	Yes	Yes
Regenerable Desiccant Absorbers	No	No	No	No	No
Desiccant Form	Cartridge	Cartridge	Bed	Bed	Bed
Catalyst Nominal Operating Temperature, °C	200	200-300	400-500	200-300	200-300
Design Basis T ₂ O Pickup by Desiccant, g	9.3	18.5	0.76	0.76	0.76
System Volume Turnovers for Cleanup Campaign	27	25	18	21	17
Heater/After-Cooler Capability, kW	0.2	1.2	10	80	700

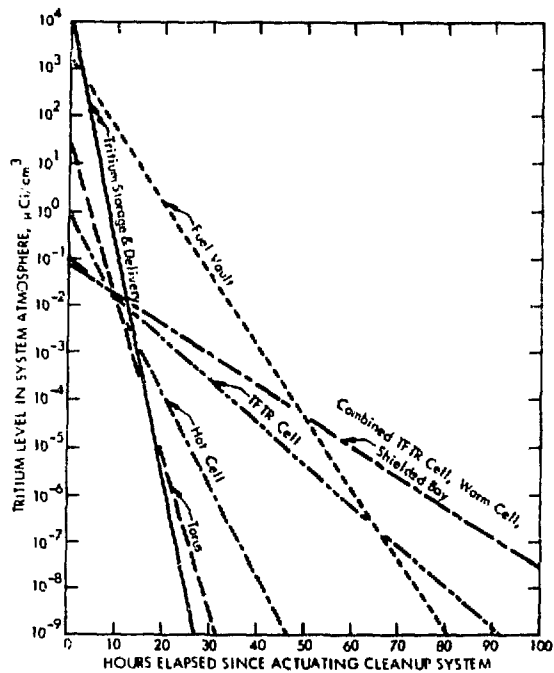


Fig. 8. Tritium Cleanup Campaigns,
Temporal Variation of
Activity Levels

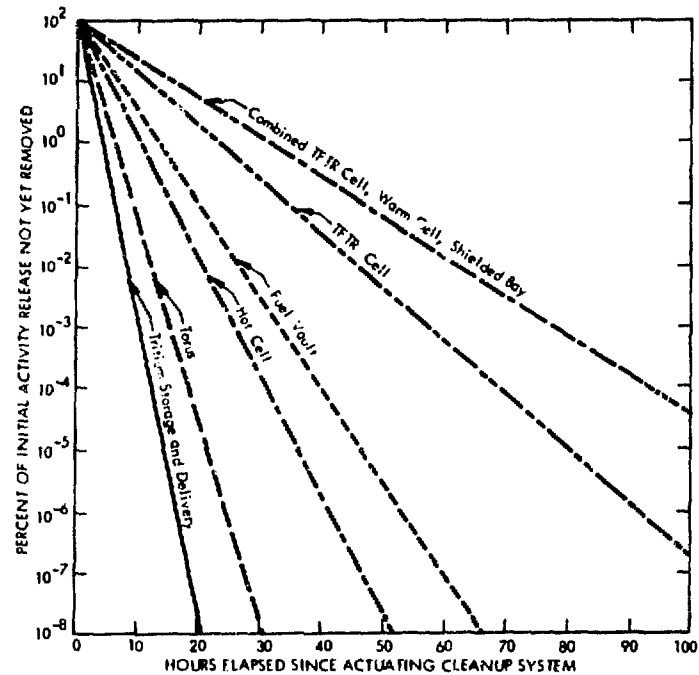


Fig. 9. Tritium Cleanup Campaigns,
Operation Time Versus Cleanup
Activities

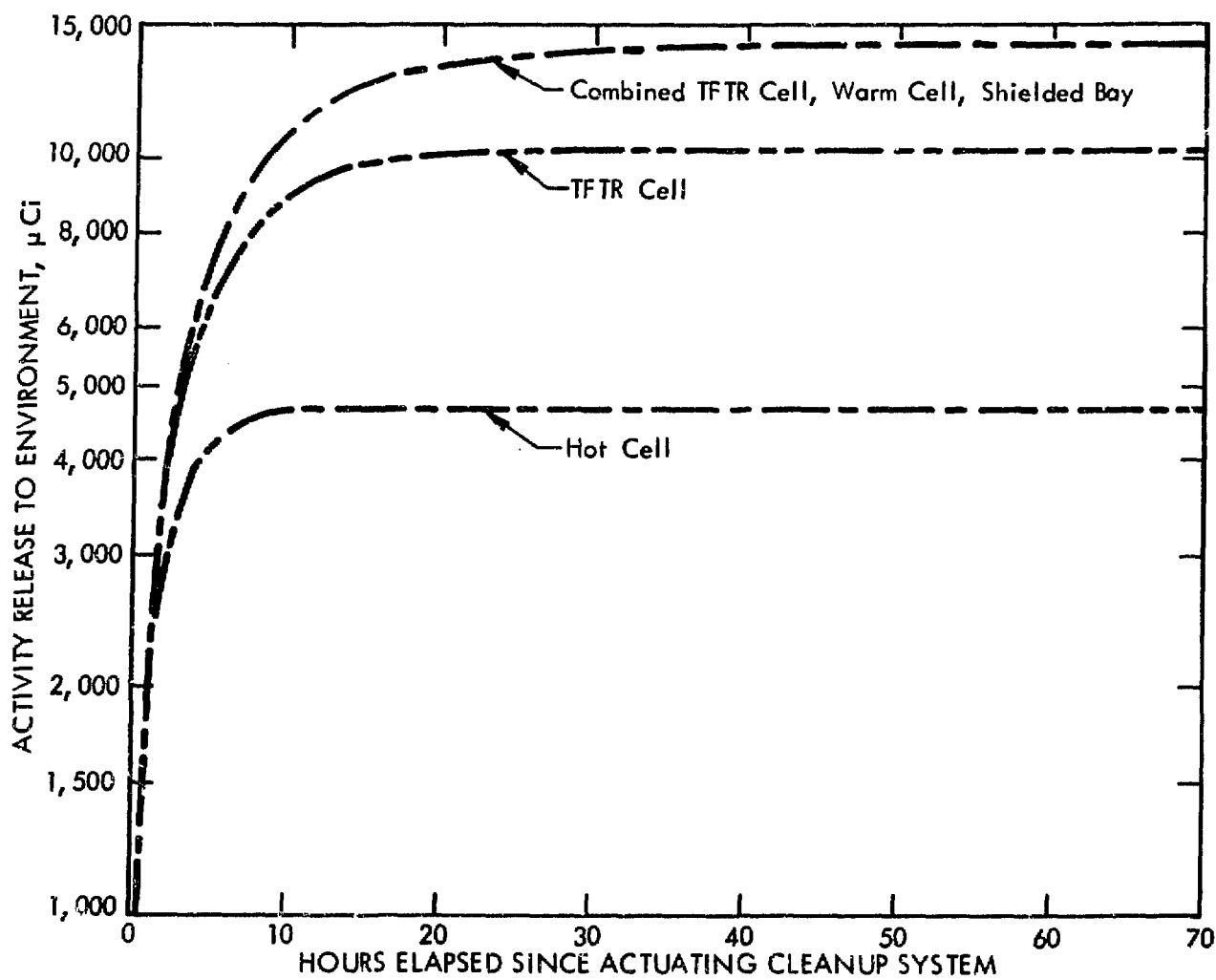


Fig. 10. Tritium Cleanup Campaigns - Activity Releases to the Environment

During normal operations, the ventilation system for the TFTR cell is designed to function in the following modes, with automatic transfer from one mode to another through appropriate valve settings and blower activations:

1. The cell is always maintained at sub-atmospheric (~ 1 inch of water negative) so as to prevent outleakage and to promote inleakage, estimated as 120 cfm.
2. During inoperative periods, the conditioned air ($\sim 21^{\circ}\text{C}$, 40% absolute humidity, two stages of filtering) flow in the cell is two changes per hour, on a once-through basis, corresponding to $\sim 23,000$ cfm.
3. During operative periods and during standby conditions subsequent to completing a pulse sequence, the cell is sealed and the cell air is re-circulated within the cell through the air cooling package to provide the requisite heat dissipation capability, at a rate equivalent to two cell turnovers per hour. During these periods, the chiller condensate is directed to the monitored retention tanks.
4. During all operation modes, an amount of air equivalent to the inleakage is exhausted to the environment, estimated as 120 cfm.
5. The duration of the sealed cell mode for a post-operative period is determined by decay requirements of neutron activated generated nitrogen (N-13 , 9.96 m; N-16 , 7.14 sec) and argon (Ar-41 , 1.83 hr) nuclides.
6. The pressure in the fuel vault is maintained ~ 1 inch of water negative with respect to ambient by tying it to the TFTR cell through a double set of check valves which permit flow in one direction, from the vault to the cell. The vault normally is in a sealed condition, so that the flow involved is both very small and intermittent. The objective is to insure that any leakages for the vault will always be inward from door seal leaks rather than outward. The vault is not otherwise ventilated.

In the event of an abnormal discharge into the TFTR cell, the air handling system is designed so as to accomplish the following actions:

1. The cell is always maintained at sub-atmospheric pressure, at ~ 1 inch of water negative, except for unusual situations when both access doors may be open. If the cell access sealed double doors were open at the time of the release, these doors would be closed rapidly to place the cell in isolation with respect to the environment.
2. The cell tritium cleanup system would be actuated and operated until monitoring of the cell atmosphere indicates that detritiation has reduced the activity level to below $5 \times 10^{-6} \mu\text{Ci}/\text{cm}^3$. Operation of this system involves recycling of the cell air in close-loop mode through the catalytic oxidizer-desiccant at 4,000 cfm. As indicated previously, the design capability of this system is substantially complete detritiation of the cell air from releases as large as 2,000 Ci within a 48 hour period of operation, with the cell air making ~ 17 complete passes through the detritiation system. This treatment eventually traps substantially all of the cell air initial humidity (~ 340 lb) and the tritiated water (~ 1 g) on the desiccant, which when spent would be disposed of by off-site burial.
3. In order to promote cell air mixing during the cleanup process, the exhaust blower of the ventilation system is operated in closed cycle mode, at the full 23,000 cfm capacity.
4. As in the case of normal operations, the ~ 1 inch negative pressure in the cell would induce air leakage at a rate of ~ 120 cfm during the cleanup process. Compensation for this is afforded by bleeding a corresponding amount of cleaned air from the treatment system to the facility exhaust duct via a 120 cfm blower.
5. Resumption of ventilation in the normal operating mode would occur when monitoring of the cell air indicates an activity level below mpc.

Figure 11 shows schematics of the air treatment hook-ups for the aforementioned operating modes. Fast acting valves and controls will accomplish changeover of the ventilation and cleanup operations to the modes shown. These manipulations are initiated at the facility central operations control.

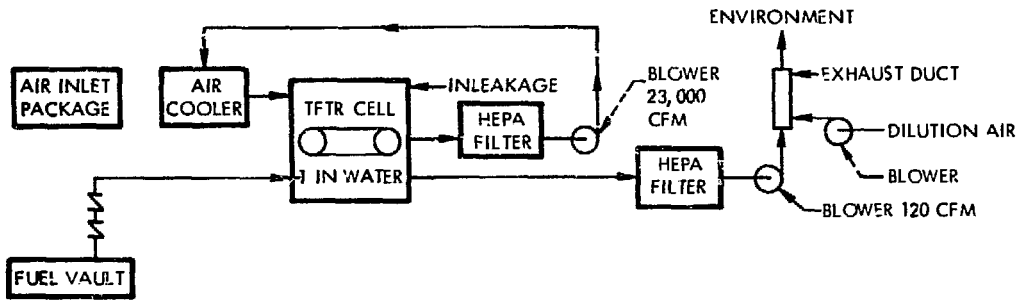
TRITIUM REQUIRED FOR T-D PULSE EXPERIMENTS

The tritium injection required for a pulse depends on a number of factors, primarily on the specific plasma experiment scenario and the quantity of gas held up in "dead-zones" within the vacuum chamber that does not get drawn into the plasma. In this connection, Table 10 summarizes the plasma characteristics under consideration for TFTR T-D experiments and the corresponding tritium required for these scenarios. These tritium requirements include the neutrals tritium contributions, based on extrapolation of data presented by Jacobsen⁶. As shown in Table 10, tritium injections of ~ 76 Ci (~ 7.9 mg) are required for an average 1 MA plasma and ~ 107 Ci (~ 11.2 mg) for 2.5 MA plasmas. Based on the expectation that the operations mix will be in the ratio of 1 MA plasmas: 2.5 MA plasmas = 9:1 the overall mean tritium injection required for a pulse experiment is ~ 80 Ci. For such mean T-D full power pulse experiments, the required neutral beam deuterium injection comes to 0.214 moles of O_2 per mole of T_2 in the plasma. This figure derives from energetics considerations, and includes both the preheat and fusion promoting energy requirements.

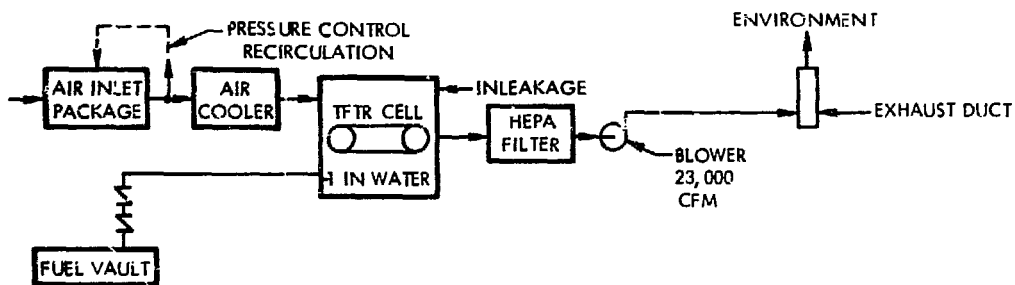
Based on the expectation that TFTR operations will be restricted to 1000 full power T-D pulses per year, with this restriction arising from neutron activation and maintenance considerations, the base annual tritium consumption amounts to $\sim 78,900$ Ci. However, the actual annual tritium consumption will be considerably greater than 78,900 Ci, with the overage determined by such details of the operations schedule as:

- a) number of T-D pulses conducted in a sequence;
- b) manner in which one component (D, H, He, He-3) plasma experiments are interspersed with the T-D pulse experiments;
- c) vacuum vessel surface conditionings required to attain the required plasma precursor gas composition. The surface conditioning requirement stems from the fact that the internal surfaces of the vacuum system under the best of circumstances are covered

NORMAL CELL SEALED OPERATION DURING CONDUCT OF PULSES



NORMAL CELL OPERATION DURING OUTAGES



EMERGENCY CELL CLEANUP OPERATION

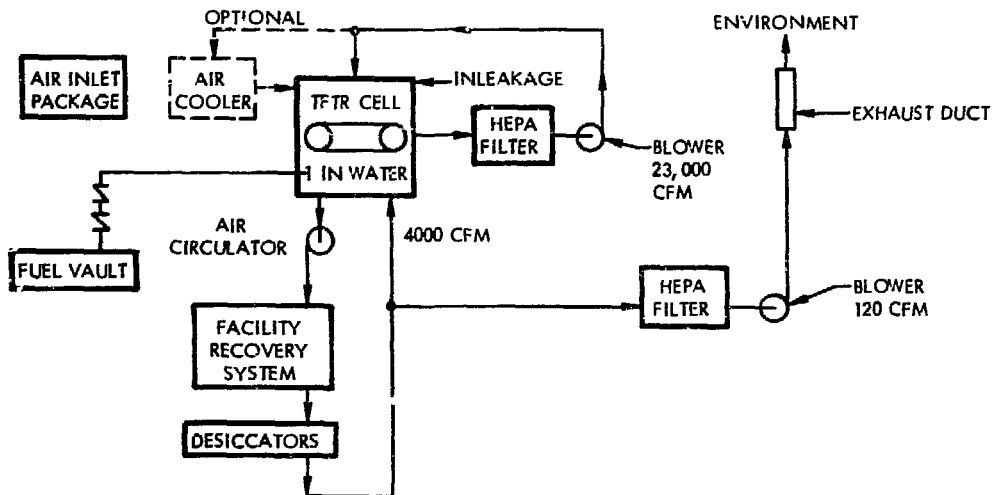


Fig. 11. Schematics of TFTR Cell Air Treatment Hookups

Table 10. Plasma Characteristics Related to Tritium Requirements

ITEM	Transient Regimes		Quasi-Static Regimes	
	Strong Compression	Weak Compression	Weak Compression	High Current
Plasma Designation	A	B	C	D
I, Compression, MA	1	1	1	2.5
R _p , Precompression, cm	314	310	310	248
R _p , Compression, cm	(209)	(248)	(248)	-
r _p , Precompression, cm	56	60	60	85
r _p , Compression, cm	(46)	(85)	(85)	-
n _e (Max (Compression), Particles/cm ³)	1.1×10^{14}	9.9×10^{13}	1.1×10^{14}	6×10^{13}
Tritium Particles in Torus	1.37×10^{21}	1.48×10^{21}	1.48×10^{21}	2.04×10^{21}
Ci/Pulse*				
In Torus	65.7	71.0	71.0	98.2
In Diagnostic Spaces	6.2	6.7	6.7	9.2
Total	71.9	77.7	77.7	107.4

ITEM	Torus	Torus and Diagnostics
Mean Tritium Injection, Ci/Pulse		
1 MA Plasmas	69.2	75.7
90% 1 MA and 10% 2.5 MA Plasmas	72.1	78.9
Molecules T ₂ Injection/Pulse	7.506×10^{20}	8.214×10^{20}
Deuterium Injection, g mole/pulse		
90% 1 MA and 10% 2.5 MA Plasmas for T:D = 1:0.214	0.00582	

*1 g Tritium = 9589.4 Ci

with adsorbed gases, so that the inter-transport of gaseous species between the adsorbed material and the contiguous gas within the torus leads to substantial "memory effects". These memory effects can be very substantial, particularly where the required plasma precursor gas composition for a new set of experiments differs significantly from the compositions involved for immediately previous experiments. This is readily understood in light of the following circumstances: a) for an estimated adsorbed population density of 8.5×10^{14} molecules/cm², the adsorbed layer population within the TFTR vessel seen by the plasma precursor gas is $\sim 7 \times 10^{21}$ molecules; b) the gas within the torus gas phase at the vacuum system base pressure of $\sim 4 \times 10^{-8}$ torr prior to plasma precursor gas injection consists of $\sim 1 \times 10^{17}$ molecules; c) the gases injected for a typical pulse experiment consists of $\sim 7 \times 10^{20}$ molecules.

The circumstance that the quantity of adsorbed gas is on the order of 8-20 times greater than the amount of gas injected for the conduct of a pulse experiment, coupled with the ready interactions between the adsorbed and injected gases has far-reaching ramifications that complicate the execution of the experimental program. The greater of these complications include the following:

1. Requirement of substantial quantities of "build-up" tritium when changing over from non-tritium to tritium based plasma experiments, and vice versa, requirement of many "flush-outs" when changing back to non-tritium experiments.
2. Relatively slow change in gas phase composition effected by each build-up or flush-out increment for these operations.
3. Imposition of a high loading on both tritium and non-tritium hydrogenous material on the getter cartridges.
4. Need for increased frequency of shipment of tritium generators for replenishment off-site.
5. Need for increased frequency of removal of spent getters canisters and shipping them off-site for regeneration or disposal.

6. Complicating the matter of recovering the gettered tritium (e.g. by cryogenic distillation) at the regeneration facility due to the lower concentration of tritium.

The nature of some of these effects is illustrated in Figures 12, 13, 14 and 15. Figure 12, for example, shows the progress of tritium concentration build-up with a number of tritium build-up injections conducted, indicating that 22 such injections are needed to attain the 0.824 tritium mole fraction required for a mean T-D full power pulse experiment. Figure 13, in contrast, shows the progress of tritium concentration drop-off during a deuterium flush-out campaign, starting out with a 0.824 tritium mole fraction. This plot shows that 140 deuterium flush-outs are required to reduce the tritium mole fraction to 10^{-6} . Figure 14 and 15 are companion plots which show the effects of the number of pure deuterium pulses conducted per year interspersed among T-D pulses conducted in sequences of 40 pulses, on the required getter changing frequency, gettered tritium per shipment, and makeup of the gettered material. The estimates shown in Figure 15 are based on attainment of a large gettering capability of 14,000 torr liters of hydrogenous species using SAES C-500 cartridges.

The quantities cited above are based on the assumption of rapid interchanges between the gas phase and adsorbed layer species, with ultimate identical composition attainment in these phases. This may not be entirely valid. Another complication is the memory effect due to embedment of plasma gases (hydrogen, deuterium tritium, etc.) into the vacuum vessel limiters, liners, and beam catchers. Gases that leave the plasma will probably penetrate into the metal a few Angstroms. Previously embedded material may also be knocked back out and can also diffuse out. Although the precise course of the associated gas recycling is difficult to define, it is clear that its path will depend on the previous events within the device. Past experience at Princeton Plasma Physics Laboratory has been that many pulses in a single working gas can be required to obliterate the memory effects from earlier discharges⁷.

As mentioned previously, the expected operating basis is 40 two-component T-D full power pulses per operating day, with the time interval between pulses equal to

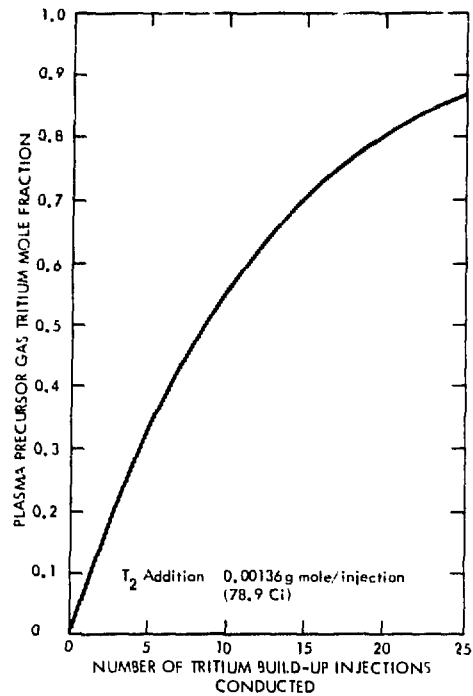


Fig. 12. buildup of Tritium Concentration with Number of Tritium Injections

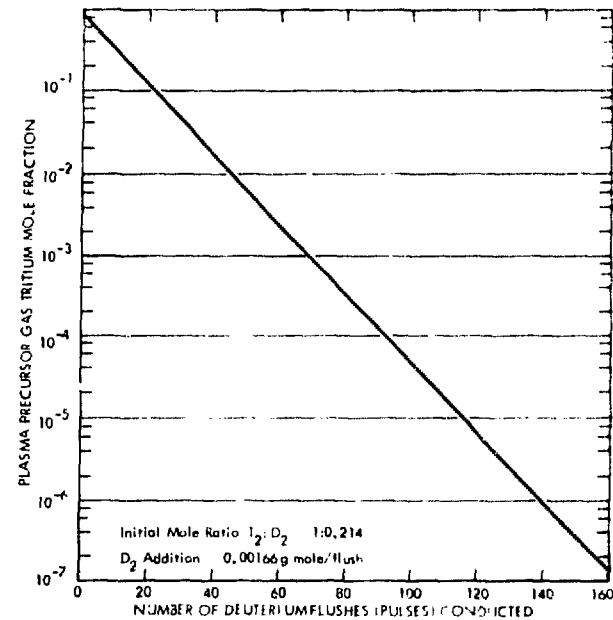


Fig. 13. Tritium Concentration Drop-Off with Number of Deuterium Flushings

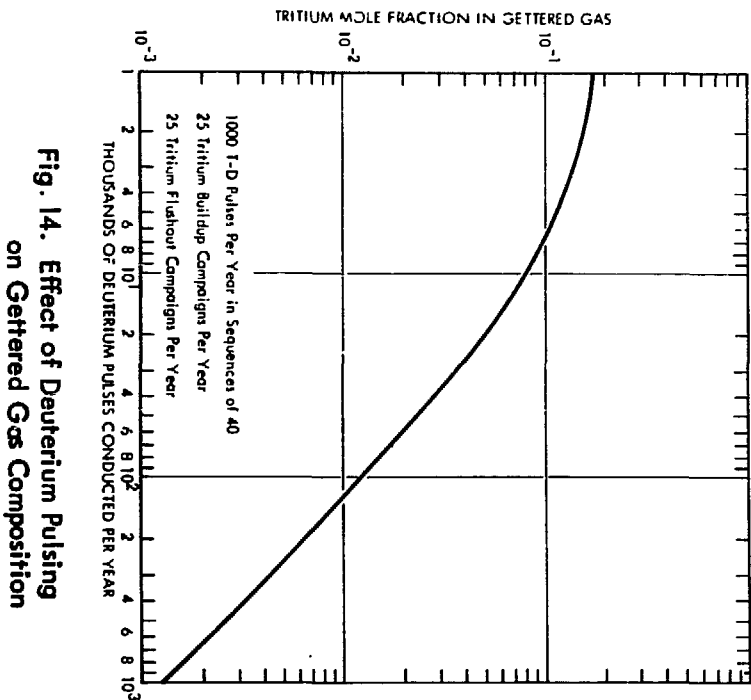


Fig. 14. Effect of Deuterium Pulsing
on Gettered Gas Composition

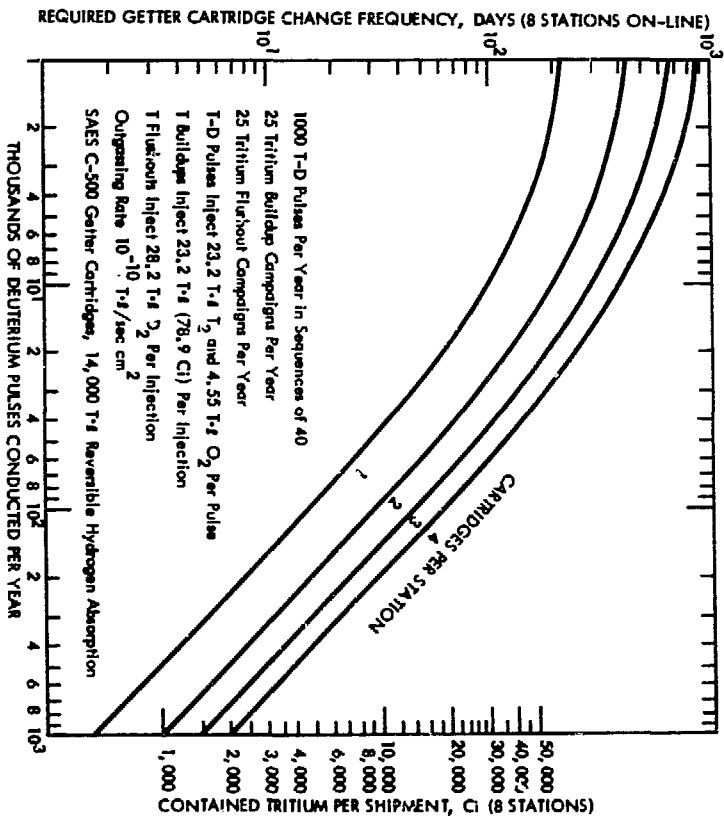


Fig. 15. Required Cartridge Change Frequency
for Torus Vacuum System

or greater than five minutes, as restricted by the design of the field coil cooling water system. Extremes may be encountered. For example, situations are anticipated where there might be as low as one full power T-D pulse per day. On the other hand, because there is a significant advantage operationswise to pulse at the maximum repetition rate when all of the equipment is working properly, a maximum of 96 pulses is anticipated over any eight hour shift. If the T-D pulsing campaigns are carried out with different numbers of pulses per sequence, and these are immediately followed by return to non-tritium operations, the gross tritium consumption per mean T-D full power pulse will vary widely as shown by the following tabulation:

<u>T-D Pulses/Sequence</u>	<u>Ci Consumed/Full Power T-D Pulse</u>
1	1815
40	122
96	97

For the 40 pulse per sequence expected operational mode, the annual tritium consumption amounts to 122,300 Ci, of which 43,400 Ci is for tritium build-up operations.

ESTIMATED TRITIUM RELEASES

The preceding sections dealt with some of the more relevant features of the system conceptual design and methodology used to handle tritium so as to limit tritium leakage and release to the environment to below significant levels. This concluding section quantifies the estimated tritium releases for normal TFTR operations.

The major chronic gaseous tritium release to be encountered will be the continual permeation-diffusion through the torus walls to the cell air on an around-the-clock basis, once the plasma test commences. During outage periods, the torus and its associated auxiliaries will be maintained at an internal pressure of $\sim 4 \times 10^{-8}$ torr, with the contained gas residue having a tritium partial pressure ranging downward from $\sim 3 \times 10^{-8}$ torr, the exact value depending on the nature of the campaign conducted immediately prior to the outage. The very low baseline tritium contents

within the equipment will give rise to "background tritium levels" in the cell air and the air discharged from the facility exhaust duct. The estimated background levels associated with three relevant outage situations, based on the two changes per hour ventilation rate are:

$\sim 1 \times 10^{-8} \mu\text{Ci}/\text{cm}^3$ for outages immediately following T-D pulsing sequences or following T buildups, and

$\sim 1 \times 10^{-11} \mu\text{Ci}/\text{cm}^3$ for outages immediately following T flushouts.

Both of these levels are substantially below the $5 \times 10^{-6} \mu\text{Ci}/\text{cm}^3$ and $2 \times 10^{-7} \mu\text{Ci}/\text{cm}^3$ mpc values for controlled and uncontrolled areas specified in ERDAM-0524 (Tables I and II).

The foregoing estimates do not account for the additional permeation that may occur during the experiments due to the higher tritium pressures that exist within the equipment during these operations where these pressures may peak to $\sim 3 \times 10^{-4}$ torr, as shown in Figure 16. The additional permeations associated with these conditions are relatively small compared to the background permeations, primarily because of the short time periods during which these higher tritium pressures prevail. Precise calculation of the tritium releases expected is exceedingly complex, and was not attempted. Instead, a simpler approach was used, both conservative and adequate for conceptual design purposes. Although all of the permeations involved are transient in character, calculation of them has been as though they were of a steady state nature, instantly responsive to changes in transport driving forces. In order to introduce additional conservatism in the estimates, an equivalent additional partial pressure contribution from the adsorbed layer tritium was incorporated into the calculation routine.

Table 11 lists the assumptions made regarding plasma scenario, operations sequence and schedule, and rudiments of the model used in making the performance estimates. As indicated in Table 11, the expected operation mode is taken as the estimation base. This presumes that: a) 40 mean T-D full power pulses are conducted in each sequence at five minute intervals during an operating day, whereupon the device is

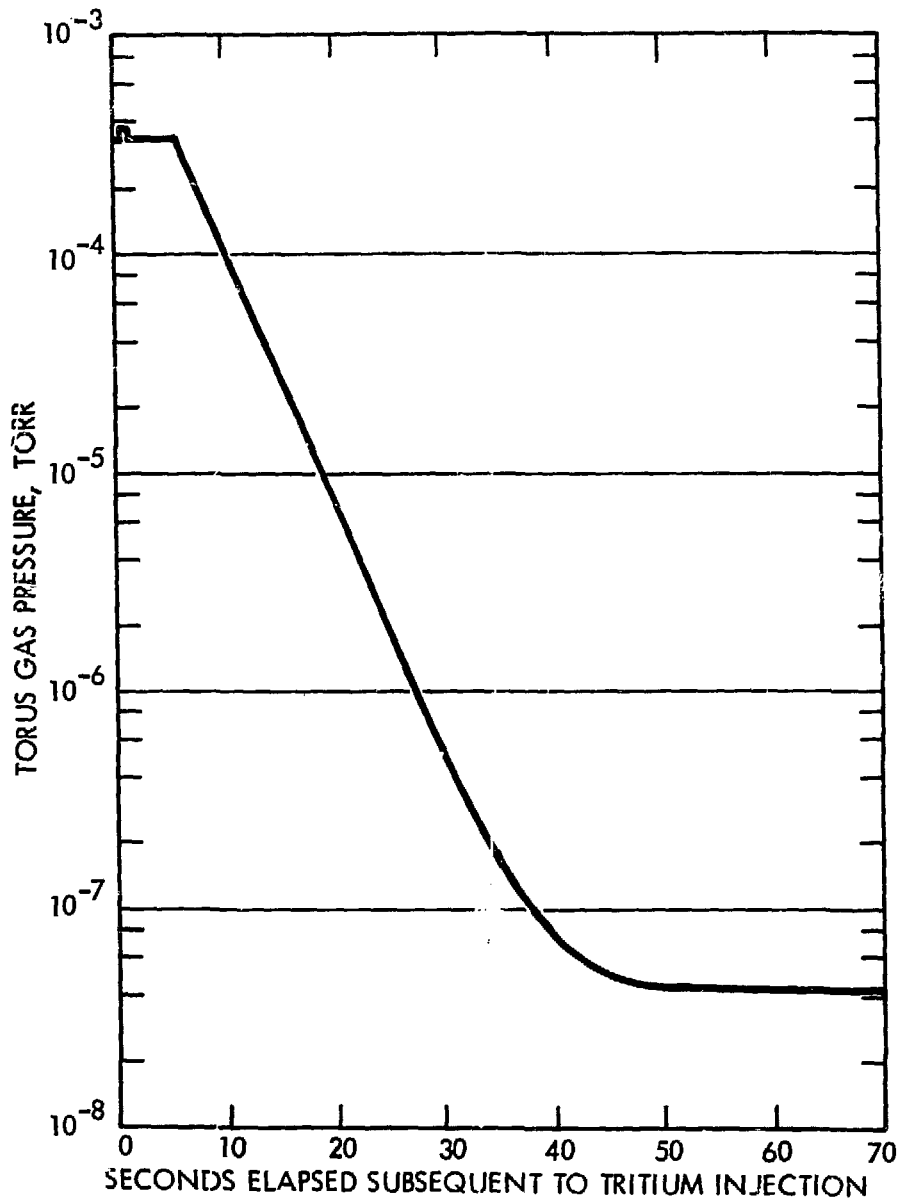


Fig. 16. Torus Pressure Variation During a Typical Pulse Experiment

Table II. Tritium Handling Assumptions and Estimations Model

- 1000 T-D Full Power Pulses Per Year, 90% 1 MA, 10% 2.5 MA
- 40 T-D Pulses in a Typical Sequence, Conducted in One Day
- 5 Minute Interval Between Pulses
- Tritium Hold Times - 1 Second for Pre-Plasma, Formation and Burn; 5 Seconds for Post-Pulse to Initiation of Pump-Down
- Base Pressure of 5.3×10^{-6} Pa (4×10^{-8} torr)
- Tritium Injection - 78.9 Ci/Pulse; 72.1 Ci to Torus, 6.8 Ci into Diagnostics
- Tritium Buildup and Flushout Campaigns Each Conducted in One Day
 - 22 Buildups - Each 78.9 Ci to Yield 0.824 Mole Fraction Tritium
 - 140 Flushouts with Deuterium - Each 0.00166 g Mole to Yield 1×10^{-6} Final Tritium Mole Fraction
- Specific Outgassing Rate - 5.9×10^{-15} g mole/sec cm² (10^{-10} torr liter/sec cm²)
- Adsorbed Layer Population - 8.5×10^{14} molecules/cm²
- Rapid, Essentially Instantaneous Equilibration Between Hydrogenous Species in Torus Gas Phase and Adsorbed Material
 - Species Mole Fraction Corresponding to Species Total Population
 - Neglect Chemical Interactions Among Hydrogen Isotopes
- Operation Temperature Essentially at Ambient - 21°C
- Neutral Beam Deuterium Injection - 0.000267 g mole/pulse
- Emergency Basis Removable Tritium Gas in Release - 2000 Ci
- Reversible Hydrogenous Species Absorption Capacity of a Getter Cartridge - 0.82 g mole (14,000 torr liters)
- Quasi-Steady State Treatment of Tritium Permeation
 - Essentially Instantaneous Response to Changes in Partial Pressure
 - Sievert's Half-Power Pressure Law Applicable Over Entire Partial Pressure Range
 - Effective Partial Pressure for Driving Permeation Includes Contribution from Adsorbed Layer
 - Effective Permeability Includes Grain Boundary Contribution, 1.4×10^{-15} STP cm³ cm/sec cm² Pa^{1/2} (1.6×10^{-14} STP cm³ cm/sec cm² torr^{1/2})
 - Discount Permeation Impedance of Bellows Assembly Cover Plates
- TFTR Cell Ventilation According to:
 - 2 Air Changes Per Hour Only after Cessation of Tests
 - Inleakage and Equivalent Continuous Exhaust for Maintenance of 2.5 cm Water (1 inch) Sub-Atmospheric Pressure - 3.4 m³/min (120 cfm)

kept at the vacuum base pressure during the rest of the day; b) on the day immediately prior to this T-D pulsing sequence, the device is prepared for this pulsing by building up the tritium mole fraction in the adsorbed layer and residual gas to 0.824 by conducting 22 build-ups, whereupon the device is maintained at the vacuum base pressure during the rest of this day; c) on the day immediately following the T-D pulsing sequence, the device is prepared for return to deuterium plasma parameter testing via conduct of 140 flushouts with deuterium. The buildups and flushouts, of course, may be pulse experiments which generate plasma data.

The tritium permeation estimates made for the various operations modes are based on an extrapolation (to lower temperature) of a least squares treatment⁸ of published transport properties of tritium in austenitic stainless steels^{9, 10, 11, 12, 13, 14, 15}, including contributions due to grain boundary transport. The principal results of these estimates are displayed in a set of plots.

Figures 17 and 18 show the temporal variations of tritium concentration in the gas within the torus and the rate of tritium release out of the device during the tritium buildup and flushout phases of TFTR operations. Figure 19 indicates how the tritium level in the TFTR cell will vary throughout the day for one day each for separate phases of tritium buildup, T-D pulsing, and tritium flushout. The estimates indicate that a peak tritium level of $\sim 1 \times 10^{-7} \mu\text{Ci}/\text{cm}^3$ can be anticipated. This level, which is 2 percent of mpc for controlled areas, occurs at the termination of a 40 T-D pulse sequence immediately before actuating ventilation of the TFTR cell and discharge of the exhaust to the environment.

Figure 20 shows how the cumulative release of tritium to the facility exhaust varies with time during the 24 hour period immediately following inception of the three principal operations phases - tritium buildup, T-D pulsing, and tritium flushout. The estimates indicate 24 hour cumulative tritium releases as indicated below:

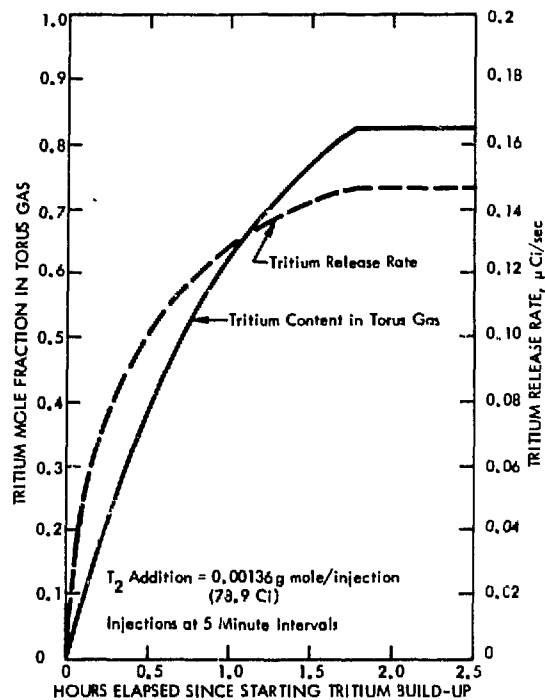


Fig. 17. Variation of Torus Gas Makeup and Tritium Release During Tritium Buildup Operations

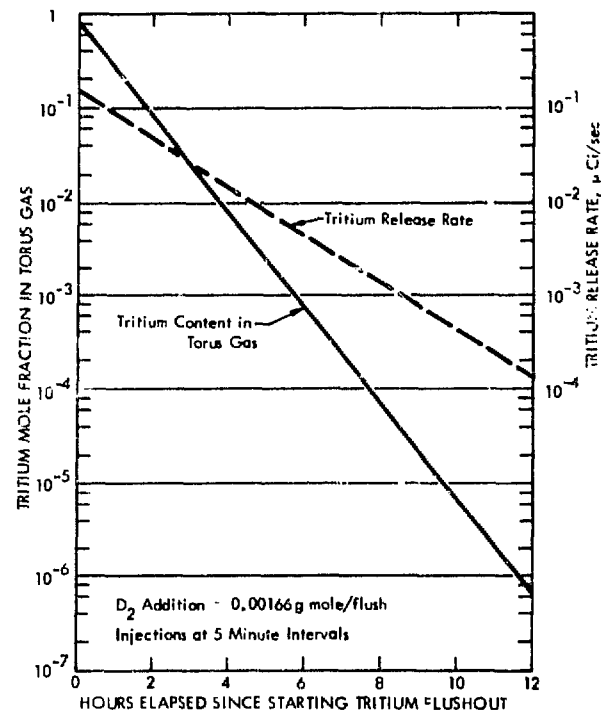


Fig. 18. Variation of Torus Gas Makeup and Tritium Release During Tritium Flushout Operations

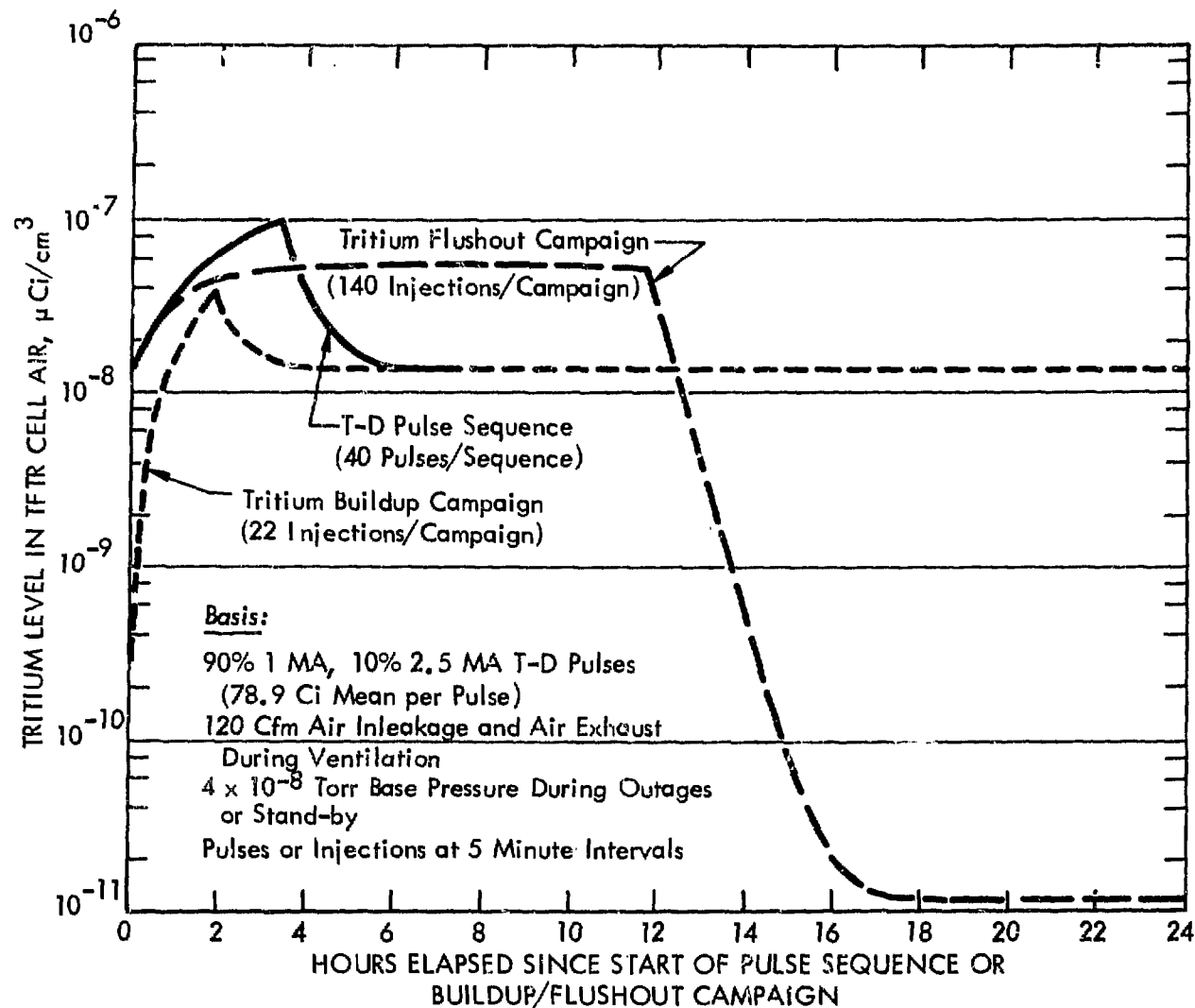


Fig. 19. Temporal Variation of TFTR Cell Air Tritium Level during Operations Periods

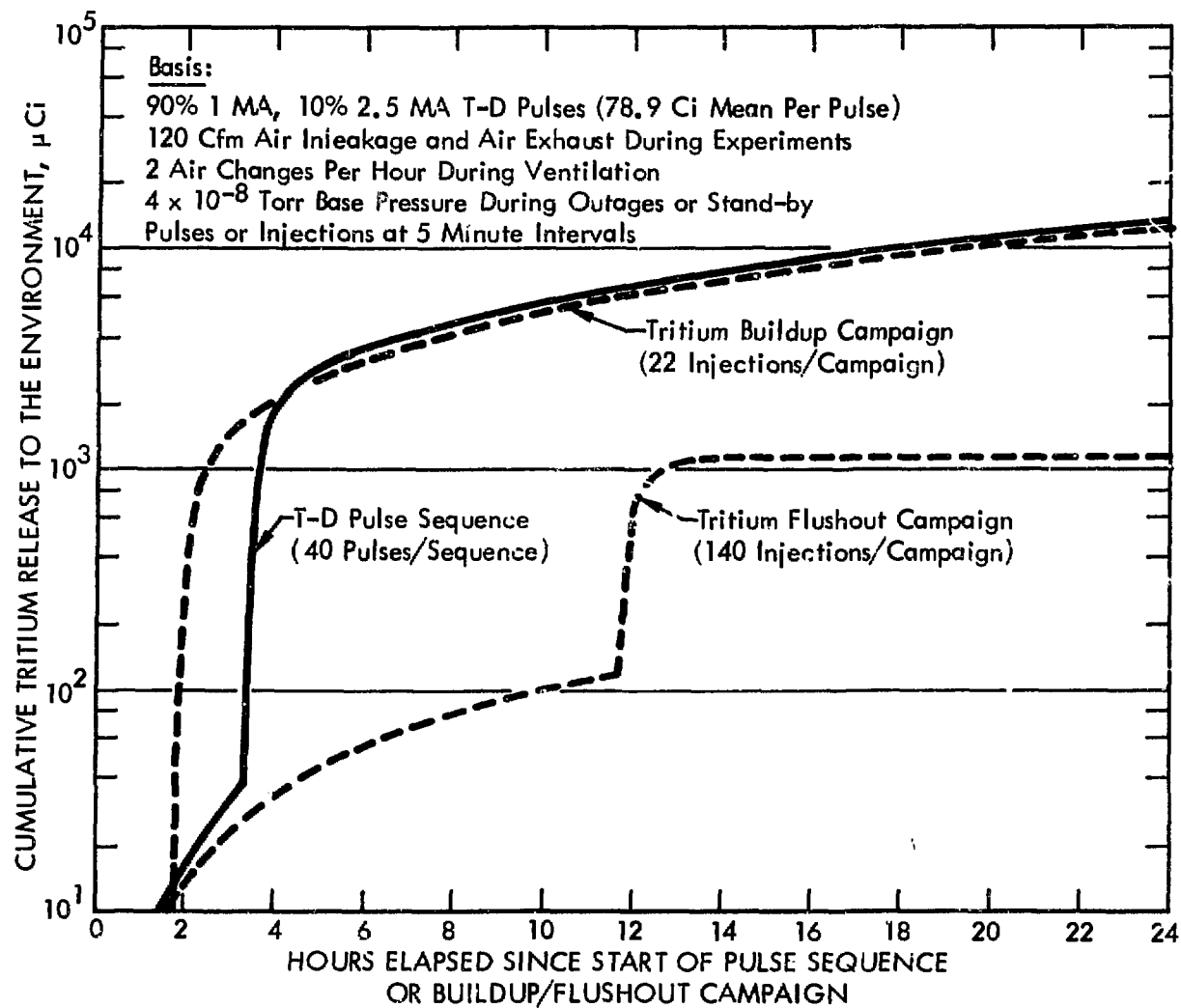


Fig. 20. Temporal Variation of Cumulative Tritium Releases during Operations Periods

<u>Operation</u>	<u>Release, μCi/day</u>
Tritium Buildup (22 buildups, then standby)	12,700
Outage after Tritium Buildup	12,700
T-D Pulsing (40 pulses, then standby)	13,200
Outage after T-D Pulsing	12,700
Tritium Flushout (140 flushes, then standby)	1,200
Outage after Flushout	10

The foregoing numbers highlight the circumstance that achievement of low annual tritium releases involves minimizing the outage days permitted without prior tritium flushout. However, this reduction in tritium release is off-set by an increased tritium consumption per reference T-D pulse. It is apparent that there is potential, for TFTR operations involving 1000 T-D full power pulses per year, to experience a wide spread in both the tritium releases and tritium consumption. The magnitudes of these depends directly on the operating schedule details. This point is illustrated by the numbers displayed in Table 12 for a variety of operating modes involving 10, 20, and 40 T-D full power pulses per sequence. The thrust of these is evident - judicious schedule planning of TFTR operations is a requisite for attainment of minimal environmental impact.

ACKNOWLEDGEMENTS

Many individuals have contributed to the concepts presented in this report. In this connection, it is a pleasure to acknowledge the comments and instructive discussions with the following: D. Green, W. Lange and D. Sink (Westinghouse Electric Corporation) concerning vacuum system features; S. Cohen and G. Lewin (Princeton Plasma Physics Laboratory) concerning tokamak wall problems and tritium transport; R. Garber (Carnegie Mellon University) relative to hydrogen-steel systems diffusion; W. Rogers (Engelhard Industries) on tritium cleanup systems; R. S. Carlson and W. Wilkes (Mound Laboratory) on tritide chemistry and tritium containment;

Table 12. Annual Tritium Consumption and Releases for Selected Operating Modes

ITEM	OPERATING MODE								
	A	B	C	D	E	F	G	H	I
Number of T-D Pulses/Sequence	10	10	10	20	20	20	40	40	40
Number of Consecutive T-D Pulsing Days	1	2	4	1	2	5	1	5	25
Number of T-D Pulsing Days	100	100	100	50	50	50	25	25	25
Number of Tritium Buildup Days	100	50	25	50	25	10	25	5	1
Number of Tritium Flushout Days	100	50	25	50	25	10	25	5	1
Number of Outage or D Pulsing Days	65	165	215	215	265	295	290	330	338
Tritium Consumption, Ci	252,500	165,700	122,300	165,700	122,300	96,300	122,300	87,600	80,600
Tritium Release, Ci	2.67	1.97	1.63	1.34	0.995	0.787	0.679	0.402	0.347

J. Watson (Oak Ridge Hollifield National Laboratory) and V. Maroni (Argonne National Laboratory) on tritium handling technology.

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CTR RELATED TRITIUM RESEARCH AT LASL *

J. L. Anderson
D. H. W. Carstens
R. M. Alire

Los Alamos Scientific Laboratory

ABSTRACT

The solubility and diffusion coefficients of H_2 in Li contained in a cylinder of Nb/1%Zr were measured in the temperature range 805-905°C at a pressure of 575 Pa. Appropriate corrections for the solubility of H_2 in Nb/1%Zr were made. As expected, a finite solid cylinder diffusion model adequately delineates the time-dependent consumption of H_2 in Li. The diffusion coefficient was found to vary from 3.88×10^{-5} to 6.92×10^{-5} cm²/sec and the activation energy was estimated to be 14.7 kcal/mole.

The use of low melting eutectic mixtures containing Y, La, and Ce for extracting tritium from molten lithium is being investigated. Eutectic mixtures being investigated include the 16% Ni in La, 12% Fe in Ce and 16% Co in Ce. At 875 K the molar distribution coefficients for tritium between these eutectic mixtures and lithium are ≤ 100 . The temperature coefficients for these distributions are also being investigated.

The pressure-composition-temperature diagram for the La₅Ni-deuterium system is being studied. A ΔH of -39.7 kcal/mole D_2 was measured for the composition D / La 1.5.

DIFFUSION COEFFICIENTS AND SOLUBILITIES OF HYDROGEN IN LITHIUM

Introduction

Any evaluation of methods for recovering tritium from Li blankets in fusion reactors requires an accurate analysis of the tritium distribution and transport within the reactor. To properly conduct the analysis, fundamental data such as diffusion coefficients and solubilities of T_2 in Li are needed. Enough information about solubilities is available or is being accumulated, but information about diffusion coefficients of H_2 in Li is not available. This lack of information has led to the present investigation. The objective was to establish a method for

*Work completed under the auspices of the United States Energy Research & Development Administration.

measuring the diffusion coefficient of T_2 in Li. The first phase of the study is the development of a method to simultaneously measure the solubilities and diffusion coefficients of H_2 in Li.

The fundamental information accumulated in this study will not only be useful for the evaluation of methods that involve permeability of T_2 , but for providing a better understanding of the migration of T_2 within the reactor.

Apparatus and Procedure

Figure 1 shows the sample configuration for the diffusion experiments. A SS304L cylinder C, with a capability of maintaining a pressure of 10^{-5} Pa at 1000°C was incorporated to ensure that the outer surfaces of cylinders B and connecting tube D would not oxidize when heated. The reproducibility of surfaces ensures that the quantity of H_2 that permeates cylinder B and connecting tube D during an experiment is reproducible. This amount was subtracted from the total H_2 consumed, determined by pressure decrease in a known volume at constant temperature, to obtain the amount of H_2 dissolved by the sample.

Hydrogen gas at a constant pressure was introduced at the bottom end of tube D. Constant pressure was maintained by using a Granville-Phillips automatic pressure controller and an MKS 0-1333 Pa Baratron differential pressure gauge. The quantity of H_2 consumed by the sample and container was determined by recording pressure loss with time in a manual volume at constant temperature.

The blank correction, the quantity that permeates cylinder C during an experiment, was determined in two ways. The first involved doing a separate experiment without sample. Since steady-state permeation through cylinder C and connecting tube D is achieved within a few seconds of exposure, the empirical correction is a linear function of time. The second method involved performing the experiment for a sufficiently long time so that the sample became saturated with H_2 and the H_2 loss with time became the linear correction. This correction was subtracted from the total H_2 consumed by the sample and apparatus to obtain the amount dissolved by the sample.

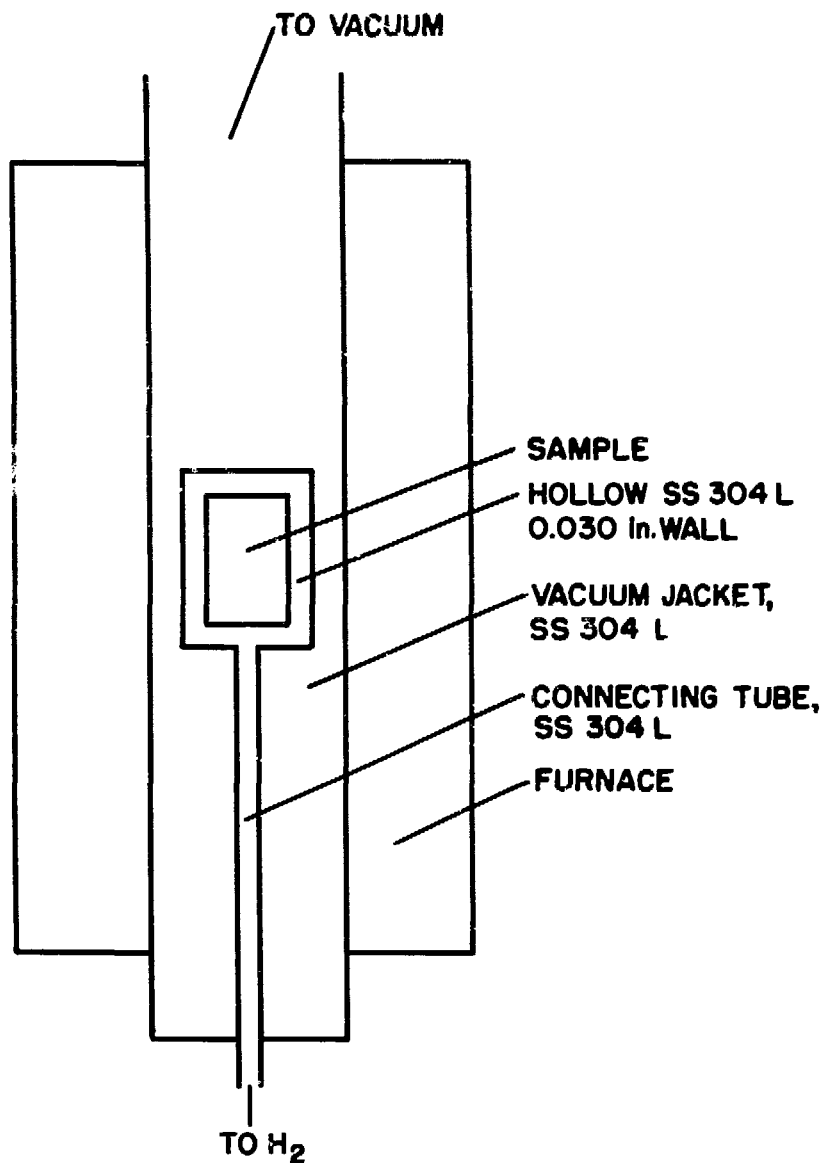


Fig. 1. Sample Configuration for the Diffusion Experiments

The second method is preferred because it eliminates the possibility of not having identical containers for the experiments with and without sample. A comparison of experiments with and without sample shows that the blank correction can be properly done without the necessity of doing a separate experiment without a sample. Figure 2 shows the data with the blank correction for two experiments with the alloy at 95.5 and 95.2Pa at 960°C. Notice that the slope of the linear correction obtained from a separate experiment without sample is the same as that obtained with sample.

Results and Discussion

Diffusion Model

Because it is simpler to fabricate cylindrical containers than other regularly shaped containers, cylindrically shaped samples were used. For experimental conditions that combine radial and axial diffusion of H_2 into a solid cylinder, it is necessary to solve the diffusion equation

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) + \frac{\partial^2 c}{\partial z^2} = \frac{1}{D} \frac{dc}{dt} \quad (1)$$

The solution for the finite solid cylinder was obtained for the following conditions:

$$c = 0 \quad (\text{diffusion into the cylinder})$$

$$0 < r < a$$

$$-l < z < l \quad t = 0$$

$$c = c_s \quad r = a$$

$$-l = z = l \quad t \geq 0,$$

or

$$c = 0 \quad (\text{diffusion out of the cylinder})$$

$$r = a$$

$$-l = z = l \quad t = 0$$

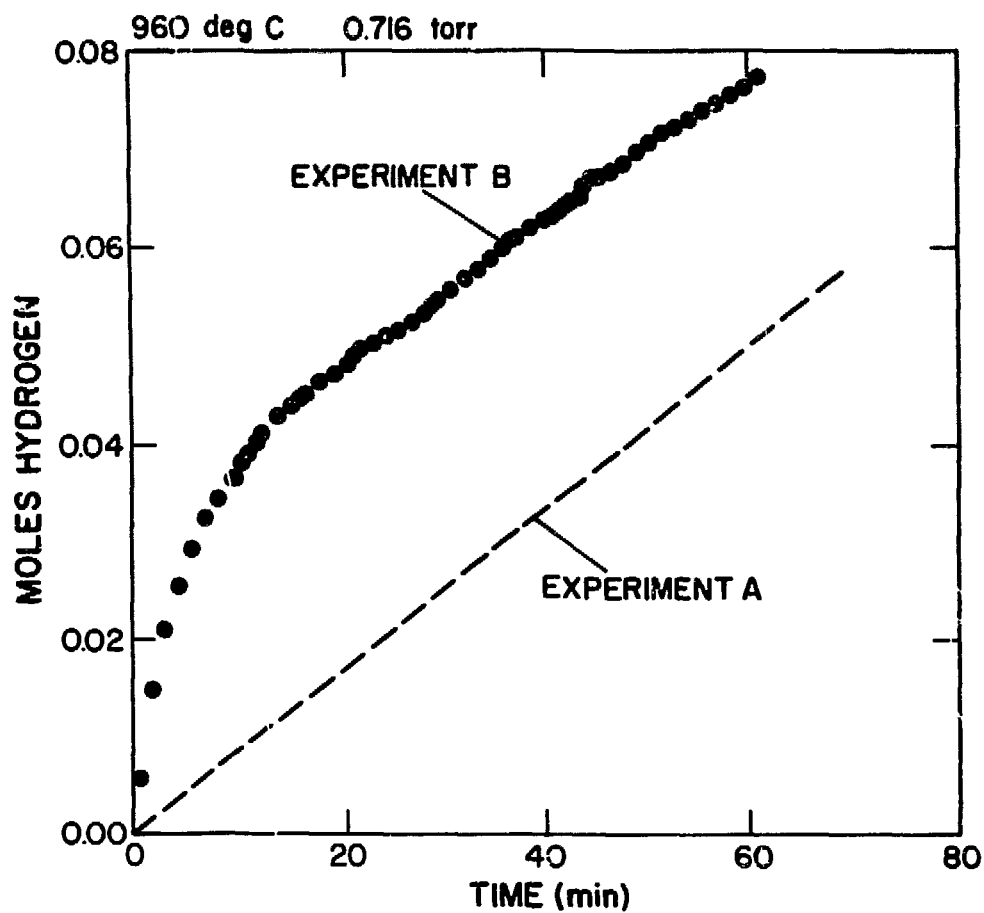


Fig. 2. Moles of H₂ Consumed vs Time for: A - Without sample (Diffusion through SS-304L), B - With Nb/1%Zr Sample.

$$c = c_s \quad \begin{matrix} 0 < r < a \\ -l < z < l \end{matrix} \quad t \geq 0$$

where a and $2l$ are the dimensions of the cylinder in the r and z directions. From the two-dimensional solution, the quantity diffusing into or out of the cylinder at time t , is found to be

$$Q = c_s V \left\{ 1 - \frac{32}{\pi^2} \sum_{m=1}^{\infty} \sum_{n=0}^{\infty} \frac{1}{a^2 \gamma_m^2 (2n+1)^2} \exp \left[-Dt \left(\gamma_m^2 + (2n+1)^2 \pi^2 \right) \right] \right\} \quad (2)$$

$c_s V$ is the product of the solubility and volume of the cylinder, D is the diffusion coefficient, and $\gamma_m a$ is the m^{th} root of the Bessel equation

$$\sum_{m=0}^{\infty} \frac{(-1)^m \left(\frac{\gamma_m a}{2} \right)^{2m}}{(m!)^2} = 0 \quad (3)$$

Diffusion into Nb/1%Zr

Several experiments to simultaneously measure the diffusion coefficient and solubility of H_2 in Nb/1%Zr alloy at 960°C and 38.7 to 1097 Pa were completed. A solid cylinder of the alloy, $r = 0.44$ cm, $l = 1.979$ cm, was used for these experiments. The finite-cylinder diffusion-model previously described was used to evaluate the two adjustable parameters D and c_s . The average diffusion coefficient for eight experiments is $4.64 \times 10^{-4} \pm 0.22 \times 10^{-4} \text{ cm}^2/\text{sec}$, which compares with an extrapolated value of $4.5 \times 10^{-4} \text{ cm}^2/\text{sec}$ at 960°C for H_2 diffusion in Nb.^{1,2} The solubilities ranged from 6.9 to 40 ppm (wt), which corresponds to a H/metal ratio of $5.2 \times 10^{-4} - 3.0 \times 10^{-3}$. A least squares evaluation of Sieverts' constant gives, $k = c_s / \sqrt{P} = 1.20 \pm .06 \text{ (ppm/(Pa)}^{1/2})$. The H/metal ratio extrapolated and normalized to 1 atm is 3.2×10^{-2} , which compares favorably with 2.6×10^{-2} extrapolated from Sieverts data for H_2 solubility in Nb.² This measurement is similar to the solubility of H_2 in a Nb/1%Zr alloy. The initial and boundary conditions of the diffusion equation were closely approximated, and the least-squares fit of the time-dependent hydrogen consumption accurately describes the experimental results.

Figure 3 shows the least squares fit of the data for an experiment at 960°C and 95.5 Pa.

Diffusion in Li

Experiments to measure the solubilities and diffusion coefficients of H_2 in Li at 575 Pa and 805, 855, and 905°C were completed. The sample was prepared by loading 0.3272g Li in a Nb/1%Zr cylinder, weighing 3.8778g; the cylinder caps were TIG welded in an argon atmosphere.

It was assumed that hydrogen does not accumulate at the container/Li interface. That is, the rate of accumulation at the container/Li interface = the rate of permeation through the container - the rate of solution into Li. If the accumulation rate is zero and the rate of solution is rate-controlling, then the quantity of H_2 dissolved with time as measured by PVT equals the quantity dissolved by Li. If these assumptions are valid, then the initial and boundary conditions of the finite-cylinder diffusion-model are not violated. The model was tested by doing a least-squares analysis on the data and comparing the solubilities obtained to those available in the literature. No other measurements of diffusion coefficients of H_2 in Li were found in the open literature.

Table 1 shows the diffusion coefficients and solubilities obtained by least squares. The solubilities were corrected for the amount of H_2 dissolved by the container. The percent of the total hydrogen dissolved by the container varies from 3.4 at 805 to 13.8 at 905°C. As shown by Table I the solubilities compare favorably with those measured by Veleckis et al.³ Figure 4 shows an example of the least squares evaluation. The solid line is the least-squares fit for an experiment done at 805°C and 575 Pa. The activation energy was estimated to be 14.7 kcal/mole.

Errors

Extra care was taken to minimize the experimental errors by measuring the system volumes against a standard volume of $37.530 \pm .007 \text{ cm}^3$ and calibrating the recording transducers for each experiment against a Texas Instrument quartz pressure gauge, a secondary standard. The standard deviation on a single measurement of moles of H_2 dissolved-vs-time varies from $\pm 2\%$ at early times to $\pm 0.5\%$ at the end of the experiment. The least-

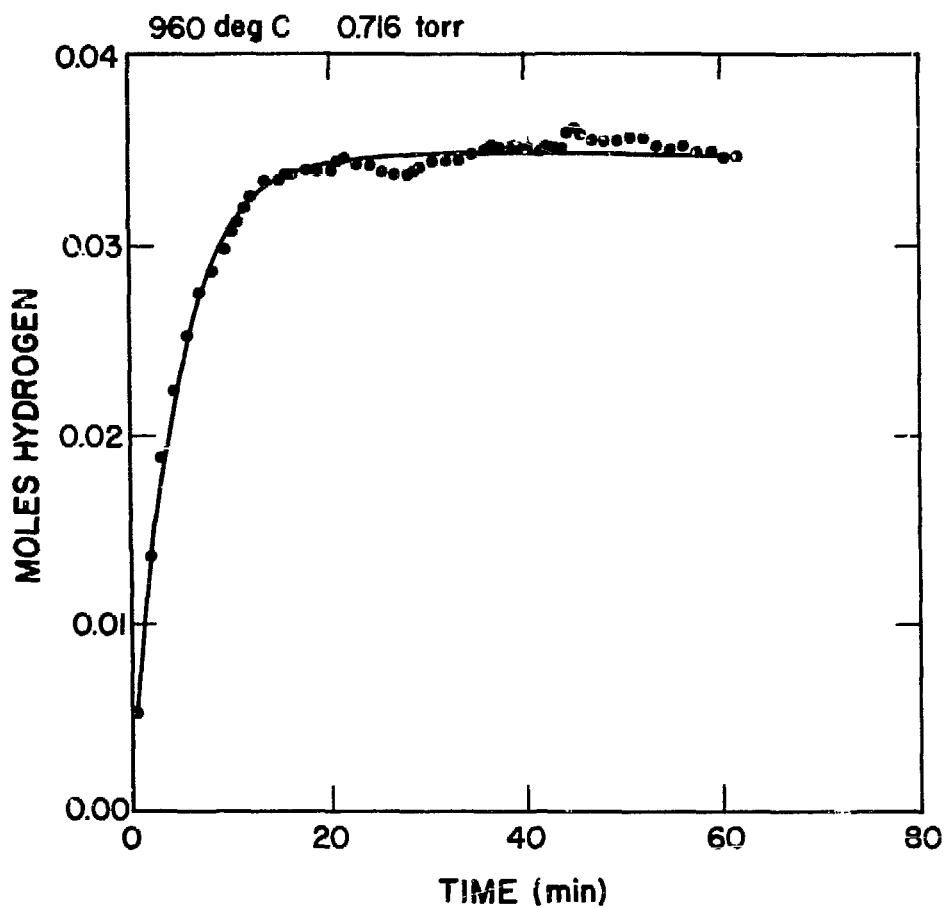


Fig. 3. Moles of H_2 Consumed vs time by Nb/1%Zr Alloy.

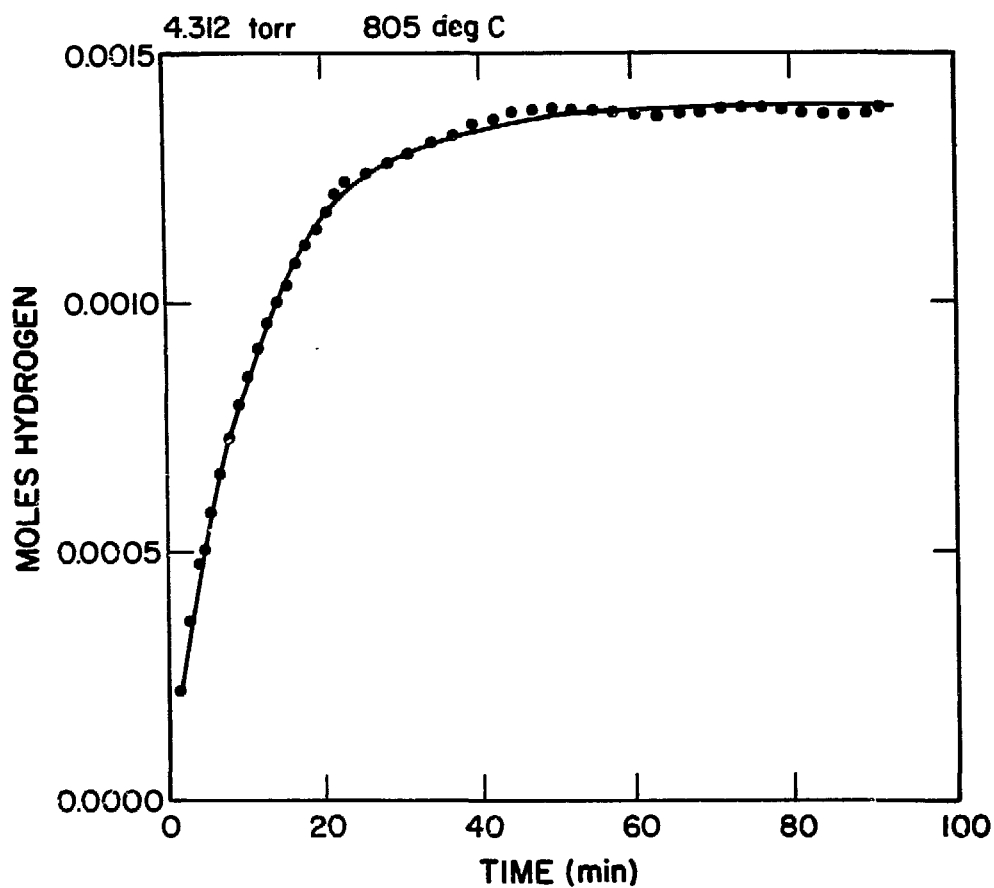


Fig. 4. Moles of H_2 Consumed vs time for a Sample of Li Contained in a Cylinder of Nb/1%Zr.

Table 1. Diffusion Coefficient and Solubility of H_2 in Li

Pres (Pa)	Temp (°C)	mole f ^a LiH/(H + Li)		Diffusion Coefficient (cm ² /sec)	%H ₂ dissolved by container
		this study	Veleckis et al		
575	805	8.1×10^{-2}	6.1×10^{-2}	3.88×10^{-5}	3.4
575	855	2.0×10^{-2}	2.5×10^{-2}	4.46×10^{-5}	7.6
575	905	5.0×10^{-3}	4.8×10^{-3}	6.92×10^{-5}	13.8

^aThis assumes that the hydrogen dissolved forms LiH in Li.

squares determinations of D and c_s were done by weighting each determination as $1/\sigma^2$. The constant pressure is controlled $\pm 0.5\%$, the temperature is measured to $\pm 0.1\%$, and the error on the pressure measurement on the PVT determination is estimated to be $\pm 0.8\%$.

H₂ Transport through Container

The transport of H_2 through a Nb/1%Zr alloy container is primarily due to grain boundary diffusion. Our basic supposition is that diffusion of H_2 through the boundaries is more rapid than diffusion into the lattice. For a thin container the boundaries quickly become saturated with H_2 , and diffusion into any given grain takes place from all sides. The grains and the container becomes saturated with H_2 quickly so that any further transport is steady state diffusion through the container into molten Li. The effects of annealing during exposure to H_2 were minimized by maintaining the container with Li at temperature in vacuo for about 15 h prior to exposure to H_2 .

Liquid lithium in the cylindrical container forms a meniscus that is concave downward. The resulting geometry is not cylindrical. The deviation is not sufficiently large to warrant using a different geometry to describe the diffusion process. The magnitude of the effect was found to be small by comparing the results from experiments done with containers having different radii.

An additional perturbation which was considered to be small was the effect of Li vapor above the liquid in the container. The amount of Li in the vapor phase is negligible compared to the amount in liquid Li. The magnitude of this effect was demonstrated to be small in the temperature range studied, by varying the quantity of liquid Li in the same size container.

The cylindrical diffusion equation adequately describes the time-dependent hydrogen consumption. The deviations from ideality are small and do not detectably affect the values reported for the solubilities and diffusion coefficients. The method developed was useful for liquid lithium and may be useful for other liquids.

THE EXTRACTION OF TRITIUM FROM LITHIUM USING LOW MELTING EUTECTIC MIXTURES

Introduction

At LASL the lithium-tritium separation program has concentrated on the study of liquid-liquid extraction of tritium from lithium using a molten metal as the extracting medium. In searching for a reactive material that can be used to getter tritium from lithium several criteria need to be met. These include:

- The reacting species (A) should be inert and insoluble in lithium.
- Species (A) should react rapidly with trace amounts of lithium tritide and remove tritium to low levels.
- The second compound (B) containing the extracted tritium should be non-reactive and insoluble in lithium.
- This compound should be easily decomposed for tritium recovery.
- A straightforward series of reactions to close the loop ($B \rightarrow A$) would be advantageous.
- Both species (A) and (B) must be completely compatible with all structural components in the lithium loop.

Liquid-liquid extraction techniques as proposed by Maroni⁵ seem to offer the best hope for achieving rapid extraction of tritium from lithium to the extremely low tritium levels (1-10ppm) desired. An attractive alternate to the fused salt systems proposed by Maroni is to use a low melting eutectic mixture containing a suitable amount of a strong hydride-forming metal such as lanthanum, cerium or yttrium as the extracting species. These elements form more stable hydrides than lithium and can therefore be expected to extract tritium from the lithium. No data are available on the solubility of tritium in these materials at the low composition range of interest. If, however, one compares the stabilities of these systems in the two-phase region of the pressure-composition diagrams, it would appear that tritium could be extracted from lithium using these materials under appropriately selected conditions. Table 2 summarizes the systems that appear to have some potential for this study. Also listed are the equilibrium dissociation pressures for the metal hydride systems at the melting point of the eutectic. The separation factor is simply the ratio of the equilibrium pressures for MH_2 vs LiH at the melting point of the eutectic. These pressures were calculated from published data (Mueller, Blackledge, and Libowitz).⁶ If the relative stabilities of these systems show the same trends for low concentrations of hydrogen then these materials offer the possibility of quite high extraction coefficients.

Experimental

A series of Sieverts -type experiments have been run using the 84 a/o La-16 a/o Ni eutectic mixture to confirm that the La is indeed available for hydride formation.

The experimental apparatus includes a temperature controlled furnace, a 120 cc standard volume for gas measurement, and 1- and 1000- torr Barocels for pressure measurements. The furnace consists of a stainless steel tube, externally heated, and the sample is contained in a stainless steel crucible. Blanks run on the system indicate that the absorption by the stainless steel can be neglected except at very low concentrations and pressures ($< 10^{-3}$ torr). Because this region is of prime interest, a furnace and crucible of another metal will probably be used for future experiments. To check out and calibrate the system a run was made on uranium

Table 2. Possible Eutectic Melts for Removal of Tritium from Lithium

Primary Component (M)	Secondary Component	Composition		Eutectic MP °C	Atomic %		Sep. Factor	$\frac{P_{LiH}}{P_{MH_2}}$
		Pri.	Sec.		P _{LiH} atm	P _{MH₂} atm		
Ce	Co	84	16	415	2.8×10^{-5}	1.1×10^{-6}	25	
	Fe	88	12	590	1.3×10^{-2}	5.1×10^{-4}	25	
	Mn	86	14	612	7.3×10^{-3}	2.8×10^{-4}	26	
	Ni	82	18	470	1.8×10^{-4}	7×10^{-6}	26	
La	Mn	83	17	715	5.5×10^{-2}	7.7×10^{-4}	71	
	Ni	82	18	495	3.8×10^{-4}	5.5×10^{-7}	69	
Y	Co	69	31	715	5.5×10^{-2}	1.2×10^{-4}	460	
	Fe	65	35	900	8.6×10^{-1}	4.4×10^{-3}	200	
	Ni	67	33	802	2.2×10^{-1}	7.7×10^{-4}	290	
Er	Co	63	37	800	2.2×10^{-1}	1.1×10^{-3}	200	
	Fe	75	25	890	7.5×10^{-1}	7.7×10^{-3}	97	
	Ni	66	34	< 880	6.6×10^{-1}	6.3×10^{-3}	105	
Dy	Fe	72	28	855	4.8×10^{-1}	not known	?	
	Ni	67	33	< 810	2.5×10^{-1}			
Gd	Ni	68	32	700	4.2×10^{-2}	2×10^{-4}	200	

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metal with no unexpected results.

The absorption-desorption of deuterium by the lanthanum was followed by adding or removing small, measured quantities of deuterium to the reactor containing the eutectic mixture and allowing the system to come to equilibrium before recording the pressure.

A different experimental technique was used in a preliminary series of extraction experiments. The eutectic mixtures used in these experiments included the 16 a/o Ni in La, 12 a/o Fe in Ce and 16 A/o Co in Ce. Experimentally, weighed amounts of lithium and the eutectic mixture were placed in a Nb/1%Zr crucible and a small amount of lithium tritide added. A lid was welded on the crucible and the crucible placed in a rotating heater. The crucible was brought to the extraction temperature and continuously rotated while holding the temperature constant for 1/2 to 1 1/2 h. The sample was then cooled rapidly to room temperature, the crucible opened and samples of each phase were separately analyzed for tritium. Tritium was determined by the complete combustion of the sample in oxygen, collecting the water formed and radiocounting tritium using a liquid scintillation counting apparatus.

Results and Discussion

Sieverts experiments have been completed on $\text{La}_{5.25}\text{Ni}$ and La_5Ni compositions. Figure 5 shows the measured pressure-composition curve for the $\text{La}_{5.25}\text{Ni}$ -deuterium system at 850 K. The equilibrium pressure of deuterium over the lanthanum is indeed low, but rises sharply as the composition $\text{D/La} = 2$ is approached. A composition of $\text{D/La} = 2.4$ is the highest composition achieved. To show the pressure at the low compositions the early part of the curve has been expanded by a factor of 1000 and is shown on the left side of Figure 5. The scatter in these points is caused primarily by lack of equilibrium which is approached slowly in this system (6-24 h being needed).

The study of the variation of equilibrium pressures of D_2 over the La_5Ni mixture for various deuteride compositions has been completed and is shown in Figure 6. It is interesting that there is no apparent break in these curves at the melting point of the eutectic. Table 3 gives the values

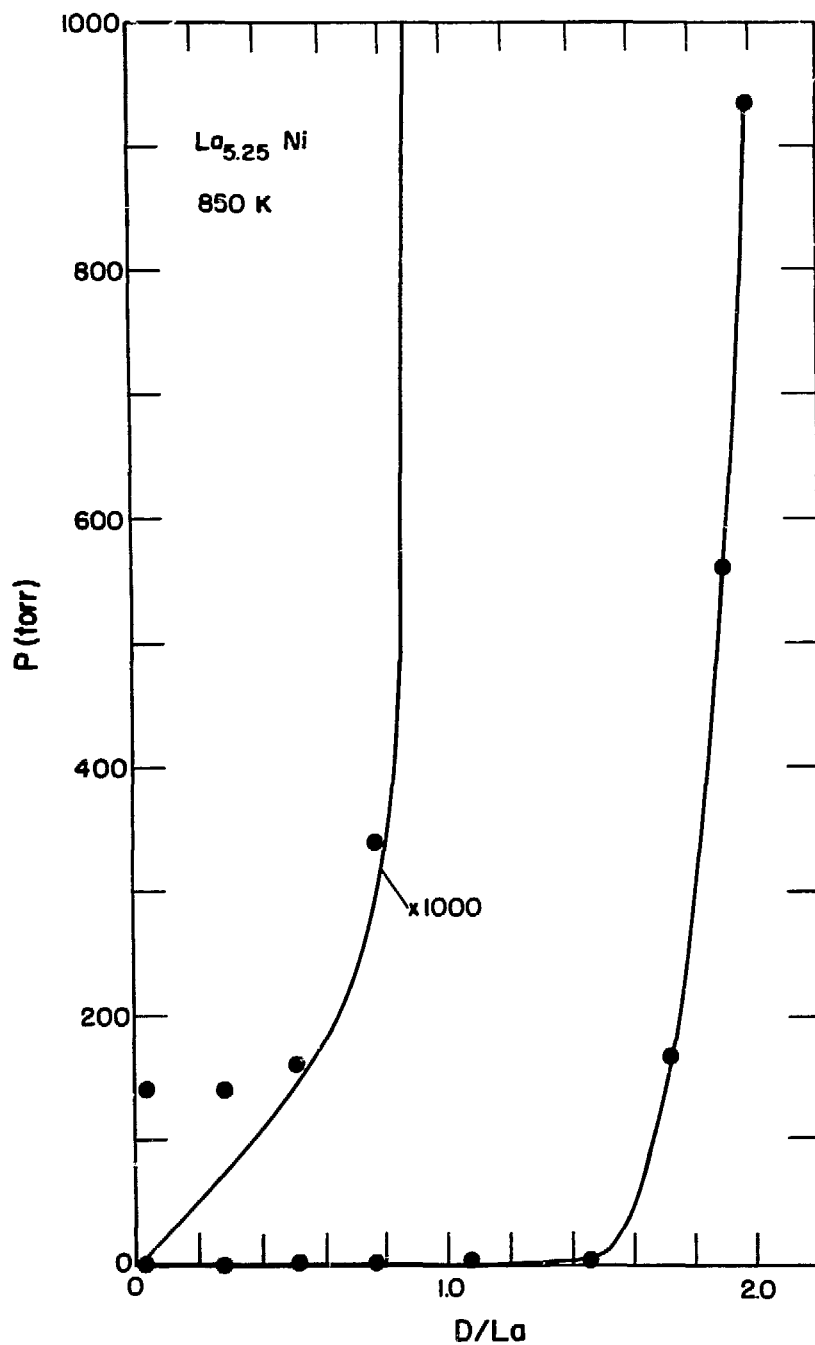


Fig. 5. Pressure-Composition Diagram for the $La_{5.25}Ni$ - D_2 System at 850 K.

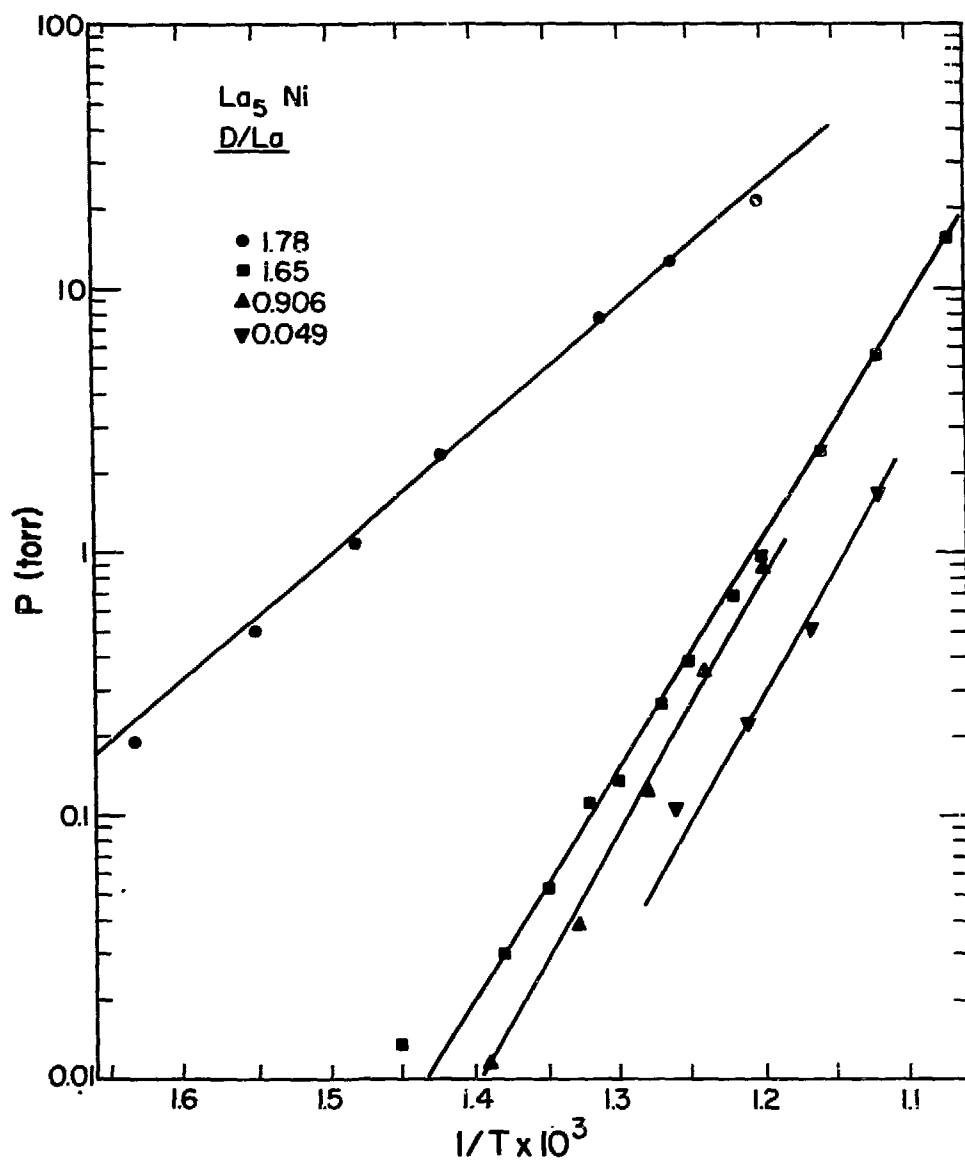


Fig. 6. $\ln P$ vs $1/T$ for La₅Ni + D₂.

of A and B for the equation

$$\ln P_{(\text{torr})} = -A/T + B \quad (4)$$

for the $\text{La}_5\text{Ni} + \text{deuterium}$ systems.

Table 3. Dissociation Pressure Data for the
 $\text{La}_5\text{Ni-D}_2$ System

$\frac{[\text{D}]}{[\text{La}]}$	A	B	$\frac{\Delta H}{\text{kcal/mole D}_2}$
.049	22,450	23.43	- 44.6
.906	21,700	25.82	- 43.1
1.65	19,980	24.01	- 39.7
1.76	11,126	16.57	- 22.1

The values of ΔH calculated from A can be compared to a published value of - 46.5 kcal/mole D_2 found for LaD_2 .⁶ The experimental value remains near this up to a composition $\text{D} / \text{La} = 1.5$ but above this the heat of formation drops rapidly. This series of experiments confirms that the lanthanum in the eutectic mixture is available for hydride formation and reacts quite similarly to pure lanthanum.

The results of the extraction experiments are given in Table 4. The measured melting points and densities of the eutectic mixtures used in these experiments are also shown. The large density differences between these materials and the molten lithium leads to a clean separation of phases when the crucibles are cooled with continuous, rapid, rotation of the crucible, from the extraction temperature to room temperature.

The distribution coefficients listed give the ratio of tritium content per mole of reactive metal to the tritium content per mole of lithium. The amount of lithium tritide added to each experiment varied over a fairly wide range with the final tritium level in the lithium phase varying from 1 to 400 weight ppm. Figure 7 summarizes the temperature effects measured for

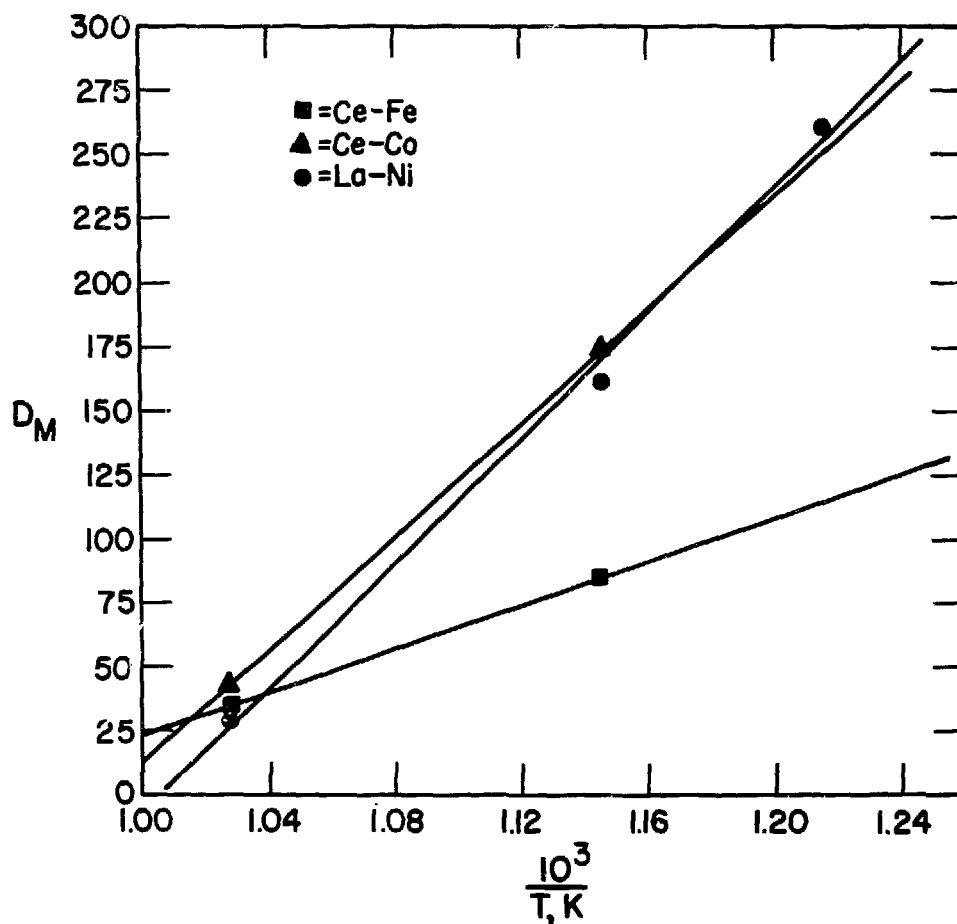


Fig. 7. Molar Distribution Coefficients, D_m , vs $1/T$ for the Extraction of Tritium from Lithium by Selected Eutectic Mixture.

Table 4. Measured Distribution Coefficients for Tritium Between Lithium and Selected Eutectic Mixtures

Eutectic Mixture	Melting point, K	Density g/cm ³	Distribution Coefficient D_m		
			823 K	873 K	973 K
La _{5.25} Ni	803	6.29	260	162	30
Ce _{7.33} Fe	848	6.97		86	35
Ce _{5.25} Co	713	7.25		175	43

these extractions.

Future work will place emphasis on those eutectic mixtures containing yttrium. The yttrium binary systems seem to have melting points that are too high to be practical. We will therefore be looking for ternary systems containing yttrium. We have recently synthesized a 76 a/o Ce-8 a/o Y-16 a/o Co mixture melting at 810 K. The first results obtained with this mixture indicate a distribution coefficient of 110 at 875 K. This value is somewhat lower than anticipated as yttrium forms the most stable hydride.

A second area receiving attention in the near future will be to determine the mutual solubilities of lithium and the eutectic mixtures in the temperature range of interest.

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TRITIUM-RELEASE FROM LiAlO_2 , ITS THERMAL
DECOMPOSITION AND PHASE RELATIONSHIP
 $\gamma\text{-LiAlO}_2\text{-LiAl}_5\text{O}_8$

- IMPLICATIONS REGARDING ITS USE AS
BLANKET MATERIAL IN FRT -

D. Guggi, H. Ihle, A. Neubert and R. Wölfle

Institut für Chemie der Kernforschungsanlage Jülich GmbH
Institut 1: Nuklearchemie
D-5170 Jülich, FRG

ABSTRACT

The release of tritium from reactor irradiated LiAlO_2 was measured using argon as carrier gas. Detection was performed by tritium gas counting. The diffusion coefficient of tritium as a function of temperature was evaluated.

The vaporization behaviour of the tetragonal $\gamma\text{-LiAlO}_2$ was studied by mass spectrometry. $\gamma\text{-LiAlO}_2$ decomposes predominantly to gaseous lithium, oxygen and solid LiAl_5O_8 . The degree of decomposition was determined by ^{58}X -ray analysis of the condensed phases. The influence of different materials used as sample container, e.g. molybdenum, stainless steel, iron, chromium and nickel, on the vapor pressure of lithium was also studied. Variation of the Li-pressure over two orders of magnitude occurs using various wall materials. Consequences of these findings in the use of LiAlO_2 as blanket material are discussed.

INTRODUCTION

Lithium metaaluminate (LiAlO_2) has been proposed for use as breeding material in the blankets of fusion reactors¹. For this purpose, however, it will be necessary to enclose the aluminate in a canning material which has, e.g. according to the UWMAK II

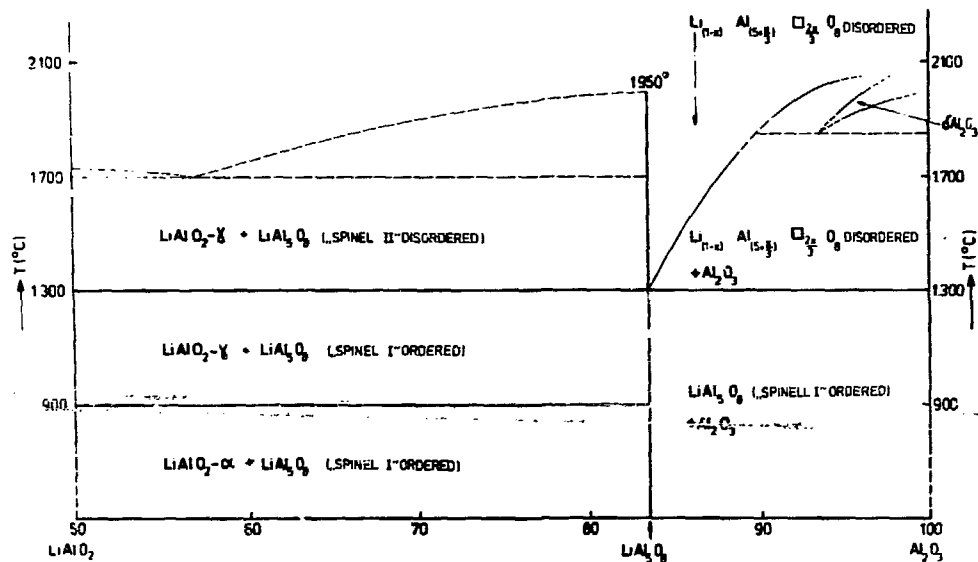
concept, a surface temperature of about 600 °C. The centerline temperature in the material would be > 1300 °C due to its low thermal conductivity². Therefore it seemed necessary to study the release of tritium from LiAlO_2 , with and without its being sealed in stainless steel, as well as the vaporization behaviour of pure LiAlO_2 and the influence of various metals on its vaporization.

The phase diagram of the system lithium metaaluminate-alumina taken from Lejus and Collongues³ is shown in Fig. 1. It is seen that two regions exist in which two solid phases coexist: one LiAlO_2 -phase and an inverted spinel-phase at compositions $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ from 1 to 5, and alumina and the same spinel-phase at $\text{Al}_2\text{O}_3/\text{Li}_2\text{O} > 5$. In this work the $\gamma\text{-LiAlO}_2$ -phase, which always contained small amounts of disordered spinel-phase, was investigated in the vaporization studies from 1300 ~ 1600 K, and also in the tritium release measurements at much lower temperatures.

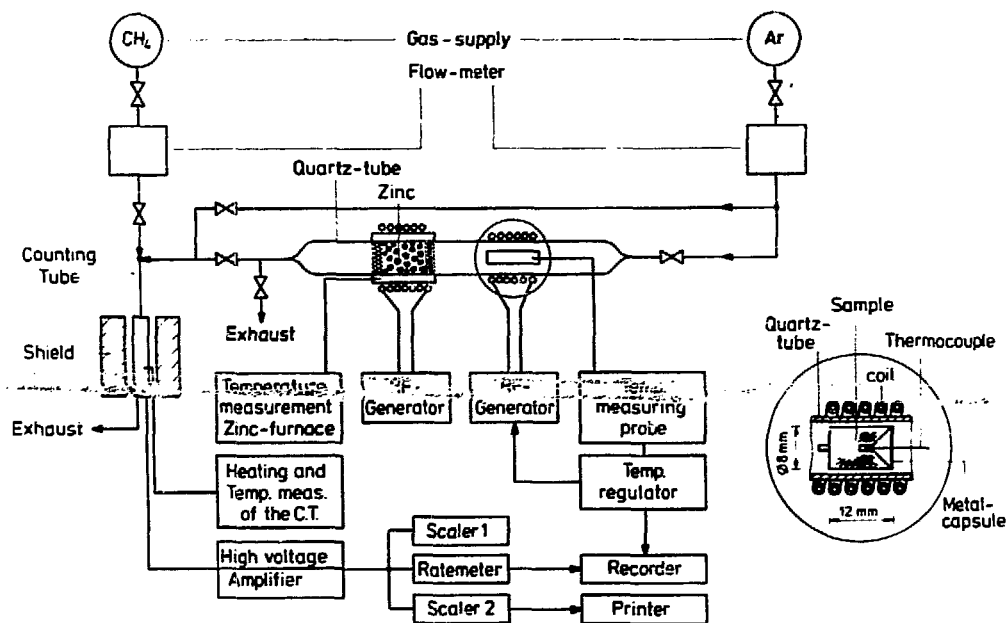
EXPERIMENTAL

For the measurement of tritium release samples of lithium aluminate were screened with a sonic sifter to a mean radius of 35 microns, heated for several hours to 800 °C in a vacuum better than 10^{-5} Torr to remove traces of water and sealed in thin walled stainless steel capsules. An atom fraction of tritium $x_T \sim 0.1$ ppm was produced by exposure to a thermal neutron flux of $\sim 10^{10}$ n/cm²sec. The irradiated samples were then introduced in the apparatus shown in Fig. 2 for the measurement of tritium release.

A stream of purified argon removes the tritium liberated from the sample upon heating to temperatures between 450 to 800 °C and carries it to a gas flow proportional counter after passage through a zinc bed, kept at 400 °C, which serves to reduce tritium oxide to tritium. Methane is admixed at a ratio



1 Phase Diagram LiAlO_2 - Al_2O_3 (after A. M. Lejus³)



2

Apparatus for Measurement of Tritium Release

1 : 1 to the argon before the gas enters the counter. The measured counting rate is proportional to the flux of tritium released from the surface of lithium aluminate after the stainless steel capsules were opened by fusion of a solder, which served to seal the capsule. Experiments were also carried out on samples hermetically sealed in stainless steel capsules of 0.1 mm wall thickness by electron beam welding.

From these capsules the tritium flux permeating the stainless steel wall after diffusing out of the lithium aluminate was measured. The sample was heated by r.f. heating, which enabled its temperature to be raised rapidly. The time constant for the measurement of the tritium concentration in a gas stream of 20 cc(STP) of argon per minute is about 1 minute. Parallel to the gas flow measurements, the tritium species desorbing from the free surface of a lithium aluminate pellet, irradiated to contain about 10 ppm tritium, were measured with a quadrupole mass spectrometer described in an earlier work⁴.

RESULTS OF TRITIUM RELEASE MEASUREMENTS

The mass spectrometric measurement of desorbing tritium species revealed that at 700 °C only T₂O and HTO are desorbed in a ratio of 4 : 3 from the free surface of a lithium aluminate pellet in vacuum. No T₂ and HT were observed. The limit of detection for these two species was 4 % of the measured ion intensity of T₂O and HTO, which desorbed with the same time constant of 4.9 minutes; this is believed to be controlled by diffusion in the solid. The evaluation of the time constant was made according to the method described by Katz et al⁵ using eq. (1),

$$p_i - p_{i,b} = \frac{\alpha}{\beta - 1/\tau} (e^{-t/\tau} - e^{-\beta t}) \quad (1)$$

where p_i and $p_{i,b}$ are the partial pressure and background pressure of species i , and α and β are constants.

The ion intensities observed are proportional to the partial pressures. The constant β was chosen to be large enough so that the second term in the bracket in eq. (1) can be neglected after a short time, and a time constant $\tau = r^2/\pi^2 \cdot D$ can be directly determined.

The results of tritium release obtained by the radiometric gas flow technique were evaluated in the same manner; β in eq. (1) is then proportional to the gas flow rate, which was high enough to enable the determination of a time constant.

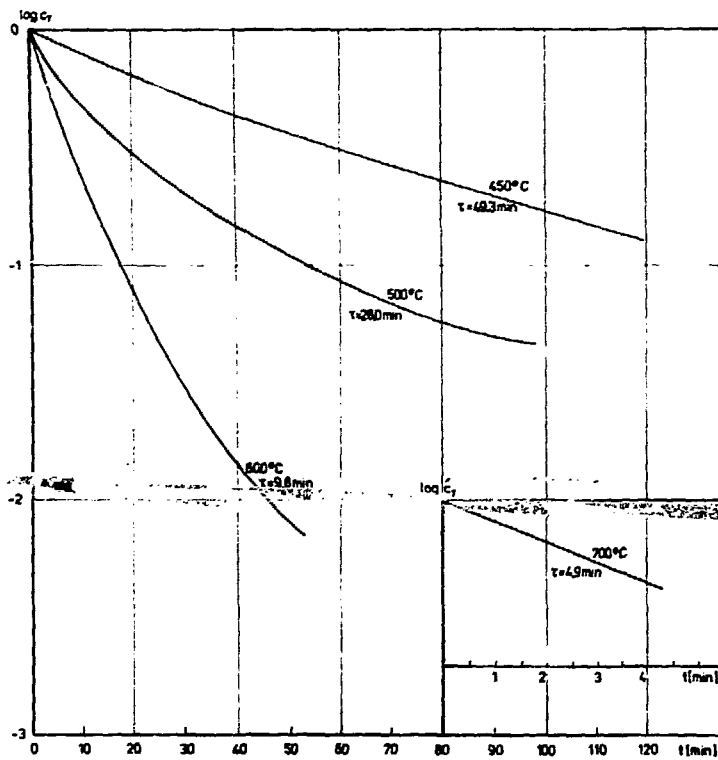
The decrease of ion intensity and tritium activity C_T , respectively, for "open" LiAlO_2 -samples at various temperatures between 450 and 700 °C is shown in Fig. 3. The result at the highest temperature was obtained in a mass spectrometer experiment, in which case the species T_2 and HTO were separated. Fig. 4 shows the corresponding tritium release vs. time curves for the stainless steel sealed samples. The time constants are an order of magnitude higher than those from the "open" sample experiments. From the time constants, diffusion coefficients for tritium in LiAlO_2 from the "open" sample experiments and reciprocal time constants from the "sealed" experiments were evaluated as a function of temperature; the results are shown in Fig. 5 and are expressed by the following equations:

"open" samples:

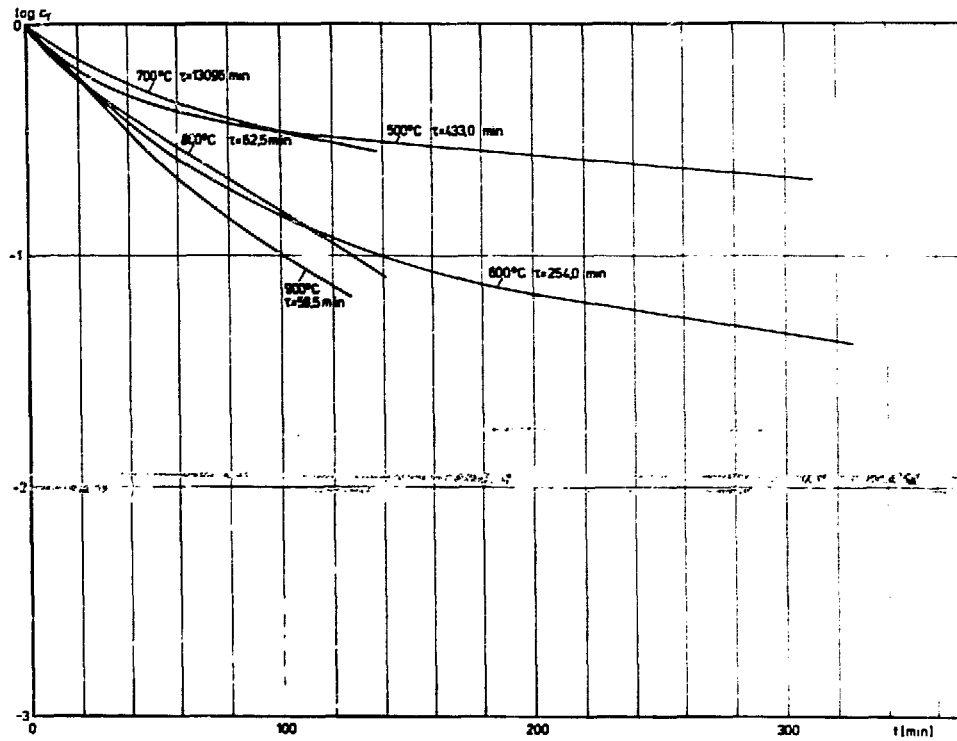
$$\log D = - \frac{(2.875 \pm 0.06) \cdot 10^3}{T} - 5.43 \pm 0.07 \quad (2)$$

stainless steel sealed samples:

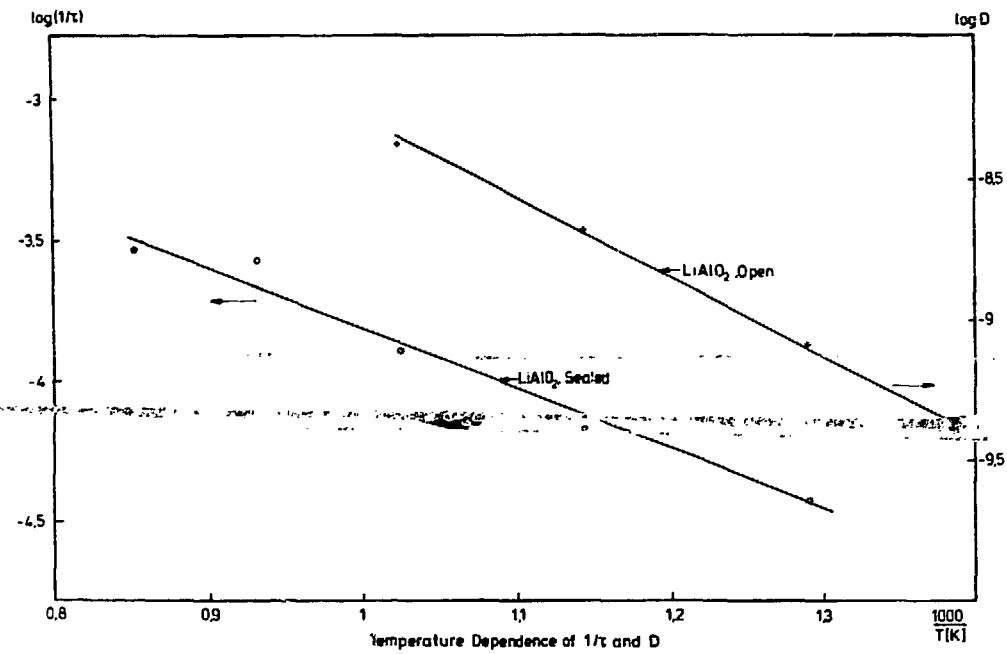
$$\log \frac{1}{\tau} = - \frac{(2.22 \pm 0.61) \cdot 10^3}{T} - 1.51 \pm 0.65 \quad (3)$$



3 Release of Tritium from LiAlO_2 vs. Time in open Vessel



4 Release of Tritium from LiAlO_2 vs. Time
Sealed in Stainless Steel



5 Temperature Dependence of Reciprocal Time
 Constant $1/\tau$ for Tritium Release from LiAlO_2 ,
 sealed in Stainless Steel and of Diffusion
 Coefficient D of Tritium in LiAlO_2

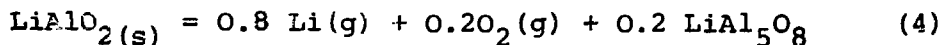
which yield an activation energy for the diffusion of tritium in LiAlO_2 of 13.2 ± 0.3 kcal in the temperature range from 450 to 700 °C.

It is interesting to note that the temperature dependence of the apparent diffusion coefficient for the release of tritium from sealed samples, which involved the complicated process of chemical reactions of T_2O at the inner wall with constituents of the wall material, is quite similar to the one observed with "open" samples.

We regard these results as preliminary for a number of reasons. The samples used are not well characterized; lithium metaaluminate of 98 % purity was used as purchased from Alfa Products, and was not analysed for impurities. X-ray analysis showed the presence of some substantial amounts of the spinel-phase LiAl_5O_8 . Despite careful degassing in vacuum at temperatures where vaporization of LiAlO_2 is negligible, we could not obtain samples free of water as is seen from the mass spectrometric results. LiAlO_2 appears also to react with traces of water in the argon gas stream which may result in changes of the sample composition and diffusion with time during the release experiment. Also, the uncertainties arising from the varying sizes and shapes of the particles used may give rise to substantial errors.

VAPORIZATION EXPERIMENTS

Mass spectrometric vaporization studies on lithium metaaluminate have been carried out by Hildenbrand et al.⁶ and by Popkov and Semenov⁷ at temperatures around 1800 K using platinum Knudsen cells. Vaporization proceeds predominantly according to eq. (4):



Small amounts of O, LiO and Li_2O are also found in the gas. In the presence of a canning metal which reacts with oxygen, this reaction must also be taken into account, and it will generally tend to decrease the oxygen pressure. The metal oxide formed may also react with LiAlO_2 or LiAl_5O_8 , thus further complicating the situation.

Mass sepctrometric measurements of the Li-pressure over LiAlO_2 contained in Knudsen cells of different wall materials were carried out to study the effect of the inner wall of a Knudsen cell⁸. In some experiments, powdered metal was added to increase the reactive surface of the metal.

An example of the effect of molybdenum as wall material on the Li-pressure is shown in Fig. 6.

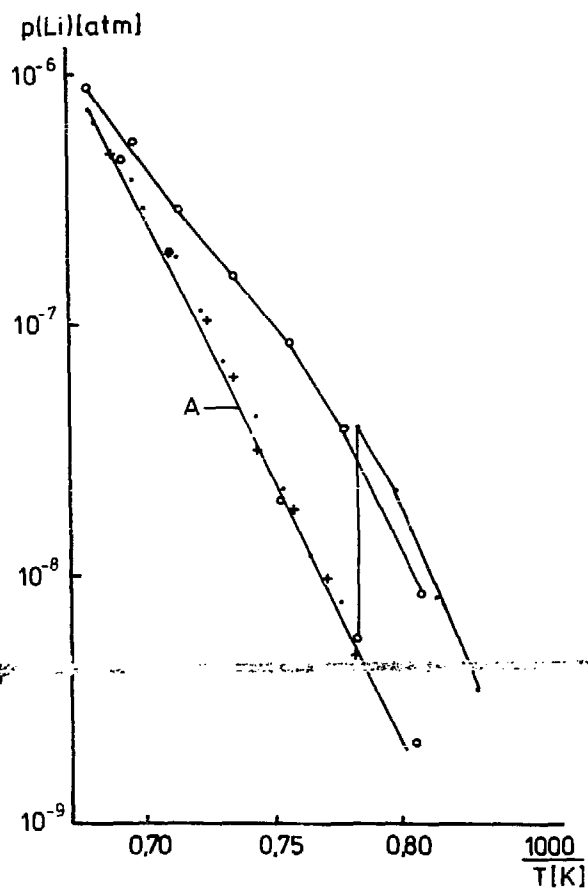
At the beginning of the measurement with a freshly loaded sample of LiAlO_2 , the Li-pressure follows a curve (•) above curve A. Maintaining constant temperature, the pressure decreases until it reaches curve A and then varies reproducibly along curve A. If the sample is taken out and stirred so that new parts come into contact with the wall, in a subsequent measurement the pressure follows the initial curve again (o). After some time, however, the pressure values reproduce again those given by curve A.

This shows that a wall reaction occurs reducing the O_2 pressure, which was found to be about 1/1000 of the Li-pressure.

X-ray analysis of parts of the sample which were close to the wall showed an increased amount of the solid product of thermal decomposition, the spinel LiAl_5O_8 , to about 5 %; while the bulk of the sample remained unchanged.

Fig. 7 shows the effect of the addition of stainless steel, Fe, Ni, Cr, Zr and Nb to LiAlO_2 on the Li-pressure.

When comparing stainless steel with its major constituent, it can be seen that chromium brings about the largest increase in Li-pressure, while zirconium has the highest effect of all the added metals. Taking into account that from the gas

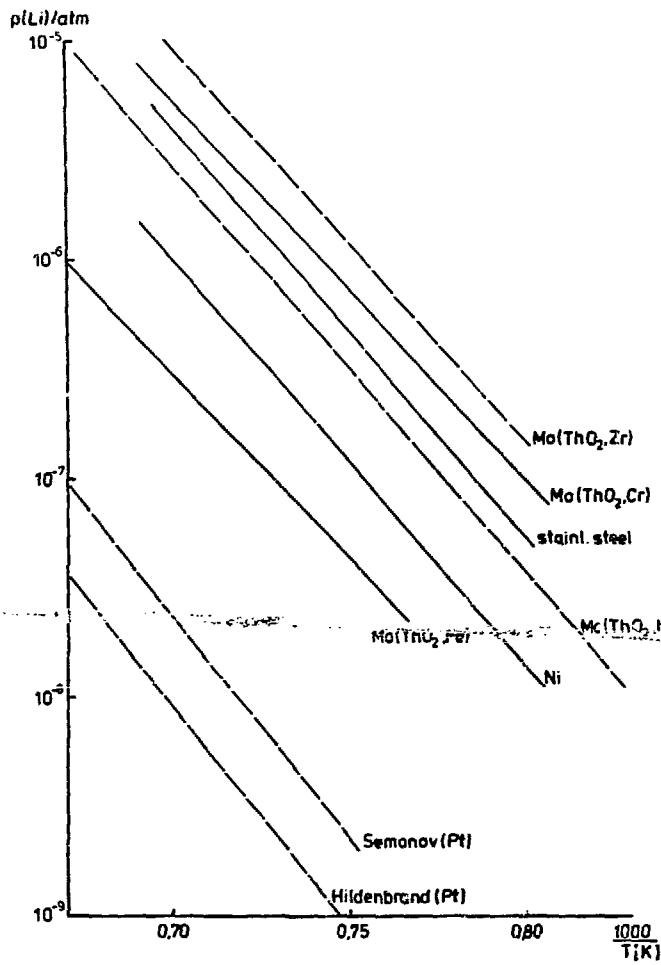


Li - pressure above $\gamma\text{-LiAlO}_2$

A : Mo - cell , Mo - liner ; final pressure

6

Variation of Li-pressure above $\gamma\text{-LiAlO}_2$ in
Molybdenum Cell, Wall Effect (cf. text)



7

Li-pressure above $\gamma\text{-LiAlO}_2$ in Contact with
Stainless Steel, its Constituents and some other
Metals

equilibrium one expects the O_2 -pressure to vary in inverse proportion to the 4th power of the Li-pressure, one can correlate the Li-pressures observed with those calculated from the O_2 -equilibrium-pressures over the added metal/metal oxide system.

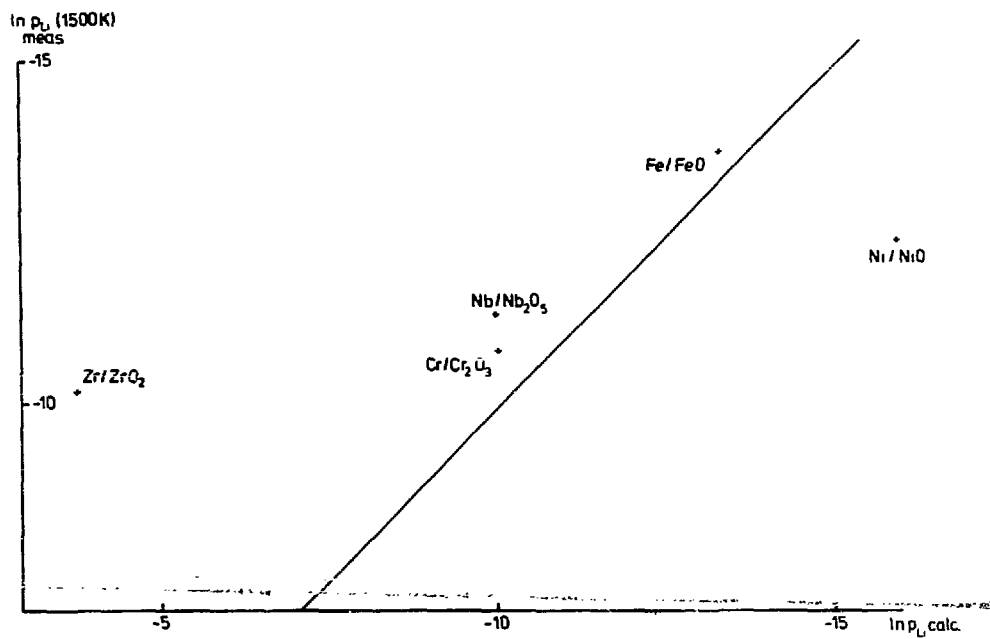
In Fig. 8 the measured Li-pressures are compared with the calculated Li-pressures. For chromium, niobium and iron we find agreement; the deviation for zirconium may be explained by the fact that the calculated O_2 -pressure over Zr/ZrO_2 at this temperature is so low ($\sim 10^{-29}$ atm) that it cannot be attained in a closed system due to the high O_2 -pressure of lithium aluminate.

Nickel shows a larger effect than it should have, and we are at present unable to provide an explanation for this.

DISCUSSION

The pronounced effects of metal walls and added metal powder on the Li-pressure and O_2 -pressure in a closed system will also influence the chemical form of tritium in the gas, because $p_{T_2O}/p_{T_2} \propto p_{O_2}^{1/2}$; Tritium is desorbed from bare lithium aluminate as T_2O as mentioned before in agreement with the thermodynamic expectation because of the relatively high O_2 -pressure of $\sim 10^{-14}$ atm over lithium aluminate at 700 °C. In the presence of zirconium, however, T_2 would predominate.

The O_2 -pressure over metal-canned lithium aluminate will therefore also effect the rate of permeation of tritium through the metal wall because this rate depends on the chemical species and type of reaction involved.



8

Comparison of Calculated and Measured Li-
Pressure above γ -LiAlO₂ + Metal

CONCLUSION

From the tritium release measurements on irradiated lithium aluminate in open and stainless steel clad form, and from the observed changes in the thermodynamic condition inside a lithium aluminate loaded vessel which are brought about by the type of wall material or added metal, one can anticipate that there will be many factors which ultimately control the tritium fluxes from a capsule. On the other hand one can expect that by appropriate choice of wall materials, and possibly the use of suitable additives, one can adjust the conditions of tritium release to the requirement of a particular fusion reactor concept.

ACKNOWLEDGEMENTS

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EQUILIBRIUM AND KINETIC STUDIES OF SYSTEMS OF HYDROGEN
ISOTOPES, LITHIUM HYDRIDES, ALUMINUM, AND LiAlO_2

J. Harding Owen
Duncan Randall

Savannah River Laboratory
E. I. du Pont de Nemours and Co.,
Aiken, South Carolina 29801

ABSTRACT

Tritium might be bred by the ${}^6\text{Li}(n,\alpha)\text{T}$ reaction in a solid lithium alloy or compound in the blanket of a controlled thermonuclear reactor to avoid problems associated with molten lithium or lithium compounds. Li-Al and LiAlO_2 systems containing hydrogen, deuterium, or tritium were studied 10-15 years ago at the Savannah River Laboratory. This paper describes measurements of (1) the distribution of tritium and helium throughout both α and β phases of irradiated Li-Al alloy, (2) the migration rate of tritium to the β phase during moderate heating, (3) equilibrium pressures as functions of temperature of H_2 , D_2 , or T_2 in contact with lithium hydrides + aluminum, Li-Al alloy, or irradiated Li-Al alloy, (4) the equilibrium constant for the reaction $\text{LiH} + \text{Al} \rightarrow \text{LiAl} + 1/2 \text{H}_2$ as a function of temperature, and (5) extraction rates of tritium from irradiated LiAlO_2 targets at elevated temperatures.

INTRODUCTION

Tritium might be bred by the ${}^6\text{Li}(n,\alpha)\text{T}$ reaction in a solid lithium alloy or compound in the blanket of a controlled thermonuclear reactor (CTR) to avoid problems associated with the use of molten lithium or a molten lithium compound. Lithium-aluminum and lithium aluminate systems containing hydrogen, deuterium, or tritium were studied 10 to 15 years ago at the Savannah River Laboratory (SRL).^{*} Although these systems

^{*} Work done by L. H. Meyer, M. O. Fulda, D. W. Tharin, Jr., and A. A. Kishbaugh.

contained higher concentrations of hydrogen isotopes (1 to 80 cm³ per cm³ of alloy) than would be expected in a low-inventory blanket,¹ the data are applicable to CTR-oriented research.

Measurements at SRL have included:

1. Distribution of tritium and helium between the alpha and beta phases of irradiated Li-Al alloy.
2. Kinetics of tritium migration in the alloy.
3. Equilibrium conditions for the reaction between aluminum and LiH, LiD, or LiT.
4. Extraction rates of tritium from irradiated LiAlO₂.

DISTRIBUTION OF TRITIUM AND HELIUM IN Li-Al ALLOY

In the 1.2, 3.2, and 7.4 wt % Li alloys of lithium and aluminum studied at SRL, an intermetallic compound, LiAl, is dispersed as a separate β phase in a dilute solid solution of Li in Al, the α phase. Figure 1 shows that at irradiation temperatures of $\sim 100^\circ\text{C}$, the solubility of Li in Al is low,^{2,3,4} so that practically all of the Li is in the β phase. But because the recoil range of tritons ($\sim 45 \times 10^{-4}$ cm in the β phase, $\sim 30 \times 10^{-4}$ cm in the α phase) is large compared to the size of the β -phase particles (radius $\sim 6.5 \times 10^{-4}$ cm) and the distance between the particles ($\sim 5 \times 10^{-4}$ cm), the newly formed tritium is distributed throughout both α and β phases, depending in part on the relative volume of the β phase (24% for 3.5 wt % Li alloy, 47% for 7.4 wt % alloy). On the other hand, helium remains predominantly in the α -phase near β -phase particles, because the helium recoil range is about equal to the average distance between the particles.

Moderate heat treatment (150° to 375°C) promotes migration of both tritium and helium. Tritium is concentrated in the β phase, which acts as a sink for tritium because of the reaction



Helium tends to collect in gas pockets in the α phase, in close proximity to the β -phase particles where most of it was formed.

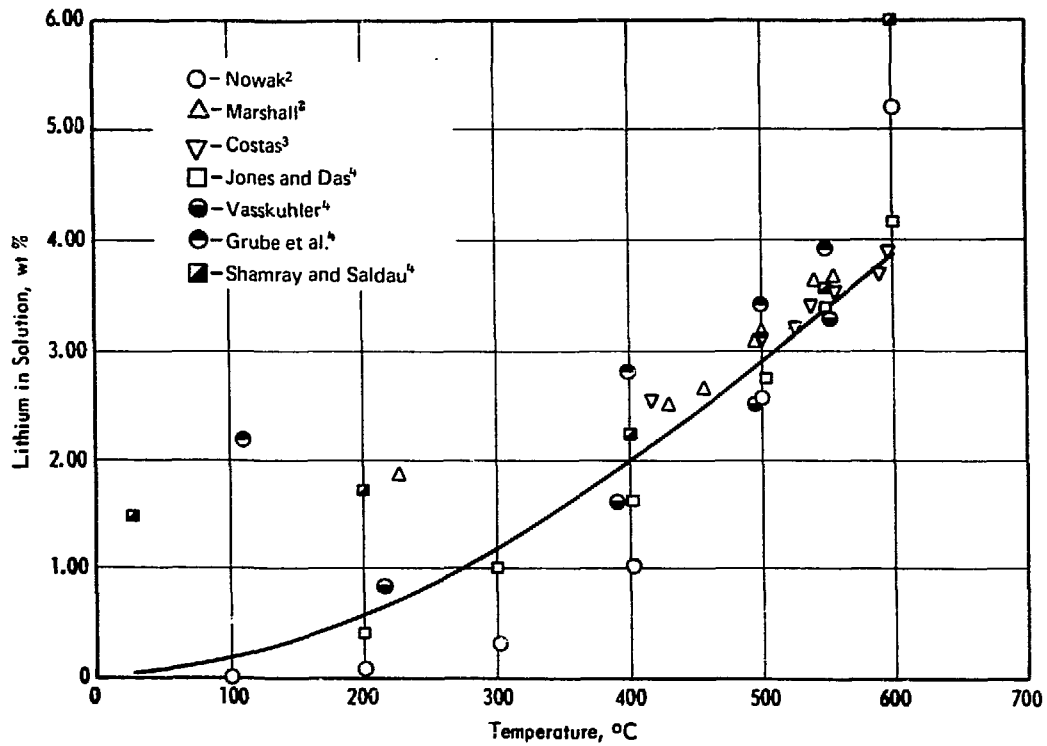
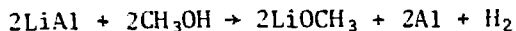


Fig. 1. Solubility of Lithium in Aluminum (Solid Phase).

Distribution of tritium and helium, before and after heat treatment, was determined by sequential dissolution of small chips of alloy machined from an irradiated slug. About 15 to 20 mg were first exposed to methanol for ~1 min, which dissolved much of the β phase:



Both gas and liquid phases were analyzed for tritium, then the liquid was evaporated and the residue analyzed for lithium and aluminum. The undissolved residue from the methanol treatment (mostly the aluminum-rich α phase) was then totally dissolved in 6N HCl, and both gas and liquid phases were analyzed. Table 1 summarizes results of 13 separate tests.

The higher density of the aluminum-rich α phase, compared to the lithium-rich β phase, hinders diffusion of tritons. Therefore, as these dissolution tests show, the α phase of the 7.4 wt % Li alloy initially contains more tritium (~81% of the total) than would be expected on the basis of its volume fraction in the alloy (53%). After heat treatment, however, most of the tritium is contained in the β phase.

These tests demonstrate that the helium content of the α phase, initially 70% to 90% of the total, is also diminished by heat treatment. The helium data are less reliable than the tritium data, because large corrections were required to allow for the solubility of helium in methanol and losses from gas pockets opened during machining and heat treatment.

KINETICS OF TRITIUM MIGRATION IN Li-Al ALLOY

The rate of migration of tritium to the β phase was measured by a second series of tests with 1/4" x 1" wafers, all cut from the same irradiated Li-Al alloy slug, then heat-treated before chips were removed for sequential dissolution and analysis. This technique reduces gas loss during heat treatment, so that the results summarized in Table 2 are probably more accurate than those for heat-treated chips in Table 1. Both sets of data are plotted in Figure 2.

Table 1. Distribution of Tritium and Helium in Irradiated Li-Al Alloy

Wt % Li in Alloy	Chips from Slug No.	Heat Treatment		Fraction of β -Phase Dissolved by CH_3OH (%)	Fraction of Total Tritium in α Phase (%) ^a	Fraction of Total Helium in α Phase (%)
		Time (hr)	Temp (°C)			
7.4	1		None	79.6	71.9	83
	1		None	78.2	84.4	89
	2		None	70.4	85.5	72
	2		None	76.2	83.4	76
	2	1	200 ^b	77.3	0.0	37
	2	1	300 ^b	79.2	0.0	44
	1	4	375 ^c	74.5	0.0	74
	1	4	375 ^c	70.6	3.5	-
	1	4	375 ^c	73.4	3.8	59
3.5	3		None	16.0	25	81
	4		None	15.5	73	93
	4		None	16.7	84	90
	4	1	300 ^b	28.7	40	66

^aCorrected for incomplete dissolution of β phase by CH_3OH .

^bChips heat-treated after machining.

^cSlug heat-treated before machining.

Table 2. Distribution of Tritium in Irradiated 7.4 Wt % Li Alloy

Heat Treatment of Wafers		Fraction of Total Tritium in α Phase of Chips
Time (hr)	Temp ($^{\circ}$ C)	Machined from Wafers after Heat Treatment (%)
	None	80
0.25	300	61
0.25	300	60
1.0	300	23
1.0	200	69
2.0	200	60
8.0	150	80
64	150	66
64	150	64
144	150	65

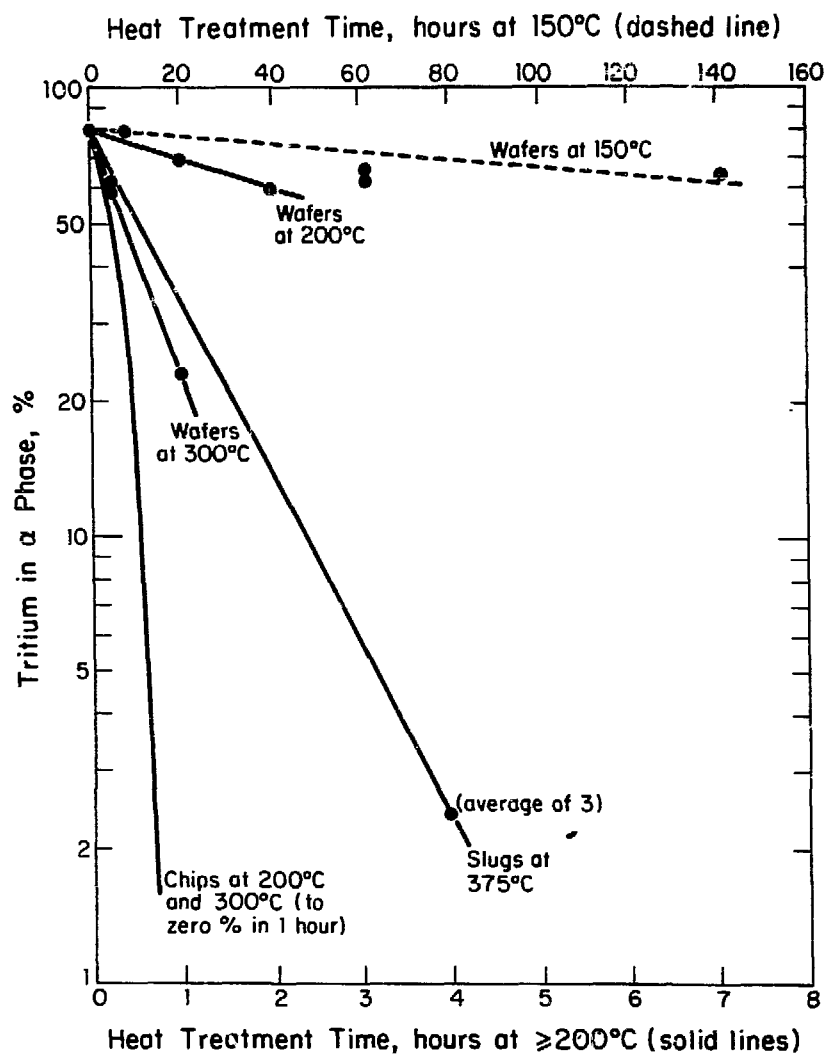


Fig. 2. Time Dependence of α Phase Tritium in Heat-Treated 7.4 wt % Li Alloy.

The linearity of $\log \% \text{ tritium}$ in the α phase vs heat treatment time for 7.4 wt % Li wafers (Figure 2) indicates that the migration of tritium from the α to the β phase is a first-order reaction. Values of the rate constant k (sec^{-1}) as a function of temperature were computed from half-times read from these curves at 150°, 200°, and 300°C (Table 3). A plot of $\log k$ vs $1/T(^{\circ}\text{K})$ is approximately linear, yielding $k = 2.35 \times 10^4 \exp(-2.00 \times 10^4/RT)$. The activation energy for the migration of tritium in the α phase is 20 ± 6 (std dev) kcal/mole.

Table 3. Measured Migration of Tritium from α to β Phase in 7.4 Wt % Li Alloy

Temperature ($^{\circ}\text{C}$)	Half-Time (sec)	Rate Constant k (sec^{-1})
150	1.26×10^5	5.50×10^{-7}
200	1.74×10^4	3.98×10^{-5}
300	2.00×10^3	3.47×10^{-4}

EQUILIBRIUM CONDITIONS FOR THE EXTRACTION OF HYDROGEN ISOTOPES

The reaction between LiT and aluminum,



is the mechanism for the release of tritium when irradiated Li-Al alloy is heated.* Figure 3 shows that around 500°C, the equilibrium pressure of tritium for this reaction is 300 to 600 times the pressure for the thermal decomposition of pure LiT.⁸

Tables 4 and 5 summarize SRL measurements of equilibrium pressures of hydrogen, deuterium, and tritium as a function of temperature; however, sufficient data to calculate equilibrium constants for the above reaction, as discussed below, were available for the 3.2 and 1.2 wt % alloys only (Table 5). Figure 4 is a schematic of the system used for these measurements.

* Addition of lead has been found to reduce both H_2 and T_2 losses during extraction from LiH or LiT, apparently by combining with condensing lithium vapors at the cooler throat of the furnace, thereby preventing resorption of the hydrogen isotopes.⁵ Lead flux reduces the amount of tritium retained in Li-Al alloy residues⁶ and permits rapid gas evolution at $\sim 490^{\circ}\text{C}$.⁷

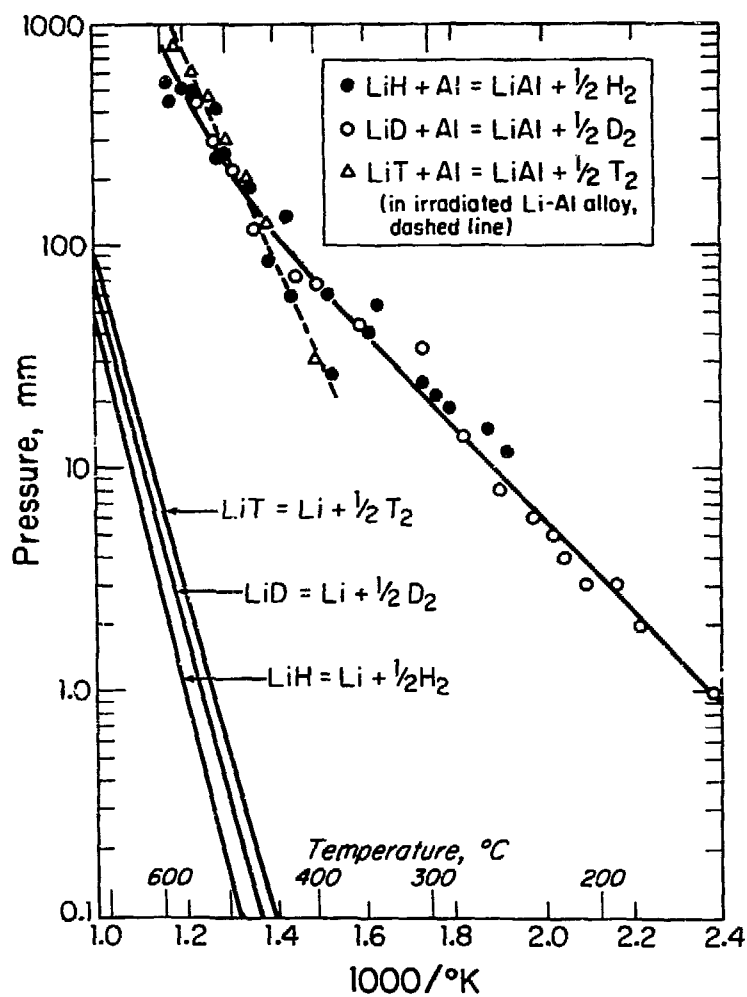


Fig. 3. Equilibrium Pressures of Hydrogen Isotopes for the Decomposition of Lithium Hydrides With and Without Aluminum.

Table 4. Equilibrium Pressures for Hydrogen, Deuterium, and Tritium

Gas	In Contact With	Temp (°C)	Press (mm)	Gas	In Contact With	Temp (°C)	Press (mm)
H ₂	LiH/Al ^a	247	12	D ₂	LiD/Al ^a	147	1
		258	15			178	2
		287	19			190	3
		296	21			206	3
		304	24			214	4
		342	54			215	4
		347	40			222	5
		360	44			231	6
		382	27			253	8
		384	60			275	14
		423	58			304	34
		424	134			354	44
		448	84			398	66
		466	181			417	71
		500	258			461	117
		501	248			492	212
		502	408			506	289
		510	477 ^b			534	433
		534	496 ^b	T ₂	Li-Al ^c	400	31
		548	478			450	123
		558	497			475	196
		583	432			500	297
		586	552			525	438
						550	588
						575	769

^aPrepared by thermal decomposition of LiAlH₄, LiAlD₄ at 200°C,⁹ e.g.,
 $\text{LiAlH}_4 \rightarrow \text{LiH} + \text{Al} + 3/2\text{H}_2$.

^bFor unirradiated 3.5 wt % Li alloy, not LiH.

^cIrradiated 3.5 wt % Li alloy.

Table 5. Equilibrium Constants for the Reaction $\text{LiH} + \text{Al} \rightarrow \text{LiAl} + 1/2\text{H}_2$

Wt % Li in Alloy	Temp (°C)	$\frac{1000}{T(^{\circ}\text{K})}$	GVR (cm ³ H ₂ /cm ³ alloy)	$P_{\text{H}_2}^a$ (mm)	$\sqrt{P_{\text{H}_2}}$ (atm) ^{1/2}	a_{LiAl}	$a_{\text{Al}} =$ $1 - a_{\text{LiAl}}$	K
3.2	375	1.543	2.5	10	0.1147	0.1260	0.8740	0.0165
			5	11	0.1203	0.1234	0.8766	0.0169
			10	12	0.1257	0.1184	0.8816	0.0169
			20	15	0.1405	0.1082	0.8918	0.0171
			30	18	0.1539	0.0981	0.9019	0.0167
			40	22	0.1701	0.0880	0.9120	0.0164
			50	27	0.1885	0.0779	0.9221	0.0159
			60	32	0.2052	0.0678	0.9322	0.0149
			70	49	0.2539	0.0577	0.9423	0.0155
			80	89	0.3422	0.0476	0.9524	0.0171
	475	1.337	2	143	0.4338	0.1265	0.8735	0.0628
			5	160	0.4588	0.1234	0.8766	0.0646
			10	175	0.4799	0.1184	0.8816	0.0644
			20	230	0.5501	0.1082	0.8918	0.0668
			30	295	0.6230	0.0981	0.9019	0.0678
			40	380	0.7071	0.0880	0.9120	0.0682
			50	500	0.8111	0.0779	0.9221	0.0685
			60	640	0.9177	0.0678	0.9322	0.0667
1.2	325	1.672	5	6	0.0889	0.0425	0.9575	0.0039
			10	9	0.1088	0.0378	0.9622	0.0043
			20	23	0.1740	0.0283	0.9717	0.0051
			30	67	0.2969	0.0189	0.9811	0.0057
			40	240	0.5620	0.0094	0.9906	0.0053
	375	1.543	5	52	0.2616	0.0425	0.9575	0.0016
			10	80	0.3244	0.0378	0.9622	0.0127
			20	180	0.4867	0.0283	0.9717	0.0142
			25	270	0.5960	0.0236	0.9764	0.0144
	395	1.497	5	140	0.4292	0.0425	0.9575	0.0191
			10	200	0.5130	0.0378	0.9622	0.0201
	460	1.364	1	530	0.8351	0.0463	0.9537	0.0405
			3	710	0.9665	0.0444	0.9556	0.9449

^aHydrogen pressures corresponding to specified GVR's were read from Figures 5 and 6.

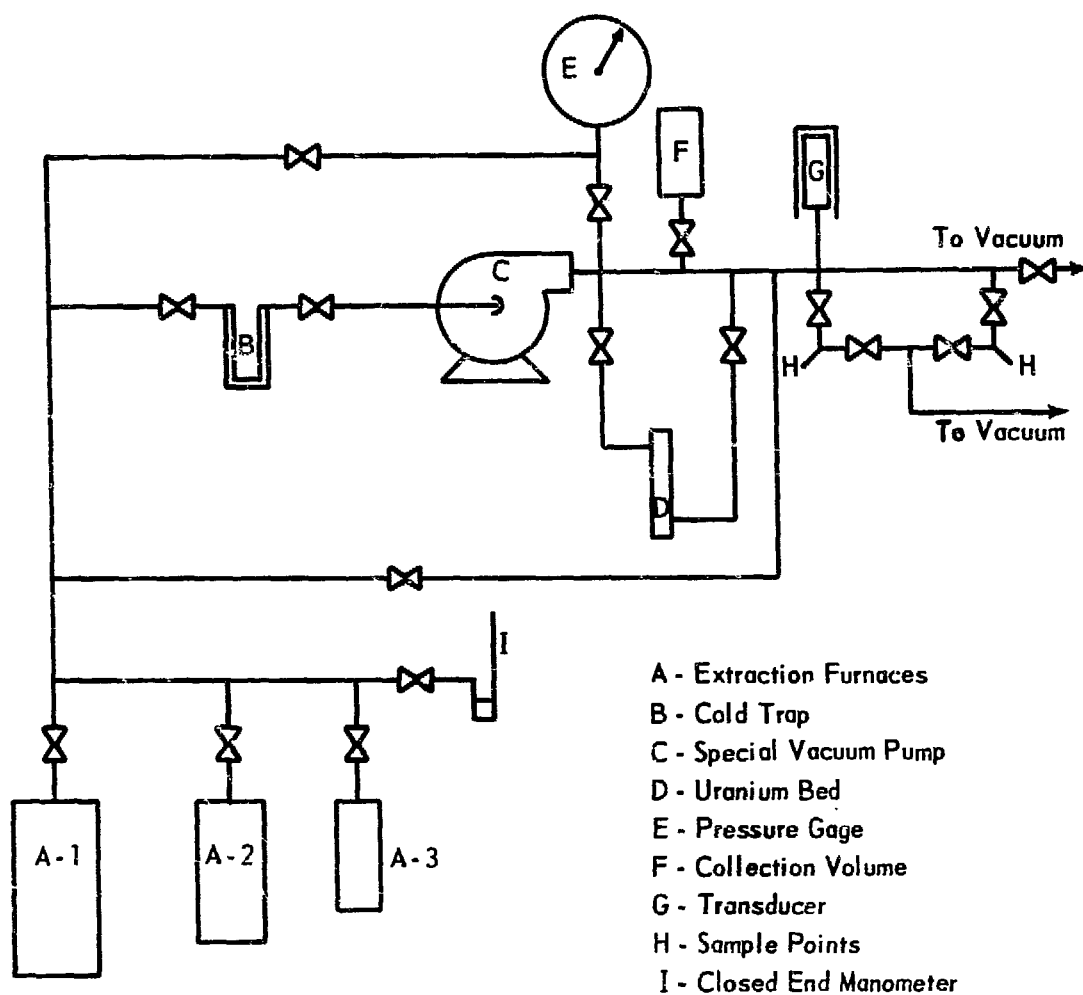


Fig. 4. Schematic Diagram of Apparatus for Measuring Pressures of Hydrogen Isotopes in Equilibrium with Reaction Mixtures.

The alloys were maintained at a constant temperature; equilibrium was assumed to have been attained after the pressure remained constant for one hour. Equilibrium pressures were measured after both increasing and decreasing the temperature to the desired level; agreement was good except at lower temperatures where re-absorption was so slow that equilibration was impractical.

Equilibrium constants for the reaction with hydrogen were calculated as follows:

$$K = \frac{a_{\text{LiAl}} \sqrt{a_{\text{H}_2}}}{a_{\text{LiH}} a_{\text{Al}}}$$

where a_{H_2} = equilibrium pressure (mm)/760 mm atm⁻¹, and where a_{LiH} = 1.00 was assumed because LiH exists as a separate phase in the binary Al-Li system.

Several assumptions are possible for the determination of a_{Al} and a_{LiAl} . First, a_{LiAl} might be taken as unity, because it exists as a separate β phase in the α -phase solid solution of Li and Al; and a_{Al} might be taken as $1 - a_{\text{Li}}$, where a_{Li} is the mole fraction of the Li that is dissolved in the α phase at saturation, as computed from Figure 1.

But Figures 5 and 6 show that the equilibrium hydrogen pressure is a function of the hydrogen content of the Li-Al system (i.e., the "gas volume ratio"*)). Therefore it would be better to assume that at high GVR's so much Li is converted to LiH that no LiAl exists as a separate β phase and even the α phase is not saturated with LiAl. Then the number of moles of LiAl in the α phase is not determined by saturation, but is the number of moles of Li originally present less the amount precipitated as LiH. At some intermediate GVR, all LiAl(β) has just been converted to LiH, and the α phase is just saturated with LiAl. Finally, for all lower GVR's, the α phase is saturated with LiAl, some LiAl is present in a separate β phase, and a small amount of LiH has been precipitated.

* GVR = cm³ of total gas/cm³ of alloy.

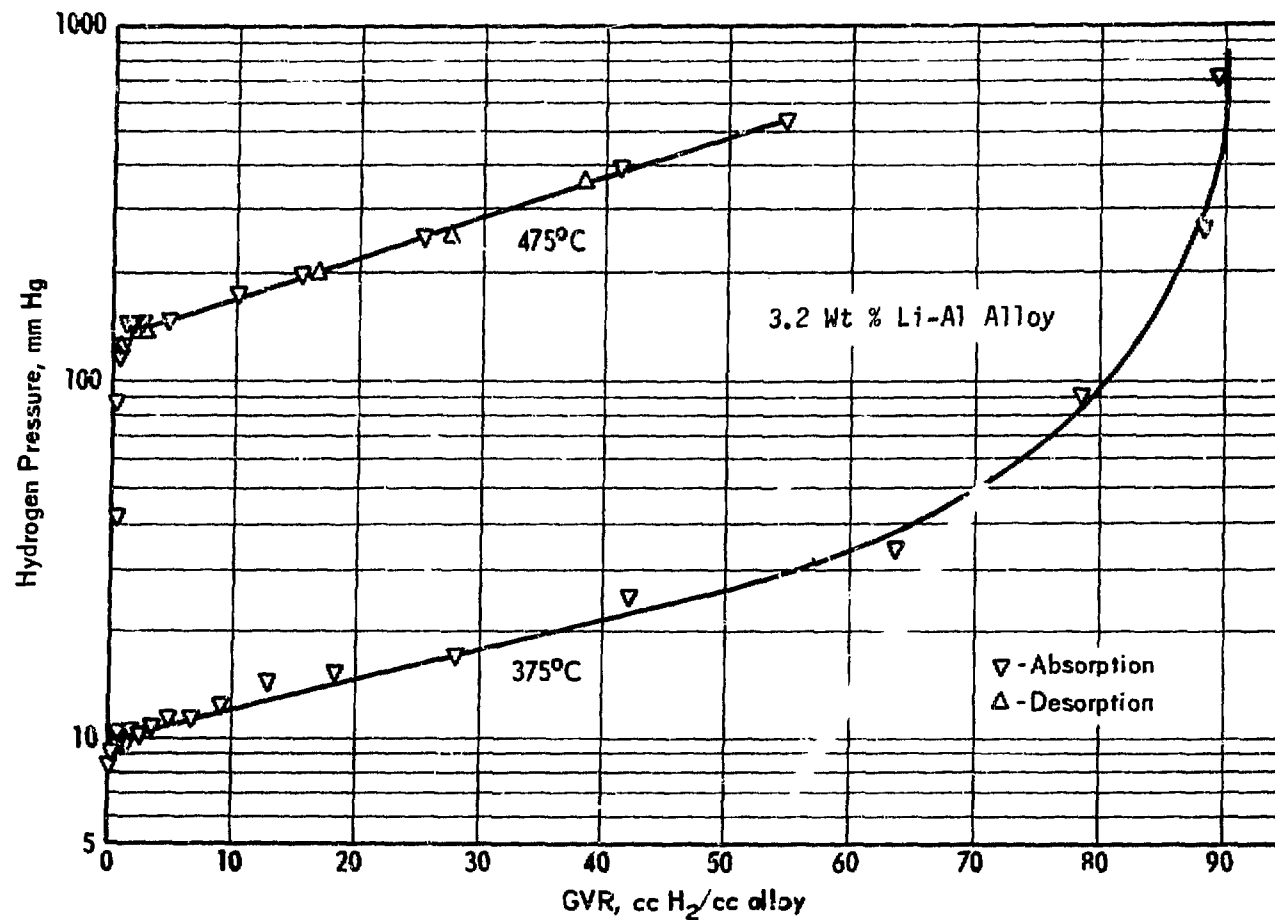


Fig. 5. Hydrogen Pressure-Concentration Isotherms for 3.2 Wt % Li Alloy.

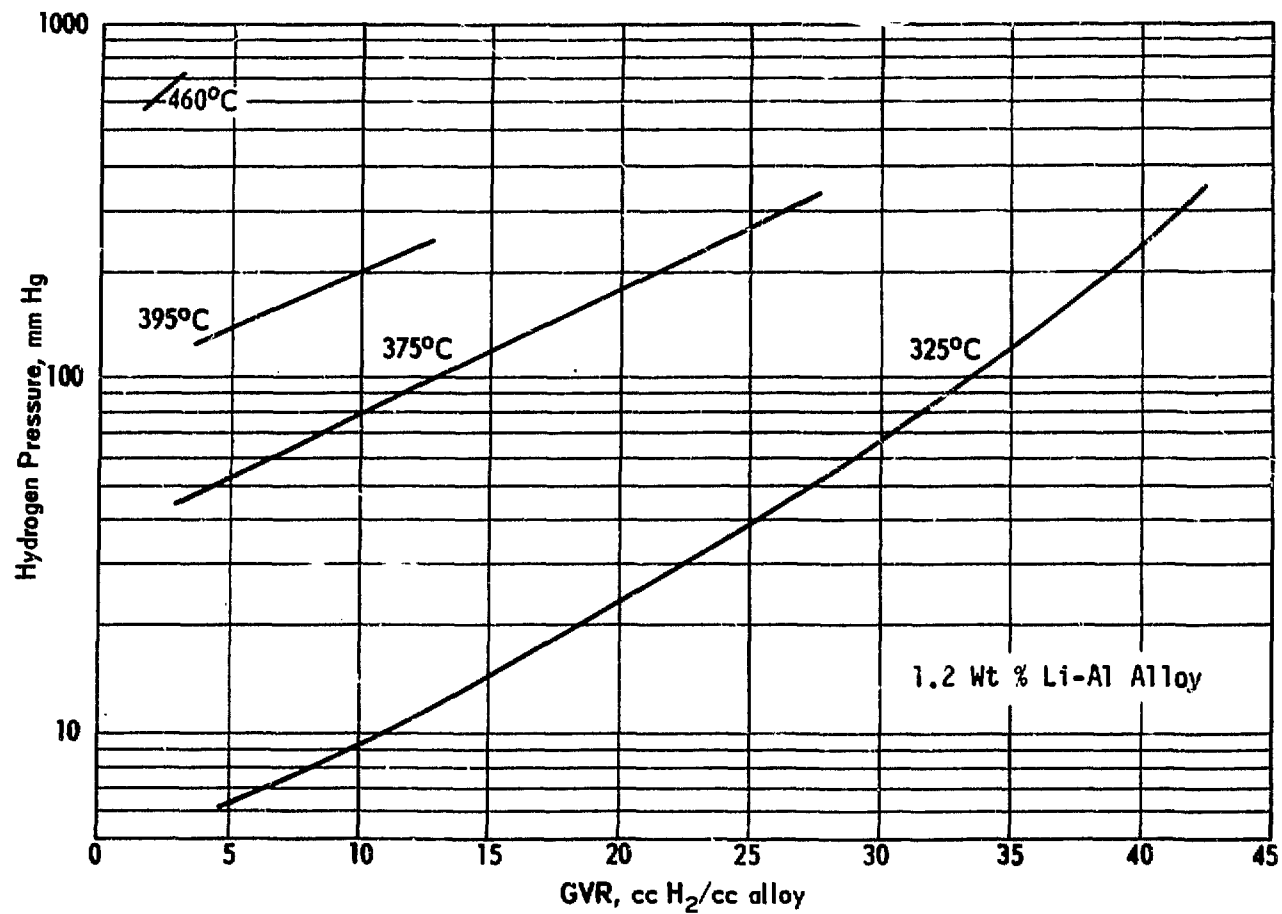


Fig. 6. Hydrogen Pressure-Concentration Isotherms for 1.2 Wt % Li Alloy.

However, this formulation does not fit the experimental data too well. First, the calculated equilibrium constants actually vary by nearly $\pm 50\%$. Second, if the activity of LiAl remains constant as long as some LiAl is present as a separate phase (above the saturation curve, Figure 1), the hydrogen pressure must also remain constant: by the phase rule for 3 components (Li, Al, H) and 4 phases (LiAl + Al in α phase, LiAl in β phase, precipitated LiH, and H_2 gas), degrees of freedom = $C - P + 2 = 3 - 4 + 2 = 1$, which requires that the hydrogen pressure be invariant at any given temperature. This invariance is not observed even at the lowest GVR values (Figures 5,6).

Since greater and greater pressures are required to force additional increments of hydrogen into the sample, regardless of whether or not a separate LiAl phase is present, it appears that LiAl *behaves* as if it were always dissolved in the α phase (then $C - P + 2 = 3 - 3 + 2 = 2$ degrees of freedom, temperature *and* pressure variable). This could occur if the activity of the LiAl decreases with increasing formation of LiH. Table 5 shows equilibrium constants calculated according to this last formulation. For example, in 1 cm³ of 3.2 wt % Li alloy (density = 2.46 g/cm³) at 375°C,

$$\begin{aligned} n_{Al}^{\circ} &= n_{Al(\alpha)} + n_{LiAl(\alpha)} = \text{moles of free Al} + \text{Al in LiAl, in } \alpha \text{ phase} \\ &= \frac{(2.46 \text{ g alloy})(0.968 \text{ g Al/g alloy})}{26.98 \text{ g/mole Al}} = 0.0883 \end{aligned}$$

$$\begin{aligned} n_{Li}^{\circ} &= \text{total number of moles of Li} \\ &= \frac{(2.46 \text{ g alloy})(0.032 \text{ g Li/g alloy})}{6.94 \text{ g/mole Li}} = 0.0113 \end{aligned}$$

$$\begin{aligned} n_{LiAl(\alpha)} &= n_{Li}^{\circ} - n_{LiH} \\ &= n_{Li}^{\circ} - \frac{\text{GVR}}{11200 \text{ cm}^3/\text{g atom hydrogen}} \end{aligned}$$

$$a_{\text{LiAl}} = \frac{n_{\text{LiAl}}(\alpha)}{n_{\text{LiAl}}(\alpha) + n_{\text{Al}}(\alpha)} = \frac{n_{\text{LiAl}}(\alpha)}{n_{\text{Al}}^{\circ}}$$

$$= \frac{n_{\text{Li}}^{\circ} - (\text{GVR}/11200)}{n_{\text{Al}}^{\circ}} = \frac{0.0113 - (\text{GVR}/11200)}{0.0883}$$

$$a_{\text{Al}} = 1 - a_{\text{LiAl}}$$

Then since $a_{\text{LiH}} = 1.00$ and $a_{\text{H}_2} = \sqrt{P_{\text{H}_2}}$, atmos,

$$K = \frac{a_{\text{LiAl}}}{a_{\text{Al}}} \sqrt{P_{\text{H}_2}} = \frac{127 - \text{GVR}}{862 + \text{GVR}} \sqrt{P_{\text{H}_2}} \text{ for 3.2 wt \% Li alloy.}$$

Similarly, for 1.2 wt % Li alloy, density = 2.58 g/cm³,

$$n_{\text{Al}}^{\circ} = 0.0945$$

$$n_{\text{Li}}^{\circ} = 0.00446$$

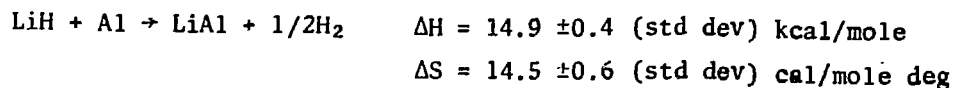
$$a_{\text{LiAl}} = \frac{n_{\text{Li}}^{\circ} - (\text{GVR}/11200)}{n_{\text{Al}}^{\circ}} = \frac{0.00446 - (\text{GVR}/11200)}{0.00945}$$

$$a_{\text{Al}} = 1 - a_{\text{LiAl}}$$

$$K = \frac{a_{\text{LiAl}}}{a_{\text{Al}}} \sqrt{P_{\text{H}_2}} = \frac{50.0 - \text{GVR}}{1008 + \text{GVR}} \sqrt{P_{\text{H}_2}} \text{ for 1.2 wt \% Li alloy.}$$

It may seem inconsistent to assume that the LiH phase is completely separate from the Li + LiAl matrix, whereas the LiAl phase is considered to be dissolved. But LiH is chemically much more like a salt than a metal and would not be expected to dissolve in aluminum. Furthermore, equilibrium constants computed on this basis (Table 5) are now constant within about $\pm 7\%$.

A plot of $\log K$ vs $1/T$, Figure 7, yields the entropy and heat of reaction:



The heat of formation of LiAl calculated from this value and from

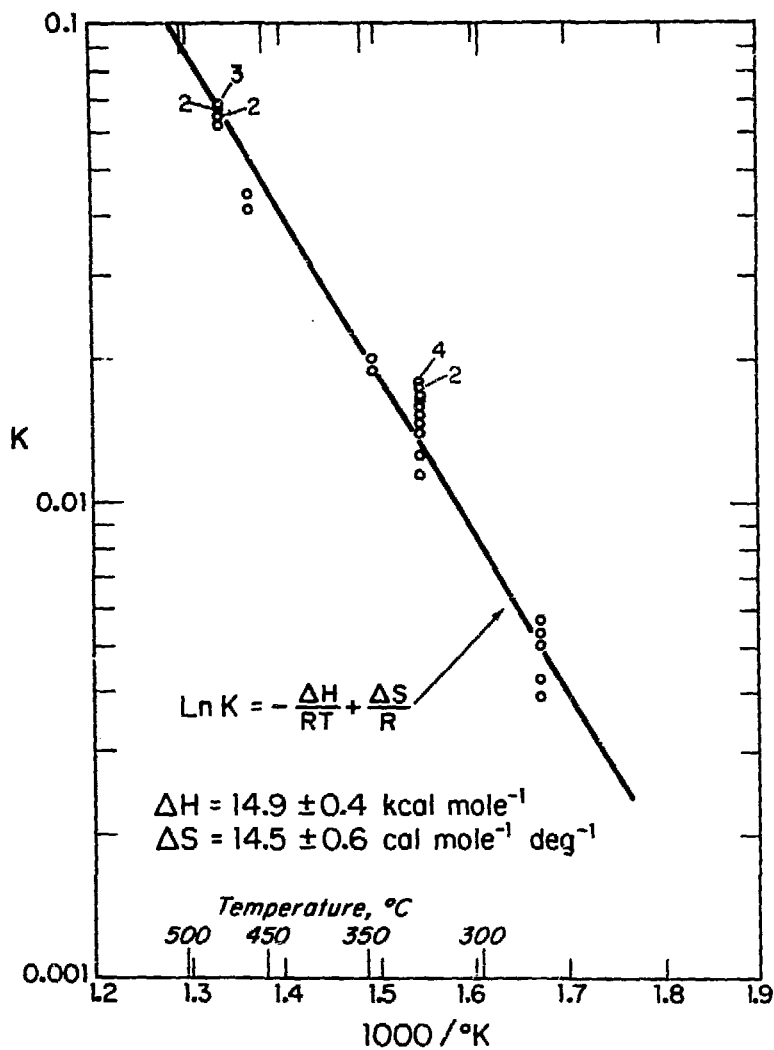


Fig. 7. Temperature Dependence of the Equilibrium Constant for the Reaction $\text{LiH} + \text{Al} \rightarrow \text{LiAl} + 1/2\text{H}_2$.

the heat of formation of LiH^{10} is -6.8 kcal/mole, in comparison with a reported value of -13.0 ± 4.0 kcal/mole.¹¹

Data were insufficient for similar calculations of equilibrium constants for deuterium and tritium.

EXTRACTION OF TRITIUM FROM IRRADIATED LITHIUM ALUMINATE

In 1966, SRL developed a process for the extraction of tritium from irradiated LiAlO_2 targets.¹² The New Production Reactor at Hanford required tritium-producing targets that would not melt even if the zirconium-clad targets were heated to $\sim 1100^\circ\text{C}$. Lithium aluminate was chosen as the most suitable target material (m.p. = 1900°C) after tests of its irradiation stability. It had been proposed to extract tritium from clad LiAlO_2 targets by dissolution in molten borax at 850°C . But experiments at SRL showed that tritium could be extracted by simply heating the targets at 850°C in a vacuum for 11 hours, leaving $<0.1\%$ of the tritium in the residue; borax flux was not only unnecessary, but increased tritium losses to 1-2%.

Typical gas evolution rates are shown in Figures 8 and 9. Table 6 shows how tritium losses can be reduced by prolonged heating and/or higher temperatures.

In these tests, hydrogen isotopes were separated from other extraction gases by Hopcalite* (catalytic oxidizer) and zeolite (water absorber) beds in series, followed by a uranium bed decomposer (Figure 10). After loading the furnace and pumping the system down to <50 microns, the furnace was heated and evolved gases were passed through the Hopcalite bed at 500°C to oxidize hydrogen isotopes. Water vapors were sorbed on the zeolite bed at 50°C while remaining gases (mainly CO , CO_2 , and He) passed through and were discharged. After completion of extraction, the zeolite was heated to 500°C and desorbed water vapors were passed through the uranium decomposer bed at 550°C to regenerate the gaseous hydrogen isotopes.

* Tradename of Mine Safety Appliances Co.; 80:20 mixture of MnO_2 , CuO_2 .

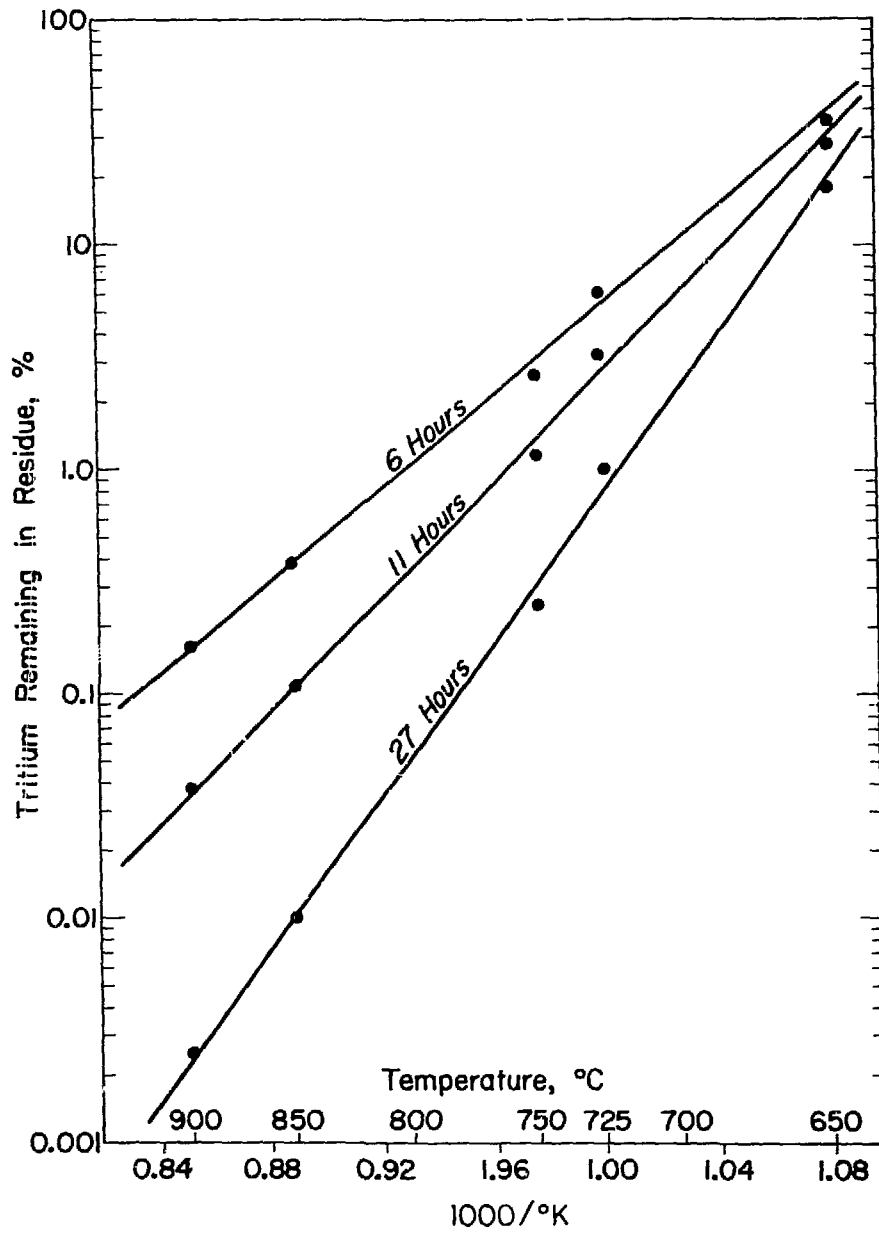


Fig. 8. Effect of Time and Temperature on Extraction of Tritium from Irradiated LiAlO_2 .

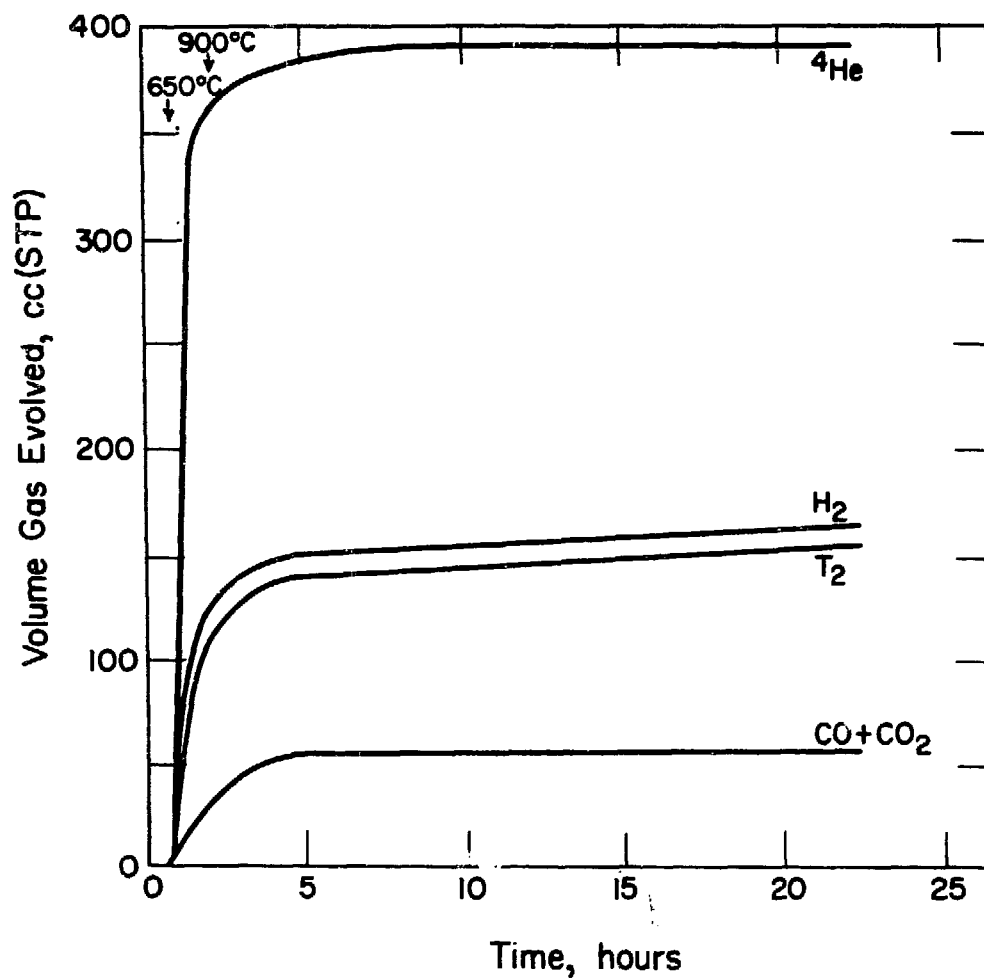


Fig. 9. Gas Evolution from Irradiated LiAlO_2 at 900°C Without Borax Flux.

Table 6. Tritium Loss to the Residue

LiAlO ₂ Density, % of Theoretical	Extraction Conditions		% of Total Tritium Retained in LiAlO ₂ Residue
	Temp (°C)	Time (hr)	
88.6	650	11	28
88.6	725	11	5.2
88.6	725	21	1.5
79.3	750	11	0.91, 1.5 ^a
79.3	850	6	0.32, 0.36, 0.41
-	850	11	0.08
88.6	850	11	0.14
79.3	850	21	0.012
79.3	900	24	0.004

^a0.64% for targets submerged in molten aluminum.

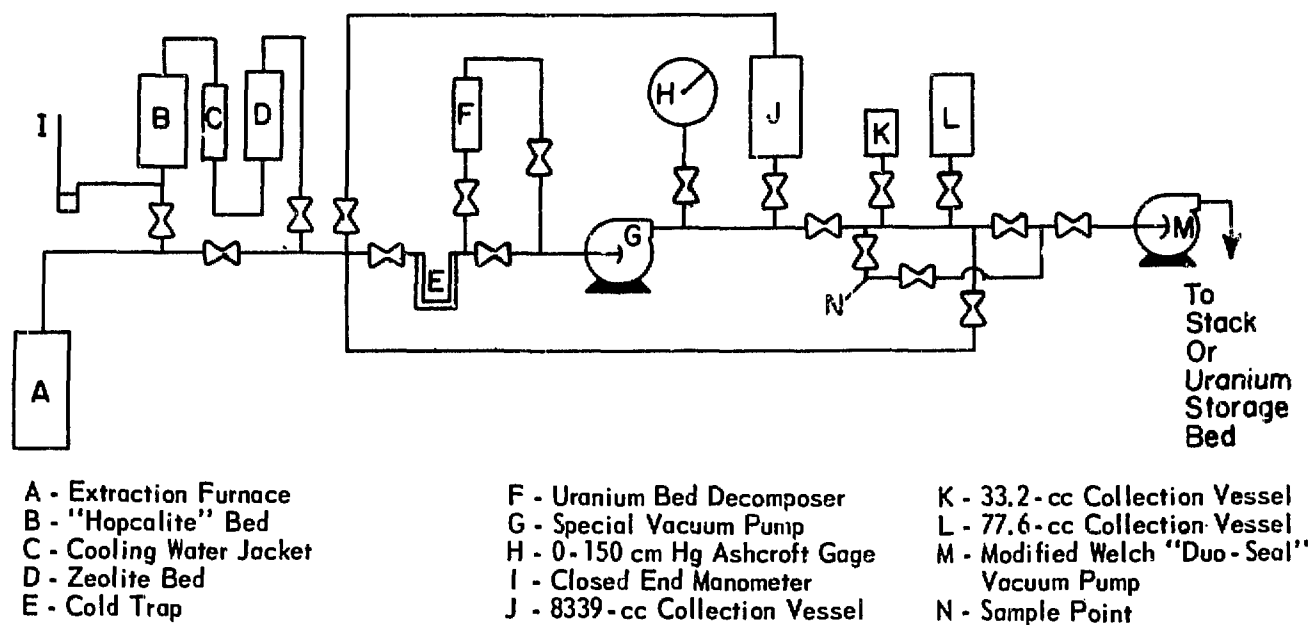


Fig. 10. Experimental Extraction Facility.

Additional experiments showed that the presence of CO and CO₂ equivalent to 10-30 volume % of the tritium did not degrade the performance of the uranium decomposer. No CH₄ was formed, which would have decreased the permeability of the palladium diffuser used in subsequent operations to separate hydrogen isotopes from ³He and ⁴He; the hydrogen permeation rate at 450°C did not change during exposure of the palladium diffuser to a mixture of H₂, CO, and CO₂ for >1700 hr. A Hopcalite-zeolite system to separate CO and CO₂ from hydrogen isotopes appears to be unnecessary for a full-scale extraction process.

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THERMODYNAMIC PROPERTIES OF SOLUTIONS OF HYDROGEN
ISOTOPES IN METALS AND ALLOYS OF INTEREST
TO FUSION REACTOR TECHNOLOGY*

Ewald Veleckis
Victor A. Maroni

Chemical Engineering Division
Argonne National Laboratory
Argonne, Illinois 60439

ABSTRACT

Recent ANL work on the solution thermodynamics of systems composed of a hydrogen isotope and either pure lithium or a lithium-containing alloy has been directed toward (1) the sources and magnitude of isotope effects in the systems Li-LiH and Li-LiD, (2) the solubility of LiD in liquid lithium (200-700°C), and (3) the solubility and decomposition pressure of hydrogen in the ternary Li-Al-H system. The H/D isotope effect appears to originate primarily in the gas phase and within the two-phase regions of the phase diagram, its range of values is 1.43 ± 0.05 . At 200°C, the solubility of LiD in lithium is ~250 appm D, thus essentially ruling out hydrogen isotope separation methods based on cold-trapping concepts. Two isotherms (at 550 and 599°C) have been obtained for solutions of hydrogen in the β -phase of the Li-Al system (48-56 mol % Li). They indicate that, at low hydrogen concentrations (<1 atom % H), the dissociation pressures are much higher ($\times 100$) than those over the lithium metal. Within the miscibility gap, which extends from 6 to 33.3 atom % D, the plateau pressures, P, may be represented by $\ln P \text{ (Torr)} = 20.46 - 11,600 T^{-1}$.

INTRODUCTION

The importance of lithium as a blanket/coolant material in thermonuclear reactors is well recognized. The knowledge of the solution behavior of hydrogen isotopes in the blanket is necessary in order to evaluate conditions for their removal or recycling. Recovery of tritium is of particular importance from the standpoint of safety and economics. A program currently in progress at ANL is directed toward the study of those physicochemical and thermodynamic properties of blanket materials

* Work performed under the auspices of the U.S. Energy and Research Development Administration.

that pertain to their use in fusion reactors. Although most of our efforts have focused on liquid lithium as a blanket material, some work is in progress on a solid blanket material - the β -phase of the Li-Al system containing ~ 50 atom % Li.

SOLUTIONS OF HYDROGEN ISOTOPES IN LIQUID LITHIUM

From an experimental viewpoint, our lithium studies may be divided into three areas: isothermal studies, plateau pressure studies and solubility studies. Recent results in each area are summarized below.

Isothermal Studies

These studies comprise extensive measurements of the decomposition pressures for the systems Li-LiH and Li-LiD under isothermal conditions, in the temperature range from 700 to 900°C. Experimental details have been described elsewhere.¹ Briefly, a ~ 2 g sample of lithium is encapsulated in a thin-walled iron crucible which forms a semi-permeable membrane around the lithium sample. The crucible is placed in a fused-silica tube and connected to the Sieverts' apparatus. Hydrogen (or deuterium) gas, introduced in small, measured quantities, diffuses through the walls of iron crucible and reacts with the lithium. After each gas addition, the sample is equilibrated (~ 8 hr) and the resulting gas pressure is recorded.

For each system, the measurements yielded a family of isotherms, as shown in Fig. 1. Each isotherm is composed of two rising portions which are connected by a pressure plateau. The first break in the isotherms corresponds to the solubility of hydride (or deuteride) in lithium; the second break - to the solubility of lithium in liquid hydride (or deuteride).

The data points in Fig. 1 are connected by smoothed lines that have no analytical significance. However, we have also fitted the data points by a consistent thermodynamic treatment¹ using the Margules forms for the activity coefficients. This treatment yields expressions for (1) the activity and activity coefficients of the dissolved hydride (or deuteride), (2) the standard free energy of formation of liquid LiH (or

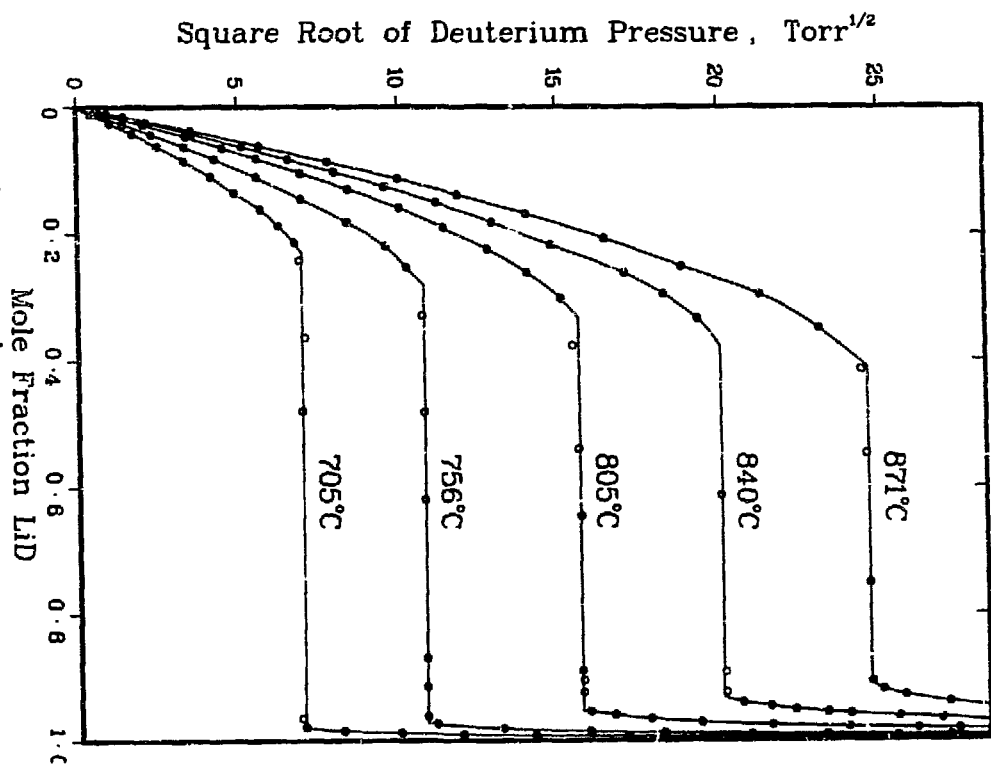
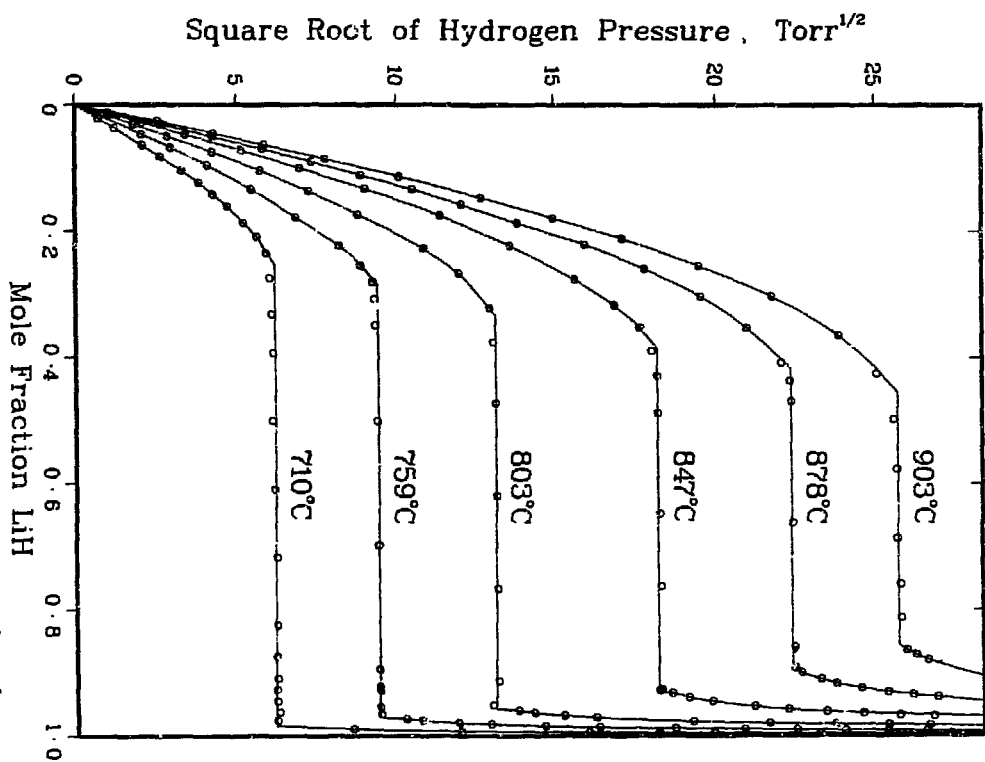


Fig. 1. Projections of the Isothermal Data on the Square Root of Pressure vs. Composition Planes for the Systems Li-LiH and Li-LiD.

LiD), and (3) the Sieverts' constants for dilute solutions of LiH (or LiD) in liquid lithium. Isotherms constructed using these expressions show very good agreement (within 1%) with the experimental data.

At low concentrations, our derived isotherms can be compared with the recent literature data,^{2,3} which are available for all three hydrogen isotopes (Fig. 2). For hydrogen and deuterium, the agreement among the various studies is very good, with possible exception of Goodall and McCracken's data at high concentrations. For tritium, no comparison can be made since Smith and Land's study² is the only one available thus far.

Plateau Pressure Studies

Isotope effects resulting from the interaction of liquid lithium with hydrogen isotopes can be conveniently evaluated by measuring the decomposition pressures over the two-phase mixtures (*i.e.*, within the miscibility gap) for the systems Li-LiH, Li-LiD and Li-LiT. Our previous studies with hydrogen and deuterium have shown that the bulk of the isotope effect can be accounted for by the differences in the decomposition pressures. Making measurements in the two-phase regions is particularly advantageous, since here the pressures fall on the plateau portions of the isotherms and do not vary with composition.

In order to obtain precise H/D isotope effects, identical experimental conditions are being maintained for both isotopes. The procedure is essentially the same as that described in the preceding section. An encapsulated lithium sample (~35 mg) is allowed to react with ~40 std cm³ of hydrogen (or deuterium) to produce a ~60 mol % LiH (or LiD) mixture. Equilibrium decomposition pressures are then determined in 25°C intervals between 600 and 800°C. This temperature range includes measurements both above and below the monotectic.

The results for the Li-LiH and Li-LiD systems are shown in Fig. 3, where the logarithms of the plateau pressures are plotted against $1/T$. For each system, the data form two linear segments. The points of their intersection correspond to the monotectic temperatures: 695°C for Li-LiH and 690°C for Li-LiD. Within the experimental errors, the H/D isotope effect appears to be identical for the liquid and for the solid phases.

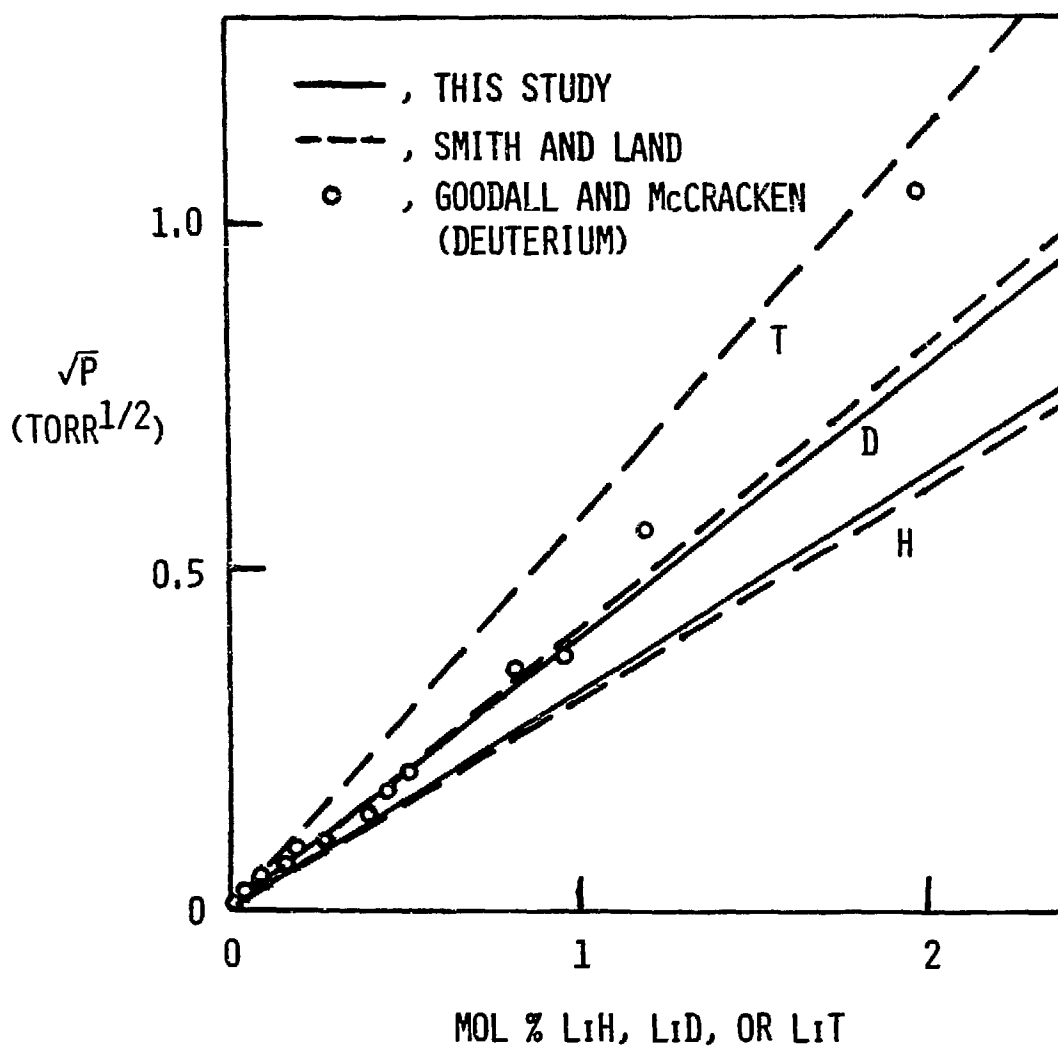


Fig. 2. Comparison of the 700°C Isotherms for the Systems Li-LiH, Li-LiD, and Li-LiT in Dilute Solution Regions.

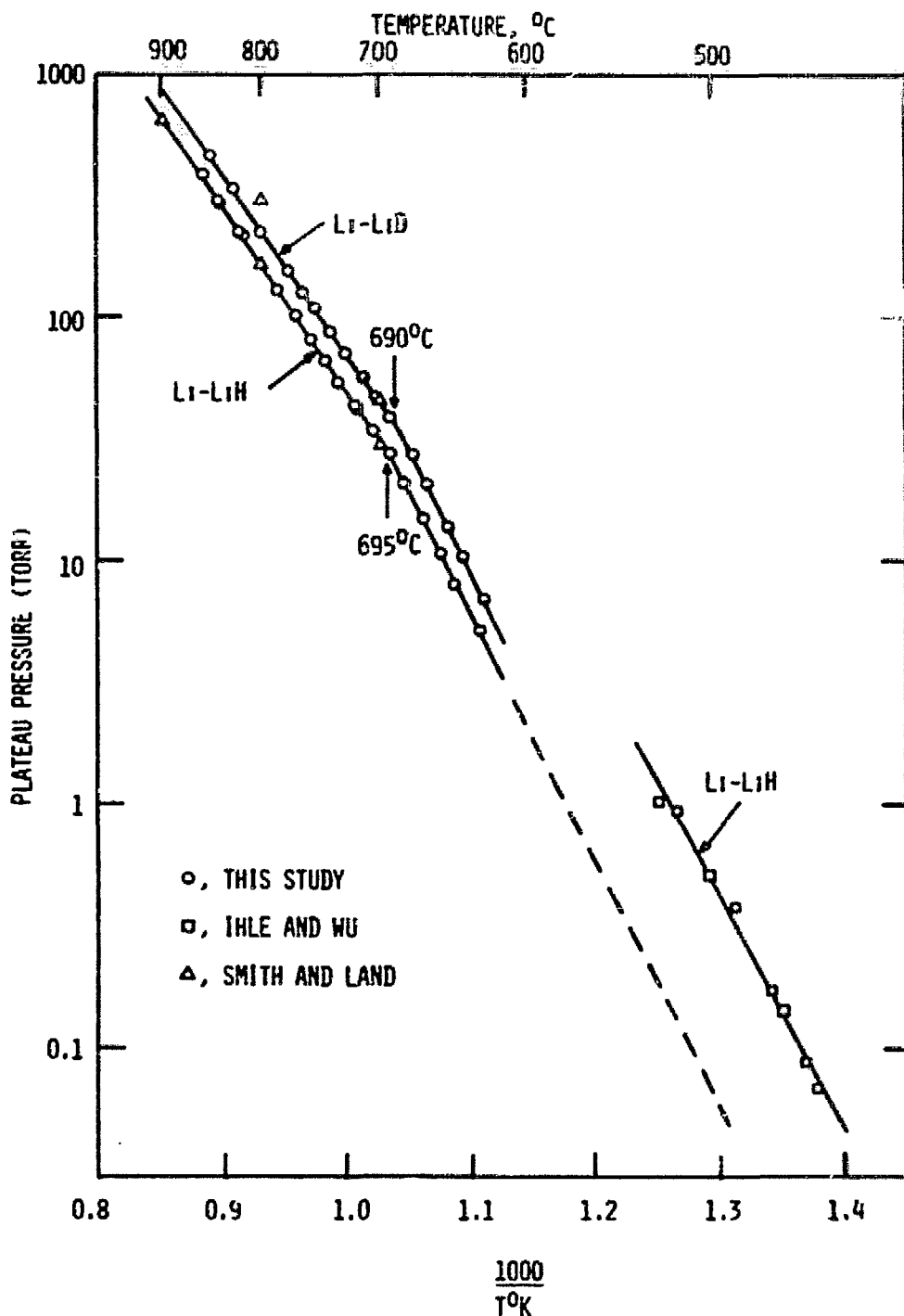


Fig. 3. Plateau Pressures of the Li-LiH and Li-LiD Systems at ~60 Mol % LiH (or LiD). ○ and △, Tensimetric Data. □, Mass Spectrometric Data.

The range of its value, 1.43 ± 0.05 , includes the square root of D/H mass ratio. Our plateau pressure data are in good agreement with those of Smith and Land² but are in obvious conflict with the mass spectrometric data of Ihle and Wu.⁵ Similar experiments with tritium are near completion.

Solubility Studies

Knowledge of the solubility of hydrogen isotopes in liquid lithium is important in selecting methods (e.g., cold-trapping) for their recovery from fusion reactor blankets. We have initiated a study to determine the solubility of LiD in liquid lithium in the range 200-600°C by a direct sampling method, which was successfully employed in our recent studies of the solubility of nitrogen in liquid lithium.⁶

Twenty-four equilibrated and filtered melt samples were taken from saturated solutions of solid LiD in liquid lithium. Although further improvements in the deuterium analyses are being sought, three tentative solubility values are available: 0.50, 0.84 and 2.30 mol % LiD at 322, 375 and 451°C, respectively. Extrapolation of these data to 200°C yields a solubility of ~250 atom ppm D. This high value appears to rule out hydrogen isotope separation from lithium based on cold-trapping methods.

SOLUTIONS OF HYDROGEN IN SOLID Li-AL ALLOYS

The use of aluminum and its alloys as low-activation structural materials for fusion reactor blankets has been considered.⁷ The β -phase of the Li-Al system (48-56 atom % Li) appears to be promising for this purpose since it has adequate physical and nuclear properties and a moderately high melting point (~700°C). Furthermore, as shown below, solutions of hydrogen in β -phase LiAl have significantly higher hydrogen dissociation pressures than do solutions of hydrogen in pure lithium at the same temperature and H/Li ratio. This latter property is especially important for designing tritium removal processes that would permit the maintenance of low tritium inventory in the blanket.

Most of the literature work on the Li-Al-H₂ system has been limited to studies of the thermal decomposition of LiAlH₄. This decomposition

is known^{8,9} to occur in at least three stages: (1) an exothermic reaction in the temperature range from 187 to 218°C, evolving ~50% of the total hydrogen; (2) an endothermic reaction from 228 to 282°C, evolving an additional ~25% H₂; and (3) a final endothermic reaction between 370 and 480°C, evolving ~22% H₂. According to the most recent thermal decomposition study,¹⁰ the losses of hydrogen in these three stages correspond, respectively, to the formation of the following compounds: (1) LiAlH₂, (2) LiAlH, and (3) a homogeneous solution of hydrogen in a Li-Al alloy of unknown composition.

In our initial studies, we are investigating the interaction between hydrogen and β -phase LiAl by measuring the hydrogen dissociation pressure over solid solutions of hydrogen in the β -phase as a function of temperature, hydrogen concentration, and alloy composition. The equipment and the procedures being used in this study are essentially identical to those previously described for the Li-LiH system.¹

To date, isotherms have been determined at 550 and 599°C. They are shown in Fig. 4, where the square root of the hydrogen pressure is plotted against atom % H. In the range from 0 to 6 atom % H, the hydrogen pressure increases monotonically with concentration—an indication of a homogeneous condensed phase. The sigmoidal shape of the isotherms, however, suggests the possibility that a miscibility gap exists at lower temperatures. At 6 atom % H, the isotherms become flat, indicating the onset of a wide miscibility gap, the upper boundary of which presumably corresponds to LiAlH (33.3 atom % H).

After completion of the second isotherm (at 550°C), the alloy contained 15.2 atom % H, *i.e.*, well within the miscibility gap, where the decomposition pressure is independent of composition. This material was used to determine hydrogen plateau pressures as a function of temperature. The results are shown in Table 1. The fluctuations in the hydrogen concentration shown in the table result from (1) changes in hydrogen content of the residual volume of the apparatus at different temperatures, and (2) additions or subtractions of small amounts of hydrogen in order to accelerate the equilibration of the system. The

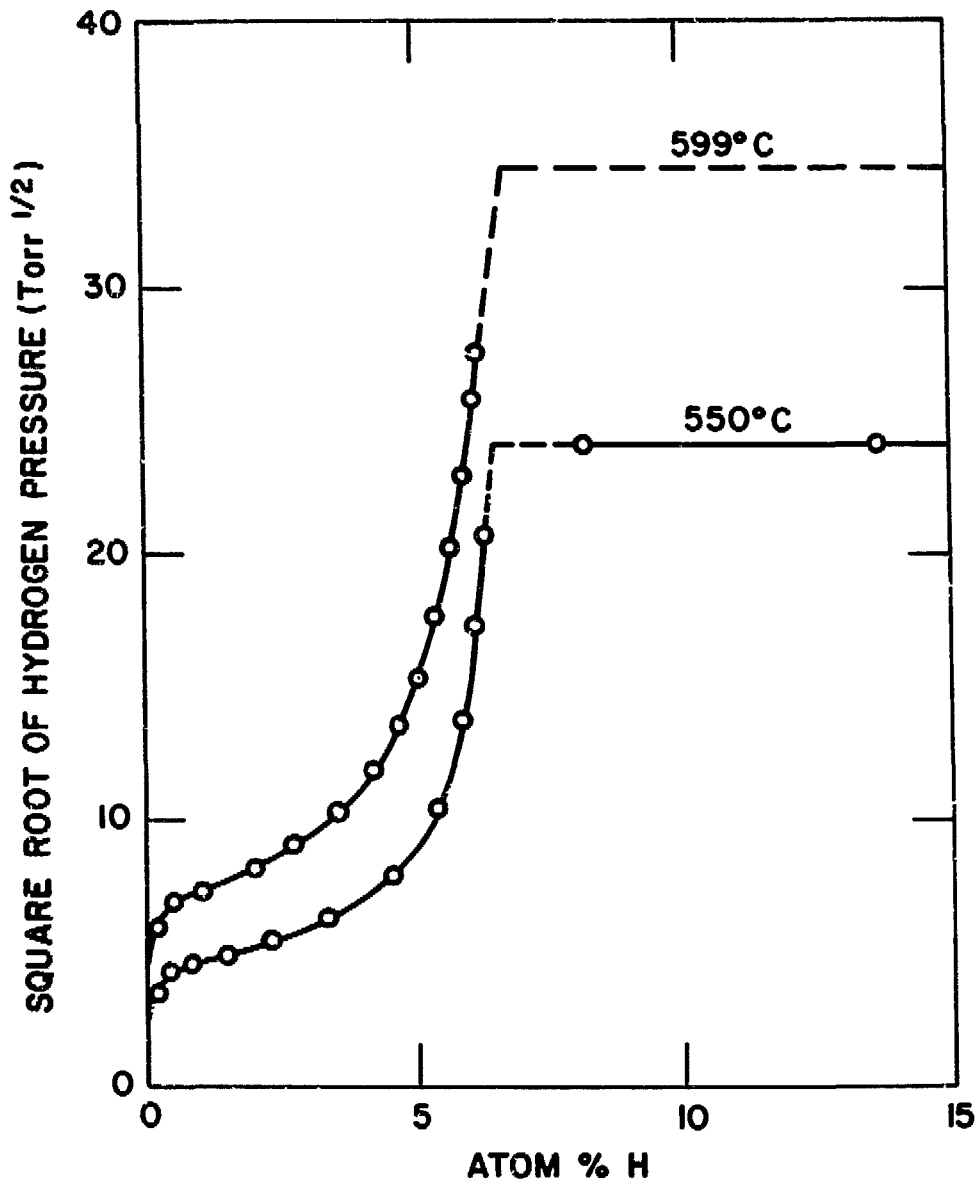


Fig. 4. Concentration Dependence of the Decomposition Pressure of Hydrogen over Solutions of Hydrogen in the β -Phase of the Li-Al System.

Table 1. Equilibrium Hydrogen Pressures Over
Two-Phase Mixtures of the System
 $\delta(\text{LiAl})-\text{H}_2$

Temperature (°C)	Hydrogen Pressure (Torr)	Concentration (at. % H)
424	45.4	17.3
443	71.4	21.4
465	117.0	20.1
492	201.0	18.5
514	311.8	23.7
528	403.1	19.1
551	582.5	15.9

plateau pressure, P, in Table 1 may be represented by the expression

$$\ln P \text{ (Torr)} = 20.46 - 11,600 T^{-1} \text{ (T in K)}$$

with a correlation coefficient of -0.99989 for the regression. It is of interest to note that our plateau pressures agree well with those reported¹⁰ for the third stage in the thermal decomposition of LiAlH_4 , thus confirming the presence of similar condensed phases in both experimental approaches.

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COLLECTION OF DEUTERIUM ON A URANIUM GETTER DURING
DYNAMIC FLOW CONDITIONS*

C. L. Folkers
M. F. Singleton

Lawrence Livermore Laboratory

ABSTRACT

We have studied uranium as a getter material under varying flow conditions using a uranium trap designed to remove tritium from inert gases. The uranium trap can remove any hydrogen isotope from an inert gas. We used mixtures of deuterium in argon at room temperatures. In the case of tritium, recovery is effected by heating the trap.

A special segmented trap was designed to prevent channeling and to promote maximum reaction rates when gas flows through it. The gas mixtures were sampled at the trap inlet and outlet and were analyzed by a mass spectrometer.

The results are expressed as a purification factor, which is the ratio of deuterium concentration at the inlet of the uranium trap to the concentration at the outlet. Purification factors vary inversely with both the ratio of deuterium to uranium already contained in the trap, and with the rate of flow of gas through the trap. The effects of varying inlet deuterium concentrations on purification factors are also discussed.

INTRODUCTION

Tritium operations frequently contend with inert gases contaminated with tritium. This tritium must be scavenged prior to disposal of the inert gas, and may be recovered for reuse.

We studied uranium as a getter material to remove tritium from inert gases under varying flow conditions. The following are several advantages of uranium:

1. The plateau pressure¹ of its hydride at room temperature is $< 0.3 \text{ mPa}$ ($< 2 \times 10^{-6} \text{ torr}$); thus it may be possible to scavenge tritium in inert gases to levels of $< 10 \text{ mCi/m}^3$.

*Work performed under the auspices of the U.S. Energy Research and Development Administration, under contract No. W-7405-Eng-48.

2. Reactive uranium powder can be made by simply hydriding and dehydriding massive uranium.²

3. Uranium hydride formed by scavenging can be dehydrided and the metal powder reused repeatedly. Also, tritium recovered here (or from any getter) as T_2 gas is much less hazardous to handle than as T_2O recovered from an oxidation-molecular-sieve-recovery process.

Because a uranium trap can be used to remove any hydrogen isotope from an inert gas, we studied mixtures of deuterium in argon at room temperature. Subsequent dehydriding is accomplished by heating the trap.

Earlier work³ indicated that the trap efficiency, expressed as a purification factor, varies inversely with both the flow of gas through the trap and the atomic ratio of deuterium to uranium (D/U ratio) already reacted in the trap. The experiments described here were intended to facilitate the design of a portable tritium scavenging system with a uranium getter for use with inert gases. We have studied the effects of varying the gas flow rate, the inlet deuterium concentration, and the D/U ratio.

EQUIPMENT AND PROCEDURES

The original experimental system was designed and built by Homer Weed.⁴ Early data³ from this system gave purification factors only for D/U ratios greater than 2.2. Difficulty was encountered with high background readings and low sensitivity in the residual gas analyzer (RGA), and also with incomplete mixing of the gases above the first sampling valve. Subsequent modifications included a mixing chamber for argon and deuterium, a UTI* 100C RGA, and faster pumping speed for the high vacuum system.

Major components of the system are shown in Fig. 1. Deuterium and argon flows are measured by thermal conductivity mass flowmeters. Total flow rates were varied from 16 to 67 cm³ (STP)/s, and deuterium concentrations ranged from 0.5 to 4.0 vol%. The gases flow together through a mixing chamber before passing the first sampling valve. Sampling valves are located directly above and below the uranium trap to sample the gas before and after it passes through the uranium bed. The total pressure

*Reference to a company or product name does not imply approval or recommendation of the product by UC or the U.S. E.R.D.A. to the exclusion of others that may be suitable.

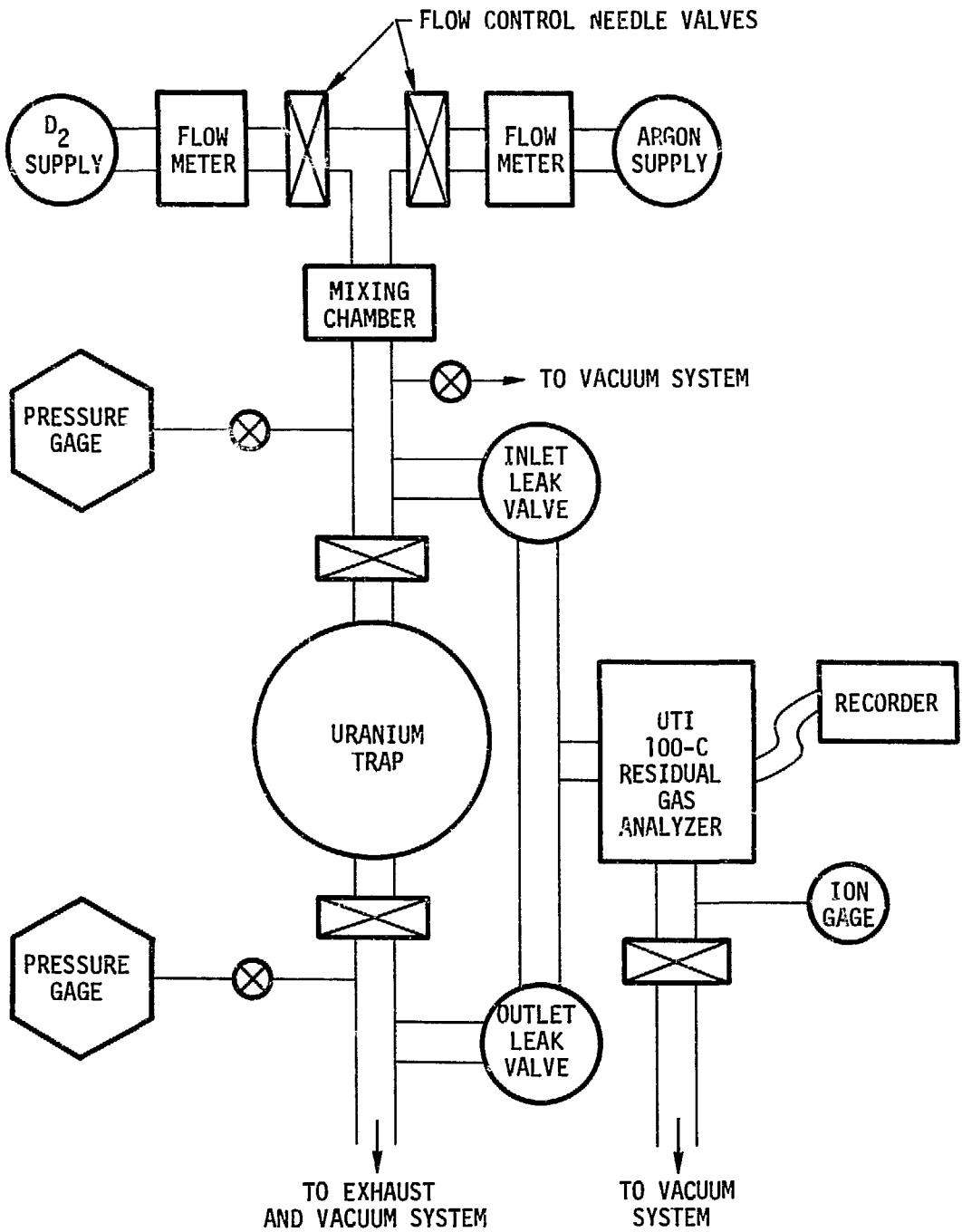


Fig. 1. Schematic of Uranium Trap System.

in the trap was usually about 100 kPa (1.0 atm) but increased to about 160 kPa (1.6 atm) at the highest flow rates. Pressure in the RGA was ~ 0.13 mPa ($\sim 10^{-6}$ torr) while sampling was in process.

The uranium trap, shown in Fig. 2, was developed by Carlos Colmenares⁵ for use in a portable cleanup system. There are 5.71 moles (1359 g) of ^{238}U arranged in three layers, each separated into eight sections, to keep the uranium powder distributed evenly. The cross-sectional area of the trap is 73.8 cm^2 , giving a uranium distribution of 18.4 g/cm^2 of flow area.

The UTI 100C RGA is capable of detecting deuterium at a concentration of ~ 3 ppm in the argon stream. Its high vacuum system includes a 300-liters/sec diffusion pump, cryotrap, and appropriate pressure gages.

The amount of deuterium introduced into the uranium trap was measured in order to calculate the D/U ratio for each run. This was measured by filling a tank of known volume with D_2 gas and monitoring the pressure change for each run.

Measurements were always made of instrument background and argon-only readings before and after the reading of the Ar- D_2 mixtures. The outlet mixture was sampled before the inlet mixture to insure the highest sensitivity at the lower D_2 concentration. Each run was maintained at steady-state for 30 min before a reading was taken. We also determined there was no significant enrichment of either gas when mixtures passed through the sample valves; this was done using a premixed gas sample without flowing through the trap.

RESULTS AND DISCUSSION

The uranium trap efficiency is expressed as a purification factor, P.F., where:

$$\text{P.F.} = \frac{\text{Concentration of } \text{D}_2 \text{ IN}}{\text{Concentration of } \text{D}_2 \text{ OUT}}$$

The atomic D/U ratio was the most significant experimental variable affecting the purification factor.

TOTAL URANIUM = 1.36 kg

CROSS-SECTIONAL AREA
FOR GAS FLOW = 74 cm^2

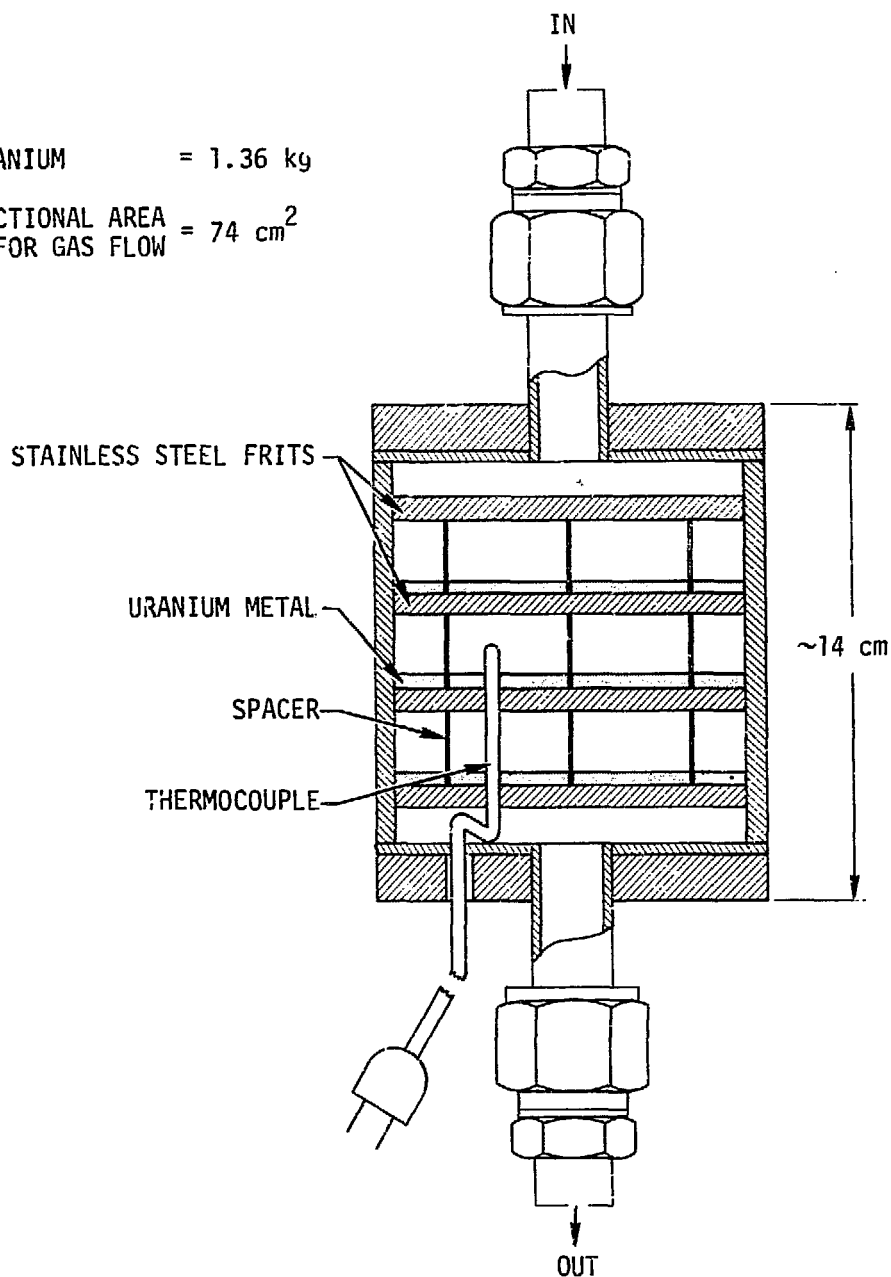


Fig. 2. Cross Section of Uranium Trap.

The effects of changing the D_2 concentration in Ar are shown in Fig. 3. The D_2 concentration was varied from 0.5 to 4.0 vol% at a constant flow rate of $17 \text{ cm}^3 \text{ (STP)/s}$ through the trap. In some cases at low D/U ratios, the outlet D_2 concentrations could not be detected above background levels. For these runs, a lower limit to the purification factor is given by:

$$\text{P.F.} > \frac{\text{Concentration of } D_2 \text{ IN}}{\text{Background } D_2 \text{ OUT}}$$

These minimum values are shown as closed symbols in Figs. 3 and 4.

Purification factors, shown in Fig. 3, vary inversely with the D/U ratio of the trap; however, we do not see any effect due to the inlet D_2 concentration for the range studied. A semilogarithmic plot suggests a straight line that extrapolates to a purification factor of 1 at a D/U ratio of 3.0. Simply stated, when the trap is fully loaded (i.e., all UD_3), there is no purification and what goes in, comes out.

The effects of varying flow rate are shown in Fig. 4. Flow rates used were 17, 33, and $67 \text{ cm}^3 \text{ (STP)/s}$ through the trap. No distinction is made for differences in inlet D_2 concentrations.

Purification factors vary inversely with the flow rate at all D/U ratios. Again, a semilogarithmic plot suggests straight lines that extrapolate to a purification factor of 1 at a D/U ratio of 3.0. The data at $33 \text{ cm}^3 \text{ (STP)/s}$ are more scattered than the data for the other flow rates.

Maienschein⁶ has developed a model for a gas-phase, mass-transfer-limited process in a packed bed. For our case, this gives:

$$\ln \left(\frac{C - C_s}{C_o - C_s} \right) = - \frac{A}{V} k_x a Z'$$

where:

- $C = D_2$ concentration at the trap outlet,
- $C_o = D_2$ concentration at the trap inlet,
- $C_s = D_2$ concentration at the uranium surface, taken as the plateau pressure over UD_3 ,

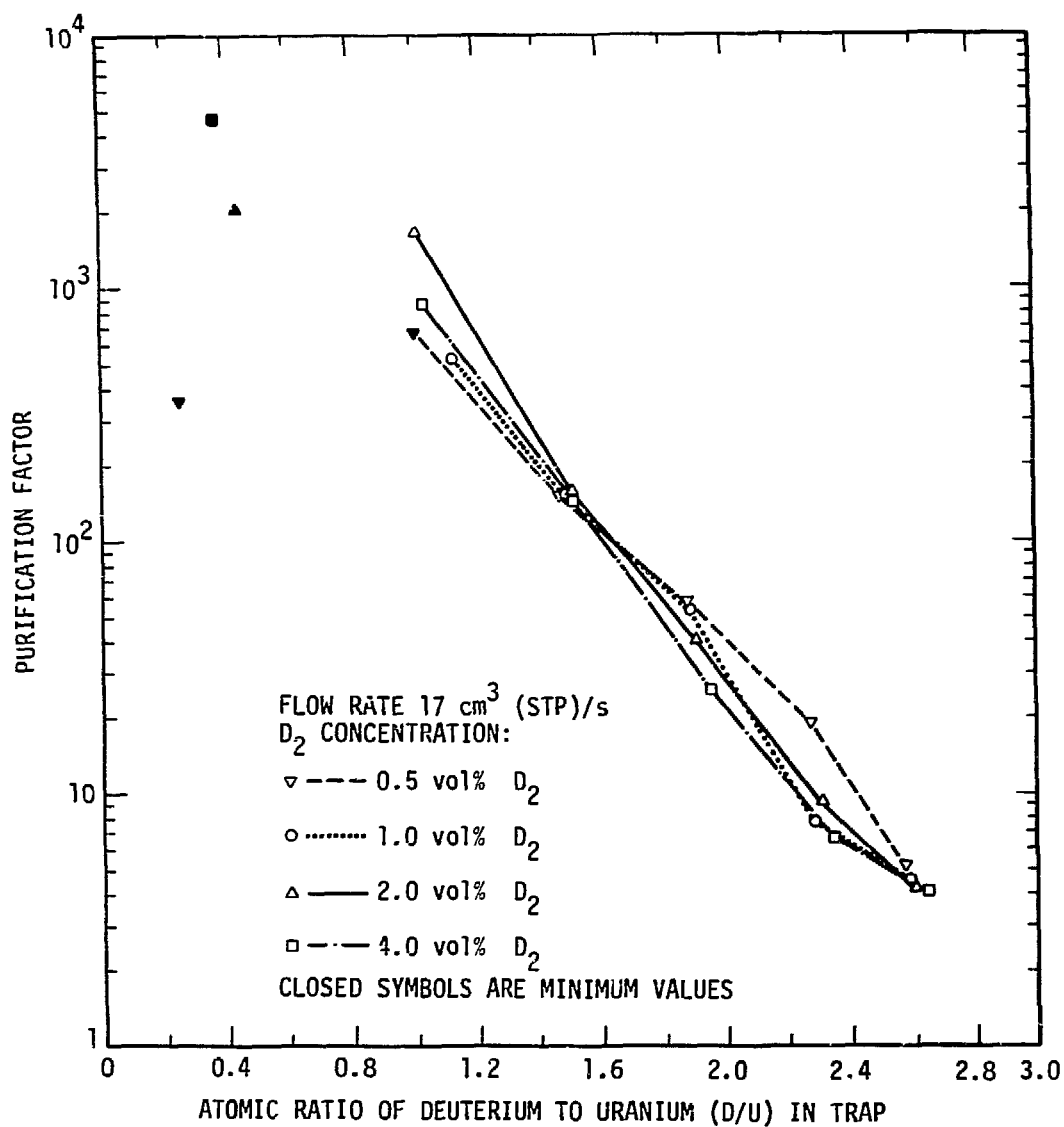


Fig. 3. Purification Factor vs Atomic Ratio of Deuterium to Uranium (D/U) in Trap, Showing Effects of Varying Inlet Deuterium Concentration.

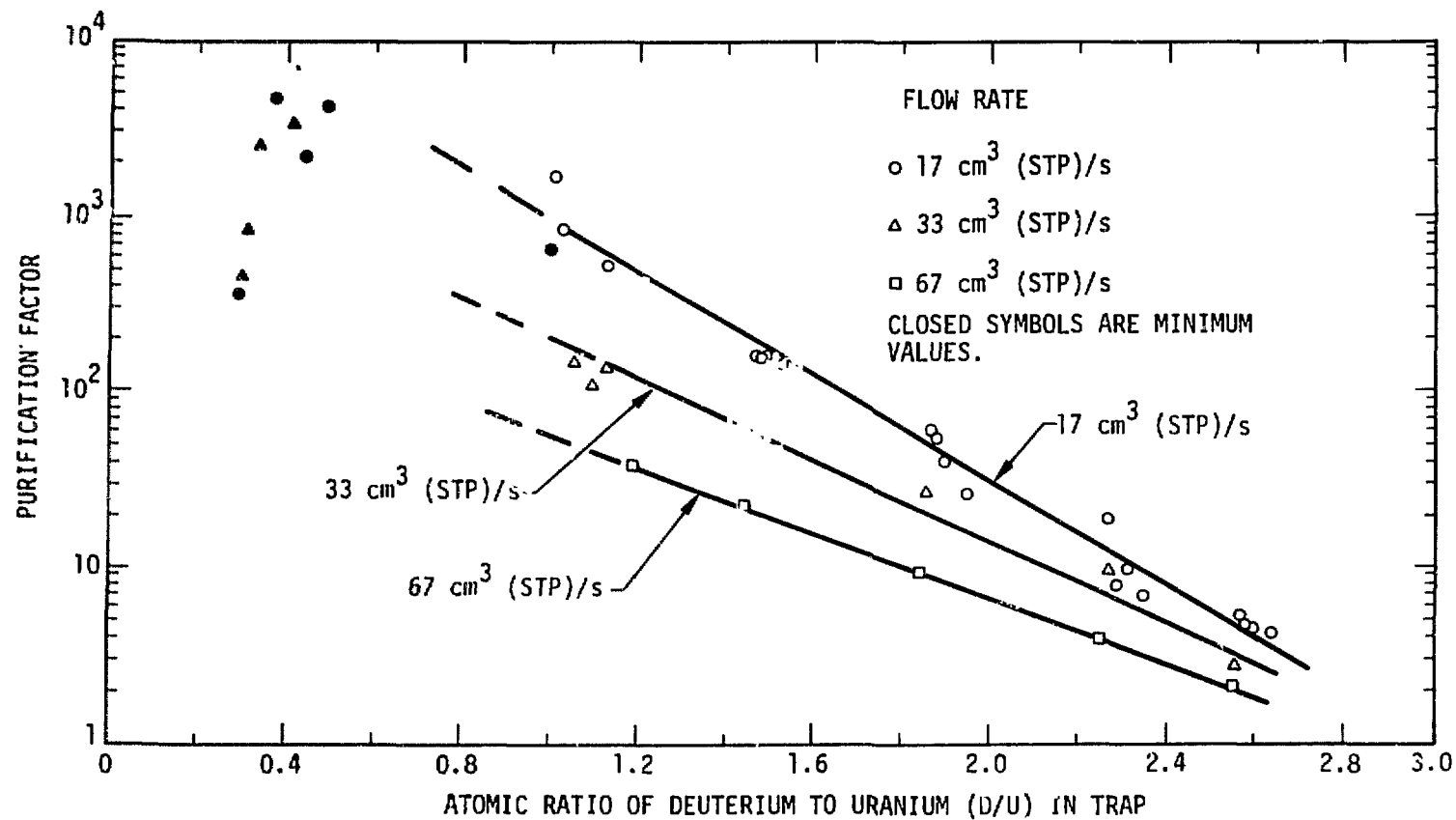


Fig. 4. Purification Factor vs Atomic Ratio of Deuterium to Uranium (D/U) in Trap, Showing Effects of Varying Flow Rate.

- A = trap cross-sectional area,
 V = volumetric flow rate,
 k_x = mass transfer coefficient,
 a = uranium particle surface area per unit bed volume,
 Z' = bed length of active material.

Here, C_s is very small compared to C and C_0 , and can be ignored.

Evaluating k_x for a given trap at constant temperature and fixed D/U ratio, the model is closely approximated by:

$$\ln \frac{C}{C_0} = -\left(\frac{P}{G}\right)^{1/2} K ,$$

where:

- P = pressure, kPa,
 G = mass flow/unit area, moles/m² - s,
 K = combined constant terms,

or,

$$\left(\frac{G}{P}\right)^{1/2} \log (P.F.) = K' ,$$

where the purification factor is $P.F. = C_0/C$, and K' represents constant terms describing the bed geometry, temperature, gas properties, etc. Our flow rates of 17, 33, and 67 cm³ (STP)/s are converted to mass flow rates, G , of 0.10, 0.20, and 0.40 moles/m² - s.

We did not originally intend pressure to be a variable. Mass flow rates up to 0.20 moles/m² - s were at about 101 kPa, but a mass flow rate of 0.40 moles/m² - s required increased pressures to about 160 kPa. Pressure data were lost for runs with D/U ratios < 1.6; we have assumed that pressures for these runs were similar to the recorded pressures for later runs. From this assumption, we conclude that observed differences in pressure from run-to-run give an uncertainty in (P.F.) of $\pm 3\%$.

A plot of $\left[\left(\frac{G}{P}\right)^{1/2} \log (P.F.)\right]$ vs D/U ratio is shown in Fig. 5. If our process is like that described by Maienschein's model, we can eliminate flow rate and pressure effects in the plot, to give a single straight line. The plot in Fig. 5 is in reasonable accord with the model and can be represented by the equation:

$$\left[\left(\frac{G}{P}\right)^{1/2} \log (P.F.)\right] = - 0.047 (D/U) + 0.142 .$$

Our existing data will permit us to design a suitable uranium getter bed for a scavenging system. We are continuing experiments in order to obtain data with lower D/U ratios and with lower inlet D_2 concentrations, as well as wider variations in mass flow rate and pressure. Finally, we plan to test our uranium trap in a scavenging system with tritium. Maienschein's model indicates that $\log (P.F.)$ is directly proportional to the length of the getter bed. Another trap will be required in order to verify this prediction.

CONCLUSIONS

The efficiency of a uranium trap, expressed as a purification factor, in scavenging deuterium from argon was found to vary inversely both with the flow rate and with the atomic D/U ratio. The inlet deuterium concentration did not affect the purification factor within the ranges studied, 0.5 to 4%. The data are described by an equation of the form:

$$\left[\left(\frac{G}{P}\right)^{1/2} \log (P.F.)\right] = - 0.048 (D/U) + 0.144 ,$$

for a trap of given geometry.

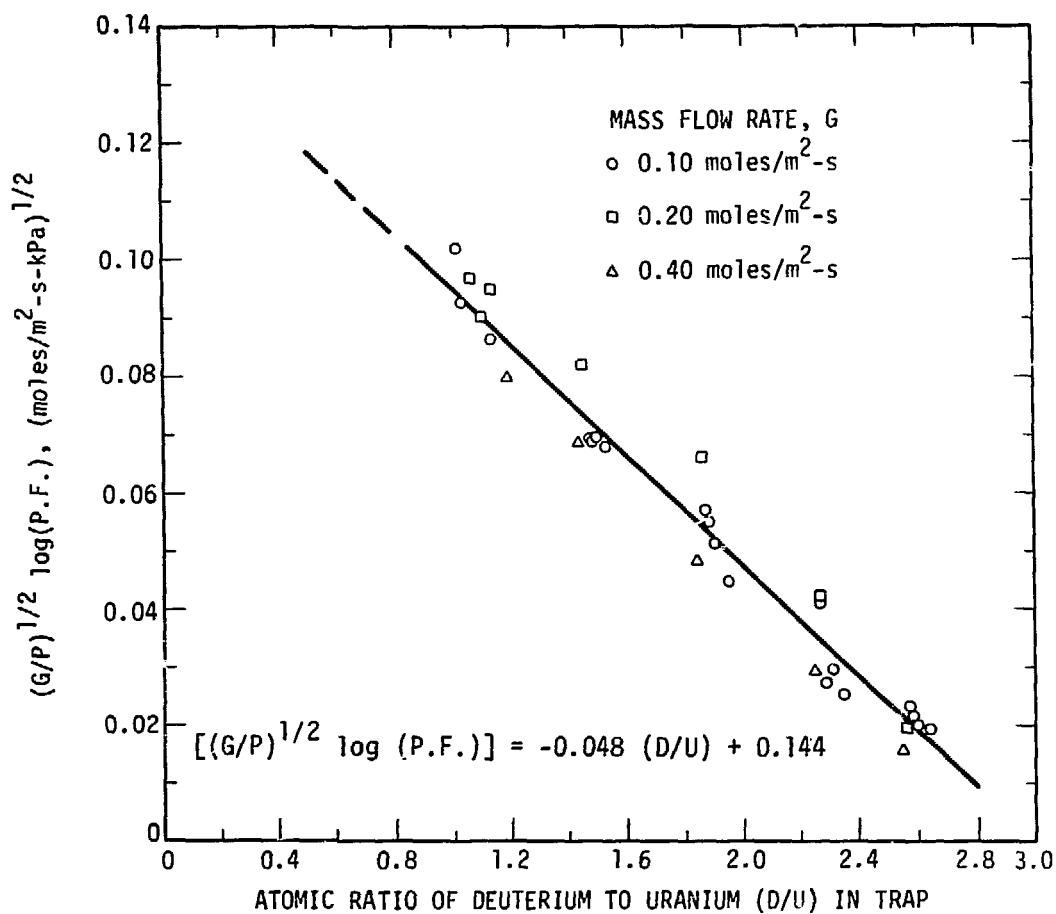


Fig. 5. $\left(\frac{G}{P}\right)^{1/2} \log(P.F.)$ vs Atomic Ratio of Deuterium to Uranium (D/U) in Trap.

ACKNOWLEDGMENTS

H. C. Weed installed and operated the original experimental equipment for this study, C. A. Colmenares designed the uranium trap, and J. Maienschein devised the model of a getter bed and assisted in its use here.

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TRITIUM REMOVAL: A PRELIMINARY EVALUATION OF SEVERAL
GETTERS*

C. W. Schoenfelder and L. A. West

Exploratory Chemistry Division 8313
Sandia Laboratories, Livermore, California 94550

ABSTRACT

The removal of hydrogen isotopes from flowing gas streams is an important aspect of CTR technology for both decontamination and tritium recovery from plasma exhausts. Several getters have been evaluated for their tritium scrubbing potential at the parts per billion level. Measurements of total capacity and dynamic response have been made for barium, erbium, palladium dispersed on molecular sieve, General Electric H-36 (zirconium alloy), Union Carbide Y-993 (Pd-MnO₂), Societa Apparecchi Eletttrici e Scientifici Getters ST101 (Zr-Al), ST171, and ST181, and a Sandia developed organic material, dimerized phenyl propargyl ether (DPPE). Preliminary flow studies were conducted by passing mixtures of either hydrogen or deuterium diluted with argon through packed beds containing the getter and periodically sampling the effluent with a gas chromatograph sensitive to 500 ppb H₂. The results of this work, similar flow experiments using tritium and total capacity measurements are presented in the text.

*Reference to a company or a product name does not imply approval or recommendation of the product by Sandia Laboratories or the United States Energy Research and Development Administration to the exclusion of others that may be suitable.

INTRODUCTION

Due to the small percentage of fuel actually consumed in the D-T reaction, a commercial CTR plant will have to handle substantial quantities of both deuterium and tritium. For instance, assuming a 4% burn-up, the conceptual design for the 5000 MW (thermal) Tokamak reactor proposed by the University of Wisconsin¹ requires a throughput of roughly 3.6 moles, or 81 liters (STP), of D-T per minute. Recovery and recycling of the unburned tritium are essential to both the economy and ecological safety of such a commercial fusion reactor.

The large throughput mentioned above implies that pumping speeds in excess of 10^6 liters/second will be needed to maintain pressures below 10^{-3} Pa in the reaction vessel. If conventional diffusion pumps or turbomolecular pumps are used to provide part of this pumping capacity, their exhausts will require extensive treatment before release to the environment. Current ERDA regulations² allow in-plant operating levels of $5 \mu \text{ Ci/m}^3$ of HTO and $2000 \mu \text{ Ci/m}^3$ of HT compared to $0.2 \mu \text{ Ci/m}^3$ of HTO and $40 \mu \text{ Ci/m}^3$ of HT in the uncontrolled environment.

The purpose of this report is to provide preliminary data on the ability of different getters to remove hydrogen isotopes from flowing gas streams, such as might be encountered in reprocessing CTR plasma exhausts. Despite the fact that many of these getters are commercial products, little information is available on their performance at room temperature. Consequently, all experiments were conducted at this temperature, even though certain getters are designed to operate at elevated temperatures.

EXPERIMENTAL

Two types of tests were used to characterize the getters. Static gas experiments were conducted to determine the hydrogen capacity of the getters and dynamic experiments were conducted to determine the effects of flow rate on gettering efficiency and to evaluate bed capacity at fixed flow rates. For the capacity measurements, a weighed sample of getter material was placed in an evacuable vessel and then attached to a vacuum system containing a measured pressure and volume of purified hydrogen or tritium. The hydrogen isotope was admitted to

the evacuated getter and the total pressure recorded as a function of time until equilibrium was attained. From the known initial and final pressures and volumes, the amount of gettered hydrogen could be calculated.

In the dynamic experiments, a deuterium or hydrogen/helium/argon gas mixture of known composition was passed through a packed cylindrical bed of getter material. The effluent from the bed was monitored at regular intervals by a gas chromatograph. This instrument is a single column, thermistor detector chromatograph capable of detecting 5 parts in 10^7 of hydrogen as shown in Fig. 1. A Hewlett-Packard Model 3370B Integrator was used in some of the experiments to measure peak areas in order to obtain a quantitative measure of the hydrogen concentration in the effluent. To prevent gas from back streaming into the getter bed and to obtain a time integrated flow rate, the exiting gas was passed through a wet test meter. Instantaneous flow rates could be measured with a bubble type flow meter. Since the driving pressure of the gas was limited to two atmospheres by the glass flow meters in the system, the flow rate through the bed was strongly affected by the bed packing density and was found to be restricted to the range 0.01-5.0 $\text{cm}^3(\text{STP})/\text{sec}$. Figure 2 shows the typical experimental set up.

Flow experiments with tritium were conducted in a slightly different manner. As shown in Fig. 3, pure tritium (97% T_2 , 3% D_2) was forced through a calibrated leak under a pressure gradient and allowed to diffuse through the getter bed into a cylindrically symmetric ionization chamber employing an electrode assembly previously described in the literature.³ A photograph of the actual experimental apparatus is shown in Fig. 4.

For the measurements described in the following sections, the ionization chamber was operated in the electron collection mode with a polarizing voltage of 90 volts. A determination of the current-voltage characteristics of the detector showed this voltage to be within the necessary plateau region. The measured sensitivity of the chamber was 0.9 $\text{pA}/\mu\text{Ci}$ with a lower detection limit of slightly less than 1 $\mu\text{Ci}/\text{m}^3$. All currents were measured using a Cary 401 Vibrating Reed Electrometer.

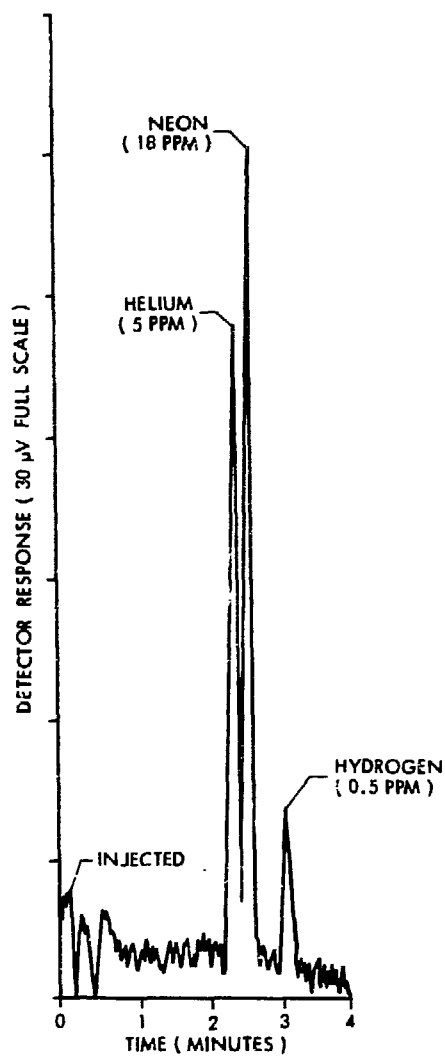


Figure 1. Typical chromatogram of a 2 cm³/(STP) air sample obtained with the apparatus shown in Figure 2.

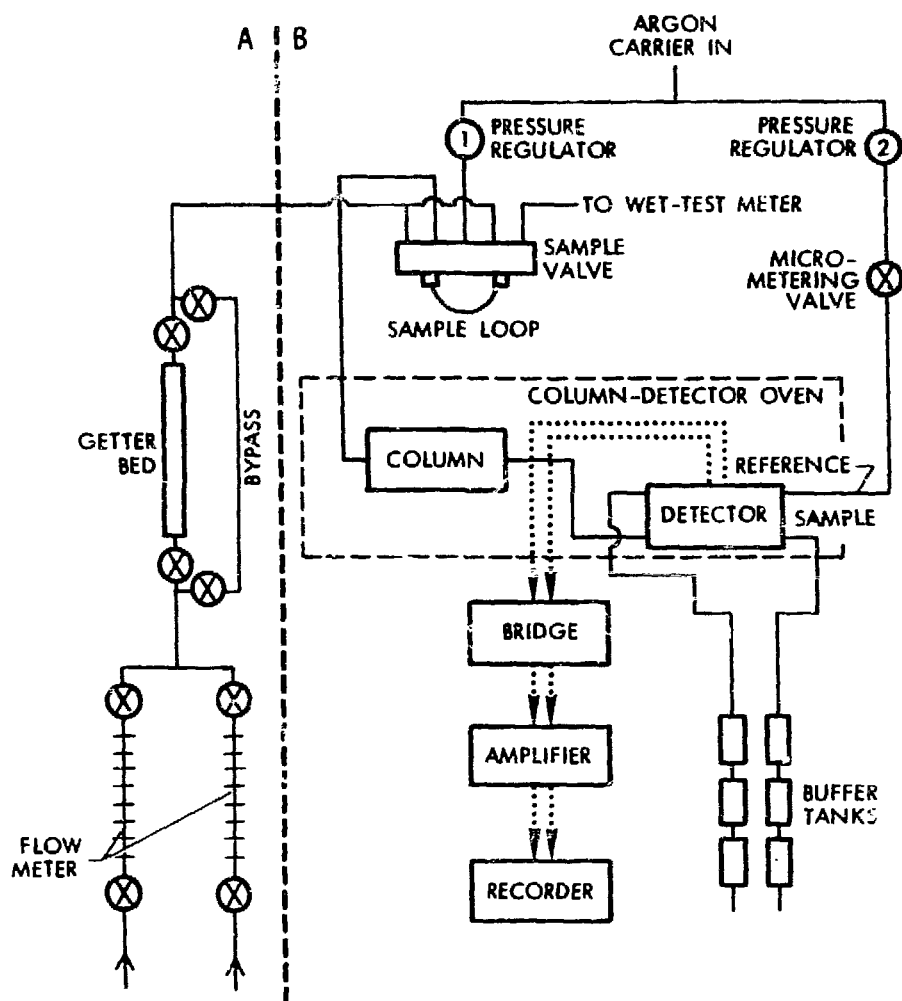
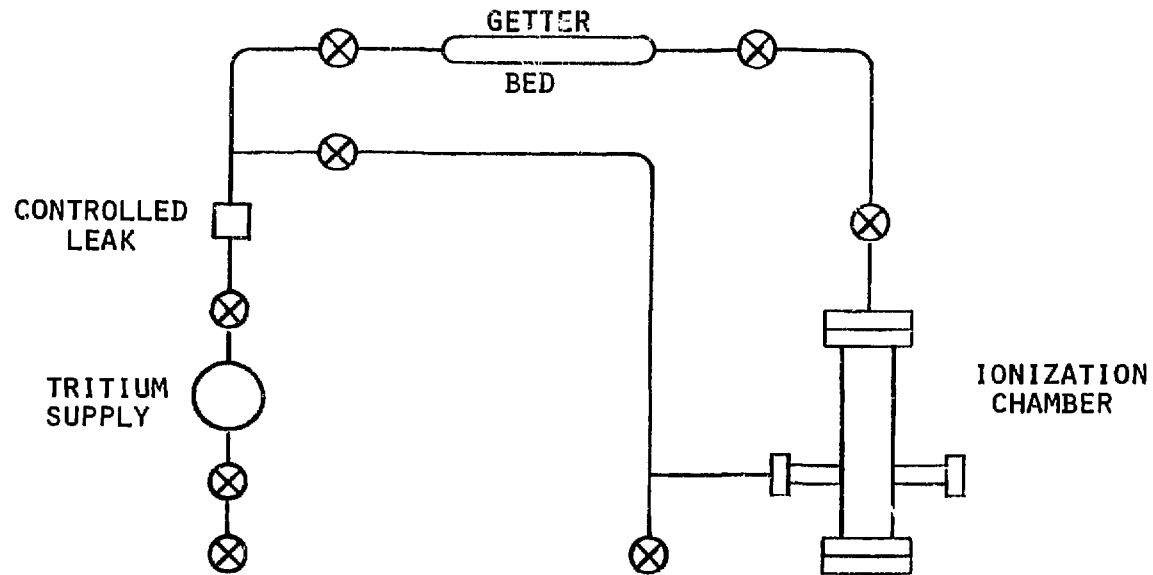


Figure 2. Flow diagram of getter bed and helium-hydrogen gas chromatograph.



TRITIUM FLOW EXPERIMENT

Figure 3. Schematic representation of apparatus for tritium flow experiments.

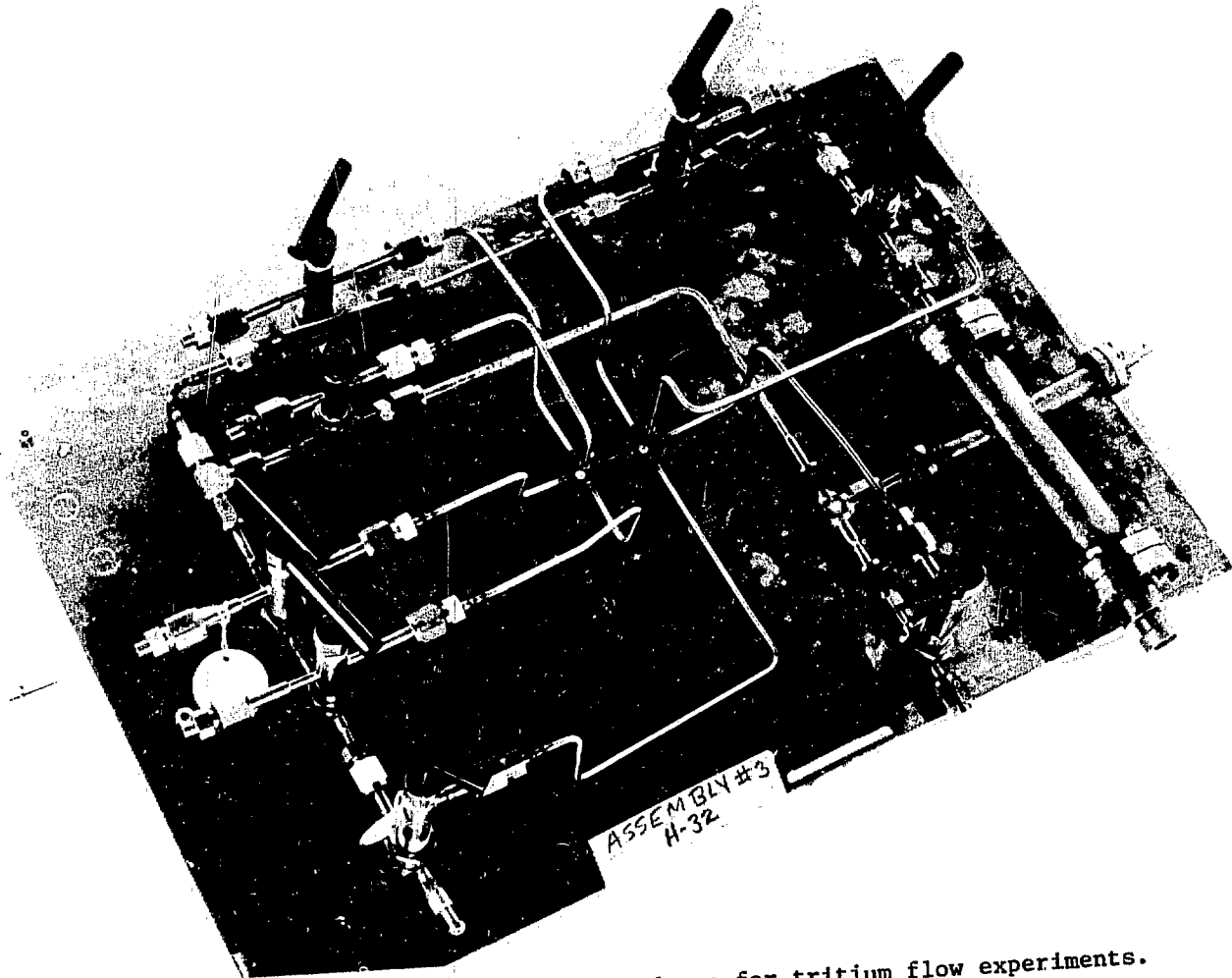


Figure 4. Photograph of actual hardware for tritium flow experiments.

Since the detector is essentially dead-ended due to the small holes in the ceramic end spacer, the measured ion current corresponds roughly to the time integral of the tritium current escaping from the getter bed.

MATERIALS

In total, nine getters were evaluated during the course of this work. Y-993 is a hydrogen absorber available in research quantities from the Union Carbide Corporation and consists of a proprietary formulation based on manganese dioxide and palladium black. The palladium/molecular sieve system (SK-100) for catalytically converting hydrogen-oxygen mixtures to water that is then strongly absorbed in the matrix of the molecular sieve was obtained from the Linde Division of Union Carbide. It was originally prepared for pentane-hexane catalytic isomerization studies and contained 0.5 weight percent palladium. Activation consisted of heating the product at 800K in the presence of $10 \text{ cm}^3(\text{STP})$ of hydrogen/gram of getter for a period of 4-6 hours. DPPE is an organic material, 1,6-diphenoxy-2,4 hexadiyne (dimerized phenyl propargyl ether) developed by Sandia Laboratories^{4,5} to getter hydrogen. The organic material is supported on a calcium carbonate substrate containing .5% palladium to act as a catalyst for the hydrogenation of acetylenic linkages in the molecule. Various concentrations up to 75% by weight of DPPE were tested. Erbium was evaluated as a getter because it has previously been used by Sandia Laboratories as a hydrogen occluder in neutron tubes. Metal powder was purchased from the Research Chemicals Division of Nuclear Corporation of America and sieved to obtain erbium particles $<300 \text{ }\mu\text{m}$ in size for testing purposes. Prior to use it was activated by heating to 673K for 30 minutes in vacuum.

The barium powder getter used in this work is commercially available from the Linde Division of Union Carbide Corporation in both powder and tablet form. It is grey-black in appearance and consists of submicron sized particles of pure barium metal with an unpacked density of 0.25 g/cm^3 . It reacts spontaneously with active gases at room temperature and has a design capacity for hydrogen of $145 \text{ cm}^3(\text{STP})$ per gram of getter

compared to the theoretical value of $163 \text{ cm}^3(\text{STP})/\text{g}$ for barium hydride (BaH_2). ST101, ST171, and ST181 are registered trade names for getters produced by S.A.E.S., S.p.A., Milan, Italy. Samples of these products in pellet form were obtained through S.A.E.S. Getters/USA for test purposes. Prior to use, the pellets were activated by heating for 10 minutes at 1073K. A sample of ST101 powder provided by S.A.E.S. was used in the flow experiments. The development and use of ST101 at elevated temperatures has been described previously in the literature.⁶⁻⁸ H-36 is a proprietary zirconium base alloy developed by the General Electric Company. The powder used in this work was screened to 75-150 μm in size and then activated for 1 hour at 823K before exposure to hydrogen.

RESULTS AND DISCUSSION

Capacity Measurements with Hydrogen

Table 1 presents a list of the getters examined in this work and their capacity to absorb hydrogen at room temperature. Y-993 was found to be slow in reacting with hydrogen in a static system, i.e. with no flow through the getter. The kinetics were roughly linear though with an uptake of 3.7×10^{-10} moles/sec/g following an initial induction period with a slightly slower rate. For proper functioning, this getter must contain approximately 15% water. In the case of the Pd/molecular sieve system, the total capacity of the getter at equilibrium was never achieved. In all cases the reaction ceased except for a small amount of physi-sorption of the gases, when the oxygen supply was exhausted. By evacuating the residual gases over the molecular sieve and then heating the sieve container, the water formed by the reaction could be condensed into a cold finger for measurement. If the molecular sieve and cold finger were both brought to room temperature and the valve between them opened, the residual pressure in the system went to zero, indicating the reabsorption of the water by the molecular sieve.

Table 1. Hydrogen Capacity of Various Getters

Getter	Capacity cc(STP) H ₂ /gm	Time to Equilibrium
Y-993	>50 ^a	>2120 hrs
Pd/Molecular Sieve	- ^b	20-300 hrs ^c
DPPE ^d	210	~10 hrs
Er	201	<15 sec
Ba	85-135	<15 sec
ST101	97	~10 hrs
ST171	192	<3 min
ST181	159	~4 hrs
H-36	0.3	16 hrs ^e

a) equilibrium not achieved

b) not measured

c) depends strongly on amount of oxygen present and exact experimental conditions

d) 75% DPPE by weight on CaCO₃ ~.5% Pd

e) duration of experiment, actual equilibration time unknown

DPPE is attractive as a hydrogen getter because it can be handled in air, needs no activation, and has an extremely low equilibrium overpressure for hydrogen. Initial experiments with 25% DPPE coated on CaCO_3 - .5% Pd showed that it absorbed hydrogen well, but that it had a pressure dependent induction period. Figure 5 shows a plot of the observed pressure-time dependence in the range 25-83 kPa (250-625 torr). Since for some applications this induction period is undesirable, ways were sought to reduce it. Figure 6 presents the effect of preexposing the getter to a small quantity of hydrogen before conducting the capacity test. Since the time of these experiments, improvements in the preparation of DPPE have resulted in significantly lower induction periods which can effectively be eliminated by the hydrogen preexposure technique. For the heavily coated supports, however, the hydrogen removal kinetics are much slower than with the lighter coatings (hours vs. minutes).

In the cases of Er and Ba, the reaction with hydrogen is sufficiently exothermic to cause the powders to glow cherry red. The Ba actually is observed to sinter into a solid mass as the result of exposure to pure H_2 at pressures greater than 150 Pa. While the Er samples absorbed the theoretical amount of hydrogen expected for the formation of the stoichiometric hydride, the Ba samples did not. Capacities between 85 and 135 cc(STP) H_2 /g were observed depending on the amount of exposure the Ba powder had to active gases during sample preparation. ST171 behaved in a manner similar to Ba and Er with regard to reaction kinetics and exothermicity. When exposed to 50 kPa of H_2 , the pellet began to glow after a few moments and the reaction was completed in less than three minutes. While ST181 showed an immediate reaction on exposure to hydrogen, it reacted at a rate much slower than the 171 alloy. More than 4 hours were needed to saturate the test pellet. The ST101 pellets absorbed hydrogen at an even slower rate than the other two S.A.E.S. getters and required roughly 10 hours to reach saturation. Both the ST171 and ST181 pellets cracked as the result of stress during hydriding but retained their massive form. The pellets of ST101 on the other hand completely disintegrated into a pile of small grains as the result of the reaction with hydrogen. Room temperature gettering tests with H-36 were conducted

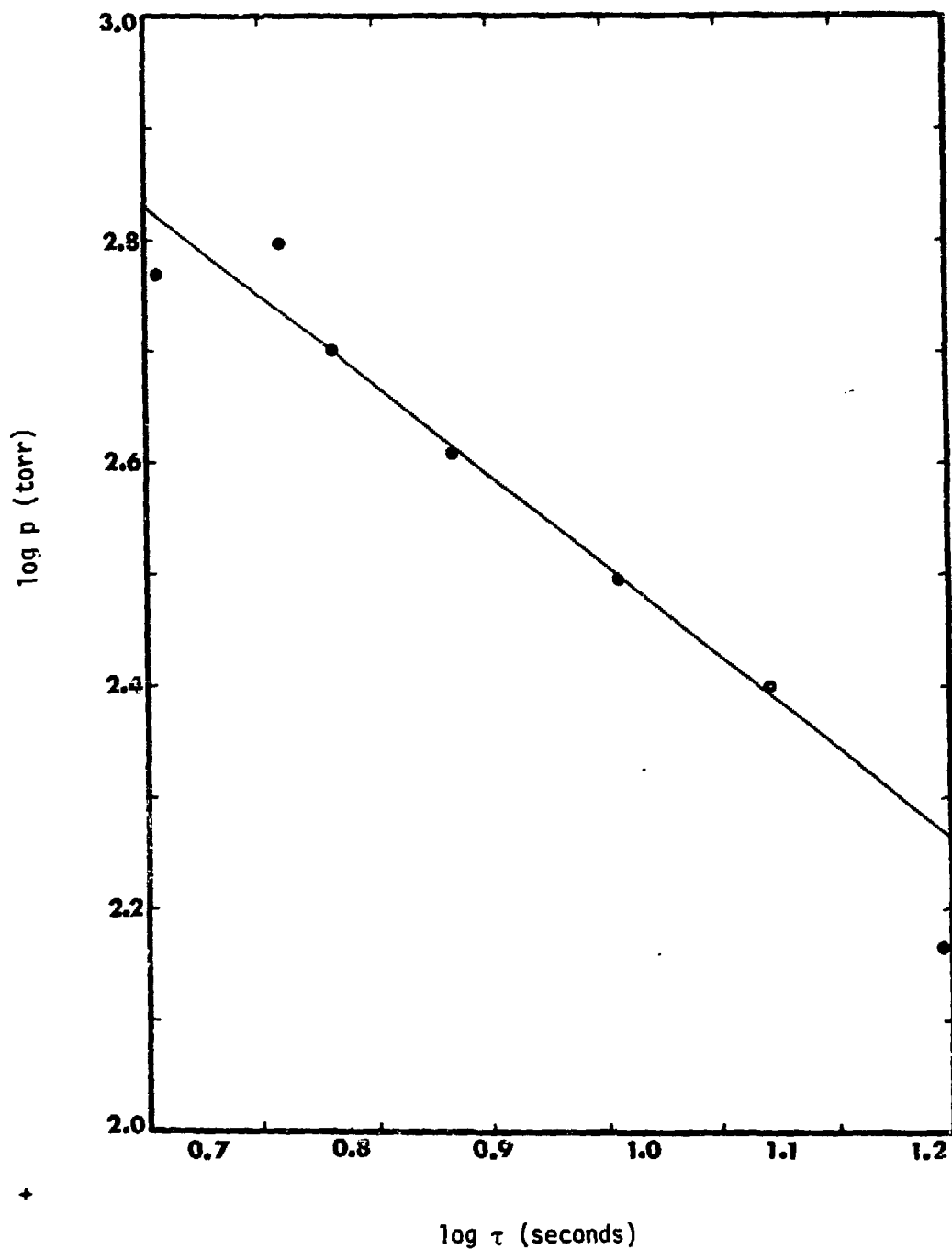


Figure 5. Pressure dependence of the induction period's duration for 25% by weight DPPE supported on CaCO_3 - 5% Pd.

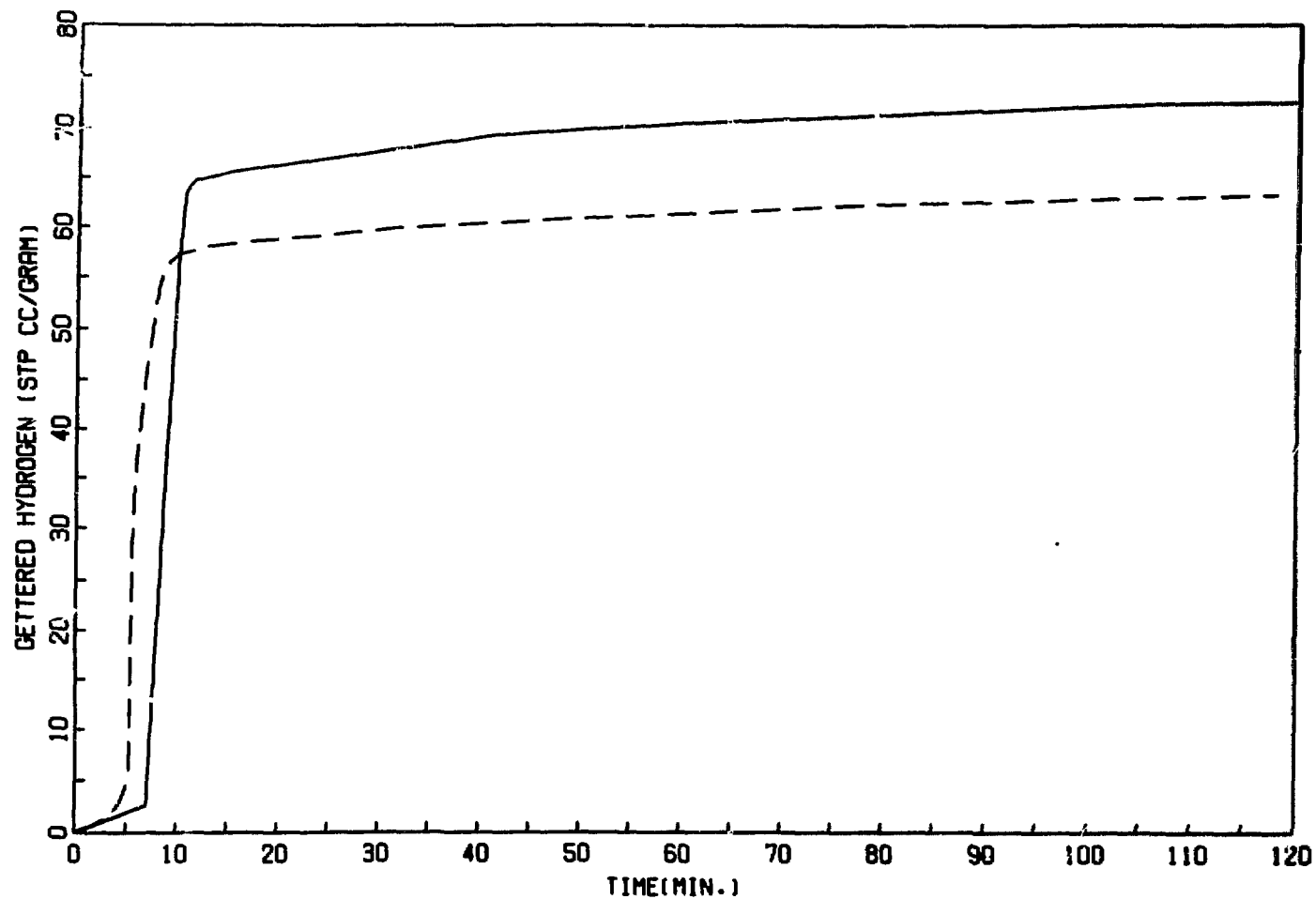


Figure 6. Effect of preexposing DPPE to hydrogen on the length of induction period and capacity. Solid line - virgin material; dashed line - hydrogen tested.

in both activated and unactivated conditions. The H_2 capacity was found to be very small in both cases.

Another type of capacity experiment is also underway. In this test the getters are contained in small evacuated capsules attached to a hydrogen manifold by palladium alloy leaks having a leak rate of roughly $6.6 \times 10^{-9} \text{ cm}^3(\text{STP}) H_2/\text{sec}$. Since this test was begun, 2800 hours have elapsed and all the getters are performing as expected.

Capacity Measurements with Tritium

Both Ba and DPPE were exposed to tritium to determine the extent of any isotopic differences. Duplicate experiments with H_2 and T_2 for Ba revealed no quantitative differences in either the gettering rates or the saturation capacity ($\sim 81 \text{ cc}(\text{STP}) H_2/\text{g}$) at exposure times < 60 minutes. The tritiated samples, however, were filled to 53 kPa with an overpressure of T_2 and examined 6 months later. At that time it was found that the gas phase pressure had decreased substantially, thus indicating that the Ba continued to react with the T_2 , although at a much slower rate than when first exposed. The total amount of T_2 consumed was about 75% of the theoretical amount necessary to form BaT_2 .

In the case of DPPE, vast differences in the reaction rate were observed in the behavior of the getter with H_2 and T_2 . Figure 7 shows the H_2 absorption data starting 70 minutes into the run subsequent to refilling the reference volume with hydrogen. After 600 minutes the reaction was essentially complete whereas with T_2 , as indicated in Fig. 8, the reaction was only 46% complete. The reaction rate with T_2 after 600 minutes became approximately linear and equal to $9 \times 10^{-9} \text{ moles/sec/g}$. After 4×10^4 minutes, however, the reaction had only reached 87% of the measured hydrogen capacity. Possible explanations for this behavior include radiation damage to the organic by the tritium and blanketing of the solid by the ^3He in the tritium ($\sim 20\%$ by volume). An analysis of the gases over the tritiated DPPE after 6 months exposure to tritium showed the presence of more methane and carbon dioxide than in the control sample. These gases probably originate from the radiolytic decomposition of the DPPE and the CaCO_3 support. As with the Ba, the DPPE

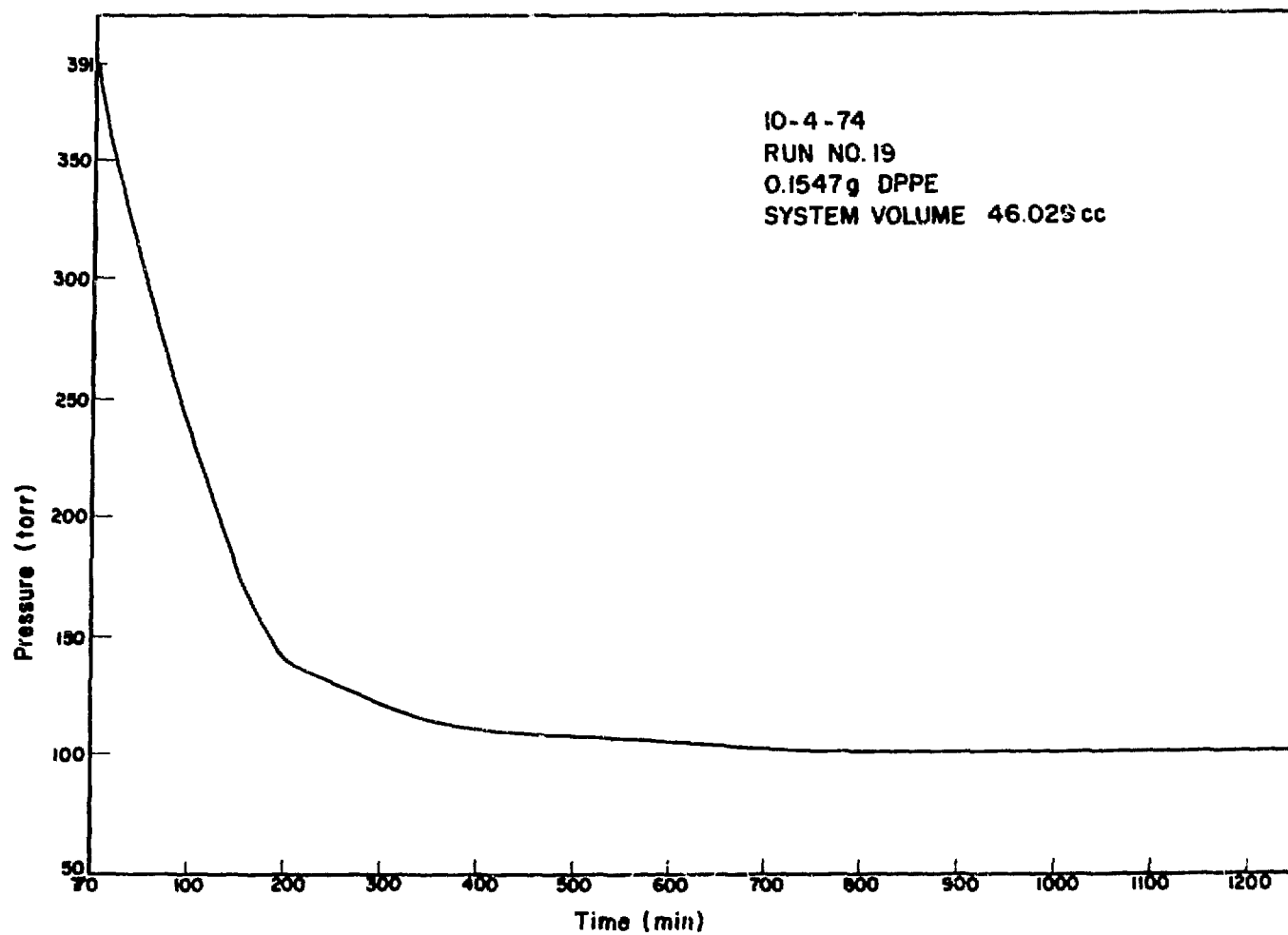
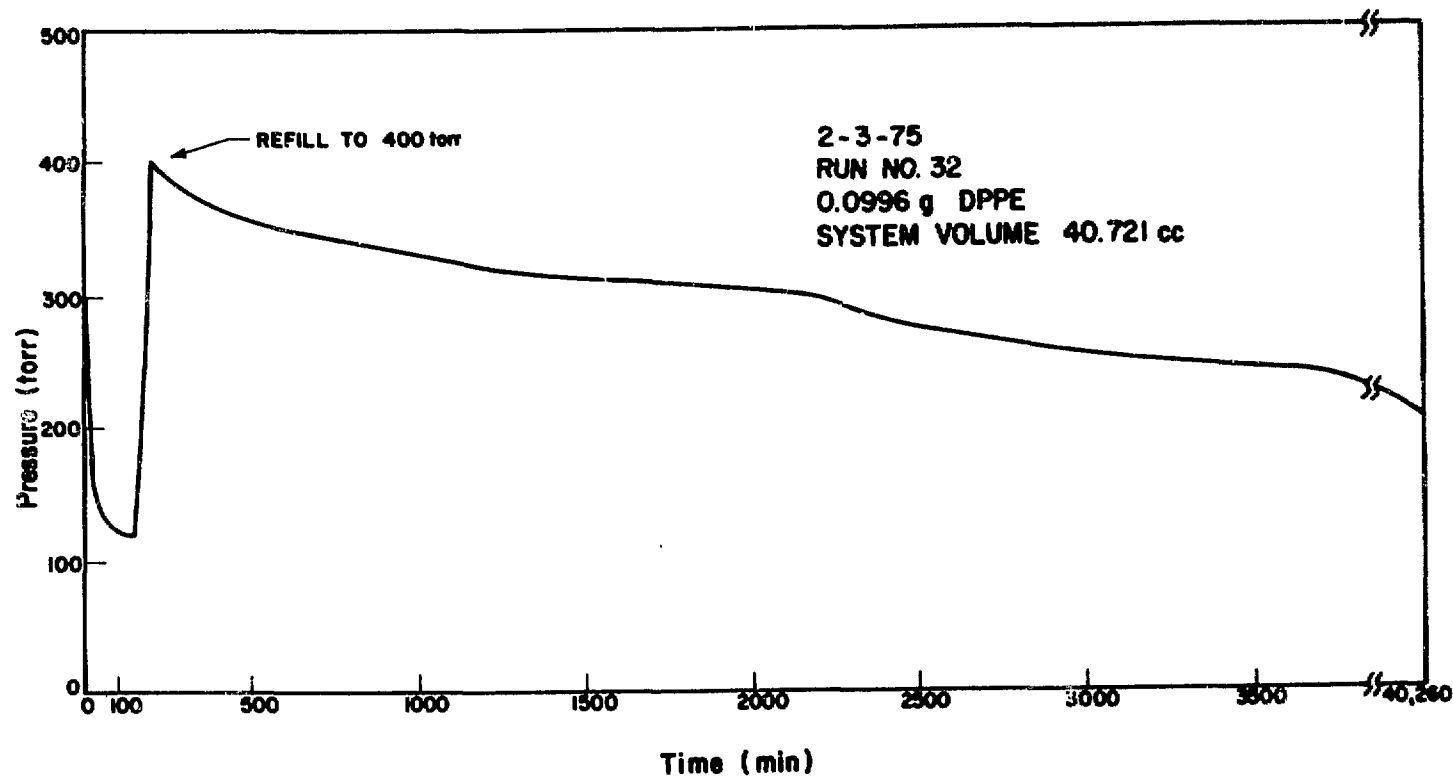


Figure 7. Hydrogen sorption curve for 75% DPPE supported on CaCO_3 starting at 70 minutes elapsed time following refill of the system to 400 torr.



154-III

Figure 8. Tritium sorption curve for 75% DPPE supported on CaCO_3 .

continued to getter the gas phase T_2 contained in the storage vessel after it was sealed.

Flow Experiments with Hydrogen and Deuterium

As described previously, a gas chromatograph was employed to assay the gas eluting from a packed cylindrical bed of getter material. In these experiments H_2 or D_2 was mixed with the argon carrier gas in known amounts with ^4He added as a tracer because its retention time is comparable to that of the hydrogen isotopes. Beds of several different sizes were employed during the course of the work. For Y-993 gas mixtures containing 48 ppm, 500 ppm, and 1550 ppm H_2 were used at flow rates between 0.2 and 5 cm^3/sec . No hydrogen was observed in the effluent of an 18 mm diameter by 30 cm long bed until the flow rate exceeded 3.6 cm^3/sec with the 1550 ppm H_2/Ar mixture. A second type of experiment was done to examine the long term behavior of the getter at a fixed flow rate. The 500 ppm H_2/Ar mixture was continually metered into the getter bed at a rate of 1 cm^3/sec for a total of 443 hours before any hydrogen was detected in the effluent. At that point, the getter had reacted with a total of 12.2 $cm^3(STP) H_2/gram$ of material.

Flow experiments were conducted in a similar manner for DPPE, Er, Ba, and ST101. Both Ba and Er behave qualitatively similar to Y-993 in that no hydrogen was observed in the gas eluted from the getter bed until the bed reached >25% of the hydrogen saturation level observed in the capacity measurements. The difference in the values observed in the two types of experiments can probably be attributed to the phenomenon of channeling. That is, the gas flowing through the column takes the path of least flow resistance and hence areas of higher than average density tend to see less gas because it is channeled around them. Since all the columns were hand packed with loose powders, it is very possible that preferential flow channels existed. Channeling would also account for the fact that large variations were observed in the amount of unreacted material at the time of hydrogen breakthrough. Table 2 summarizes some of the chromatography results.

Table 2. Gas Chromatograph Results

Getter	Column Dimension		Time to Breakthrough (hr)	Gas Composition H ₂ /Ar	Flow Rate (cm ³ /sec)
	diameter (mm)	length (cm)			
Y-993	18	30.0	443	500 ppm	1.0
Ba	3	26.4	217	970 ppm	0.9
Er	3	26.4	226	970 ppm	1.0
ST101	3	26.4	0.5	970 ppm	0.9

The ST101 behaved differently than the three other getters described above. Breakthrough was observed after only one-half hour exposure to the flowing hydrogen mixture. A possible explanation is found in the published data on ST101. At elevated temperatures the gettering process is thought to be diffusion controlled⁷ and high temperatures undoubtedly facilitate the migration of hydrogen into the bulk. At room temperature, on the other hand, the activated getter is primarily surface active, and once a layer of hydrogen forms on the surface, gettering ceases until that hydrogen can diffuse into the bulk. In the dynamic experiments there was insufficient time for the diffusion to occur and once the surface capacity of the bed was exhausted, hydrogen was detected in the effluent.

DPPE also behaved quite differently from Y-993, Ba and Er. Figure 9 shows the time history of the hydrogen concentration in the effluent from a 14.0 cm long by 3 mm I.D. bed of DPPE subjected to a $0.02 \text{ cm}^3/\text{sec}$ flow of argon containing 220 ppm of D_2 . The activation period is clearly apparent in that initially very little of the deuterium entering the bed was absorbed. After reaching full activation, this bed then behaved similarly to those made of Y-993, Ba and Er. The effect of flow rate on the activation process can be observed in Fig. 10. Here the upper curve was obtained at a flow rate of $0.26 \text{ cm}^3/\text{sec}$ and the lower one at $0.02 \text{ cm}^3/\text{sec}$. The abscissa on the graph is the total amount of D_2 that has entered the bed. The effect of the contact time between the hydrogen isotope and the getter can be explained by the following simple model. For a first order reaction, the time rate of change of the hydrogen concentration C at any point in the bed is given by

$$\frac{dC}{dt} = -kC \quad (1)$$

whereas the spatial distribution of the hydrogen along the bed is given by

$$\frac{dC}{dx} = \frac{dC}{dt} \cdot \frac{dt}{dx} = -kC \frac{1}{v_f} \quad (2)$$

where the flow velocity v_f of the gas has been substituted for (dx/dt) . In the case of an inert gas carrier sweeping hydrogen through the bed, v_f is a constant, and so Eq. (2) can be integrated to give

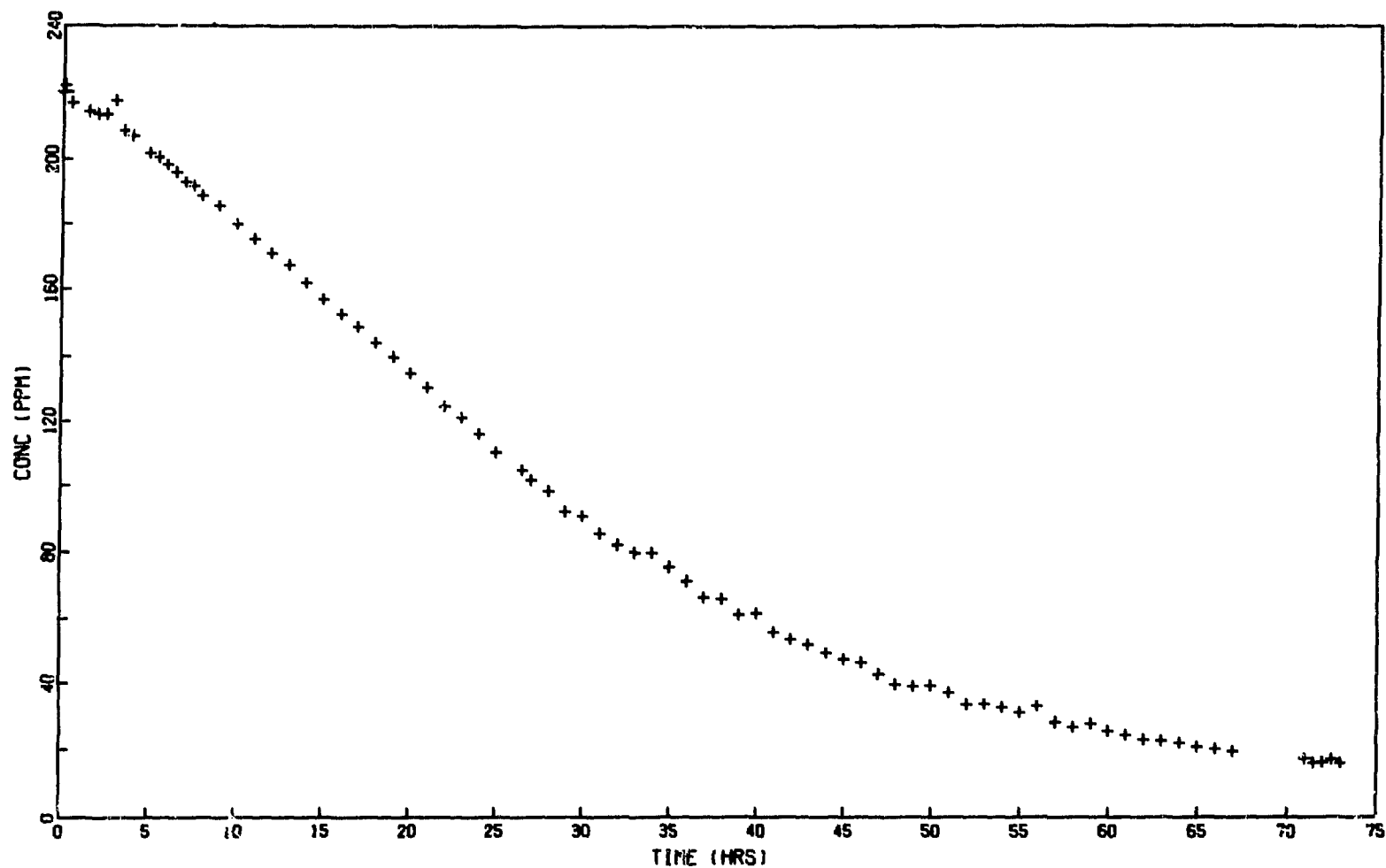


Figure 9. Concentration of deuterium in effluent from DPPE getter column as a function of time. 220 ppm D_2/Ar . Flow rate $0.02 \text{ cm}^3/\text{sec}$. Bed length 14.0 cm.

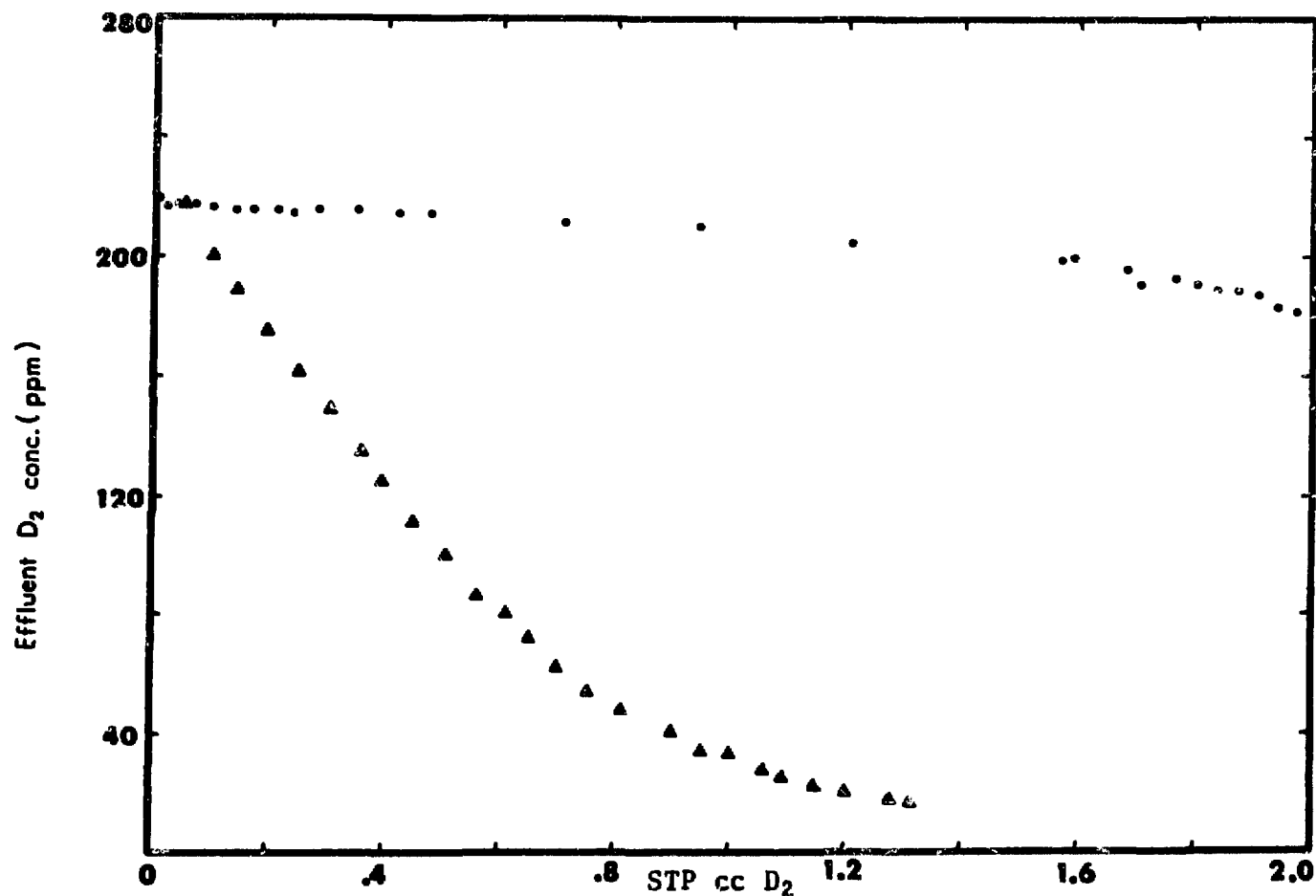


Figure 10. Comparison of the effect of flow rate on the amount of D₂ in the effluent from a DPPE getter bed. Dots: 220 ppm² D₂/Ar at 0.26 cm³/sec. Triangles: 220 ppm D₂/Ar at 0.02 cm³/sec. Abscissa plotted in terms of the total amount of D₂ having entered the bed.

$$C = C_o \exp\left(-\frac{kx}{v_f}\right) . \quad (3)$$

Thus, at the exit of the bed where x is a constant, increasing the flow velocity should increase the observed concentration in the gas in qualitative agreement with the data.

Flow experiments with the Pd/molecular sieve getter were conducted in a somewhat different manner due to the required presence of oxygen. In this case a 13 cm long by 18 mm diameter bed of getter was placed in series with a stainless steel bellows pump in a circulation system. After the sieve had been activated at 800K in hydrogen, it was cooled to room temperature and exposed to a nearly stoichiometric hydrogen-air mixture. Within 5 minutes after starting the bellows pump, the pressure had dropped to that previously calculated for the complete removal of hydrogen from the system. The reaction proceeded so rapidly that the temperature of the molecular sieve bed rose to a point uncomfortable to the touch. This temperature rise is attributable to the ΔH for the hydrogen-oxygen reaction.

Flow Experiments with Tritium

To date, tritium flow experiments have only been conducted with H-36, DPPE and Ba. Figure 11 summarizes the data obtained in these tests. Since H-36 does not react appreciably with the hydrogen isotopes at room temperature, the H-36 curve really portrays the system response to a 10^{-6} cm³/sec tritium leak. At early times, the DPPE curve follows the H-36 curve except for small differences in leak rate and system volume. At later times though, the activation of the getter is apparent and the amount of tritium exiting from the bed decreases significantly. With the barium getter, three facts are apparent. First, the time to the initial tritium breakthrough is longer by roughly a factor of four than for either H-36 or DPPE. The probable reason for this behavior is the faster hydriding kinetics of the Ba. Second, the slope of the curve is smaller, indicating that less tritium is exiting from the bed per unit time than in the other two instances. Third, since the data represent the integral of the total amount of ungettered tritium, the Ba is clearly the most efficient getter of the three. A

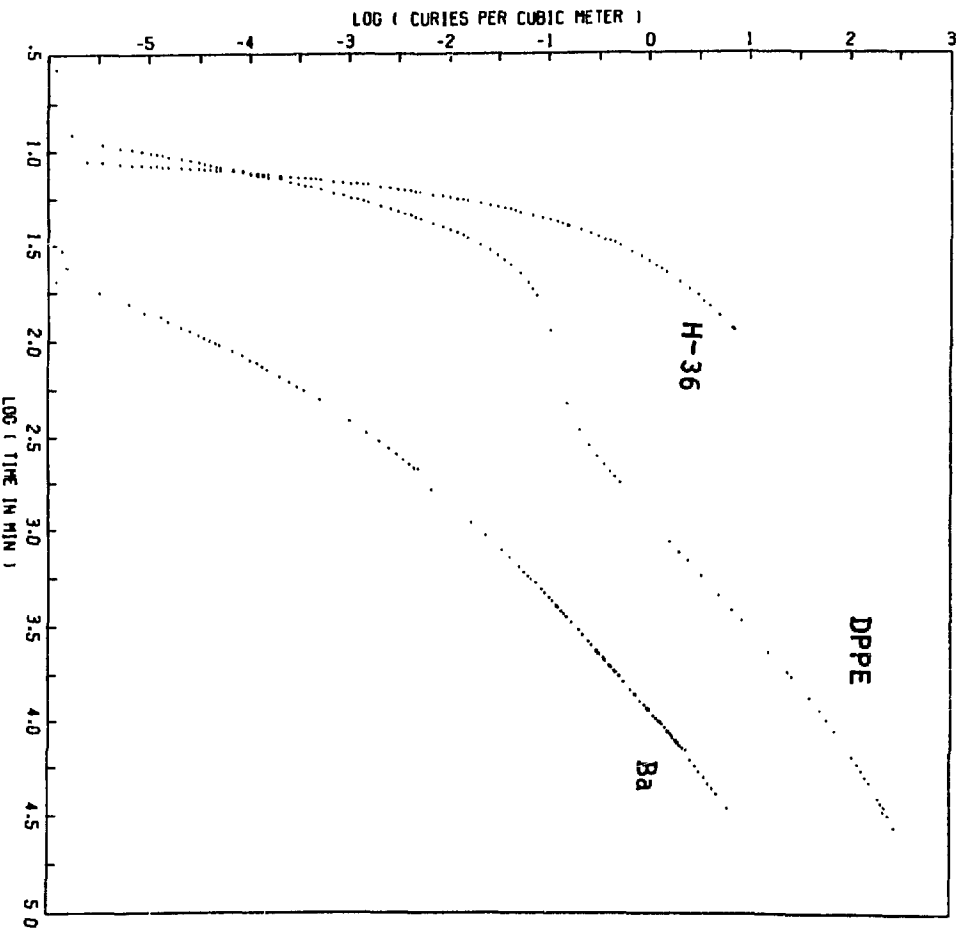


Figure 11. Tritium concentration in the ionization chamber as the result of 1×10^{-6} cm³/sec of tritium entering getter beds of H-36, DPPE and Ba. See Figs. 3 and 4.

test with hydrogen pre-exposed DPPE has not yet been conducted, however. Future tests are also planned with Y-993, ST171, and ST181 using T_2 to compare these getters with those already evaluated.

SUMMARY

A total of nine getters have been evaluated for their ability to remove hydrogen isotopes from flowing gas streams under room temperature conditions. Table 1 summarizes the observed hydrogen capacities under static conditions. Of the nine, H-36 and ST101 were the least effective getters under dynamic flow conditions. Although both barium and erbium proved to be excellent hydrogen getters in this mode, their one disadvantage is that they must be handled in an inert gas atmosphere to retain full activity. ST171, ST181, and SK-100 Pd/molecular sieve can be handled in air prior to activation and work well once activated. On the other hand, Y-993 and DPPE can be handled in air, need little or no activation, and can remove hydrogen from flowing gas streams at room temperature. These reasons may give the latter two getters a slight advantage for use in scrubbing CTR pump exhausts. For any of the getters mentioned in this report, however, one area that still remains to be investigated is the effect of organic pump vapors and other poisons on getter kinetics and capacity.

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A METHOD FOR RECOVERY OF TRITIUM FROM FUSION PLASMA
BY RADIO FREQUENCY PREFERENTIAL PLUGGING

A. Miyahara^{*}, S. Kawasaki^{**} and T. Sato^{*}

^{*}Institute of Plasma Physics, Nagoya University, 464 Nagoya, Japan

^{**}Department of Physics, Faculty of Science,
Kanazawa University, 920 Kanazawa, Japan

ABSTRACT

For toroidal fusion reactor, fuel recovery especially tritium recovery is very important, because fractional burn up is low and breeding rate at blanket is approximately one. When fusion plasma are exhausted through cusp field with rf plug, which is located between reactor core and pumping system, D^+ , T^+ , He^+ and impurity ions are separated by means of preferential plugging. Preliminary experiment has been carried out successfully for H^+ , H_2^+ and H_3^+ plasma.

INTRODUCTION

In tokamak reactor, it will be expected 5 ~ 10 % fractional burn up, so that large amount of tritium will be contained in exhausting gases evacuated through divertor. In this case, exhausting gases from reactor core, will be mixtures of low temperature fuel plasma, ashes and impurities. From the stand point of fuel economics and environmental pollution, they must be carefully separate into isotopes. Fuel gas must be recovered and utilized once more because breeding rate at blanket will not exceed one very much. For impurities, they must be treated carefully as radioactive wastes.

In fusion reactor, because exhausting gases are originally plasma state, it is not reasonable to separate into isotopes after they are

neutralized by touching on cold walls of pumping systems. They must be separate while they are in plasma state. Here we propose a method of isotope separation which can be inserted between reactor core and evacuating system. This method is an application of rf plugging of cusp plasma, which was developed in the Institute of Plasma Physics, Nagoya University.

PHYSICAL BACKGROUND

When one cycle operation has been over, we must stop a reactor and exhaust fuel gases, ashes and impurities. But because reactor core is still hot, it is filled with plasma. Then, by changing the polarity of one of the toroidal coils, we can produce magnetic configuration as illustrate in fig.1, and a pair of disk shaped plasma sheet will be formed. If we add sufficiently strong rf field at electrode, D^+ and T^+ are plugged simultaneously,⁽¹⁾⁽²⁾ but α -particles (ashes) are come out beyond plugs because their energies are too high (~ 500 keV after α -heating). Also impurity ions are passed through plug, because their cyclotron frequencies are largely apart from those of fuel ions.⁽³⁾⁽⁴⁾ Usually, hydrogen isotopes are not necessarily separated from fuel gases, but extraction of He gases and impurities is important. In this case, simple plugging for D^+ and T^+ is sufficient to recover fuels.⁽¹⁾ If we want to recover tritium separately, rf plugging for D^+ ions must be added. After certain time, percentage concentration of tritium becomes sufficiently low, then the rf potential must be reduced and outcoming D^+ ions must be introduced into the pumping system for deuterium gas.

To determine the magnetic field strength, rf field and electrode radius of proposed system, we push the discussions along the theory of adiabatic rf plugging developed by Hatori and Watanabe.⁽⁵⁾ To fulfil adiabatic condition, ion temperature T (eV) of plugged particles must be low compared to the critical energy W_c (eV).

$$T \ll W_c = 7.00 \times 10^3 A_1^{\frac{3}{5}} \frac{(E_0 R_0)^{8/5}}{(B_0 R_0)^{6/5}} \quad (1)$$

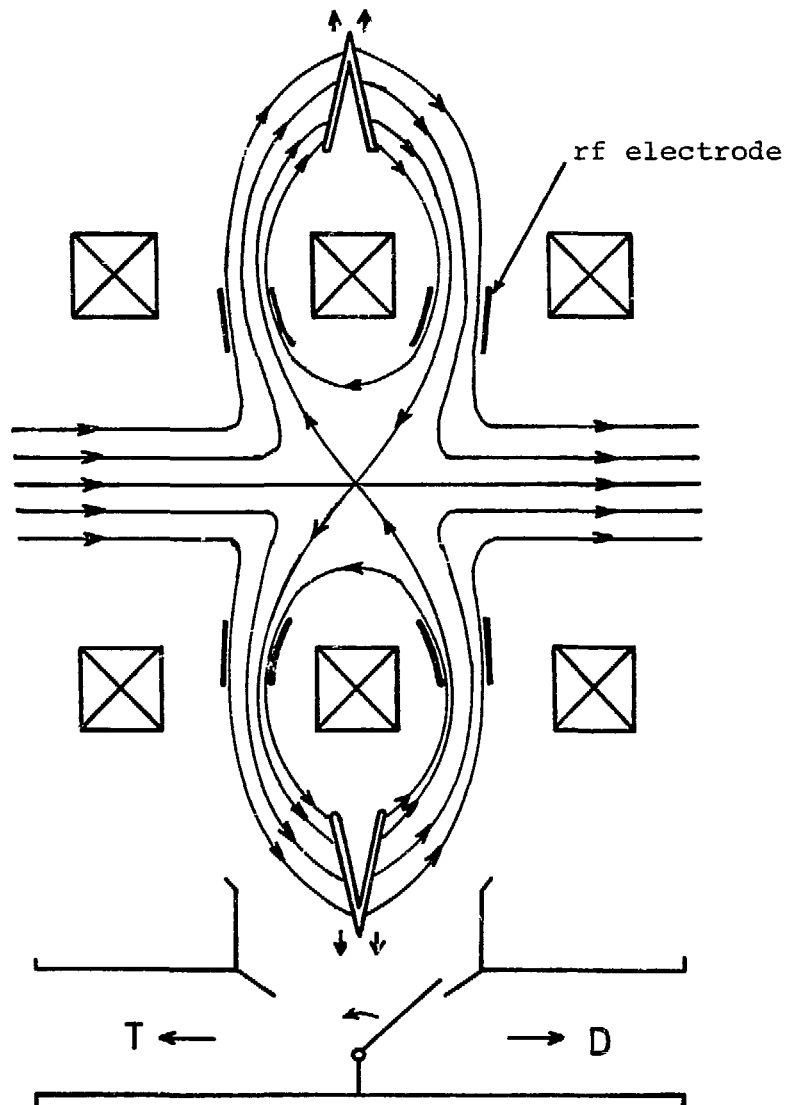


Fig.1. Conceptual drawing for rf plugging Isotope Separator.

where

E_0 (kV/cm) = rf field strength in plasma,

B_0 (kG) = magnetic field at rf electrode,

R_0 (m) = distance from plasma center to rf electrode,

A_i = ratio of ion mass to proton mass.

Also additional two conditions are necessary.

$$\bar{E} = \frac{ZeE_0}{M\omega^2 R_0} = 5.2 \times 10^{-2} \frac{A_i}{Z} \frac{E_0 R_0}{(B_0 R_0)^2} \ll 1 \quad (2)$$

$$\rho_i / R_0 \ll 1 \quad (3)$$

where ρ_i = ion Larmor radius at R_0 . Equation (3) is fulfilled usually for confinement devices, and if we give values of $W_c = 500$ eV and $\bar{E} = 2 \times 10^{-3}$, we can obtain hatched region as in fig.2, and cross point will give the minimum values of $E_0 R_0$ and $B_0 R_0$. We adopt twice of these minimum values. In table 1, list of $E_0 R_0$, $B_0 R_0$ values for $T_i = 10$ eV, 100 eV, 1keV has been given, where $T/W_c = 2 \times 10^{-2}$ kept constant. On the other hand, n_{RD} , density of D^+ at rf electrode without rf field, can be written⁽⁶⁾ $n_{RD} = 0.15 n_0$, where n_0 is density at separatrix. If we set $n_0 = 5 \times 10^{13} \text{ cm}^{-3}$, n_{RD} becomes $7.5 \times 10^{12} \text{ cm}^{-3}$, and magnetic field can be determined from the relation of $(\frac{\omega_{pi}}{\omega_{ci}})^2 < 1000$. Here we adopt the values of $B_0 = 20$ kG and $(\frac{\omega_{pi}}{\omega_{ci}})^2 = 690$, then we can obtain B_0 , R_0 , and E_0 values as in table 2 for $T \approx 10, 100, 1000$ eV each. In the following discussion, we use the values of $B_0 = 20$ kG, $R_0 = 5.3$ m and $E_0 = 20$ kV/cm, which correspond to the values for $T_i = 1$ keV. We can expect better adiabaticity if the temperature of plasma become lower.

Radio frequency field can be penetrated into plasma if we set frequency equal to resonance frequency of eigenmode. This eigenfrequency can be written $\omega = \sqrt{2} \omega_{ci}$ ⁽¹⁾⁽⁷⁾ for $(\frac{\omega_{pi}}{\omega_{ci}})^2 \gg 1$ plasma. On the other-hand, quasi-potential ψ (eV) for rf plugging, can be written as follows.⁽⁵⁾

$$\psi(r) = \frac{M}{4} \left(\frac{ZeE_0}{M} \right)^2 \frac{1}{\omega^2 - \omega_{ci}^2(r)} = 2.61 \times 10^3 A_i \left(\frac{E_0 \text{ (kV/cm)}}{B_0 \text{ (kG)}} \right)^2 \left(\frac{\omega^2}{\omega_{ci}^2} - 1 \right)^{-1} \quad (4)$$

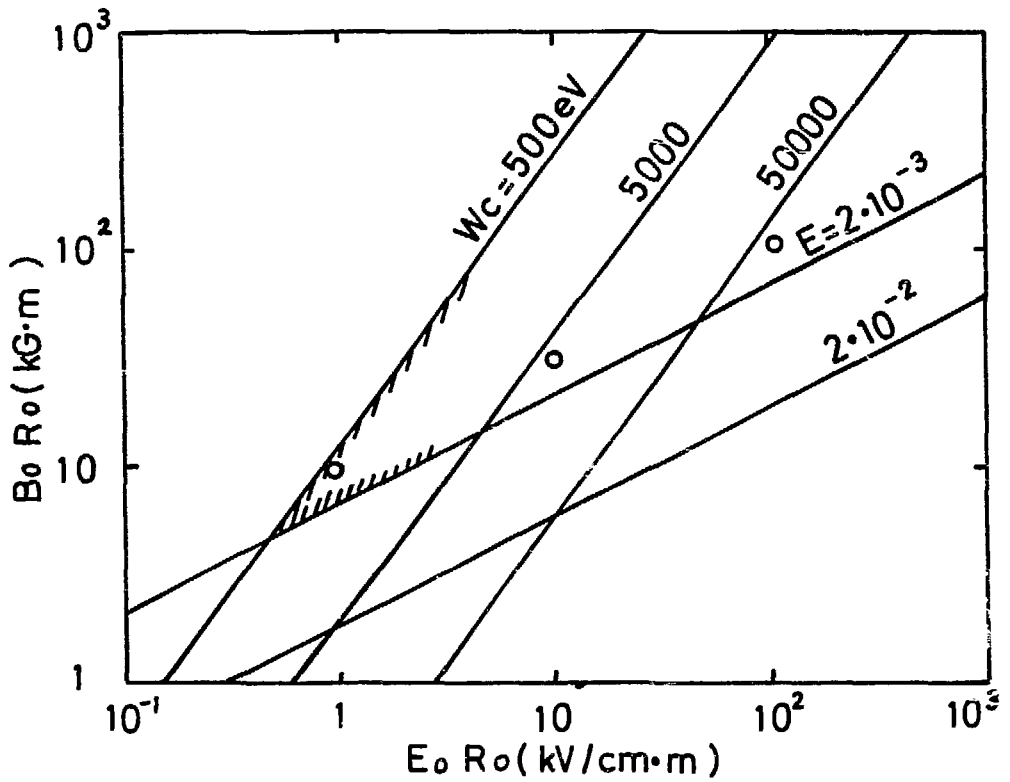


Fig.2. Determination of $B_0 R_0$ and $E_0 R_0$ from adiabatic condition for each W_c and $\bar{E}$ values.

$T(\text{eV})$	$E_O R_O$	$B_O R_O$
10	1.0	10
100	10	32
1000	106	106

Table 1. Typical values of $E_O R_O$ (kV/cm·m) and $B_O R_O$ (kG·m) for ion temperature of 10, 100 and 1000 eV. Each value corresponds to circle point of Fig.2.

$T(\text{eV})$	B_O (kG)	R_O (m)	E_O (kV/cm)
10	20	0.5	2.0
100	20	1.6	6.3
1000	20	5.3	20

Table 2. B_O , R_O and E_O values for each ion temperature 10, 100 and 1000 eV.

With the fixed frequency of $\omega = \sqrt{2} \omega_{CD}$, quasi-potential ψ_D^* for D^+ is 5200 eV and ψ_T^* for T^+ is 2230 eV. Because the density decrease by $\psi^*(D)$ is given by

$$n_D = n_{R0} \exp\left(-\frac{\psi_D^*}{2T}\right) \quad (5)$$

Here, in equation (5), we took into consideration about ambipolar effect. From these, selectivity S for rf plugging system is given as equation (6).

$$S = \frac{n_T}{n_D + n_T} = \frac{1}{1 + \exp\left(-\frac{\psi_D^* - \psi_T^*}{2T}\right)} \quad (6)$$

In table 3, n_D , n_T and S have been given for various ion temperature with above mentioned quasi-potential.

If the plasma temperature is below 200 eV, selectivity S is essentially equal to one, while $n_T/n_{RT} < 10^{-3}$, that means T^+ ions are also plugged very well. On the other hand, with the temperature above 2 keV, T^+ ions will be plugged 50 % but at the same time, about 30 % D^+ ions leak from the rf plug. From these considerations, ion temperature of 500 eV is optimum, and at the same time reduction of rf field E_0 is necessary when the plasma temperature become lower. The relation between T and E_0 is given in table 4 with fixed $S = 0.95$.

To estimate the recovery time for T^+ , we have calculated T^+ flux which pass through rf electrode as follows.

$$F_T = \frac{1}{4} n_T v_T \cdot 2\pi R_0 \cdot 2\rho_T = 1.25 \times 10^8 \frac{n_T(\text{cm}^{-3}) R_0(\text{m}) T(\text{eV})}{B_0(\text{kG})} \quad (7)$$

If we treat by six systems such as fig.1 around torus, recovery time τ can be obtained as (8)

$$\tau = \frac{N_T}{6F_T} \quad (8)$$

where N_T is total number of T^+ in reactor core. In table 4, τ has been given under various conditions.

In fusion reactor, energy balance plays an essential part, so the estimation of necessary rf power is important. In this case, because

T (eV)	n_D/n_{RD}	n_I/n_{RT}	s
10	~ 0	3.8×10^{-49}	1.00
100	5.1×10^{-12}	1.4×10^{-5}	1.00
200	2.3×10^{-6}	3.8×10^{-3}	0.999
500	5.5×10^{-3}	1.1×10^{-1}	0.951
1000	7.4×10^{-2}	3.3×10^{-1}	0.815
2000	2.7×10^{-1}	5.7×10^{-1}	0.678

Table 3. Selectivity vs. ion temperature.

T (eV)	E_O (kV/cm)	τ (sec)
10	2.9	320
100	8.9	29
1000	28	2.7

Table 4. Recovery time vs. ion temperature.

rf adiabatic plugging has been adopted, rf energy will not go into plasma. Dissipations are only due to losses of rf cavity. As an example, six copper cavities of ID = 10 m, OD = 16 m and distance 0.05 m, operated at frequency of $\sqrt{2} f_{CD} = 2.18 \times 10^7$ MHz and $E_0 = 20$ kV/cm, dissipate the power of 13 MW.

EXPERIMENTAL BACKGROUND

The experiment for rf preferential plugging was first done by Hidekuma et al.⁽²⁾ by using TPD-II devices. Although their experiment did not fulfil adiabatic condition completely, two experimental results illustrated important indications for tritium recovery system.

The first, N^+ and N_2^+ ions mixed as impurities for He^+ plasma, pass through He^+ rf plug without any influence. This is due to large difference of cyclotron frequency between He^+ and N^+ , N_2^+ . In a reactor, ions of wall material such as Nb ions are considered as main impurities. If the electron temperature is high, impurities become multiple charged ions and approach to $eZ/m \sim \frac{1}{2}$, but at the end of cycle operation of reactor, it is expected lower electron temperature and smaller eZ/m values.

The second result is in respect of three component plasma H^+ , H_2^+ and H_3^+ . This is a simulation of H^+ , D^+ and T^+ mixture plasma at lower plasma temperature. One of the experiments is rf plugging preferentially for H_2^+ , another is rf plugging preferentially for H^+ . Both of them illustrate that with moderate rf field, preferential plugging have been achieved, but with stronger rf field, all of ion species are plugged effectively.

CONCLUSION

A method for tritium recovery by rf preferential plugging has been proposed and explained by conceptual drawing. Other possibility is to insert an extracting pipe to divertor region, then the plasma will be exhausted through guiding pipe and rf plugged cusp separator. This case, we can adopt multistage separator system to improve efficiency.

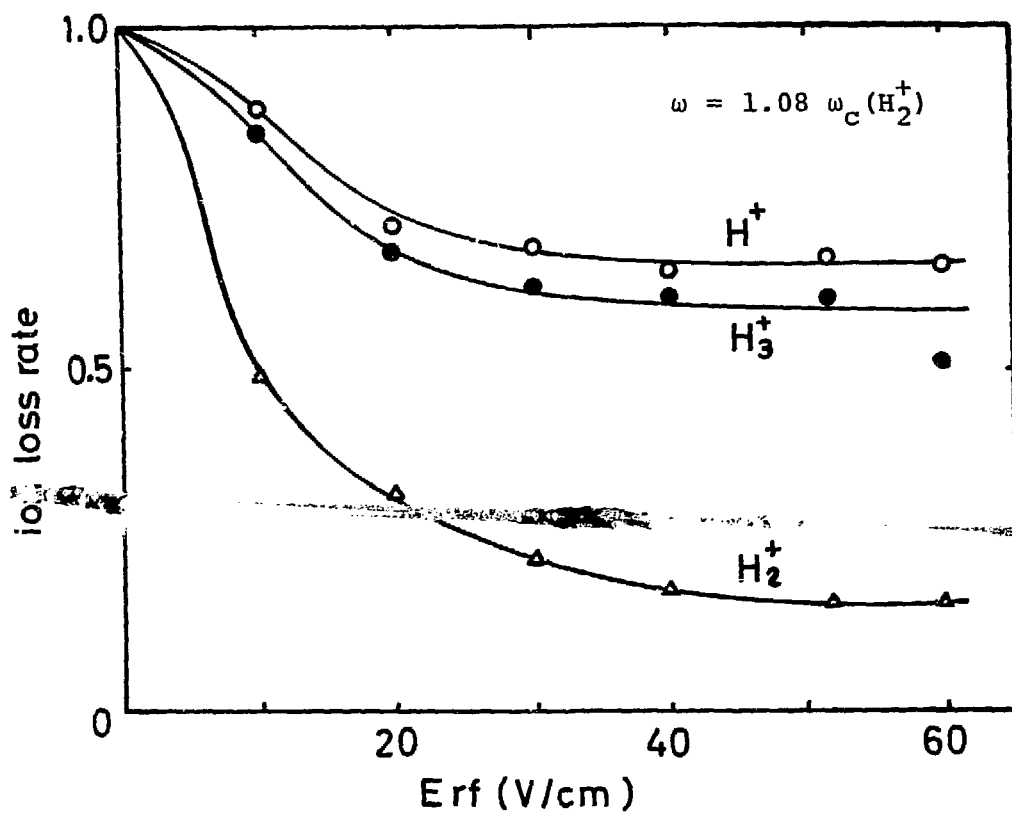


Fig.3. Plot of loss factor of three ion species (H^+ , H_2^+ and H_3^+) against the applied rf field. The rf frequency is adjusted to the resonance frequency of the H_2^+ ion.

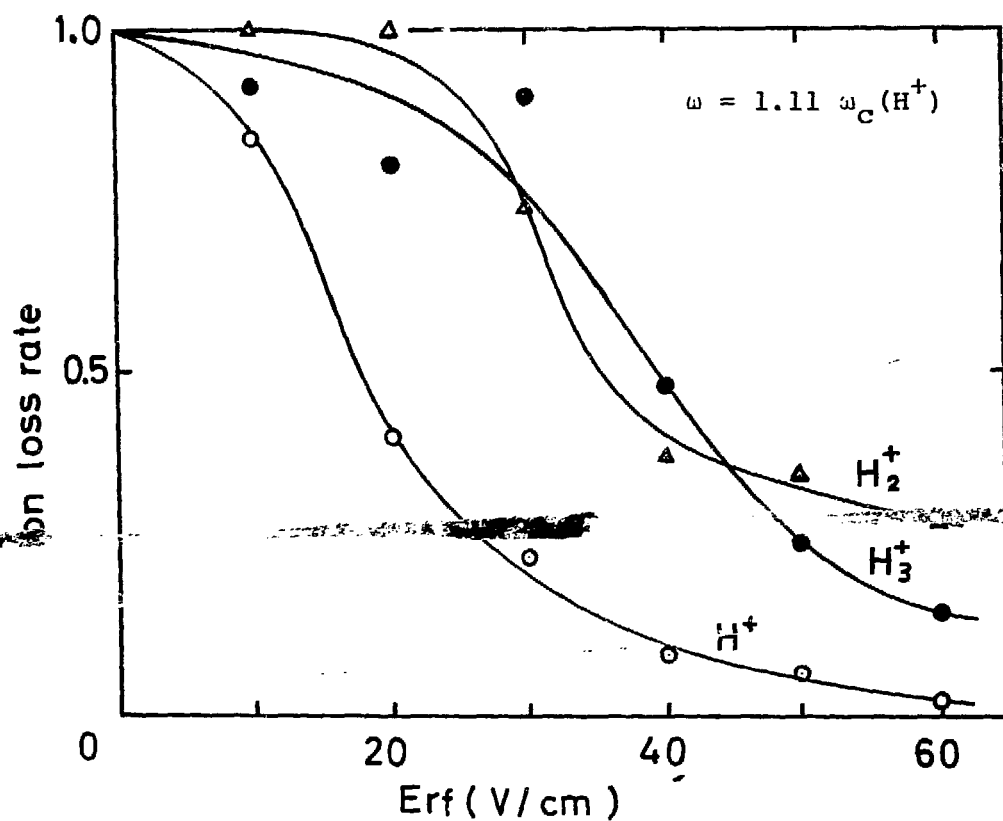


Fig.4. Plot of loss factor of three ion species (H^+ , H_2^+ and H_3^+) against the applied rf field. The rf frequency is adjusted to the resonance frequency of the H^+ ion.

On the other hand, the fact that D^+ and T^+ will be plugged simultaneously by stronger rf field, suggest us that the recovery of fuel gas, namely D_2 and T_2 mixture, is easier than tritium recovery itself. This time, He^+ and He^{++} will escape from the system because they have higher energy. For impurities, they will come out easily because of large difference of cyclotron frequencies at lower electron temperature.

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RECENT EXPERIMENTAL ENGINEERING STUDIES RELATED
TO CONTROLLED THERMONUCLEAR REACTORS⁺

S. D. Clinton	J. B. Talbot
P. W. Fisher	J. S. Watson
F. J. Smith	

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

Recent experimental engineering studies at ORNL on tritium handling systems for controlled thermonuclear reactors (CTRs) include investigations of: (1) metal sorbers for removal of tritium from liquid metals, (2) tritium solubility in lithium-bismuth (Li-Bi), (3) oxidation of hydrogen permeating a metal surface, and (4) cryosorption pumping of hydrogen. A yttrium metal sorber has shown significant tritium removal rates from molten potassium. The tritium sorption mass transfer coefficient was measured to be 3.0×10^{-2} cm/hr at 300°C. The slow mass transfer rate would dictate a large metal sorber system for tritium recovery; however, the results are encouraging enough to merit further sorbent studies with tritiated lithium. At 600°C the tritium solubility in Li-Bi (15 at. % Li) ranged from 0.01 to 0.1 ppb at respective tritium partial pressures of 10^{-2} to 10^{-1} torr. Due to the low solubility, further experimentation with Li-Bi as a possible extractant for tritium does not appear to be justified at the present.

INTRODUCTION

Experimental studies have begun which relate to: (1) tritium recovery from the blanket, (2) tritium containment, and (3) tritium recovery from plasma. This paper will emphasize the oldest

⁺Research sponsored by the Energy Research and Development Administration under contract with Union Carbide Corporation.

experimental effort, which is an evaluation of metal sorbers for removing tritium from liquid metals, and a brief study of tritium uptake by lithium-bismuth (Li-Bi). Paul Barton of Penn State University proposed Li-Bi as a possible extractant for removing tritium from a molten salt blanket. Since Penn State has no facility for handling tritium, studies of tritium solubility in Li-Bi were performed at ORNL.¹ Two recently initiated studies dealing with hydrogen permeation-oxidation and hydrogen pumping will be mentioned; however, the results from these studies are preliminary.

TRITIUM RECOVERY FROM CONTROLLED THERMONUCLEAR REACTOR (CTR) BLANKETS

A molten lithium blanket appears to be the most promising means of achieving tritium breeding for Tokamak fusion reactors. Three recovery techniques are currently being considered at ORNL for the recovery of tritium from liquid lithium: (1) extraction with a molten salt, (2) permeation through a niobium window, and (3) sorption on a hydrogen-gettering metal such as yttrium or zirconium.

Metal Sorbers

Tritium sorption rates from liquid metals are being measured in a batch contactor (20 cc volume) using selected metal sorbents. The metal sorbents tested were yttrium, zirconium, uranium, and titanium. A sample of the sorbent metal was contacted with a known amount of potassium (a potential blanket coolant) containing 620 ppb tritium for time periods ranging from a few hours to several days at temperatures of 150 to 400°C. After the desired contact time, the potassium was drawn into a sample tube and analyzed for the remaining tritium content.

Experimental equipment. A schematic diagram of the equipment being used to contact tritiated liquid metals with selected metal sorbents is shown in Fig. 1. Basically, the equipment consists of a tritiated liquid metal reservoir, two sampling valves, two contacting chambers, a vacuum source, and an argon supply (less than 5×10^{-4} %

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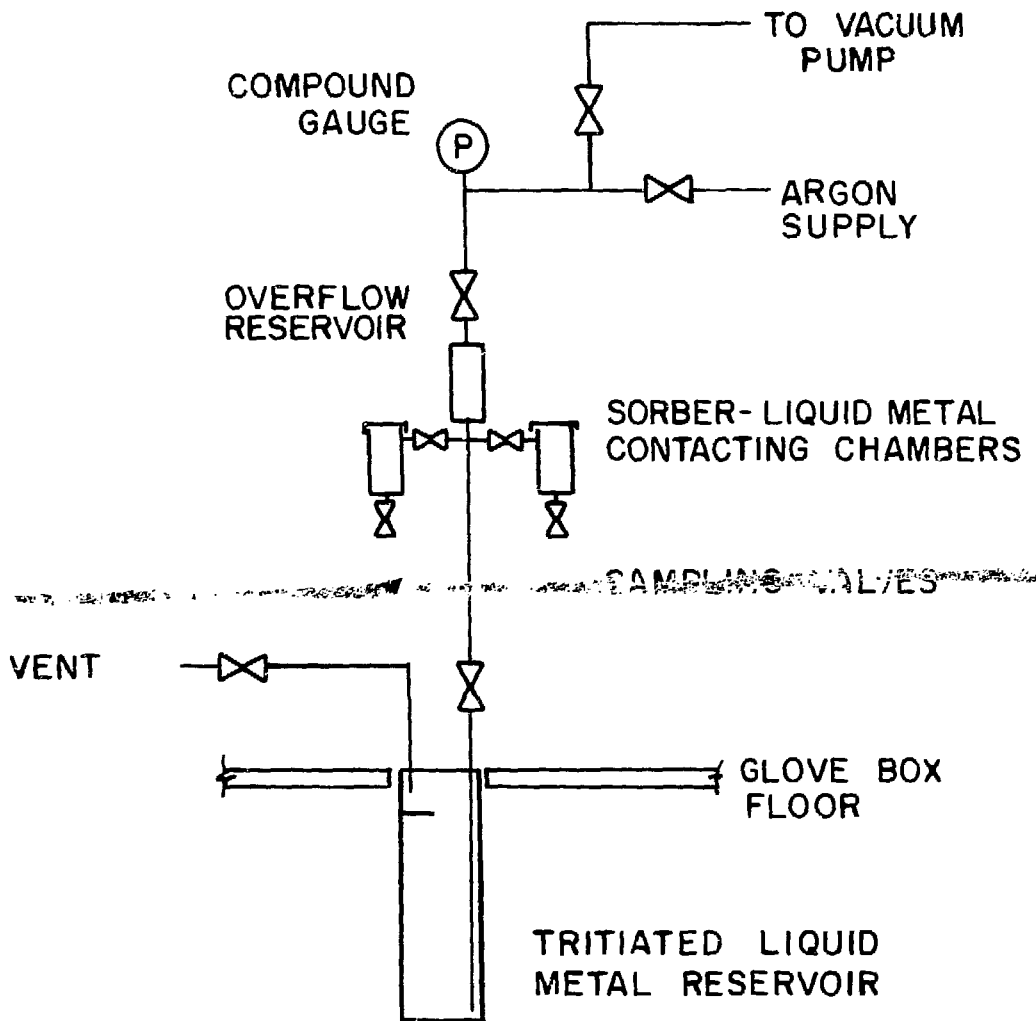


Fig. 1. Contacting apparatus for tritium-metal sorption studies.

total impurities). The tritiated liquid metal is drawn into the two contactor chambers at a temperature of 150 to 400°C. One chamber contains the metal sorbent, and the other chamber serves as a control sample. To terminate the experiment, the two liquid metal samples are removed from the contactor chambers and analyzed for tritium.² To reduce the problems of oxygen contamination, the entire process is enclosed in a glove box with a once-through, dry argon atmosphere. The glove box exhausts to a hot off-gas system and is eventually discharged via a stack to the environment. Figure 2 shows the contacting apparatus as seen through the glove box window.

Initial sorption measurements were made with liquid potassium, and preparations are under way to evaluate metal sorbents in tritiated lithium. Since preliminary tests indicated that tritium removal by metal sorbents was slow and controlled by solid diffusion, an earlier ~~batch contactor was abandoned~~ in favor of the batch contactor.³ Two-dozen metal sorbent samples were contacted with tritiated potassium at temperatures from 150 to 400°C and time periods up to several days before any significant mass transfer of tritium was observed. Several zirconium samples were given different surface treatments to reduce or eliminate the solid film resistance, but none were successful.

A yttrium metal sample obtained from Research Chemicals (Division of Nuclear Corp. of America) removed a significant amount of tritium from the molten potassium. Photographs of the yttrium sorbent sample are shown in Fig. 3. The sample dimensions are 0.06-in. x 0.5-in. x 1.5-in. (geometric surface area, $A = 11.2 \text{ cm}^2$) and the weight is 3.42 g. The yttrium metal sample appears to have a layered structure and is grayish in color.

Results and discussion. The results of the yttrium-tritium sorption experiments in molten potassium are tabulated in Table 1. The yttrium sorber was not removed from the contacting chamber until after run 12, and the two subsequent runs (13 and 14) were made with a second yttrium sample of the same dimensions and weight. Runs 7 through 11 were conducted at 400°C, and the remaining runs were

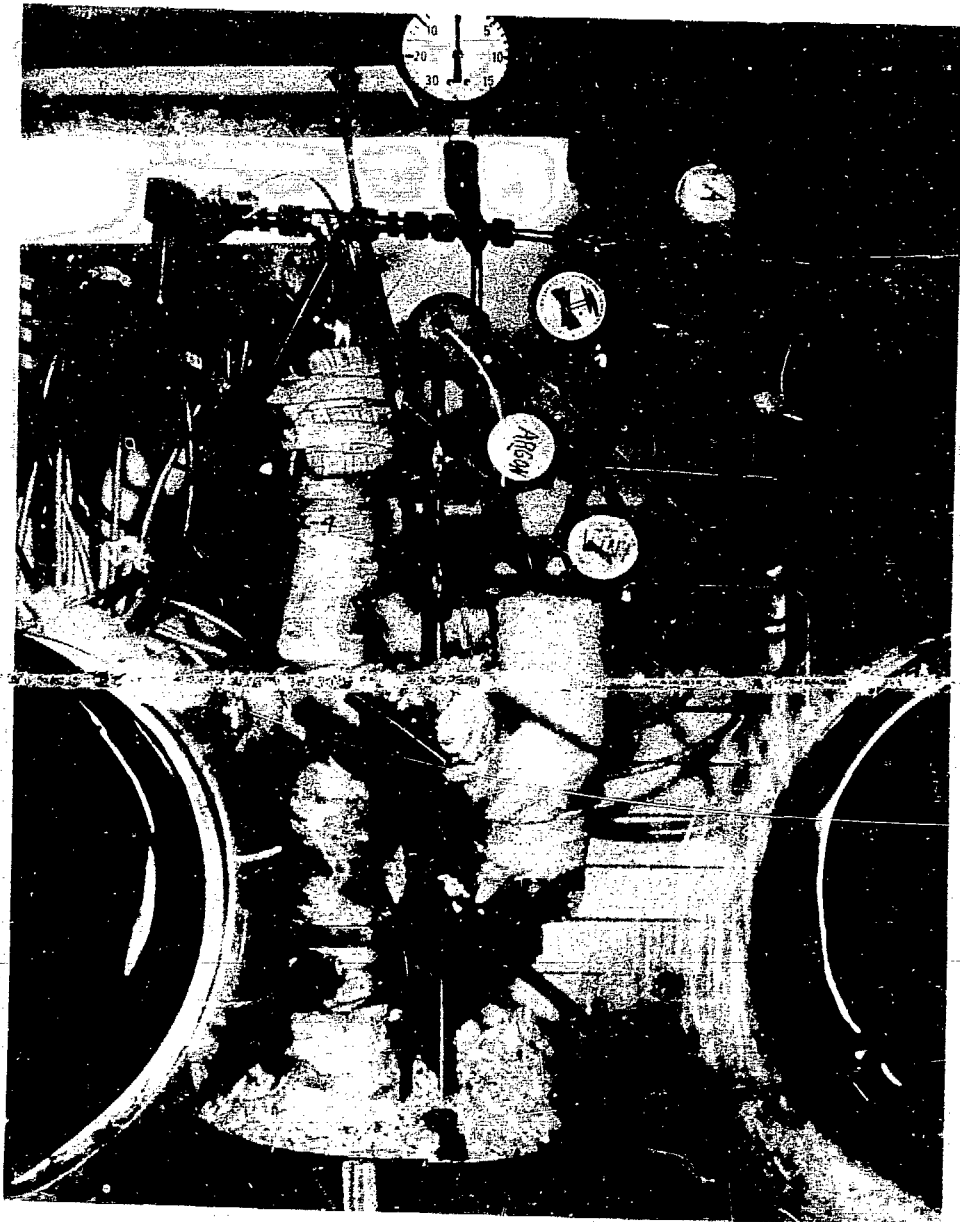
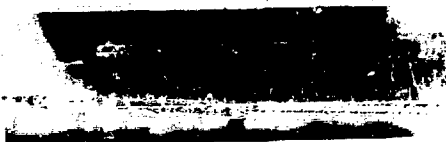


Fig. 2. Tritium-metal sorbent contacting apparatus as viewed through the glove box window.

Y133096



(a) SIDE VIEW OF YTTRIUM SAMPLE.



Y133097



(b) EDGE VIEW OF YTTRIUM SAMPLE.

Fig. 3. Yttrium metal sorbent samples.

Table 1. Results of the tritiated potassium-yttrium sorption experiments

Run No.	Contact time, t (hr)	Tritium concentration in potassium		Potassium volume, V (cc)	(At/V) ^a (hr/cm)	(C _y /C) ^b (ppb/ppb)
		Sorber, C (ppb)	Control, C ₀ (ppb)			
1	51	483	639	18.9	30.2	1.2
2	99	80	579	19.5	56.8	37.1
3	145	30	646	14.6	111	163
4	24	347	590	17.2	15.6	17.2
5	4	620	643	21.0	2.1	9.6
6	48	241	612	12.4	43.3	29.2
7	24	40	618	13.9	19.3	220
8	16	54	611	12.9	13.9	206
9	6	266	637	18.2	3.7	47.3
10	30	22	673	10.0	33.6	631
11	12	319	592	17.5	7.7	47.1
12	72	490	609	18.8	42.9	31.8
13	72	68		18.3	44.1	30.6
14	24	257		19.8	13.6	13.8

^a A = yttrium geometric surface area, 11.2 cm²,

^b C_y = tritium concentration in yttrium, ppb.

at 300°C. The yttrium-tritiated potassium contact times (t) are given in column 2, and the tritium concentrations (C) remaining in the potassium are shown in column 3. Column 4 tabulates the tritium concentrations (C_0) in the potassium control samples. From the twelve control analyses, the average tritium concentration measured in the potassium feed reservoir was 621 ± 27 ppb. These values demonstrated the precision of our measurements and showed that the tritium concentration in the potassium supply did not vary with time. The potassium volumes (V) which were recovered from the sorber contacting chamber are shown in column 5, and column 6 tabulates the product of yttrium area per unit volume of potassium (average $A/V = 0.72 \pm 0.18 \text{ cm}^{-1}$) and the contact time, t . The last column tabulates the ratio of tritium concentration in the yttrium to tritium concentration remaining in the potassium, (C_y/C) at the end of each run. The tritium concentration in the yttrium was estimated by summing accumulations from previous runs.

Except for runs 1 and 12, tritium concentration in the potassium decreased as a first order reaction. The low mass transfer observed in run 1 could indicate that yttrium must be activated to sorb tritium; however, a similar yttrium sample used in run 13 did not require significant time to activate the surface. The low mass transfer rate observed in run 12 could have resulted from the yttrium and tritium concentration approaching saturation (bulk tritium concentration in the yttrium was 15.6 ppm). Yttrium capacities for tritium at these temperatures and pressures can only be estimated by extrapolating existing data,⁴ but higher capacities were expected. The results from run 12 could be explained by a tritium concentration gradient within the yttrium. That is, the concentration at the metal surface may be higher than the average bulk concentration.

Using data from the remaining runs with the first yttrium sorber, the time required to reduce the tritium concentration in potassium by a factor of 2 was 32 hrs at 300°C and 6 hrs at 400°C. Due to a limited available supply of tritiated potassium, only two

runs were completed with the second yttrium sorber. The second sample sorbed tritium at a slightly higher rate, and the tritium concentration was reduced by a factor of 2 in approximately 22 hrs at 300°C. Although the geometric areas of the two yttrium samples were the same (11.2 cm²), the effective overall sorption rate of the second yttrium sample appears to be about 50% greater. This probably represents differences in properties of the two samples.

The tritium concentrations in potassium for the first yttrium sample are plotted in Fig. 4 as a function of the contact area (A) and time (t) per unit volume (V) of potassium. With a surface-resistance controlled process and a tritium concentration in the solid phase far below saturation, the driving force can be approximated by the tritium concentration in potassium at any time. The tritium sorption mass transfer coefficient is then equal to the slope of the lines shown in Fig. 4. The mass transfer coefficient increases from 3.0×10^{-2} cm/hr at 300°C to 1.5×10^{-1} cm/hr at 400°C. With these two values, the activation energy of the reaction is estimated to be 12 kcal/g-atom.

After runs 12 and 14, parts of the two yttrium samples were analyzed for tritium by dissolving the metal in nitric acid and determining tritium concentration by liquid scintillation counting. From previous analyses of the potassium for tritium, the first yttrium sorber was estimated to have accumulated 0.52 Ci of tritium and the second 0.13 Ci. Analysis of the first yttrium sample indicated recovery of 81% (0.42 Ci) of the estimated tritium content. While removing the second sample from the contactor, adherent potassium oxidized and damaged the sample. This prevented quantitative comparisons of estimated and measured accumulated tritium with the second sample. Prior to dissolution, the first yttrium sample was cut into three pieces (0.5-in. x 0.5-in. x 0.06-in.), and the second sample was divided into three layered sections (inner layer was about 0.04-in. thick). The tritium concentration appeared to be uniform in both directions; however, layer measurements with the second sample are not conclusive.

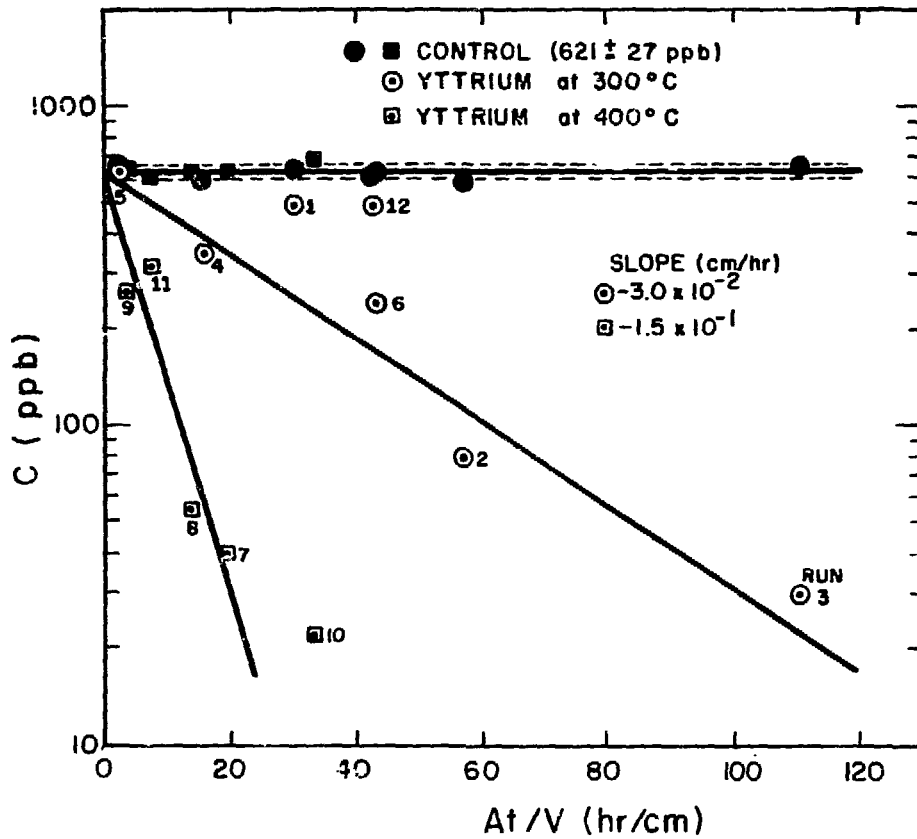


Fig. 4. Tritium concentration in potassium vs the product of yttrium area per unit volume and time.

Although a metal sorber system could be designed to remove tritium from a liquid metal blanket or coolant, the existing data indicate that the sorber size and tritium inventory in the reactor blanket and yttrium sorber may be impractical. The results, however, are encouraging enough to merit limited further sorption studies with tritiated lithium.

Li-Bi Extraction

A suggested process for recovery of tritium from molten salt fusion blankets prompted an investigation of tritium sorption in molten Li-Bi. The Li-bi has been proposed as a possible extractant for removing tritium from a molten salt (Li_2BeF_4) blanket.

Apparatus and procedures. The equilibration and sorption of tritium in Li-Bi were conducted similarly to a method used previously.⁵ About 600 g of bismuth and 3.47 g of lithium were loaded under an argon atmosphere into a molybdenum crucible placed inside the reaction vessel. The Li-Bi mixture was heated to 600°C under argon. The system was evacuated, and tritium was added to the molten alloy by breaking the seal in the ampule attached to a molybdenum sparge tube extending into the heated metal phase. The system pressure was increased to and maintained at 1-5 psi static argon pressure throughout the experiment by adding argon through the sparge tube. At least 24 hrs were allowed for equilibrium to be attained. Pairs of liquid and gas samples were removed for analysis. Metal sampling was performed as described previously.⁵ The metal samples were dissolved in nitric acid while a stream of argon, containing one percent hydrogen, was flushed over the nitric acid solution, through a hot (600°C) copper oxide bed, and finally through a series of water bubblers. Any evolved tritium was thereby converted to tritiated water and trapped in the water bubblers. The nitric acid and water solutions were analyzed for tritium by liquid scintillation counting. Gas phase samples were taken by filling an evacuated 4.5 ml tube with the gas samples. The samples were then slowly flushed with argon into a tritium monitor or to a copper oxide bed and tritium trapping system.

Results and discussion. Measured tritium solubilities in Li-Bi (15 at. % Li) at 600°C ranged from 0.01 to 0.1 ppb at respective tritium partial pressures of 10^{-3} to 10^{-1} torr. Although a few data were taken at 500 and 700°C, most of the simultaneous gas and metal samples were obtained at 600°C. A least-square fit of the tritium pressure-solubility data at 600°C is shown in Fig. 5.

The solubility of tritium in bismuth has not been measured, but it is expected to be low since bismuth does not form a stable hydride at the experimental conditions. The 2×10^{-7} at. % tritium solubility in Li-Bi at 600°C and 10^{-2} torr is approximately 6 orders of magnitude lower than the tritium solubility of 0.3 at. % in pure lithium at the same conditions.⁶ The lower solubility in Li-Bi is consistent with the low activity of lithium in Li-Bi solutions⁷; that is, little if any lithium in bismuth is free to associate with tritium.

The 95% confidence interval for the slope of the line in Fig. 5 is 1.29 ± 0.54 . This does not follow Sieverts' law (slope equal to two), and a slope of one, which is within the 95% confidence interval, could indicate molecular tritium sorption. The data, however, are not sufficiently accurate to propose a sorption mechanism. Due to the low tritium solubility in Li-Bi, further experimentation does not appear to be justified at the present time.

TRITIUM CONTAINMENT

Due to the large permeation rates of tritium through containment barriers at even moderate temperatures (300 to 500°C), the handling of tritium (specific activity of 10^4 Ci/g) in fusion reactors can create a hazardous situation. The oxidation of tritium to a nonpermeating and recoverable form could make effective secondary containment possible. In addition, an oxidation technique may be useful for recovering tritium produced in the blanket. One proposed recovery method entails permeation of tritium into a helium coolant from which it is continuously oxidized and removed.⁸ The technique under investigation in this study is oxidation of tritium as it permeates through the first containment or

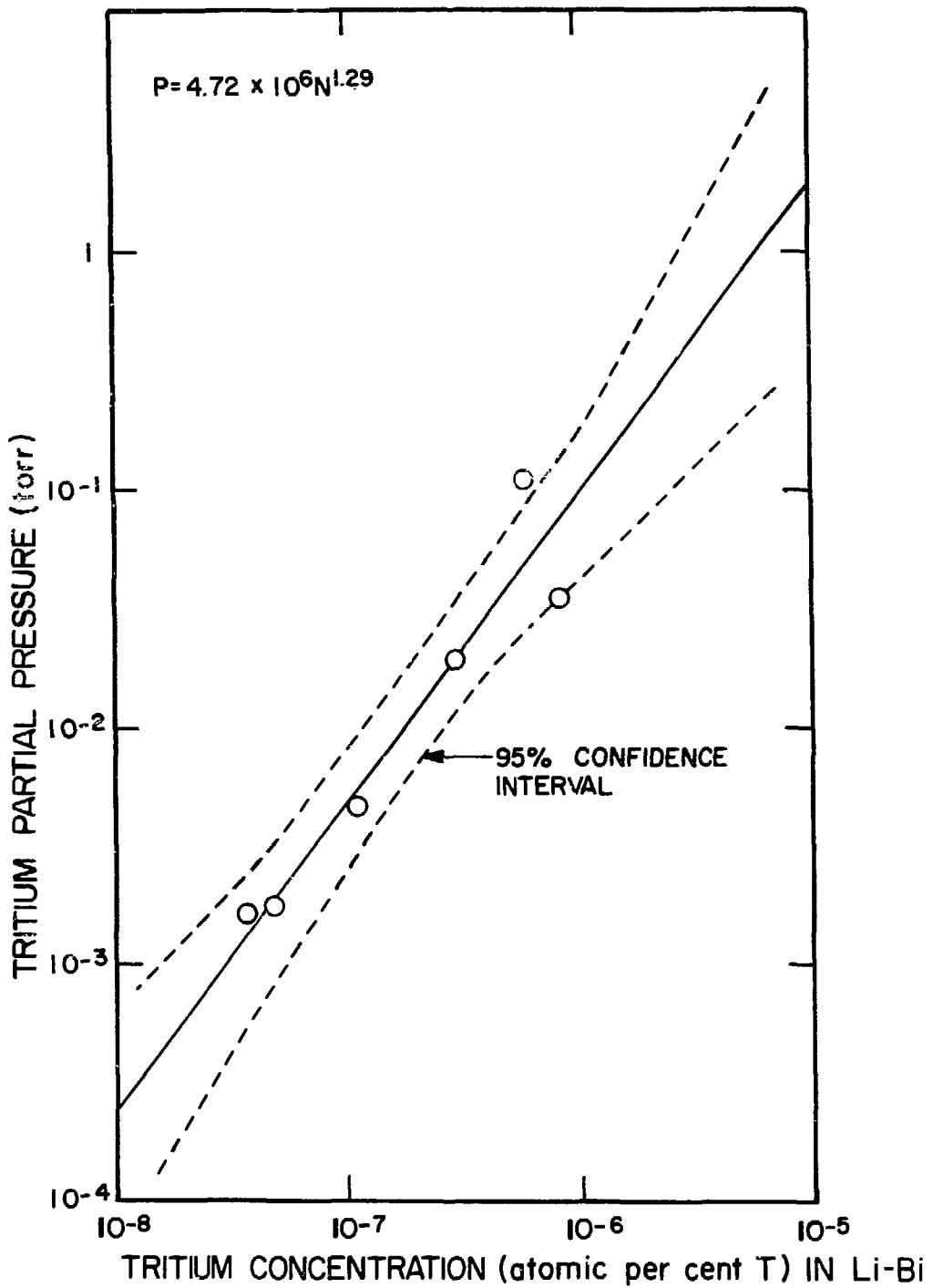


Fig. 5. Tritium partial pressure vs the tritium concentration in Li-Bi (15 at. % Li) at 600°C.

heat exchange surface. An important consideration is the chemical form of the tritium as it leaves the permeated surface. Low concentrations of oxygen are likely to be present in either a helium coolant or reactor containment atmosphere, and higher concentrations of oxygen could be added. Atomic tritium, permeating a metal barrier, may react with oxygen at the metal surface to form the nonpermeating oxide; however, the catalytic effectiveness of most metals considered for fusion reactor piping and heat exchangers is unknown. The goal of the experiment is to determine the oxidation of permeating hydrogen to water at conditions which can be expected to prevail within fusion power reactor systems.

Experimental Equipment

A schematic equipment diagram for the hydrogen isotope permeation-oxidation studies is shown in Fig. 6. The basic system consists of a permeation tube surrounded by a 1 1/2-in.-diam tubular vacuum chamber and furnace, a VacSorb roughing pump, a 20 liter/sec noble ion pump, and a variable leak valve for introducing oxygen. Two nude ion gauges [millitorr and ultrahigh vacuum (UHV)] measure the system pressure, and the gas composition within the vacuum chamber is monitored by a mass spectrometer (UTI Model 100 C). Since the maximum operating pressure for the gas analyzer is 10^{-3} torr, the vacuum chamber contains a 2-mil-diam orifice to permit higher oxygen partial pressures at the permeation tube surface. Deuterium is used as a stand-in for tritium, and to date, exploratory measurements have been made with two metal surfaces, 304 stainless steel and palladium. Figure 7 shows the permeation-oxidation system and the associated instrumentation.

Results and Discussion

Stainless steel is an obvious choice as a permeation surface, whereas, palladium was chosen as a control to compare with other metals. At room temperature, the permeation rate of hydrogen through palladium is controlled by the exit surface reaction.⁹ Palladium can sorb large quantities of hydrogen, and the diffusion rate is high. But little hydrogen is reported⁹ to leave the metal surface at temperatures below

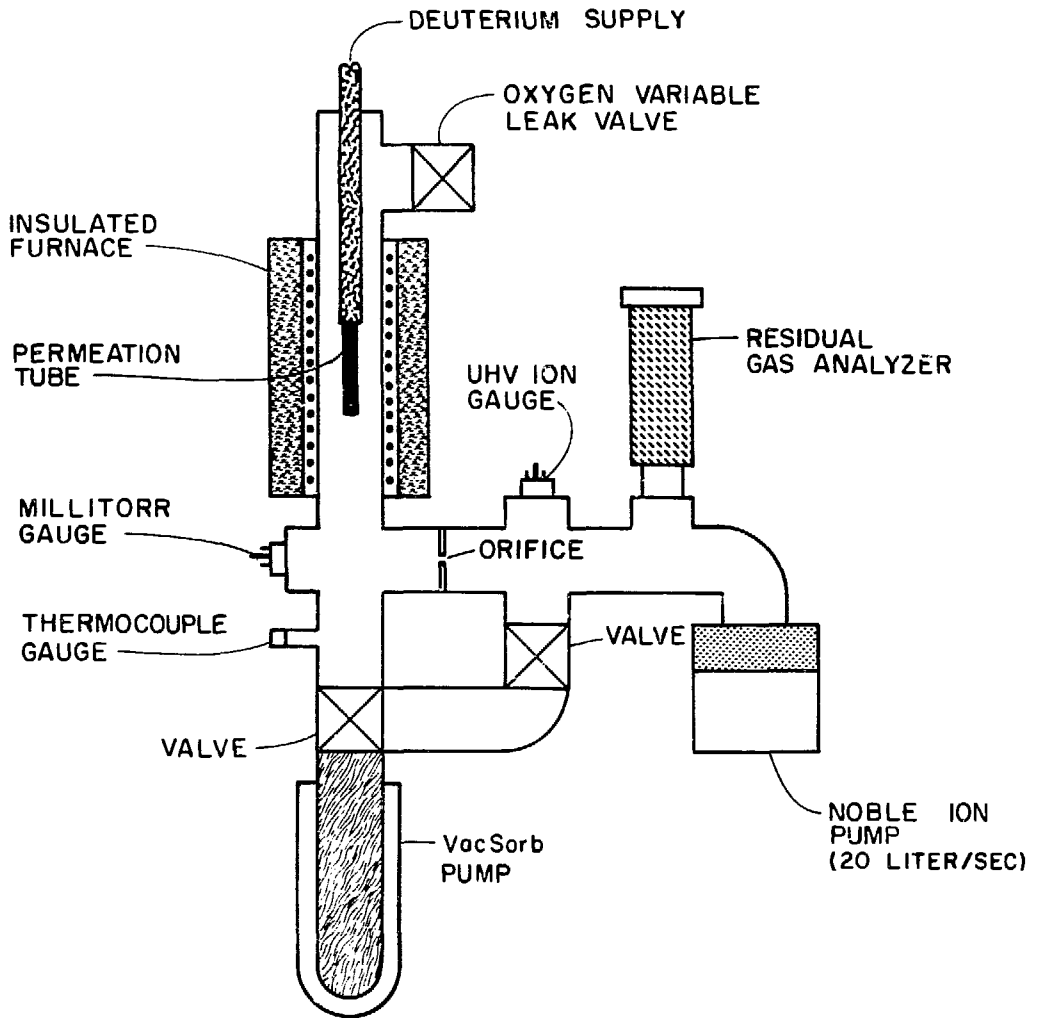


Fig. 6. Schematic equipment diagram for permeation-oxidation studies.

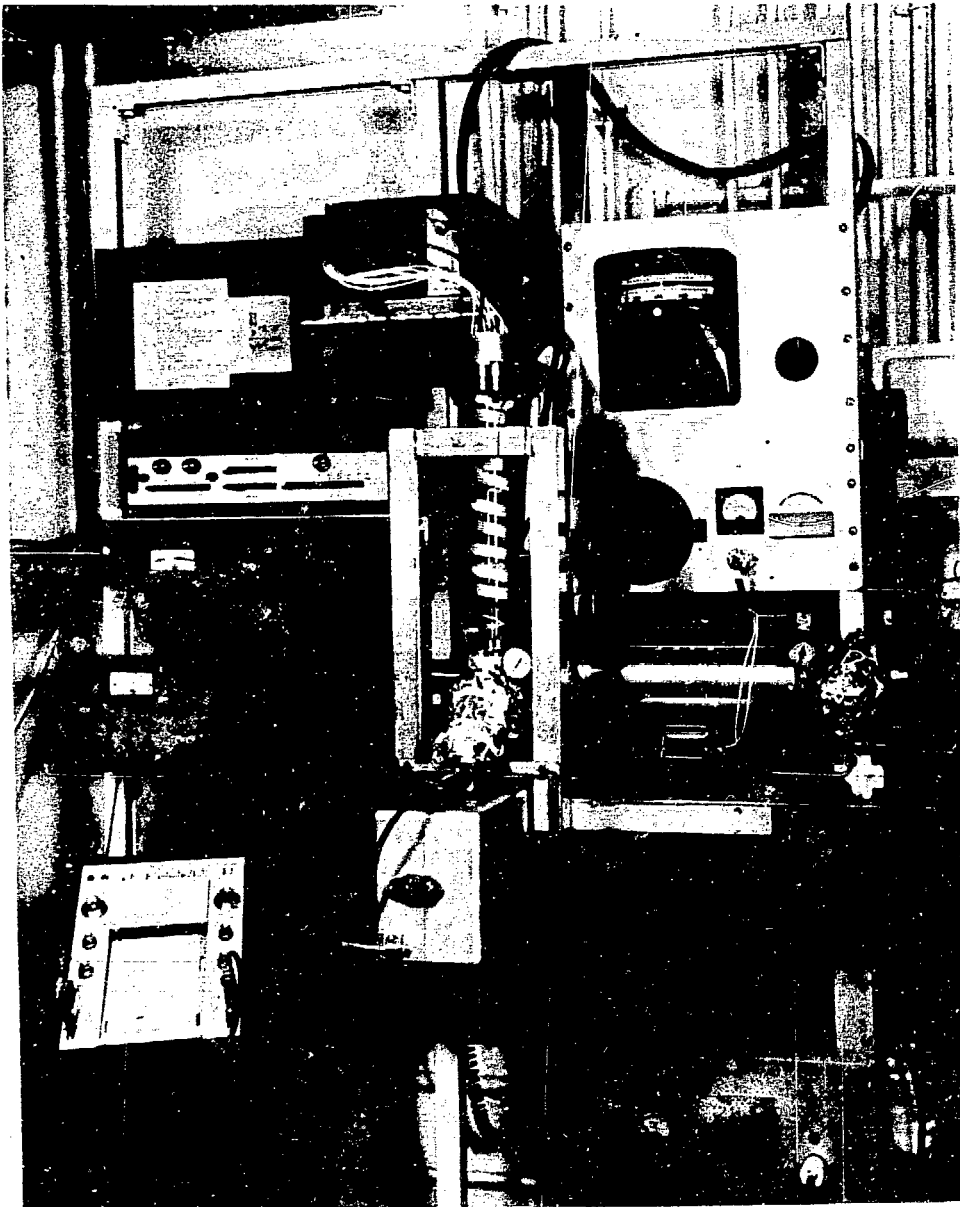


Fig. 7. Permeation-oxidation system and the associated instrumentation.

100°C. However, even at room temperature, a palladium surface will lose hydrogen to an atmosphere containing oxygen, and the release is apparently caused by a reaction of the sorbed hydrogen with oxygen on the metal surface.

All of the deuterium-stainless steel data were taken at very low pressures (orifice not installed between the permeation tube and gas analyzer shown in Fig. 6). At 300 - 500°C and with an oxygen partial pressure of 10^{-6} torr, the conversion of permeating deuterium to water was 40 to 50%. With deuterium permeating through palladium and with an 8-mil-diam orifice to the vacuum pump, the oxygen partial pressure at the metal permeation surface was increased to 10^{-3} torr. With the palladium at 25°C, approximately 80% of the deuterium was converted to water. More data are required for different metals at higher oxygen pressures and a wider range of temperatures to determine optimum conditions for the oxidation of permeating hydrogen.

PLASMA RECOVERY

Tokamak fusion reactors require large pumps for evacuation of the plasma liner following each heating cycle and for recovery of the deuterium (or tritium) not accelerated by the neutral beam injectors. The unburned deuterium and tritium contained in the plasma exhaust must be recovered and recycled. Cryogenic pumps can achieve low operating pressures by condensing or sorbing the pumped gases on molecular sieves which have been cooled to liquid helium temperatures. Such pumps require no lubricants or operating fluids within the vacuum chamber and are extremely clean, vibration-free, and unaffected by magnetic fields. In this study, a cryosorption pump from Excalibur Corp. is being tested to determine the pump operating characteristics under CTR conditions.

Experimental Equipment

The equipment for the cryosorption pump evaluation experiment is shown in Fig. 8. The pump (model CVR-1106) is flanged to a 6-in.-diam vacuum chamber which contains an orifice plate for flow rate

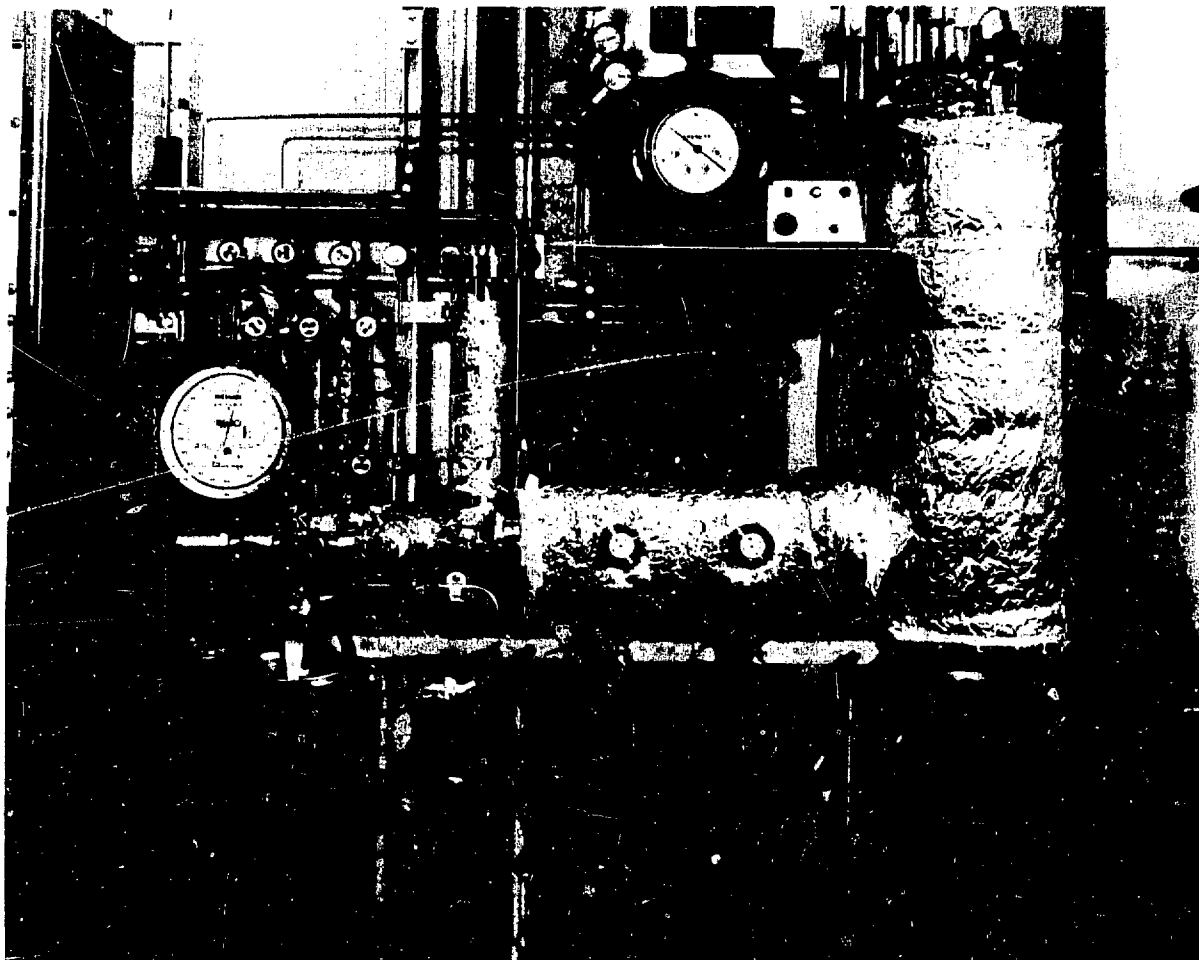


Fig. 8. Cryosorption pump and the associated instrumentation.

determinations. The system attachments include four ion vacuum gauges, a variable leak valve for hydrogen, a gas analyzer probe (UTI), two VacSorb roughing pumps, and a 20 liter/sec ion pump. The hydrogen supply is connected to a calibrated reservoir and differential pressure gauge to measure pumping speeds.

Results and Discussion

Pumping tests are in progress with protium and deuterium, however, only preliminary results are available at the present time. The variables to be investigated include pumping speeds for selected gases and mixtures at specified pressures and loadings, pump sorption capacities, and regeneration characteristics (especially at lower temperatures). The pumped gases will include all of the isotopes of hydrogen and hydrogen-helium mixtures.

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CHEMICAL EQUILIBRIUM STUDIES OF TRITIUM-LITHIUM
AND TRITIUM-LITHIUM ALLOY SYSTEMS*

F. J. Smith J. B. Talbot
J. F. Land J. T. Bell

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

In deuterium-tritium fusion reactors currently under design, the production of tritium is accomplished by utilizing a lithium-bearing blanket. Lithium metal is presently the leading candidate for the blanket material, although molten Li_2BeF_4 , solid Li-Al (50-50 at. %) alloy and other lithium-containing materials are distinct possibilities. This paper summarizes progress of ongoing studies of the thermodynamics of some of these lithium containing systems. The individual solubilities of hydrogen, deuterium, and tritium in lithium as a function of temperature (700 to 1000°C) and pressure are presented. Recent work with the solid alloy Li-Al (50-50 at. %) has shown that the tritium solubility between 400 and 600°C is low. When the tritium pressure was between 0.14 and 0.52 torr, the Li-Al samples contained only 1 to 4 ppm tritium.

INTRODUCTION

Vapor-liquid equilibria in hydrogen isotope-lithium systems are being studied to support development of Controlled Thermonuclear Reactors (CTRs) with lithium metal blankets. Data from these equilibrium studies aid in the definition of the tritium pressures that will exist in a CTR system and in the prediction of the permeation behavior of hydrogen isotopes in the system. The data are also useful in devising or assessing processes required to maximize recovery of bred tritium and to minimize the loss of tritium to the environment.

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The Li-H₂ system has recently been extensively studied by Veleckis, Van Deventer, and Blander.¹ The Li-D₂ system was briefly examined by Heumann and Salmon,² and is currently being investigated by several groups.^{3,4,5} Heumann and Salmon give the only prior information on the Li-T₂ system,² but their data are inconsistent, both in magnitude and with respect to pressure dependence of the solubility, with all other reported data on lithium-hydrogen isotope systems. The primary purpose of this work was to obtain data on the Li-T₂ system, particularly in the dilute solution range. The Li-H₂ and Li-D₂ systems were also studied to provide a complete and systematic study by the same investigators of all three hydrogen isotope-lithium systems. The results of these studies, particularly those with H₂, provide a basis for comparison with the results of other workers and give additional credibility to our tritium data.

The intermetallic compound Li-Al (50-50 at. %) has been suggested as a minimum activation and low tritium inventory CTR blanket material.⁶ The removal of tritium from irradiated LiAl samples was studied by Wiswall and Wirsing.⁷ This study reports preliminary results on the solubility of hydrogen and tritium in LiAl at 500°C.

EXPERIMENTAL

The equilibrium pressures of the hydrogen isotopes in the Li-H₂, Li-D₂, and Li-T₂ systems were measured using the modified Sieverts apparatus⁸ shown in Fig. 1. Samples of lithium were sealed in metal (iron or nickel) capsules which have high permeation coefficients for the hydrogen isotopes, and the equilibrium hydrogen isotope pressure was established inside and outside the capsule. The equilibrium pressure was measured externally relative to the capsule.

The procedure used in a typical experiment was as follows: A weighed amount (0.2 to 2 g) of pure lithium was sealed under vacuum in a small iron capsule which was placed in the quartz envelope. The envelope was then connected to the system, and its volume calibrated. The system was evacuated at ambient temperature, heated to a preselected temperature,

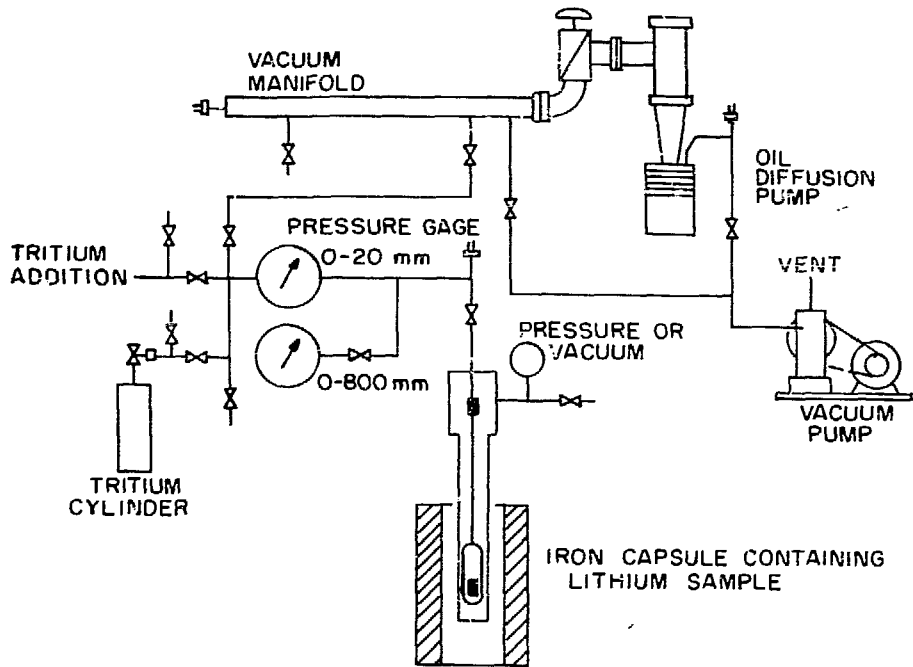


Fig. 1. Sieverts Type Absorption Apparatus.

and evacuated further until the pressure was reduced to about 10^{-4} torr. The quartz envelope containing the capsule was subsequently valved off, and the hydrogen isotope (H_2 , D_2 or T_2) was admitted to the rest of the system until a predetermined pressure was obtained. Finally, the valve to the quartz envelope was opened and the change in pressure with time was recorded until an apparent equilibrium was reached. Additional equilibrium points for a given temperature were obtained by adding more of the same hydrogen isotope and repeating the above procedure. The concentration of hydrogen in the lithium at each equilibrium point was calculated using the initial weight of lithium, the total amount of hydrogen added, and the amount of hydrogen gas remaining in the system after equilibration.

The solubility of hydrogen in the LiAl samples was also measured with the Sieverts apparatus. A rod of LiAl was loaded under argon into a quartz tube which was then connected to the Sieverts apparatus. After heating to $500^\circ C$, the sample was outgassed and a known quantity of hydrogen was allowed to equilibrate with the LiAl sample. In general, 4 hr was sufficient to obtain equilibrium. The concentration of hydrogen dissolved in the sample was calculated from the initial and final quantities of hydrogen gas.

In order to measure the tritium solubility in LiAl (50-50 at. %), LiAl samples, in both rod and powder (<20 mesh) form, were loaded under an inert atmosphere into stainless steel-lined quartz sample tubes. The tubes were connected to a manifold and pumping system, as illustrated in Fig. 2. The system was evacuated, the samples were heated to the desired temperature, and tritium was added from an ampule. At least 24 hr was allowed for the LiAl samples and tritium to equilibrate before the samples were quickly cooled to ambient temperature. The samples were removed and dissolved in nitric acid in preparation for analysis. During the dissolution, a stream of argon containing about 1% hydrogen was flushed over the nitric acid solution, through a hot ($600^\circ C$) CuO bed, and finally through a series of water bubblers. Any evolved tritium was thereby converted to HTO and trapped in the water bubblers. The tritium content of the sample was determined by liquid scintillation counting of the nitric acid and water solutions.

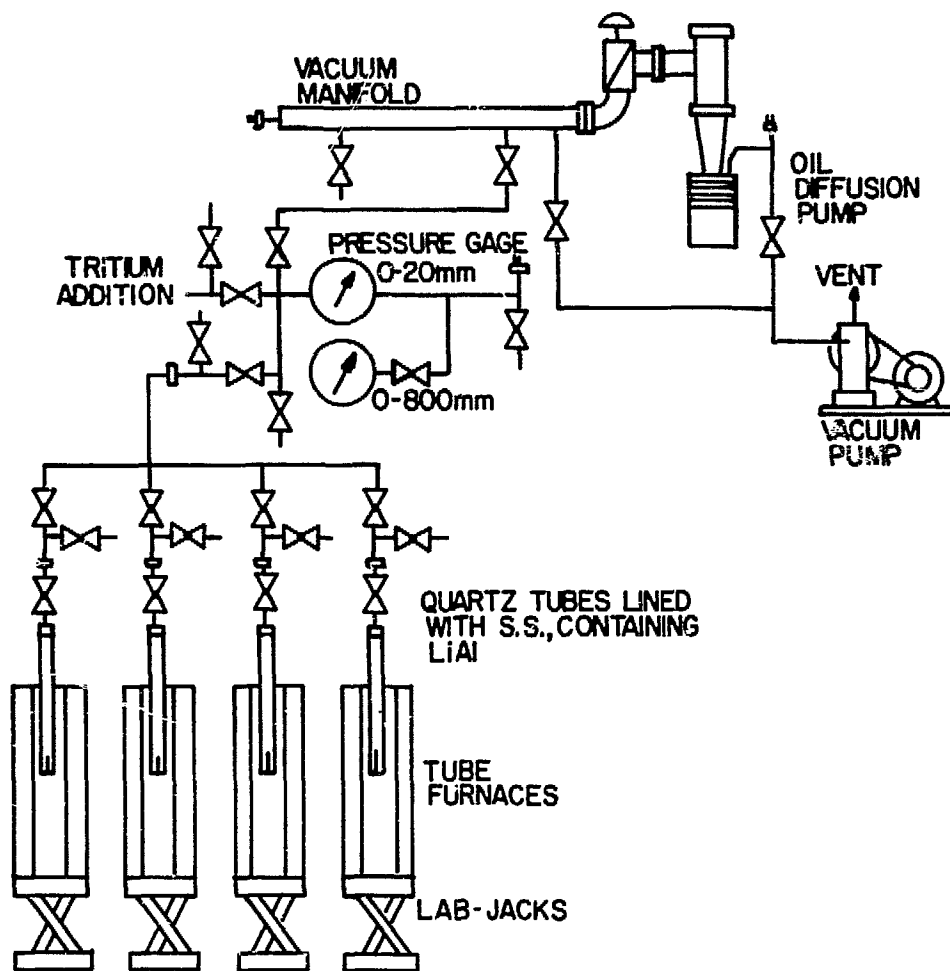


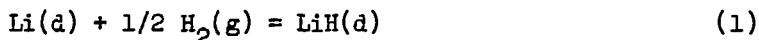
Fig. 2. The LiAl-Tritium Sorption Apparatus.

RESULTS AND DISCUSSION

The solubility of hydrogen in lithium, measured as a function of pressure at several temperatures, is shown in Fig. 3. Additional measurements were made at 750, 850, and 950°C. The pressure limitation of the apparatus was 800 torr. Below 900°C, each of the isotherms is comprised of three regions. The first rising portion represents a homogeneous liquid phase of lithium hydride dissolved in lithium. The second rising portion represents the homogeneous phase of lithium dissolved in lithium hydride. The constant-pressure plateau between the two portions just mentioned defines the two-phase coexistence region. Several points were obtained by decreasing the hydrogen pressures and no evidence of hysteresis was observed. Identical results were obtained using two different Sieverts apparatuses and several different capsules containing between 0.2 and 2 g of lithium.

The solubilities of deuterium and tritium in lithium at several temperatures are shown in Figs. 4 and 5, respectively. Again, additional measurements were made at 750, 850, and 950°C. The tritium measurements were limited to 150 Ci total tritium which, in our system, was about 50 torr maximum pressure.

The experimental data were considered in terms of the equilibrium



in which (g) and (d) indicate the gas and the liquid Li-LiH phases, respectively, and H represents the hydrogen isotope. When the mole fraction (N) of LiH, LiD, or LiT was less than about 0.1, (the first rising portion of the curves shown in Figs. 3, 4, and 5) the Sieverts relationship,

$$\sqrt{P_{\text{H}_2}}(\text{g}) = K_s N_{\text{LiH(d)}}, \quad (2)$$

was obeyed by each system. In this equation, K_s is the Sieverts constant and $N_{\text{LiH(d)}}$ is the mole fraction of lithium hydride in the liquid phase. The experimental results for several temperatures are summarized in Table 1 and are shown as a plot of the Sieverts constant vs temperature

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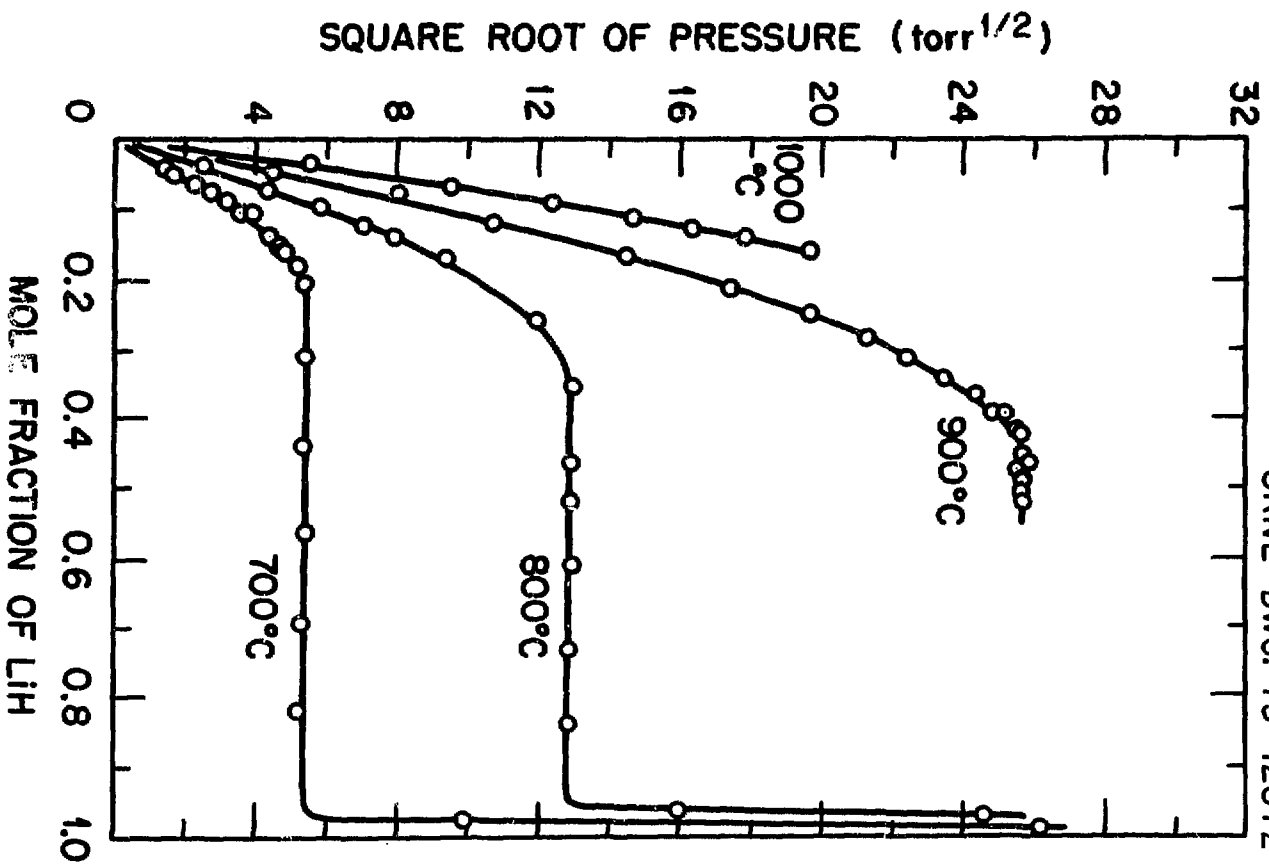


Fig. 3. Hydrogen Solubility in Lithium.

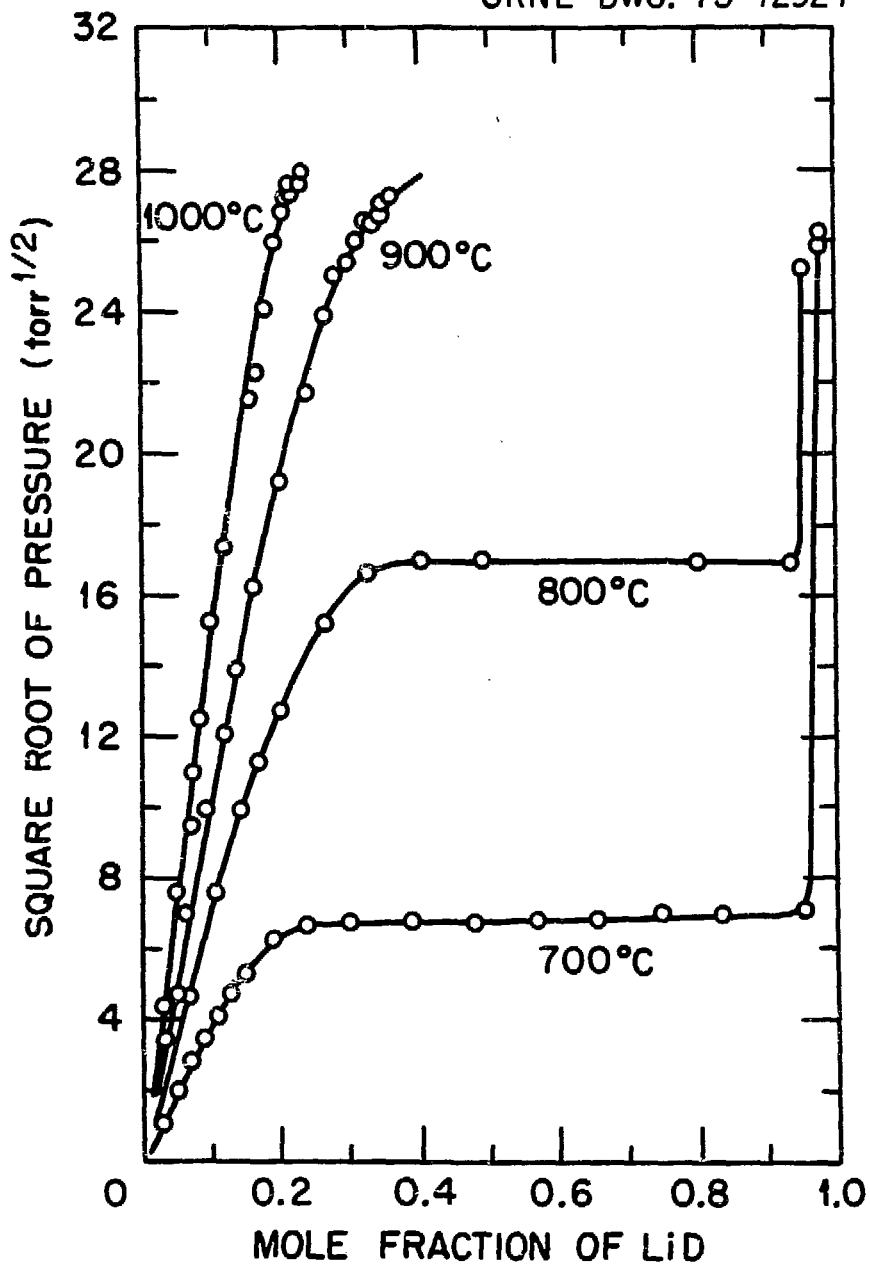


Fig. 4. Deuterium Solubility in Lithium.

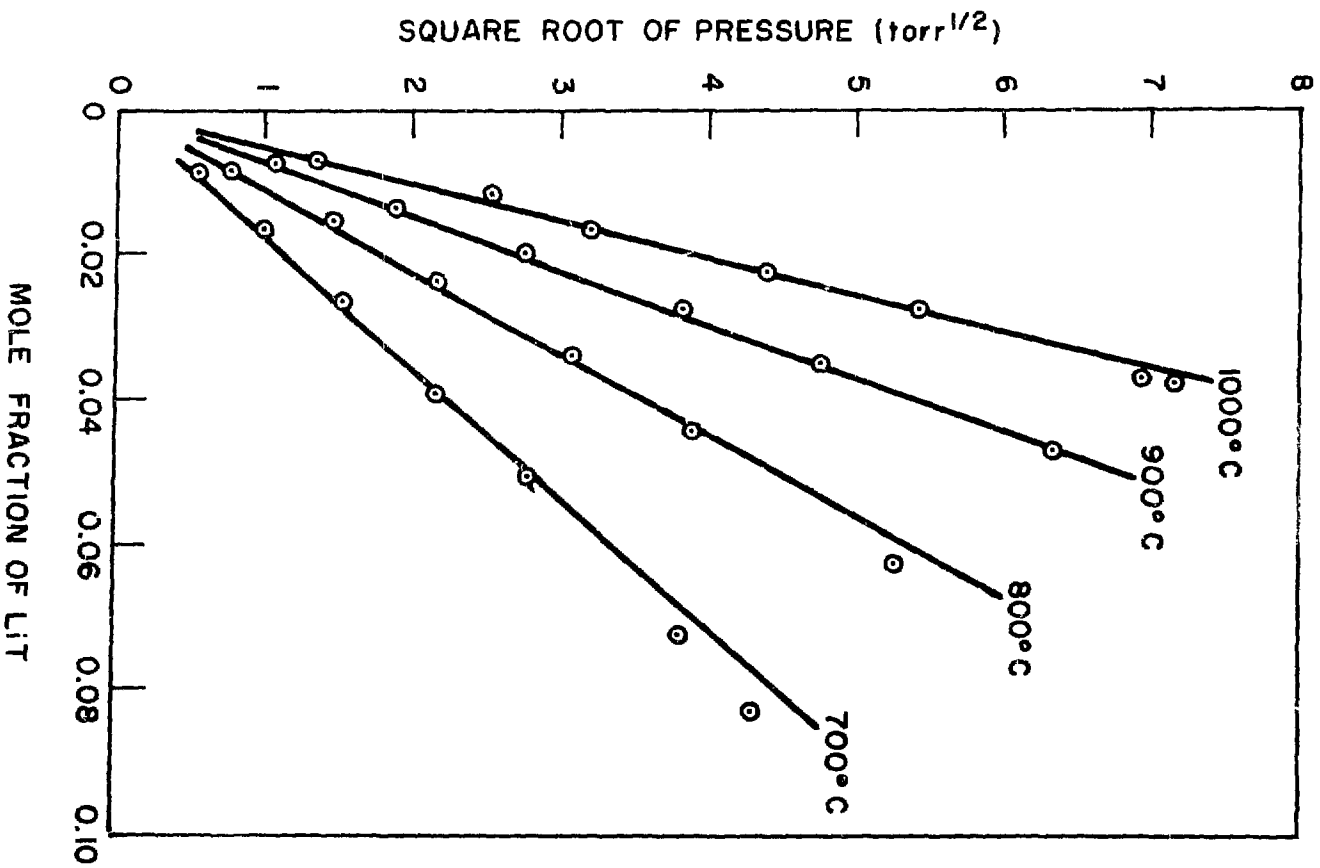


Fig. 5. Tritium Solubility in Lithium.

Table 1. Equilibrium in Liquid Lithium-Hydrogen Isotope Systems

Temperature (°C)	K_s (torr ^{1/2} /mole fraction)			Equilibrium Plateau Pressure (torr)	
	Hydrogen	Deuterium	Tritium	Hydrogen	Deuterium
700	31	41	57	30	46
800	56	76	89	164	287
900	93	112	130	650	>750
1000	137	160	190		

in Fig. 6. The values for hydrogen are in good agreement with those recently reported by Veleckis, Van Deventer and Blander,¹ and the deuterium results are in reasonable agreement with the limited literature values.^{2,3,4,5} No reliable data for the lithium-tritium system have been reported previously. Both the magnitude and the temperature dependence of the Sieverts constant for tritium are in good agreement with predictions made utilizing the data obtained with hydrogen and deuterium.

For hydrogen and deuterium, the measurements included the constant-pressure plateau region which defines the two-liquid phase coexistence region. Several of the measured plateau pressures are given in Table 1. Again, the hydrogen results are in good agreement with previously published data.

The solubility of hydrogen in the Li-Al (50-50 at. %) compound was measured at 500°C as a function of hydrogen pressure between 153 and 537 torr. The results are presented in the first two columns of Table 2. The last column gives the square root of the hydrogen gas pressure divided by the atom fraction of hydrogen in the alloy for each equilibrium point. The constancy of these values shows that Sieverts behavior is followed for hydrogen dissolution in the LiAl alloy. The measured Sieverts constant at 500°C is $1.9 (\pm 0.1) \times 10^{+4} \text{ torr}^{1/2}/\text{atom fraction}$.

Several experiments were conducted in an attempt to measure the solubility of tritium in the LiAl. Tritium sorption rates were low and equilibrium conditions were not achieved in many experiments. In many cases the tritium sorption time was several days as compared to about 4 hr for hydrogen in the hydrogen solubility experiments. The pressure of hydrogen was greater than 153 torr, whereas the tritium pressure was limited to less than 1 torr because of the health hazard. The slow tritium sorption rate was probably due to a surface oxide film and the low pressure. No pressure dependence data were obtained; however, the tritium concentration in the rod samples ranged from about 1 to 4 ppm at respective tritium pressures of 0.14 to 0.52 torr. Since Sieverts behavior was observed for hydrogen solubility in LiAl (50-50 at. %), Sieverts constants were calculated for those most reliable cases in

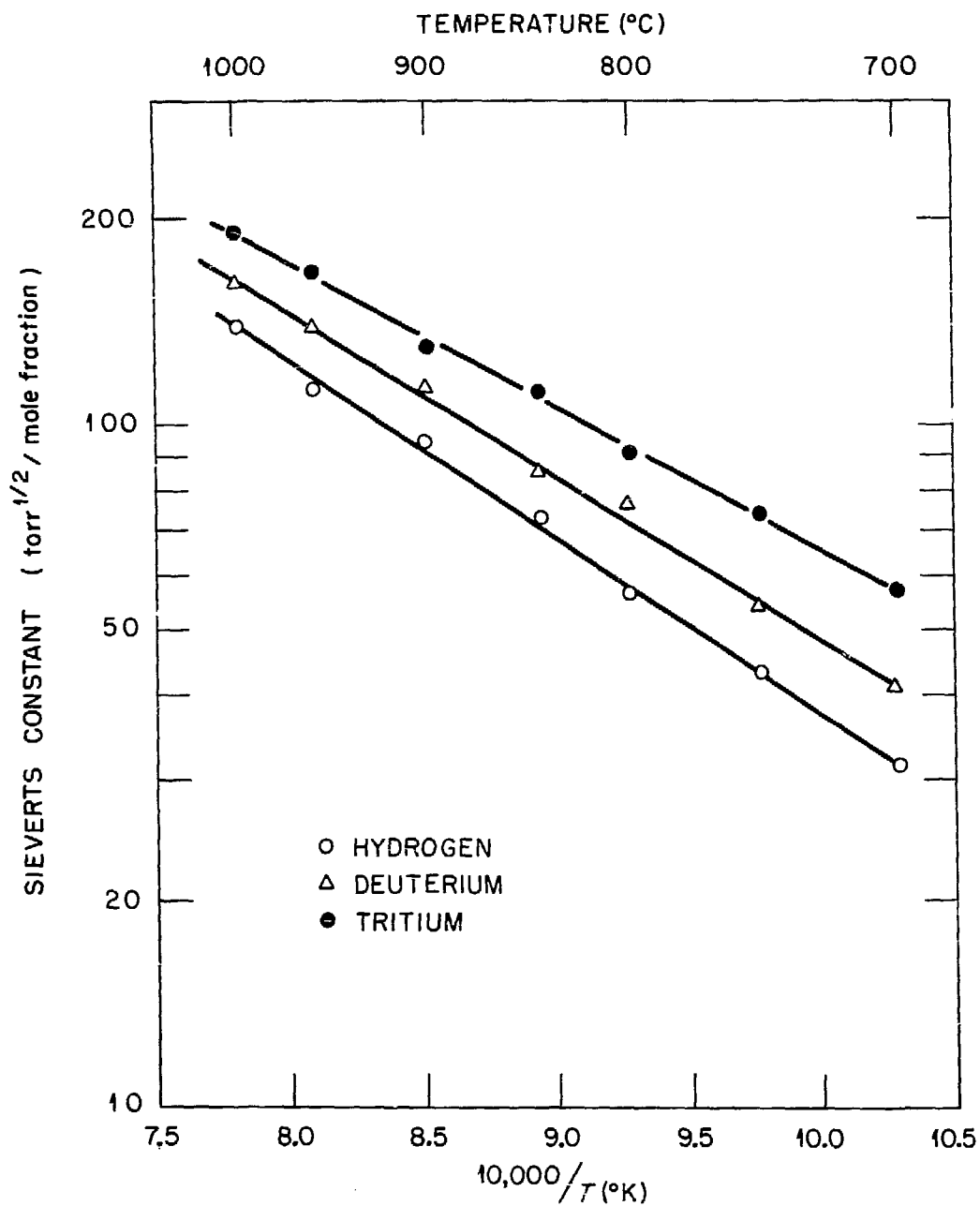


Fig. 6. Temperature Dependence for Hydrogen Isotope Solubility in Lithium.

Table 2. The Solubility of Hydrogen in LiAl (50:50 at. %) at 500°C

Hydrogen Pressure, P (torr)	Hydrogen Concentration in LiAl, N (at. fraction)	Sieverts Constant $\sqrt{P}/N$ (torr ^{1/2} /at. fraction)
153	6.04×10^{-4}	2.05×10^4
230	8.07×10^{-4}	1.88×10^4
315	9.94×10^{-4}	1.79×10^4
537	1.22×10^{-3}	1.89×10^4
		average $1.90 (\pm 0.1) \times 10^4$

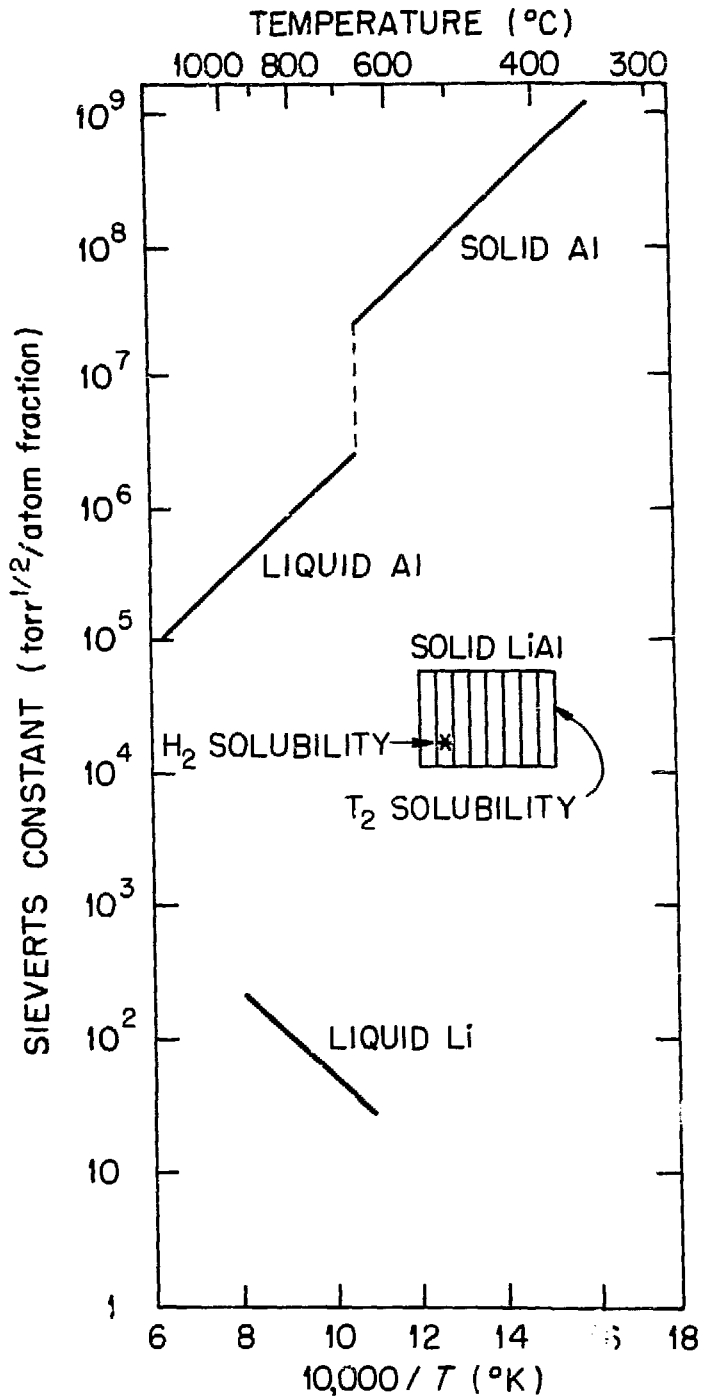


Fig. 7. Comparison of the Hydrogen Solubility in Aluminum and Lithium to the Hydrogen and Tritium Solubility in LiAl (50-50 atom %).

which equilibrium seemed to be achieved. The values fall within the band shown in Fig. 7 with an average value of about $3 \times 10^4 \text{ torr}^{1/2}/\text{atom}$ fraction. The Sieverts constant for hydrogen solubility in the LiAl is shown along with similar data for hydrogen solubility in liquid lithium and aluminum.⁹ The Sieverts constants for LiAl fall between the lithium and aluminum data and are in agreement with the value reported by Wiswall and Wirsing⁷ for tritium at 500°C, $1.22 \times 10^4 \text{ torr}^{1/2}/\text{atom}$ fraction. Wiswall and Wirsing were not able to verify the applicability of Sieverts law as we did with the hydrogen data given in Table 2.

The amount of tritium dissolved seemed to be higher for the powdered samples than the rod-shaped samples. Also, partial dissolution of LiAl rod samples showed that the concentration of tritium decreased as more of the sample was dissolved. Therefore, surface and bulk solubilities also need to be determined before evaluation of LiAl as a fusion reactor blanket material is completed.

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