

27
11-20-75
2508 E.N.75



DEPARTMENT of APPLIED SCIENCE

TRITIUM RECOVERY FROM FUSION BLANKETS USING SOLID LITHIUM COMPOUNDS

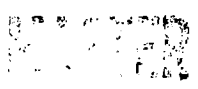
I: DESIGN AND MINIMIZATION OF TRITIUM INVENTORY

J. R. Powell

II: EXPERIMENTS ON TRITIUM REMOVAL AND ABSORPTION

R. H. Wiswall and E. Wirsing

October 1975



**BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973**

INFORMAL REPORT



N O T I C E

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$5.45; Microfiche \$2.25

October 1975

NOTICE

52 copies

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TRITIUM RECOVERY FROM FUSION BLANKETS USING SOLID LITHIUM COMPOUNDS-
I: DESIGN AND MINIMIZATION OF TRITIUM INVENTORY

J.R. Powell

Department of Applied Science
 Brookhaven National Laboratory
 Upton, NY 11973

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees or their employees' makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

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 (?)
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 Bi

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 UWMAR-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

<u>BREEDER TYPE</u>	<u>SOLID LITHIUM COMPOUND</u>	<u>ENRICHMENT STATE</u>	<u>STRUCTURAL MATERIAL</u>	<u>MODERATOR</u>	<u>NEUTRON MULTIPLIER</u>	<u>NOTES</u>
<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	LiAl, LiAlO ₂ Li ₂ SiO ₃	ENRICHED	Al, SS, Nb, V, Mo	C, SiC, Al ₂ O ₃	NONE	BR ~0.8
<u>SUSTAINER-BREEDERS</u> (1≤BR≤1.3)						
I	LiAl, LiAlO ₂ , Li ₂ SiO ₃	ENRICHED	Al, SS, Nb, V, Mo	C, SiC, Be BeO, Be ₂ C	Be, Be ₂ C, BeO, PbO, PbS	
II	Li ₇ Pb ₂ , Li ₃ Bi	NATURAL	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	NONE	Pb or Bi ARE NEUTRON MULTIPLIERS
III	Li ₂ Be ₂ O ₃	NATURAL	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	NONE	Be IS NEUTRON MULTIPLIER
IV	Li ₄ Si, Li ₃ Sn, Li ₄ Sn	NATURAL	Al, SS, Nb V, Mo	C, SiC (SECONDARY)	NONE	SOME COMBINATIONS MAY HAVE BR<1
<u>SUPER-BREEDERS</u> (BR>1.3)						
I	LiAl, LiAlO ₂ , Li ₂ SiO ₃	ENRICHED	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	Be, Pb, Bi	MAX BR ~1.5
II	Li ₇ Pb ₂ , Li ₃ Bi	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_2SiO_3 OR $LiAlO_2$, AND BERYLLIUM (Be, BeD, Be,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 (~900°C)	Be (RESOURCE LIMITED?)
IV	NO RESOURCE LIMITATION	MAXIMUM TEMPERATURE LIMITED (~500°C). Sn ACTIVATES IF Li_7Sn 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 BERYLLIUM

DESIRED CHOICE

1. SUSTAINER-BREEDER-I WITH Be
OR Be₂C AND LiAlO₂

OR

2. SUB-BREEDER-I (HIGH TEMPERATURE
C AND LiAlO₂)

AND

SUPER-BREEDER-I WITH Be AND LiAlO₂

NOTES

MINIMUM Be REQUIREMENTS - HIGH
TEMPERATURE CAPABILITY

HIGH TEMPERATURE CAPABILITY -
SUB-BREEDER HAS MINIMUM RADI-
ATION DAMAGE - REQUIRES DEVEL-
OPMENT OF 2 BLANKET TYPES

SECOND CHOICE

3. SUB-BREEDER-III WITH LiAlO₂

AND

SUPER-BREEDER-I WITH Be AND LiAlO₂

HIGH TEMPERATURE CAPABILITY -
REQUIRES 2 BLANKET TYPES -
SOME REACTORS OPERATE WITHOUT Be

INSUFFICIENT BERYLLIUM

DESIRED CHOICE

4. SUSTAINER-BREEDER-I WITH PbO AS
NEUTRON MULTIPLIER AND LiAlO₂

GOOD TEMPERATURE CAPABILITY

SECOND CHOICE

5. SUPER-BREEDER-II WITH Li₇Pb₂

AND

SUB-BREEDER-I OR SUB-BREEDER-III
WITH LiAlO₂

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 neutronic 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

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

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_7Pb_2 , Li_4Si , 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_7Pb_2 , Li_4Si , etc.) ² WITH SS , Mo, V, OR Nb STRUCTURE	SAME	ONLY MODE FEASIBLE	NOT FEASIBLE	NOT FEASIBLE

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

$$I_T = 3 \times 10^4 \tau_T \dot{N}_T = 3 \times 10^4 \tau_T \frac{P_0 (BR)}{QN_0} \text{ curies} \quad (1)$$

where

τ_T = mean holdup time of T in particles, sec

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

P_0 = 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_0 = 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 temperature¹⁴, 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 elsewhere¹⁴ 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

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, $\text{torr}^{1/2} [\text{atom fraction}]^{-1}$

with

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

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,

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

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 ($90\% \text{ Li}^6$) 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

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

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

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 recovering 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 desiccant.

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 desiccant, 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

$$P_{\Sigma T_2} = \frac{P_{He} (BR) (C_p \Delta T)}{2 f_p Q N_0} \quad (9)$$

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.

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 desiccant is used with an adsorption/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

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 T_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 coolant 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.

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

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

where

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

for a typical circulation type 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

The author wishes to express his appreciation to Dr. Richard Wiswall and Mr. Edward Wirsing for many stimulating and useful discussions about the properties of solid lithium compounds, to Dr. Otto Lazareth for carrying out neutronic calculations on a large variety of blanket designs, to Miss Carolyn Eterno for typing and preparation of the manuscript, and to Mr. Stan Majeski for preparation of the drawings.

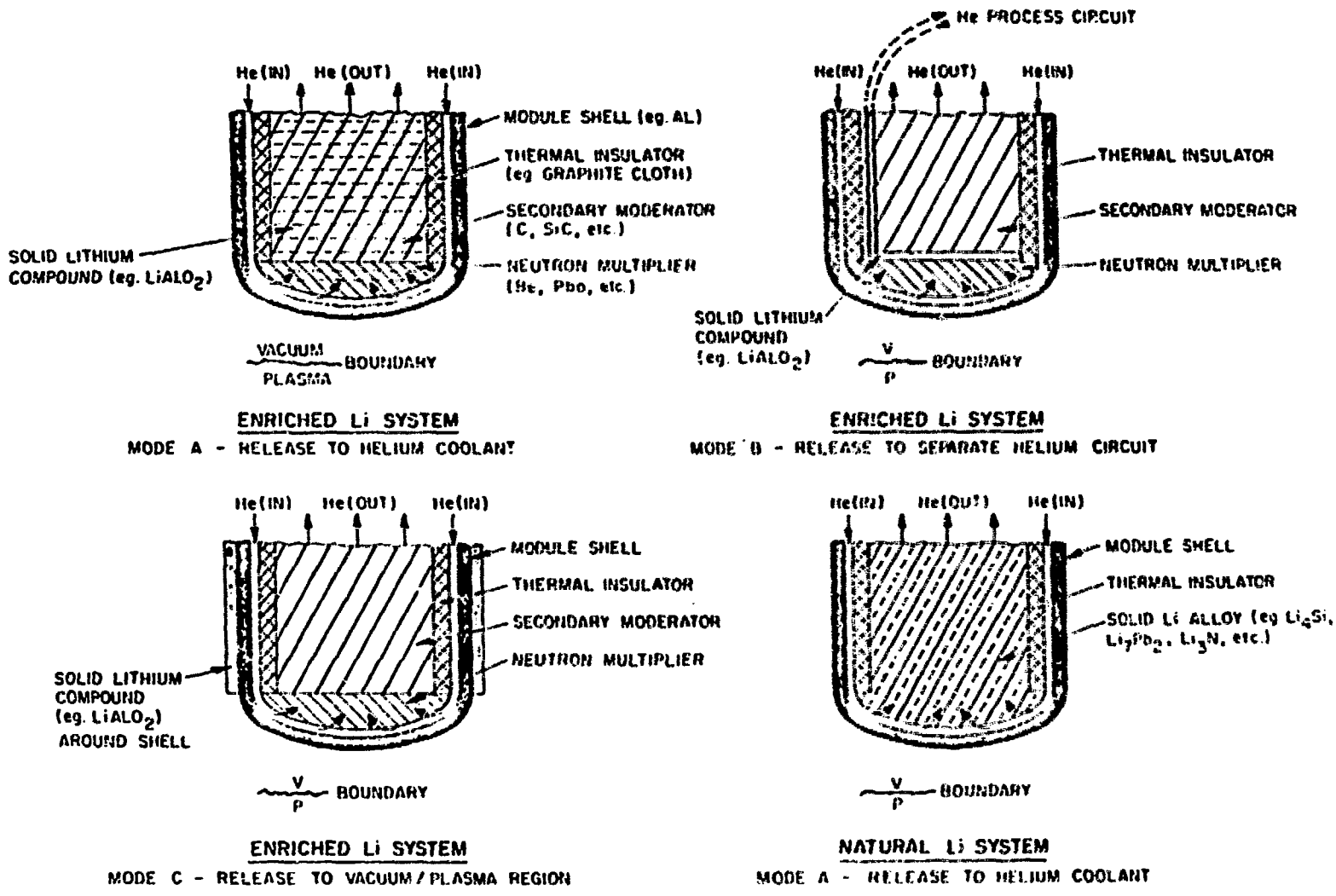
REFERENCES

1. J. R. Powell et al., Studies of Fusion Reactor Blankets with Tritium Breeding in Solid Lithium Compounds: A Preliminary Report, BNL 18236 (June 1973).
2. J. R. Powell et. al, Proc. 5th Symposium on Engineering Problems of Fusion Research, p. 163 (1973).
3. J. R. Powell et. al, Proc. First Topical Meeting on Technology of Controlled Nuclear Fusion, Vol. I, p. 533 (1974).
4. J. R. Powell et al., Preliminary Reference Design of a Fusion Reactor Blanket Exhibiting Very Low Residual Radioactivity, BNL 19565 (Dec., 1974).
5. M. Hansen, Constitution of Binary Alloys, McGraw Hill (1958).
6. R. C. Weast (ed.), Handbook of Chemistry and Physics, 45th Edition, Chemical Rubber Company (1965).
7. P. P. Turner, and B. F. Bartram, J. Inor. Chem. 6, 833 (1967).
8. F. Shunk, Constitution of Binary Alloys, 2nd Supplement, McGraw Hill (1969).
9. R. Elliott, Constitution of Binary Alloys, 1st Supplement, McGraw Hill (1965).
10. K. Sato, Proceeding Culham Conference, paper #31, Culham, England (1974).
11. J. R. Powell, Beryllium and Lithium Resource Requirements for Solid Blanket Designs for Fusion Reactors, BNL 20299 (1975).
12. D. A. Brobst and W. P. Pratt (ed.), United States Mineral Resources, Geological Survey Professional Paper 820 (1973).
13. J. R. Powell, O. W. Lazareth, P. Tichler, Trans. Am. Nucl. Soc. 21, 50 (1975).
14. R. H. Wiswall, E. Wirsing, The Removal of Tritium from Solid CTR Blanket Materials: A Progress Report, BNL 19766 (Feb. 1975).
15. E. A. Gulbransen and K. F. Andrew, J. Metals 1, 741 (1949).

FIGURE LIST

- 10-105-75 Fig. 1 Modes of Tritium Release for Modular CTR Blankets Using Solid Lithium Alloys or Compounds
- 11-227-74 Fig. 2 High Temperature Graphite Blanket Structures
- 8-719-74 Fig. 3 Aluminum Blanket Module Design Incorporating Solid LiAl and LiAlO₂
- 10-108-75 Fig. 4 Tritium Inventory in CTR Blankets As a Function of Mean Tritium Holdup Time
- 10-106-75 Fig. 5 Sieverts' Constant Required to Achieve Given Tritium Blanket Inventory if Tritium Release is Controlled by Equilibrium
- 10-107-75 Fig. 6 Methods for Recovering Tritium from Helium Coolant Stream
- 12-365-74 Fig. 7 Conceptual Design of Metal Hydride Absorber Beds for Tritium
- 5-569-75 Fig. 8 Trapping Characteristics of Metal Hydride Absorbers for Tritium Trapping

FIGURE 1 - MODES OF TRITIUM RELEASE IN MODULAR BLANKETS



Neg. #10-105-75

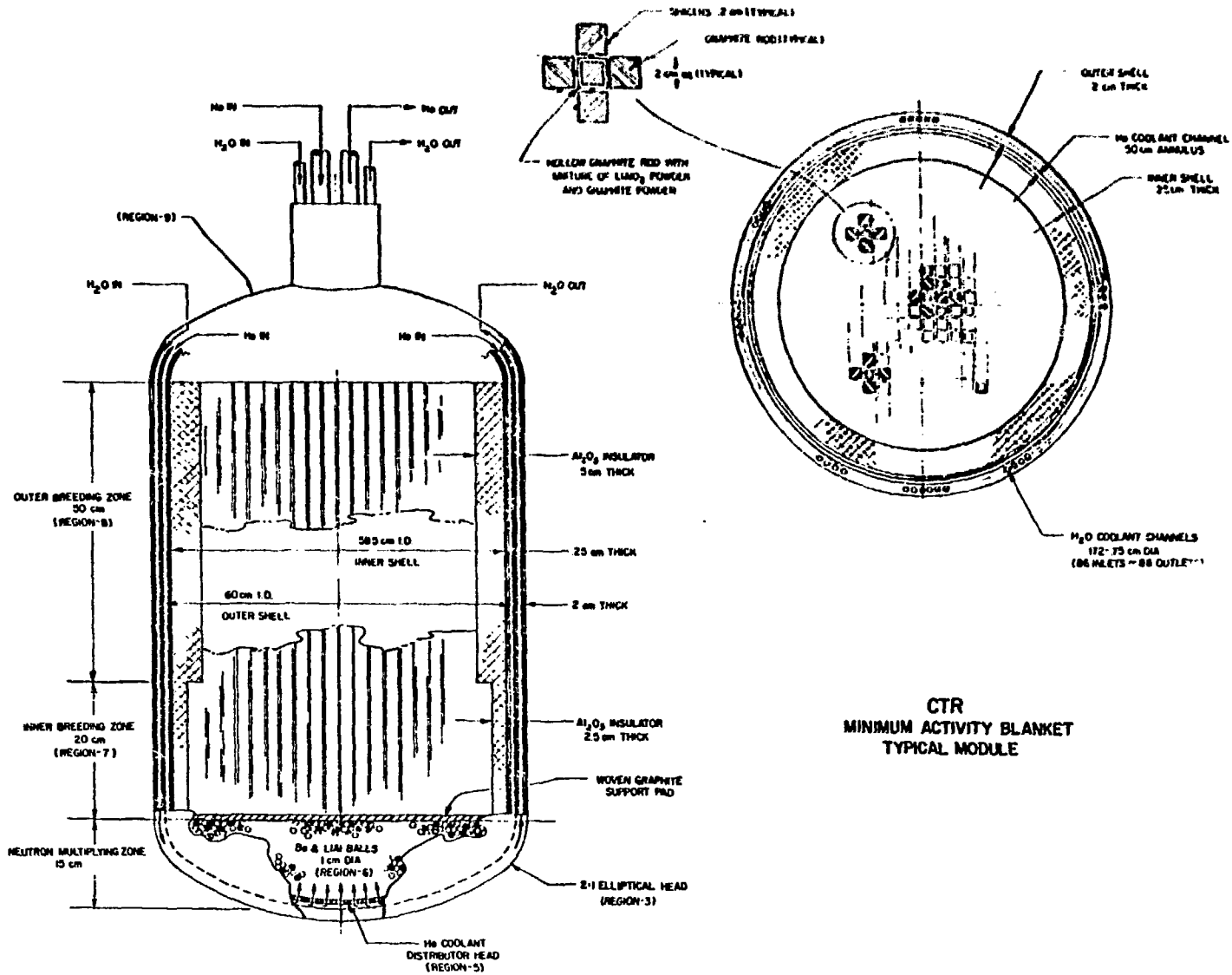
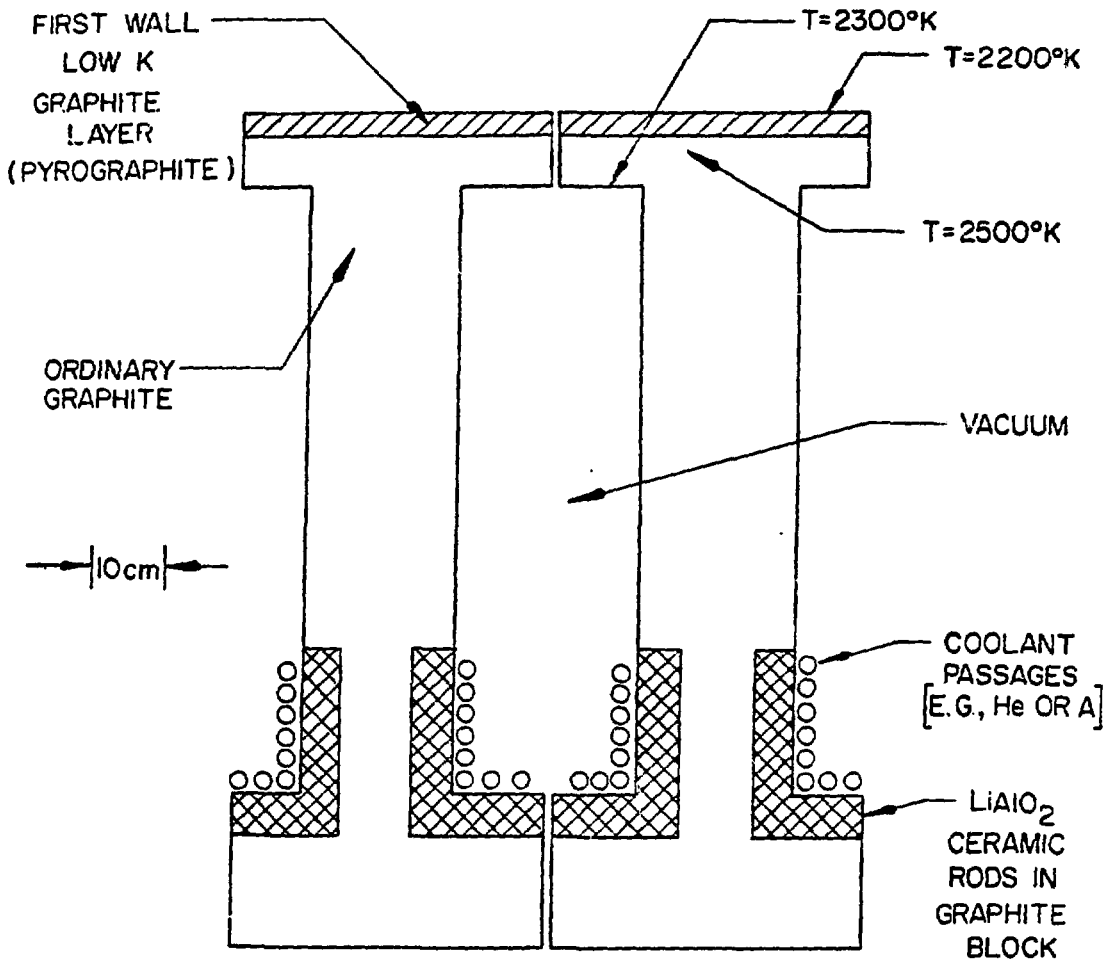


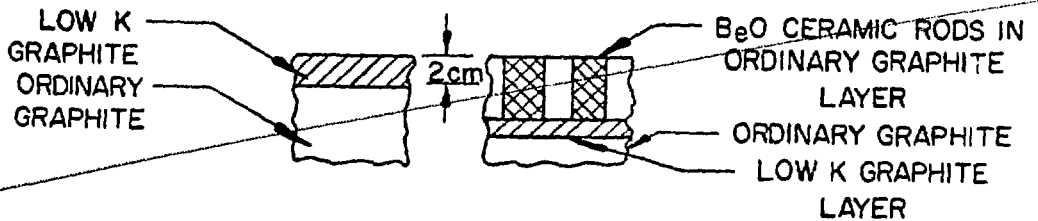
Fig. (I)-2

Reg. #11-227-74

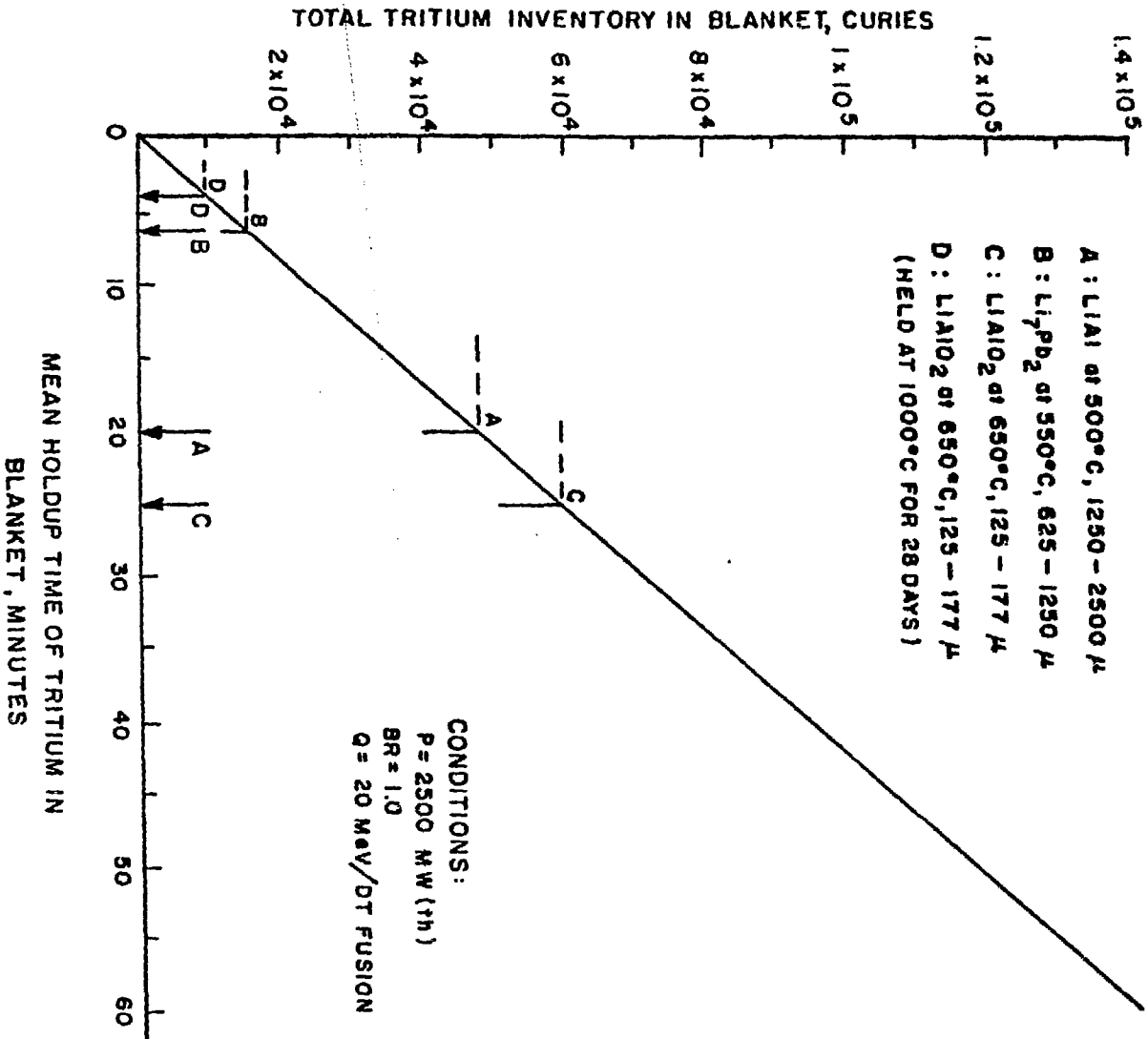
TYPE B-1 BLANKETS



ALTERNATIVE FIRST WALLS



TRITIUM BLANKET INVENTORY VS HOLDUP TIME



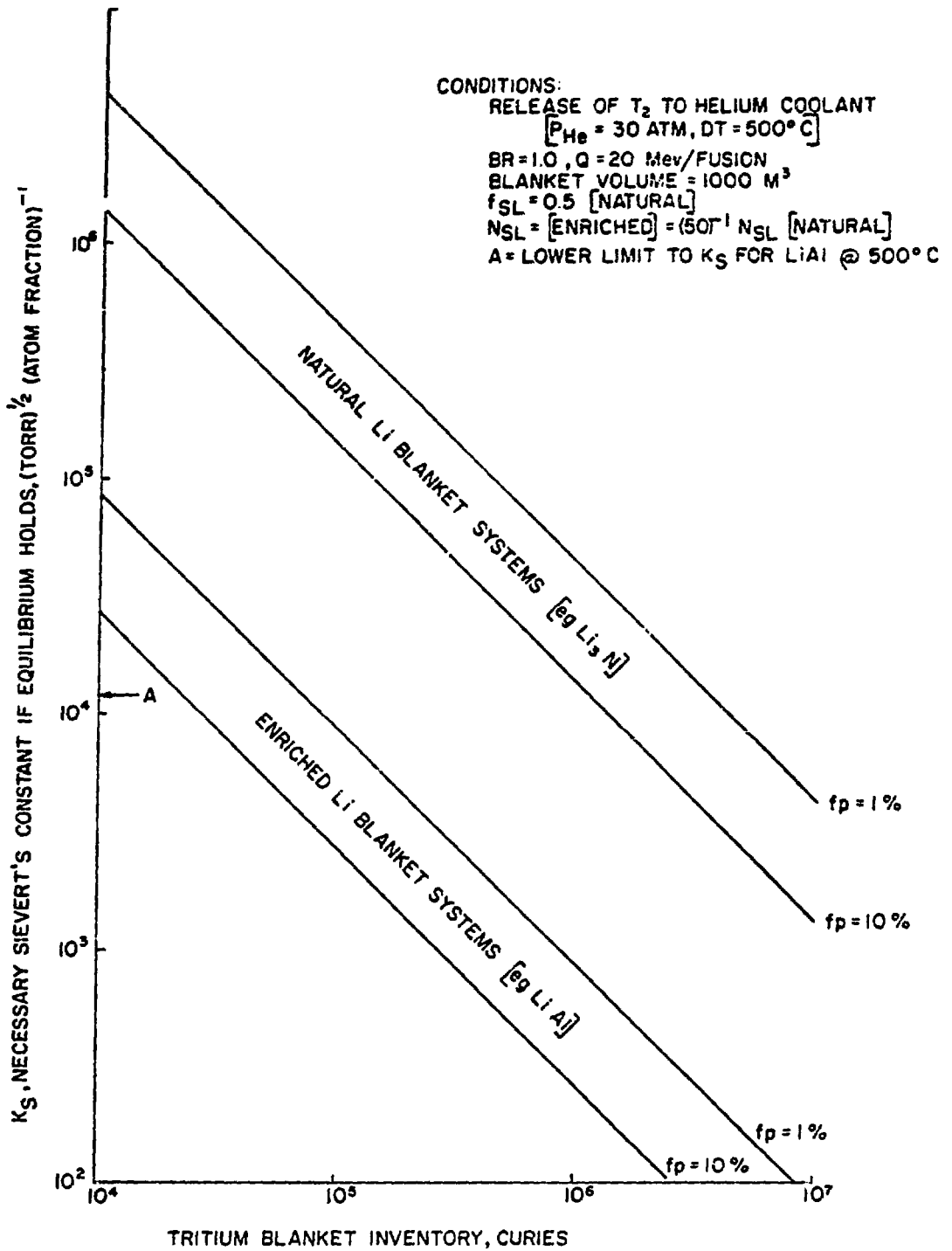
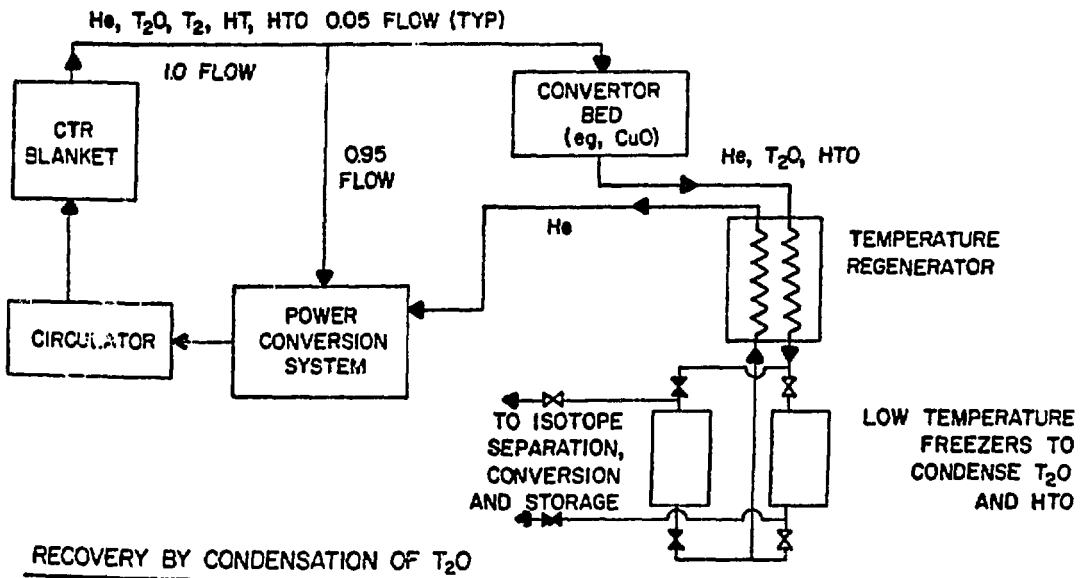
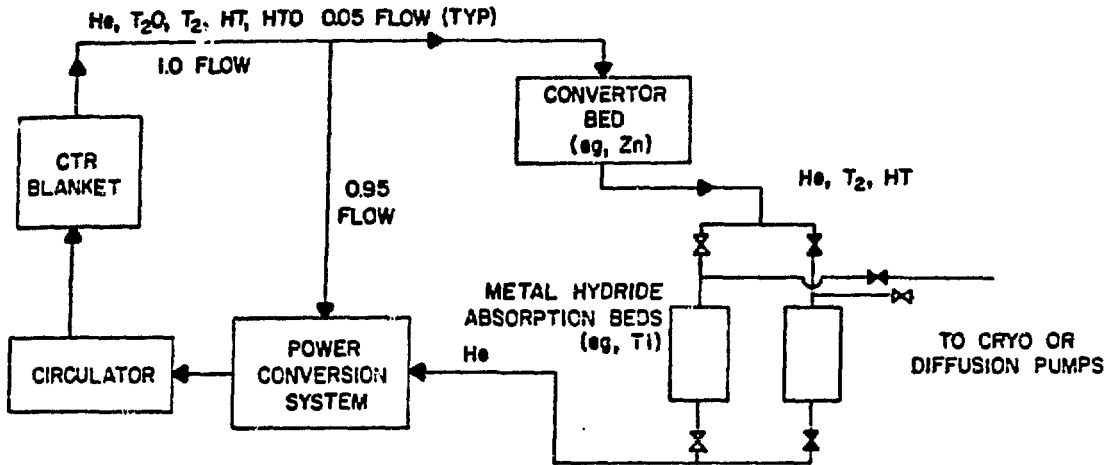


Fig. (I)-5

MODES OF TRITIUM RECOVERY
FROM HELIUM COOLANT



ABSORBING-DESORBING BEDS FOR T₂ RECOVERY
FROM HELIUM COOLANT

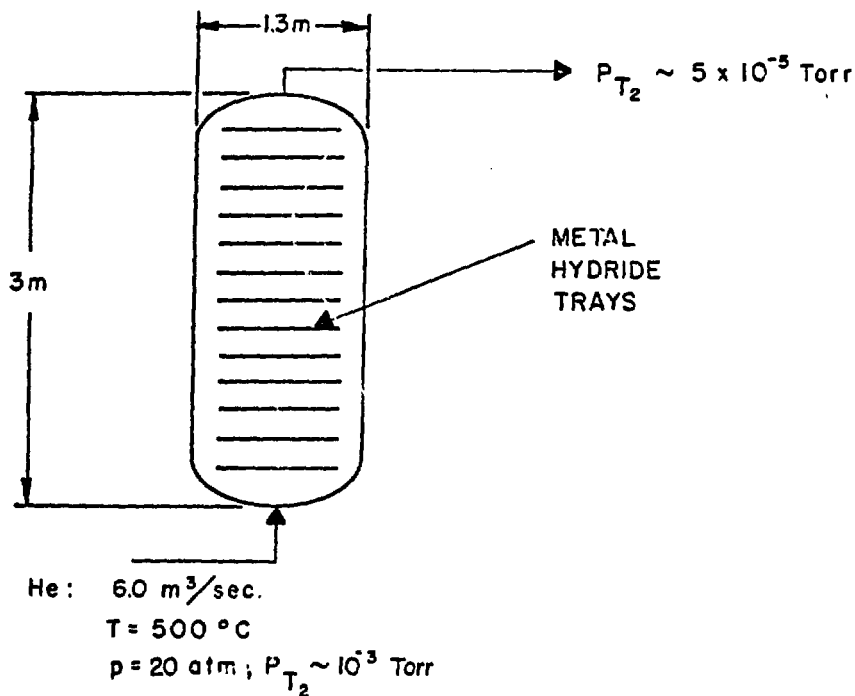
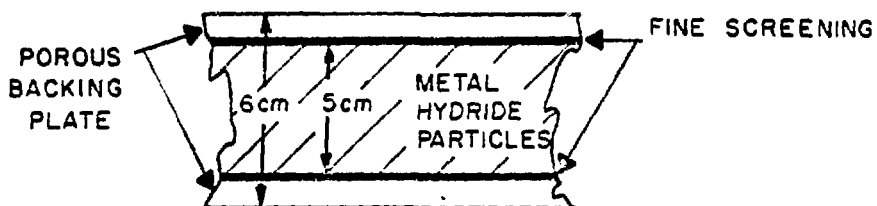
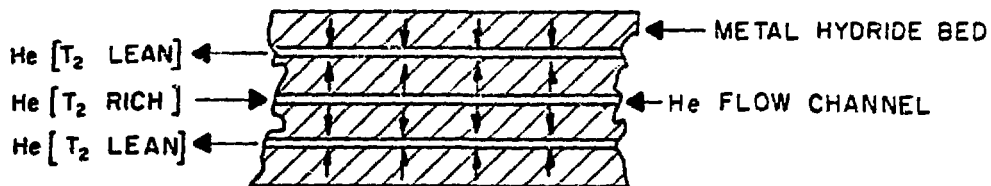


Fig. (I)-7

H₂ PRESSURE ABOVE METAL HYDRIDES
 VS
 H₂ CONCENTRATION IN METAL
 [T=500°C]

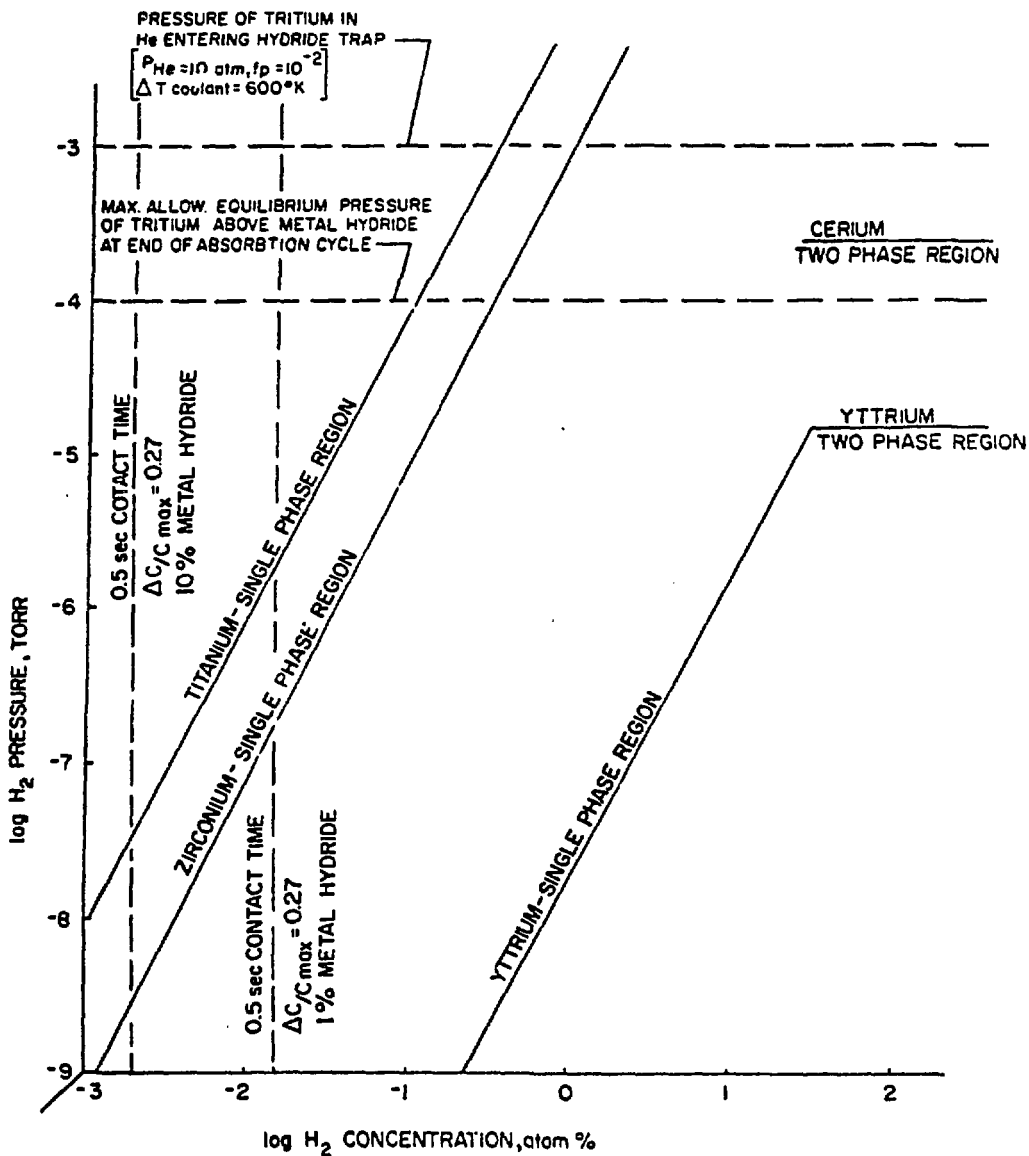


Fig. (I)-8

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 (?)
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 B11

Table 2. Breeding Characteristics
of Blankets Using Solid Lithium Compounds

<u>BREEDER TYPE</u>	<u>SOLID LITHIUM COMPOUND</u>	<u>ENRICHMENT STATE</u>	<u>STRUCTURAL MATERIAL</u>	<u>MODERATOR</u>	<u>NEUTRON MULTIPLIER</u>	<u>NOTES</u>
<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	LiAl, LiAlO ₂ , Li ₂ SiO ₃	ENRICHED	Al, SS, Nb, V, Mo	C, SiC, Al ₂ O ₃	NONE	BR ~0.8
<u>SUSTAINER-BREEDERS</u> (1≤BR≤1.3)						
I	LiAl, LiAlO ₂ , Li ₂ SiO ₃	ENRICHED	Al, SS, Nb, V, Mo	C, SiC, Be BeO, Be ₂ C	Be, Be ₂ C, BeO, PbO, PbS	
II	Li ₇ Pb ₂ , Li ₃ Bi	NATURAL	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	NONE	Pb or Bi ARE NEUTRON MULTIPLIERS
III	Li ₂ Be ₂ O ₃	NATURAL	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	NONE	Be IS NEUTRON MULTIPLIER
IV	Li ₄ Si, Li ₃ Sn, Li ₄ Sn	NATURAL	Al, SS, Nb V, Mo	C, SiC (SECONDARY)	NONE	SOME COMBINATIONS MAY HAVE BR<1
<u>SUPER-BREEDERS</u> (BR>1.3)						
I	LiAl, LiAlO ₂ , Li ₂ SiO ₃	ENRICHED	Al, SS, Nb, V, Mo	C, SiC (SECONDARY)	Be, Pb, Bi	MAX BR ~1.5
II	Li ₇ Pb ₂ , Li ₃ Bi	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

<u>BREEDER TYPE</u>	<u>ADVANTAGES</u>	<u>DISADVANTAGES</u>
<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_2SiO_3 OR LiAlO_2 AND BERTLLIUM (Be , BeO , Be_2C) 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
I Ib	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_2Sn 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
I Ib	GOOD TEMPERATURE CAPABILITY (~800°C) WITH Li_3Bi	Bi RESOURCE LIMITATION

Table 4. Assessment of Favored Alternate Solid Blankets

AMPLE BERYLLIUM

DESIRED 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

NOTES
MINIMUM Be REQUIREMENTS - HIGH
TEMPERATURE CAPABILITY

HIGH TEMPERATURE CAPABILITY -
SUB-BREEDER HAS MINIMUM RADI-
ATION DAMAGE - REQUIRES DEVEL-
OPMENT OF 2 BLANKET TYPES

SECOND 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 Be

INSUFFICIENT BERYLLIUM

DESIRED 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

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_7Pb_2 , Li_4Si , 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_7Pb_2 , Li_4Si , etc.) ² WITH SS^4 , Mo, V, OR Nb STRUCTURE	SAME	ONLY MODE FEASIBLE	NOT FEASIBLE	NOT FEASIBLE

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 $cm^{-2} sec^{-1}$. 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

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

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.

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,

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

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,

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.

-

FIGURE LIST

<u>Photo No.</u>	<u>Caption</u>
9-643-75	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.
7-148-74	Fig. 2. Removal of tritium from LiAl of 5-10 mesh.
7-146-74	Fig. 3. Removal of tritium from LiAl of 10-20 mesh.
7-2-74	Fig. 4. Removal of tritium from LiAl; effect of temperature and particle size. A. 5-10 mesh, 500° B. 5-10 mesh, 600° C. 10-20 mesh, 400° D. 10-20 mesh, 500°
7-147-74	Fig. 5. Removal of tritium from LiAl of 10-20 mesh at 500°; effect of helium flow rate.
7-149-74	Fig. 6. Removal of tritium from LiAl of 10-20 mesh at 400°; effect of added H ₂ .
9-642-75	Fig. 7. Removal of tritium from Li ₇ Pb ₂ .
1-657-75	Fig. 8. Removal of tritium from LiAlO ₂ of 70-100 mesh. Dashed line has slope of 1/2.
9-641-75	Fig. 9. Removal of tritium from sintered LiAlO ₂ at 650°.
1-658-75	Fig. 10. Removal of tritium from Li ₂ SiO ₃ of 70-100 mesh at 500°.

REFERENCES

1. J. R. Powell, F. T. Miles, A. Aronson and W. E. Winsche, Studies of fusion reactor blankets with minimum radioactive inventory and with tritium breeding in solid lithium compounds: a preliminary report, BNL 18236 (June 1973).
2. W. Bernstein and R. Ballentine, Rev. Sci. Instr. 21 158 (1950)
D. R. Christman, Nucleonics 19 (5), 51 (1961).
3. F. T. Miles, R. J. Heus and R. H. Wiswall, The extraction of protactinium from solid thorium fluoride, BNL 482 (November 1954).
4. J. J. Reilly and R. H. Wiswall, Inorg. Chem. 13 218 (1974); also, unpublished BNL results.
5. A. M. Lejus and R. Collongues, Comptes Rendus de L'Academie des Sciences, Ser. Chim. 254, 2005 (1962).

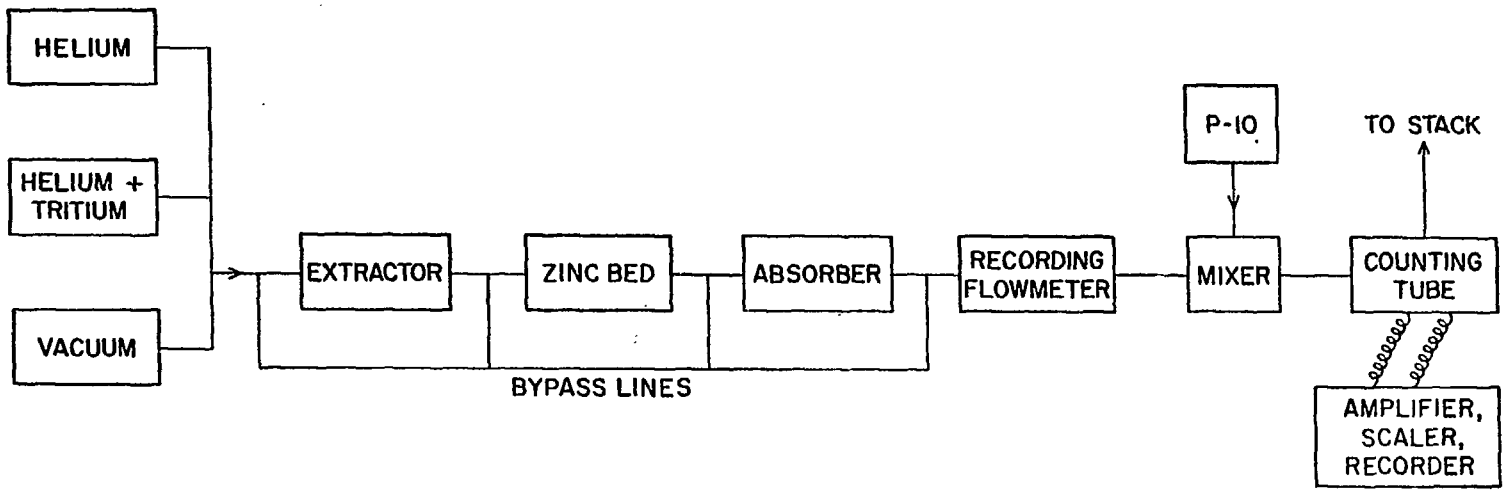


Fig. (II)-1

Neg. #9-643-75

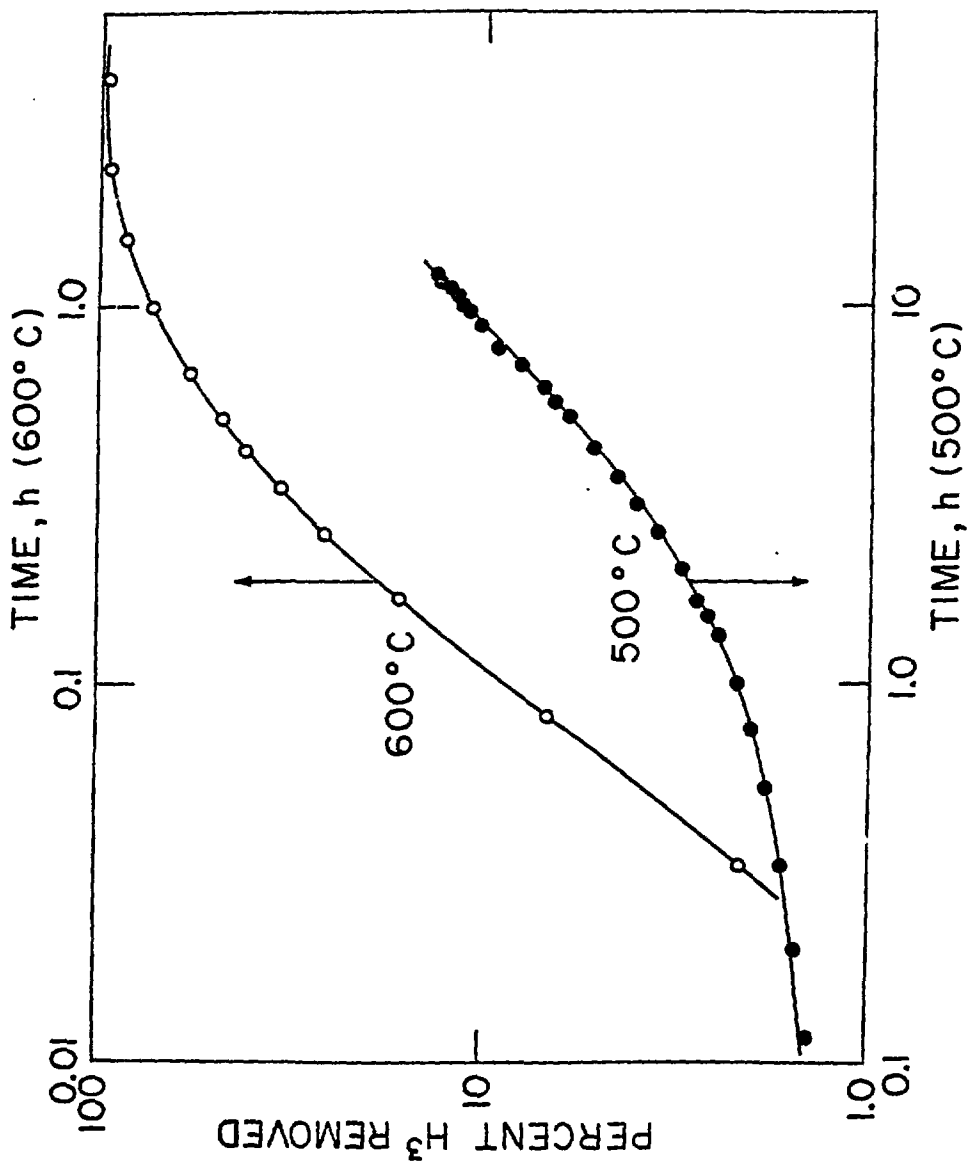


Fig. (II)-2

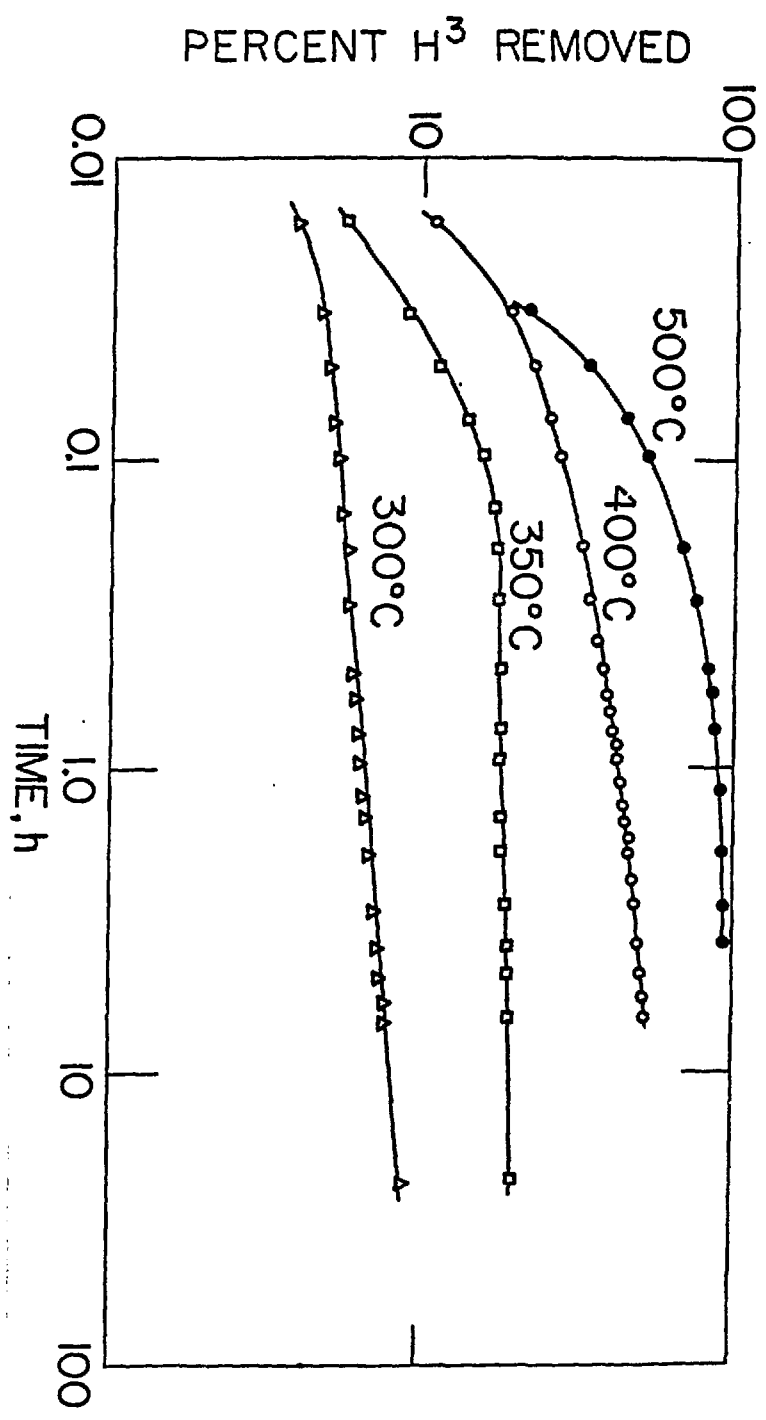


Fig. (II)-3

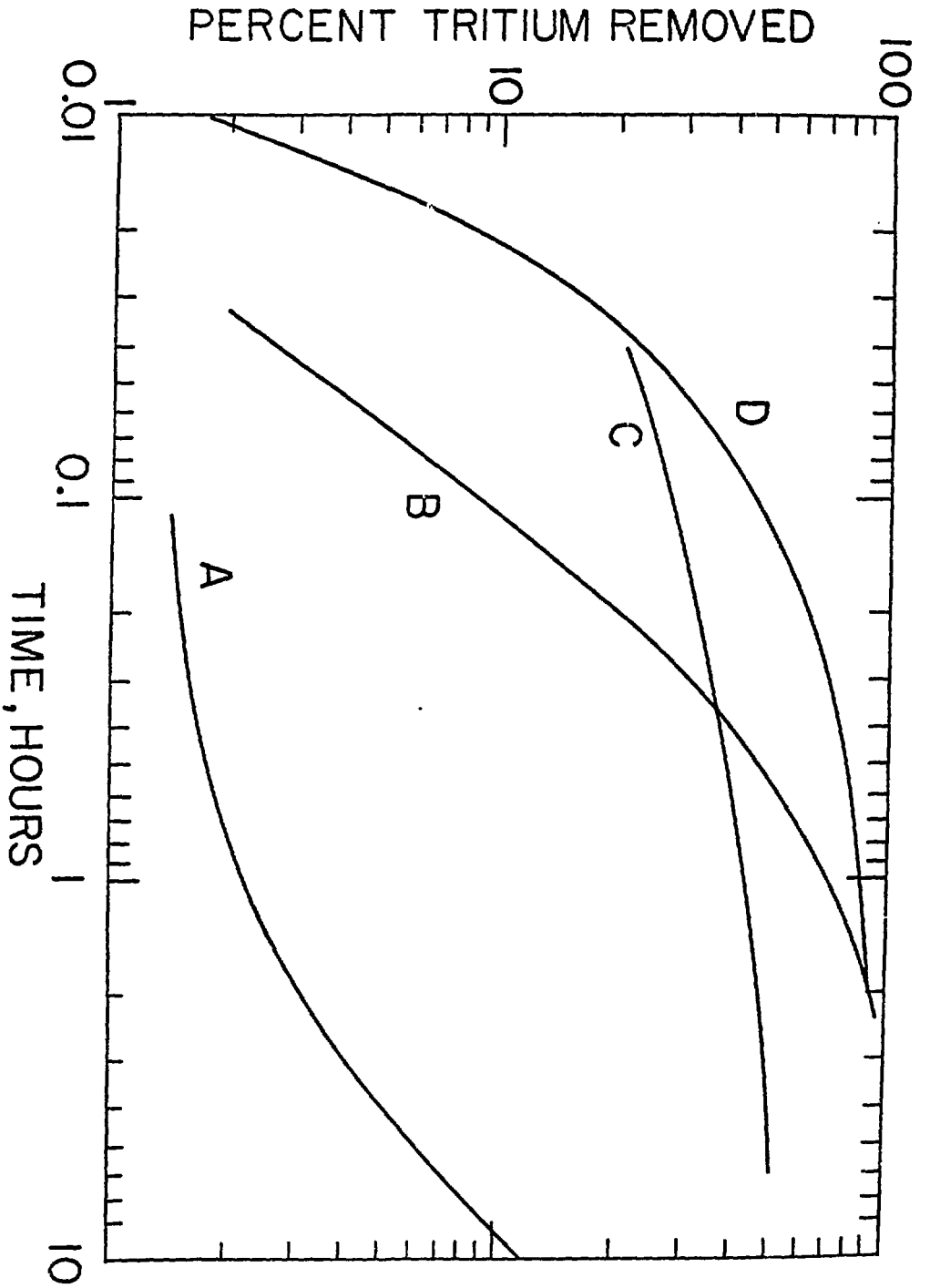


Fig. (II)-4

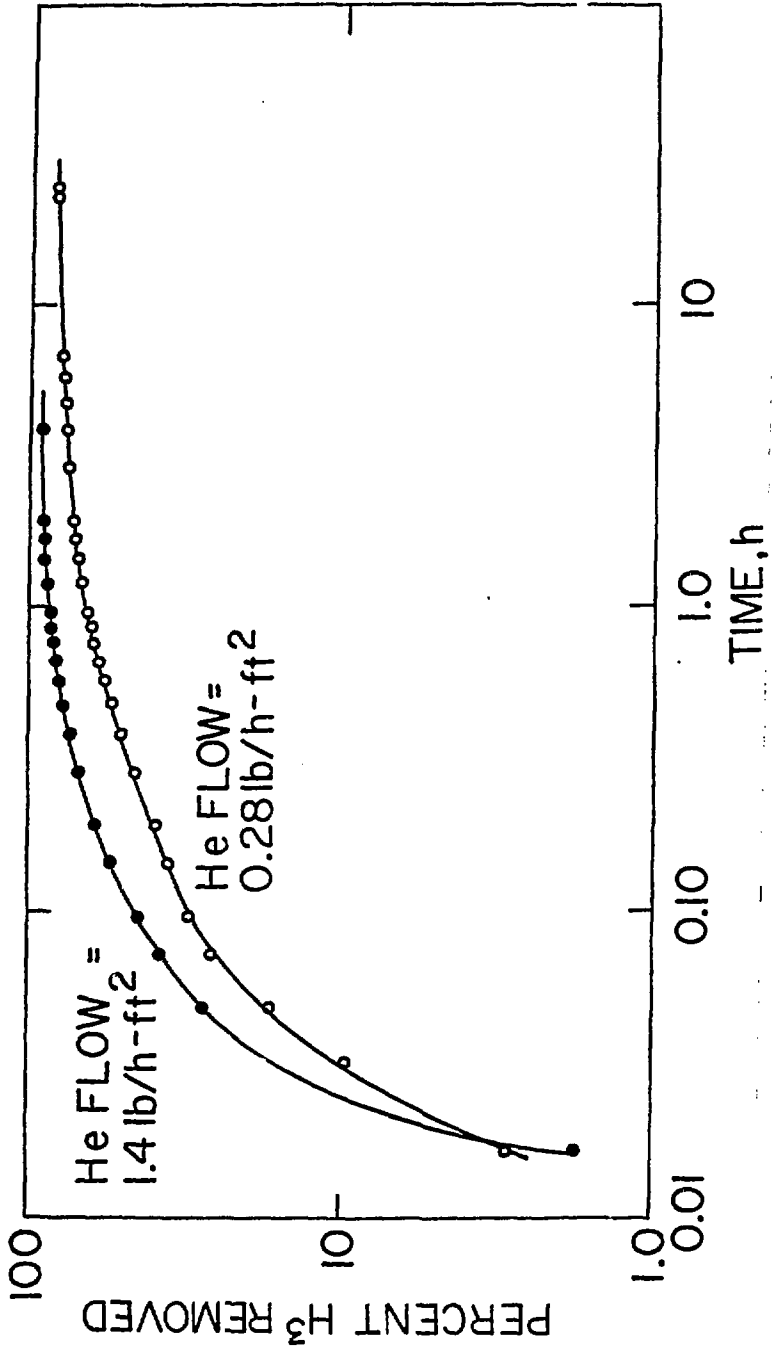


FIG. (II)-5

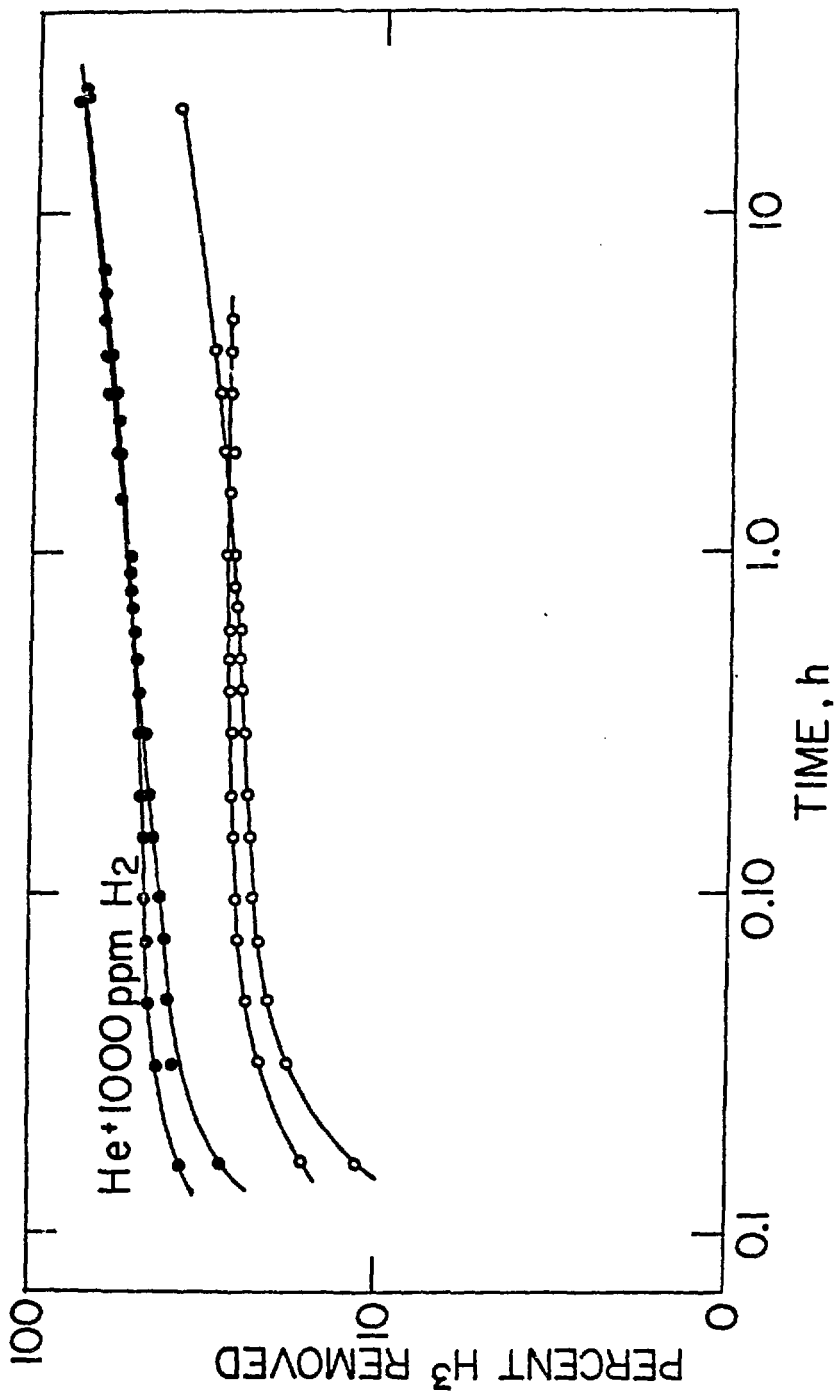


Fig. (II)-6

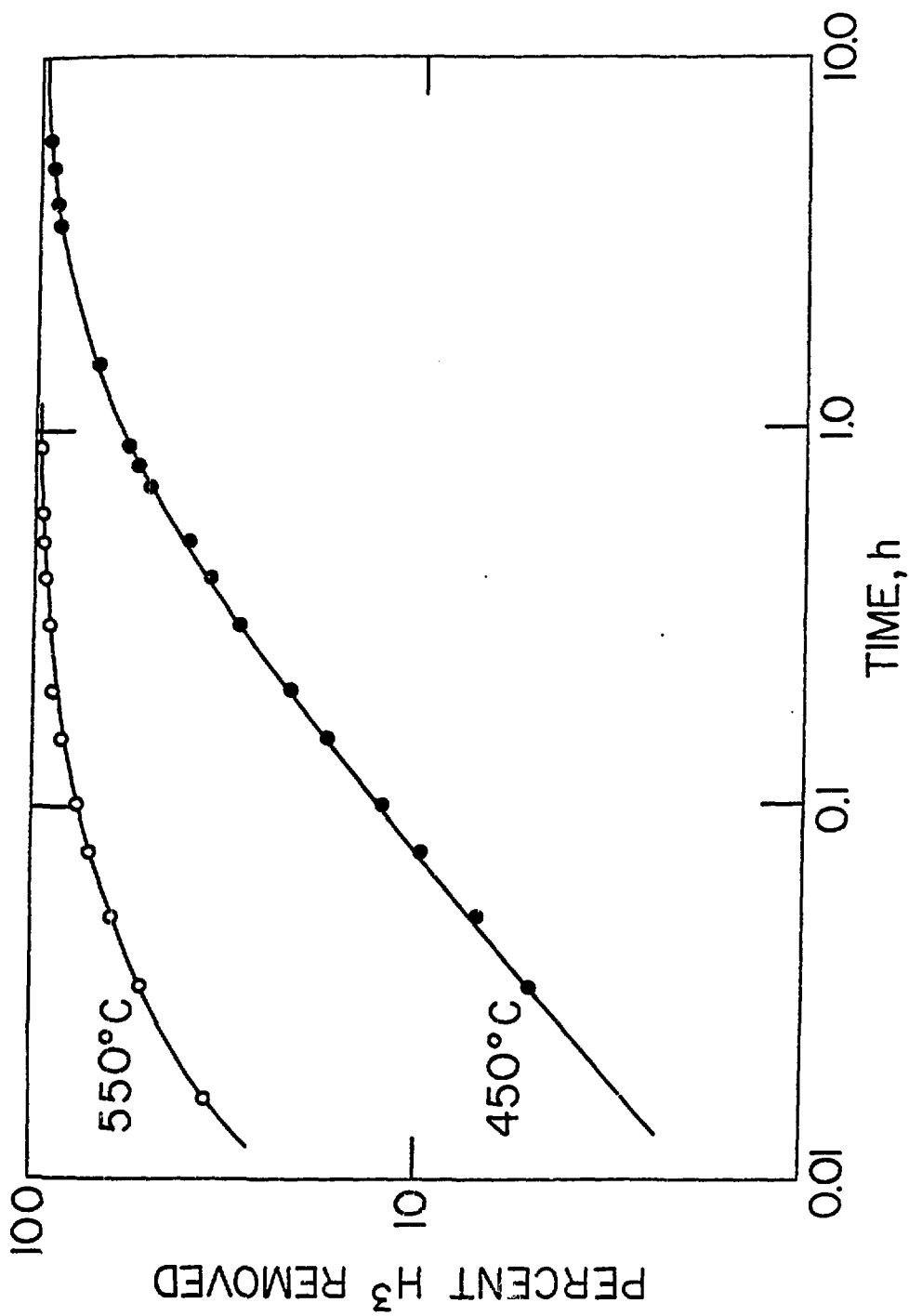


Fig. (II)-7

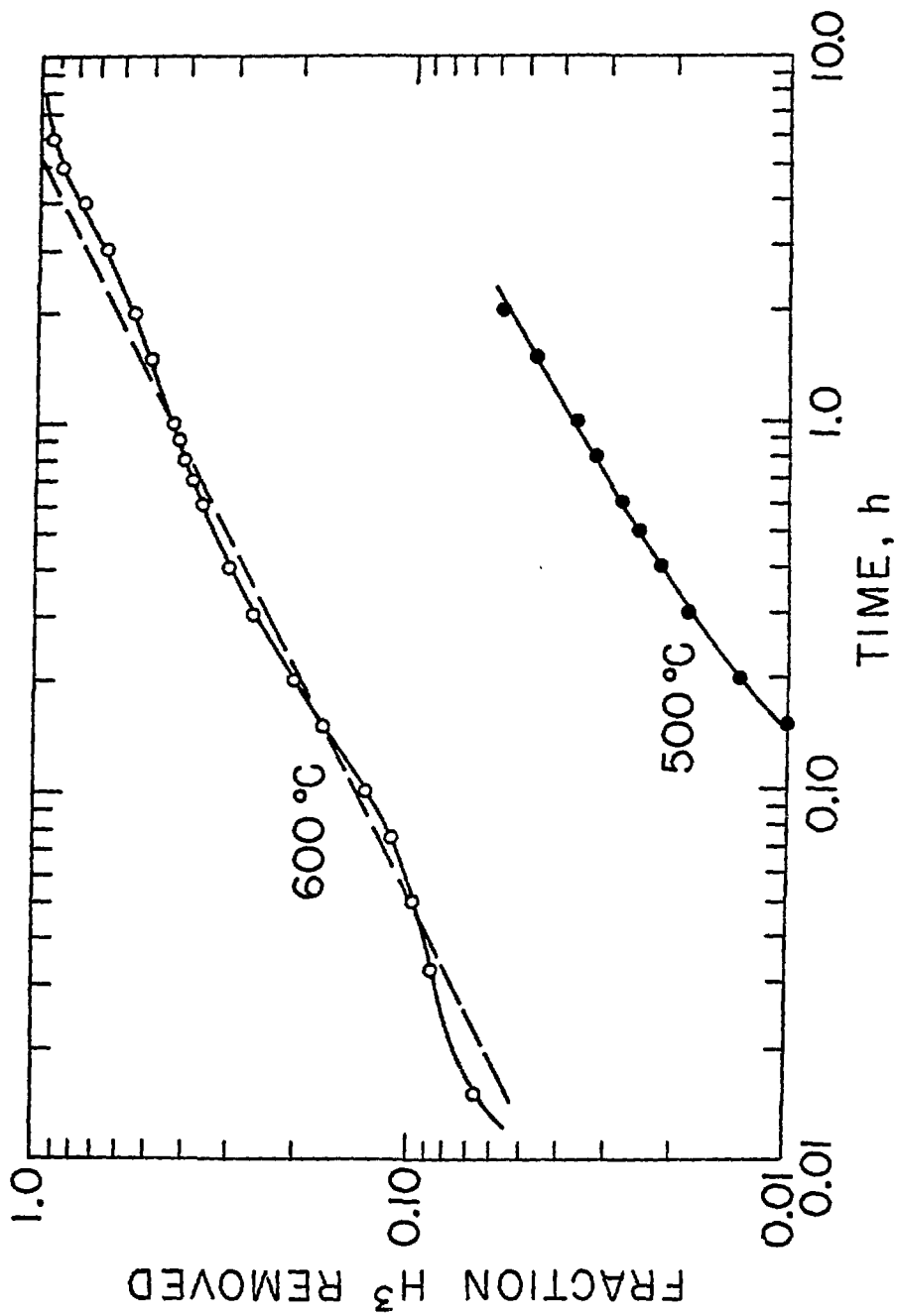


Fig. (II)-8

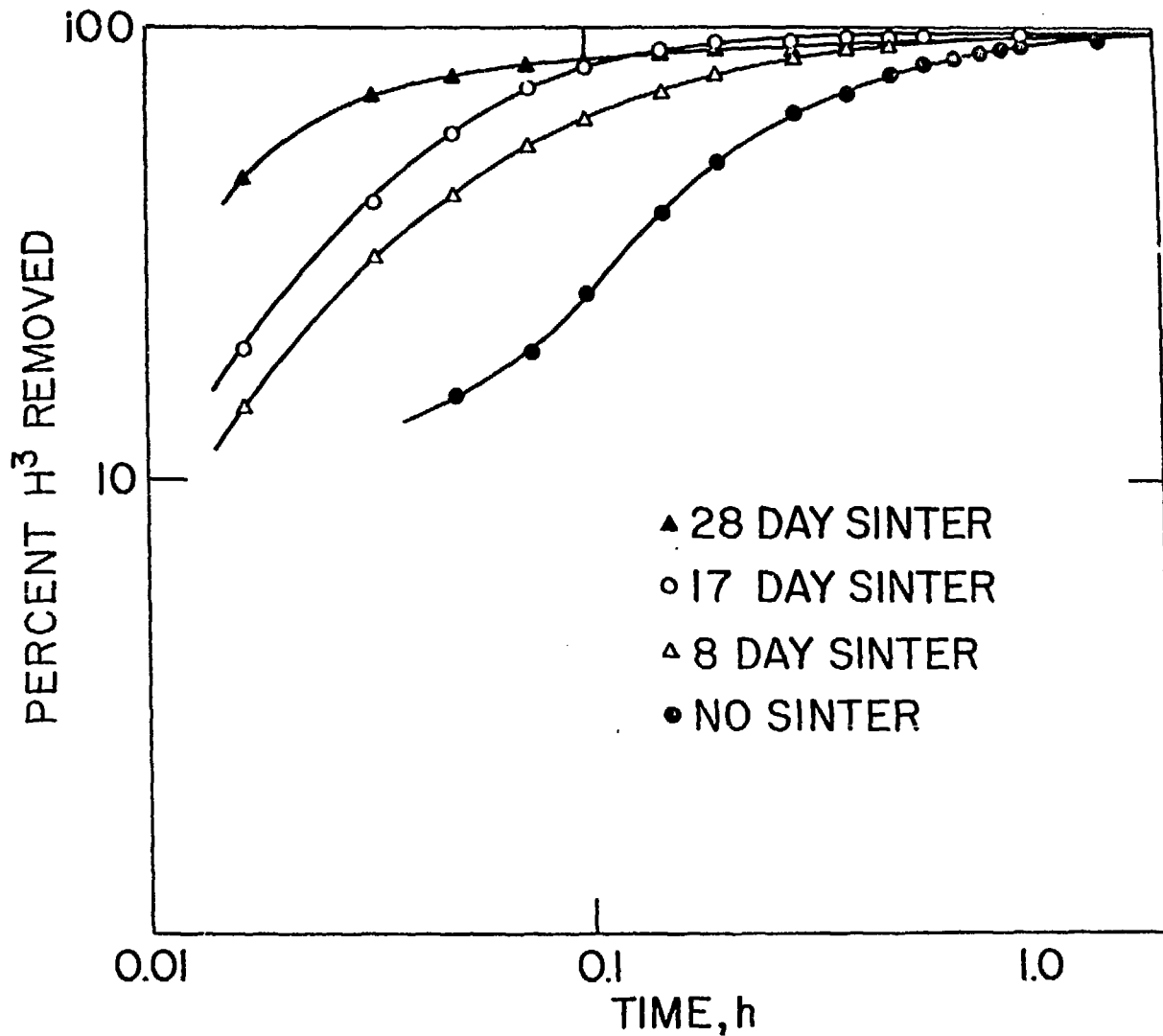


Fig. (II)-9

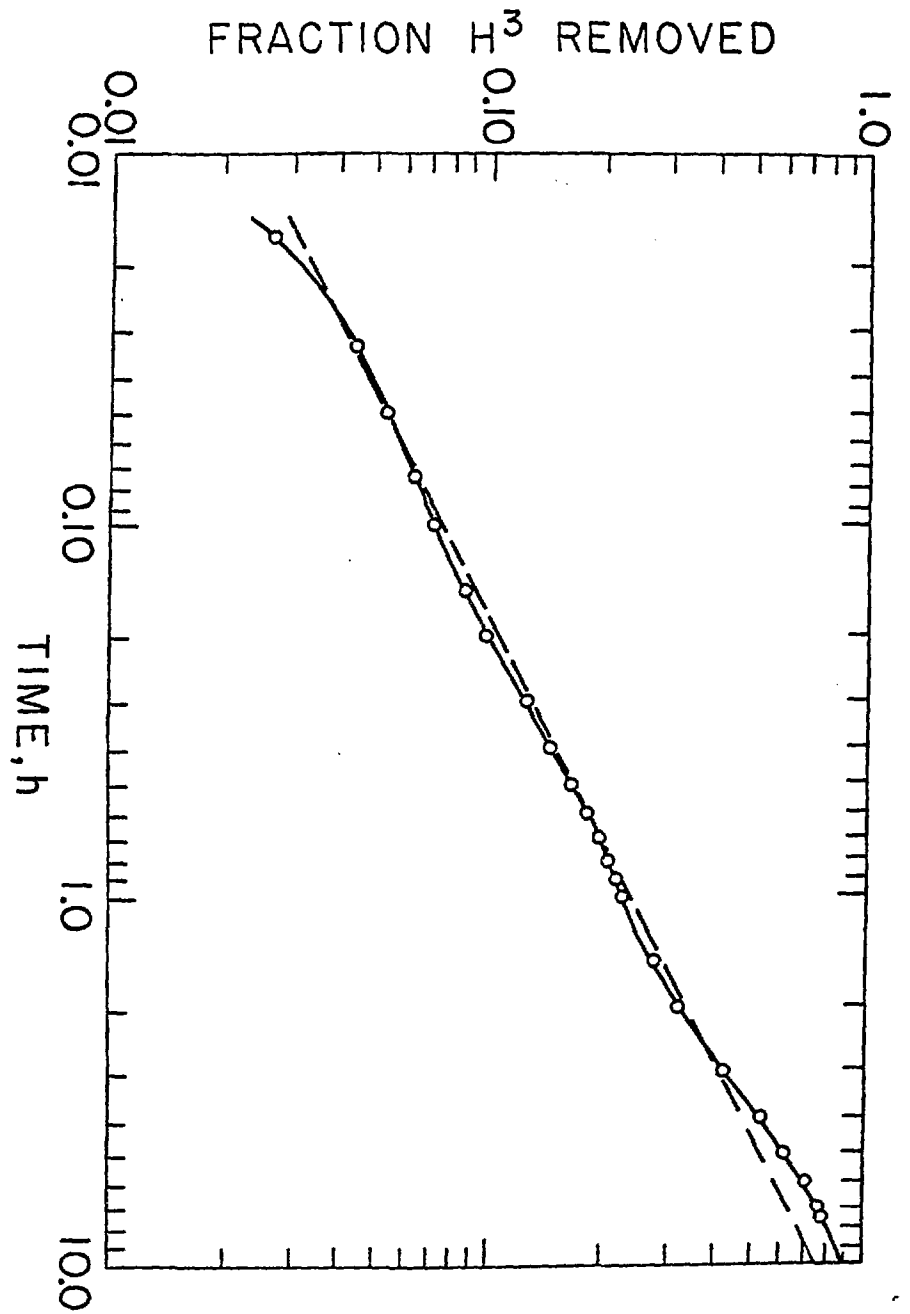


Fig. (II)-10