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COMBINED GETTERING AND MOLTEN SALT PROCESS
FOR TRITIUM RECOVERY FROM LITHIUM*

by

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ABSTRACT

A new tritium recovery concept from lithium has been developed as part of the U.S./Japan collaboration on Reversed-Field Pinch Reactor Design Studies. This concept combines the γ -gettering process as the front end to recover tritium from the coolant, and a molten salt recovery process to extract tritium for fuel processing. A secondary lithium is used to regenerate the tritium from the gettering bed and, in the process, increases the tritium concentration by a factor of about 20. That way, the required size of the molten salt process becomes very small. A potential problem is the possible poisoning of the gettering bed by the salt dissolved in lithium.

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1. INTRODUCTION

The self-cooled lithium blanket is the most widely studied fusion reactor blanket concepts. It was top rated by the Blanket Comparison and Selection Study [1]. The more recent major fusion reactor studies such as Tokamak Power System Studies (TPSS) [2], the TITAN-1 Study [3], and REPUTER [4] all use the self-cooled lithium blanket for energy recovery and tritium production. By combining the cooling and breeding functions into one, the blanket system becomes very simple.

There are various issues remained to be resolved. Some major engineering issues are tritium recovery, MHD and lithium safety. The tritium recovery problem arises from the high tritium solubility in the lithium, and the required low tritium inventory. A design goal is to reach a tritium concentration in lithium to about 1 wppm. The tritium partial pressure over lithium at this concentration is about 1×10^{-7} Pa. Therefore, the tritium containment is not a severe problem for such a blanket system.

Three tritium recovery methods have been experimentally studied. These are molten salt extraction [5], a permeation window [6] and gettering [7]. Technical issues still exist which may affect the feasibility of all three methods. A new concept was developed as the result of the U.S./Japan collaboration on reversed field pinch reactor design studies. This new concept is to combine the gettering and molten salt process to eliminate some of the critical issues included on either separate concepts.

This paper reviews the state-of-the-art of the tritium recovery methods and associated issues. The combined gettering and molten salt process will be described and its critical issues outlined.

2. MOLTEN SALT RECOVERY METHOD

The molten salt method [5,8] of recovering tritium from liquid lithium is a three-step process. First, lithium which contains tritium is intimately mixed with a salt mixture of lithium halides in a centrifugal contactor/separator. The tritium which is in the form LiT, lithium tritide, preferentially distributes to the salt phase. The salt phase, which has higher density than the lithium, is separated from the lithium by centrifugal force. Second, the salt phase is circulated to an electrolysis unit in which the LiT is dissociated to form molecular tritium. The molecular tritium is swept from the salt phase by bubbling helium through the electrolysis unit. Third, the helium is circulated to a cleanup unit which recovers the tritium and removes impurities from the helium gas.

Although individual steps in the molten salt recovery method have been experimentally verified, the integrated process has not been demonstrated. The engineering problems associated with the integrated process are unknown. Prior to a detailed design of a system for a commercial fusion reactor, engineering prototypes for the centrifugal contactor, the electrolysis unit and the cleanup unit would be designed, built and tested. The testing would be conducted both in independent and integrated operation to assess the actual magnitude of the problems. Some of the anticipated problems are mentioned below.

For the integrated process, entrainment of the two liquids must be prevented. Therefore, a minimum of three contactor/separator units in series

may be required. Separation of the lithium from the salt prevents recombination of the dissociated tritium with excess lithium in the electrolysis unit. Separation of the halide salt from the lithium keeps the halides out of the fusion reactor in which they could be activated, could enhance corrosion, and could precipitate out in the colder parts of the lithium coolant loop. The three contactor/separators in series should prevent entrainment, however, mutual solubility of the two liquids can cause the above problems to a limited extent. The limit on these problems should therefore be the solubility limits for these two liquids.

For the electrolysis unit, the role of impurities (metal corrosion products) on the operation and the lifetime of the electrodes is not known. Metal or oxide precipitation on the electrodes could reduce their capacity either by clogging the electrode pores and reducing the efficiency of the helium sweep gas or by increasing the voltage over-potential required. If reduced capacity is expected over the unit's life, either replacement of units at specified intervals or the use of units with excess capacity might be required. The design of the electrolysis unit will also have to control tritium permeation from the unit since the unit will be at temperatures $> 500^{\circ}\text{C}$.

The cleanup unit must separate the helium from the tritium and all impurity species as quickly and as efficiently as possible. Expected impurities are radioactive gases and entrained halides. A sacrificial bed may be used to trap the entrained halides followed by a palladium diffuse to remove the tritium from the helium and radioactive gases. The major engineering issue may be the time required to remove the tritium from the helium.

3. GETTERING RECOVERY PROCESS

This method utilizes one of the following principles: (i) Sieverts' constant of tritium in yttrium (eq. (1)) [9] is larger than that in lithium (eq. (2)) [10]:

$$K_{Y-T}(wppm/Torr^{1/2}) = 0.55 \exp (22900/RT) \quad (1)$$

$$K_{Li-T}(wppm/Torr^{1/2}) = 42.8 \exp (10104/RT) \quad (2)$$

(ii) When yttrium tritide is formed, tritium concentration in lithium is controlled by dissociation of yttrium tritide as given by [11],

$$C_{Li}(at.fr.) = 25.1 \exp (-8323/T) \quad (3)$$

Tritium recovery by gettering has advantages of being a simple process and no impurity mixing to lithium as considered in salt extraction.

Bed packed with sintered pebble consisted of small particle is considered here. For calculating mass transfer rate, tritium diffusivities in lithium and yttrium must be evaluated. For tritium diffusivity in lithium, values given by Buxbaum and Johnson [12] can be used.

$$\log D_{Li}(cm^2/sec) = -9.038 + 1.737 \log T - 110/T. \quad (4)$$

However, measured values of diffusivity in yttrium are much scattered as shown in Fig. 1, especially at low temperatures. Abrupt decrease at lower temperature (A) may be attributed to surface reaction.

For the reference design, yttrium pebble (1 mm in radius, 0.5 of void fraction) made by sintering particle (20 μm in radius) was adopted and smaller diffusivity (A in Fig. 1) was used.

Flow sheets of tritium recovery by yttrium getter are shown in Fig. 2-4, which were considered in the conceptual design of REPUTER-II studied at the University of Tokyo [4]. Tritium concentration in the blanket is limited to 1 wppm from considerations of inventory and leakage to the environment. In the flow sheet of Fig. 2 solid solution regime in yttrium-tritium system is used. Breakthrough curve for this case is shown in Fig. 5. In the reference case ($K_{FaV}=22.1 \text{ hr}^{-1}$), breakthrough curve is not so good and there exists incentive to improve mass transfer rate. In this design, bed height of 2.0m and lithium velocity of 10 m/hr are assumed, total amount of yttrium is 15 ton. When yttrium tritide is used to recover tritium, the flow sheet is shown in Fig. 3. If smaller diffusivity in yttrium (Case A in Fig. 1) is used, capacity coefficient is 1.1 l/hr, which is too small to be used for recovering tritium. If larger diffusivity (Case B) is used, capacity coefficient is 21.4 l/hr and breakthrough time (2.0 m in bed height) becomes 280 days, it means efficient yttrium utilization in the case of yttrium tritide. To improve mass transfer rate, one method is to operate at higher temperature. However, at high temperature equilibrium relations (dissociation pressure over yttrium tritide or Sieverts' constant) are not suitable. In order to overcome this shortcomings, hydrogen swamping method can be used. Considered flow sheet is shown in Fig. 5, where yttrium tritide is used at high temperature of 400°C and hydrogen is added at the inlet of bed to about 200 wppm, equilibrium hydrogen concentration over yttrium hydride at 400°C is 15 wppm. In the case of 2.0 m in bed height and 10 m/hr of lithium velocity ($K_{FaV}=43.5 \text{ hr}^{-1}$) breakthrough time is 2.2 days.

For desorption of tritium from yttrium, gas-phase degassing is a usually considered. In this process, yttrium is heated to high temperature (for example, 800°C) and helium gas is used for purging desorbed tritium. However, difficulties in this process arises from a very low equilibrium pressure even at high temperature. Equilibrium tritium pressure over tritium-containing yttrium used in the Fig. 2 (average T/Y=308 wppm) is 1.47×10^{-4} Torr, and desorption time will becomes as long as 300 days if purging He velocity is 10,000 m/hr. If yttrium tritide is used, equilibrium dissociation pressure is 0.29 Torr at 800°C, and required time for desorption is still too long as 50 days.

In order to shorten the required period for desorption, we proposed a new method. This method used a second lithium loop, namely different lithium from main blanket lithium, for desorbing tritium from yttrium. This idea makes uses of large tritium solubility in lithium and differences in temperature dependences for Sieverts' constants between tritium-yttrium system and tritium-lithium system. If tritium concentration in liquid lithium is 1 wppm, equilibrium tritium concentration in yttrium at 300°C is 980 wppm. And if yttrium containing this concentration of tritium is contacted with another lithium at 600°C, equilibrium tritium pressure in lithium becomes 48 wppm. This means that enrichment of tritium in lithium is conducted. For desorbing tritium from yttrium which contains average concentration of 38 wppm (corresponding to Fig. 2), desorption time is 19.5h and outlet tritium concentration is 15 wppm at 600°C.

Key problems relating to yttrium gettering are: (1) Fear of cracking or powdering of yttrium especially for yttrium tritide. There is a possibility to improve integrity by making alloy, (2) Uncertainty in the mass transfer rate at low temperature. Tritium diffusivity in yttrium and surface reaction rate must be experimentally studied.

4. PERMEATION WINDOW PROCESS

This process utilizes permeation of tritium through metal at high temperature. Metal membrane which has both a good compatibility with liquid lithium and a large tritium permeability such as niobium is contacted with liquid lithium and the other side of the membrane is evacuated or tritium partial pressure is reduced by chemical reaction such as $T_2 + 1/2O_2 = T_2O$. If diffusion in the metal bulk is rate determining, tritium recovering rate is given by the equation:

$$J = \frac{PA}{d} (\sqrt{P_{Li}} - \sqrt{P_{Vac}}) \quad (3-1)$$

where P is permeability, A area of the membrane, d membrane thickness, P_{Li} tritium equilibrium pressure in lithium and P_{vac} tritium pressure in the vacuum side.

For example, required membrane area for recovering 500g/day of tritium from liquid lithium (1 wppm of tritium concentration) by niobium membrane (0.5mm in thickness) becomes $1.5 \times 10^4 \text{ m}^2$, when temperature is 600°C, $P_{vac} = 0$, and permeability is $101 \text{ cc(STP).mm/hr.cm}^2.\text{atm}^{1/2}$. Tritium equilibrium pressure in liquid lithium is $4.8 \times 10^{-9} \text{ Torr}$, which is too low to be evacuated by pump. Adding oxygen on the downstream side and decrease of T_2 pressure is one solution, but in this case Pd coating will be necessary to

prevent niobium from oxidation. Permeability used is extrapolated from the experimental data by Rudd, et al. [14] which was measured in the temperature range of 950°C-1065°C using hydrogen.

The required area is comparable with that of heat exchanger. Tanaka, et al., measured hydrogen permeability of niobium contacting with liquid lithium [15] and found that the values are one to two orders of magnitude lower than anticipated from extrapolation of Rudd's data. This was explained by slow surface process which was caused by the formation of surface layer on the lithium side of the membrane. This means that required area will be enlarged by the same factor by the slow surface process. To control impurity (mainly nitrogen) in liquid lithium by hot trapping was tested, however, improvement of permeability was limited. From these considerations, tritium permeation window is not an attractive method to recover low concentration of tritium from blanket, though this process has a possibility to be used for recovering tritium of high concentration. Deterioration of metal membrane and tritium leakage by permeation are also matters of problem.

Hsu and Buxbaum recommended of using palladium-coated zirconium membrane for permeation extraction [16]. If similar slow surface process caused by the formation of surface layer on the lithium side of the membrane will reduce the permeation by one-to-two orders of magnitude, the feasibility of this method will be questionable. It is important, therefore, to demonstrate the permeation process with an upstream lithium with similar impurity concentrations to that of a fusion reactor system.

5. CONCEPT OF COMBINED GETTERING AND MOLTEN SALT PROCESSES

A new tritium recovery process concept from lithium has been developed as the result of U.S./Japan collaborations on RFP (Reversed Field Pinch) reactor

design studies. This collaboration is between the U.S. TITAN RFP [3] reactor design team, led by UCLA, and the Japanese REPUTER team, [4] led by the University of Tokyo. Both designs investigated the using of lithium as the coolant and breeding material, and tritium recovery from lithium becomes an important issue for such a blanket.

A molten salt recovery process, developed by ANL, and a gettering process have been proposed by the TITAN and REPUTER team, respectively, for the candidate method for tritium recovery from lithium. Both processes have been developed to a certain extent to establish its technical feasibility. Critical issues exist, however, for each process. For molten salt recovery process, the key problem is caused by the salt carried by the lithium back to the reactor. For the gettering process, the key problem is caused by the recombination of the tritium atoms on the surface of the gettering bed to be released on T_2 form. If tritium is regenerated by gas purging, very low dissociation pressure of tritium over yttrium getter requires too long a period for tritium recovery.

The combined gettering and molten salt recovery process uses yttrium gettering bed to remove tritium from lithium at 300°C. An important innovation is to use a secondary lithium to regenerate tritium from the gettering bed. The regenerating occurs at 600°C and since the solubility of tritium in yttrium decreases much faster than that in lithium with increasing of temperature, the tritium concentration in the secondary lithium can be increased from 1 wppm in the coolant, to 20 wppm in the secondary lithium stream. At this high concentration, a very small secondary lithium loop, with a lithium flow rate of .5 kg/sec, will be required. Molten salt recovery process will be used to recover the tritium from the secondary lithium. The flow rate in the salt loop will be 2 kg/sec.

The schematic flow diagram of the process is shown on Fig. 6. There are two units of yttrium gettering bed for recovering and regenerating. A very small secondary lithium loop is used for regenerating. The major parameters of the tritium recovery system is shown on Table 1. Some of the features of this process are described here.

1. For desorption of tritium from yttrium, gas-phase degassing is usually considered. The difficulty arises from a very low tritium equilibrium pressure even at 800°C. In this process, a secondary lithium is used for tritium regeneration. This takes advantage of the much stronger temperature dependency of tritium solubility in yttrium than lithium.

2. One of the concerns of the molten salt recovery process is the carrying back of the salt by the lithium to the blanket. The following problems may occur:
 - a. More Corrosion.
 - b. Activation
 - c. Salt precipitation in the cold part of the loop.For this process, there is no direct access of the salt to the blanket. In addition, the secondary lithium loop and the salt loop can be operated at constant temperature so that salt precipitation is not a problem.

3. There are engineering problems associated with the centrifugal contactor and electrolysis unit in which mainly caused by the required high efficiency. In this process, the required size of the salt process is so small, that high efficiency is not essential. For instance, a mechanical

stirrer may be sufficient, instead of a centrifugal contactor. The life time of the electrolysis unit is not critical either.

There is a potentially critical issue. The secondary lithium is saturated with the salt. The interaction of the salt with the yttrium getter, and its possible effect to the gettering and regeneration of tritium must be investigated.

6. CONCLUSIONS:

Tritium recovery from lithium to a concentration of about 1 ppm is an issue associated with a lithium breeding blanket. Different tritium recovery concepts have been proposed, and limited amount of experimental results are available for each concept. However, there are still practical problems associated with each method. Recovering tritium from lithium under the constraints of inventory, cost and tritium containment remains to be questionable.

A less tritium recovery concept from lithium has been developed and is described in this paper. This method combines the gettering method and molten salt method for tritium recovery. A number of innovative ideas have been incorporated into the design. It appears that this concept is able to alleviate some of the issues facing each individual concept. The potential poisoning of the gettering material by the salt dissolved in the lithium may be a problem and has to be experimentally studied.

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**Table 1 -- Parameter of Blanket Tritium Recovery System Using
a Combined Gettering and Molten Salt Process**

Fusion Power	2288 MW
Thermal Power	2918 MW
Blanket Tritium Production Rate	420 g/d
Coolant Flow Rate	10^7 kg/hr
Tritium Concentraion in Coolant	1 wppm
Lithium Flow Rate to Tritium Recovery System	2×10^4 kg/hr
Tritium Concentration in Secondary Lithium Loop	20 wppm
Lithium Flow Rate in Secondary Lithium Loop	1200 kg/hr
Salt Flow Rate in Molten Salt Recovery Process	7000 kg/hr

FIGURE CAPTIONS

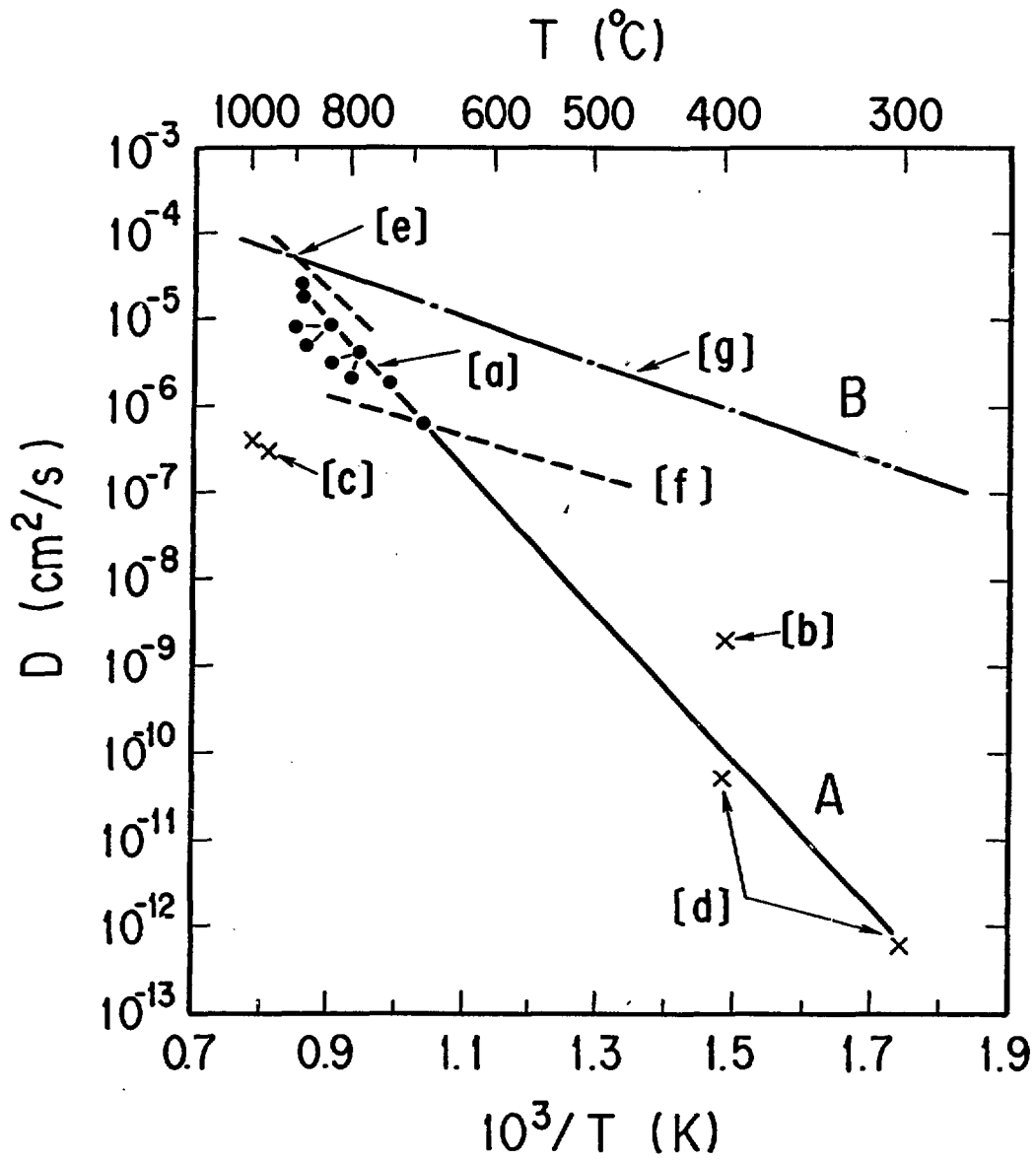
Figure 1 Tritium (Hydrogen) Diffusivity in Yttrium, Summarized by Fisher and Tanase [13], Data (B) Evaluated by Buxbaum and Johnson [12] is also included.

Figure 2-4 Flow Sheets for Recovering Tritium by Yttrium Getter:

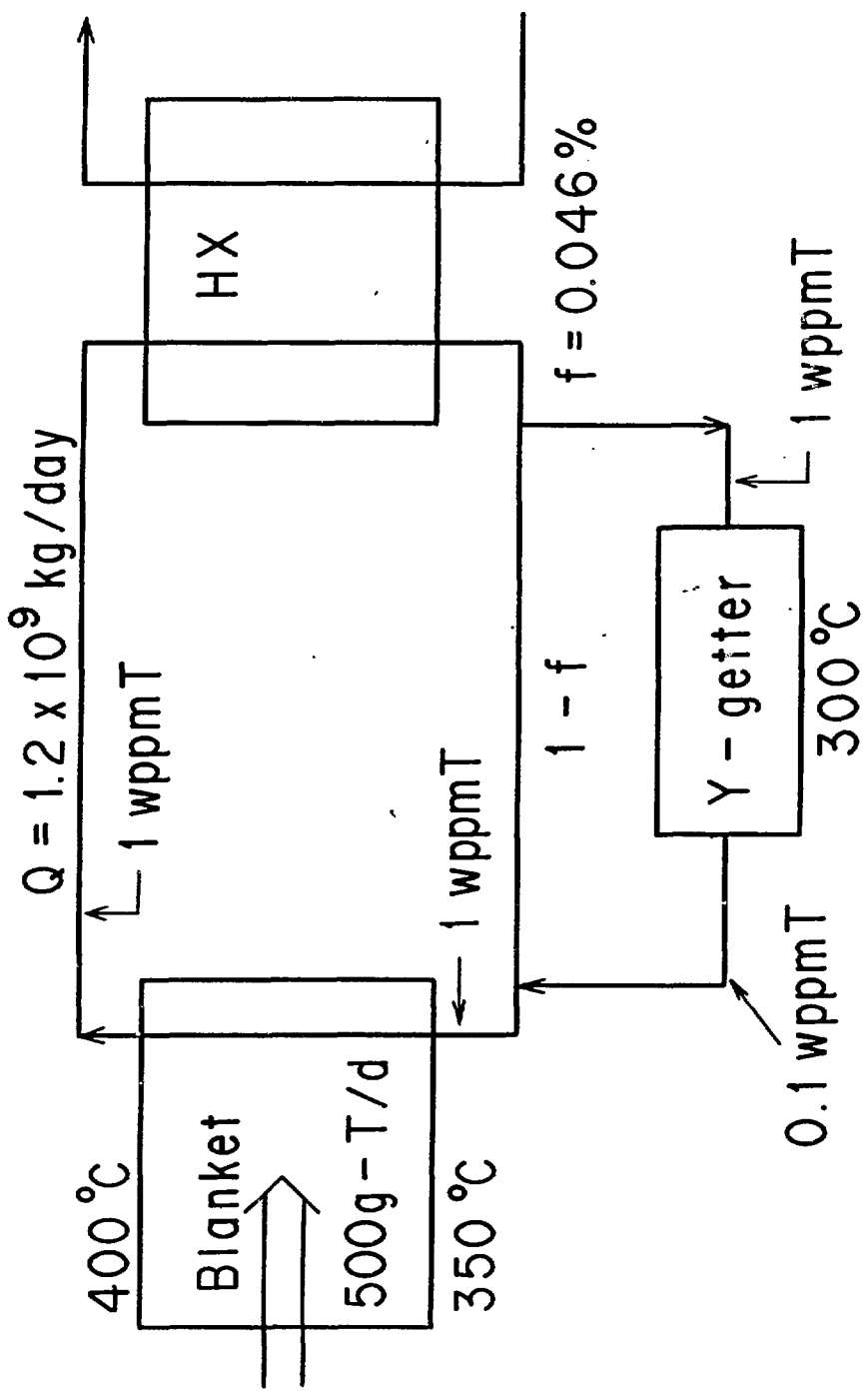
- (2) Solid Solution Regime.
- (3) Yttrium Tritide is Formed.
- (4) Yttrium Tritide Formed and Swamped by Hydrogen.

Figure 5 Tritium Breakthrough Curve, Corresponding to Flow Sheet of Fig. 2.

Figure 6 Combined Gettering and Molten Salt Recovery Concept.



- Figure 1 (D.K. Sze et al.) -



- Figure 2 (D.K. Sze et al.)

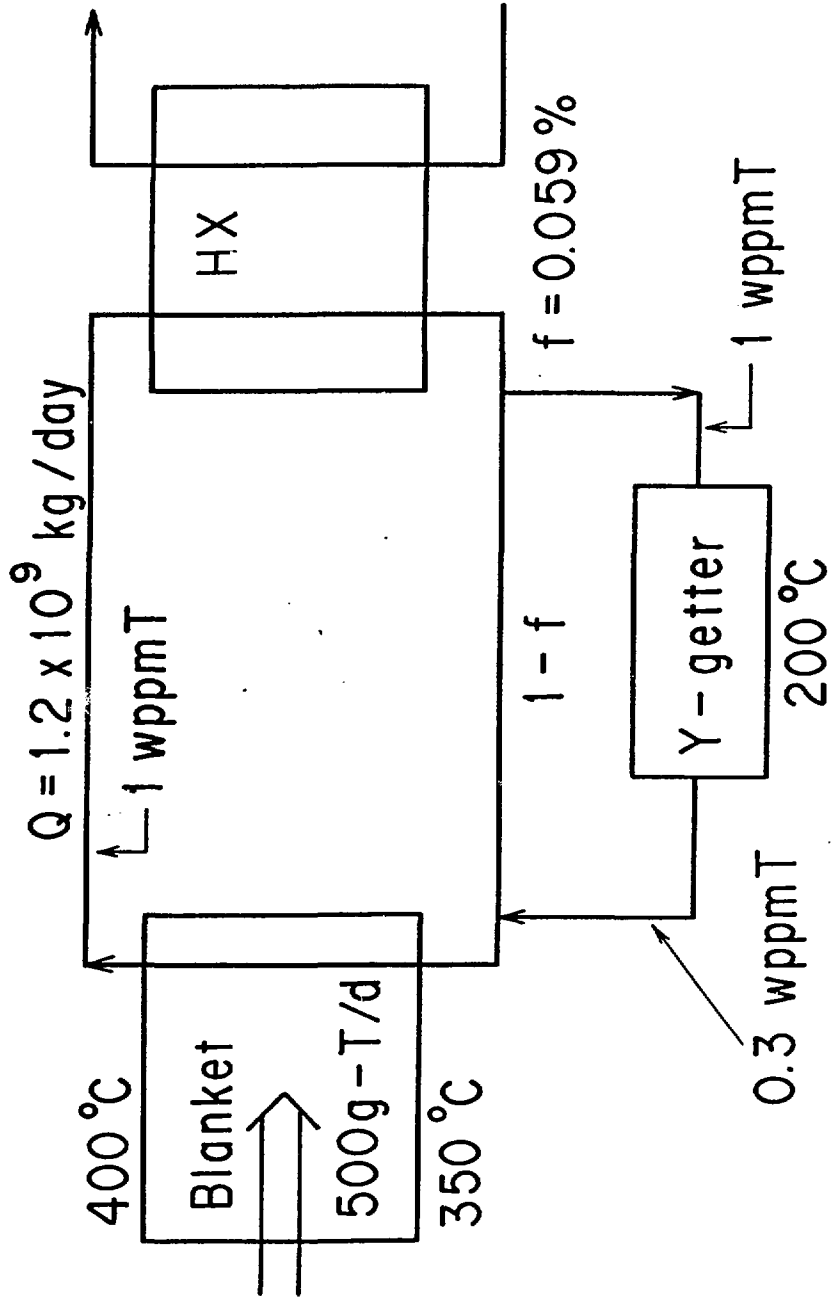


Figure 3

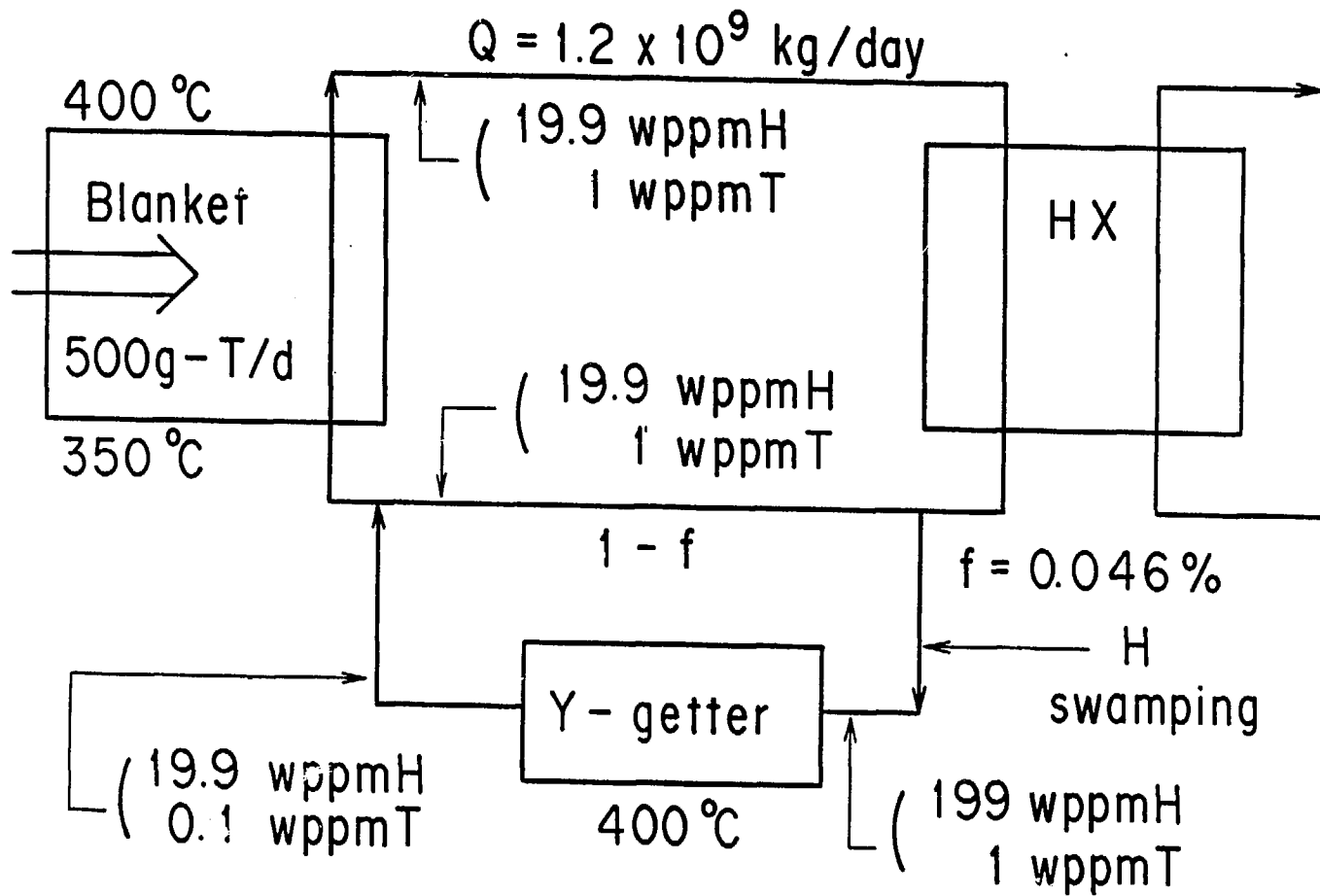


Figure 4

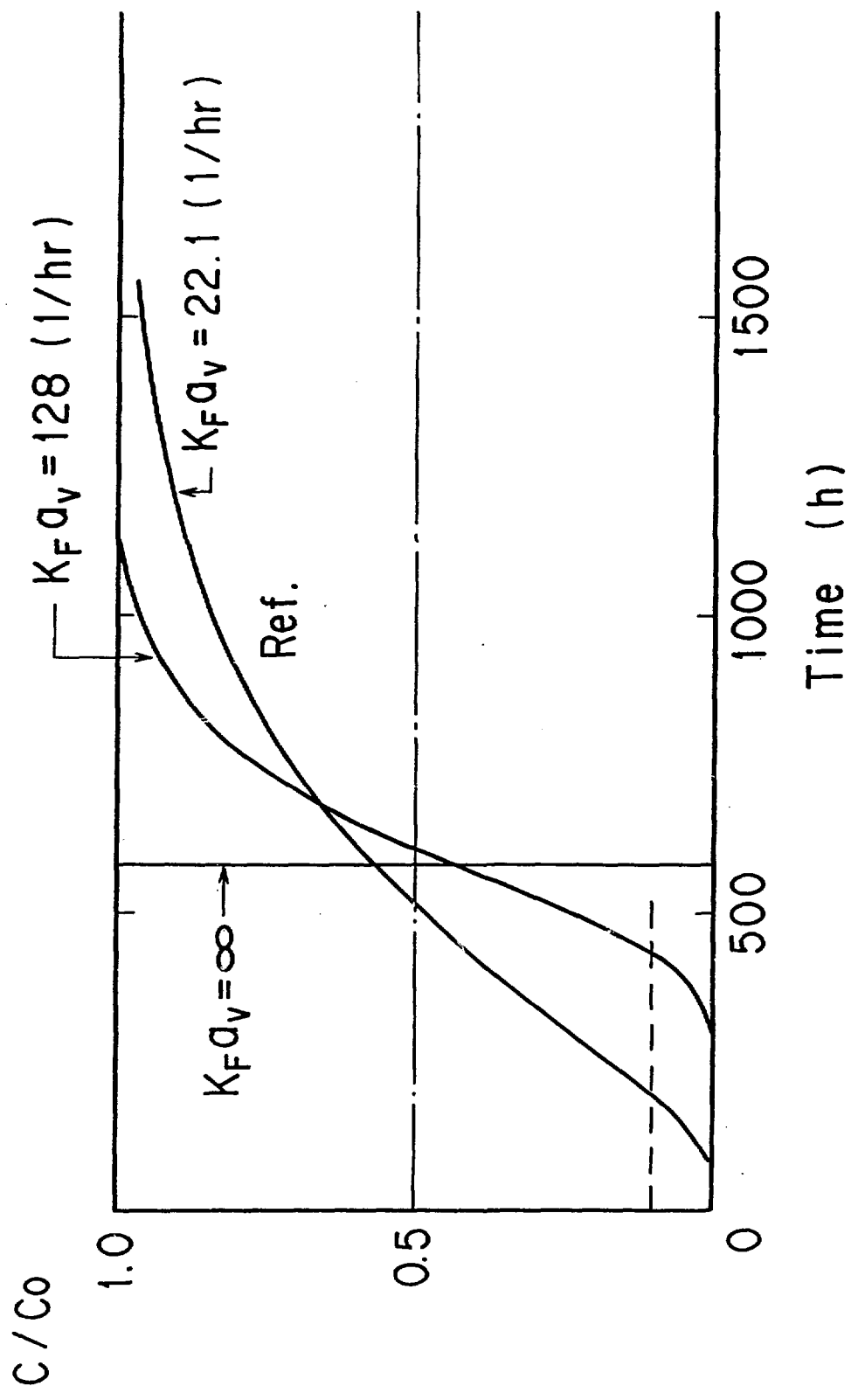


Figure 5 (D.K. Sze et al.)

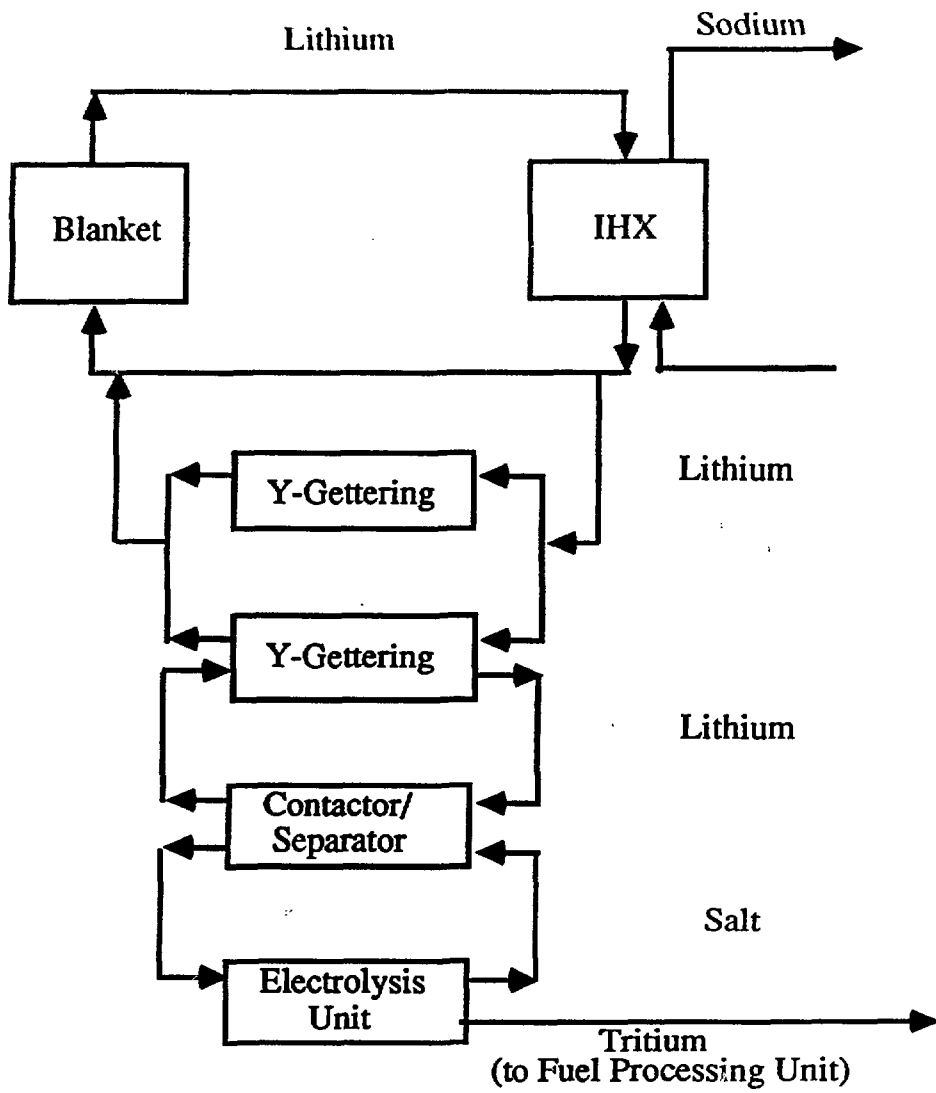


Figure 6
(Sze et al.)