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TRITIUM CONTROL IN HIGH-TEMPERATURE
FUSION REACTORS

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GENERIC PROBLEMS WITH Li_2O BREEDERS AND TRITIUM CONTROL IN HIGH-TEMPERATURE FUSION REACTORS

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Abstract

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Within the past year, major reactor design studies have been performed using Li_2O as a breeder material. These are the INTOR¹ and STARFIR / DEMO² projects. We in our studies on fusion/synfuels are embarking on another, but our blanket will operate at significantly higher temperatures than these two. Some of the problems inherent in using this material are aggravated and some are diminished by operating at higher temperatures. For the conditions of the above two design studies many of the problems we mentioned in the respective references. This report reviews the available data, the educated guesses about unavailable data, and the design options that have been and are being chosen. The review of this information is a needed part for our proposed use of Li_2O as a breeder in a fusion/synfuel reactor blanket. Further details will be available in various appropriate sections of our FY82 project report.

Description of INTOR

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The INTOR study was aimed at developing a large, relatively long lived tokamak reactor for physics and engineering experiments. It would burn tritium, and it was believed necessary to breed a significant fraction (60%) of that needed to operate the reactor. The breeding material temperature was tailored for that sole purpose. Power production was not a consideration. A schematic of the breeding zone is shown in Fig. 1. It is configured to allow a modest purge flow rate of He through the annulus and center of the cylindrical assembly. This He sweeps out the tritium that has been produced. It is separated and recovered outside the reactor. Because of the low coolant temperatures (100 °C), permeation of tritium through metal surfaces is considered to be negligible. The first choice breeder material is lithium meta silicate, with Li_2O as a backup. The breeder is a 70% dense porous ceramic.

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Description of STARFIRE/DEMO

The original STARFIRE design used lithium metasilicate as the breeding material. The follow-on workshop that developed the demonstration reactor switched to Li_2O . Because this would be a real power reactor, the temperatures are much higher than in the INTOR. Consequently, many of the problems associated with the use of Li_2O and large-scale tritium breeding were studied and discussed at length. A schematic of the breeding zone is given in Fig. 2 and other data of interest are presented in Table 1. A good effort was put forth to estimate the tritium inventory based on the steps required to remove tritium from the point at which it is bred. This was done at a variety of temperatures.

A rather narrow operating range was defined for Li_2O : 410 °C to 660 °C. The lower end of the range was set by the onset of LiOT separation as a separate phase in the breeder. Higher temperatures were judged to cause LiOT vaporization and to allow sintering to occur, particularly in a radiation field and with trace amounts of LiOH present. This was unacceptable. Sintering would produce lower porosity, possibly larger grains, and an increase in the tritium inventory. This breeder is produced in the form shown in Fig. 3. Very fine grains ($\sim 1 \mu$) are formed into clusters ($\sim 1 \text{ mm}$) and then consolidated to form a 70% dense breeder with a bimodal distribution of open porosity.

Table 1. STARFIRE/DEMO Li_2O Breeder Reference Design

Breeder	Li_2O (70% dense)
Breeder coolant	$\text{H}_2\text{O}(l)$ (260 °C inlet, 300 °C outlet)
Breeder coolant tubing	~ 316 stainless steel
Breeder sweep (T_2 recovery)	He (50 kPa), low velocity
Breeder temperature range	410 °C - 660 °C

Breeder temperature maintained by putting ceramic spacers on the coolant tube exteriors.

Lithium Hydroxide Formation in the Solid Phase

When water vapor contacts Li_2O , it is possible to form LiOH in the solid phase. The extent to which it forms depends on the temperature and partial pressure of water vapor. Based on experience with HTGR's, we should anticipate about 5×10^{-5} atm of water vapor to be present in the main helium coolant flow. Local concentrations in purge streams can be more than this. If LiOH forms, it can be present in three states in the solid phase. It can be dissolved uniformly (or nonuniformly if it is being bred), it can separate as a new solid phase, and it can separate as a liquid phase. The latter relationship is shown approximately in Fig. 4.³ This phase diagram fails to show the possibility of coexistence of Li_2O and LiOH at any temperature and water vapor partial pressure. If LiOH forms, the equilibrium amount dissolved in the Li_2O is shown in Fig. 5 for 5×10^{-5} atm H_2O .⁴

Water vapor can be present due to various kinds of leakage in the coolant systems. It can also be present because tritium breeding produces LiOT by transmutation which can dissociate to form water and Li_2O .

Ordinarily we would not expect LiOH to separate as a second solid phase. The configuration of the breeder material can have a major effect on this, however. If the H_2O in the clean helium is 5×10^{-5} atm (5 Pa) then according to Fig. 4, the LiOH should stay dissolved above 300°C . Without knowing the details of the porosity distribution, we cannot calculate the partial pressure of water in the gas that is in contact with the solid deep within the pores. Eventually concentration gradients will be established in the gas phase that remove T_2 and HTO (or T_2O) from the porous body at the same rate at which it is generated and released. The low end of the water partial pressure gradient will be 5 Pa. The high end of it may be from several Pascals to several hundred Pascals higher, if all the porosity is open.⁵ Again, Fig. 4 suggests that this is acceptable for temperatures above 450°C . The presence of closed porosity could probably cause separation of LiOH as a new phase, however.

Lithium Hydroxide Formation in the Gas Phase

At elevated temperatures, hydroxides typically are stable in the vapor

phase if a modest amount of water vapor is also present. These data for LiOH are given in Table 2. This phenomenon could be of concern if a substantial amount of LiOH was vaporized in a very hot part of the blanket and it was subsequently deposited elsewhere. The real question centers on the tolerable upper limit for a given reactor design.

Table 2. Volatilization of LiOH as Functions of Temperature and Partial Pressure of Water Vapor⁶

p_{LiOH} (atm) for various $p_{\text{H}_2\text{O}}$ (atm) and temperatures

T, K	$p_{\text{H}_2\text{O}}=10^{-7}$ atm	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}
900	5.817×10^{-10}	1.840×10^{-9}	5.817×10^{-9}	1.840×10^{-8}	5.817×10^{-8}	1.840×10^{-7}
1000	6.768×10^{-9}	2.140×10^{-8}	6.768×10^{-8}	2.140×10^{-7}	6.768×10^{-7}	2.140×10^{-6}
1100	4.989×10^{-8}	1.578×10^{-7}	4.989×10^{-7}	1.578×10^{-6}	4.989×10^{-6}	1.578×10^{-5}

Diffusion in Li₂O

The rate limiting step for removal of tritium from Li₂O is generally solid state diffusion. This is true even though great efforts are made to keep the diffusion distance in the solid short. For example, the lower temperature operating limit for Li₂O in the STARFIRE/DEMO study was set by the slow rate of removal of bred tritium from inside the grains to the grain surfaces. The grains are very tiny (i.e., ~ 1 micron) so the longest diffusion distance would be half a micron, and the mean diffusion distance would be only a quarter micron. A plot of diffusion coefficients as a function of temperature is given in Fig. 6.⁷ The first observation is that

a very large scatter exists between different investigators. The second is that even at high temperatures the diffusion coefficient may be as low as 10^{-11} cm²/sec. From these data, it is easy to appreciate the concern over sintering and grain growth that could occur. This is particularly true if total tritium inventory in the blanket becomes a design constraint. Some brief and concise insights into sintering were provided in one of our earlier studies.⁸

The disagreement between different investigators' results is so large, it is difficult to put believable bounds on tritium inventory. Extrapolating any of the data to other temperatures looks risky. We can at least assert that tritium inventory will increase rapidly with an increase in diffusion path length. Lower temperatures will decrease solid state diffusion rates and favor precipitation of LiOH as a separate phase.

During irradiation with neutrons, the breeder is in a nonequilibrium chemical situation. A neutron that reacts with a lithium atom forms T and He. Both of the new atoms have sufficient recoil energy to move them away from the lattice site at which they were formed. Viewed from afar, it looks as if we have simply converted Li₂O to LiOT. On an atomic scale, we have created a lithium vacancy in the lattice. The electrons that had been part of the lithium atom can remain associated with the vacancy or they can follow the newly formed particles or they can be knocked elsewhere in the crystal, at least temporarily. The new tritium atom and helium atom are probably initially present as interstitials. The attraction of the vacancy (assuming it's charged) for the new tritium atom (assuming it too is charged) is limited to several lattice parameters. The mean recoil distance is greater than a micron. Thus, combination to form LiOT will be diffusion limited.

It would be entirely possible for some of the tritium to escape from the crystal surface before it ever becomes chemically bound to form LiOT. the probability of a tritium atom combining to form LiOT increases as the number of tritium atoms being created increases. It also increases as the crystal size increases, and with increasing time. It decreases with increasing trap concentration.

This discussion leads to the conclusion that more than one diffusion mechanism participates in the release of tritium from lithium oxide. In an experiment with irradiated Li₂O, the observed release rate of T from the

Li_2O will depend on the flux and fluence of neutrons, the irradiation temperature, the particle size, and the temperature and duration of storage between the end of irradiation and the beginning of the outgassing experiment. This perhaps is a partial explanation for the differences in the reported data. Obviously, the most appropriate measurement would be on material prepared as it would be for a reactor, with the irradiation and tritium release being performed simultaneously at the reactor's proposed temperature.

Returning to the published data in Fig. 6, we can probably say that the diffusion coefficient at 400°C will be no less than $10^{-11} \text{ cm}^2/\text{s}$ and that at 1000°C it will be no less than the same number. *This is a pessimistic assumption, but is a fair representation of our knowledge.*

Something might also be said with regard to the fate of the helium formed at the same time as the tritium. Ionic crystals usually swell when exposed to a radiation environment. The swelling is due to the formation of internal voids, which in turn result from radiolysis of the crystal. Thus, swelling occurs with exposure to gamma rays when no alpha particles are formed. When alpha particles are formed, the voids can act as sinks for the bred helium. Compared to the other effects, this is considered to be of little consequence. Some of the helium escapes from the surface of the crystal before it diffuses to an internal void. Accumulated helium in the radiation-induced voids can exert high enough pressures to actually fracture the crystal. This would allow escape of helium to the grain boundaries, but more importantly it could shorten the diffusion distances for the tritium.

Tritium Permeation

At low temperatures, such as will be used in INTOR, permeability of tritium through common structural metals is low enough so permeation losses are of little concern. At modest operating temperatures as found in the STARFIRE/DEMO designs, permeation becomes an important consideration. Depending on the design details, it may become necessary to use intermediate heat exchangers and create permeation barriers of oxide films. Low permeability metals can be selected. Some oxide films are far less permeable

than others and it depends on the thickness and grain structure as well as its chemical composition. These matters have been discussed in some detail over the years, although little data is available.

At high temperatures, as in our present study for a synfuel blanket, no metals are sufficiently impermeable. It appears that some and perhaps all naturally occurring oxide films that form on common high temperature structural metals are too permeable. Special claddings and coatings, along with different breeding blanket processing strategies, will probably be required. At least two ceramic materials can be formed into polycrystalline bodies to have their hydrogen permeabilities measured. These are silicon carbide and alumina. They show remarkably low permeability at high temperatures and obey the equations.⁹

$$\text{Al}_2\text{O}_3 \quad P = 6.6 \exp\left(\frac{-53 \text{ kcal/mole}}{RT}\right) \frac{\text{std cc} \cdot \text{cm}}{\text{sec} \cdot \text{cm}^2 \cdot \text{atm}^{1/2}}$$

$$\text{SiC} \quad P = 3.36 \times 10^{-8} \exp\left(\frac{-93 \text{ kcal/mole}}{RT}\right) \frac{\text{std cc} \cdot \text{cm}}{\text{sec} \cdot \text{cm}^2 \cdot \text{atm}^{1/2}}$$

The suitability of these materials to act as tritium permeation barriers in a wide variety of MFE applications still needs to be demonstrated.

Synfuel Blanket Designs

A distinguishing feature of reactors designed for the production of synthetic fuels via thermochemical cycles is that they have relatively hot blankets (~850-1100 K coolants as compared with 750-800 K coolants). As used here, synfuel means hydrogen derived from water, and we recognize this is quite a restrictive definition. For such a process (assuming it's not electrolytic), high temperature heat is required. Peak blanket material temperatures can be as high as 1250 K.

One type of synfuel blankets with Li₂O breeder are the flowing micro-sphere designs. A ten-zone version is shown schematically in cross section in Fig. 7.⁸ The spheres move at various slow speeds around the plasma in their respective tubes and exit into a direct contact heat exchanger below. In this design, the speed of the microspheres is adjusted in each zone to allow them

all to exit at the same temperature of 1250 K. Although sodium is shown as the coolant fluid, high pressure helium was also a desirable design option.

Our two-zone blanket design used the flowing microspheres in the lower temperature inner region of the blanket.¹⁰ They still moved directly to a heat exchanger. Peak operating temperatures within the low temperature Li_2O region ranged from 850 to 950 K. Conceptually this part of the blanket is very similar to the ten-zone design. The high temperature zone provided helium at 1060 K.

Some problems are recognized with this approach. One is that all the bred tritium is expelled into the main coolant flow. This requires processing a few to several percent of the main coolant flow to extract the tritium. Another is that mechanical abrasion of the Li_2O microspheres is more likely to occur than if they were stationary. This deterioration in size and shape might be reduced by coating the friable ceramics with a tough ceramic. With this, however, comes the attendant problem of tritium removal. A strong coating such as SiC would not allow the bred tritium to escape.

At General Atomic Co., another synfuel blanket design was conceived, as shown in Fig. 8.¹¹ Helium is the coolant for both major heat removal streams, and the bred tritium is released into the lower temperature stream. The exact details of the lithium oxide configuration in terms of porosity and grain size were not given, but it was a massive porous ceramic body. Sintering was recognized as a potential problem and was one of the reasons for keeping the Li_2O at relatively low temperature.

A current design under development in our FY82 fusion/synfuel study is called the canister blanket. The Li_2O , in the form of small, hollow, cylindrical cartridges, is encapsulated in tubes, much as in the INTOR design. A small purge stream of He is used to remove the bred tritium from the canisters. Thus, most of the tritium is kept out of the main helium coolant stream. Some small fraction of the tritium gets into the helium coolant, but only a very small fraction (10^{-4}) of the mainflow needs to be processed to keep the tritium at acceptably low levels. The blanket material temperatures may be as high as 1100 K, so permeation barriers are needed on the canisters. Also, instead of trying to prevent sintering from occurring, we are deliberately forming Li_2O ceramic breeder elements at 90% of theoretical density.

Tritium Inventory

In view of what has already been said, if we allow high temperatures in our blanket, then grain growth and sintering can and probably will occur. If the constituent particles making up the Li_2O cartridge remained spherical, their steady-state inventory, I , would be given by⁷

$$I = \frac{G}{15} \frac{r^2}{D}$$

for the homogeneous boundary condition where G is the generation rate, r is the particle radius, and D is the solid-state diffusion coefficient. At one significant figure accuracy, $G = 2 \times 10^{-3} \text{ g/s-GW}_{\text{th}}$ (or $10^{-11} \text{ g/cm}^3 \cdot \text{sec}$). Take the view that $D = 10^{-10} \text{ cm}^2/\text{s}$ and that the grains grow to full density and 2 mm diameter with open porosity. Then the inventory per GW_{th} is 13 kg, but we have reason to hope it will be substantially less, perhaps by a factor of 100. Offsetting some of the anticipated reduction is the fact that the homogeneous boundary condition is incorrect. All this assumes that LiOH doesn't form as a separate phase.

Inventories of this size are large compared to what the fusion community has become accustomed to expect. They are not larger than the largest inventories suggested as possible in the STARFIRE report, however. Even with these inventories, the blanket is quite safe. In fact, the reason the inventories may be large is that it is very difficult to remove the tritium, and that makes it inherently safe. That is particularly true for the $\text{He-Li}_2\text{O}$ combination, where there is also no combustible material used as the breeder/coolant. Even with the larger tritium inventories, these reactor designs should be more socially acceptable than fission reactors. It is time to stop advertising fusion reactors as a nearly nonradioactive power source, for someday people will surely believe they were deliberately misled.

Conclusions

Good data are lacking on the phase relationships in the $\text{H}_2\text{O-LiOH-Li}_2\text{O}$ chemical system. Little is known about the solubility of LiOH in Li_2O . Nothing is known about the details of migration of bred tritium from within a

Li_2O grain to its surface. In this respect, the available data on apparent diffusion coefficients vary widely. There are no data on sintering of Li_2O in a radiation field with trace amounts of water vapor present.

Tritium inventories cannot be accurately predicted. This does not mean that Li_2O cannot be used successfully, however. The information that is lacking should be acquired. Questions on tritium inventory can then be based on acceptable doubling times. Arbitrary limits on total tritium inventory should be avoided because designing an attractive fusion power reactor is difficult enough without imposing artificial constraints.

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Fig. 1 Arrangement of solid breeder material in the INTOR. Helium-filled gaps are adjusted to maintain the breeder temperature.

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Fig. 2 Schematic diagram of STARFIRE blanket showing the arrangement of breeder, coolant, and helium for tritium purge.

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Fig. 3 Close-up view of the Li_2O breeder in the STARFIRE/DEMO design.

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Fig. 4 Phase diagram for $\text{H}_2\text{O}(\text{g}) - \text{LiOH} - \text{Li}_2\text{O}$.

Fig. 5 Preliminary results on the solubility of LiOH in Li₂O.

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Fig. 6 Diffusion coefficients of tritium in Li_2O by three investigators.

Fig. 7 Schematic diagram showing the ten-zone flowing microsphere blanket.

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Fig. 8 General Atomic syngas blanket module streams A and C are helium coolant but stream B is an oxygen-enriched helium purge for tritium control.