

SOLID BREEDER MATERIALS*

C. E. Johnson and R. G. Clemmer

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

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G. W. Hollenberg

Hanford Engineering Development Laboratory
P.O. Box 1970
Richland, Washington 99352

Increased attention is being given to the consideration of lithium-containing ceramic materials for use as breeder blankets in fusion devices. These materials, e.g., Li_2O , $\gamma\text{-LiAlO}_2$, Li_4SiO_4 , Li_2ZrO_3 , etc., are attractive because of their inherent safety advantages. At present, there is a broad scope of laboratory and irradiation activities in force to provide the requisite data enabling selection of the prime-candidate solid breeder material.

1. INTRODUCTION

The element lithium, in some form, appears to be the only material suitable for breeding tritium in a commercial fusion reactor. The status of breeder blanket technology was recently reviewed (1), and it appears that the most promising breeder materials are liquid lithium and certain solid lithium compounds. Because of their overall desirable properties, the lithium-containing ceramic-type solid breeder materials (e.g., Li_2O , $\gamma\text{-LiAlO}_2$, Li_4SiO_4 , Li_2SiO_3 , Li_2ZrO_3 , and Li_2TiO_3) have received increasing attention. The data base for liquid lithium is comparatively large and most of the breeder blanket feasibility issues, including tritium release, appear to be well defined. (2) The data base for the lithium-containing ceramics, the subject of a recent workshop (3), is not as large, but the inherent safety advantages of these materials provide strong incentives for consideration as candidate breeder materials. The goal of current solid breeder programs is to develop the data base for the candidate solid breeder materials so that appropriate breeder concepts can be developed. This paper will discuss the status of the candidate breeder materials with regard to the requisite materials properties and also give attention to efforts being made to improve the materials properties data base.

2. MATERIALS PROPERTIES REQUIREMENTS

The lithium compound selected for breeding tritium in a fusion reactor must satisfy many requirements. The candidate breeder material must possess desirable neutronic and irradiation characteristics, exhibit chemical stability at

operating temperatures, be compatible with other blanket and structural materials, and must breed and release tritium. Any compound selected will eventually release tritium at the rate at which it is formed; however, the release must be at a sufficiently high rate so that the tritium inventory is not excessive. Further, because of nuclear heating during tritium production, the temperature of the breeding material may greatly exceed the average temperature of the blanket and sintering take place. The required blanket performance criteria have been established by design studies such as STARFIRE (4), and these criteria translate to the materials properties listed in Table I.

Table I. Required Properties of Solid Breeder Materials

Neutronics
Thermochemical Properties
Physical Properties
Tritium Release
Compatibility
Radiation Effects
Fabrication

The status of the materials properties data base was the subject of a DOE-sponsored workshop. (3) It is not the purpose of this paper to reiterate the findings of that workshop; however, it can be said that the data base was and still is very limited.

3. DISCUSSION: MATERIALS PROPERTIES

3.1 Neutronics

At low neutron energies the major tritium (and heat) producing neutron reaction in lithium

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ceramics is associated with the ${}^6\text{Li}$ isotope:



In Figure 1 the cross section for this neutron capture reaction is presented as a function of neutron energy. Lithium-6 has a very high neutron capture cross section (3,000 barns) for thermal neutrons ($E \sim 10^{-1}$ to 10^{-2} eV). However, most (99%) of the thermal neutrons would even be absorbed in a 1-cm thick sheet of natural LiAlO_2 , which has a low ${}^6\text{Li}$ atom density.

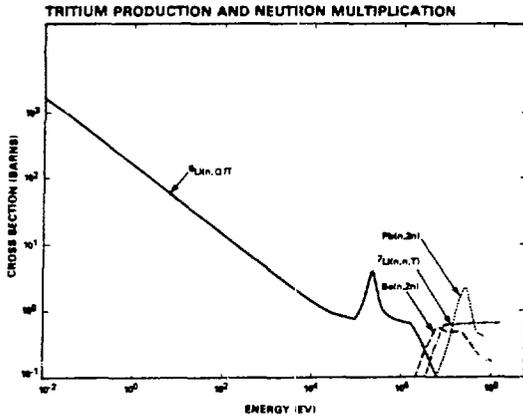


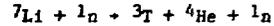
Figure 1: Tritium production and neutron multiplication.

Consequently, irradiation testing of lithium ceramics in thermal neutron reactors is complicated by self-shielding. Fast neutron fission reactors, *i.e.*, FFTF and EBR-II, present far less of a problem since the neutron capture cross section for lithium-6 is approximately 1 barn, which results in less than 10% self-shielding at 1 cm.

At the high neutron energies (14 MeV) found near the first wall of a fusion reactor, the neutron capture cross section of lithium-6 drops to less than 0.1 barn. This means that the direct capture of a 14 MeV neutron is very unlikely. What really happens is that, as the high energy neutrons are moderated by collisions with the first wall and blanket materials, their energy is reduced. These moderated neutrons are then available for neutron capture by lithium-6 atoms. Consequently, the ability of the first wall and blanket to moderate high energy neutrons is essential in determining the lithium-6 reaction rate. Neutron multipliers such as lead and beryllium not only moderate the 14 MeV neutrons, thereby yielding a softer spectrum, but also generate an additional neutron by the $(n, 2n)$ reaction.

Lithium-7 atoms possess a low but still significant cross section ($\sigma \sim 1$ barn) for neutron

energies greater than 5 MeV. Hence, direct



neutron capture by lithium-7 atoms yields not only a tritium atom but also a slower neutron which is immediately available for capture by lithium-6 atoms. In neutronics calculations on a model fusion blanket, Jung has reported (5) that the lithium-7 reaction is actually more important than the lithium-6 reaction in an Li_2O blanket without a neutron multiplier.

Of the solids being considered only Li_2O is potentially capable of attaining adequate breeding without a neutron multiplier; however, experimental verification is certainly required. It is recognized that tritium breeding optimization is strongly configuration dependent and thermal hydraulic factors and tritium recovery considerations may impose severe constraints.

3.2 Thermochemical Properties

Thermochemical properties data (*e.g.*, vapor pressure, phase equilibria, thermal stability, thermodynamics) are critically needed for objective evaluation of candidate breeder materials. Of the materials being considered only lithium oxide (Li_2O) has received significant attention, that being due to its high lithium atom density and potential for breeding without the aid of a neutron multiplier. A major question regarding the viability of Li_2O relates to its thermodynamic equilibria with T_2O and its impact on tritium inventory. Equilibrium tritium concentrations in candidate solid breeder materials for a T_2O partial pressure of 1.3 Pa (10^{-2} torr) were calculated from available thermodynamic data and are presented in Figure 2.

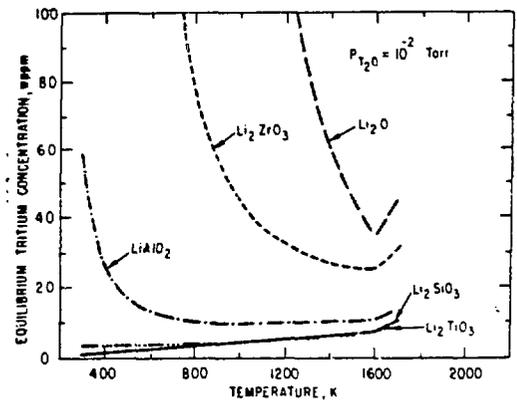


Figure 2: Calculated equilibrium tritium concentrations in candidate solid breeding materials at $P_{\text{T}_2\text{O}} = 1.3 \text{ Pa}$.

The calculations indicate that tritium dissolution in Li_2O is unacceptably high for

temperatures of interest, leading to high tritium inventory and uncertainty. All of the ternary oxides appear to have significantly lower tritium "solubilities" and, with the possible exception of Li_2ZrO_3 , have levels of 10 wppm or less (10 wppm corresponds to a ~ 1 kg inventory). The thermodynamic data base for the $\text{Li}_2\text{O-LiOH-H}_2\text{O}$ system is not well established but is receiving increasing attention.(6,7) Most recent information suggests a much lower T_2O solubility in Li_2O than shown in Figure 2. However, increasing volatility was observed for increasing moisture content of the gas phase passing over solid lithia.(7,8)

With the exception of lithium aluminate (LiAlO_2) there is a paucity of thermochemical data for the ternary ceramic oxides. Of critical importance to these materials is their stability as lithium deficient solids. Presently, there are two irradiation experiments and out-of-pile mass spectrometry studies which give attention to this issue.

3.3 Physical Properties

The lithium-containing ceramic breeder materials are characterized by high melting point and high lithium atom density. However, the performance of the solid breeder will be strongly affected by its thermal conductivity and sintering characteristics. It is the in-reactor thermal performance of the candidate material that largely determines the ultimate blanket design. Since ceramic materials characteristically exhibit low thermal conductivity, any degradation in this parameter during irradiation would have a severe impact on the solid breeder performance.

The sintering characteristics of the candidate breeding materials have received only very limited investigation. In general, the thermal sintering characteristics of stable oxides are quite similar. Temperatures in excess of $0.8 T_m$ (the absolute melting point) are required before significant sintering occurs. However, neutron radiation typically enhances the sintering characteristics and lowers the temperatures at which sintering is observed. The effects of radiation are expected to reduce the sintering temperature to $0.6 T_m$.(4)

Sintering and grain growth are phenomena that could significantly affect the restructuring of the lithium ceramics. In Table II preliminary experimental data of sintering temperatures for $\sim 0.85 T_m$ material is compared with calculations using the $0.6 T_m$ postulate. It should be noted that the experimental results indicate that temperatures above 850°C are required to induce densification which might cause closed porosity. Irradiation damage could cause enhanced diffusion and a reduction in the sintering temperature, but inferences from materials other than those of Table II must be made cautiously. For instance, in fission reactor fuel steep temperature gradients ($\Delta T > 1000^\circ\text{C}/\text{cm}$) can cause porosity to

migrate from the colder circumference into the central core with a greater driving force than surface tension alone. Under these conditions sintering occurs at ~ 0.6 of T_m .

Table II. Sintering of Lithium Ceramics

Material	Sintering Temperature ($^\circ\text{C}$)		Melting Point ($^\circ\text{C}$)
	Observed ^a	Calculated ^b	
Li_2O	1050	750	1427
Li_2ZrO_3	1350	860	1615
LiAlO_2	1200	855	1610
Li_2TlO_3	1350	820	1550
Li_4SiO_4	850	670	1300

^aPreliminary data (9) for sintering of $\sim 0.85 T_m$ material.

^bCalculated on basis of $0.6 T_m$.

3.4 Tritium Release

Tritium release in the solid breeder blanket will depend upon kinetic, thermodynamic, and structural factors. In a recent design study (4) tritium generated in the solid breeder material is removed by a low pressure helium purge that circulates through the pores of the ceramic. The tritium is considered to be removed by the following recovery mechanisms:

- bulk diffusion in the grain
- desorption of T_2O at the grain surface
- migration through interconnected grain boundary porosity to the particle surface
- percolation through the porosity of the packed breeder bed
- convective mass transfer out of the blanket into the processing stream

The tritium inventory in the breeder material will be determined both by diffusion rates and thermodynamic constraints. The tritium inventory is predicted to possess a very strong temperature dependence and is predicted to be extremely sensitive to the diffusion path length. Hence, it is not surprising that some analyses conclude that some solids will have very low tritium inventories, while others conclude that these same solids may have very high inventories. Further, it is noted that the solid breeder material must maintain interconnected porosity and small grain size ($\sim 1 \mu\text{m}$) throughout its irradiation history to enable maximum tritium recovery.

Bulk diffusion is considered to be a significant contributor to the tritium inventory. For spherical particles of radius r , assuming zero surface concentration, the tritium inventory I is given by

$$I = (1/15) \dot{i} r^2/D \quad (1)$$

where \dot{i} = the tritium generation rate and D = diffusivity. It is very significant that the tritium inventory is a function of the square of the particle size. Clearly, small ($\sim 1 \mu$) grain sizes are required for minimum tritium inventory, and the grains must not enlarge significantly during the lifetime of a reactor blanket. While diffusivity values for hydrogen have been measured for many solids, there is a rather large uncertainty for what the correct values for tritium in solid breeders will be. Kinetic experiments of postirradiation tritium release from several candidate solid breeders have been performed. In these experiments, the kinetics are non-steady state and the diffusivity D is given by:

$$D = 0.16 r^2/\tau \quad (2)$$

where τ is the mean residence time defined as the time required to extract 87.4% of the tritium.(10)

Because the grains in experiments are often very small ($\sim 1 \mu$), non-spherical, and non-uniform, it is very difficult to determine r and, therefore, D in Eq. (2). However, Eqs. (1) and (2) can be combined, yielding:

$$I = 0.5 \dot{i} \tau \quad (3)$$

Since τ is readily measured, one can estimate the diffusive inventory in a blanket, provided the particle microstructure in the blanket corresponds to that in the experiments. The tritium generation rate per GWth, assuming a breeding ratio of 1.2 and 20 MeV/fusion, is 1.87×10^{-3} g/s. Substitution into Eq. (3) yields

$$I = 3.3 \cdot \tau(h) \quad (4)$$

where I = the diffusive tritium inventory in grams per GWth and $\tau(h)$ = the mean residence time determined in postirradiation annealing experiments. Calculations from the above model show a temperature dependence which is consistent with a diffusion-controlled process.

The gas-phase mass transfer mechanisms (steps b to e) are not quantitatively understood at this time, although fission gas models of this form have been used successfully.(4) Experiments performed to date, in which tritium is removed after neutron irradiation of a solid breeder, do not permit delineation of the importance of these steps. The TRIO experiment, wherein tritium is dynamically recovered during irradiation, should significantly enhance our understanding of the tritium release phenomenology.

3.5 Compatibility

The chemical compatibility of the candidate material with structural materials is an important consideration. During breeding T_2O will form and, in combination with the solid breeder,

could present a very corrosive environment. In the case of Li_2O one would expect $LiOT$ to form. Once formed, the $LiOT$ will contribute species to the vapor phase, altering its characteristics. Depending on the solubility of $LiOT$ in Li_2O , single-phase liquid $LiOT$ may form in the blanket and result in an extremely corrosive environment. Studies of the compatibility between candidate breeder materials and structural materials have received little attention. What data are available suffer from two important deficiencies: poorly characterized candidate breeder materials and no experiments simulating an amount of T_2O characteristic of what one might expect in reactor under steady-state conditions. Recent research on this topic is reported in other papers (11).

3.6 Radiation Effects

The irradiation performance of candidate breeder materials has received little or no attention. While in reactor, the materials will be subjected to high temperatures explicitly testing their chemical and physical stability. In addition, the neutron environment is likely to change the breeder materials characteristics. The neutron capture reaction $n^1 + Li^6 \rightarrow T^3 + He^4$ produces significant lattice damage during irradiation. Not only are two large gas atoms produced, one of which is not expected to be soluble in the parent material, but also a lithium vacancy is produced. Several plausible radiation damage mechanisms are listed in Table III. How these atomistic changes are manifested in microstructural damage (i.e., helium bubbles, dislocation loops, or crystallographic transformations) can only be evaluated during irradiation.

Table III. Radiation Effects in Solid Breeders

<u>Displacement Damage</u>
Vacancies
Loops, Clusters, etc.
Interstitials
<u>Reaction Products</u>
Bubbles
Interstitials
Substitutional Defects
<u>Lithium Depletion</u>
Vacancies
Oxygen Excess
Nonstoichiometry
<u>Microstructural</u>
Sintering
Grain Growth
Microcracking

In metals, displacement damage by neutrons is of considerable concern. Each elemental atom possesses its own particular nuclear cross section for "direct-knock-on." After a "direct-knock-on," an atom (or ion) cascades through the lattice normal positions. If the displaced atoms are lost from the crystal, then a vacancy is created. If the displaced atoms are deposited into interstitial positions, then Frenkel defect pairs are created. In lithium ceramics, however, there are a minimum of two sublattices composed of anions and cations. Creation of more defects on one sublattice than the other, for instance on the oxygen lattice, would lead to charge separation within the matrix.

If sufficient defect mobility exists, the newly formed defects can annihilate or cluster, hence forming voids or precipitates within the crystal. The displacement damage to the lattice is measured by a computed value called displacements per atom, dpa. In actual blanket application, solid breeder materials will receive substantial displacement damage from the very high energy neutrons of the plasma. Lower energy neutrons, like those predominant in a fission reactor, will produce much less displacement damage.

Helium and tritium will be generated in the solid breeder material during irradiation. If present design postulates are realized, almost all of the tritium will migrate out of the solid breeder material. In such a case, irradiation effects by tritium would appear minimal. Tritium ions in the matrix could substitute for the lithium vacancies left after neutron captures, hence making chemical trapping in the matrix likely. However, owing to its inert character, helium will have a much lower solubility in these ceramics than tritium, since only interstitial positions are available. This impacts its damage potential in two ways. First, the lower solubility for helium will result in a lower permeability so that the rate of migration out of the lattice will be less. Secondly, this low solubility will enhance bubble formation. In other materials, inert gasses form bubbles extensively: helium in B_4C (12) and xenon and krypton in fission reactor fuel. (13)

A consequence of the neutron capture process would be the loss of lithium atoms from the lattice. This loss creates either a lithium vacancy or a localized excess of oxygen, *i.e.*, oxygen interstitials. Since tritium ions are created during the neutron capture of a lithium ion, the overall electrostatic equilibrium of the crystal is maintained. When the tritium ions are subsequently released to the cover gas, it necessarily follows that the oxygen ions must also be released in order to avoid a charge buildup in a single valency system. If multivalent ions (Fe^{+2} , Fe^{+3}) were present, then a change in oxidation states would balance the charge of the excess oxygen. In the Li_2O system the observation that tritium is released as T_2O ,

rather than a hydrocarbon or T_2 , during post-irradiation annealing appears logical if not obvious. (10)

If lithium depletion occurs to a significant extent, *i.e.*, $\approx 5\%$, the resultant nonstoichiometry in the ternary lithium oxides ($Li_xM_yO_z$) could establish a multiphase rather than single-phase condition. For instance, if stoichiometric Li_4SiO_4 were irradiated, then lithium neutron captures would cause an excess of silica. An examination of the Li_2O-SiO_2 phase diagram reveals that the incipient melting point would be reduced from $1300^\circ C$ to a eutectic temperature of $1024^\circ C$. Similarly, in other systems lithium depletion and the nonstoichiometry that is produced will bring about phase changes during irradiation.

3.7 Fabrication

In selecting a solid breeder fabrication method, one must take into consideration the need for a tailored microstructure to facilitate tritium release, the need for purge channels within the breeding material, all within the complexity of blanket assembly design. A low density material having a fine grain size ($<1 \mu m$) and a bimodal pore distribution [*i.e.*, small grain size and fine porosity within particles that are fairly coarse ($\approx 1 mm$) with a much coarser porosity between the particles] is believed to be the most desirable microstructure. Potential methods for fabrication of the candidate breeder material into blanket modules include sintered blocks, vibratory compaction, and slip casting. Development work has shown that lithium aluminate ($LiAlO_2$) can be fabricated with a bimodal pore distribution. (14)

Integral to the fabrication of blanket modules is the preparation of starting material. Techniques have been developed for the preparation of Li_2O and the ternary ceramic oxides from Li_2CO_3 and the metal oxide precursor. These techniques are discussed in two other presentations (15-17) at this conference.

4. RESEARCH FOCUS

Recent fusion reactor conceptual designs have highlighted the potential for lithium-containing ceramic materials being selected as candidate breeding materials. These design studies have identified the need for a more detailed data base from which selection can be made. The near-term data needs are most pressing if we are to be in a position to select the candidate material for further development. The recognition of an inadequate data base has stimulated a diversified effort involving thermochemical and thermophysical properties studies to improve our present position. Complimentary to this laboratory effort is the initiation of irradiation experiments to enlarge our experience on the behavior of candidate materials in a neutron environment. Recently (3), General Atomics

encapsulated four materials (Li_7Pb_2 , Li_4SiO_4 , LiAlO_2 , Li_2O) for study in the Oak Ridge Reactor (ORR). The irradiation phase of this work is now complete and the postirradiation examination of these materials is soon to be initiated. The DOE/OFE is sponsoring two irradiation experiments that are to commence in about October 1981. One experiment (TRIO) will be carried out in ORR and is to be a dynamic study of tritium recovery from $\gamma\text{-LiAlO}_2$. The other is a scoping study of the four most promising materials (Li_2O , $\gamma\text{-LiAlO}_2$, Li_4SiO_4 , and Li_2ZrO_3) and is to be carried out in EBR-II. This latter study is significant in that it will be the first time these candidate materials will be exposed to a neutron environment prototypical of that expected in a fusion reactor.

The activities covering thermochemical and thermophysical properties needs are too numerous to list. The single most concentrated effort is that of the Japanese (6) on Li_2O . These latter studies are extremely important in that Li_2O is a key compound in the makeup of the ternary ceramic oxides.

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