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ASSESSMENT OF SOLID BREEDING BLANKET OPTIONS FOR COMMERCIAL TOKAMAK REACTORS

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by

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ASSESSMENT OF SOLID BREEDING BLANKET OPTIONS FOR COMMERCIAL TOKAMAK REACTORS*

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Summary

This study examines the materials and design implications regarding the use of solid breeding materials with respect to compatibility with structure and coolant, tritium processing, chemical and radiation stability and thermal-hydraulics. Four solid breeding materials considered, viz., Li_7Pb_2, Li_2O, Li_2SiO_3 and $LiAlO_2$, are representative of the metallic and ceramic compounds available. The major design problems regarding the use of solid breeding materials relate to the limited range of operating temperatures acceptable for tritium release and chemical stability or compatibility. The allowable ranges of breeder temperatures for which in-situ tritium recovery is potentially viable are evaluated for the candidate breeding materials.

Introduction

Lithium in some form appears to be the only material suitable for breeding tritium in a commercial fusion reactor. In addition to liquid lithium, several solid lithium compounds are potentially viable tritium breeding materials. Of the relatively large number of stable lithium compounds, three types of lithium compounds are the most promising. These include the metallic compound Li_7Pb_2, lithium oxide (Li_2O), and the complex oxides Li_2SiO_3 and $LiAlO_2$. Although other compounds have been proposed, the compounds listed here are the favored compounds of each type. For example, LiAl is similar to Li_7Pb_2 in many respects, however, Li_7Pb_2 provides superior breeding capability because of the neutron multiplication of the lead and is the favored compound of this type. Lithium oxide is unique because of its high lithium atom density and higher melting temperature compared to compounds such as Li_2Si and Li_2C_2. The Li_2SiO_3 and $LiAlO_2$ generally provide a better combination of high temperature stability and high lithium atom density compared to other complex compounds.

The critical properties of these primary candidate breeding materials are summarized and their viability for tritium breeding in a commercial tokamak reactor blanket is assessed in this paper. Aspects considered include physical properties, neutronics properties, chemical stability and compatibility and tritium release characteristics.

Physical Properties

Key physical properties of the primary candidate breeding materials are summarized in Table 1. Also shown for comparison are the corresponding properties for liquid lithium. Of the solid breeding materials considered, Li_7Pb_2 has the lowest melting temperature, and hence, the lowest maximum operating temperature. This compound also has a significantly higher density than the ceramics. The unique feature of Li_2O is the high lithium-atom density. However, as will be discussed in more detail later, the effective density of Li_2O and the other ceramics will be reduced because of tritium release requirements. Thermal conductivity is an important property, however, the data for these compounds are very limited. The value for Li_7Pb_2 is estimated from data for similar types of compounds. Figure 1 summarizes available data for Li_2O[1] at two densities. Since no data were found for Li_2SiO_3 and $LiAlO_2$, data for other silicates and aluminates are shown.[2] In the present analyses, the thermal conductivities of the two complex oxides are assumed to be similar to that of Li_2O. As indicated by the results, the thermal conductivity is significantly affected by the density and, in general, is quite low for these ceramics.

Neutronics Properties

Two neutronics characteristics of the solid breeding materials have been evaluated, viz., breeding capability and long-lived activation products. Since the breeding capability or breeding ratio is sensitive to the specific design details, only a general assessment is presented here. The Li_7Pb_2 possesses very good breeding characteristics because of the neutron multiplication provided by the lead. The Li_2O has an inherently high lithium atom density; however, this advantage is somewhat reduced since the actual material used may contain ~ 20% porosity. Also, the effective breeding capability of the ceramics is impacted by the relatively high structural material fraction required because of the low thermal conductivity. It is generally concluded that Li_2SiO_3 and $LiAlO_2$ will require a neutron multiplier to obtain adequate breeding because of the parasitic absorption of the other elements present.

Of the candidate breeding materials, only ^{205}Pb from Li_7Pb_2 and ^{26}Al from $LiAlO_2$ present long-term activation problems unless significant amounts of impurities are present.

Chemical Stability and Compatibility

The chemical stability and compatibility of the solid compounds in the reactor environment are important considerations in the selection of the most viable options. Water and helium are the prime candidate coolants for use with solid breeding materials since lithium would most likely be used as the breeding material if it were selected as the coolant. The major consideration regarding a water-cooled blanket relates to the fact that all of the candidate breeding materials react to some degree with H_2O.

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Table 1. Summary of Properties of Candidate Breeding Materials

	Lithium	Li_7Pb_2	Li_2O	Li_2SiO_3	$LiAlO_2$
Physical and Chemical Properties					
Melting point, °K	453	999	1970	1470	1880
Density, g/cm³	0.51	4.59	2.01	2.52	2.60
Li atom density, g/cm³	0.51	0.49	0.93	0.36	0.27
Thermal cond. W/m-°K	∿ 50	∿ 20	∿ 3	∿ 3	∿ 3
Stability	Significant vapor pressure above 600°C	Reduced solidus if not stoichiometric	Significant vapor pressure above 1200°C (sublimes)	Reduced solidus (∿ 1025) if not stoichiometric	
Chemical Compatibility					
Helium coolant	Oxidizes	Oxidizes	impurity interactions		
Water coolant	Very reactive → H_2	Very reactive → H_2	Reacts → LiOH	Soluble - hot water	Soluble - hot water
Air (elevated temperature)	Very reactive	Very reactive	Reacts	Hygroscopic	Hygroscopic
Neutronics					
Breeding	Very good	Very good	Good	Requires neutron multiplier	Requires neutron multiplier
Activation	No long term	^{205}Pb	No long term	No long term	^{26}Al
Radiation Effects					
Tritium breeding	Helium generation	Changes stoichiometry	Forms LiOT	Changes stoichiometry	Changes stoichiometry
		Lowers solidus temperature		Lower solidus temperature	
		Helium production may cause swelling and T-retention		Phase instability	Phase instability
Neutron damage	None	Swelling/densification (?)	Swelling/densification (?)	Swelling/densification (?)	Swelling/densification (?)
		Reduced T-release	Reduced T-release	Reduced T-release	Reduced T-release
		Enhanced sintering	Enhanced sintering	Enhanced sintering	Enhanced sintering

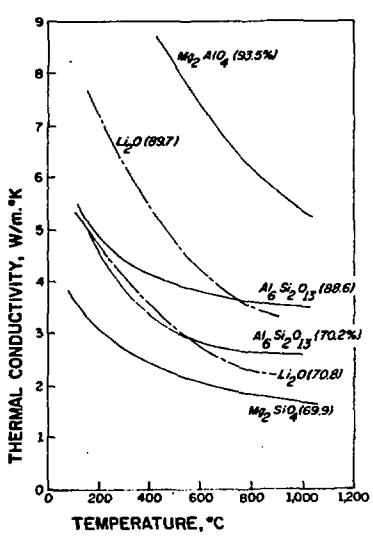

Fig. 1. Thermal conductivities of oxides with effective densities given in parentheses.

The following hydrolysis reactions will occur on contact of water with Li_7Pb_2 and Li_2O.

$$1/7\ Li_7Pb_2 + H_2O \rightarrow LiOH + 1/2\ H_2 + 2/7\ Pb$$

$$\Delta H_{hyd}(298°K) = -47.9\ \text{Kcal/mole}$$

$$1/2\ Li_2O + 1/2\ H_2O \rightarrow LiOH$$

$$\Delta H_{hyd}(298°K) = -15.4\ \text{Kcal/mole}$$

Both of these compounds react exothermically with water to form LiOH which has a melting temperature of 470°C. Since liquid LiOH is extremely corrosive to nearly all structural materials, the integrity of the structure would be severely degraded in the event of a reaction that forms LiOH. In addition, hydrogen formed in the reaction of H_2O with Li_7Pb_2 presents a safety problem which probably eliminates this system as a viable blanket option. The reaction of Li_2O with water is considerably less exothermic and, since hydrogen is not evolved, this reaction does not pose a major safety problem. As shown in Fig. 2, the free energy of the Li_2O reaction decreases to zero at ∿ 1200°K, which indicates that the reaction should stop as the

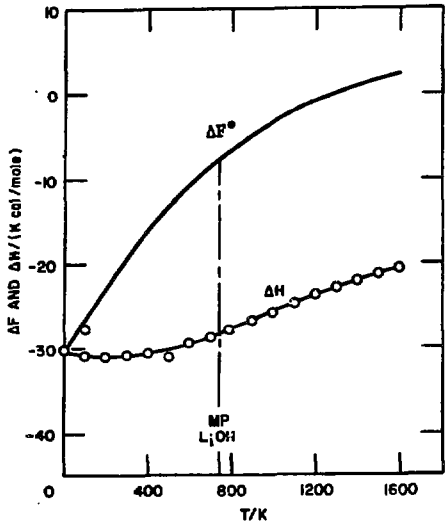

Fig. 2. Thermodynamics of the reaction Li_2O (C) + H_2O (g) ⇄ 2 LiOH (C or ℓ)

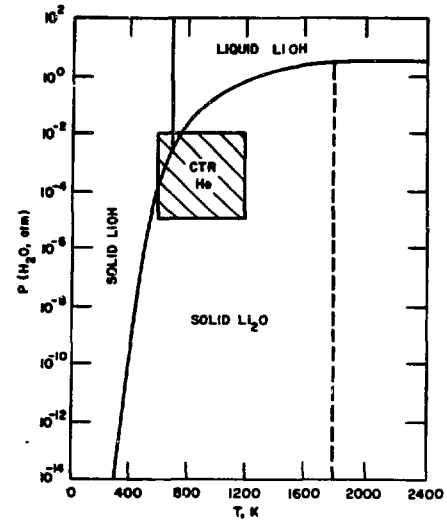

Fig. 3. Calculated Li_2O/LiOH phase equilibria as a function of P_{H_2O} and temperature.

temperature is increased. The reactions of H_2O with Li_2SiO_3 and $LiAlO_2$ are even less severe. The Li_2SiO_3 will decompose in hot water and probably form some hydroxide. Although data are limited, $LiAlO_2$ appears to be more stable than the silicate.

Although helium is chemically inert to the candidate breeding materials, trace impurities typical of large heat-transport systems can react. The Li_7Pb_2 will react with minute levels of oxygen in helium to form an oxide film that will inhibit tritium release. Subsequent changes in stoichiometry of the breeding material caused by oxidation of the lithium will lower the melting temperature of the system.

Under certain conditions, trace amounts of water vapor in helium will react with Li_2O to form solid or liquid LiOH. Figure 3 is a plot of the calculated Li_2O/LiOH phase equilibria as a function of P_{H_2O} and temperature. The shaded region indicates the conditions anticipated in a fusion reactor environment. At the lower temperatures and higher water-vapor pressures, formation of LiOH is predicted. Further calculations indicate that the vapor pressure of LiOH over Li_2O is significant at temperatures of > 1000°K if water vapor is present. Experimental results in Table 2, which were reported by A. Johnson, et al.,[3] tend to support the calculations. These results show significant weight losses of Li_2O when exposed to 1270°K to low water-vapor pressures. At water-vapor pressures required to maintain low tritium pressures, i.e., 0.01 to 1 Pa, the weight losses are excessive and direct contact of helium coolant with Li_2O is not considered acceptable at the higher temperatures. Although Li_2SiO_3 and $LiAlO_2$ are less susceptible to this reaction, the present data base is insufficient for a reliable evaluation of the problem.

The data are also very limited on the compatibility of the candidate solid breeding materials with potential structure or cladding materials. Recent

Table 2. Weight Loss of Li_2O Exposed at 1000°C to Low Water-Vapor Pressures

P_{H_2O} Pa	Exposure Time hours	Weight Loss %
Evacuation	2.5	3.3
10^{-6}	2	3.2
10^{-2}	2.5	6.4
10^{0}	2.0	12.4
10^{2}	0.5	18.4

data[4] on the compatibility of Li_2O with Fe-Ni-Cr alloys are given in Fig. 4. These corrosion rates are much higher than typical corrosion rates of stainless steel in reactor grade sodium and are probably excessive at temperatures above ∿ 500°C. Another corrosion problem of concern relates to the formation of LiOH as discussed above or LiOT from the breeding reaction. The LiOH is highly corrosive to most structural materials and could present problems in the heat transport or tritium processing circuits.

Tritium Release from Solid Breeding Materials

For solid breeders, tritium most likely will be recovered as T_2O from a helium purge stream by sorption on molecular sieves. The tritium inventory in the solid breeder will be determined by both diffusion rates and thermodynamic constraints.

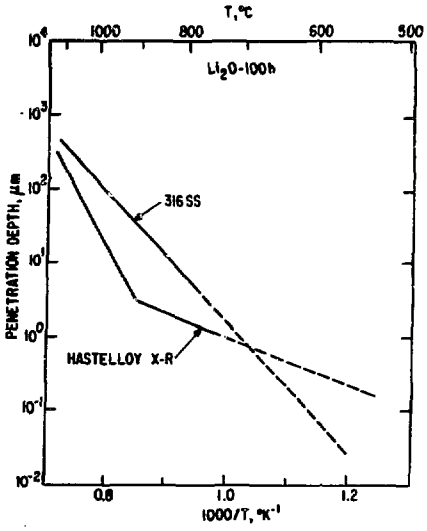

Fig. 4. Corrosion of structural alloys exposed to Li_2O for 100 h.

Diffusion Considerations

In a fusion blanket, the tritium concentration in the solid breeder will build up until the rate of diffusion out of the solid is equal to the tritium generation rate, and steady state is achieved. For infinite slab geometry with zero surface concentration, the steady state relationship is described by

$$I = \frac{1}{3}\,\dot{I}\,\frac{r^2}{D} \qquad (1)$$

where I = tritium inventory (g),

$\dot{I}$ = tritium generation rate (g/s),

r = half-thickness of the slab, and

D = diffusivity.

In typical experiments,[5] when diffusion rates are measured by first irradiating the sample and then heating to remove tritium, the diffusion kinetics are not steady state. The steady state diffusivity, which will give a conservative estimate of the tritium inventory, is given by

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

where τ = mean residence time for tritium in solid, i.e., the time to extract 87.4% of the tritium.

In the experiments, τ can be readily measured; but, it is much more difficult to determine r, and therefore, D. However, assuming the r in the experiments is representative of material in a reactor blanket, equations (1) and (2) can be combined to eliminate r and D. The tritium inventory is then given by

$$I = 5\,\dot{I}\,\tau \quad . \qquad (3)$$

For a 1000 MWth reactor (steady state) at 20 MeV/fusion and a breeding ratio of 1.20, the tritium generation rate ($\dot{I}$) is 1.87×10^{-3} g/s. If τ is expressed in hours, then

$$I(g) = 33.6 \cdot \tau(h) \qquad (4)$$

Using this relationship, the calculated tritium inventories for candidate solid breeders are shown in Fig. 5. In view of the very strong temperature dependence and the fact that the inventory is extremely sensitive to the diffusion path length r ($I \propto r^2$), it is not surprising that some analyses conclude that solids will have very low tritium inventories, while others conclude that solids may have very high inventories.

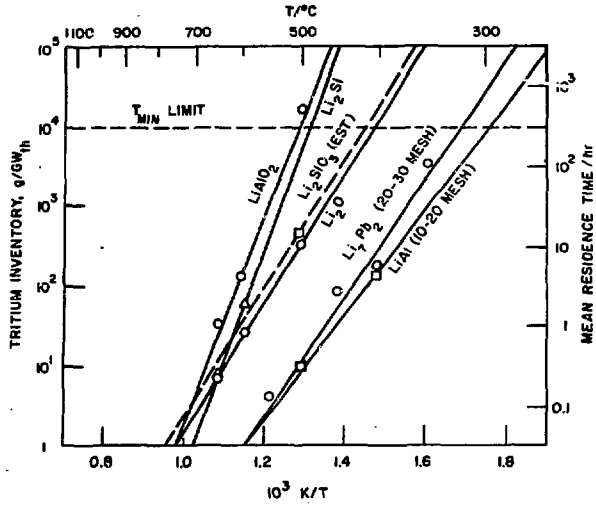

Fig. 5. Predicted tritium inventory in candidate solid breeding materials (20 mesh) as a function of temperature after low-fluence irradiation.

The design solution to this dilemma is proper temperature control. The minimum temperature must be sufficiently high that tritium will diffuse out at an adequate rate, and the maximum temperature must not permit excessive agglomeration and sintering, which could increase the diffusion path length and thereby reduce diffusion rates. It is suggested that, as a design criterion, the inventory of any 5% of the blanket not exceed 500 g per GWth. Therefore, on the basis of thermal diffusion, not more than 5% of the blanket can be below the minimum temperatures indicated in Fig. 5. These minimum temperatures are given in Table 3 for the same breeding materials. Increases in particle size caused by thermal sintering will tend to inhibit tritium release. Estimated temperatures below which thermal sintering will not be important are given in Table 3. Wiswall[5] performed prolonged heat treatments on several materials at 80- to 90% of the absolute melting temperature and observed only limited structural changes.

It is expected that the radiation environment may have some effect on the tritium release characteristics. Radiation-induced trapping of solutes has been observed in irradiated materials. Wiswall observed that tritium release rates from certain oxides decreased with increasing fluences (up to 10^{20} n/cm^2). Figure 6 shows the effect of neutron fluence on the tritium release characteristics of $LiAlO_2$ at 650°C. At the higher fluences the fractional release under similar conditions is reduced by about an order of magnitude. From Fig. 5, a decrease in inventory by an order of magnitude translates to about a 50°C increase in temperature. Therefore, minimum release temperatures under irradiation are increased as indicated in Table 3. The effects of radiation-induced

Table 3. Temperature Limits (°C) for Solid Breeders

Breeder	m.p. °C	Thermal Effects		Radiation Effects	
		T_{min} [1]	T_{max} [2]	T_{min} [3]	T_{max} [4]
Li_2O	1700[5]	410	1000	460	910
$LiAlO_2$	1610	500	1000	550	850
Li_2SiO_3	1200[6]	420	900	470	610
Li_2Si	760	480	550	530	420
LiAl	700	300	500	350	380
Li_7Pb_2	726	320	530	370	390

[1] Diffusion limited.

[2] Thermal sintering.

[3] Radiation-induced trapping (factor of 10 degradation in tritium release estimated).

[4] Radiation enhanced sintering (0.6 T_m for oxides and 0.67 T_m for other compounds).

[5] Li_2O reportedly sublimes at temperatures below the melting point.

[6] Li_2SiO_3 is a line compound with a solidus temperature of ∿ 1030°C for slightly hypo- or hyperstoichiometric compositions.

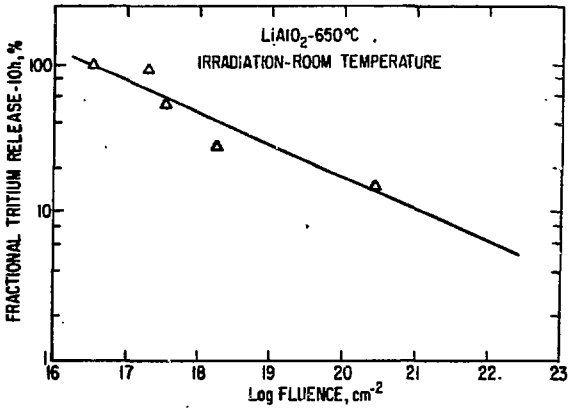

Fig. 6. Effect of neutron fluence on the tritium release characteristics of $LiAlO_2$ at 650°C.

sintering are also considered. The maximum allowable temperature for ceramics is estimated from results on oxide fuels in fission reactors, wherein radiation-enhanced sintering occurs at ∿ 0.6 of the absolute melting temperature. For the metallic compounds, the radiation sintering temperature is assumed to be 2/3 of the absolute melting temperature.

Provided the breeding materials are maintained within the listed temperature constraints, the estimated tritium holdup by diffusion will be less than 1 kg/GWth. It is evident that the ceramic breeding materials provide the largest operating temperature ranges. Of the three ceramics, Li_2O appears to be the most favorable.

Thermodynamic Considerations

The tritium release and recovery characteristics are also affected by thermodynamic considerations. Since experimental results on the phase equilibria are limited, the following calculational approach has been used to evaluate this effect. The vapor phase composition above Li_2O was calculated using the available thermochemical data.[6] The tritium is assumed to be present as LiOT in ideal solid solution in Li_2O. The tritium content of the Li_2O was taken to be 1.0 wppm (mole fraction = 1×10^{-5}) and the mole fraction of H (as LiOH) in Li_2O was assumed to be 1×10^{-3}. The relevant equilibria are:

$$2LiOT(c) \rightleftharpoons Li_2O(c) + T_2O\ (g)$$

$$LiOH(c) + LiOT(c) \rightleftharpoons Li_2O(c) + HTO(g)$$

$$2LiOH(c) \rightleftharpoons Li_2O(c) + H_2O(g)$$

Roult's Law was used to estimate LiOH and LiOT vapor pressures. Accordingly, the calculated vapor phase compositions are shown in Fig. 7. At 800°K, the HTO pressure is 10^{-6} torr and the T_2O pressure is 10^{-8} torr. From mass transfer considerations, a T_2O (or HTO) pressure of about 10^{-3} torr is required in the purge stream, in order to remove the tritium at reasonable purge flow rates. It appears that the tritium concentration in the solid Li_2O would have to be increased to ∿ 300 wppm in order to effectively recover tritium by a purge stream. This would correspond to a tritium inventory of about 40 kg per GWth. The compounds $LiAlO_2$ and Li_2SiO_3 are expected to have significantly higher T_2O vapor pressures, and hence, lower inventories. Additional data are required to reliably determine these values.

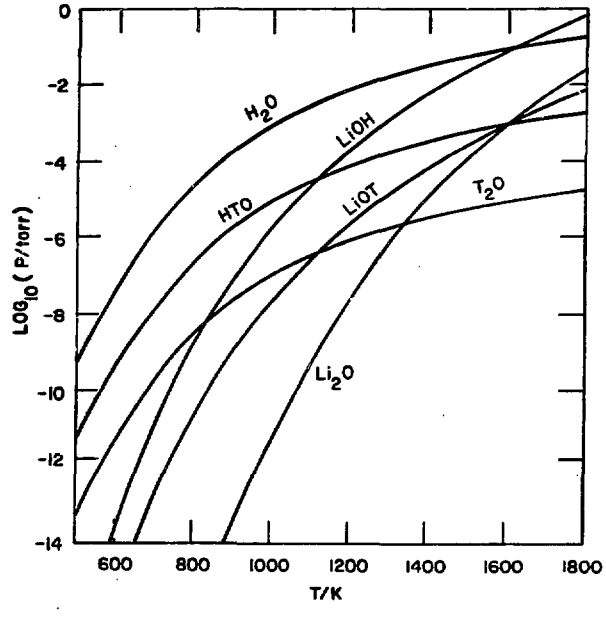

Fig. 7. Vapor phase species in equilibrium with Li_2O.

Conclusions

The major design problems regarding the use of solid breeding materials in fusion reactor blankets relate to the capability to remove tritium from the solid. The temperature window for tritium release appears to be acceptable only for the ceramics. Of the ceramics, Li_2O has the largest temperature range. However, thermodynamic calculations indicate that the tritium concentration in Li_2O at anticipated T_2O pressures will be greater than 10 kg/GWth. The corresponding T_2O pressures over Li_2SiO_3 and $LiAlO_2$ are higher, and therefore, lower tritium concentrations in these solids may be attainable. Additional thermodynamic data are required to more accurately determine the tritium holdup in solid breeders.

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