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Thermal Conductivity and Tritium Retention in Li$_2$O and Li$_2$ZrO$_3$*

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Abstract

Lithium oxide (Li$_2$O) and lithium zirconate (Li$_2$ZrO$_3$) are promising ceramic breeder materials for fusion reactor blankets. The thermal and tritium transport databases for these materials are reviewed. Algorithms are presented for predicting both the temperature distribution and the retained tritium profile across sintered-product and pebble-bed regions. Sample design calculations are also performed to demonstrate the relative advantages of each breeder ceramic.

For Li$_2$O, the thermal conductivity of sintered-product material has been measured over a wide range of temperatures and densities. Data are also available for the effective thermal conductivity of a pebble bed (in atmospheric helium) with 55% packing fraction for the 5-mm-diameter/75%-dense pebbles. Similar results are available for sintered-product and pebble-bed (60% packing fraction for 1.2-mm-diameter/80%-dense pebbles in atmospheric He) Li$_2$ZrO$_3$. Hall and Martin model predictions are in reasonable agreement with both sets of pebble bed data. Thus, the databases and calculational algorithms are well established for performing thermal analyses.

Laboratory data for tritium behavior in Li$_2$O are available for diffusion, desorption, adsorption and solubility, as well as the critical temperatures and moisture pressures for LiOH precipitation. These data have been used to determine the model parameters in the steady-state TIARA code. In addition, TIARA has been validated to 20 data points from in-reactor, purge-flow tests after which tritium inventory measurements were obtained directly for samples irradiated at 495 - 1000°C. The database for individual rate mechanisms in Li$_2$ZrO$_3$ is less complete. However, it has been observed that the Li$_2$ZrO$_3$/H$_2$O system is less likely to result in LiOH precipitation in the temperature ranges of interest. Rather than use a TIARA-type approach (which requires data for individual mechanisms), a more straightforward algorithm is proposed for calculating tritium inventory in Li$_2$ZrO$_3$ based on the 31 inventory data points obtained after in-reactor purge-flow tests at 315 - 1000°C. A reasonable upper-bound fit to these data normalized to the tritium generation rate is obtained vs. temperature. This inventory/generation-rate (i.e., residency time) correlation can be used directly to bound the tritium inventory in blanket designs. The major uncertainty in this approach is in the extrapolation to temperatures below the database. Results of design calculations for each of these ceramics are presented.

**Introduction**

Lithium oxide (Li$_2$O) is an attractive ceramic breeder material because of its high lithium atom density for tritium breeding, high thermal conductivity, good tritium release properties and low activation. However, at temperatures below a moisture-pressure-dependent critical value (e.g., 366°C at 10 Pa), LiOT/LiOH will precipitate out as a separate phase, thereby increasing tritium retention to unacceptable levels. At high temperatures (e.g., 800-1000°C), transport of vapor phase LiOT/LiOH, as well as chemical incompatibility with structural materials, may cause design problems. Thus, controlling moisture pressure is essential to Li$_2$O performance.

Lithium zirconate (Li$_2$ZrO$_3$), while not as attractive as Li$_2$O with regard to breeding, heat transport, and activation, has the advantage of being a more practical engineering material for large scale production, handling and blanket operation because of its stability. It also exhibits low tritium retention at low operating temperatures. Its performance in the areas of compatibility and stability (chemical, irradiation, and microstructural) is at least as good as the other ternaries (Li$_4$SiO$_4$ and LiAlO$_2$) and much better than that of Li$_2$O.

In the current work, algorithms are presented and validated to data for calculating temperature and tritium-retention profiles across Li$_2$O and Li$_2$ZrO$_3$ breeder zones. Results are presented for an ITER/EDA breeding blanket design concept.

**Thermal Performance**

Takahashi and Kikuchi [1] have measured the thermal conductivity [k in W (m K)$^{-1}$] of Li$_2$O in vacuum in the temperature range of 473 ≤ T ≤ 1173 K and the porosity range of 0.066 ≤ p ≤ 0.292. A good correlation to the data is

$$k = (1 - p)^{1.96} \left[39.79 \left(1 + 7.067 \times 10^{-3} T\right)^{-1}\right]$$  \hspace{1cm} (1)

Gierszewski [2] has summarized the thermal conductivity data for Li$_2$ZrO$_3$ in He in the temperature range of 373 ≤ T ≤ 1063 K and porosity range of 0.187 ≤ p ≤ 0.211. The data correlate well with

$$k = (1 - p)^{5/3} \left[3.643 \left(1 + 1.549 \times 10^{-3} T\right)^{-1} + 7.579 \times 10^{-10} T^3\right]$$  \hspace{1cm} (2)

The Hall and Martin [3] model for the effective thermal conductivity ($k_{eff}$) of a single-size pebble bed is summarized by Billone et al. [4] and validated to data for Li$_2$O (Yoshida [5]), Li$_4$SiO$_4$ (Dalle Donne and Sordon [6]) and Li$_2$ZrO$_3$ (Sullivan et al. [7]) pebble beds in atmospheric helium. Hall and Martin derived the model for a cubic lattice of spheres with a theoretical packing fraction of 52.4%. In comparing the predictions of the $k_{eff}$ model to data for packing fractions of 55 - 62%, particle sizes from 0.5 - 5.0 mm, and temperatures in the range of 52 - 613°C, it was found that the radiation term, which increases linearly with particle diameter, should be limited by the value corresponding to 1 mm diameter and that $k_{eff}$ scales with packing fraction (in absolute units) as 1.26 P$_f$.

The modified model is shown in Fig. 1 to have good agreement with the data.

A set of reference densities and configurations is established for design calculations presented in this work: an 87%-dense sintered product; a single-size pebble bed composed of coarse (0.75 mm diameter) pebbles (87% dense) at 60% packing fraction...
and a net smear density of 52.2%; and a binary bed composed of the same packing fraction of coarse particles and 20% packing of fine (0.25 mm diameter) particles with a net smear density of 69.6%.

The thermal conductivities of 87% dense Li$_2$O and Li$_2$ZrO$_3$ are compared in Fig. 2 as functions of temperature. Also shown in Fig. 2 is the conductivity for these materials at a sintered density of 69.6%. This result sets the upper limit on the $k_{\text{eff}}$ for the reference binary bed. The $k_{\text{eff}}$ values for the reference single-size pebble beds are also shown. The decrease in effective conductivity from an 87% sintered product to a single-size pebble bed with 52.2% smear density is more significant for Li$_2$O than for Li$_2$ZrO$_3$. On the average, the Li$_2$O pebble-bed $k_{\text{eff}}$ is only 1.45 times higher than that of the Li$_2$ZrO$_3$ pebble bed, as compared to a factor of 3 for the sintered-product form. Thus, there is relatively little thermal performance penalty for pebble-bed vs. sintered-product Li$_2$O, while there is a much larger penalty for pebble-bed vs. sintered-product Li$_2$O. These calculations assume no significant source of external contact pressure on the pebble beds.

For the reference binary bed (69.6% smear density), the enhancement in $k_{\text{eff}}$ over the single-size bed is a factor of < 2. For Li$_2$ZrO$_3$, the binary bed can enhance the single-size-bed $k_{\text{eff}}$ by a factor of < 1.28, based on the equivalent-density sintered-product upper bound. A more sophisticated model is needed to perform the detailed binary bed calculation. For low-conductivity Li$_2$ZrO$_3$, there is relatively little gain in effective conductivity from a single-size bed to a binary bed.

**Tritium Retention**

Laboratory data for tritium behavior in Li$_2$O are available for diffusion, desorption, adsorption, solubility and LiOT/LiOH precipitation. As described by Billone [8,9], these data have been used to determine the model parameters in the steady-state TIARA code. In addition, TIARA has been validated to 20 data points from in-reactor, purge-flow tests after which tritium inventory measurements were obtained directly. A residency-time-correlation approach is also developed in the following and compared to the inventory data and the TIARA predictions. The purpose of this exercise is to learn more about the relative strengths and weaknesses of this approach for a material which has a well-developed data base and modeling code. The residency-time approach is then used to model tritium retention in Li$_2$ZrO$_3$ for which there are 31 inventory data points, but very little fundamental data.

The tritium residency time ($\tau$, in hours) is the steady-state inventory ($I$ in wppm) divided by the steady-state generation rate ($g$ in wppm/hour). The residency time is related to the temperature of the breeder by a correlation which is what would be derived from a diffusion or a first-order surface desorption model:

$$\tau = \exp\left[A - Q/(RT)\right]$$  \hspace{1cm} (3)

where A and Q are empirically-determined parameters, $R = 8.314 \times 10^{-3}$ kJ·mole$^{-1}$·K$^{-1}$ and $T$ is temperature in K. The parameters A and Q are determined by a two-step process. Approximate values ($A'$, $Q'$) are first determined from an Arrhenius plot of the data for ($I/g$) vs. the inverse of volume-averaged temperature ($T_{\text{ave}}$) for the samples by
matching the calculated $\tau(\text{Tave})$ to the measured $I/g$. However, the algorithm $I = g \cdot \tau_{\text{ave}}$, where $\tau_{\text{ave}}$ is the spatial average (determined by integration) of Eq. 3 across the breeder region, is recommended for design calculations. Thus, $A'$ and $Q'$ are refined to give $A$ and $Q$ for Eq. 3 by matching $g \cdot \tau_{\text{ave}}$ to the measured values for $I$.

Figure 3 summarizes the measured $I/g$ vs. the inverse of $T_{\text{ave}}$ (515 - 955°C) for the Li$_2$O samples used in the EXOTIC-2, SIBELIUS, VOM-15H, CRITIC-1 and BEATRIX-II in-reactor purge flow tests. The inventory data are divided into two categories: the reference conditions of He + 0.1% H$_2$ purge and as-fabricated densities in the range of 80 to 86%, which are believed to be optimum from a tritium inventory point of view; and higher densities and/or lower protium contents, both of which tend to result in higher tritium inventories than the reference conditions. Also shown in Fig. 3 are the residency times deduced from the tritium release rate data in the MOZART experiment. These data have a higher source of error and are not considered as reliable as the direct inventory data. The solid line in Fig. 3 is a reasonable upper bound of the reference-condition data and corresponds to Eq. 3 with $A' = -8.45$ and $Q' = 56$. These values also give good agreement between the calculated values of $g \cdot \tau_{\text{ave}}$ and the measured values of $I$. Thus, $A = A' = -8.45$ and $Q = Q' = 56$ for this data set which includes local breeder temperatures in the range of 494-1000°C.

The use of Eq. 3 in the algorithm $I = g \cdot \tau_{\text{ave}}$ should yield a reasonable upper bound prediction for the tritium inventory within the fabrication (80-86% dense) and operation ($\geq 0.1$% H$_2$ in the purge, $T \geq 494$°C and $g = 3.4-33.0$ wppm/day) ranges of the database. The major uncertainty in using the correlation is in the extrapolation to temperatures lower than 494°C. Depending on the moisture pressure in the purge, additional inventory may be accumulated (as LiOT) if the temperature drops below a critical value: 368°C for 10.7 Pa, 328°C for 2.14 Pa and 312°C for 1.07 Pa. Also, based on desorption data and TIARA models, the single effective activation energy in the residency time approach would result in an under-prediction of inventory for $T < 471$°C, at which temperature the desorption activation energy increases.

The TIARA code has been validated to the inventory data base shown in Fig. 3 and the individual models in TIARA have been validated to a wide database: diffusion (300-900°C), desorption (256-653°C and ~0-5000 Pa of H$_2$), hydrogen solubility for Li$_2$O/H$_2$O (512-1000°C and 2-106 Pa of H$_2$O), hydrogen solubility for Li$_2$O/H$_2$ (400-670°C and 17-500 Pa H$_2$), and precipitation for Li$_2$O/H$_2$O (300-617°C and 0-1250 Pa H$_2$O). Thus, there is more confidence in using TIARA to calculate tritium inventory for $T < 494$°C, for microstructure and purge-protium contents different from the reference conditions and for design cases in which the moisture level is significant with respect to either solubility or precipitation.

Tritium inventory data are available for Li$_2$ZrO$_3$ irradiated in the EXOTIC-3,4,5,6 tests (11 data points) as reported by Kwast [10] the SIBELIUS test (1 data point) as reported by Kopasz and Johnson [11] and the BEATRIX-II (Phase II) pebble-bed test (19 data points) as reported by Verrall [12]. The measured inventories for Li$_2$ZrO$_3$, normalized to the tritium generation rate, are shown in Fig. 4, along with the residency times determined from the MOZART tritium release data. The horizontal axis represents the average temperature (360 - 1001°C) for the sample region in which the inventory was
measured. The solid line in Fig. 4 is a reasonable upper bound to the data and is given by Eq. 3 with $A' = -7.0282$ and $Q' = 48.94$. The values of these parameters are then refined based on the inventory data and the $I = g^* \tau_{\text{av}}$ calculational methodology to give $A = -7.7213$ and $Q = 50.75$. The use of Eq. 3 with these coefficients gives a reasonable upper-bound prediction for tritium inventory for the local temperature range (315-1044°C) of the database. While most of the densities for the Li$_2$ZrO$_3$ experimental samples are 73 - 86%, the data set also includes the EXOTIC-6 pebble bed with pebbles of 94% density and 10 - 40 $\mu$m grain size, pebble-bed smear density of 52.5% and pebble-bed temperature profile of 315 - 425°C. The predicted and measured inventories are 3.45 wppm and 2.3 wppm, respectively. It is also shown in Fig. 4 that the inventories implied by the MOZART transient release data (local temperatures of 270 - 650°C) are bounded by the recommended residency-time approach.

Based on the lessons learned from the Li$_2$O comparison, some caution must be exercised in using the Li$_2$ZrO$_3$ residency time correlation for design applications which may have higher moisture levels than the experiments, particularly at the lower temperatures. Kawamura and Nishikawa [13] studied the adsorption of water vapor for the Li$_2$ZrO$_3$/H$_2$O system at 120 - 400°C and for moisture partial pressures of range 20 - 160 Pa. The adsorbed moisture increased continuously as the temperature was lowered and/or the moisture pressure was increased. Thus, LiOT precipitation does not seem to be an issue for an Li$_2$ZrO$_3$ breeding blanket in the range of operating conditions of interest. In order to complete the validation of the residency time approach for Li$_2$ZrO$_3$, direct inventory data for samples irradiated at 200 - 300°C and/or data for fundamental mechanisms (e.g., diffusion and desorption) in this range are needed.

**Design Application**

Tritium inventory calculations are compared in Fig. 5 for layers of Li$_2$O (TIARA) and Li$_2$ZrO$_3$ (residency time) vs. the minimum breeder temperature ($T_{\text{min}}$) with the temperature increase across the breeder, $\Delta T = T_{\text{max}} - T_{\text{min}}$, shown as a parameter. The tritium generation rate is taken as 184 g/day (Gohar et al. [14] for ITER/EDA) and the peak moisture pressure is assumed to be 10.7 Pa (Billone et al. [15] for the ITER/CDA). The predicted tritium inventories for both breeders and all $\Delta T$ cases are relatively small for $T > 368^\circ$C. For $T \leq 368^\circ$C, LiOT precipitation initiates in Li$_2$O and inventories are predicted to be quite large. However, for Li$_2$ZrO$_3$ which does not precipitate out LiOT in this range, the minimum breeder temperature at which the inventory is one-day's-generation (184 g) is 232°C for $\Delta T = 100^\circ$C and < 200°C for $\Delta T = 300$-500°C. Thus, Li$_2$ZrO$_3$ has an a distinct advantage with regard to tritium inventory over Li$_2$O for low temperature operation.

The ITER design described in Ref. 14 includes three outboard and two inboard layers of 10-mm-thick binary-pebble-bed Li$_2$ZrO$_3$ with effective smear density of 70%. Each layer is surrounded by layers of beryllium multiplier. The temperature range for the breeder is 272-699°C and the tritium generation rate is 184 g/day. Using the proposed residency time correlation for each layer gives a total tritium inventory of only 24 g. An alternate design has been proposed with two outboard and one inboard layer of 87%-dense sintered-product Li$_2$O. The $\Delta T$ across each breeder layer for this design is much less than the $\Delta T$ for the Li$_2$ZrO$_3$ pebble-bed. However, the $\Delta T$ from coolant to breeder surface is much greater for the Li$_2$O design in order to maintain $T_{\text{min}} > 368^\circ$C, such that the total $\Delta T$ from coolant to breeder centerline is greater for the Li$_2$O case than for the
Li2ZrO3 case. This result, along with the temperature limits for both materials, gives more flexibility to the Li2ZrO3 design in accommodating thermal powers greater than the nominal value.

Conclusions

Thermal conductivity correlations for sintered-product Li2O and Li2ZrO3 are reviewed. These correlations are based on data in the temperature and porosity ranges of 200-900°C and 6.6-29.2% for Li2O and 100-790°C and 18.7-21.1% for Li2ZrO3. Using these correlations in a modified Hall and Martin model gives reasonable agreement with data for single-size pebble beds in He with particle porosities of 6.7-25%, packing fractions of 55-62% and particle diameters of 0.5-5.0 mm.

While the Tiara code is recommended for predictions of steady-state tritium inventory in Li2O, a residency-time correlation is proposed for Li2ZrO3. The TIARA code is validated to 20 data points for sintered-product (80-91% dense) Li2O irradiated at 494-1000°C with tritium generation rates of 3.4-33.0 wppm/day and He purge with ~0-300 Pa of H2. The Li2ZrO3 residency time correlation is validated to 31 data points for sintered-product (73-86% dense) and pebble-bed (about 52% smear density) forms at 315-1044°C with tritium generation rates of 0.38-10.6 wppm/day and purged by He +0.1% H2. In comparing the thermal and tritium performance of these two breeders, it appears that Li2ZrO3 is better than Li2O for low temperature operation because it is less likely to trap tritium as LiOT precipitates. This makes Li2ZrO3 more attractive as a breeder ceramic for low-coolant-temperature machines such as ITER. However, tritium inventory data and/or fundamental mechanistic data are needed to validate tritium inventory predictions for this material at temperatures lower than about 300°C.

References


Fig. 1. Predicted vs. measured effective thermal conductivities of single-size packed beds in atmospheric helium. The numbers in parentheses indicate the packing fraction in % and the pebble diameter in mm.
Fig. 2. Predicted effective thermal conductivities ($k_{\text{eff}}$) of sintered product (SP) and pebble bed (PB) forms of Li$_2$O and Li$_2$ZrO$_3$. The numbers in parentheses are smear densities.
Fig. 3. Tritium residency times for Li$_2$O determined from post-irradiation tritium inventory measurements as compared to residency times determined from transient tritium release data (e.g. MOZART). The solid line is a recommended design correlation for He + 0.1% H$_2$ purge, 80-86% density and 5-20 μm grain diameter.
Fig. 4. Tritium residency times for Li$_2$ZrO$_3$ determined from post-irradiation tritium inventory measurements as compared to residency times determined from transient tritium release data (e.g. MOZART). The solid line is a recommended design correlation for He + 0.1% H$_2$ purge, 73-86% density and ≤ 3 μm grain diameter.
Fig. 5. Predicted tritium inventory in an ITER/EPP driver blanket design composed of Li$_2$O or Li$_2$ZrO$_3$ ceramic breeder. The tritium generation rate is 184 g/day. Results are for temperature increases (Tmax - Tmin) across the breeder layers of 100, 300 and 500°C and a peak moisture pressure of 10.7 Pa.