Ceramic Breeder Materials: Status and Needs*

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Abstract

The tritium breeding blanket is one of the most important components of a fusion reactor because it directly involves both energy extraction and tritium production, both of which are critical to fusion power. Because of their overall desirable properties, lithium-containing ceramic solids are recognized as attractive tritium breeding materials for fusion reactor blankets. Indeed, their inherent thermal stability and chemical inertness are significant safety advantages. In numerous in-pile experiments, these materials have performed well, showing good thermal stability and good tritium release characteristics. Tritium release is particularly facile when an argon or helium purge gas containing hydrogen, typically at levels of about 0.1%, is used. However, the addition of hydrogen to the purge gas imposes a penalty when it comes to recovery of the tritium produced in the blanket. In particular, a large amount of hydrogen in the purge gas will necessitate a large multiple-stage tritium purification unit, which could translate into higher costs. Optimizing tritium release while minimizing the amount of hydrogen necessary in the purge gas requires a deeper understanding of the tritium release process, especially the interactions of hydrogen with the surface of the lithium ceramic. This paper reviews the status of ceramic breeder research and highlights several issues and data needs.

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1. Introduction

Lithium-based ceramics have long been recognized as promising tritium-breeding materials for fusion reactor blankets [1]. These materials have exhibited excellent tritium release, as well as thermophysical and thermomechanical characteristics. In particular, their thermal stability and chemical inertness add to their attractiveness from a safety point of view. Probably the most important qualification for a candidate ceramic breeder material is its ability to withstand the rigors of long-term irradiation at high temperature and under large temperature gradients.

Tritium breeder blanket designs are of a varied nature, and blanket designers for the different applications have tended to use different breeding materials. For example, Li$_2$ZrO$_3$ and Li$_2$TiO$_3$ are being considered for the ITER driver blanket; Li$_2$O is being considered for the DEMO blanket being developed in Japan (with Li$_2$TiO$_3$ as the alternative); and Li$_4$SiO$_4$+SiO$_2$ is being considered for the helium-cooled pebble bed (HCPB) DEMO blanket being developed by the European Union, with either Li$_2$ZrO$_3$ or Li$_2$TiO$_3$ as alternatives. Blanket designs are maturing, and with this maturation has come the realization that consideration must be given to development of improved materials that are less expensive to prepare, are easier to fabricate into desired shapes, exhibit excellent thermal as well as irradiation performance, and demonstrate tritium release to low temperatures.

A significant feature of fusion energy is that it has the potential of being an environmentally attractive energy form. Every effort must be made to ensure that this advantage is not lost in the development of fusion technology. An acceptable guideline could be that all materials should meet the requirements for near surface burial as radioactive waste. Long-lived nuclides and pathways to the biosphere are certainly among the primary considerations for evaluation of acceptable blanket and structural materials. From a ceramic breeder perspective, Li$_2$O, Li$_2$TiO$_3$, and Li$_4$SiO$_4$ are more attractive than Li$_2$ZrO$_3$ because of its long-term radioactive characteristics.

This paper describes the status of ceramic breeder development and identifies needs that have yet to be addressed in the development of these materials. The topics covered include:
- Development of preparation and fabrication methods for the ceramic breeder materials,
- Laboratory testing and evaluation of materials performance,
- Determination of irradiation behavior of candidate breeder materials,
- Fundamental studies to better understand and/or clarify several complex phenomena governing tritium release and breeder material behavior, and
- Issues that remain for performance optimization of lithium ceramics.
2. Preparation and Fabrication of Ceramic Breeders

Four ceramics have emerged as offering excellent potential for use in current designs of ceramic breeder blankets: Li$_2$O, Li$_2$ZrO$_3$, Li$_2$TiO$_3$, and Li$_4$SiO$_4$. For the Zr-, Ti-, and Si-containing materials, small amounts of the parent oxide remain in the final product for optimization of materials performance. Large quantities of these ceramics will be needed in the near future for the fabrication of DEMO blanket modules to be tested in ITER and for the fabrication of the ITER driver blanket. Thus, the fabrication processes should be scalable to requisite quantities. Also, consideration should be given to developing processes that are amenable to recovery of unburnt lithium from the ceramic breeder after service in the reactor. In the fabrication of large quantities of lithium ceramics, the hygroscopic nature of several of the candidate lithium ceramics must be considered. For example, sensitivity to moisture increases as the lithium oxide content increases and as the specific surface area of the ceramic increases. Due to the deleterious effects of moisture adsorption on materials properties, precautions will have to be taken during fabrication, during storage of the ceramics before loading in the reactor, and also during loading to ensure material integrity. Avoiding moisture contamination of hundreds of kilograms of materials is not a trivial problem.

Both pebbles and pellets have been considered as configurational options for the tritium breeding blanket design; the pebble configuration has been selected as the current option because of its potential advantages in assembly of blankets with complex geometry and in anticipated relief of thermal stress and irradiation cracking. Though a spherical pebble shape is desired, there is no experimental evidence that slight deviation in spherical form is critical. Pebble size is dictated by both design (pressure drop, heat transfer, and packing fraction) and material characteristics (thermal stress and irradiation cracking resistance). The desired pebble diameter is in the 0.1-1.0 mm range, with those ceramics exhibiting poorer thermal, mechanical, and irradiation behavior being limited to the smaller size. For tritium breeding ratio (TBR) considerations, the density of the pebbles should be near theoretical to ensure a maximum smear density for the pebble bed.

A number of methods are available to produce pebbles, but few can simultaneously meet current requirements for shape, size, density, purity, yield, and production rate. Processes that have been, or are being, explored or developed include:

a) A melting/spraying process was used at FZK, in collaboration with Schott Glaswerke, for the production of 0.1-0.2 mm and 0.25-0.63 mm Li$_4$SiO$_4$ and Li$_4$SiO$_4$+SiO$_2$ pebbles [2]. After annealing, spherical pebbles of 98% theoretical density (TD) exhibiting satisfactory mechanical strength were obtained. A melting/dropping process was used by JAERI in collaboration with Mitsubishi to produce 1 mm Li$_2$O spheres [3].

b) Sol-gel type processes are being investigated at JAERI, with NFI Ltd., to produce 1 mm Li$_2$O [4,5] and 1.5 mm Li$_2$TiO$_3$ pebbles [4,6]. After sintering, densities in the range of 80-85% TD were obtained for both materials [4,6]. In addition, these processes are attractive as effective use of resources and reduction of radioactive wastes [7]. The sol-gel type processes were also employed at ECN to produce 0.5-1.0 mm Li$_2$TiO$_3$ pebbles.
In the case of ECN, the pebble densities were less than 80% TD. Also being explored is a solution process [9] for the fabrication of Li₂TiO₃ pebbles, which uses lithium and titanium ions in solution as primary precursors. This process is attractive because of the ease of gelling sol droplets in a proper medium that can be shaped as "spheres" directly. Also, it has possible application in reprocessing of the irradiated breeder material.

C) A process consisting of extrusion, spheronization, and sintering has, for several years, been used by AECL to produce 1.2 mm LiAlO₂, Li₂ZrO₃, and Li₂TiO₃ pebbles in collaboration with Ceramics Kingston [10]. Material densities are in the 80-90% TD range. Good yield and high production rates are expected. Using the same process, preliminary trials were made at CEA to produce 1 mm Li₂ZrO₃ pebbles [11].

d) An agglomeration/sintering process has been used by JAERI, in collaboration with Kawasaki, for producing ~1 mm Li₂O, Li₄SiO₄, and Li₂ZrO₃ pebbles. Pebble densities in the 90% TD range were obtained [12]. This process is also being investigated at CEA for producing ~1 mm Li₂TiO₃ pebbles. Pebble density of 90% TD and good mechanical strength were obtained [11].

3. Materials Performance

Properties data are needed for blanket design and analysis. In the last decade an extensive effort was devoted to developing a properties data base as a function of key parameters, and from that data base, properties correlations were derived for LiAlO₂, Li₄SiO₄, Li₂O, and Li₂ZrO₃ [13]. However, for Li₂TiO₃ the properties data base is somewhat limited. Additional properties measurements are in progress internationally.

The thermal conductivity of bulk Li₂O, LiAlO₂, Li₄SiO₄, and Li₂ZrO₃ has been measured, and correlations have been derived as a function of porosity and temperature [13]. For materials of the same density, thermal conductivity ranks in the order Li₂O > LiAlO₂ > Li₂ZrO₃ > Li₄SiO₄. Thermal conductivity values for Li₂TiO₃ are intermediate between those for LiAlO₂ and Li₂ZrO₃ [14-16]. Thermal conductivity measurements at FZK on Li₄SiO₄ + SiO₂ showed that its values are greater than that obtained with pure Li₄SiO₄. Recall that the thermal conductivity of a pebble bed is controlled by the thermal conductivity of the gas phase and the gas pressure. It is expected that the thermal conductivity of the pebble bed will follow the ranking as given above, provided the same packing fraction, pebble size, and pebble density are maintained. Indeed, this was confirmed in measurements on pebble beds of Li₂O, Li₂ZrO₃, and Li₄SiO₄ [17,18]. Measurements are planned for Li₂TiO₃ pebble beds. Since experimental values for pebble beds are in reasonable agreement with theoretical model predictions, the latter can be used to estimate the thermal conductivity until actual values are available.

Limitation of the ceramic breeder operating temperature may be dictated by the potential for lithium loss by vaporization during tritium recovery. To evaluate the maximum allowable temperature for the ceramic breeder, vapor pressures over the lithium ceramics were measured as a function of temperature, in vacuum, and in the presence of D₂ and/or...
D₂O [19-21]. Measurements from Knudsen effusion mass spectrometry [19,20] show the following ranking for increasing lithium oxide vapor pressures: LiAlO₂ < Li₂TiO₃ < Li₂ZrO₃ < Li₄SiO₄ < Li₂O [20]. There is a desire to perform the measurements under prototypical purge gas conditions, namely, He + 0.1% H₂ or He + H₂O vapor such as done by Yamawaki et al. [21]. Results reported by Yamawaki et al. show that for a D₂ partial pressure of 100 Pa (current H₂ pressure in the helium purge gas), Li₂TiO₃ and LiAlO₂ should be comparable with respect to lithium loss and better than Li₄SiO₄. Mass transfer of lithium could lead to blockage of the sweep gas path and limit blanket operation. However, a drop in pressure of the moisture-containing (about 30 ppm) helium sweep gas was not observed for Li₂ZrO₃ and Li₂O pebble beds operated at 600°C for 300 h [22].

Thermomechanical testing involves integrated tests that incorporate relevant blanket geometry and operating conditions. During blanket operation, the ceramic breeder will be subjected to a number of stresses induced by thermal expansion, thermal gradients, thermal shocks, and thermal cycling, which may cause fracture of the ceramic. Fracture has to be limited to avoid purge gas pressure drops and downstream particulate transport. Thermal cycling tests were conducted at ENEA on LiAlO₂, Li₂ZrO₃, and Li₂TiO₃ pellets under conditions representative of an operating reactor. An overall good behavior of the pellets was observed under DEMO conditions [23]. Similarly, several thermal cycling tests were made by FZK on pebbles of various formulations of Li₄SiO₄; by JAERI on Li₂O, Li₂TiO₃, and Li₄SiO₄ pebbles; and by AECL on Li₂ZrO₃ and Li₂TiO₃ pebbles. Results have been summarized in [17,24]. Good performance of FZK pebbles was observed up to temperature change rates of 50°C/s at 400-500°C, to be compared with a maximum rate of 20°C/s in the DEMO HCPB blanket. The thermal cycling behavior of 1.2 mm Li₂ZrO₃ and Li₂TiO₃ pebbles from early AECL developmental production runs showed a decrease in pebble strength with increasing number of cycles. Such behavior was thought to be due to the anisotropic thermal expansion of both ceramics combined with the large grain size of the materials tested [17,24]. Utilization of smaller grain size materials should improve the Li₂ZrO₃ and Li₂TiO₃ behavior. This will be checked through testing CEA material with a typical grain size of 1-2 μm, as compared to 10-50 μm for the AECL material. An extended test campaign of 1000 cycles was performed on a water-cooled breeder-in-tube (BIT) ITER blanket mock-up (one pin) with AECL Li₂ZrO₃ pebbles to test their thermal hydraulic and thermomechanical performance. The test confirmed the capability of the proposed blanket design in terms of functionality, thermal hydraulic response, and temperature control [25]. Thermal cycling behavior of 1 mm pebbles was also examined by JAERI under the conditions of 20°C/s at 400-800°C for up to 10,000 cycles, where some fragmentation of the pebbles was noted [26,27].

While the mechanical behavior of bulk ceramics has been reported [13,14], there are few data on mechanical strength of ceramic pebbles. Crush load values for single pebbles of Li₂O, Li₂ZrO₃, Li₄SiO₄, Li₄SiO₄+SiO₂, and Li₂TiO₃ are reported in [4,11,17]. Crush load depends on a number of factors, among which are ceramic composition, pebble density, pebble diameter, pebble microstructure, and the pebble fabrication
process. The broad range of values observed reflects the effect of the above-mentioned factors. Studies at JAERI showed the crush load of Li$_2$O, Li$_2$ZrO$_3$, and Li$_4$SiO$_4$ to decrease with increasing number of thermal cycles [26]. Of greatest interest is the behavior of pebble beds under blanket operating conditions, namely, under stress caused by pressure, thermal gradients, thermal expansion, thermal shock, and thermal cycling. Such work is planned for Li$_2$ZrO$_3$ and Li$_2$TiO$_3$ pebbles in the European Blanket Program.

4. Irradiation Performance - Laboratory and In-reactor Tests

Laboratory tests were performed by several research groups for investigation of tritium release mechanisms and identification of key material parameters that might influence the release of tritium from the ceramic. Results are in good agreement with in-reactor tests with respect to the ranking of materials performance. Recent laboratory tests indicated excellent tritium release behavior of Li$_2$ZrO$_3$ and Li$_2$TiO$_3$ to low temperatures [11,14]. In addition, tritium diffusivity in single-crystal Li$_2$TiO$_3$ was measured over the temperature range 352-1103°C to provide baseline properties for tritium transport [28]. While its role has yet to be fully understood, the importance of hydrogen in the helium purge gas to the tritium recovery process has been amply demonstrated both in these laboratory tests and in the in-reactor tests described below. Also, helium behavior in ceramic breeder materials may have a significant impact on the irradiation durability of candidate ceramics. Helium diffusion in the grains and release from closed pores was recently examined for Li$_2$O [29].

A number of in-reactor tests were conducted in the HFR, NRU, and FFTF reactors.

The EXOTIC-6 irradiation test at HFR Petten focused on tritium release studies of candidate ceramics in pellet and pebble configurations [30]. A tritium residence time of one day, in He+0.1%H$_2$ purge gas, was found at ~400°C for 76% TD LiAlO$_2$ pellets, at ~350°C for 94% TD Li$_4$SiO$_4$ pebbles, and at ~250°C for 73% TD Li$_2$ZrO$_3$ pellets. In the EXOTIC-7 irradiation test, 50% $^6$Li-enriched Li$_2$ZrO$_3$ and LiAlO$_2$ pellets and Li$_2$ZrO$_3$ and Li$_4$SiO$_4$ pebbles were irradiated to 6-18% burnup [31,32]. Pellet stacks and pebble beds remained essentially intact during irradiation. Tritium inventory measurements confirmed values obtained from previous EXOTIC tests. Tritium release from Li$_2$ZrO$_3$ ceramic was excellent. Tritium residence times were not affected by lithium burnup. Postirradiation examination of the mixed Be-Li$_4$SiO$_4$ pebble bed showed implanted tritium in beryllium when lithium ceramic and beryllium were intimately mixed. The tritium inventory was found to be very high, with the smaller pebbles having the largest inventory. The first phase of the EXOTIC-8 experiment was initiated in June 1997 with specimens of Li$_2$TiO$_3$ pebbles. The second phase, to be initiated in 1998, will include pebble specimens of Li$_2$TiO$_3$ and Li$_2$ZrO$_3$. Irradiation capsules will accommodate ~50% $^6$Li enriched specimens of Li$_2$TiO$_3$ and Li$_4$SiO$_4$, allowing them to achieve lithium burnups of 7-10% representative of DEMO end-of-life performance.
The CRITIC-II irradiation test in the NRU reactor at Chalk River focused on the irradiation of Li$_2$ZrO$_3$ pebbles [33]. The temperature gradient in the pebble bed ranged from 200°C at the outer edge to ~1100°C at the center. The final burnup achieved 0.5% total lithium after 272 full power days (FPD). Postirradiation examination of the pebbles indicated very low tritium inventory, except at the lowest temperature. Tritium inventory ranged from ~5 wppm to 0.01 wppm for the operational temperature range. Lifetime tritium release from Li$_2$ZrO$_3$ pebbles showed very low tritium inventory and excellent performance at the target burnup. Currently in progress is the CRITIC III test, which focuses on the irradiation of Li$_2$TiO$_3$ pebbles; a lithium burnup of about 0.5% is expected to be achieved. The tritium release behavior of Li$_2$TiO$_3$ pebbles in CRITIC III is comparable to that of Li$_2$ZrO$_3$ pebbles in CRITIC II.

For the BEATRIX II irradiation test in the FFTF fast reactor at Richland, burnups in excess of 5% were achieved. The Li$_2$O solid pellets and the Li$_2$ZrO$_3$ pebble bed operated at a centerline temperature of ~1000°C and edge temperature of ~400°C. In spite of these extreme conditions, Li$_2$O and Li$_2$ZrO$_3$ performed very well; Li$_2$O exhibited good tritium release throughout the irradiation, and this was confirmed by a measured very low tritium inventory [34]. Ceramic integrity was maintained during irradiation (burnup 5%), although some structure changes and swelling occurred along with a very small loss of lithium [34,35]. For Li$_2$ZrO$_3$ at this burnup level, tritium release was constant, with no indication that second phase formation degrades tritium release behavior. Material fracture was not observed in the ceramic breeder material. Lifetime tritium release of Li$_2$ZrO$_3$ pebbles showed very low tritium inventory and excellent performance of pebbles to 1100°C for ~200 FPD [36].

5. Tritium Transport and Release

The liberation of tritium from neutron-irradiated lithium ceramics involves the diffusive motion of the tritium atom within the solid and its subsequent release from the ceramic surface [37-41]. It is important to distinguish the rate-controlling step contributing to tritium release. The rate-controlling step has been observed to change from surface phenomena to diffusion as the grain size of the specimen increases and as temperature increases [42-48]. In order to address tritium release issues, one needs a firmer understanding of the mechanism through which hydrogen enhances tritium release. Generally, the method for determining the diffusion and desorption rate constants has been to observe tritium release from the ceramic and analyze the time dependence of the release process. The data are analyzed using a diffusion, desorption, or a mixed diffusion-desorption model. Complementary measurements that would indicate whether release is in the diffusion- or desorption-controlled regime are not always made.
Tritium Transport in the Bulk

Bertone [49] may have been the first to address the boundary conditions that define whether bulk diffusion or surface desorption is the rate-limiting step in tritium release. This study indicated that tritium release is controlled by: 1) diffusion of tritium through the crystal when the dimensionless group \( \frac{ak}{D} \) is > 10, 2) desorption of tritiated water from the crystal surface when \( \frac{ak}{D} \) is < 1, and 3) a combination of these processes when 1 < \( \frac{ak}{D} \) < 10, where \( a \) is a characteristic crystal size, \( k \) is the governing desorption rate constant, and \( D \) is the governing diffusion coefficient. As both the diffusion coefficient and the desorption rate constant are temperature dependent, this approach indicates that the form of the rate controlling mechanism depends primarily on crystal size and release temperature. These theoretical studies were followed by the experimental work of Quanci [50] on single-crystal Li2O, and this work more clearly demonstrated the boundary conditions as outlined by Bertone.

Too often in experimental studies, the initial release behavior does not follow the prescribed mathematics due to time delays in the recorded tritium release or because of the vagaries in the mathematics and the experimental apparatus. Verrall [51] established a more rigorous methodology for the Bertone [49] approach when he identified the need to initiate analysis at a particular time in the tritium release process. In practice, the release rate of tritium will never follow the diffusion-controlled relation at short times, even when the release of tritium is controlled by diffusion, because the formula diverges (goes to infinity) at \( t = 0 \). Also, ionization chambers and proportional counters have a relatively large internal volume that contains the tritium that is being measured. As the tritium enters the chamber, the tritium concentration in the chamber increases from zero to a finite maximum and then decreases. Under these conditions, the measured release rate does not follow the relation \( \frac{\partial \ln(f)}{\partial \ln(t)} = \frac{1}{2} \), especially at short times. Surprisingly, no matter what the shape of the release curve and no matter what point along the curve is selected as \( t \) goes to zero, the relation \( \frac{\partial \ln(f)}{\partial \ln(t)} \) was found to be equal to 1. Although this limit is 1 for all tritium release curves, diffusion and desorption control can still be distinguished by examining \( \frac{\partial \ln(f)}{\partial \ln(t)} \), not in the limit as \( t \) goes to zero, but for longer times, i.e., many times the detector time constant. Thus, the shape of the logarithmic derivative over long times can be used to distinguish between diffusion- and desorption-controlled release.

Also, impurities in the lithium ceramic were thought to affect the transport rate. Impurities can alter the diffusivity by creating vacancies, interstitials, or other defects. In lithium aluminate, it has been postulated that tritium diffusion occurs via a lithium-vacancy tritium complex [52]. If this is the case, then impurities that affect the number of lithium vacancies should also affect the tritium diffusivity. The sensitivity of the tritium diffusivity to these impurities depends on the number of lithium vacancies caused by the impurity relative to those defects present in the pure material. However, tritium diffusivity was observed [53,54] to follow a simple Arrhenius-type temperature dependence, with the diffusivity determined for the doped and undoped materials being the same within experimental error. This suggests that impurities which create lithium vacancies have little
or no effect on tritium diffusion in lithium aluminate over the temperature range investigated.

**Tritium Desorption from the Ceramic Surface**

While desorption has been determined to be the rate-limiting step in tritium release [49,55,56], the details of the release process are still not well understood. Early on, tritium desorption was treated as occurring from one site with one desorption activation energy. However, in laboratory studies [57-59], the rate of evolution of H₂O(g) was observed to go through several maxima. This was interpreted as indicating that evolution proceeded from several types of desorption sites, each with its corresponding activation energy. Isotherms and isobars derived from the adsorption data revealed two processes with different activation energies for adsorption. Also, the heats of adsorption were found to depend upon the degree of surface coverage.

In developing theoretical models of tritium release from ceramic breeder materials, the activation energy of desorption is an important variable. The activation energy for desorption is equal to the sum of the heat of adsorption and the activation energy of adsorption. Usually, the activation energy of adsorption is small so that the activation energy of desorption is approximated by the heat of adsorption. It follows that the activation energy of desorption is a function of surface coverage, as is the heat of adsorption. The observed range of values for the heat of adsorption indicates a range of activation energies for desorption. The physical basis for such a range is the existence of multiple types of sites for adsorption and, hence, multiple types of sites from which desorption occurs [61,62]. For example, a theoretical analysis of the types of OH⁻ sites possible on the surface of alumina, characterized in terms of the number of O²⁻ nearest neighbors, showed five types of sites to be present.

The complexity of the H₂O(g) adsorption/desorption process for lithium aluminate has been examined [60]. Reactivity differences in adsorption sites could be that one kind of adsorption site involves lithium ions and adjacent oxides, and another kind of site involves aluminum ions and adjacent oxides. Further evidence from a number of studies on candidate ceramic breeder materials indicates that multiple types of sites, with their associated activation energies for desorption, are involved in the desorption of H₂O(g), HTO(g), or T₂(g) from the ceramic breeder surface [61]. The degree of surface coverage by adsorption of H₂O(g) or H₂(g) and diffusion of tritium to the grain surface will determine which type of site is dominant in the release process and what the desorption activation energy will be at that time. Related studies have shown that multiple desorption processes are involved in the evolution of H₂O (T₂O) from the lithium ceramics [61,62]. These processes differ in several respects: 1) they can involve chemisorption or physisorption, 2) there can be different degrees of surface coverage by OH⁻ groups, and 3) there can be differing types of surface sites from which desorption occurs. The distinction in sites may involve defects and impurities, as well as differences in ions on different crystallographic planes exposed to the gas phase.
Complementary to the above are the studies of the tritium release process through various analytical means using Fourier transform infrared spectroscopy (FTIR), work function measurements, and deuterium as tracer material. In an FTIR study, the deuteroxyl group OD was directly observed on the Li$_2$O surface at high temperature and under controlled atmosphere. Multiple peaks were observed in the O-D stretching vibration region and exhibited varied dependence on temperature and oxygen potential of the surface [63]. Yamaki et al. [64] emphasized that tritium release from Li$_2$O is affected both by swamping effects with H$_2$ and H$_2$O and by the surface oxygen potential. Work function techniques were used to examine the defect structure of Li$_4$SiO$_4$ [65]. The work function was found to depend upon the oxygen potential and the defect structure in the near surface region. Irradiation defects were shown to have an impact on tritium release at low temperatures, and this may become important for low temperature operation of the breeder blanket [66,67].

**Fundamental Studies**

Present understanding of tritium release is that the release rate cannot be enhanced by simply increasing the hydrogen partial pressure in the helium purge stream. This can be understood from Hartree-Fock theoretical calculations [68-71] of dissociative hydrogen chemisorption on the (110) and (111) surfaces of Li$_2$O. These calculations indicate that a majority of the surface sites (i.e., the terrace sites) are not available for hydrogen chemisorption. Only a minority of sites, such as step ledges and point defects, are favorable. Once those sites are occupied, further increases of the hydrogen partial pressure would not be useful.

The ab-initio calculations on the dissociative hydrogen chemisorption on lithium oxide surfaces [64,68] provide one component of the quantitative basis for an understanding of the role of hydrogen in affecting the release of tritium from lithium ceramic breeders. These calculations suggest heterolytic adsorption of hydrogen onto the ceramic surface. The presence of hydrogen in the purge gas stream provides a very different environment. The hydrogen is chemisorbed onto the lithium ceramic surfaces, forming OH$^-$ and Li$^+$H$^+$Li$^+$. 

There are two possible reactions with the T$^+$:

\[
\text{Li}^+\text{H}^+\text{Li}^+ + \text{T}^+ = 2 \text{Li}^+\text{solid} + \text{HT}
\]

\[
\text{OH}^- + \text{T}^+ = \text{HTO} + \text{O}^{2-}\text{vacancy}
\]

In both tritium release processes, the rate scales as the product of the surface coverage of the chemisorbed hydrogen species and the tritium concentration. However, the rate is not well characterized, so some doubt remains as to the details of the surface interactions in the tritium release process. As the hydrogen coverage is usually much larger than the tritium concentration, the tritium release rate is proportional to the first power in the tritium concentration and not to its square, as is the case in the absence of hydrogen from the purge gas.
Also note that the present model suggests that relying on the "intrinsic" hydrogen impurity level in nominally pure helium (present to the level of a few ppm) as contrasted to hydrogen added to the purge gas is unlikely to be effective. In that case, the chemisorbed hydrogen surface coverage would be correspondingly very low. The rates of HT and HTO formation would be no better or lower than that of $T_2$ and $T_2O$. One needs to add hydrogen to a level substantially above the nominal impurity level in order for its presence to be effective in enhancing tritium release. The present model also suggests that the tritium release rate cannot be arbitrarily enhanced by simply increasing the hydrogen partial pressure in the helium purge stream, as there is a saturation effect. This can be understood from the fact that our simulations have indicated that a majority of the surface sites (i.e., terrace sites) are not available for hydrogen chemisorption. Only a minority of sites, such as step ledges and point defects, are favorable. Once those sites are all occupied, further increases in the hydrogen partial pressure would not be useful.

6. Needs and Summary

Four ceramics continue to be tested by the international fusion-blanket community. These are Li$_2$O, Li$_2$ZrO$_3$, Li$_4$SiO$_4$, and Li$_2$TiO$_3$. Tritium release performance and materials properties are suitable for current DEMO concepts, while irradiation behavior up to end-of-life has to be confirmed with high burnup and high dpa neutron irradiation using fast neutrons. Neutron activation is not a concern for Li$_2$O and of little concern for Li$_4$SiO$_4$ and Li$_2$TiO$_3$. While Li$_2$O and Li$_4$SiO$_4$ exhibit the highest lithium atom density, they also have the highest lithium vaporization rate and greatest sensitivity to moisture. Lithium metazirconate exhibits greater thermal stability than Li$_2$O and Li$_4$SiO$_4$ and is less sensitive to moisture. Even though mass production of Li$_2$ZrO$_3$ pebbles is not yet demonstrated, its feasibility is expected. Excellent irradiation behavior and excellent tritium release for Li$_2$ZrO$_3$ specimens were observed in several worldwide irradiation tests to lithium burnups up to 10%. Activation of zirconium is a concern, though it is small in comparison to that from current structural materials. The overall performance characteristics for Li$_2$TiO$_3$ are excellent with respect to tritium release, insensitivity to moisture, and low activation. Emphasis on low activation materials places great importance on candidate ceramics such as Li$_2$O, Li$_4$SiO$_4$, and Li$_2$TiO$_3$.

Additional properties data remain an urgent need for breeder blanket design activities and in support of optimization of blanket performance. Only with equivalent data bases of requisite properties can all materials be fairly evaluated and a sound selection made. With the conservation of $^6$Li in mind, it is important to develop preparative schemes that are suitable for processes that would be used for recycle of $^6$Li. Such methodology may be critical to the larger focus of developing cost-effective preparation and fabrication methodologies.
The forthcoming construction of test blanket modules for ITER/DEMO requires base engineering data. Thus, emphasis must be placed upon both out-of-pile and in-pile engineering tests of blanket submodules.

Irradiation testing to high burnup and high dpa levels with fast neutrons needs to be done for candidate ceramic breeder materials for DEMO reactors to ensure proper perspective on tritium release behavior and the irradiation durability of candidate materials to end-of-life expected for current blanket designs. International plans for long-term irradiations have been delayed by the successive shutdown of several fast breeder reactors. Due to the limited options for conducting irradiation experiments in fast reactors, the ceramic breeder community may have to consider the use of a mixed spectrum reactor to obtain the minimum materials data set required for designs of test blanket modules for ITER and DEMO fusion reactors within a limited time period. In such a case greater attention must be given to design details like grain size and $^6$Li enrichment to ensure an appropriate tritium production rate and uniform damage production in the specimen. Tailoring of the neutron spectrum may be an alternative way to ensure a hard spectrum, but with some loss of neutron fluence.

Attention also needs to be given to the characteristics of tritium release at low H/T ratios, or stated another way, a better understanding is needed of $H_2$ addition to the purge gas and the H/T ratio on tritium release. Currently, tritium release experiments operate at H/T ratios of 500 or greater when blanket designers are calling for H/T ratios about 10. The lower H/T ratios can be achieved through lower $H_2$ concentrations in the purge gas, lower purge gas flow rates, or a combination of both.

The ongoing irradiation program needs to give greater attention to the release characteristics of neutron-generated helium. What data are available suggest that helium releases much slower than tritium and, therefore, could cause a blanket swelling problem if helium gas could not escape from the ceramic. In testing of candidates in small grain form, this may not represent too great a problem. However, a demonstration experiment would help define the boundary conditions for helium behavior.

From the above, it appears obvious that modeling of tritium/helium release and blanket performance needs to be re-energized on the international level. There is much that has been accomplished recently; unfortunately, there has not been a concerted effort to bring these various data together in a "performance" model.

In summary, the development of the properties data base for lithium containing ceramics has yet to identify a critical issue that would negate their use as tritium breeding materials in a fusion reactor. Several of the candidate materials have performed well to burnups in excess of 10% under some very demanding in-reactor conditions. Issues of current interest are reactor-relevant-scale fabrication of ceramics, thermal mechanical and thermal hydraulic behavior of blanket submodules, tritium release, tritium inventory, tritium transport/release modeling, irradiation behavior to end-of-life burnup, and dpa.
7. References