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# Research and Development Status of Ceramic Breeder Materials

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Carl E. Johnson
Chemical Technology Division
Argonne National Laboratory
Argonne, Illinois 60439 USA

## ABSTRACT

The breeding blanket is a key component of the fusion reactor because it directly involves tritium breeding and energy extraction, both of which are critical to development of fusion power. The lithium ceramics continue to show promise as candidate breeder materials. This promise was also recognized by the International Thermonuclear Experimental Reactor (ITER) design team in its selection of ceramics as the first option breeder material. Blanket design studies have indicated areas in the properties data base that need further investigation. Current studies are focusing on issues such as tritium release behavior at high burnup, changes in thermophysical properties with burnup, compatibility between ceramic breeder and beryllium multiplier, and phase changes with burnup. Laboratory and in-reactor tests are underway, some as part of an international collaboration for development of ceramic breeder materials.

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## 1. Introduction

The development of ceramic breeder materials has progressed systematically in complementary laboratory experiments, in-reactor testing, and modeling activities. These efforts have resulted in a broad properties data base for several materials in differing configurations (i.e., sintered pellets, pebbles, single crystals) [1,2]. The lithium-containing ceramics ($Li_2O$, $LiAlO_2$, $Li_4SiO_4$, and $Li_2ZrO_3$) have been determined to have excellent potential as tritium breeders in a near-term reactor such as ITER because of the ease of tritium recovery, thermal performance, and good irradiation behavior. Also, these efforts have indicated that optimum materials performance information is obtained when a candidate material is tested in a fashion that results in multiple effects (gas production, recoil effects, neutron multiplier, tritium production, release, and recovery).

Current research is addressing issues identified in the ITER design activity, for example, compatibility of the breeder with beryllium multiplier, tritium release behavior at high burnup, effects of breeder burnup on thermophysical properties, and operation at lower temperatures (i.e., $<623$ K). The design studies, place a greater emphasis on neutron irradiation effects and the current experimental effort reflects interest in multiple effects experiments. However, complementary separate-effects laboratory studies are still required to ensure correct interpretation of the irradiation experiments. This paper summarizes the status of ceramic breeder materials with respect to research on tritium transport, vaporization behavior, and irradiation behavior.

## 2. Tritium Transport

The solid-state defect structure of the ceramic (lithium vacancy, defects, traps, etc.) can strongly influence the tritium transport and release

process. The origin of the lithium vacancy ($V_{Li}$) can arise from (1) the $^6Li(n,\alpha)T$ reaction, which generates many defects in transforming Li into $^3H$ and $^4He$ atoms, (2) defects created by displacement damage, i.e., recoil of energetic $^3H$ and $^4He$ atoms, and (3) the extrinsic impurity-induced defects that control lithium diffusion.

To permit lower temperature operating conditions for solid breeders non-thermal methods of increasing tritium release need to be developed. Addition of hydrogen into the helium purge gas stream has proven to be useful in increasing tritium release. For various design scenarios, however, further increase is desirable. Impurity/defect induced increase of tritium release may represent a viable method of meeting this goal. In fact, existing experimental tritium release data from $Li_2O$ have indicated a correlation between lithium and tritium transport [2a,2b]. Furthermore, impurity/defect induced increase of the hydrogen transport (as an impurity) in a number of non-lithium oxides has been observed [2c,2d]. The presence of (selected) impurities may affect tritium diffusion by (1) changing the local concentration of free vacancies, (2) changing the activation energy and jump frequency of lattice atoms due to electronic effects, or (3) changing the correlation factor for diffusion by changing the ratios of jump frequencies near impurities. Solids modification in which $Li^+$ ions are substituted with $Mg^{2+}$ ions appears an appropriate testing scheme for tritium release.

Tritium transport and release have been the subject of two recent modeling workshops [3,4]. Much of the modeling effort has been focused on a transport mechanism that considers diffusion and desorption as the rate-limiting processes. Quanci [5] has demonstrated that limiting mechanisms are very dependent upon grain size in that desorption is limiting for small grain materials ($<$200 $\mu$m diameter) and diffusion is limiting for large grain

materials (>2000 μm diameter). Recently, however, unusual tritium release behavior has been observed in the CRITIC purge flow tritium release experiment on $Li_2O$ [6]. In the CRITIC tests at 773 K with a temperature increase of 50-100 K and purge gas containing 0.1% hydrogen, the tritium release initially decreased, increased to a maximum, and then decreased back to steady state. This unusual behavior can be accounted for by an activation energy for desorption that is surface coverage dependent [7].

The effect that surface coverage has on the desorption activation energy can be understood by examining more closely the desorption process. In tritium release experiments, what is regarded as the desorption step really involves two processes: (1) a surface reaction between tritium (which has diffused to the surface as $T^+$) and chemisorbed hydrogen to form surface bound HTO or HT, and (2) desorption of the surface bound HTO or HT.

The activation energy of the surface reaction or the desorption of the surface bound molecule may be dependent on the surface coverage. If there are two or more adsorption sites for hydrogen on lithium oxide (e.g., $H^+$ bound to an O on a normal oxygen site, $H^+$ bound to an O adjacent to a lithium vacancy), then at high surface coverage both the low and high energy sites will be occupied. Reaction of $T^+$ at the surface will occur with the hydrogen <u>least</u> tightly bound to the surface, i.e., the hydrogen in the <u>highest</u> energy sites. At low surface coverage, the hydrogen will occupy the <u>lowest</u> energy sites on the surface (i.e., sites with <u>largest</u> binding energy), and the high energy sites will be unoccupied. In this case, because the $T^+$ must now react with a hydrogen which is more tightly bound, the activation energy for the surface reaction will be <u>larger</u> than that for the high surface coverage case.

The tritium release observed for temperature changes in the region of 723-823 K under conditions of 0.1% hydrogen in the purge gas could not be

explained by a simple diffusion model, a one-mechanism desorption model, or a diffusion-desorption model with one desorption rate constant. however, a diffusion-desorption model which allows for a change in the desorption activation energy with temperature can reproduce the tritium release curves observed for these conditions [7]. The temperature dependence of the desorption activation energy is most likely due to a dependence of the activation energy on surface coverage. The results from CRITIC and the surface coverage dependent model suggest that knowledge of surface phenomena involved in tritium desorption is crucial for the accurate calculation of tritium inventory changes resulting from temperature variations.

3. Vaporization Behavior

Within the ceramic breeder material, tritium may be found as LiOT, which, during irradiation, may transport lithium (and tritium) to cooler parts of the blanket. This transport may cause loss of lithium from the blanket, blockage of flow paths, and an increase in the tritium inventory. Laboratory studies have established the pressure of LiOH(g) for reaction of $Li_2O$(s) with water vapor [8,9]. The pressure of LiOT and HTO or $T_2O$ above $Li_2O$ is essentially the same as that for reactions involving hydrogen.

Analysis of experiments [9a] on the transport of LiOH(g) under varying temperature, He purge gas flow rate, and water vapor partial pressure showed that two interconnected, simultaneous processes were taking place, namely: (1) water vapor carried by the helium purge diffused to the surface of the $Li_2O$ where LiOH was formed, and (2) the LiOH diffused into the flowing helium. It was proposed that each of these processes is controlled by the diffusion rate of water ($D_{water}$) and LiOH ($D_{LiOH}$) in helium for residence times (t) limited by the gas velocity and the diffusion length (slab thickness, L). The fractional saturation for each process as a function of $Dt/L^2$ was calculated

with standard equations [9a]. It was assumed that the overall fractional saturation process can be calculated from the product of each fractional saturation (for $H_2O$ and LiOH in He). The experimentally measured fractional saturation of LiOH in helium agreed reasonably well with the calculated fractional saturation within the experimental uncertainty. Fractional saturations between 0.07 and 0.999 were measured.

These studies established conditions for calculating LiOH undersaturation in helium as a function of $Li_2O$ purge channel volume and the velocity of the purge gas. It is proposed that the fractional saturation of two-step reactions which are independent can be treated as the product of each fractional saturation in which each process is diffusion controlled.

## 4. Irradiation Behavior

### 4.1 Irradiation Effects

Lifetime testing of the ceramic breeder materials is required to evaluate materials behavior at long burnups and under large temperature gradients. The low cross section of $^6Li$ for high energy neutrons (>1 MeV) results in an almost homogeneous reaction throughout the breeder sample. This "global" effect then leads to high internal heat generation and development of large differences in temperature between the center and edge of the sample. Such experiments can provide an approximation of operating a ceramic material under reactor-like conditions. The current FUBR [10,11,12] series of irradiations is one example of lifetime tests in a hard spectrum reactor.

The FUBR tests indicate that tritium retention is lowest for $Li_2ZrO_3$ and highest for $LiAlO_2$, and that helium retention follows a similar order. In the FUBR tests, $Li_4SiO_4$ showed a tendency for fragmentation as compared with $LiAlO_2$ and $Li_2O$, while $Li_2ZrO_3$ remained relatively crack free during irradiation. Fragmentation was not burnup dependent and was thought to

result from thermal stresses and thermal expansion [11]. In the ALICE experiments [13], no significant fragmentation of $LiAlO_2$ was observed up to 873 K and 1 at.% burnup; severe fragmentation was observed at 1023 K with thermal gradients of 100 K/min.

The thermal conductivity of irradiated $Li_2O$ and $LiAlO_2$ has been investigated by Ethridge [14] in the temperature range 373-1173 K. Samples were irradiated at 773-1173 K to lithium burnup of $11.5 \times 10^{20}$ captures/$cm^3$. In general, the measured conductivity of the irradiated material was quite similar to that for non-irradiated material. Reductions in thermal conductivity at temperatures $<573$ K were observed for lithium oxide samples as a result of irradiation-induced lattice damage, whereas at temperatures $>573$ K the thermal conductivities approached values well within the error band of non-unirradiated lithium oxide. This is consistent with the general expectation that at higher temperatures the annealing of irradiation-induced defects would improve thermal conduction. The thermal conductivity of non-irradiated lithium aluminate samples remained relatively constant with temperature for all irradiation times and temperatures and was only slightly lower than that of non-irradiated $LiAlO_2$ at high temperatures. Botter et al.[13] reported that $LiAlO_2$ samples showed no measurable change of thermal conductivity after irradiation in OSIRIS to 1% burnup at 873 K and 2% burnup at 1073 K.

### 4.2 Compatibility with Neutron Multiplier

The use of beryllium in intimate contact with lithium ceramics simplifies blanket design, improves tritium breeding, and improves thermal heat transfer. Laboratory compatibility tests on beryllium/ceramic compacts [14a] have shown little or no reaction between materials. Due to the large free energy driving force for oxidation of beryllium, a concern has been

raised as to whether or not neutron irradiation will change the currently observed reaction rate. A collaborative (EEC/USA) in-reactor test (SIBELIUS) is planned to assess the compatibility characteristics of beryllium/ceramic and beryllium/ structural compacts. Emphasis will be placed on understanding the potential for acceleration of beryllium oxidation in the neutron environment due to irradiation-enhanced diffusion of oxygen, or altered phase stability.

The experiment will be an in-situ tritium release experiment conducted in the core of the SILOE reactor in Grenoble, France. The irradiation vehicle is comprised of eight capsules, seven of which are independently purged with He/0.1%$H_2$ gas mixture. Four capsules are used to examine beryllium/ceramic ($Li_2O$, $LiAlO_2$, $Li_4SiO_4$, and $Li_2ZrO_3$) and beryllium/steel (316L and 1.4914) compacts. Two capsules, containing ceramic only ($Li_2O$ and $LiAlO_2$), will be used for comparing tritium release characteristics between capsules with beryllium and those without beryllium. It is hoped that the tritium release behavior will give an early signal of reactions between the materials in the compacts. One capsule contains large beryllium pellets for obtaining information on lifetime void swelling. The last capsule contains $Li_4SiO_4$ pebbles (0.5 mm dia) in contact with beryllium discs.

The experiment will operate for four cycles (~2000 hours) at a temperature of 823 K (the capsule containing the pebbles will operate at 723 K). Upon completion of the irradiation period, an extensive post-irradiation examination (PIE) will be initiated. The PIE will measure the tritium retention and helium retention in each ceramic and beryllium, perform detailed microscopic examination of the Be/ceramic and Be/steel interfaces using SEM, EPMA, and SIMS, conduct extensive ceramographic examination of the

couples, measure void swelling of the beryllium pellets, and perform x-ray diffraction analysis of the ceramics. Should it become necessary to clarify phenomena, $^{6}Li/^{7}Li$ isotopy, $\gamma$-spectrometry, and measurements of physical dimensions and weights will also be carried out.

4.3 Purge-Flow/High-Burnup Test

Current in-reactor testing is usually done in thermal spectrum facilities. To ensure attainment of a more balanced data base, tests are planned to add information on spectral effects and burnup effects. This test, BEATRIX-II, is sponsored by the International Energy Agency and includes vented and nonvented capsules [15]. The objective of BEATRIX-II is to conduct in-situ tritium recovery in the high energy neutron environment of the Fast Flux Test Facility (FFTF) that incorporates high damage and tritium production rates in a fully instrumented test on a larger volume of solid breeder material. The BEATRIX-II test has two experimental phases. During Phase I, two in-situ tritium release capsules containing $Li_2O$ are being irradiated with higher tritium production levels than in previous experiments. One capsule has the capacity for temperature change experiments, while the other has a temperature gradient for evaluating the stability of temperatures in an engineering blanket configuration. Nonvented capsules were included for measurement of irradiation damage, thermal diffusivity, PIE release kinetics, and beryllium compatibility.

For Phase I, special materials and components including a channeled nickel layer, tritium barrier coatings, tritium removal system, etc., were developed and adapted for BEATRIX-II. Many of these materials and components could have application in future blanket systems. Phase II is not defined at this time; however, it is likely that the testing will follow a similar approach and include a ternary ceramic.

### 4.4 Integral Effects

An issue of great concern for ceramic breeder materials is the ability of a blanket to maintain temperature profiles suitable for acceptable tritium release. While overwhelming evidence indicates that tritium release from the ceramic is effective for controlled conditions [6,16-36], there remains a concern about the performance of a blanket when the ceramic is integrated with a neutron multiplier, coolant, and helium purge gas under conditions representative of a prototypic design. Therefore, suitable "integral" testing is desired.

Such a test should also address breeder size, volumetric ratio of ceramic to structural material, temperature gradients, temperature transients, tritium generation rates, and breeder morphology. To achieve uniform tritium production, either a hard spectrum or a tailored spectrum irradiation facility is favored. Within limits, neutron flux is considered to be of lesser importance than uniform, homogeneous tritium production. Production rates of ~5 Ci/day are desirable. Capability for testing at low temperature ($<300^{o}C$) is a must if the experiment is to address the low temperature limitations to tritium release that are relevant to the ITER design. Irradiation for a one year period is appropriate.

The design of the test module could follow essential features of a current ceramic breeder design concept. For example, the ceramic breeder and beryllium multiplier could be in the form of flat plates. Active temperature control for the blanket can be obtained through the use of a gas gap, electrical heaters, or insulating material around the test section. The test should also have one or more internal coolant channels to provide a good test of the heat transfer performance of this blanket concept. The coolant could be low-temperature water. The most important issues in testing this concept are heat transfer and tritium transport.

The ceramic breeder could be in the form of a fairly large slab, at least 10 cm x 40 cm, with thickness about 2 cm. The beryllium, also in large slabs, would be the order of 1 cm thick, with additional insulation provided by a gas gap. A possible arrangement is a central slab of ceramic separated from beryllium on each side by cladding. On the outer face of the beryllium is a coolant channel comprised of a gas gap and a coolant zone. The outer zone is a ceramic slab encased in cladding. The arrangement would have multiple gas lines and a very large number of sensors such as thermocouples and neutron detectors. Tritium recovery from the ceramic breeder would be accomplished by a helium purge. If the breeder material is in the form of high-density sintered product, it may be necessary to provide flow paths for the purge gas. Such flow paths could be obtained either by cutting parallel channels or grooves on the outer surfaces of the ceramic or by surrounding the ceramic with a porous metal layer to permit purge gas flow.

The test matrix for this experiment should strive to address the following issues: (1) solid breeder tritium release performance as a function of burnup effects, phase change in solid, low-temperature limitations to tritium release, temperature cycling, and morphology changes; (2) ability of the blanket to accommodate power variations (examine thermomechanical and thermochemical effects on tritium release and ceramic stability) (3) thermal behavior of ceramic/steel and beryllium/steel interface (does high burnup change the conductance characteristics across these interfaces?).

## 5. Future Efforts

The current data base for the candidate ceramic breeder materials indicates that all materials exhibit acceptable thermodynamic, thermophysical, mechanical, and low-burnup (3%) irradiation behavior. In-situ tritium recovery experiments show very low tritium inventories for all candidates.

Fabrication of kilogram quantities of candidate ceramic materials has been achieved, and technology is available for further scaleup.

The next phase of experimental efforts must give more attention to integrated experiments that focus on materials behavior under neutron irradiation. Experiments of this type would combine ceramic, multiplier, structural material, coolant, and purge gas into a single, well-instrumented module. Such irradiations would facilitate testing of multiple effects that are not possible with single-effect tests.

Tritium-release modeling activities would need to address the interaction of tritium with inhomogeneities in the breeder such as precipitates, bubbles, and porosity. A more realistic understanding of the impact of hydrogen in the purge gas on tritium release (including both bulk and surface effects) is also needed. The response of these considerations to both short-term and long-term pulsed operation should be addressed in an integral test.

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