117
3-22-78

BNL 50748

Dr. 1945

MASTER

THE REMOVAL OF TRITIUM FROM FUSION REACTOR BLANKETS

ANNUAL REPORT FOR FY 1977

R. WISWALL AND E. WIRSING

October 1, 1977

DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

UNDER CONTRACT NO. EY-76-C-02-0016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THE REMOVAL OF TRITIUM FROM FUSION REACTOR BLANKETS

ANNUAL REPORT FOR FY 1977

R. WISWALL AND E. WIRSING

October 1, 1977

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Research sponsored by the
DIVISION OF MAGNETIC FUSION ENERGY,
U.S. DEPARTMENT OF ENERGY, WASHINGTON, D.C.

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

REA

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy (DOE), nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$4.00; Microfiche \$3.00
December 1977 190 copies

1. Introduction

This report summarizes the recent results of experimental research on tritium management in solid fusion-reactor blankets carried out at Brookhaven for ERDA's Division of Magnetic Fusion Energy (budget activity ED-02-04-e). It covers the work of FY1977, and also includes some unpublished results from the preceding Transition Period.

The program is concerned with investigating the chemistry of those compounds and alloys of lithium which have acceptable physical and neutronic properties. In particular, information is needed on whether tritium can be removed rapidly, and how removal rates are affected by particle size, temperature, dose rate, etc.; how stable the solids are under long irradiation; and whether they are chemically compatible with the other materials that will be present in a blanket. The ultimate objective is to specify an optimum compound or alloy; to describe methods of synthesizing it and incorporating it, with or without diluents, into blanket modules; and to be able to predict its long-term behavior under operating conditions.

2. Experimental Procedures

The greater part of the year's work consisted of tritium extraction experiments. The procedure was the now standard one of irradiating small samples of lithium-bearing materials with thermal neutrons and extracting the tritium thus generated by means of a helium stream at elevated temperatures. Proportional counter measurements on the effluent helium yielded data on the fraction of tritium removed in a given time interval. Details of the procedure can be found in CONF-750989, v. III, p. 232, and in BNL 20563.

A variation of the procedure was tried in one case. Usually, the sealed capsules in which samples are irradiated are cut open in a glove box and the sample is transferred to a stainless steel tube for the extraction test. This operation would result in the loss of any tritium which might have passed

from the solid into the gas phase during irradiation. To find whether such loss is appreciable, apparatus was designed which permitted the capsule to be broken open inside the extraction system. Gas-phase tritium would be carried by the helium stream into the usual counting apparatus, and would register counts while the sample was still at room temperature. When this system was used on a LiAlO_2 sample, no counts were observed; evidently the tritium remains in the solid until it is heated.

Extraction experiments were supplemented by optical studies with a scanning electron microscope and by the determination of surface area changes by means of gas adsorption measurements.

3. Lithium Aluminate, LiAlO_2

(a) Without diluents

Previous work having shown good tritium extraction from LiAlO_2 powder at 650°C , the effect of compacting the powder into pellets was determined; in a blanket, compacted shapes will probably be desirable. Cylindrical pellets, $1/4" \times 1/4"$, were put through the usual procedure. As Figure 1 shows, the extraction curve was indistinguishable from that of loose powder.

The extraction behavior of LiAlO_2 was, as previously reported (CONF 750989, v. III, p. 232), unimpaired by long exposure to 975° to 1000°C . The surface areas of the samples used in these experiments were determined by nitrogen adsorption (B.E.T. Method) and found to undergo a gradual decrease. Figure 2 gives the specific areas as a function of time of sintering. It can be seen that little change was occurring toward the end of the period. At this time, the extraction behavior was still very satisfactory.

The effect of even higher temperatures on LiAlO_2 sintering was investigated in one experiment at 1300°C . A pelletized sample was exposed to that temperature for eight days, irradiated, and extracted. Figure 3 gives the tritium release curves. It can be seen that sintering caused a considerable change in the 650°C performance, about 24% of the tritium

being retained after 5 hr. By raising the temperature to 750°C, however, satisfactory extraction was obtained. In any case, exposure to so high a temperature as 1300°C is unlikely in practice.

Knowledge of the "absolute" surface area of a LiAlO_2 powder, combined with an analysis of its tritium extraction behavior, can in principle yield values of the diffusion coefficient of tritium in LiAlO_2 . In practice, several assumptions must be made, such as that the powder consists of uniform spherical particles and that diffusion within the crystallites of the solid is the rate-limiting step in tritium release. If the latter were strictly true, the time required for 87.4% extraction of the tritium would be equal to τ , the mean life of the diffusate under conditions of continuous generation and continuous extraction. This quantity is inversely proportional to the diffusion coefficient, D:

$$D = \frac{r^2}{15\tau}$$

where r is the particle radius. With this formula, a value of $1 \times 10^{-14} \text{ cm}^2 \text{ sec}^{-1}$ was obtained on fresh LiAlO_2 at 650°C. After treatment at 975°C, values ranged from 2 to $4 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$. No great precision can be claimed for these figures since the extraction curves do not have the slope that would be predicted by the simple diffusion-controlled model in which all tritium atoms are in energetically equivalent situations. Such curves would be straight lines on the log-log plot, with a slope of 1/2. The observed curvature suggests that part of the tritium is more strongly held than the rest.

(b) LiAlO_2 - graphite mixtures

Since mixtures of lithium aluminate and graphite have been proposed for blanket use, their extraction performance was studied. In one series of experiments, LiAlO_2 powder was intimately mixed with 9 parts of spectroscopic-grade graphite powder, irradiated and tested for tritium release at 650°C. The greater part of the tritium was extracted very soon, as in

the case of pure LiAlO_2 ; however, some 30% remained unextracted after 2 hr. (With pure LiAlO_2 , only 3% was left.) If the residue was adsorbed by the graphite after release from the LiAlO_2 , a repetition of the experiment might result, we surmised, in a smaller retention. This proved to be the case; on re-irradiation of the extracted sample and re-extraction, 76% of the new tritium was recovered in 2 hr; and on still another repeat, 90% was recovered. Figure 4 gives the three curves. Evidently, the graphite surface becomes saturated with tritium. The amount required for this was calculated from our results to be only about one curie per 100 kilograms--a negligible amount for practical purposes.

Loose powder having been used for these runs, a parallel experiment was conducted on pelletized material of the same composition. At 650°C , much larger retention of tritium was observed than with the loose powder, and even at 800°C extraction was incomplete. Figure 5 shows the extraction behavior of a single pellet at successively higher temperatures (note that here we use linear, not log-log scales).

In the hope of improving the situation, mixtures were made up in which the diluent was nuclear grade rather than spectroscopic graphite. A mixture of 10 parts graphite to one of LiAlO_2 was made up, compressed at 5000 psi into pellets, and irradiated. Extraction was carried out this time at 800°C rather than 650°C ; but even at the higher temperature it was rather slow, and the value of τ was >3 hr.

Figure 6 shows the course of the extraction. For a more direct comparison with earlier runs, a 650°C extraction was subsequently carried out on a different but similarly prepared pelletized sample. The result is graphed as curve A of Figure 7; the amount removed leveled off at about 30%.

An interesting observation made during this series was that the relatively mild reactor irradiation used in our activation procedure caused serious disintegration of the pellets; some were completely reduced to powder. A sample of

this powder which was tested separately for tritium extraction gave the results shown as curve B of Figure 7.

It is possible that the poor results obtained with LiAlO_2 -graphite pellets are attributable to retention of tritium by a limited number of active sites on the graphite and that when these were filled the extraction behavior would improve. A thorough testing of the hypothesis would have required a rather lengthy series of extraction runs. Such a series did not appear worth doing because of the rather discouraging results of the chemical stability tests, which indicated that at 975°C a slow reaction takes place in LiAlO_2 -graphite mixtures. This conclusion is based on the gradual loss of weight of such mixtures when maintained at temperature in the presence of a slow stream of helium. The purpose of the helium is to carry away volatile reaction products such as CO , CO_2 , and (at 975°) Li . Experimental difficulties have so far prevented the obtaining of very accurate results, and no reaction products have been identified; but the observed weight losses would be consistent with a reaction such as

going to completion in the course of a few weeks.

The procedure used was to weigh a mixture of LiAlO_2 powder with a large excess of powdered nuclear-grade graphite into a stainless steel tube from which it could be withdrawn by means of a wire for periodic weighings, and maintain it at 975° . Ultrapure helium flowed through the tube at a rate of a few cc per minute. The weight loss increments did not follow a smooth curve, and in one experiment the total loss was even larger than the reduction reaction could account for; so that the present results should be accepted with some reserve. We believe, however, that something is happening and plan to try for a clearer picture through the use of mass spectrometry. It must be noted that H. R. Ihle and his colleagues at Jülich have

already found indications of a reaction between carbon and LiAlO_2 (Proc. 9th Symp. Fusion Technology, EUR 5602, Pergamon Press, 1946, p. 635).

4. Lithium Oxide, Li_2O

A study of lithium oxide as a breeder material was begun, since this compound would be of interest for blanket designs in which a high ratio of lithium to other atoms was desired. Most of the experiments were done on a commercial product (Ventron-Alfa) in powder form. It was sieved to obtain the usual 80 to 120-mesh fraction, dehydrated by heating to 600° to 650°C for 1 hr under vacuum, and then irradiated and extracted at various temperatures. Figure 8 shows the results at 500° , 600° , and 650°C . The corresponding values of τ , taken as the time for 87.4% extraction, are 8, 0.75, and 0.23 hr. The curves had the same general shape as those of LiAlO_2 and extraction times were comparable.

For a check on these results, a parallel experiment at 650°C was carried out on the product of another manufacturer, Atomergic. The comparison is shown in Figure 9. The difference is surprising, since the two oxides appear almost identical in the scanning electron microscope and have nearly identical specific surface areas as determined by the B.E.T. gas adsorption method: $0.17 \text{ m}^2/\text{g}$ for Ventron-Alfa and $0.19 \text{ m}^2/\text{g}$ for Atomergic. In both cases, the surface areas as estimated from the electron micrographs were in good agreement with the B.E.T. results; that is, the fairly uniform particles that were seen in the micrographs did not possess internal porosity, and the material could be considered as constituted, approximately, of equal spheres of a diameter calculable from the surface area. With this approximation, and the additional assumption of diffusion-limited kinetics, diffusion coefficients can be calculated from the values of $t_{0.874}$. Some values so obtained were:

Ventron Alfa, 600°:	$2 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$
Ventron-Alfa, 650°:	5×10^{-11}
Atomergic, 650°:	1×10^{-11}

These are significantly larger than the corresponding values for LiAlO_2 .

5. Lithium-Lead Alloy

Pure metals were melted together in a graphite crucible in a proportion to give the intermetallic compound Li_7Pb_2 . The product was ground into coarse particles, irradiated, and extracted as usual under varying conditions. Figure 10 shows the effect of temperature on tritium extraction from 20 to 30-mesh material, under the usual helium flow rate of 60 cc/min. The times for 87.4% removal are, in hours: 350°, >10; 400°, 5.5; 450°, 2.6; 500°, 0.29; 550°, 0.13.

To determine the effect of particle size, a 450°C run was carried out on a sample of 60 to 80-mesh material, other conditions being the same. Figure 11 shows the comparison. With the finer material, 87.4% extraction was reached in 0.46 hr.

To find whether the flow rate of the extracting helium was an important variable in this system, a 500°C run was carried out on 20 to 30-mesh alloy with a fivefold slower flow. As Figure 12 shows, extraction was somewhat slower but still satisfactory.

A modification that had had a significant accelerating effect on tritium extraction from LiAl was the addition of a little hydrogen to the helium stream; presumably this was due to the facilitation of the escape of tritium from the metal surface through the formation of HT molecules. We therefore tried adding 100 ppm H_2 to the hydrogen in runs on Li_7Pb_2 (20 to 30-mesh, flow rate 60 cc/min) at 400°C and 500°C. Figure 13 shows that the addition resulted in a slightly faster extraction at both temperatures.

Finally, the effect of maintaining Li_7Pb_2 at an elevated temperature for long periods was tested. A temperature of 550°C was chosen, as being sufficiently close to the melting point, 726°C , to be likely to cause sintering; for the extraction tests, 450°C was chosen, since it gave satisfactory rates on fresh material. Figure 14 shows the surprising result that the extraction behavior improved with the "aging" of the material. Microscopic examination of aged samples showed, not normal sintering, but an apparent separation into two phases. Not enough is known about the Li-Pb system to preclude such a possibility. Whatever is happening at least seems to be beneficial.

6. Lithium Silicide

Since silicon is one of the elements that are acceptable in a minimum-activity blanket, compounds in the system Li-Si are worth investigating. There are two: Li_2Si , which melts congruently at 760° , and Li_4Si , which undergoes peritectic decomposition at 634°C . Samples of the former were prepared by heating the elements together in graphite crucibles to 800°C , under argon, in a resistance furnace. The product was brittle and very sensitive to moisture. Samples were ground and sieved in an inert atmosphere and subjected to the usual routine of our tritium generation and extraction runs. Material of 80 to 120-mesh was treated at 550° , 600° , and 650°C , with the results shown in Figure 15. From the curves the times at 87.4% extraction are as follows: 550° , >10 hr; 600° , 1.8 hr; 650° , 0.19 hr. To see whether particle size has an important effect, two runs were carried out on a coarser material of the same composition: 20 to 30-mesh grains. As Figure 16 shows, the 550°C curve was almost exactly congruent with that of the finer material, and the 600°C curves were sufficiently close that the effect of gross particle size (in this range) can be considered negligible.

7. Lithium Nitride

An attempt was made to measure the rate of tritium extraction from lithium nitride, Li_3N . This is less stable than the lithium compounds previously tested, and could not be given the usual 500° to 600°C evacuation pretreatment without decomposing. A room-temperature vacuum treatment had to suffice, after which the usual thermal-neutron irradiation was given. The resulting tritium-containing sample was exposed to flowing helium at a series of temperatures from 300°C up, with the downstream gas being analyzed as usual for tritium. None was observed at up to and including 550°C . At 600°C the nitride began to decompose, with some release of tritium. It may be concluded that the nitride is not a promising material for blanket purposes.

Figure 1. Removal of tritium from irradiated LiAlO_2 at 650° .

Figure 2. BET surface area of LiAlO_2 powder vs. time of sintering at 1000°C .

Figure 3. Removal of tritium from irradiated LiAlO_2 at 650°C effects of sintering on pellets.

Figure 4. Removal of tritium from an irradiated mixture of LiAlO_2 and graphite at 650°C ; successive irradiations of a single sample.

Figure 5. Removal of tritium from pelletized mixture of LiAlO_2 and spectroscopic graphite.

Figure 6. Removal of tritium from pelletized mixture of LiAlO_2 and nuclear graphite at 800°C .

Figure 7. Removal of tritium from irradiated mixture of LiAlO_2 and nuclear graphite, at 650°C .

Figure 8. Removal of tritium from irradiated Li_2O powder (alfa).

Figure 8. Removal of tritium from irradiated Li_2O powder (Alfa).

Figure 10. Effects of temperature on the removal of tritium from irradiated Li_7Pb_2 . Particle size: 20-30 mesh.

Figure 11. Removal of tritium from irradiated Li_7Pb_2 alloy at 450°C , effect of particle size.

Figure 12. Effects of helium flow rate on the removal of tritium from irradiated Li_7Pb_2 alloy at 500°C .

Figure 13. Removal of tritium from irradiated Li_7Pb_2 alloy, effect of hydrogen in the gas stream.

Figure 14. Removal of tritium from irradiated Li_7Pb_2 alloy at 450°C , effect of previous sintering at 550°C .

Figure 15. Removal of tritium from irradiated Li_2Si . Particle size: 80-120 mesh.

Figure 16. Removal of tritium from Li_2Si . Particle size: 20-30 mesh.