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DEPARTMENT of APPLIED SCIENCE

THE REMOVAL OF TRITIUM FROM SOLID CTR
BLANKET MATERIALS; A PROGRESS REPORT

R. H. Wiswall
E. Wirsing

February 11, 1975

MASTER

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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**Brookhaven National Laboratory
Upton, New York 11973**

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SOLID CTR BLANKET MATERIAL

ABSTRACT

It has been shown experimentally that tritium can be easily removed from certain solid lithium compounds that have been proposed as components of CTR breeder blankets. The compounds tested were LiAl , LiAlO_2 and Li_2SiO_3 in granular or powder form; the procedure was to pass a stream of helium through a bed of material maintained at a temperature in the range $400\text{-}600^\circ\text{C}$. As the tritium, which had been previously generated in the materials by exposure to thermal neutrons, diffused out and was carried away, its concentration was continuously monitored by radioactive assay of the gas stream. From the data, it was possible to calculate average lifetimes of tritium in a continuously extracted breeder blanket. Lifetimes of a few hours were found for LiAl at $400\text{-}500^\circ$, LiAlO_2 at 600° and Li_2SiO_3 at $500\text{-}600^\circ$.

THE REMOVAL OF TRITIUM FROM SOLID CTR BLANKET MATERIAL

Introduction

It has recently been proposed by J.R. Powell⁽¹⁾ et al. that blankets in which lithium is present in a solid form offer certain advantages over systems containing it in the form of the liquid metal or in a fused salt mixture. These authors have elaborated a conceptual scheme involving the alloy LiAl, which is solid up to 718°. Other possible solid vehicles for lithium are the silicate, Li_2SiO_3 , and the aluminate, LiAlO_2 . The first criterion in the selection of candidate solids is that they do not acquire long-lived induced radioactivity under blanket conditions, since a primary goal of the solid-blanket concept is to achieve a system with a low inventory of radioactive, and therefore hazardous, material. This goal also requires, and the concept postulates, that bred tritium will be removed from the blanket after a very short average residence time. The purpose of the research described in this Report was to find out whether tritium could indeed be moved from a lithium-bearing solid of suitable nuclear properties at reasonable rates under practically attainable conditions. An affirmative answer having been obtained early on, a more detailed study of the removal kinetics was undertaken, and is continuing. In this, we determine the effect on tritium removal rates of changes in a number of variables, such as chemical composition of the solid, particle size, temperature, helium flow rate, presence of normal hydrogen in the helium, etc. We hope eventually to establish a model of the tritium removal process which will permit us to explain the dependence of removal rates on amount removed in terms of the successive steps involved - diffusion in solid, escape from surface, etc.

Experimental Procedure

Experimental procedure parallels the processes that are postulated for our blanket concept as closely as possible. Small concentrations of tritium are generated uniformly throughout small (ca. 0.5g) samples of a solid compound or alloy of lithium by exposure to thermal neutrons in the Brookhaven Medical Reactor. A typical exposure is one hour at a flux of 10^{13} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. This results in the formation of about ten millicuries of tritium per gram of lithium, or an atom fraction of tritium, relative to lithium, of 2.4×10^{-6} . For comparison, an atom fraction of not more than 1.0×10^{-6} is desired as the steady-state concentration in an actual blanket; this would give a tritium holdup of 160g in a 1000 MWe reactor. In some respects (temperature, radiation flux) the irradiation conditions are very different from those of a blanket, and in-pile experiments must eventually be resorted to in order to confirm present results.

Material is customarily crushed, if necessary, and screened to approximately uniform particle size before exposure in the reactor. After irradiation, a sample of about 250 mg is transferred to the extraction tube, which is simply an 11 mm OD tube of Pyrex, Vycor or stainless steel provided with a frit of the same material to support the sample. This is connected into the extraction and analysis train, a schematic diagram of which is given in Figure 1. Helium ("Typical analysis": 99.96% He, 0.3 ppm H_2 , 5.8 ppm CO_2 , dew pt., -60°C) flows up through the frit and carries away whatever tritium is released by the sample. The helium flow is monitored by a Matheson mass flowmeter, type H-500M, model ALL-500; its readings are continuously recorded on a strip chart. Except where otherwise noted, a flow of 60 cc/min, or 1.4 lb/hr-ft^2 , was used. A tube furnace and its associated controller can maintain the reaction zone at any temperature up to 850° . The sample temperature, as determined by a thermocouple on the outside of the tube, can be raised from room temperature to 500° in 20 minutes. In the range 500° to 850° , the temperature fluctuates about $6-7^\circ$ above and below the control point.

The tritium content of the helium leaving the extraction tube is determined from radioactivity measurements by means of an internal proportional counter.⁽²⁾ For this purpose, the helium first goes to a mixing device where one part of helium is mixed with 10 parts of P-10 counting gas (90% argon, 10% methane). Rotameters measure the helium and P-10 flows; proportioning is done manually with a Matheson Flow Proportioner Mixer, Model 665-1 and is probably accurate to within about 2 percentage points of helium. The mixture flows through a counting tube of conventional construction - an internally silvered Pyrex tube of 23 mm OD, with central tungsten wire anode. The silvered length is 30 cm.

In runs on the oxygen-containing compounds Li_2SiO_3 and LiAlO_2 , it was found that the tritium yields as determined by counting the gas stream were often much less than the loss of tritium from the solid samples as determined by scintillation counting before and after the runs. Apparently the tritium failed to reach the counting chamber or for some other reason failed to register. It was suspected that tritium might be coming off the compounds in question as T_2O or HTO , rather than as T_2 or HT , which were believed to result from the helium extraction of LiAl . A unit was therefore inserted into the reaction train for the purpose of reducing oxygen-containing species. It consists of a 3/16" i.d. stainless steel tube filled for about 9" of its length with 30-mesh zinc powder, which has first been cleaned with dilute HNO_3 . A furnace maintains it at a temperature of 400° during a run. Its use has resulted in the obtaining of total counts of the same order for the oxygen-containing materials as for alloys, and the reproducibility is much improved.

In order to determine the optimum voltage (about 2000 V), count rates vs. voltage are determined from time to time on a Na-22 source. Reasonably level plateaus are found, so small voltage variations are not considered to be a source of error. Neither is the count very sensitive to the helium-P-10 ratio; in a typical experiment, changing the ratio from 1:10 to 1:11 resulted in the count rate changing from 5315 to 5095 counts/15 minutes.

Tritium disintegrations are registered and recorded on standard counting equipment. It can measure either "instantaneous" count rates (with a variable time constant) or it can integrate the total number of counts recorded over a period. The latter mode has been the more usual in our work. The number obtained does not have an absolute significance, but relative counts provide all the needed information in these runs. It is only necessary to make sure that the helium and P-10 flow rates are constant throughout a run. Results are analyzed more easily if the total tritium activity that has been removed at any point can be expressed as a fraction of the total activity in the sample at the beginning of the run. Whenever possible, this quantity was obtained by driving the entire tritium charge into the helium stream. In low-temperature runs, where only a fraction of the tritium was extracted in a reasonable time, the temperature was raised at the end to a point where removal was essentially complete in an hour or two. Completeness of removal was usually verified by dissolving part of the material at the end and analyzing the aqueous solution by scintillation counting.

Materials

Although only a few elements have nuclear properties which permit their use in a low-activity CTR blanket, their combinations with lithium and each other constitute a sizeable group of solid compounds: LiAl , Li_3Al_2 , Li_4Si , Li_2Si , LiAlO_2 , Li_2SiO_3 and Li_2BeO_3 are only some of the possible candidates. Experiments have so far been carried out on LiAl , LiAlO_2 and Li_2SiO_3 .

The intermetallic compound LiAl is a brittle solid which crystallizes in the b.c.c. NaTl (B32) type of structure. It is a phase of variable composition, extending from about 45 to 56 atom percent lithium. The equiatomic composition melts congruently at 718° . Its room temperature density is 1.73, corresponding to 0.35g Li per ml. For the present series of experiments, samples were made by melting Li and Al together under an inert atmosphere in a stainless steel crucible heated by an induction furnace. The cooled product was transferred to an argon-filled glove box for grinding, screening and encapsulating prior to irradiation.

Lithium metasilicate, Li_2SiO_3 , was obtained from Alfa Products as a fine powder of "98 + %" purity. Lithium aluminate, LiAlO_2 , was obtained from Alfa Products as a palpable powder stated to contain 21.4% Li_2O (theoretical for LiAlO_2 , 22.7%). Both the silicate and aluminate were classified into various size fractions by means of wire sieves.

Results

The removal of tritium from coarsely granular LiAl proved relatively easy. Even as low as 400° , half of the tritium was carried away by helium in 5 hours. The initial removal rate was always fast, but decreased rapidly, so that the results are most conveniently plotted on log-log paper. Figures 2 and 3 show several graphs of this sort. These illustrate the effect on the extraction kinetics of changes in the principal variables of the present series, namely particle size and temperature. Figure 4 repeats selected curves from figures 2 and 3 for cross-comparison purposes.

The helium flow is another variable quantity, one which could be important if transfer of tritium across the solid-gas interface were rate-limiting. A tendency for tritium in the gas phase to be redeposited on to the alloy would be lessened by increased flow. In Figure 5, two runs are shown in which everything was kept constant except the helium flows, which differed by a factor of five. The difference is probably significant, although it must be admitted that "identical" pairs of runs have differed nearly as much. Further experiments are needed on the effect of flow rate.

Another test of the role of surface reactions in the overall extraction process was obtained by comparing runs with and without added hydrogen. If the combination of tritium atoms to form T_2 at the solid-gas interface were rate-limiting, the addition of hydrogen to the helium should hasten the removal by permitting the formation of HT molecules. Figure 6 shows the course of tritium removal in four runs. In two, the usual tank helium was used; in the other two, 1000 ppm H_2 was added to the helium. It is clear that the tritium was removed faster by the H_2 -He mixture, especially in the early stages of the runs. The difference is much larger than the difference between the members of either pair of similar runs.

Less complete data have been obtained on lithium aluminate and lithium silicate. In both cases, good extractions were achieved, but it was necessary to resort to smaller particles and higher temperatures than with LiAl . Figure 7 illustrates the course of tritium removal from LiAlO_2 particles of 70-100 mesh (150 to 210 micrometers particle diameter) at 500° and 600° . At the higher temperature some 44% was removed in one hour and 90% in five hours. The dashed line, which has a slope of $1/2$, was drawn in to show how closely the 600° kinetics conform to those expected for a diffusion-controlled reaction; see the discussion section below. The 500° curve also approaches a slope of $1/2$.

Figure 8 gives a similar graph for Li_2SiO_3 particles of the same size as the LiSiO_2 , 70-100 mesh, extracted at 500° . Here too a slope - one-half line is included. About 23% of the tritium was extracted in one hour.

Discussion

It is clear that low tritium inventories can be attained by the continuous extraction of LiAl blankets at 500° , or LiAlO_2 or Li_2SiO_3 blankets at 600° . An exact determination of the hold-up times to be expected requires an analysis of the kinetic behavior illustrated in Figures 2 through 8 and the development of a physical model of what is happening. It is reasonable to expect the removal rate to be limited by slow diffusion of tritium from the interior of a particle to the surface; although a slow transfer of tritium from the surface to the gas phase may also play a role. A mathematical analysis of diffusion-limited extraction was worked out several years ago in connection with a similar problem and was presented in a Brookhaven report⁽³⁾. A rigorous analysis yields a rather complex function relating fraction removed to time, but certain approximations are permissible and useful. At relatively short time,

$$f \approx \frac{6}{r\sqrt{\pi}} \sqrt{Dt}$$

where f is the fraction removed, r is the particle radius, D the diffusion coefficient and t the time. In a regime where this equation held, our log-log removal plots should be linear, with a slope of $1/2$. With LiAl , no such linear regions are observed; nevertheless, diffusion coefficients calculated by (1) from the data in those parts of the curve closest to a slope of $1/2$ may have some significance. With LiAlO_2 and Li_2SiO_3 , the extraction behavior is consistent with equation (1) and the diffusion coefficients should be more trustworthy.

Hold-up times in a continuously irradiated, continuously extracted material are related to the diffusion coefficient and the particle radius by the equation

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

Some representative values of D and τ thus derived from the results graphed in Figure 2-8 are the following:

<u>Material</u>	<u>T, °C</u>	<u>D, cm² sec⁻¹</u>	<u>τ, hours</u>
LiAl, 5-10 mesh	500	7×10^{-10}	1500
LiAl, 5-10 mesh	600	3×10^{-8}	14
LiAl, 10-20 mesh	400	2×10^{-8}	6
LiAl, 10-20 mesh	500	3×10^{-7}	0.3
LiAl, 10-20 mesh H ₂ added to He	400	1×10^{-7}	1
LiAlO ₂ 70-100 mesh	500	3×10^{-12}	500
LiAlO ₂ 70-100 mesh	600	3.8×10^{-10}	3.9
Li ₂ SiO ₃ 70-100 mesh	500	1×10^{-10}	13.9

The discrepancies in the D values among the LiAl runs as particle sizes and other factors varied illustrates the inadequacy of the kinetic model and the low reliability of the values. The more reliable values found for LiAlO₂ and Li₂SiO₃ may be compared with the results of G. Caskey (4) on tritium diffusion in rutile at 600°C (extrapolated). He found D values of 1×10^{-9} and 4×10^{-8} cm² sec⁻¹ in the a and c directions respectively.

Attempts were made to interpret the LiAl results in other ways but without much success. "First order plots" of the logarithm of the fraction remaining vs. the time proved far from linear; the rate fell off much faster than called for by $-dy/dt = ky$. A more probable differential equation would be $-dy/dt = ky^2$. This would result if the surface reactions were limiting and Sieverts' law were obeyed; i.e., if the escaping tendency of tritium were proportional to the square of its concentration in the solid, assumed to be uniform throughout each particle. The integrated form of this is such that a plot of $f/(1-f)$ vs. t should be a straight line. This was sometimes but not generally observed. Certain qualitative considerations point to a combination of slow steps. The fact that removal rates from LiAl were increased both by increasing the flow of helium and by adding 1000 ppm H₂ to the helium shows that surface reactions are important. On the other hand, the great increase in

extraction rate on going from 5-10 mesh to 10-20 mesh particles indicates that slow internal diffusion is playing an important part.

It is possible that not all the tritium atoms are in equivalent situations. For example, an analysis of one 400° run (by Dr. F. T. Miles) indicated that about 25% of the tritium came off almost at once; 15% came off with a half-life of 0.36 hours; and the removal of the remaining 60% approximately obeyed diffusion-law kinetics, with a mean life of 12 hours.

One fact established by the experiments is that the equilibrium tritium pressure over LiAl is much greater than over pure Li, for a given T/Li ratio in the metal phase. For lithium, Sieverts' constant values have been estimated by ANL workers as follows (5):

<u>Temp., °C</u>	<u>$K_s \text{ (torr)}^{\frac{1}{2}} (\text{atom fraction tritium})^{-1}$</u>
1000	243
900	157
800	93
700	51

For LiAl, a lower limit can be calculated on the assumption that the tritium in the gas stream leaving the sample is in equilibrium with a surface whose tritium content is given by the average tritium concentration in the sample. A typical value found was 12,200 at 500°. It could be in error by as much as a factor of two, since it is derived from the slope, at a particular point, of a curve such as those of Figures 2 and 3 and these slopes were not very reproducible. Making due allowance for this, however, it is clear that the pressure, at a given tritium content, is orders of magnitude higher in LiAl than in Li. That is, the presence of aluminum greatly reduces the affinity of lithium for hydrogen. Without aluminum, the fugacity of hydrogen over Li-H systems is so small that separation cannot be accomplished by any sparging or distillation process. With aluminum, it is clear that a simple physical separation is feasible.

The writers thank J. R. Powell and F. T. Miles for stimulating discussions and useful suggestions.

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SCHEMATIC DIAGRAM OF EXPERIMENTAL UNIT
USED FOR TRITIUM EXTRACTION

Figure 1

REMOVAL OF TRITIUM FROM
LiAl OF 5-10 MESH

Figure 2

REMOVAL OF TRITIUM FROM
LiAl OF 10-20 MESH

Figure 3

REMOVAL OF TRITIUM FROM LiAl: EFFECT OF TEMPERATURE AND PARTICLE SIZE.

A	5-10	MESH, 500°
B	5-10	MESH, 600°
C	10-20	MESH, 400°
D	10-20	MESH, 500°

Figure 4

REMOVAL OF TRITIUM FROM
LiAl OF 10-20 MESH AT 500°
EFFECT OF HELIUM FLOW RATE

Figure 5

REMOVAL OF TRITIUM FROM
LiAl OF 10-20 MESH AT 400°:
EFFECT OF ADDED H₂

Figure 6

REMOVAL OF TRITIUM FROM
 LiAlO_2 OF 70-100 MESH.
DASHED LINE HAS SLOPE OF $\frac{1}{2}$.

Figure 7

REMOVAL OF TRITIUM FROM Li_2SiO_3
OF 70-100 MESH AT 500°

Figure 8