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TRITIUM RECOVERY FROM LITHIUM OXIDE PELLETS

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ABSTRACT

The TFTR Lithium Blanket Module is an assembly containing 650 kg of lithium oxide that will be used to test the ability of neutronics codes to model the tritium breeding characteristics of limited-coverage breeding zones in a tokamak. It is required that tritium concentrations as low as 0.1 nCi/g bred in both metallic lithium samples and lithium oxide pellets be measured with an uncertainty not exceeding $\pm 6\%$. A tritium assay technique for the metallic samples which meets this criterion has been developed. Two assay techniques for the lithium oxide pellets are being investigated. In one, the pellets are heated in a flowing stream of hydrogen, while in the other, the pellets are dissolved in 12 M hydrochloric acid.

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III. INTRODUCTION

The Lithium Blanket Module (LBM) program being conducted for the Tokamak Fusion Test Reactor (TFTR) program at the Princeton Plasma Physics Laboratory (PPPL) will test the ability of advanced neutronics codes to model the tritium breeding characteristics of limited-coverage breeding zones in a toroidal fusion device.¹ A 1500 kg module called the LBM, consisting of 920 breeder rods that contain 23000 reactor-prototypical lithium oxide pellets and a few diagnostic metallic lithium samples, will be irradiated by the extended fusion neutron source of the TFTR. The tritium inventory of numerous lithium oxide pellets and metallic lithium samples will be measured and used to test the neutronics codes. It is vital that tritium concentrations as low as 0.1 nanocurie per gram of lithium (nCi/g_{Li}) be measured with an uncertainty not exceeding $\pm 6\%$. This paper reports the manufacture of the metallic samples to be used in the LBM and describes a tested method of accurately measuring the tritium bred in them. This paper also reports ongoing work to develop and test methods of accurately measuring tritium bred in LBM-type lithium oxide pellets.

II. METALLIC LITHIUM SAMPLES

At Argonne National Laboratory (ANL) during 1982, natural lithium samples that were appropriate for use in the LBM were produced, clad in No. 1100 aluminum, irradiated in the thermal column of the Argonne Thermal Source Reactor (ATSR), and assayed for tritium. These experiments allowed us to gain experience producing such samples, allowed us to identify errors associated with the tritium assay procedure, and allowed us to prove the feasibility of measuring tritium concentrations as low as $0.1 \text{ nCi/g}_{\text{Li}}$ in 2 g samples with an absolute accuracy of $\pm 6\%$.

A. Fabricating metallic samples

At ANL, 26 metallic lithium samples were fabricated in an argon atmosphere by first melting a solid billet of natural lithium and then pouring it into an extrusion cylinder. After reaching room temperature, a solid lithium rod, having a diameter of 1.78 cm, was extruded using a hydraulic jack, and was then cut into 3.5 g samples.

To protect the cylindrical lithium samples from atmospheric contamination, they were sealed in aluminum capsules shaped like top hats, which are shown in Fig. 1, by cold welding the parallel flanges using a hydraulic press. A faulty seal would have been indicated by a slow weight gain, so the sealed samples were weighed to the nearest 10 μ g. This sealing technique was highly satisfactory because none of the samples exhibited any weight gain after five months.

In the LBM, a few of the lithium oxide pellets will be replaced by metallic lithium samples of a various isotopic content. These clad metallic samples will be 2.5 cm in diameter and 1.3 cm long, and contain approximately 2.0 g of lithium.

B. Extracting ^3H from metallic samples

In the LBM program, tritium will be extracted from the irradiated aluminum-clad lithium samples using a method similar to one that has been successfully employed at ANL since the late 1960s for samples with much larger tritium inventories.² At temperatures above the melting point of LiH(s), 680°C, the following a reaction occurs rapidly:

This is an equilibrium phenomenon, with the equilibrium partial pressure of hydrogen being approximately 40 torr at 700°C. Therefore, the tritium-bearing sample is first surrounded with a known amount of hydrogen and the temperature is raised to 700°C, whereupon the hydrogen reacts with the lithium and the pressure drops toward the equilibrium value. After one hour, hydrogen is continually bled from the system so that the reaction is reversed:

This tritiated gaseous sample is converted, using $\text{CuO}(\text{s})$, into a tritiated water sample, which is then collected in a cold trap at liquid nitrogen temperature. Finally, the activity of the collected water is determined with a liquid scintillation counter that has been calibrated with a NBS tritiated water standard. For the LBM experiments, the resulting mass of tritiated water will be approximately 1.0 g. The tritium extraction apparatus to be used in the LBM program appears schematically in Fig. 2, while the extraction procedure is summarized in Fig. 3.

C. Testing the assay method

To test the tritium assay procedure for metallic samples, accurately known tritium inventories between 0.16 and 7.21 nCi were bred in the 3.5 g natural lithium samples by irradiating them in the graphite thermal column of the ATSR. For each irradiation, the samples were fastened to an aluminum wheel, which was uniformly rotated to ensure that they were identically

irradiated. For these experiments, gold foils were secured to the exterior of three samples. During the irradiation, tritium was produced by the ${}^6\text{Li}(n,\alpha){}^3\text{H}$ reaction and the foils were activated by the ${}^{197}\text{Au}(n,\gamma){}^{198}\text{Au}$ reaction. After irradiation, the gold foil activities were measured by gamma counting with a calibrated sodium iodide detector, and the tritium content of the irradiated samples was measured as described above.

Predicting the tritium inventories was complicated because large self-shielding effects were present. To overcome these difficulties, Bretscher at ANL precisely modeled the ATSR thermal column and performed Monte Carlo calculations to predict the tritium inventories from the measured gold foil activities.³ For our experiments, the model was composed of cylindrical natural lithium samples of varying size surrounded by an air gap, aluminum cladding, and a 1 mil thick gold foil. The continuous energy Monte Carlo Code VIM, and the ENDF/B Version IV cross-sectional data base were used to calculate the $A({}^3\text{H})/A({}^{198}\text{Au})$ activity ratio present at the end of the irradiation. Sufficient neutron histories were followed to provide a 10 precision of 1%. As can be seen in table 1, the model consistently predicted larger tritium inventories than those measured, but the discrepancy was always less than 2.8%.

Error estimates associated with the above tritium assay procedure for a 2 g lithium sample with a tritium inventory of 0.2 nCi are summarized in table 2 and are discussed in detail by Bertone.⁴ The errors associated with the incomplete recovery of tritium were difficult to quantify, but all evidence indicates that the Fig. of 3% is extremely conservative.

III. LITHIUM OXIDE SAMPLES

Currently, we are investigating two methods of measuring tritium concentrations as low as $0.1 \text{ nCi/g}_{\text{Li}}$ in LBM lithium oxide pellets with an uncertainty not exceeding $\pm 6\%$. These pellets are 2.54 cm in both diameter and length, have a density that is 80% of the theoretical density, and have a natural lithium mass of 9.63 g. The tritium assay methods of interest are a dissolution technique and a thermal extraction technique.

A. The thermal extraction method

The primary method of measuring tritium bred in LBM lithium oxide pellets will be a thermal extraction procedure that is similar to those employed in past experiments, which have been conveniently summarized by Tanifuji.⁵ These experiments were concerned with measuring the rate at which much larger amounts of tritium escape from irradiated lithium oxide; the LBM program is concerned with accurately measuring total tritium inventories, so a simpler procedure can be employed. The experimental apparatus to be employed in the LBM program appears schematically in Fig. 4.

The bred tritium will be thermally driven from the irradiated LBM pellets into slowly flowing hydrogen which subsequently passes over a hot bed of copper oxide. In this bed, the hydrogen and the tritiated species will be converted into tritiated water and then collected in a trap operating at liquid nitrogen temperature. The amount of tritium in the collected sample, which is expected to weigh less than 5 g, will be accurately assayed using a standard liquid scintillation counter.

Unlike past experiments, hydrogen will be used as the carrier gas for a number of reasons. First, a closed system can be employed, which eliminates the possibility of tritiated water being swept out of the system by an inert

carrier gas. Secondly, the amount of hydrogen used during the extraction can be measured and compared to the amount of tritiated water that is actually collected, so any material losses can be detected. Finally, the presence of hydrogen may, by isotopic exchange, minimize the amount of tritium that is lost by adsorption onto the walls of the apparatus.

Using the procedure outlined above, it is expected that the removal of tritium from a typical LBM pellet will be completed in a few hours at extraction temperatures between 650 and 850°C. This is supported by the Wiswall and Wirsing experiments which indicated that more than 95% of the tritium bred in small powdered lithium oxide samples can be removed in one hour at 650°C, and the Tanaka experiment which indicated that tritium bred in small lithium oxide pellets with densities as high as 88.5% of the theoretical density is released at the same rate as from lithium oxide powder.^{6,7}

B. The dissolution method

The amount of tritium bred in LBM pellets can also be measured by dissolving the oxide in acid, thereby incorporating the tritium into a water molecule. Unfortunately, this simple procedure creates a voluminous tritiated water sample which, in turn, causes substantial counting errors. We are developing a procedure that minimizes the final volume of tritiated water by using a concentrated acid.

Concentrated hydrochloric acid has been used in our experiments. When irradiated lithium oxide reacts with 12 M hydrochloric acid, a clear and colorless tritiated salt solution results:

It is thought that all the tritium is liberated as a tritiated water molecule:

This water sample can be distilled from the lithium chloride and subsequently assayed using a standard liquid scintillation counter.

This superficially simple procedure is complicated by three factors. First, the reaction between lithium oxide and concentrated hydrochloric acid is exothermic and extremely rapid. Secondly, some tritium might escape from the liquid phase. Finally, this procedure may require a lithium oxide purity that is greater than that in the conventional LBM pellets. When contaminated pellets are dissolved, the tritium might be incorporated into an insoluble form precluding its incorporation into the water sample.

The random counting errors associated with this tritium assay technique will be acceptable. When 12 M hydrochloric acid dissolves a 21 g LBM pellet containing tritium, 100 ml of tritiated water is produced. It is possible to assay 5 ml of this water sample as a single liquid scintillation sample with an efficiency approaching 50%, so random counting errors below 2% can be expected for counting times longer than three hours.

C. Testing the assay methods

It will be tremendously important to test both methods of assaying tritium that has been bred in lithium oxide pellets. Three independent checks will be used.

The first test of the assay methods is simple: the results will be

compared. Accordingly, many irradiations are planned in which multiple lithium oxide pellets will be identically irradiated.

A second method of testing the assay methods utilizes the recent work by Bretscher at ANL outlined above. Basically, lithium oxide pellets, metallic lithium samples, and diagnostic gold foils will be simultaneously irradiated by thermal neutrons in the ATSR. The tritium inventory of the metallic samples and the activity of the gold foils will be measured as described above, and will be used to calculate the expected tritium inventory in the lithium oxide pellets.

The final method of testing the assay methods involves the irradiation with energetic neutrons. Metallic lithium samples and LBM-type lithium oxide pellets will be produced from isotopically pure ^7Li . These samples will be identically irradiated with the 14 MeV neutron generator at PPPL. Under these circumstances, self-shielding effects will be minimized and the tritium inventory of the lithium oxide pellets can be more readily predicted from the measured tritium inventory of the metallic samples.

IV. SUMMARY

The LBM program requires the measurement of tritium concentrations as low as $0.1 \text{ nCi/g}_{\text{Li}}$ in both metallic lithium samples and lithium oxide pellets. The measurement technique for metallic samples has been developed and successfully tested. Initial experiments indicate that the thermal extraction and dissolution measurement techniques for lithium oxide pellets are both likely to meet the design criterion of an assay uncertainty not exceeding $\pm 6\%$.

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REFERENCES

- ¹D.W. Graumann, R.L. Creedon, B.A. Engholm, J.R. Lindgren, and L. Yang, in Proceedings of the 5th Topical Meeting on the Technology of Fusion Energy, Knoxville, TN, 1983.
- ²D.L. Smith, M.M. Bretscher, and J.W. Meadows, Nucl. Sci. Eng. 78, 359 (1981).
- ³M.M. Bretscher, in: Proc. 10th Symp. on Fusion Engineering, 1983, in print.
- ⁴P.C. Bertone, to be published.
- ⁵T. Tanifuji, K. Noda, S. Nasu, and K. Uchida, J. Nucl. Mater. 95, 108 (1980).
- ⁶R.H. Wiswall and E. Wirsing, BNL-50748 (1977).
- ⁷K. Tanaka, H. Kudo, and H. Amano, in Proceedings of the International Conference on Radiation Effects and Tritium Technology for Fusion Reactors, Gatlinburg, TN, 1975.

TABLE 1

Predicted and Measured Tritium Inventories
Bred In Metallic Lithium

<u>Sample</u>	<u>Measured Inventory (nCi)</u>	<u>Predicted Inventory (nCi)</u>
Li-02	0.718	0.735
Li-22	2.038	2.095
Li-23	2.029	2.046

TABLE 2

Estimated Maximum Errors Associated With The
Tritium Assay Procedure For Metallic Samples

<u>Error</u>	<u>Type</u>	<u>Magnitude(%)</u>
Scintillation	Random	1.
Counting		
NBS Tritiated	Systematic	1.
Water Standard		
Extraction System	Systematic	1.
Background		
Incomplete	Systematic	3.
Recovery of Tritium		

FIGURE CAPTIONS

FIG. 1 Aluminum Cans To Seal Lithium Samples.

FIG. 2 Metallic Lithium Extraction Apparatus.

FIG. 3 Metallic Lithium Extraction Procedure.

FIG. 4 Lithium Oxide Extraction Apparatus.

#83P0147

WALL THICKNESS: 0.41 mm

Fig. 1

Major Components: 304 and 316 SS

Fig. 2

Fig. 3

Major Components :304 and 316 SS

Fig. 4

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