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TRITIUM RELEASE FROM LITHIUM SILICATE
AND LITHIUM ALUMINATE, IN-REACTOR AND OUT-OF-REACTOR

A. B. Johnson, Jr.

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TRITIUM RELEASE FROM LITHIUM SILICATE
AND LITHIUM ALUMINATE, IN-REACTOR AND OUT-OF-REACTOR

By

A. B. Johnson, Jr.
Metallurgy Research Section
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TRITIUM RELEASE FROM LITHIUM SILICATE
AND LITHIUM ALUMINATE, IN-REACTOR AND OUT-OF-REACTOR

INTRODUCTION

Considerable technology has developed for production of tritium in metallic target systems by the reaction

At normal N-Reactor temperatures ($\sim 300^\circ\text{C}$), aluminum-lithium alloys appear to offer a satisfactory system for tritium production.⁽¹⁾ However, reactor safety requirements have generated interest in a target system which will hold the lithium in place at temperatures to 1200°C . At the same time, gas retention at irradiation temperatures ($\sim 300^\circ\text{C}$) must be acceptable, and extraction of the product must be practical.

From a survey of lithium compounds,⁽²⁾ it was concluded that the requirement of high temperature stability was best met by lithium silicates, lithium aluminates and lithium aluminosilicates. However, behavior of the materials under irradiation and extraction was unknown. SAP* materials containing LiAlO_2 , Li_2CO_3 , LiF and Li_2SiO_3 were prepared at NMI,⁽³⁾ but were not irradiated.

Initial radiation studies at Hanford were performed on swaged rods of lithium aluminate and lithium silicate. Thermal extractions of the irradiated targets in the laboratory resulted in gas recoveries which were considerably below predicted values. However, gas balances were in doubt, since gas released in-reactor was lost in decladding.

*Sintered aluminum powder

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To determine in-reactor gas release characteristics of the silicate and aluminate materials, targets were irradiated in quartz and aluminum capsules. Following irradiation, the gas (condensable and noncondensable fractions) released in-reactor was recovered by drilling the capsules. Subsequently, the targets were recovered and heated in a laboratory vacuum system to investigate characteristics of tritium and helium evolution as a function of temperature. The experimental procedures are discussed briefly, with details in the Appendix. The results of the study are discussed in terms of in-reactor release and later in terms of laboratory extractions.

SUMMARY

Studies were conducted to determine the generation and evolution of tritium and helium in lithium aluminate (LiAlO_2) and lithium silicate (Li_2SiO_3) by the reaction:

Targets were irradiated in the K-West Reactor snout facility. (Silicate GVR* ~ 2.0 cc/cc; aluminate GVR ~ 1.4 cc/cc.) Gas release in-reactor was determined by post-irradiation drilling experiments on aluminum ampoules containing silicate and aluminate targets. In-reactor tritium release (at $\sim 100^\circ\text{C}$) was found to decrease linearly with increasing target density. Tritium released in-reactor was primarily in the noncondensable form (HT and T_2), while in laboratory extractions (300 - 1300°C), the tritium appeared primarily in the condensable form (HTO and T_2O). Concentrations of HT (and presumably HTO) were relatively high, indicating moisture pickup in canning operations or by inleakage of moisture after the capsule was welded.

Impurities in extracted gases included H_2O , CO_2 , CO , O_2 , H_2 , NO , SO_2 , SiF_4 and traces of hydrocarbons.

Analysis for condensable tritium by a mass spectrometer method was unreliable, but analysis by scintillation counting appears to give consistent results. Approximately 80% of the generated helium was evolved from a low density pressed-sintered aluminate target prior to post-irradiation drilling.

$$*GVP = \frac{\text{cc T}_2 + \text{He}}{\text{cc Target}}$$

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In-reactor helium evolution from the remaining targets could not be determined directly, due to inleakage from the capsule atmosphere.

CONCLUSIONS

1. Tritium extracted from aluminate and silicate targets appeared primarily (65 to 95%, depending on target density) in the condensible form. A corresponding increase (compared to metallic target processing) in product recovery by conversion to elemental tritium will be required, presumably by the uranium bed process currently used at the Savannah River Plant.
2. Control of gas evolution in-reactor can be accomplished by choice of target density. However, gas generations as high as 30 GVR in swaged silicate targets have not resulted in cladding distortion.
3. Moisture contents of the targets were excessively high, resulting in product dilution with hydrogen. Prime consideration must be given to development of a dry target. Preliminary results indicate that this will require complete isolation from atmospheric moisture, following final outgassing.
4. Appearance of CO_2 and CO in the extracted gases indicates incomplete conversion of lithium carbonate in the preparation of the aluminate and silicate powders. Residual lithium carbonate and lithium oxide may contribute appreciably to the hygroscopic character of the target materials. Attention also should be given to the effects of the impurity gases in product recovery operations.
5. Gas extractions from aged samples (96-111 days at room temperature) indicated that 89-94% of the tritium and 75-90% of the helium was evolved during the room temperature aging.
6. Preliminary results on aged samples indicated that 4-hr 800°C anneals result in 92% recovery of tritium remaining in the target after aging. Anneals of 30-60 min at 400-800°C did not result in acceptable recovery; anneals of 10-15 min at 1300°C apparently resulted in complete recovery from swaged aluminate but not from impacted (high density) aluminate. Heating the silicate above the melting point resulted in complete (>99.9%) product recovery.

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EXPERIMENTAL

Targets

The capsule irradiation included three lithium aluminate targets and one lithium silicate target. Three of the targets (swaged lithium aluminate, swaged lithium silicate, pressed-sintered lithium aluminate) were in the form of cylindrical pellets, ~0.65 in. diameter and 0.25 in. thick. The fourth target was pneumatically-impacted (Dynapak) lithium aluminate, in the form of a rectangular pellet, length 0.35 in., width, 0.25 in., thickness, ~0.1 in. Details of sample preparation are given in Appendix A. Emission spectra and lithium analyses for the materials are given in Appendix B.

Capsule Design

The three cylindrical pellets were encapsulated in aluminum ampoules. A diagram of the capsule containing one quartz ampoule and three aluminum ampoules is shown in Figure 1. The ampoules were drilled from a solid rod, leaving a blind end. Closure of the other end was made by electron beam welding. Prior to welding, the open ampoules containing the targets were heated to 500°C overnight. The capsules were placed hot into a dessicator and stored until welding. However, exposure of the samples to the atmosphere occurred during adjustment of sample position and transfer to the electron beam welder. The ampoules were evacuated before the final closure was made. After welding, the ampoules were placed in a chamber, pressurized with helium at 70 psig, followed by a leak check with a helium sensor.

The impacted lithium aluminate sample was sealed into a quartz ampoule. The capsule was heated to ~500°C, while being evacuated through the hollow break seal. When the pressure fell below 10^{-5} torr (at room temperature), the break seal tube was sealed off. However, post-irradiation analysis of the gas in the ampoule indicated that helium and moisture had leaked into the ampoule. It is possible that a small crack formed in the ampoule as a result of charging or welding, although no defects were detected in visual inspection before and after irradiation.

FIGURE 1

CAPSULE ASSEMBLY FOR IRRADIATION OF LITHIUM SILICATE
AND LITHIUM ALUMINATE TARGETS

The quartz and aluminum ampoules were welded inside a doubly-contained aluminum capsule. Helium was placed in the space around the ampoules for subsequent leak checking; however, air also was admitted to the capsule during closure. A 20-ft, 1/16-in. diameter Chromel/Alumel thermocouple was used to monitor the temperature at the center of the lithium silicate target. The thermocouple tip rested inside an aluminum thermal well which was an integral part of the ampoule cap. The well extended through the center of the target.

Capsule Irradiation

The capsule was irradiated in the snout facility of the Hanford K-West Reactor. The snout arrangement is shown schematically in Figure 2. The capsule can be charged and discharged while the reactor is in operation and the capsule position can be changed during the irradiation.

The thermocouple in the silicate target read 103°C upon charging and rose to 107°C at the end of the [REDACTED] exposure. The aluminate capsules likely ran cooler, due to a lower lithium content.

The estimated flux to the capsule was [REDACTED] (thermal). The estimated (Appendix C) gas contents ($T_2 + He^4$, cc STP, per gram of target) at the end of the [REDACTED] exposure were 0.95 cc/g for the silicate target and 0.65 cc/g for the aluminate targets, assuming theoretical lithium contents (10.52 wt% for the aluminate, 15.4 wt% for the silicate) and natural Li^6 content (7.42 at.%). The corresponding GVR's* are 2.4 cc/cc for the silicate and 1.6 cc/cc for the aluminates. The calculated Li^6 burnup in the [REDACTED] exposure was 1.4% (Appendix H).

Gas Recovery from Irradiated Ampoules

The aluminum and quartz ampoules were removed from the capsule in Radiometallurgy. The aluminum ampoules were drilled in a vacuum apparatus (Appendix D) to release the gases evolved in-reactor. The gases were

*Gas Volume Ratio = $\frac{cc T_2 + He^4}{cc Target}$, STP, based on target densities of 2.55 g/cc for the aluminate and 2.52 g/cc for the silicate.

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FIGURE 2

Capsule Irradiation in Snout Facility

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separated into condensible (T_2O and HTO) and noncondensable (T_2 and HT) fractions. The condensible fraction was removed from the vacuum-system in the trap and diluted with 100 cc of distilled water while the trap was still cold. The tritium content of the water was determined by scintillation counting. The tritium concentration was converted to equivalent cc T_2 , STP using as the activity of tritium, 2.5 curie/cc T_2 , STP.*

The volume of the noncondensable gas fraction was determined in the standard volume of the drilling apparatus. The species were identified by mass spectrometer analysis.

Gases were recovered from the quartz ampoule by cracking the break seal in a vacuum system. Condensible and noncondensable gas fractions were analyzed as described above.

Target Appearance

Following the drilling operation, the targets were removed from the ampoules. The pneumatically-impacted (Dynapak) aluminate and swaged aluminate and silicate targets remained intact during irradiation and removal from the ampoules. The pressed-sintered aluminate broke into a number of pieces while being removed from the ampoule. The target fractured into two pieces ~0.5 g each, plus a distribution of smaller pieces. Appearances of the lithium aluminate samples did not change during the irradiation. The lithium silicate turned black, but the original light gray color was restored by high temperature anneals. The darkening may have resulted from a phenomenon similar to F-center coloration of other materials, which also bleaches at high temperature.

Laboratory Extractions

Thermal extractions on the irradiated targets were conducted in two laboratory vacuum furnace systems (Appendix E) capable of 800 and 1300°C, respectively. The targets were stored in dessicated vials. Fragments of the targets weighing about 0.25 g were used in the extraction runs. Runs

*The value calculated from the most recent half-life of tritium (12.26 yr) is 2.6 curie/cc, STP.

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at 1300°C were above the melting point of the silicate (m.p. 1256°C), but below the melting point of the aluminate (~1700°C). A silicate sample which obviously had melted was dissolved in 5 vol percent HF solution; a scintillation counter analysis of the solution indicated essentially complete extraction of the tritium (3.2×10^{-2} % tritium retention in the melted silicate). Tritium and helium were extracted from the pressed-sintered aluminate target by dissolution in molten sodium borate by W. H. Yunker, Chemical Separations Unit.

Extraction runs in the vacuum furnace systems were conducted by moving the sample into the hot zone of the furnace with a magnetic couple. Condensable and noncondensable tritium fractions were analyzed by scintillation counting and by mass spectrometer analysis, respectively. Gas evolution was followed by pressure rise measured with a McLeod gage. Extractions were continued until the pressure rise approached the system leak rate.

While some fracturing of the targets occurred in high temperature extractions, the aluminate targets generally remained intact after heating as high as 1475°C; the silicate targets remained coherent in 1000°C extractions, but melted in 1300°C extractions.

Dissolution of the ceramic targets in concentrated hydrofluoric acid was attempted. The silicate dissolved readily at room temperature in about 80 min; the aluminate compact disintegrated, but did not completely dissolve in a 3-day exposure.

RESULTS

In-Reactor Gas Release

In-reactor tritium release from the four capsule targets is summarized in Table I. Tritium release is shown in terms of cc, STP/g of target, including noncondensable (HT and T₂) and condensable (HTO and T₂O) tritium. The fourth column shows the release as percent of total tritium (reactor and laboratory extractions) recovered from each target. Indicated in column 5 is the percent of the tritium recovered after the in-reactor exposure, occurring as noncondensable (HT and T₂). It will be seen later that the

TABLE I
IN-REACTOR TRITIUM RELEASE FROM LITHIUM ALUMINATE
AND LITHIUM SILICATE TARGETS

Target	Target Density, Percent of Theoretical	Target Weight g	Tritium Evolution cc T ₂ /g Target	Percent of Total Tritium*	Percent Evolved as Noncondensable (HT + T ₂)
Pressed-Sintered Aluminate	68	2.26	4.9×10^{-2}	28.7	99.1
Swaged Aluminate	79	2.77	3.2×10^{-2}	17.1	97.2
Pneumatically-impacted Aluminate	96	0.13	0.6×10^{-2}	4.5	95.3
Swaged Silicate	78	2.47	4.5×10^{-2} (3.1×10^{-2})**	17.0	97.3

Irradiation Time - [REDACTED]

Irradiation Temperature (lithium silicate) 103-107°C.

*Based on total tritium (in-reactor and laboratory, condensible and noncondensable) evolved from each target.

**Normalized to lithium aluminate lithium content.

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relatively high percent of noncondensable recovered from the ampoules is in contrast to the release of condensable in high temperature laboratory anneals.

A plot of tritium evolution versus percent theoretical density is shown in Figure 3. For the three lithium aluminate targets, tritium evolution decreased linearly as target density increased, passing through zero at 100% theoretical density.

The point for the lithium silicate target falls above the lithium aluminate line when plotted in units of cc/g of target. However, the lithium contents are 15.42 wt% for the silicate and 10.52 wt% for the aluminate, and the tritium content of the silicate is correspondingly higher. If the silicate lithium content is normalized to the aluminate lithium content (i.e., cc/g divided by 1.46), the normalized point falls near the aluminate line. Stated another way, when the tritium evolution is expressed as a percent of the total tritium generated, the evolution is similar for the two materials, under the conditions of the in-reactor exposure ($\sim 100^\circ\text{C}$).

A relatively large proportion of the tritium evolved in-reactor was in the form of HT. The relative proportions of H_2 , T_2 , and HT are shown in Table II. Also shown are the approximate pressures (at 0°C) of each hydrogen species in the ampoules at the end of the exposure. To evaluate the total tritium evolved, the assumption was made that HT was formed from the reaction

The HT concentration (in mole %) therefore was divided by 2 and added to the T_2 concentration to calculate the evolved tritium. If an exchange mechanism of the type

is assumed, the division of the HT concentration by 2 is not made. While trace amounts of hydrocarbons (~ 0.1 mole %) did appear in the evolved gases, they were always much less than the hydrogen concentrations, and exchange reaction 2 was assumed to be negligible. In all cases, HT concentrations were in relatively good agreement with values calculated from the room temperature equilibrium constant.

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

○ Lithium Aluminate
△ Lithium Silicate
□ Lithium Silicate Normalized
to Lithium Aluminate Lithium Content

Percent of Theoretical Density

In-Reactor Tritium Evolution
From Irradiated Lithium Aluminate
and Lithium Silicate
as a Function of Target Density

FIGURE 3

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TABLE II
RELATIVE PROPORTIONS OF H_2 , T_2 AND HT IN AMPOULES

	Approximate Pressures** (torr)			Relative Mole %*			
	H_2	T_2	HT	H_2	T_2	HT	HT(calc)***
Pressed Lithium Aluminate	2.2	5.4	5.2	17.6	41.7	40.7	42
Swaged Lithium Aluminate	2.6	2.5	3.7	29.6	28.8	41.6	46
Pneumatically-impacted Lithium Aluminate	0.77	0.009	0.13	85.2	1.0	13.8	14
Swaged Lithium Silicate	260	0.12	10.7	96.1	0.1	3.8	51

*Based on $H_2 + T_2 + HT = 100\%$

**Pressures were calculated at $0^\circ C$

***HT calculated from the HT , T_2 , H_2 equilibrium

$$\text{at } 25^\circ C, K = 2.5 = \frac{(HT)^2}{(H_2)(T_2)}$$

In a laboratory test (Appendix F) firing at $600^\circ C$ produced silicate and aluminate which were analytically dry ($>1100^\circ C$ firings). It is likely that the dilution of the tritium in the ampoules resulted from pickup of atmospheric moisture during sample adjustment and transfer prior to welding and to inleakage of moisture. Even though the capsules appeared to be tight in helium leak checks, it is clear from the helium contents that inleakage did occur. The latter source of moisture is difficult to evaluate, since the moisture content of the capsule atmosphere is unknown. Prior to welding, the aluminates were exposed to the atmosphere only 3 to 4 min, but the silicate was exposed for ~15 min, although, in each case the temperatures were $>100^\circ C$. The longer atmospheric exposure of the silicate appears to correlate with the relatively high hydrogen content of the gas evolved in-reactor.

Laboratory Extractions from Capsule Targets

Portions of the capsule targets were heated in vacuum furnace systems to determine a) the total gas content and b) the gas release characteristics of the targets. Results of the laboratory extractions are summarized in Table III. Total tritium release (condensable and noncondensable) is shown

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in Table III. The relative amounts of condensible and noncondensable tritium at various outgassing temperatures are shown in Table IV. In-reactor helium evolution was in doubt, due to inleakage of helium from the capsule atmosphere. Helium extractions and estimated in-reactor helium evolutions are shown in Table V. The estimates represent the difference between calculated He^4 and He^4 recovered in laboratory extractions.

In Table III, the tritium release data are presented in terms of cc T_2 (STP) per gram of target and as a percentage of the total tritium, condensible and noncondensable, from in-reactor and laboratory extractions. Tritium evolved as condensible (HTO and T_2O) was converted to equivalent gaseous tritium at STP, using as the factor for tritium activity, 2.5 curie/cc, STP.

Details of the extractions will be discussed for the individual targets, but some generalizations will first be pointed out from Tables III, IV, and V. Tritium evolution at 300°C was 2 to 5% of the total tritium and was a relatively small fraction of the tritium evolved in-reactor. From Table IV it is apparent that a basic difference between in-reactor and laboratory tritium evolution lies in the relative proportions of condensible and noncondensable tritium. The relatively high fraction of condensible observed in laboratory extractions begins to show up in the 300°C extractions.

$\text{GVR} \left(\frac{\text{cc T}_2 + \text{He}^4}{\text{cc target}} \right)$ values shown in Table III were calculated from the total tritium evolved from each target, using the property of the $\text{Li}^6(n, \alpha)$ reaction ($\text{Li}^6 + n \rightarrow \text{T} + \text{He}^4$) that the He^4 generated is equal to two times the T_2 generated. Multiplying the total tritium by 3 thus gives helium plus tritium. If the GVR for the lithium silicate target is multiplied 0.682 (wt% lithium in the aluminate divided by wt% lithium in the silicate) to normalize the lithium contents, the value is $1.4 \frac{\text{cc gas}}{\text{cc target}}$ in agreement with the GVR calculated for the swaged lithium aluminate. GVR's for the other two aluminate targets are low compared to GVR's for the swaged targets.

In-reactor helium values (Table V) are generally in doubt due to leakage of helium into the ampoules from the capsule atmosphere. The magnitude of the inleakage is evident from a comparison of the last two columns in Table V.

TABLE III
LABORATORY EXTRACTION OF TRITIUM FROM CAPSULE TARGETS

Target	Tritium Release (Condensable + Noncondensable)					
	In-Reactor	300°C	800°C	1300°C	Total Tritium Content	GVR*
	<u>cc/g</u>	<u>cc/g</u>	<u>cc/gm</u>	<u>cc/g</u>	<u>cc/g</u>	<u>cc/cc</u>
Pressed-Sintered Aluminate	0.05 28.7%	$(0.87 \times 10^{-2})^a$ 5.1%	$(0.11)^b$ 66.2%		0.17 100%	1.3
Swaged Aluminate	0.03 17.1%	$(4.3 \times 10^{-4})^c$ 0.2%		0.16 82.7%	0.19 100%	1.4
Pneumatically-impacted Aluminate	6.4×10^{-3} 4.5%	Lost in Sampling**		0.14 95.5%	0.14 100%	1.1
Swaged Silicate	Run No. 1	0.04 17.0%	0.53×10^{-2} 2.0%	0.12 (Sum to 800°C is 64.7% of total yield, Run No. 2) 45.8%		
	Run No. 2	0.04 17.0%	$(1.16 \times 10^{-2})^d$ 4.5%	0.20 78.5%	0.26 100%	2.0

- a. 300-350°C - 24 hr data from W. H. Yunker, Chemical Separations Unit, PNL.
b. 800°C dissolution in sodium borate - W. H. Yunker, Chemical Separations Unit, PNL.
c. 320°C - Noncondensable only.
d. 340°C - Noncondensable only.

* $\frac{\text{ccT}_2 + \text{He}^4}{\text{cc Target}}$ Calculated by multiplying total T₂ by 3 and dividing by target density, 2.55 g/cc for aluminate, 2.52 g/cc for silicate.

**The noncondensable tritium in a 100 cc mass spectrometer bulb was lost. The loss was a negligible fraction of the total tritium (~0.02%).

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TABLE IV

CONDENSIBLE AND NONCONDENSIBLE FRACTIONS IN TRITIUM EXTRACTIONS

Target	In-Reactor		300°C		800°C		1300°C	
	Cond	Noncond	Cond	Noncond	Cond	Noncond	Cond	Noncond
Pressed-Sintered Aluminate	0.9	99.1%	(90.8%) ^a	(9.2%) ^a	(87.6%) ^b	(12.4%) ^b		
Swaged Aluminate	2.8	97.2%	ND*	0.2%			97.7%	2.3%
Pneumatically-Impacted Aluminate	4.7	95.3%					99.9%	0.1%
Swaged Silicate								
Run No. 1	2.7	97.3%	91.2%	8.8%	99.4%	0.6%		
Run No. 2	2.7	97.3%	ND	4.5%			92.4%	3.1%

a. 300-350°C - 24 hr data from W. H. Yunker, Chemical Separations Unit, PNL.

b. Dissolution in sodium borate at 800°C, W. H. Yunker, Chemical Separations Unit, PNL.

*ND - not determined

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TABLE V
HELIUM-4 EVOLUTION FROM IRRADIATED CAPSULE TARGETS

<u>Target</u>	<u>In-Reactor cc/g</u>	<u>300°C cc/g</u>	<u>800°C cc/g</u>	<u>1300°C cc/g</u>	<u>Total Out-of- Reactor Helium-4 cc/g</u>	<u>Total Helium-4 Extracted</u>	<u>Helium-4* Generation cc/g</u>
Pressed-Sintered Aluminate	0.35 (Actual) 81.2%	(0.025) ^a 5.7%	(0.057) ^b 13.1%	-	0.08	0.44 100%	0.34
Swaged Aluminate	0.53 (Actual) 0.12 (Est.) **	0.076	-	0.17	0.25	0.78	0.37
Pneumatically- Impacted Aluminate	0.72 (Actual) <0.22 (Est.)	Lost In Sampling		0.064	-	0.78	0.28
Swaged Silicate o Run	0.61 (Actual)	0.074	0.22	-	0.30	0.91	0.52
No. 1	0.22 (Est.)						
Run	0.61 (Actual)	-	-	0.094	0.17	0.83	0.52
No. 2	0.35 (Est.)	0.076	-				

a. 300-350°C - 24 hr data from W. H. Yunker, Chemical Separations Unit, PNL

b. Dissolution in sodium borate, 800°C, W. H. Yunker, Chemical Separations Unit, PNL.

*Calculated from total tritium generation, i.e., $T_2 \times 2 = He^4$

**In-reactor helium release, estimated from He^4 generated (column 8) minus He^4 extracted out-of-reactor (column 6).

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Only in the case of the pressed-sintered aluminate does the in-reactor helium evolution approach agreement with the expected helium generation, calculated from tritium yield. Even for the sintered aluminate, the extracted helium was too high, but the calculated GVR for this target indicates that the tritium yield may be in error by ~7% on the low side.

The data summarized in Tables III, IV, and V are discussed below for each target.

Pressed-Sintered Aluminate

The laboratory extractions of this target were performed by W. H. Yunker of Chemical Separations Unit, Pacific Northwest Laboratory, at 300-350°C by thermal extraction and at 800°C in a sodium borate melt. The behavior of this target is characterized by high in-reactor release of tritium and a relatively high noncondensable fraction (compared to thermal anneals) in the sodium borate extraction. The calculated GVR for this target was ~7% low compared to the swaged targets. However, since the samples were small (the majority of this target was lost when it fragmented while being removed from the ampoule), it is likely that the difference is within experimental error.

Swaged Aluminate

Two sections of the same target were extracted in separate runs. In one case, noncondensable samples were taken at 320 and 1300°C; a condensable sample was taken at the end of the run. The sample was held at 1300°C for 10 min, until the gas evolution was essentially complete. The fact that the GVR for this sample agrees with the value for the swaged silicate, where extraction is known to have been complete, suggests that the 10-min exposure was sufficient for complete extraction.

The second run was made at 800°C, with a holding time of 4 hr, followed by an extraction at 1300°C. In both runs, condensable and noncondensable tritium was collected.

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Pneumatically-Impacted (Dynamak) Aluminate

The entire impacted target (0.13 g) was heated to 300 and 1300°C. At the end of the 300°C run a gas sample taken was lost in sampling. However, from the noncondensable tritium remaining at the end of the 1300°C run, the loss was estimated to be ~0.02% of the total tritium. Condensable and noncondensable samples were taken at the end of the 1300°C run. The sample was held for 15 min at 1300°C. However, the fact that the calculated GVR is ~20% low for this sample suggests that extraction was not complete. A sodium borate dissolution of the spent sample is contemplated to determine the residual product. While extraction of the swaged aluminate appeared to be complete after 10 min at 1300°C, the bulk density of the aluminate sample is high (96%), and extraction may occur less rapidly than it did for the relatively porous (bulk density 79%) swaged target.

Swaged Silicate

The swaged silicate was thermally extracted in two sets of runs, one at 300 and 800°C (3 to 4 hr holding times) and one at 340 (noncondensable only) and 1300°C, the latter temperature being above the melting point of the silicate (m.p. 1256°C). To determine if extraction of the tritium was complete at the melting point, the fused sample was dissolved from the platinum boat, using a 5 vol% HF solution. Scintillation counter analysis of the HF solution showed only 0.03% of the generated tritium remaining in the spent sample. The reliability of the calculated GVR for this sample is further substantiated by close agreement with the GVR for the swaged aluminate, when the values are normalized for lithium content.

Comparing the results of the runs on the separate silicate samples, approximately 35% of the tritium was left in the sample heated only to 800°C. This indicates that a large fraction of the HTO and T₂O species are strongly bound in the silicate and therefore are not amenable to straight thermal extractions at 800°C or below, at least for holding times of 3-4 hr.

Loss of tritium and helium either during the irradiation or during decladding were considered as an explanation for the fact that expected gas yields were not recovered in laboratory extractions.

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LABORATORY EXTRACTIONS - SWAGED TARGETS

The following irradiations were performed on swaged rods of the aluminate and silicate targets.

<u>Test</u>	<u>Material</u>	<u>Irradiation Time, Days</u>	<u>Estimated GVR*</u>
K-2-22**	LiAlO ₂		10.1
	LiSiO ₃		14.7
K-1-23**	LiAlO ₂		21.6
	LiSiO ₃		31.6
K-C-3***	LiAlO ₂		20.1

*See Appendix C and Reference 18.

**Targets from KER loop irradiations

***Target from capsule irradiation K-East Peactor, sidehole 2A

Laboratory extractions were conducted in two vacuum systems: a resistance furnace operating to 800°C and an induction furnace operated as high as 1475°C. However, softening of the quartz tube limited the induction-heated furnace to 1300°C. This temperature still was above the melting point of the lithium silicate (m.p. 1256°C).

Initial extractions from aluminate samples from irradiation K-C-3 indicated a low yield of tritium and helium-4, compared to the estimated yields. A series of extractions therefore were conducted in which the liquid nitrogen trap was not cooled, to check the extracted gases for condensable tritium. Extractions from silicate and aluminate targets are shown in Table VI. The trapped runs were performed consecutively on the same sample. In all runs, HTO and T₂O were essentially absent in mass spectrometer analyses. However, of greater concern was the relatively low recovery of He⁴, since loss of this gas by adsorption was unlikely. Laboratory extractions (Table VII) on targets from irradiations K-2-22 and K-1-23 showed a low recovery of He⁴ and of tritium (as HT and T₂).

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TABLE VI

GAS COMPOSITIONS FROM TRAPPED AND UNTRAPPED EXTRACTIONS

Sample: Li_2SiO_3 , [REDACTED] Test K-2-22

Gas	Untrapped Runs					Trapped Run
	220°C		380°C		800°C*	1000°C
	Mole %	ppm	Mole %	ppm	Mole %	Mole %
CO_2	78.6	830	53.1	920	47.9	<0.05
O_2	0.25		0.05		0.21	10.0
N_2	1.1		0.75		1.83	2.4
CO_4	0.7		1.42		17.1	27.0
He^4	1.9		4.37		3.78	2.7
H_2	3.5		2.83		11.6	51.0
HT	0.22		0.5		5.0	2.2
T_2	0.03		<0.01		1.5	0.5
H_2O	13.5	60	35.8	250	11.0	2.2**
HTO	<0.1		0.1		0.1	<0.1
T_2O	<0.1		<0.1		<0.1	<0.1
NO	<0.1		<0.1		<0.1	0.7
CH_4	0.1		0.15		0.05	1.1
CxHy	<0.1		0.4		0.6	0.7
SO_2	<0.05		<0.05		<0.05	<0.05

*During the run at 800°C, a crack developed in the vacuum system and the final gas pressure could not be determined.

** H_2O likely occurred from reaction of H_2 and O_2 in the mercury diffusion pump.

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TABLE VI (cont)

Sample: LiAlO_2 , [REDACTED] Test K-2-22

Gas	Untrapped Runs							
	250°C		405°C		795°C		1475°C	
	Mole %	ppm	Mole %	ppm	Mole %	ppm	Mole %	ppm
CO_2	19.2	530	72.2	1900	36.4	1200	30.1	2000
O_2	0.56		0.45		4.83		0.4	
N_2	0.72		1.92		2.08		0.94	
CO	0.58		1.39		23.7		7.4	
He^4	0.98		2.02		3.6		1.56	
H_2	0.68		3.12		13.8		3.21	
HT	0.05		0.5		1.4		0.05	
T_2	<.01		0.1		0.06		0.02	
H_2O	75.0	750	16.0	170	11.6	155	55.5	1400*
HTO	<0.1		0.1		<0.1		---	
T_2O	<0.1		<0.1		<0.1		---	
Cxly	0.2		1.0		0.5		0.5	
NO	1.2		0.8		1.0		<0.1	
CH_4	0.07		0.15		0.07		0.03	
SO_2	<0.05		<0.10		0.9		0.1	

*Sample exposed to atmosphere in transfer between vacuum systems after 795°C run.

[REDACTED]

TABLE VII

SUMMARY OF TRITIUM AND HELIUM YIELDS
FROM LABORATORY EXTRACTIONS,
USING MASS SPECTROMETER DETECTOR

Species	Target					
	LiAlO_2		LiAlO_2	Li_2SiO_3	Li_2SiO_3	
	K-C-3		K-2-22	K-2-22	K-1-23	
	Sample 1 to 800°C	Sample 2 to 1000°C	to 1490°C	to 1300°C	Sample 1 to 1000°C	Sample 2 to 1300°C
He^4	30.9%*	32.5%	8.5%	4.5%	5.8%	21.1%
Tritium	2.7	2.9	2.4	3.5	12.9	16.3

Species	Target	
	LiAlO_2	
	K-1-23	
	Sample 1 to 1000°C	Sample 2 to 1300°C
He^4	8.3%	6.2%
T_2	2.0	0.5

*Percent of calculated yield

Loss of tritium and helium either during the irradiation or during de-cladding were considered as an explanation for the fact that expected gas yields were not recovered in laboratory extractions.

Arguments against release of large fractions of the gas in-reactor were a) failure to observe distortions of the target cladding and b) failure to release appreciable gas by drilling through the cladding after irradiation. However, regarding the latter argument, it was not certain that released gases would permeate the swaged target and escape through the drill hole. The capsule irradiation discussed earlier therefore was undertaken to provide a complete tritium balance and to clarify the question of in-reactor release.

Analysis of the condensible tritium from the capsule targets by scintillation counting showed that the major tritium fraction from laboratory extractions was evolved in the condensible form. The mass spectrometer method failed to detect the full tritium yield due to adsorption and exchange in the collection and analyzer systems.

The status of He^4 in-reactor still is not clear. There is evidence that the proportion of helium release in-reactor from the pressed-sintered capsule target is large. It is also otherwise difficult to rationalize the He^4 recovery from laboratory extractions. In the K-C-3 irradiation, the temperature was $\sim 90^\circ\text{C}$, while in the K-2-22 and K-1-23 irradiations, the temperatures were ~ 260 - 280°C . Helium retention was correspondingly high in the low temperature irradiation, suggesting a thermally-controlled release. At 700°C permeation of quartz by helium is a factor of 10 higher than permeation by hydrogen.⁽⁵⁾ Even at room temperature, helium permeation rates through glasses are measurable. However, permeation and diffusion coefficients for helium migration through the crystalline aluminate and silicate are not currently available.

EXTRACTIONS FROM SWAGED ALUMINATE CAPSULE TARGETS
AGED AT ROOM TEMPERATURE

Extractions were performed on two swaged aluminate samples (from the capsule irradiation) which had been at room temperature for 96 and 111 days, respectively, following the irradiation. In one set of extractions, an aluminate sample was heated consecutively to 400, 600, 800 and 1280°C , in each case, until gas evolution approached the system leak rate (30-60 min holding times; 15 min at 1280°C). In the second run, the sample was heated consecutively to 800 and 1280°C . In all runs, condensible and noncondensable fractions were collected separately.

Results of the runs are shown in Table VIII. The surprising aspect of the results is that in both cases, the yields of tritium and helium were much lower than those obtained in extractions performed on the same targets soon after discharge, indicating appreciable gas evolution at room temperature. A confirmatory extraction by dissolution of a section of the same target in

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TABLE VIII

GAS EXTRACTIONS FROM ALUMINATE TARGETS
AGED AT ROOM TEMPERATURE

<u>Extraction Temp. °C</u>	<u>Noncondensable Tritium, cc/g</u>	<u>Condensable Tritium, cc/g</u>	<u>Total Tritium, cc/g</u>	<u>% Original Tritium Content</u>	<u>Helium-4 cc/g</u>	<u>% Original Helium-4</u>
400	$<3 \times 10^{-5}$	1.2×10^{-4}	1.2×10^{-4}	0.06	2.8×10^{-2}	11.2
600	2.2×10^{-4}	2.4×10^{-4}	4.6×10^{-4}	0.24	5.9×10^{-3}	2.4
800	2.9×10^{-3}	1.7×10^{-3}	4.6×10^{-3}	2.4	6.6×10^{-3}	2.6
1280	1.9×10^{-4}	6.1×10^{-3}	6.3×10^{-3}	3.2	2.2×10^{-2}	8.8
	3.3×10^{-3}	8.1×10^{-3}	11.4×10^{-3}	5.9	6.3×10^{-2}	25.0
800	1.2×10^{-3}	1.8×10^{-2}	1.9×10^{-2}	10.2	1.2×10^{-2}	4.8
1280	Not Detectable	1.8×10^{-3}	1.8×10^{-3}	1.0	1.1×10^{-2}	4.4
	1.2×10^{-3}	2.0×10^{-2}	2.1×10^{-2}	11.2	2.3×10^{-2}	9.2

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sodium borate was not completed, due to an equipment malfunction. The apparent loss of gases at room temperature needs further investigation, since it has implications both to analytical and gas recovery operations.

In the set of runs at 800 and 1280°C, extraction of the tritium remaining in the sample was 91% complete after the 4-hr, 800°C run. It appears from the gas yields in the set of runs at 400, 600, 800 and 1280°C that the 60 min exposure at 800°C was insufficient to extract all tritium which is recoverable at that temperature. A yield above 90% for the 4-hr, 800°C run suggests that tritium recovery from the aluminate is possible in extended thermal extractions at 800°C.

Total tritium recoveries were in relatively good agreement (6 and 11%) for the two runs. Total helium recovery was considerably lower (9 versus 25%) for the last set of runs; however the sample with the lower helium yield was exposed longer (15 days) at room temperature.

IMPURITIES IN LITHIUM SILICATE AND LITHIUM ALUMINATE TARGETS

While complete chemical analyses of the targets are not available, a large number of gas analyses and several emission spectra give considerable information about target purity and point to several aspects of purity which require further study. The inferences of the analyses of gases from thermal extractions will be discussed first, followed by a discussion of emission spectra.

Thermal extractions of the targets were conducted at temperatures from 250 to 1475°C. In some runs the condensible fraction was trapped out, while in other runs, the condensible and noncondensable products were collected together for mass spectrometer analysis. The impurity gases in the mass spectrometer analyses are discussed below, assuming that the only constituent gases to be expected are T_2 and He^4 , with traces of He^3 from decay of tritium (half-life, 12.26 yr).

HT, H_2 , and H_2O

The formation of HT results in undesirable dilution of the tritium product. While HT can be separated from T_2 in a thermal diffusion column, it

would likely be uneconomical to attempt recovery of T_2 from HT. [REDACTED]

[REDACTED] (6) The HT diluent can occur either by exchange with hydrogen-bearing materials such as moisture or organics, or by reaction with gaseous hydrogen. As previously indicated, considerable moisture, HT and H_2 occurred in thermally-extracted gases. In thermal extractions from 12 separate target samples, HT was the major gaseous tritium product in 11 cases. In thermal extractions at 275, 1000, and 1300°C from one silicate sample, the HT dilution was 11.3, 6.2, and 13.7%, respectively, compared to concentrations of 50 to 100% HT in extractions from the other samples. The hydrogen (gas phase) contents were correspondingly low for the silicate sample. The sample was obtained from a swaged silicate target, irradiated in KER loop No. 2 (Test K-1-23). The favorable T_2 /HT ratio resulted from a relatively low moisture content and a high tritium generation (estimated GVR of 31.6, equivalent to 10.5 cc T_2 /cc target). The favorable T_2 /HT ratio from the silicate target offers hope that production of an acceptably dry target is feasible, although production at lower GVR's demands a concomitantly lower moisture content. As previously noted, 10 ppm moisture in a 10-GVR aluminate target potentially represents a 1% product dilution if conversion to HT is complete.

CO_2 , CO , and O_2

The procedure recommended by Nuclear Metals⁽⁷⁾ for preparation of lithium aluminate involves the reaction*

The reaction is conducted in a 24-hr exposure at 1200°C. A similar reaction

is used to prepare the silicate.

*It should be noted that a species referred to as lithium aluminate also is produced by a hydrothermal reaction,⁽⁸⁾ but the x-ray diffraction patterns for the two aluminates differ (Appendix G).

[REDACTED]

Analysis of gases from the irradiated targets show relatively large concentrations of CO_2 (in untrapped runs) at the lower temperatures and of CO and oxygen at the higher temperatures. This is assumed to indicate residual Li_2CO_3 in the targets.

In the target system, the potential for generation of CO_2 , CO and O_2 has implications in temperature excursions, where gas release would contribute to pressure generation. However, since tritium and helium release would also presumably have the same result, the effect of the additional gases is perhaps only to cause rupture at a temperature lower than it otherwise would occur. Since the irradiated targets have remained largely intact in high temperature extractions, it is not likely that copious gas evolution would carry large fractions of the target out through ruptures in the cladding.

The presence of the gases also has implications in the extraction process, where oxidation of the uranium beds and the palladium valve will result if the oxidizing constituents are not removed. While removal of the gases from the T_2/He stream likely can be accomplished, elimination of the excess carbonate during formation of the aluminate is an alternative and likely more desirable solution.

Nitrogen and NO

Nitrogen in widely varying concentrations occurred in the gas samples, presumably from air contamination. Nitric oxide (NO) occurred in some samples in concentrations as high as 4.7 mole %. Considerable NO (up to ~1%) occurred in extractions as low as 300°C; it is not likely to have formed by the reaction

since the kinetics and equilibrium are both unfavorable below ~1500°C.⁽⁹⁾ The source therefore appears to be radiolytic generation.

Hydrocarbons

Hydrocarbons of the form CH_4 , C_2H_x and C_xH_y (3 and 4 carbons) occurred in essentially all samples (in at least one form) in concentrations of 0.1 to

1 mole %. In addition, tritiated methanes (CH_3T) appeared in a few samples in amounts of 0.1 to 0.2 mole %. The fact that the hydrocarbons were largely untritiated suggests that they were not present in the capsule during irradiation. However, care in eliminating grease and oil from target preparation is important, since they represent potential sources of product dilution.

Sulfur Dioxide

In untrapped gas samples from thermal extractions of irradiated targets, SO_2 occurred in amounts as high as 13 mole %. In two samples, small amounts ($\sim 0.2\%$) of CS_2 appeared. In untrapped runs from capsule targets, SO_2 appeared in the gas from the swaged silicate, but was not present in the gas from the swaged aluminate. The sulfur compounds are presumed to have come from sulfur impurity in the compacts, but the source and form have not yet been identified. Chemical analyses of swaged and pneumatically-impacted aluminates showed <0.5 wt% sulfur, determined by a barium sulfate method. It is recommended that sulfur contents of future target materials be determined; improved sensitivity can be obtained using a combustion analysis method. However, since the targets were stored over Drierite (CaSO_4) it is possible that small particles of dessicant account for the observed evolution of SO_2 .

Silicon Tetrafluoride

In two samples, SiF_4 occurred in concentrations of 1 mole %. The source is not clear, since in both cases the samples were trapped; SiF_4 did not appear in any of the untrapped samples. The impurity likely comes from a source external to the target system. However, the use of teflon in blending of powders for compacts suggests a potential if not actual source of fluorinated compounds in the targets. In compacts prepared using teflon, the degree of teflon pickup should be determined. Hydrogen fluoride is one of the reaction products of SiF_4 and water. The combination of tritiated water and SiF_4 in the radiation field appears to be an undesirable combination which can be avoided by minimizing or eliminating fluorinated compounds.

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DISCUSSION

To summarize the results of the in-reactor and out-of-reactor gas release,

- a) In-reactor tritium release occurred in the noncondensable form,
- b) The in-reactor release decreased linearly with increasing target density,
- c) Tritium released in laboratory extractions at 300°C was less than that released in-reactor at 100°C,
- d) Tritium release in laboratory extractions was primarily in the condensable forms (HTO and T₂O),
- e) Helium recovery in laboratory extractions was 23 to 68% of calculated helium content, based on tritium recoveries.
- f) The predominant tritium species was HT (and undoubtedly HTO in the condensable phase), due to exchange with moisture in the targets.
- g) Under various conditions, CO₂, CO, O₂, SO₂, CS₂, SiF₄, NO and traces of hydrocarbons (tritiated and untritiated) appeared in extracted gases.
- h) Gas evolution appears to proceed at an appreciable rate at room temperature.

Since tritium was extracted primarily in the condensable form in high temperature (300-1300°C) laboratory extractions, in-reactor release of non-condensable tritium must involve one or both of the following release mechanisms:

- a) Diffusion to the surface as T (unlikely due to high affinity for oxygen) T₂, HT, T₂O or HTO,
- b) Ejection from surface and lattice fission sites as recoils before reaction with lattice oxygen can occur.

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The diffusion characteristics of tritium in the aluminate and silicate targets are unknown, and it is therefore of interest to review what is known about tritium behavior in other materials.

While information regarding tritium behavior in nonmetallic systems is meager, a few studies of irradiated lithium salts have been reported. Tritium release from lithium fluoride plates was low below 700°C.⁽¹²⁾ Release from massive LiF was complex and depended on temperature history, initial tritium concentration and trapping of molecular tritium in imperfections in the LiF plates.

Tritium release from lithium-doped nickel oxide during irradiation was less than 1% of the total activity.⁽¹³⁾ This activity was almost equally divided between condensible and noncondensable fractions. At 100°C, free tritium was released, but was a small fraction (apparently less than 1%) of the total tritium. T₂O was the only product at higher temperatures (to 800°C).

The tritium release characteristics of a number of lithium salts (halides, chromate, nitrate and hydrides) were investigated.⁽¹⁴⁾ As in the previous reference, the in-reactor release was low (~1% of activity released at 750°C). From lithium chloride, the condensible fraction was smaller than the noncondensable fraction at corresponding temperatures, and the total release was low at 150°C. However, the oxygen-bearing salts (nitrate and chromate) released only condensible tritium (probably T₂O).

The relatively small tritium release from the aluminate and silicate targets at 300°C could be interpreted to indicate low tritium diffusion rates at 100°C. Alternatively it could result from an increase in reaction between tritium and lattice oxygen or other available oxygen (CO₂, CO and O₂). Stability of tritium in other oxygen-bearing lithium salts also is high at

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100°C. However, it is again not clear if the stability is due to low diffusion rates of atomic or molecular tritium or to chemical reaction of tritium with lattice oxygen. However, stability of tritium in other lithium salts, and the appearance of molecular tritium in the low temperature in-reactor gas suggest in-reactor release by a mechanism other than diffusion.

It then remains to evaluate release due to recoils from surface and bulk fission sites. Release related to surface area is at least qualitatively-consistent with the observed density dependence. Calculation of the surface area required to result in the observed tritium release (at fission sites in the surface) from the pressed-sintered target (Appendix H), indicates that a specific surface area of $\sim 1000 \text{ m}^2/\text{g}$ is necessary. The surface area of a pressed-sintered (1325°C) lithium aluminate pellet was $3.5 \text{ m}^2/\text{g}$, determined by the B.E.T. method. The in-reactor release therefore involved more than the release of atoms fissioning at surface sites.

Loss of tritium by recoils from the aluminate lattice was calculated from the equation⁽¹⁵⁾

$$P_a = \frac{3}{4} \left(\frac{\lambda}{a}\right) - \frac{1}{16} \left(\frac{\lambda}{a}\right)^3$$

where P_a is the fraction of the recoils which escape from a particle of radius a and λ is the fission fragment range. Recoil ranges calculated from the Bragg-Kleeman relation⁽¹⁶⁾ were 31 and 4 microns for tritium and helium respectively. The above equation applies rigorously only for independent particles and application to a system of compacted powders is subject to considerable interpretation.

Sieve analyses⁽¹⁷⁾ of Lithium Corporation of America LiAlO_2 powders showed a mean particle radius of the order of 40 μ . Using this value for parameter a in the above equation, the fraction of tritium recoils which escape from a given particle is 55%. However, in the compacts, only a fraction (dependent on void volume) of the recoils will escape, since some recoils will come to rest in adjacent particles. In a material with $\sim 30\%$ void volume, $\sim 1/3$ of the recoils will come to rest outside the lattice. Thus in a compact

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with a mean particle radius of 40μ and a void volume of 30%, the fraction of recoils escaping to the voids will be one-third of 55% or $\sim 18\%$. Tritium evolved in-reactor was 4.5 to 28.7% for the four targets. The calculated tritium escape is of the right order of magnitude and it is possible that close agreement between observed and calculated tritium release could be obtained in each case if the effective particle size and void volume distributions of the compacts were known precisely. The variation of recoil release with particle size is shown in Figure 4 for tritium and helium assuming independent particles.

The fact that the gas is released in-reactor in the elemental form, without interaction with lattice oxygen is consistent with a recoil release mechanism, since in laboratory extractions, the tritium appeared primarily in the oxidized form. However, it admittedly is not clear whether the reaction with oxygen occurred when the tritium recoil came to rest in the lattice or whether it occurred as a result of the temperature increase.

On the other hand, the apparent in-reactor release of helium (81%) from the pressed-sintered aluminate is not consistent with a recoil escape mechanism, since the expected release from particles with $a = 40\mu$ is only $\sim 5\%$. The rate of diffusion of helium in quartz is a factor of 10 faster than the diffusion rate of hydrogen at higher temperatures⁽⁵⁾ and the release of helium may occur by diffusion. This question likely can be answered when helium release data from a subsequent capsule experiment are available.*

Problems of target purity should involve a program to identify and reduce to acceptable levels impurities in the following categories:

- Moisture
- Unreacted carbonates
- Organic materials (lubricants, teflon, binders)
- Inorganic materials (elements which have a high cross section, those which cause a high radiation background and those which result in undesirable product gases such as sulfur compounds).

*Capsule irradiation by W. H. Yunker and J. Weber, in progress.

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FIGURE 4
Theoretical Loss of Tritium and He Recoils
from LiAlO_2 and Li_2SiO_3 Lattices
as a Function of Particle Size
Recoil Ranges: Tritium, 31 μ , Helium, 4 μ

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Pickup of surface moisture appeared to occur rapidly within 3 to 4 min based on the results from the capsule targets. Required handling procedures can best be determined from kinetic studies of moisture pickup rates. However, it is desirable and perhaps necessary to avoid contact with moist air in precompaction as well as canning stages of target preparation.

A solution to the problem of unreacted carbonate appears to lie in a longer high temperature outgas (perhaps under vacuum) of the uncompacted powders. It should also be noted that disappearance of CO_2 in off-gases from unirradiated targets may not guarantee that CO_2 will not be evolved from irradiated targets, due to radiolytic decomposition of carbonates which resisted thermal decomposition.

Organic contaminants occurred at relatively minor levels in the extractions reported here. However, surveillance of the target preparation procedure for sources of organic contamination obviously is essential.

While relatively high contamination of sodium (5000 ppm), zirconium (500 ppm), iron (100 ppm) and magnesium (500 ppm) have appeared in spectrochemical analyses, 1 to 2 gram samples of the targets could be handled in the laboratory without shielding (100-200 mr at 6 in.). Boron appeared in one sample at the trace-to-moderate level. However, a chemical analysis of the sample indicated only 0.007 wt% boron. Indications of sulfur contamination (SO_2 and CS_2) were observed in extractions where traps were not used; chemical analyses indicated 0.5 wt% sulfur. The sulfur may have come from particles of dessicant (CaSO_4) picked up by the targets. However, because the potential of sulfur compounds for fouling of palladium valves and as corrosive agents, it is recommended that sulfur analyses of target materials be conducted.

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APPENDIX A

PREPARATION OF TARGET MATERIALS⁽¹⁷⁾

I. Pneumatically-Impacted Lithium Aluminate

- Lithium aluminate powders were obtained from Lithium Corporation of America (LCA, batch two)
- Aluminate powder density -- 2.43 g/cc (95.3% of Theo)
- Particle sizing -- none.
- Processing before compaction -- none -- carried in stainless steel at 1.24 g/cc.
- Impaction Process (Dynapak)
 - a. Heated to 1200°C. Held 90 min at temperature; pressure -- 50μ.
 - b. Can extracted from furnace; immediately impacted.
 - c. Can, and contents quenched to room temperature.

II. Pressed-Sintered Lithium Aluminate (N.M.I. Process)⁽⁷⁾

- Aluminate powders were obtained from Lithium Corporation of America (first batch)
- Processing before fabrication -- none.
- Pressing procedure (See reference 7):
 - a. Pressed at 21,000 psi on 0.620 die (tool steel), using lithium stearate lubricant on die walls.
 - b. Placed in furnace on a platinum sheet at 1000°C. Temperature raised to 1325°C, held for 20 hr.
 - c. Samples removed from furnace hot; stored in dessicated vials inside a dessicator.

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III. Swaged Lithium Aluminate and Lithium Silicate

- Compacts made from Lithium Corporation of America powders.
- Particle sizing -- none.
- Procedure:
 - a. Powders outgassed at $\sim 400^{\circ}\text{C}$.
 - b. Outgassed powders loaded into C-64 aluminum cladding and swaged.
 - c. Swaged columns cut in sections; aluminum cladding machined off.
 - d. Swaged rods fired to 1100°C by placing in a cold furnace, heating to temperature (2 hr) and slow cooling immediately after temperature was reached.
- All pieces weighed and measured upon cooling; stored in dessicated vials inside a dessicator.

IV. Canning Procedure

Targets to be irradiated as rods were swaged in an aluminum cladding. End caps were welded into place. One end cap had an outgassing hole. Prior to closure of the hole, the clad target was heated to $\sim 400^{\circ}\text{C}$ for 4 hr to attempt removal of surface moisture. The aluminum-clad targets were then clad with Zircaloy-2 prior to loop exposures.

Capsule targets were placed inside aluminum ampoules, heated to 500°C and stored in a dessicator. Immediately prior to welding, the ampoules were removed from the dessicator, final adjustments in sample position were made, the ampoules were placed in the electron beam welder, evacuated and welded. Total contact time with air was $\sim 3-4$ min for the aluminate targets and ~ 15 min for the silicate target due to complications in positioning the thermal well. The ampoules were heated with a hand torch, placed in the electron beam welder and evacuated.

APPENDIX B

EMISSION SPECTRA AND CHEMICAL ANALYSES

Sample	Commercial Aluminate* Powder	Commercial Silicate* Powder	Aluminate Press-Sintered by NMI**	Swaged*** Aluminate	Pressed-Sintered*** Aluminate	Impacted*** Aluminate
		Swaged Aluminate				
Al	S	S	50	S	S	S
B	10		5	T	<T	<T
Cr	<10		<10	T-M	M	-
Cu	5	<T	5	T-M	T-M	T
Fe	100	T-M	100	T-M	T-M	T-M
Ga	500	M	<10	M	T-M	T-M
Li	SS	SS	SS	SS	SS	SS
Mg	1	<T	500	T	T	<T
Mn	5	T	5	T	T	T
Mo			<T	T	T	T
Na	5000	M-S	100	M-S	M	M-S
Ni	<10		100	T	T	<T
Si	500	M	SS	M	M	M
Sn	x					
Ti	100		50	T-M	T-M	T-M
Zr	500		<100			
Total	6200 ppm		900 ppm			

*Numbers indicate estimated levels in ppm.

**Nuclear Metals, Inc.

***Capsule targets

x Interface

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APPENDIX B

(Cont.)

ANALYSIS OF TARGETS FOR LITHIUM AND LITHIUM-6

Method for Lithium Analysis

Lithium aluminate was dissolved in HCl solution in silica capsules at 300°C. In some samples dissolution obviously was incomplete, accounting for low values for the lithium content. A more recent dissolution process being investigated by J. C. Langford, Chemical Analysis, involves heating the aluminate in H_3PO_4 -HF solutions. In this case, dissolution appears to be complete.

Analysis of the dissolved lithium is conducted by flame photometry by J. C. Langford.

Analysis for lithium-6 was done by mass spectrometry, performed by N. Wing, 234-5 Bldg., 200 Area (Hanford).

Due to instrument problems, Li^6 analyses have not been performed on samples from capsule targets.

Lithium Analysis

	<u>Wt% Li</u>	<u>Theoret. Li</u>	<u>Error</u>
NMI Pressed Pellet (Aluminate)	10.25	10.54	-2.7%
	9.97	10.54	-5.4%
Swaged Pellet (Aluminate)*	8.3	10.5	-21%
Pneumatically-Impacted* Pellet (Aluminate)	8.3	10.5	-21%
Swaged Pellet (Silicate)*	13.5	15.4	-12.3%

*Low values apparently resulted from incomplete dissolution of the samples in HCl bomb dissolutions. A new dissolution technique is being developed and tested.

Lithium-6 Analysis

	<u>Li^6 (Analyzed)</u>		<u>Li^6 (Theoret.)</u>	<u>Error</u>
	<u>Wt%</u>	<u>Atom %</u>	<u>Atom %</u>	
Swaged Aluminate	6.0	6.9	7.4	-6.7%

Li^6 analyses not yet available on target samples.

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APPENDIX C

ESTIMATED GAS GENERATION IN ALUMINATE AND SILICATE TARGETS

In the absence of data on gas generation in the aluminate and silicate targets, gas contents were calculated using experience with aluminum-lithium targets as a basis, making the assumptions that gas generation is dependent only on flux, exposure time, and lithium-6 concentration. Knowing the gas generation in one system, gas generation in a second system can be calculated from the relationship:

$$\frac{(\text{Gas Content})_1}{(\text{Gas Content})_2} = \frac{\phi_1 (\text{Li}^6)_1 t_1}{\phi_2 (\text{Li}^6)_2 t_2}$$

where ϕ is thermal flux, Li^6 is lithium-6 concentration and t is the length of exposure.

APPENDIX D

PROCEDURE FOR DRILLING IRRADIATED ALUMINUM AMPOULES

Following removal from the capsule, the aluminum ampoules were drilled in a fission gas collection apparatus.⁽¹⁹⁾ The elements are sealed into drilling blocks with neoprene vacuum seals. The gas is released by drilling through the aluminum capsule. The released gas expands through a cold trap and into an evacuated standard volume. Gas pressures are followed with a thermocouple gage and are measured with a Todd gage. After the gases had equilibrated with the cold trap, the noncondensable fraction was pumped into a mass spectrometer bulb with a Toepler pump. To collect the condensable tritium, the collection system was brought slowly to atmospheric pressure by introducing helium. The cold trap was removed and immediately rinsed with 100 cc of distilled water. The tritium content of the water was analyzed by scintillation counting.

RADIOMETALLURGY FISSION GAS DRILLING AND COLLECTION SYSTEM

APPENDIX E

Furnace: Resistance Type (Chemical Metallurgy Unit)
 Induction Type (Physical Analysis Unit)

VACUUM SYSTEM FOR GAS EXTRACTIONS

APPENDIX F

MOISTURE ANALYSIS OF ALUMINATE AND SILICATE TARGETS

I. Analysis by Electrolysis of Phosphorus Pentoxide

Samples of swaged unirradiated aluminate and silicate were ground in a mortar and pestle open to the atmosphere. The powder was heated in a furnace. Evolved moisture was determined by electrolysis of phosphorus pentoxide.⁽⁴⁾ Results are shown below in terms of ppm of moisture evolved as a function of temperature. The powder picks up considerable surface moisture in the grinding process, but evolution of surface moisture was complete at 600°C for the silicate, and by 800°C for the aluminate.

<u>Temperature Ranges, °C</u>	<u>Swaged Lithium Silicate</u>	<u>Swaged Lithium Aluminate</u>
20 - 200	750 ppm	1840 ppm
200 - 400	100 ppm	845 ppm
400 - 600	ND	200 ppm
600 - 700	ND	
600 - 800		ND

ND: Not detectable - <10 ppm

A sample of powdered lithium aluminate was heated* at the rate of 2°C/min to 600°C. Moisture evolution appeared to be complete at this temperature. The weight loss during the heating sequence was 8.0 wt%. The sample had been in contact with air prior to the heating sequence.

* Analysis performed by Glen Benedict, Chemical Separations Unit.

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APPENDIX G

X-RAY DIFFRACTION PATTERNS

LiAlO_2 (swaged)		LiAlO_2 (powder)		LiAlO_2 (fired)		$\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ (19)	
$\underline{d}$	$\underline{I/I_0}$	$\underline{d}$	$\underline{I/I_0}$	$\underline{d}$	$\underline{I/I_0}$	$\underline{d}$	$\underline{I/I_0}$
7.50A	12	7.50A	15				
5.25	5	5.25	2				
4.75	100	4.73	35	4.40A	10		
4.40	5	4.40	5	4.43	10		
3.99	100	3.98	100	3.98A	100	3.98	100
3.86	40	3.77	9				
3.65	15	3.65	12	3.65	15	3.64	24
3.48	12	3.48	14			3.52	7
3.15	25	3.15	20	3.16	20	3.16	28
3.12	12						
2.97	5	2.97	2	2.97	3		
2.86	5	2.86	2	2.86	3	2.79	16
2.80	5	2.80	2	2.80	3		
2.68	80	2.68	80	2.69	70	2.68	82
2.63	15						
2.58	90	2.59	90	2.59	75	2.58	88
2.55	81						
2.45	25	2.49	6				
2.38	20	2.39	12	2.39	12	2.38	45
2.32	5	2.30	3				
2.22	15	2.22	4				
2.17	8	2.17	5	2.17	10	2.16	12
2.08	15	2.08	9				
2.00	65	2.00	25	1.98	4	1.97	18
1.86	15	1.86	13	1.86	14	1.86	20
1.81	16	1.81	12	1.82	10	1.82	10
1.74	4	1.74	4				
1.63	7	1.63	6	1.63	8	1.63	10
1.60	8	1.60	6	1.51	28	1.58	10
				1.40	10	1.57	10
						1.52	14
						1.51	43
						1.40	26

The patterns of the samples do not correspond to any of the aluminum oxides or lithium aluminates listed in the ASTM files, but do correlate with a pattern

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reported by Hummel⁽¹⁹⁾ (right-hand column) for lithium aluminate formed by reacting Li_2O and Al_2O_3 for 15 hr at 1500°C . The compound listed as lithium aluminate in the ASTM card files was formed by a hydrothermal reaction⁽⁸⁾ $[\text{Al}(\text{OH})_3 + \text{LiOH} (\text{aq}) \text{ at } 300^\circ\text{C}]$ and the x-ray diffraction pattern differs from the above patterns.

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APPENDIX H

Estimation of surface area required to release observed T_2 from fissioning Li^6 in surface positions.

1. Assume 10^{15} surface positions per cm^2 of target.
2. In $LiAlO_2$, one-fourth of the atoms are lithium, and 7.4% of the lithium is Li^6 . Therefore,

$$0.25 \times 0.74 \times 10^{15} = 1.8 \times 10^{13} Li^6/cm^2$$

3. Tritium released in-reactor from the irradiated pressed-sintered aluminate target:

$$\frac{0.11 \text{ cc } T_2, \text{ STP}}{22,400 \text{ cc/mole}} \times 6.02 \times 10^{23} \frac{\text{molecules}}{\text{mole}} = 3 \times 10^{18} \text{ molecules of } T_2$$

corresponding to 6×10^{18} fissions, i.e.,

$$3 \times 10^{18} \text{ molecules } T_2 = 6 \times 10^{18} Li^6 \text{ fissions.}$$

4. Total Li^6 burnup:

$$\frac{0.77 \text{ cc He}^4}{22,414 \text{ cc/mole}} \times 6.02 \times 10^{23} = 2.1 \times 10^{19} \text{ fissions}$$

$$\begin{aligned} \text{Total } Li^6 &= 2.26 \text{ gm of target} \times 0.105 \frac{gLi}{g \text{ target}} \times \frac{0.0645 gLi^6}{gLi} \\ &= 1.5 \times 10^{-2} g \end{aligned}$$

$$\frac{1.53 \times 10^{-2} gLi^6}{6.015 g/mole} \times 6.02 \times 10^{23} \sim 1.5 \times 10^{21} \text{ atoms } Li^6$$

$$\begin{aligned} Li^6 \text{ burnup} &= \frac{2.1 \times 10^{19} \text{ fissions}}{1.5 \times 10^{21} \text{ atoms } Li^6} \times 100 \\ &= 1.4\% \end{aligned}$$

5. Assume equal surface and bulk burnup of Li^6 .

$$\begin{aligned} \therefore \text{ surface fissions} &= 1.4 \times 10^{-2} \times 1.8 \times 10^{13} \frac{\text{atoms } Li^6}{cm^2} \\ &= 2.5 \times 10^{11} \frac{\text{fissions}}{cm^2} \end{aligned}$$

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6. Surface area required to release observed T_2 and HT (pressed-sintered $LiAlO_2$):

$$\frac{6 \times 10^{18} \text{ fissions}}{2.5 \times 10^{11} \frac{\text{fissions}}{\text{cm}^2}} = 2.4 \times 10^7 \text{ cm}^2 = 2.4 \times 10^3 \text{ m}^2$$

$$\frac{2.4 \times 10^3 \text{ m}^2}{2.26 \text{ g}} \sim 10^3 \frac{\text{m}^2}{\text{g}}$$

The above estimate is conservative, since some tritium recoiling from the surface will come to rest in adjacent grains. In the pressed-sintered target, the void volume was 32% and the probability of a recoil stopping in a void therefore is $\sim 1/3$, assuming uniform distribution of voids.

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ACKNOWLEDGMENTS

Thanks are due R. L. Dillon, T. W. Evans, and W. H. Yunker for discussions on various phases of target irradiation and analysis. Targets were provided by W. J. Weber and W. E. Girwell of Metallurgy Development. The author is grateful for irradiation and analytical services from the following: R. Elder, R. Fullerton, L. C. Kellog, J. C. Langford, D. A. Wallace, P. J. Zimmerman, and A. E. DeMers.

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