SEPTEMBER 1990 ECN-RX--90-070

NL91C0224

COMPARISON OF THE TRITIUM RESIDENCE TIMES OF VARIOUS CERAMIC BREEDER MATERIALS IRRADIATED IN EXOTIC EXPERIMENTS 4 AND 5

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PAPER PRESENTED AT THE 16TH SYMPOSIUM ON FUSION TECHNOLOGY (SOFT),
LONDON, UK, SEPTEMBER 3-7, 1990

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The work described in this paper has been carried out in the frame of the European Fusion Technology Programme, tasks B11-B16, with financial support from the Commission of the European Community.

ABSTRACT

Tritium residence times have been determined for various ceramic tritium breeding materials from in-situ tritium release measurements. The irradiations, codenamed EXOTIC (EXtraction Of Tritium In Ceramics), were carried out in the High Flux Reactor (HFR) at Petten. During the irradition more than 450 transients were performed and the corresponding tritium release measured. Materials supplied by SCK/CEN (Li_2ZrO_3), CEA (Li_2ZrO_3 and $LiAlO_2$), ENEA ($LiAlO_2$, KfK (Li_4SiO_4), NRL ($Li_6Zr_2O_7$) and ECN (Li_8ZrO_6) were irradiated in EXOTIC-5 to compare the tritium residence times obtained under equal conditions. Apart from differences in density, grain size, pore size and OPV it appeared that the tritium residence times of the lithium zirconates (pellets) were shorter than those of the Li_4SiO_4 pebbles. The tritium residence times of the Li_4SiO_4 pebbles were shorter than those of the $LiAlO_2$ pellets.

CONTENTS

1. INTRODUCTION

Within the European programme on Fusion Blanket Technology a series of in-situ tritium release experiments have been performed with $LiAlO_2$, Li_2SiO_3, Li_4SiO_4, Li_2O, Li_2ZrO_3, $Li_6Zr_2O_7$ and Li_8ZrO_6 [1-5] to determine tritium residence times. These experiments have been performed in different reactors and at different conditions. Moreover, the analysis of the data and the definition of the material temperature has not been quite the same. This makes direct comparison of the results difficult. The main objective of experiment EXOTIC-5 was to irradiate under similar conditions the best available materials from: SCK/CEN-Mol, NRLSpringfields, ENEA-Casaccia, CEA-Saclay, KfKKarlsruhe and ECN-Petten to determine tritium residence times from transient tritium release and to compare the results also with earlier experiments [1-5]. The main differences between the lithium zirconates of EXOTIC-4 and -5 was the ^6Li abundance which was 0.6 and 7.5 % respectively.

2. EXPERIMENTAL

2.1. Materials

The samples irradiated in EXOTIC-5 were annular pellets of $LiAlO_2$, Li_2ZrO_3, $Li_6Zr_2O_7$ and Li_8ZrO_6 with outer and inner diameter of 10 mm and 6 mm respectively. In a few cases the inner diameter was 4 mm. One capsule was filled with 0.5 mm diameter Li_4SiO_4 pebbles. This capsule had an outer diameter of 10 mm and an inner diameter of 5 mm. The stack length of all materials was 100 mm. The ^6Li abundance was 7.5 %. The loading of the materials in the capsules, their suppliers and characteristics are given in [6] and summarized in table 1.

2.2. Irradiation facility

Irradiation of EXOTIC-5 was performed in a four channel rig (TETRA) each channel containing one sample holder which consisted of two stainless steel capsules [7]. All eight capsules are independently controlled and continuously purged. In-situ tritium release rates were meausured by eight ionization chambers, one for each capsule. The instrumentation included thermocouples, neutron fluence detector sets and gamma scan wires. The temperatures were adjusted by changing the helium/- neon gas mixture in the gas gaps surrounding the sample holders. The avarage temperature was defined as a volume averaged temperature, considering radial and axial gradients, based on measured data and calculated two dimensional fields.

2.3. Irradiation conditions

The irradiation was carried out in the HFR Petten at a nominal reactor power of 45 MW and lasted 6 cycles (136 FPD), 3 cycles in peripheral HFR core position H2 and 3 cycles in H6. During irradiation in each position the nuclear conditions remained constant. The capsules were purged with dry helium + 0.1 vol % hydrogen at a flow rate of 100 cm^3/min. The hydrogen content in the purge gas was changed from 0.1 % to 0.01 % and to 1 % during the last cycle. The purge gas downstream was continuously analysed on released tritium and on water vapour. The temperatures, the purge gas flow and the pressure were

also continuously monitored. A large number of temperature transients were performed between 300°C and 650°C, at different temperature levels and with different temperature steps, both by increasing and decreasing the temperature. The relevant process parameters were scanned every two minutes by a computerized data logger. During the temperature transients the data were, for a period of two hours, scanned every 10 seconds.

3. RESULTS AND DISCUSION

3.1. Tritium release with reference purge gas

A review of all transients is given in ref. [6].

3.2. Effect of purge gas composition

The effect of hydrogen content in the purge gas has been investigated by changing the H_2 percentage from 0.1 vol.% to 0.01 % and subsequently to 0.1 % and 1 %. Examples of the effect of hydrogen content in the purge gas on the transient tritium release are illustrated in figs. 1 and 2. Fig. 1 shows a positive peak of the tritium release rate when the hydrogen content was increased from 0.1 % to 1 %. A decrease in tritium release rate was observed, fig. 2, when decreasing the hydrogen content from 1 % to 0.1 %.

3.3. Tritium residence times

From the transient tritium release curves tritium residence times were determined by data fitting using a diffusion model for a spherical geometry with a constant internal tritium source and zero surface concentration [3]. The tritium residence time is defined as

$$\tau = I/\dot{G} \,, \tag{1}$$

where

I = tritium inventory, mCi

$\dot{G}$ = tritium production rate, mCi/min.

The tritium inventory, ^{T}, is given by the relationship:

$$I = (a^2/15D)\dot{G} \,, \tag{2}$$

where,

a = grain radius, cm

D = diffusion coefficient, cm^2/s

The tritium residence time can thus be written as:

$$\tau = a^2/15D_2 \quad . \tag{3}$$

where D_2 is determined from:

$$\dot{R}/\dot{G} = 1 + \frac{6}{\pi^2}\left(\frac{D_2}{D_1} - 1\right) \sum_{n=1}^{\infty} \frac{1}{n^2} \exp.(-n^2\pi^2 D_2\ t/a^2) \tag{4}$$

where,

$\dot{R}$ = tritium release rate, mCi/min

t = time, min

Sofar, a limited number of transients have been analysed. The tritium residence times determined from positive transients (temperature increase) of the Li_2ZrO_3 of all three capsules, 17.1, 17.2 and 18.1, were longer than those of negative transients with equal final temperatures. For Li_8ZrO_6 an increase in tritium residence time was observed after the first irradiation cycle when the rig was moved from core position H2 to H6. Sofar, no explanation can be given for the behaviour of this Li_2ZrO_3 and Li_8ZrO_6. The preliminary results given in table 2 and illustrated in fig. 3 represent the residence times, determined from the positive transients of Li_2ZrO_3 and from the transients of the second cycle for Li_8ZrO_6. The straight lines of the Arrhenius plot represent the least square fit of the available data. To improve the reading of this figure the data points were not plotted. The tritium residence times of Li_2ZrO_3 of the capsules 17.2 and 18.1 are practically the same. Therefore, only one line has been drawn for both materials.

To compare the tritium residence times of the various breeding materials one has to take into account the material characteristics like: density, open pore volume, grain size and pore size, see table 1. In general, tritium residence times can be reduced not only by increasing the temperature but also by using material with a smaller grain size, a smaller fraction of closed porosity (CPV) and a lower density.

From table 1 it can be observed that the three lithium metazirconates had almost an equal average grain size (1 μm) and pore size (0.25 μm). The density and CPV are somewhat higher for the Li_2ZrO_3 of capsule 17.1 (77.5 % TD and 4 %) than those of capsules 17.2 and 18.1 (74 % TD and 0 %). Nevertheless, the tritium residence times of the Li_2ZrO_3 of capsule 17.1 are slightly shorter.

The grain size and density of $Li_4Zr_2O_7$ (2 µm and 79 % TD) and Li_8ZrO_6 (5/10 µm and 84 % TD) differed largely. This might mean that for Li_8ZrO_6 shorter tritium residence times can be achieved by using material with a smaller grain size and a lower density.
The difference in tritium residence time between the two lithium aluminates is rather small. The different slopes of the lines shown for $LiAlO_2$ in fig. 3 result at temperatures above 475°C in shorter tritium residence times for $LiAlO_2$ of capsule 19.1. At temperatures below 475°C the tritium residence time of $LiAlO_2$ of capsule 19.2 is shorter.

3.4. Comparison of the tritium residence times

The tritium residence times of EXOTIC-5 have been compared with those determined from the experiments EXOTIC-4 [3] and MOZART [1] for the lithium metazirconates and with those of experiments MOZART [1] and TEQUILA [2] for the lithium aluminates. The tritium residence times of the experiments MOZART and TEQUILA are presented in the same way, in the figs. 4 and 5 for Li_2ZrO_3 and $LiAlO_2$ respectively, as those of EXOTIC-5. This means that the lines in these figures are the best fit of all experimental data. For the experiments MOZART and TEQUILA this is not in agreement with the graphs presented in refs. [1] and [2], where the plotted lines have two different slopes. The slope of the Li_2ZrO_3 (MOZART) line given in fig. 4 differs significantly from the two original ones [1]. However, the first part of this plot consisted of three data and the second part of only two. The low values of the first part may have been influenced by the time constant of the measuring system. Therefore, taking the best fit of the available data in fig. 4 seems to be reasonable. The slope of the $LiAlO_2$ (TEQUILA) line in fig. 5 does not differ much from the original ones [2].
From fig. 4 it can be observed that the tritium residence times of Li_2ZrO_3 of MOZART S6 are in very good agreement with those of EXOTIC-5, capsules 17.1 and 18.1. The material characteristics are similar as can be seen in table 3. The lithium metazirconates of EXOTIC-4 have longer tritium residence times than those of MOZART and EXOTIC-5. Moreover, the slopes of the graphs are different. The density of the materials of capsules 14.1/2 is significantly higher

which results in longer residence times. The much lower ^6Li abundance in the materials of EXOTIC-4 gives during irradiation a smaller tritium production rate, a more homogeneous tritium distribution and a smaller temperature gradient across the pellets. However, it is not yet clear whether the lower ^6Li abundance causes the longer tritium residence times. Comparison of the lithium aluminates, fig. 5, illustrates that the material with the highest density, and the largest grain size, MOZART S5, has the longest tritium residence times. The EXOTIC-5 values are in reasonable agreement with those of TEQUILA P. On the basis of the material characteristics this could have been expected. The $LiAlO_2$ of EXOTIC-5 (19.1) and of TEQUILA P are both made by ENEA.

4. CONCLUSIONS

The EXOTIC-5 experiment has confirmed previous literature results that the tritium residence times of Li_2ZrO_3 are shorter than those of $LiAlO_2$.

The tritium residence times of the Li_4SiO_4 pebbles of EXOTIC-5 were shorter than those of $LiAlO_2$ pellets but larger than those of Li_2ZrO_3.

Comparison of the EXOTIC-5 data irradiated in the HFR Petten with those of MOZART and TEQUILA irradiated in the MELUSINE reactor in Grenoble revealed that the difference in experimental conditions has no significant effect on the tritium residence times.

The differences observed in the tritium residence times of Li_2ZrO_3 irradiated in EXOTIC-4 and -5 can only partly be explained by a lower density for the materials of EXOTIC-5. Most likely, the results are also influenced by the difference in Li-6 abundance, 0.6 % for EXOTIC-4 and 7.5% for EXOTIC-5.

The tritium residence times of the EXOTIC-5 materials $Li_6Zr_2O_7$ and Li_8ZrO_6 are almost equal. By decreasing the grain size of both materials to about 1 um even shorter residence times can be expected.

At temperatures of around 300°C the tritium residence times of the Li_8ZrO_6, $Li_6Zr_2O_7$ and Li_2ZrO_3 of EXOTIC-5 are almost identical.
For the materials of EXOTIC-5 a tritium residence time of one day can be achieved at temperatures of approximately

- 430°C for $LiAlO_2$
- 375°C for Li_4SiO_4 and
- 300°C for Li_2ZrO_3, $Li_6Zr_2O_7$ and Li_8ZrO_6.

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Table 1. Summary of EXOTIC-5 material characteristics.

Caps. no.	Material	Supplier	Density (% TD)	OPV (%)	Weight (g)	Grain size µm	Pore size µm	Pellet OD/ID mm
17.1	Li_2ZrO_3	SCK/CEN	77.5	22.5	21.3	0.9	0.26	10/4
17.2	Li_2ZrO_3	SCK/CEN	74.0	26.0	20.0	0.8	0.28	10/4
18.1	Li_2ZrO_3	CEA	74.1	25.9	16.0	1.1	0.24	10/6
18.2	$Li_6Zr_2O_7$	NRL	79.1[1]	20.9	17.9	2.0[2]	0.5	10/4
19.1	$LiAlO_2$	ENEA	80.9	19.1	10.8	0.7	0.17	10/6
19.2	$LiAlO_2$	CEA	74.7	25.3	9.9	0.35	0.06	10/6
20.1	Li_4SiO_4	KfK	80.8	19	6.4	-	-	Pebbl.
			51.9[3]	48	6.4	0.5	-	10/5
20.2	Li_6ZrO_6	ECN	84.1	14	12.6	5/10	<0.8	10/6

1) one pellet of 72.7 % TD, otherwise average 79.8 % TD.
2) individual grains, agglomerates range: 2-20 µm.
3) density of pebble bed (1.24 g/cm³); measured: 1.09 g/cm³.

Table 2. Tritium residence times of various ceramic breeding materials irradiated in EXOTIC-5.

End of transient temp.,(°C)	Time, (h)	End of transient temp.,(°C)	Time, (h)	End of transient temp.,(C)	Time, (h)
Li_2ZrO_3-SCK/CEN, caps. 17.1		Li_2ZrO_3-SCK/CEN caps. 17.2		Li_2ZrO_3-CEA caps. 18.1	
305	12.4	333	11.1	332	10.5
388	1.1	416	0.94	406	1.6
392	1.2	421	1.9	411	1.5
396	2.4	454	0.74	502	0.55
424	0.6	461	0.6	504	0.49
426	0.6	522	0.49	528	0.23
436	0.65	580	0.12	611	0.15
487	0.4	585	0.10	614	0.13
550	0.14				
552	0.16				
$Li_8Zr_2O_7$-NRL caps. 18.2		Li_8ZrO_6-ECN caps. 20.2		Li_4SiO_4-KfK caps. 20.1	
331	7.0	457	3.2	408	6.5
336	8.3	457	2.0	460	9.5
338	12.0	485	2.3	463	8.6
414	1.8	525	0.6	501	5.5
448	2.1	535	2.1	505	2.1
460	3.7	549	2.6	506	0.5
462	4.5	596	0.5	520	1.6
464	1.2	600	0.9	520	1.5
477	1.4			598	0.8
517	1.7			607	0.7
561	1.1				
587	0.8				
589	1.0				
$LiAlO_2$-ENEA caps. 19.1		$LiAlO_2$-CEA caps. 19.2			
463	21.3	471	15.1		
462	14.3	472	15.4		
463	12.7	508	5.1		
502	2.9	512	4.8		
502	7.1	549	2.6		
550	0.94	551	3.4		
551	1.8	551	1.2		
552	0.83	552	1.7		
553	1.8	553	1.25		
585	0.8	600	1.6		
		681	0.9		
		686	0.55		

Table 3. Comparison of the material characteristics of Li_2ZrO_3 and $LiAlO_2$ of the experiments EXOTIC-4, EXOTIC-5, MOZART, and TEQUILA.

Material	Experiment	Density, % TD	Average grain size, µm	Average pore size, µm	Li-6 abundance, %
Li_2ZrO_3	MOZART, S6	80	1	-	7.5
	E4, 16.1	79	0.4-1	0.3	0.6
	E4, 14.1/2	85.5	1	0.14	0.54
	E5, 17.1	77.5	0.9	0.26	7.5
	E5, 18.1	74.1	1.1	0.24	7.5
$LiAlO_2$	MOZART, S5	92.7	5	-	7.5
	TEQUILA, P	80	0.3	-	7.5
	E5, 19.1	80.6	0.3-1	0.17	7.5
	E5, 19.2	74.7	0.35	0.06	7.5

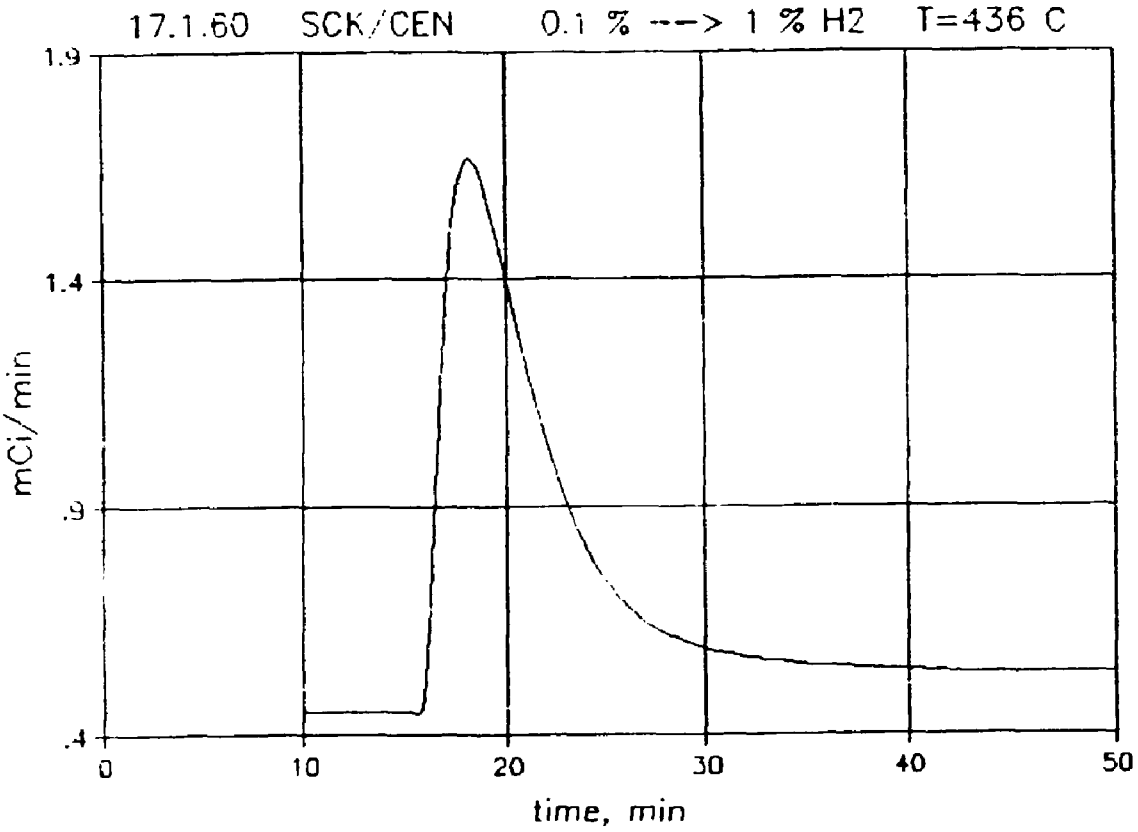

Fig. 1. Transient tritium release from Li_2ZrO_3 by changing the hydrogen content in the purge gas from 0.1 to 1%.

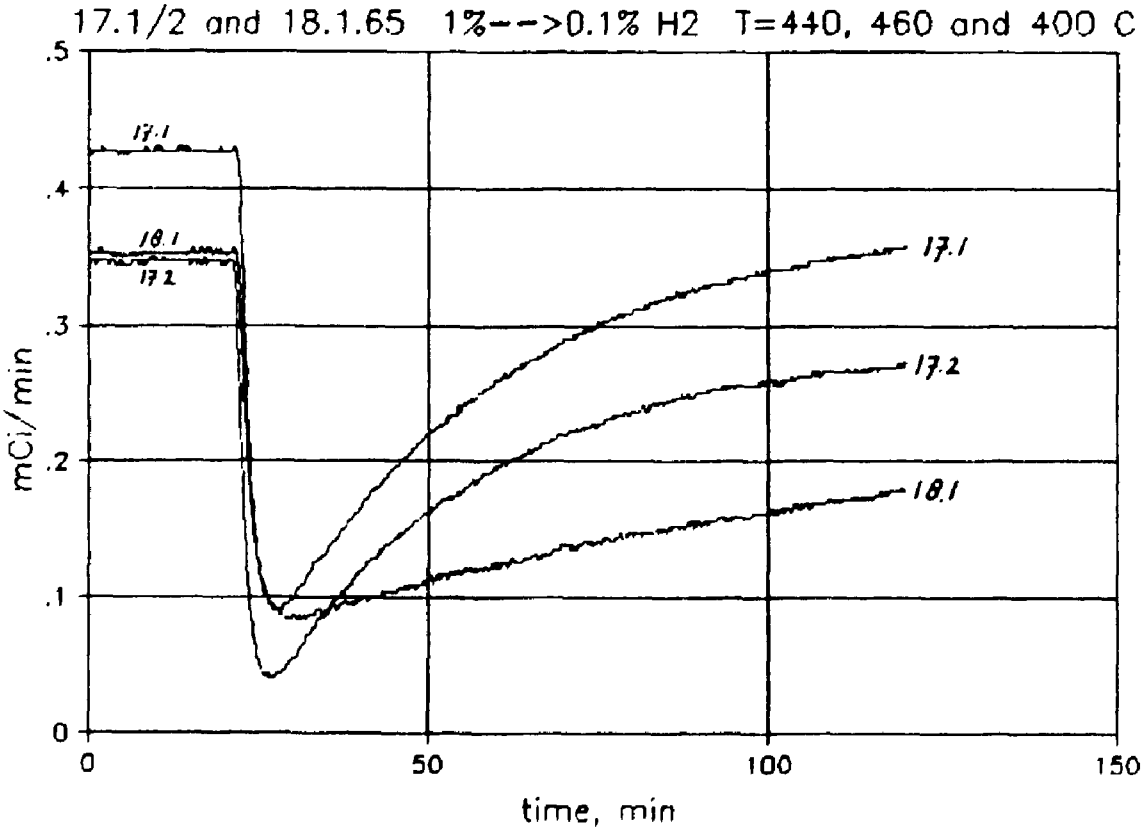

Fig. 2. Transient tritium release from Li_2ZrO_3 by changing the hydrogen content in the purge gas from 1 to 0.1%.

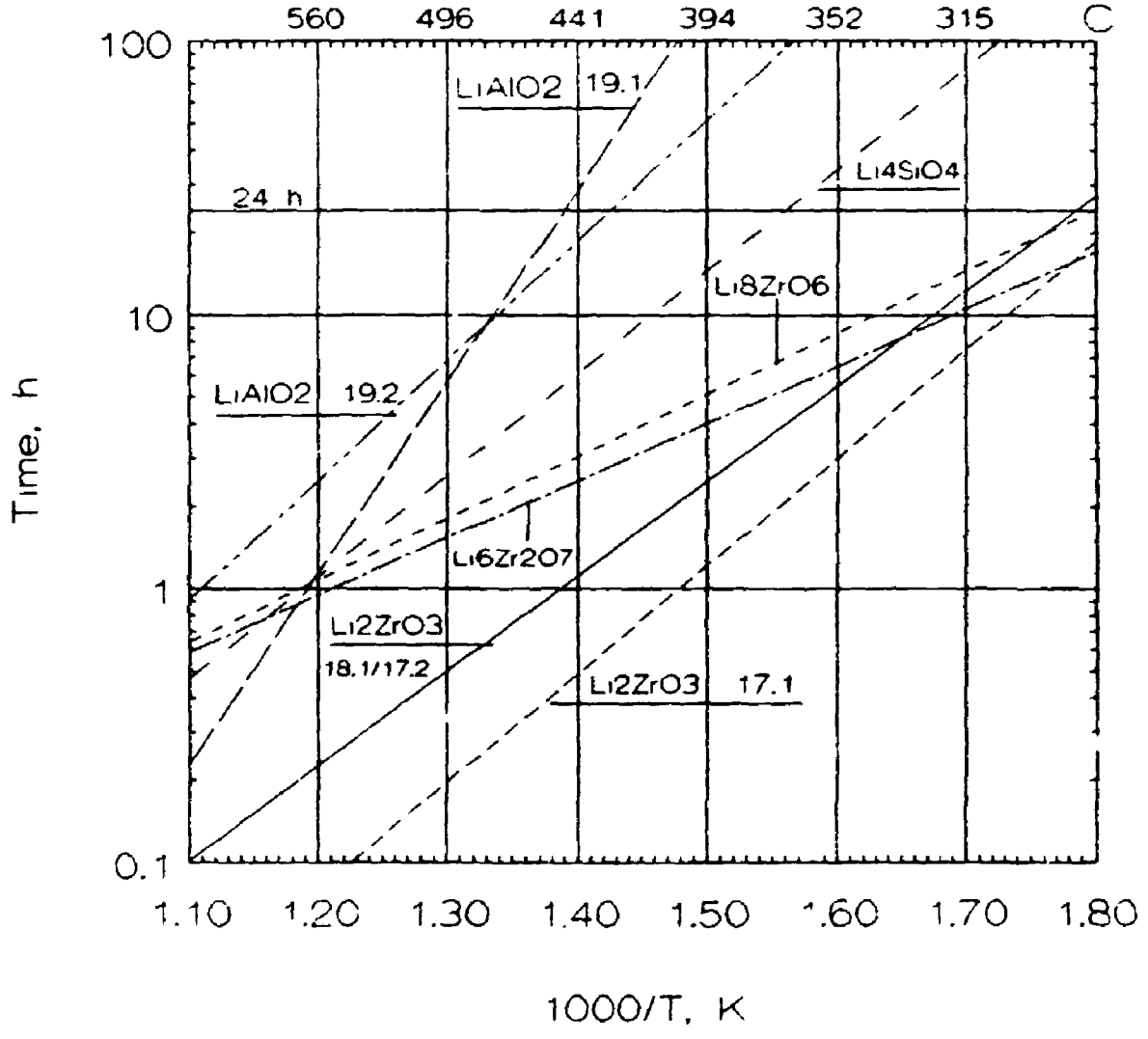

Fig. 3. Tritium residence times of Li-ceramics irradiated in EXOTIC-5.

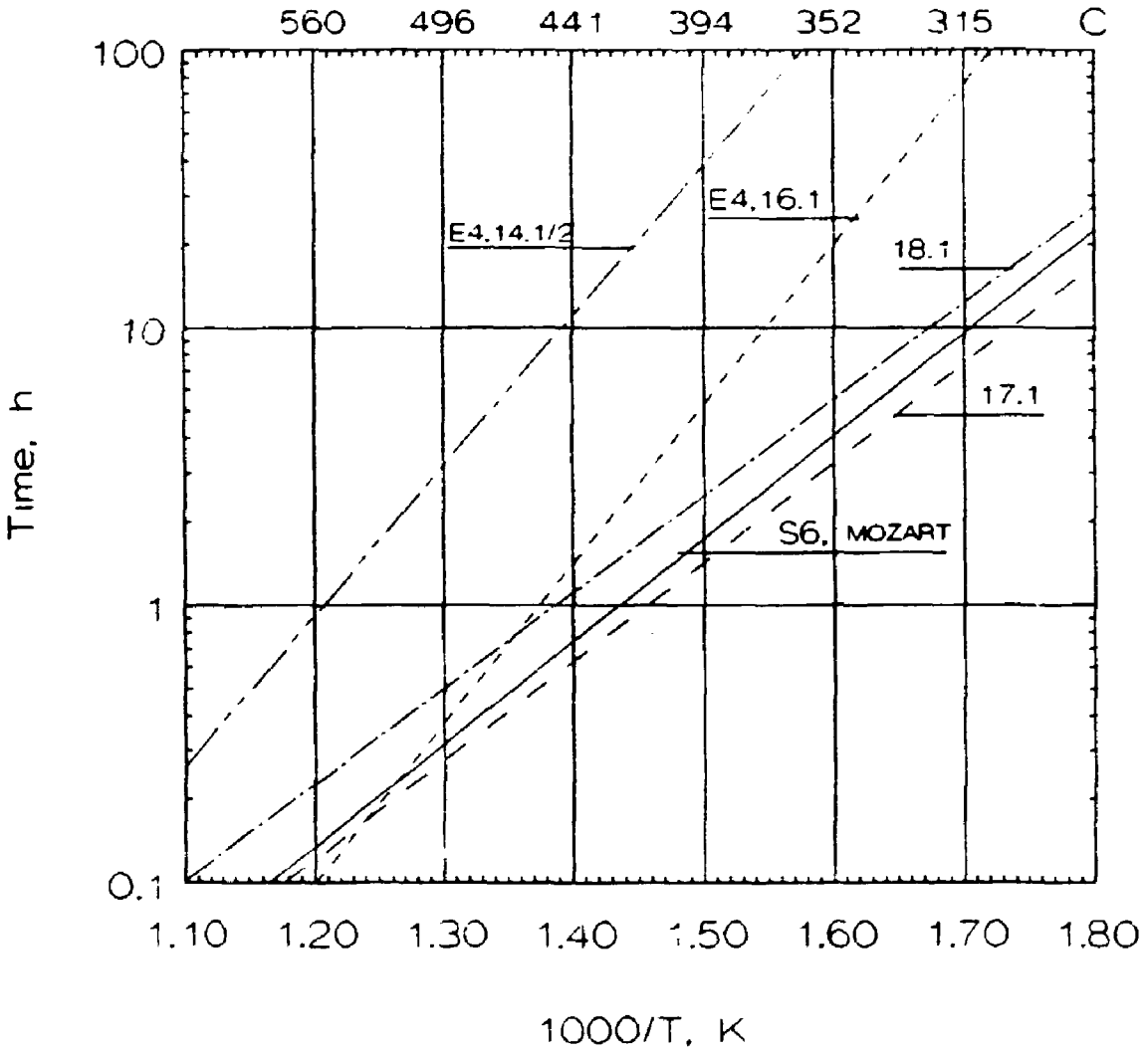

Fig. 4. Tritium residence times of Li_2ZrO_3 from experiments EXOTIC-4 and -5 and MOZART.

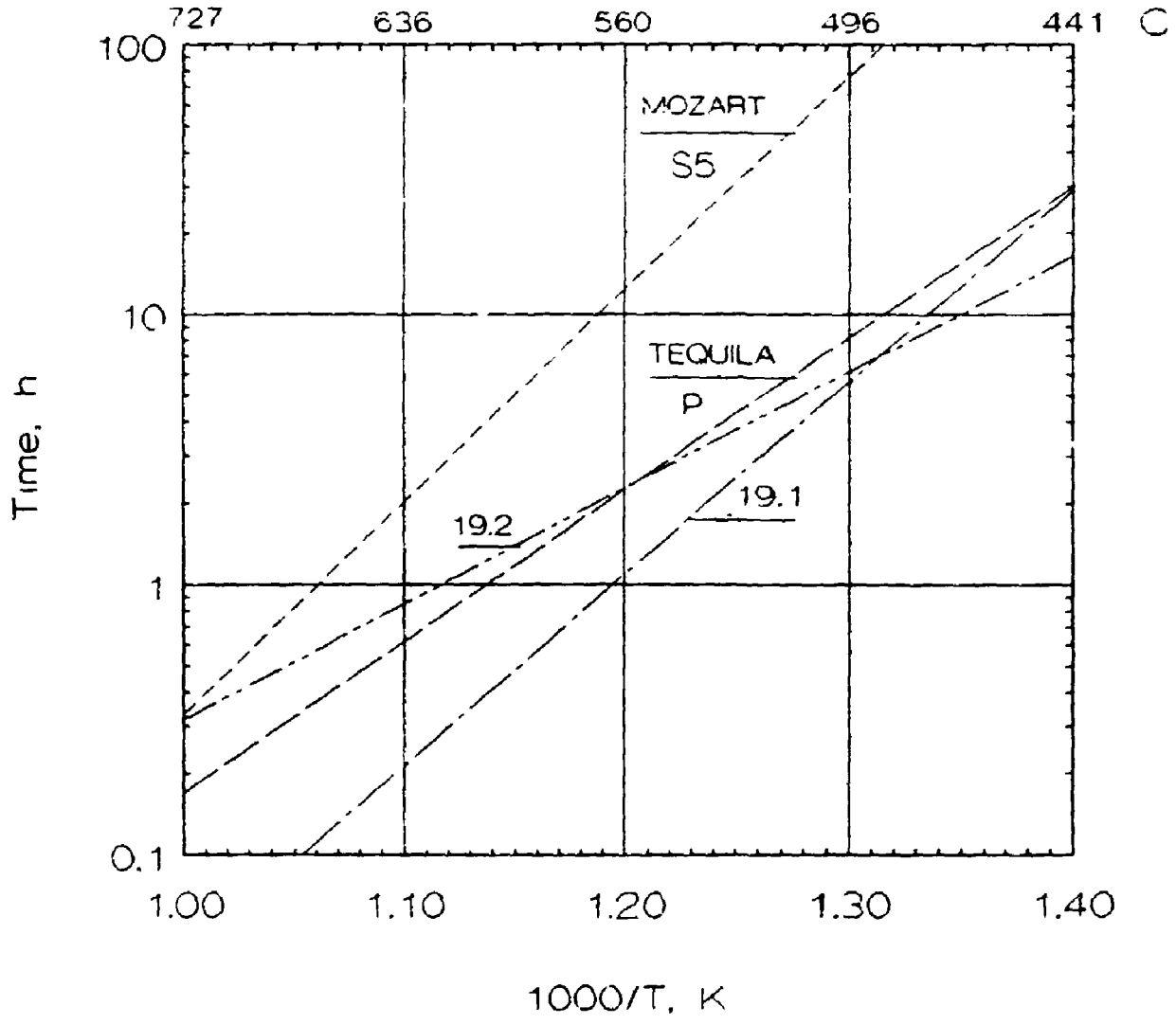

Fig. 5. Tritium residence times of $LiAlO_2$ from experiments EXOTIC-5, MOZART[1] and TEQUILA[2].