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Post-irradiation examinations of Li_4SiO_4 pebbles irradiated in the EXOTIC-7 experiment

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Abstract

Extraction of tritium in ceramics-7 (EXOTIC-7) was the first in-pile test with ^6Li-enriched (50%) lithium orthosilicate (Li_4SiO_4) pebbles and with DEMO representative Li-burnup. Post-irradiation examinations (PIEs) of the Li_4SiO_4 have been performed at the Forschungszentrum Karlsruhe (FZK) to investigate the tritium release kinetics, the effects of Li-burnup, of the contact with beryllium during irradiation and the changes in the mechanical stability of the pebbles due to irradiation. Based on these data one can conclude that neither the contact with beryllium nor a burnup up to 13% have a detrimental effect on the tritium release of Li_4SiO_4 pebbles, but at 18% Li-burnup the residence time is increased by about a factor of 3. The mechanical strength of both irradiated and unirradiated pebbles has been examined by means of crush tests. According to the PIE no significant changes in the mechanical stability of the pebbles have been observed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The Helium cooled pebble bed (HCPB) blanket, which is being developed within the European Fusion programme, is based on the use of lithium ceramic pebble beds as breeder material and of binary beryllium pebble beds as neutron multiplier [1]. Irradiation behaviour of the various breeder materials up to medium lithium burnup (~3%) has been studied in previous extraction of tritium in ceramics (EXOTIC) tests [2]. The goal of EXOTIC-7 was to study the irradiation behaviour (mainly mechanical integrity and tritium release) up to and beyond DEMO relevant lithium burnup (~7%). When EXOTIC-7 was planned (1993) the breeder-out-of-tube (BOT) blanket concept was being studied [3], and mixtures of Li_4SiO_4 and beryllium pebbles were also considered as blanket material. Therefore in EXOTIC-7 pure Li_4SiO_4 and mixed Li_4SiO_4/beryllium pebble beds were irradiated. One irradiation capsule containing a mixed bed was made of DEMO relevant steel (MANET) in order to study chemical interactions, and determine irradiation induced swelling by changes in the measured radial temperature gradient of the bed. In this paper, the result of the post-irradiation examinations (PIEs) of Li_4SiO_4 pebbles performed at the research center of Karlsruhe are discussed. In-pile and PIE results from the Netherlands Energy Research Foundation (ECN) Petten have been presented elsewhere [4].

2. Samples and irradiation conditions

Overstoichiometric ($Li_4SiO_4 + 1.4$ wt% SiO_2) lithium orthosilicate pebbles with diameter in the range 0.1–0.2 mm were irradiated in the EXOTIC-7 experiment. The pebbles were produced by Schott Glaswerke by the melting-spraying process, and their ^6Li-enrichment was about 52% [4]. The content of impurities was low (0.07 wt% Al, 0.3 wt% C and <0.009 wt% for the other impurities). The presence of carbon was due to the fabrication process which uses high ^6Li-enriched lithium carbonate. The material from Forschungszentrum Karlsruhe (FZK) was irradiated in three capsules, and Table 1 shows the loading characteristics. More detailed information about the loading can be found in Ref. [4].

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Table 1
Loading characteristics of the irradiated capsules

Capsule number	Material (pebbles)	Mass (g)	Pebble bed density (g/cm^3)[a]	ρ_{bed}/ρ_{th} (%)
26.2	Li_4SiO_4	1.40	0.408	17.3
	Be[b]	3.53	1.029	55.9
28.1	Li_4SiO_4	4.99	1.476	61.8
28.2	Li_4SiO_4	1.88	0.233	9.9
	Be[b]	9.81	1.217	66.2

[a] For mixed beds the density of both beryllium pebbles and lithium orthosilicate pebbles are indicated.
[b] A DEMO relevant binary beryllium pebble bed with 0.1–0.2 and 2 mm diameter were used.

The stainless steel capsule 28.1 contained only Li_4SiO_4 pebbles. The pebble bed height was separated into three parts, each of 20 mm length, in order to enable three different temperature levels (28.1-1, 28.1-2 and 28.1-3). The pebble bed diameter for the upper part was 6.3 mm, in order to achieve the required temperature of 400°C. The pebble bed diameter of middle and lower parts was 8 mm. Capsule 28.2 contained Li_4SiO_4 pebbles of 0.1–0.2 mm diameter and Be pebbles of 2 and 0.1–0.2 mm diameter. The pebble bed diameter was 11.35 mm and the pebble bed height 80 mm. The pebble bed of this capsule was enclosed in a MANET tube (DEMO relevant steel) of 1.75 mm thickness. The objective was to determine indirectly the beryllium swelling during the irradiation, by measuring the radial temperature gradient of the pebble bed. Capsule 26.2 also contained Li_4SiO_4 and beryllium pebbles as the previous one, but was done of stainless steel and the pebble height was separated into three parts each of 20 mm length (26.1-1, 26.1-2 and 26.1-3). The pebble bed diameter was 8 mm for the upper part and 7.2 mm for the middle and the lower parts. The peak neutron fluences near the capsule walls were: fast fluence (^{54}Mn) 1–2 $\times 10^{25}$ n/m^2, thermal fluence (^{60}Co) 1–1.6 $\times 10^{25}$ n/m^2. The depression of the thermal fluence at the capsule centres was a factor of 2–4. Other irradiation conditions are given in Table 2 [5].

3. Dismantling and visual inspection

Neutron radiography just after irradiation and before dismantling revealed no irregularities, and the pebble beds were found essentially intact. This was confirmed by visual inspection during and after unloading. The dismantling of capsules 26.2 and 28.2, containing a mixture of Li_4SiO_4 and beryllium pebbles, was difficult because of blocked regions. The unloading of capsule 28.1 was easy, and a small number of fractured pebbles were observed [4].

4. Experimental results

4.1. Optical microscopy

In the unirradiated initial condition (specimen 28.1, unirradiated), the orthosilicate material has a dendritic structure with a network of interdendritic micropores. In some pebbles there are also spherical freezing shrinkage voids and oblong intercrystalline cavities. After the irradiation, the visual inspection of the Li_4SiO_4 pebbles showed that only a small number of pebbles were fractured, whilst scanning electron microscopy showed the presence of surface cracks [6]. By comparing the pebbles before and after the irradiation (Figs. 1 and 2) it is possible to see that the orthosilicate pebbles from the capsule 28.1 (10% Li-burnup) show both an increase in smaller cracks in the kernels of the pebbles, and the presence of larger throughcracks. The throughcracks start underneath the pebble surface and open towards the pebble centre. They occur as radial and tangential cracks with different shapes. Fig. 3 shows that after the irradiation very few pebbles were broken or deformed. In capsule 26.2 (14% Li-burnup) a higher amount of cracks was observed in the pebbles and cracking progressed further (Fig. 4). In the case of the highest Li-burnup occurring in capsule 28.2 (18% Li-burnup) a still higher degree of cracking occurred, resulting in increased fragmentation.

A comparison of the pebbles at the three burnup levels indicates a large scatter in conditions: at the lowest

Table 2
Irradiation conditions: central temperature and total lithium burnup

	26.2	28.1	28.2
Central temperature (°C)	410–545	465–730	410–480
Lithium burnup (%) (calculated)	14 ± 2	7 ± 2	19 ± 2
Lithium burnup (%) (experimental)	–	10 ± 2	18 ± 2

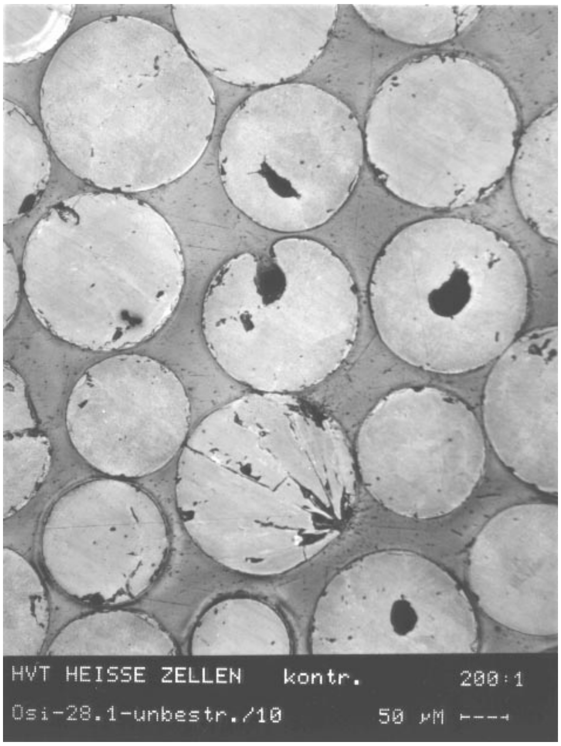

Fig. 1. Lithium orthosilicate pebbles before irradiation (capsule 28.1).

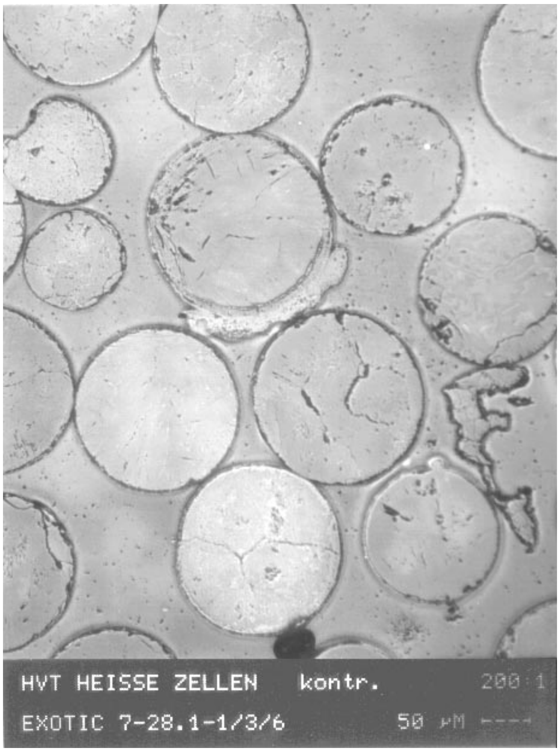

Fig. 2. Lithium orthosilicate pebbles after irradiation (capsule 28.1, 10% Li-burnup).

burnup individual pebbles were broken as a result of cracking while, at the highest burnup, there were still several undamaged pebbles with very compact structures. The reason of this must be sought in the different glass-ceramic structures, which arose during the pebble fabrication process. The post-crystallisation of the glass phase and the release of produced tritium and helium influence strongly the effects of the irradiation. The strong reduction due to crystallisation, the volume of the glass phase causes freezing shrinkage voids and microporosities to be generated. Crystallisation spreads through the crystal–glass contact points and, consequently, it occurs preferably in the kernel of the pebbles where there is a higher mixing of crystal and glass. This explains cracking and the opening of throughcracks in the inner part of the pebbles at the onset of irradiation. Afterwards, as irradiation is continued, crystallisation begins also in the outer, rich in glass, part of the pebbles. Cracks frequently open towards the surface of the pebble. Cracking is increased by the precipitation of gas bubbles in the crystalline structure. The glass phase, with its larger interatomic gaps, can retain much higher gas fractions in solution than the more closely packed crystal lattice. Pebbles, which are still intact at high burnups are probably made up largely of the glass phase.

4.2. Mechanical behavior

Crush tests at room temperature have been performed to characterise the mechanical behaviour of the single pebbles before and after the irradiation. In these tests, a continuously increasing load is imposed by a piston to a single pebble until it breaks. The very small quantity of irradiated material available did not allow any statistics on the total amount of pebbles broken during the irradiation. Therefore, the quite small fraction of broken pebbles present in the material delivered by the ECN Petten was not taken into account in our considerations on the mechanical behaviour of the pebbles. The crush tests showed practically no reduction of the mechanical stability of single pebbles after the irradiation.

Also the measurements of microhardness indicated no significant radiation induced changes. Measurements according to Vickers indicated hardness levels of 283 for unirradiated orthosilicate, and 319 for orthosilicate with about 10% burnup (capsule 28.1).

4.3. Tritium release

The tritium release rate and total amount of released tritium were studied by purging with He + 0.1% H_2 and

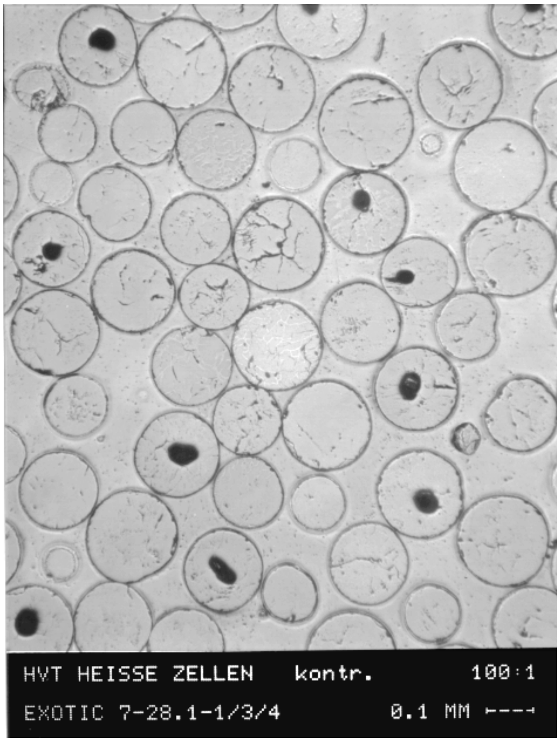

Fig. 3. Lithium orthosilicate pebbles after irradiation (capsule 28.1, 10% Li-burnup).

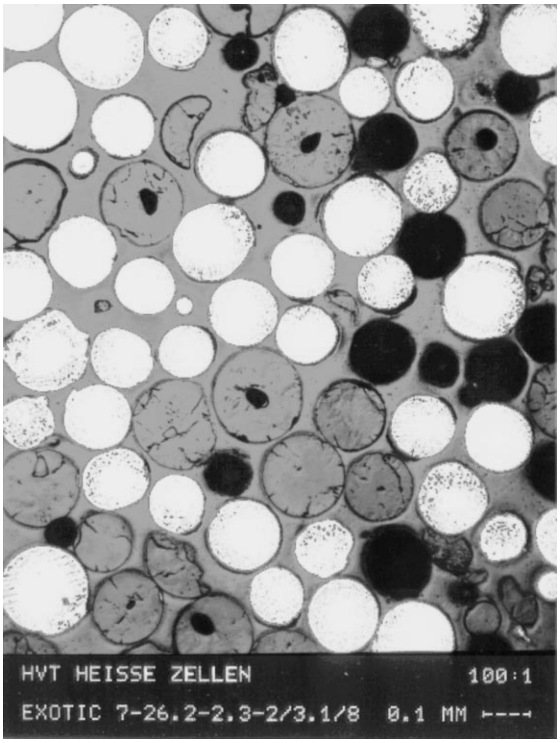

Fig. 4. Lithium orthosilicate and beryllium pebbles after irradiation (capsule 26.2, 14% Li-burnup). The beryllium pebbles are the white ones.

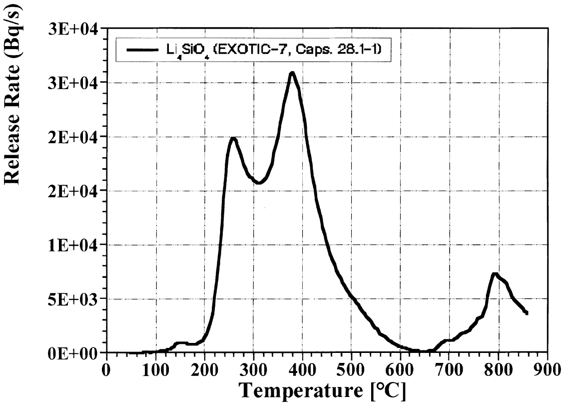

Fig. 5. Tritium release rate from lithium orthosilicate: capsule 28.1 (only Li_4SiO_4 pebbles).

heating at a rate of 5°C/min up to 850°C, and holding this temperature for several hours [7]. The release rate of Li_4SiO_4 pebbles from the pure Li_4SiO_4 bed of capsule 28.1-1 is characterised by a broad main peak at about 400°C, and a smaller peak at about 800°C. Totally, about 4×10^9 Bq/g are released. Broad peaks in the region 300–600°C were generally observed in all previous studies of specimens irradiated at low Li-burnup (~3%) [7]. The release rate of the Li_4SiO_4 pebbles from the mixed beds of capsule 28.2 and 26.2-1 shows again these two peaks, but most of the tritium is now released from the 800°C peak. Fig. 5 shows the results for capsule 28.1 [7].

Usually, along the Be/Li_4SiO_4 contact surfaces, a reaction zone (i.e., $BeO + Li_2Si + Li_2Be_2O_3$) has been observed, the growth rate of which can be described by a parabolic rate law. According to this law, the Li_4SiO_4 pebbles from capsule 26.2 and capsule 28.2 should show a reaction zone of about 7–10 μm at the Be/Li_4SiO_4 contact points. Qualitative and quantitative chemical analyses in μm range were recently performed on EXOTIC-7 metallographic sections [8]. The analyses showed that in case of direct contact of Be and Li_4SiO_4 during the irradiation, a two phase reaction layer of about 30 μm thickness has formed. The layer consists of BeO and probably of a Li–Be oxide of the composition $Li_2Be_2O_3$ on the Be rich side and of Li_2BeSiO_4 on the Li_4SiO_4 side. Furthermore, the Si content in the Li_4SiO_4 pebbles was higher than in the Li_4SiO_4 standard indicating a reasonable fraction of a Si richer phase, e.g., Li_2SiO_3, in these pebbles. The presence of the above cited reaction layer as well as the increased presence of Li_2SiO_3 in the pebbles from capsules 28.2 and 26.2-1 might justify the experimentally observed shift of tritium release from low to high temperature.

Due to the contact with beryllium during irradiation, the total tritium release from Li_4SiO_4 from both capsules 26.2-1 and 28.2 ($\sim 4 \times 10^{10}$ Bq/g) is about a factor of 10 higher than that from capsule 28.1-1. At the ECN Petten under the same conditions (He + 0.1% H_2, 5°C/min up to 860°C) essentially the same release kinetics as in the FZK tests has been observed for Li_4SiO_4 pebbles from capsules 28.1-1, 28.2 and 26.2-1 [6]. In addition, the total tritium release determined at ECN Petten for Li_4SiO_4 pebbles from all capsules agrees, within the experimental scatter (standard deviation for samples from the same capsule about 50%), with the FZK results. The very high scattering in the in-pile tritium release data made impossible for any reasonable interpretation of the EXOTIC-7 in-pile tritium release curves. Therefore, the residence time ($\tau =$ inventory/production rate) has been estimated on the basis of the out-of-pile tests performed at ECN Petten and FZK. The tritium residence time for Li_4SiO_4 pebbles from capsule 28.1 irradiated to 10% Li-burnup agrees quite well with the EXOTIC-6 data (irradiation of only lithium orthosilicate pebbles with Li-burnup ~3%). In spite of the observed shift in the release peaks from low to high temperature, the residence time for Li_4SiO_4 pebbles from capsule 26.2-1 irradiated to 14% Li-burnup agrees quite well with the EXOTIC-6 data. On the other hand, the tritium residence time for Li_4SiO_4 pebbles from capsule 28.2 (Li-burnup 18%) lies slightly above the EXOTIC-6 line and is about a factor of 1.7–3.8 higher than that for capsule 26.2-1. Based on these data it can be concluded that the tritium release from Li_4SiO_4 pebbles is not influenced by Li-burnup up to 13%. On the contrary, the contact of beryllium with ceramics during the irradiation seems to influence tritium release at higher Li-burnup by increasing the tritium residence time by about a factor of 3.

5. Summary and conclusions

PIEs of Li_4SiO_4 pebbles irradiated in the HFR reactor during the EXOTIC-7 experiment have been performed at both ECN Petten and FZK. The results of the optical microscopy showed for the specimen 28.1 (about 10% Li-burnup) an increase in smaller cracks in the kernel of the pebbles. After the irradiation very few pebbles were broken or deformed. In capsules 26.2 (14% Li-burnup) and 28.2 (18% Li-burnup) a higher degree of cracking occurred resulting in increased fragmentation. The crush load tests on the lithium orthosilicate pebbles from the three capsules showed practically no decrease of the mechanical stability. In agreement with previous studies it was found that from lithium orthosilicate, which was not in contact with beryllium during the irradiation (Li-burnup about 10%) tritium was mainly released at about 400°C. On the contrary, the lithium orthosilicate pebbles which were in contact with beryllium (Li-burnup 14% and 18%) release tritium mainly at about 800°C. It is not yet clear if this shift of the release peaks from low to high temperature is due to contact with beryllium or to the higher Li-burnup. The total release of tritium determined at ECN for Li_4SiO_4 pebbles from all capsules agrees, within the experimental scatter, with the FZK results. In spite of the observed shift in the release peaks from low to high temperature, the residence time for Li_4SiO_4 from capsule 26.2 irradiated to about 14% Li-burnup agrees quite well with the EXOTIC-6 results (~3% Li-burnup). Therefore, it can be concluded that the residence time is not influenced by Li-burnup up to 14%. On the contrary, the tritium residence time for pebbles irradiated up to 18% Li-burnup is slightly larger than for EXOTIC-6 pebbles. This increase might be caused by Li-burnup or a combination of Li-burnup and interaction with beryllium during irradiation.

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