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# Tritium release behavior of $Li_4SiO_4$ pebbles with high densities and large grain sizes

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## HIGHLIGHTS

- Tritium release behaviors of two batches of $Li_4SiO_4$ pebbles with different densities and grain sizes were compared.
- The temperature of tritium release from the M-OSi sample was much higher than that from the W-OSi sample.
- The fraction of tritium gas released from the M-OSi sample was much larger than that from the W-OSi sample.
- The difference in tritium release from the two batches of samples can be explained reasonably by the effect of grain sizes.
- This study can provide a guideline for optimizing the fabrication process of $Li_4SiO_4$ pebbles.

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## ABSTRACT

Tritium release behavior from the $Li_4SiO_4$ pebbles with high densities (~96%TD) and large grain sizes (100–300 μm) fabricated by a melt-based method (the M-OSi sample) was investigated through out-of-pile experiments. Another batch of $Li_4SiO_4$ pebbles with relatively low densities (~86%TD) and small grain sizes (10–50 μm) fabricated by a wet method (the W-OSi sample) was used for comparative study. Comparing with the W-OSi sample, the temperature of tritium release from the M-OSi sample was found much higher. Moreover, the fraction of tritium gas released from the M-OSi sample was much larger, especially under helium purge gas. The big differences between the characteristics of tritium release from the two batches of samples can be explained reasonably by the effect of grain size, implying that the grain size played an important role in the tritium release behavior. This study can provide a guideline for optimizing the fabrication process of $Li_4SiO_4$ pebbles.



## 1. Introduction

Lithium orthosilicate ($Li_4SiO_4$) and lithium metatitanate ($Li_2TiO_3$), in the form of ceramic pebbles, have been considered as the most promising tritium breeder materials for solid breeding blankets of fusion reactors [1]. Specifically, $Li_4SiO_4$ is the preferred breeder material for Chinese HCCB-TBM to be tested in ITER [2].

For fabrication of ceramic breeder pebbles, a wet method including freeze, drying and sintering processes has been developed by CAEP since 2004 [3,4]. The wet method was considered to be clean, economical and easy for mass production. The $Li_4SiO_4$ pebbles fabricated by the wet method showed good properties, such as small pebble diameter, good sphericity, high crush load, porous structure, small grain size and good tritium release performance [4,5].

However, the densities of the $Li_4SiO_4$ pebbles fabricated by the wet method, with a typical value in the range of 75–85%TD (TD: theoretical density), are considered to be relatively low. According to the present design of Chinese HCCB-TBM, the density of $Li_4SiO_4$ pebbles is required to be higher than 91%TD. To fulfill the design requirement of Chinese HCCB-TBM, a melt-based method, which is similar to the well-known melt-spraying method developed by the Karlsruhe Institute of Technology (KIT) and Schott AG (Mainz, Germany) [6], for fabrication of high-density $Li_4SiO_4$ pebbles, was

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initiated in 2014. Through this new fabrication method, the first batch of $Li_4SiO_4$ pebbles with a density of ~95%TD was obtained. Moreover, this batch of $Li_4SiO_4$ pebbles were found to have large grain sizes, typically in the range of 100–300 μm.

It is commonly known that the grain size is an important parameter for the tritium release behavior of ceramic breeder materials. Generally speaking, the breeder pebbles with small grain sizes (e.g. < 5 μm) are more desired in consideration of fast tritium release [7]. This point of view is mainly based on that the smaller the grain size, the shorter the tritium migration path will be in the breeder grain. However, it should be noted that the rate-controlling step of tritium release can be either bulk diffusion process or surface desorption process. In previous studies [8,9], tritium diffusion in the grains of $Li_4SiO_4$ was found to be very fast, and the surface reactions dominated the overall tritium release behavior.

It has been reported that the grain size of $Li_4SiO_4$ pebbles increased from 10–15 to 20–40 μm after neutron irradiation to high burn-up [10]. Consequently, the effect of grain growth on tritium release behavior should be evaluated properly. In addition, according to the prediction by Hanada et al. [11], the optimum grain size for $Li_4SiO_4$ was about 100 μm from the viewpoint of reducing total tritium inventory in the breeder materials. So far, the $Li_4SiO_4$ samples used in tritium release studies have relatively small grain sizes, mostly in the range of 1–50 μm [5,8–10,12–21]. Thus it is interesting to know what will the tritium release behavior of $Li_4SiO_4$ pebbles be like if the grain sizes are much larger, e.g. > 100 μm.

In this work, we performed out-of-pile tritium release experiments to investigate the behavior of tritium release from $Li_4SiO_4$ pebbles with high densities and large grain sizes that were fabricated by a melt-based method. For comparative study, tritium release experiments were also performed on $Li_4SiO_4$ pebbles with relatively low densities and small grain sizes that were fabricated by the wet method. The effect of grain size on tritium release behavior of $Li_4SiO_4$ pebbles will be discussed.

## 2. Experimental

### 2.1. Experimental samples

In this work, two batches of $Li_4SiO_4$ pebbles were used as the experimental samples for comparative study. In the following paragraphs, the $Li_4SiO_4$ pebbles fabricated by melt-based method and wet method will be denoted as “M-OSi” and “W-OSi”, respectively.

The melt-based method applied for fabrication of the M-OSi sample in this work included three main steps. Firstly, $Li_4SiO_4$ powder was prepared by solid-state reaction using lithium hydroxide monohydrate ($LiOH \cdot H_2O$) and silica ($SiO_2$) as raw materials. Secondly, the $Li_4SiO_4$ powder was heated to the melting point in a platinum crucible, and the molten $Li_4SiO_4$ was dropped into liquid nitrogen through a nozzle. At the outlet of the nozzle, a helium gas flow was continuously supplied to control the droplet size of the molten $Li_4SiO_4$. Finally, the green pebbles of $Li_4SiO_4$ collected in liquid nitrogen were dried in air and then annealed at 1000 °C for 5 h in air atmosphere to eliminate the internal stresses and surface impurities.

The wet method applied for fabrication of the W-OSi sample has been described in detail by Gao et al. [4]. However, instead of lithium carbonate ($Li_2CO_3$), lithium hydroxide monohydrate ($LiOH \cdot H_2O$) was used as the raw material for preparing $Li_4SiO_4$ powder precursor in the present study.

Table 1 shows the main characteristics of the experimental samples. The cross sections of the experimental samples were observed by scanning electron microscopy (SEM). The SEM photographs for the microstructures of the M-OSi and W-OSi samples are shown in Figs. 1 and 2, respectively.

### 2.2. Neutron irradiation

Before neutron irradiation, the samples were first heated at 850 °C for 2 h under helium atmosphere to remove the surface adsorbed water and other impurities. Then the samples were sealed in quartz capsules filled with ~90 kPa helium gas. The amount of samples in each quartz capsule was ~50 mg. Neutron irradiation of the quartz-encapsulated samples was finished at the China Mianyang Research Reactor (CMRR) in the Institute of Nuclear Physics and Chemistry (INPC), CAEP. The reference thermal neutron flux was $1.57 \times 10^{13}$ n/(cm$^2$ s), and the irradiation time was 72.5 h. The temperature of the samples during neutron irradiation was estimated to be lower than 100 °C.

### 2.3. Tritium release experiments

Tritium release experiments were carried out in the Tritium Recovery System (TRS) located at INPC. Fig. 3 shows the flow diagram of the experimental setup. The collecting pipes in the TRS were not heated during the experiments. Therefore, adsorption of tritium species (e.g. HTO) on the pipes was possible to occur. However, the adsorption effect was considered to be not significant due to small pipe diameter (1/8 inches). The irradiated samples were transferred to the sample holder where the quartz capsules were broken online without exposing to air. The samples were heated from room temperature (RT) to 900–950 °C at a heating rate of 5 °C/min. The temperature was kept at 900–950 °C for 1–2 h before shutting down the furnace. The tritium species (HT, $T_2$, HTO and $T_2O$) released from the samples were purged out from the sample holder by He or He+0.1%$H_2$ gas with a flow rate of 100 mL/min. The purge gas was dried by a molecular sieve bed (MS5A) before entering the sample holder. In the downstream of the sample holder, the purge gas containing tritium species first passed through an ionization chamber (I.C.1, 50 mL), where the concentration of total tritium in the purge gas was measured. The lag-time of tritium species from the outlet of furnace to the inlet of I.C.1 was negligible, and the residence time of tritium species in the IC was about 30 s. Then the purge gas passed through a group of glycol bubblers, where the tritium species in the form of tritiated water (HTO/$T_2O$) was trapped. Afterwards, the purge gas containing tritium gas (HT/$T_2$) only passed through another ionization chamber (I.C.2, 50 mL), where the concentration of tritium gas in the purge gas was measured. The time-lag between I.C.1 and I.C.2 was estimated to be about 25 s. Then the purge gas passed through a cooper oxide bed maintained at 400 °C, where the tritium gas in the purge gas was converted into tritiated water. Finally, the purge gas passed through another group of glycol bubblers, where the tritiated water converted from tritium gas was trapped. The tritium collected in the glycol bubblers was measured by the conventional liquid scintillation counting (LSC) method.

## 3. Results and discussion

### 3.1. Tritium release behavior under purge gas of He

Tritium release experiments were first conducted using He as purge gas. The behaviors of tritium release from the M-OSi and W-OSi samples are shown in Figs. 4 and 5, respectively. As can be seen from Figs. 4 and 5, the tritium release curves for the two batches of samples show very different characteristics.

For the M-OSi sample, the majority of tritium was released in the form of tritium gas. According to the LSC measurements, the