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Tritium release experiments on Li_4SiO_4 pebbles from TRINPC-I experiments: Effects of water adsorption and hydrogen gas

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ABSTRACT

Out-of-pile tritium release experiments under different water uptake contents and purge gas chemistry were performed on Li_4SiO_4. Water measurement was performed on samples under different experimental procedures. It was found that water was adsorbed on the sample during its transferring and storage process. A strong dependence of tritium release behavior on water uptake was determined. By doping H_2 in the sweep gas, the formation of water in orthosilicate was observed in addition to the isotope exchange reaction with H_2 gas. Thermal desorption peaks of the water formation reaction and H_2 isotope exchange reaction appeared at 668 °C and 463 °C, respectively, at ramping rate of 5 °C/min.

1. Introduction

Knowledge of the Li-ceramics tritium release behavior is needed for designing fusion reactor blankets based on solid-state breeding materials. Among the various Li-ceramics, Li_4SiO_4 (lithium orthosilicate) is one of the main candidates for tritium breeding material in the Helium Cooled Pebble Bed Blanket (HCPBB) and is selected as solid ceramic breeder material for Chinese He-cooled Solid Breeder (CH HC-SB TBM). There have been several researches focused on the release of tritium from lithium orthosilicate [1–10]. In these experiments, effects of the composition of sweep gas, material microstructure, irradiation defects and neutron fluence on the tritium release behavior were studied. It is found that different experimental results exist in these references. Among them, differences in tritium release chemical form and temperature are notable, which is crucial to tritium containment and processing.

According to previous studies [11,12], Li_4SiO_4 is a material with large water adsorption capability. Thus, it is reasonable to assume that, among other factors, water uptake may be one of reasons for different results in those experiments mentioned above. To examine this belief, the influence of water content on tritium release behavior from orthosilicate is studied in this work, which is rarely involved in other investigations. In addition, effects of sweep gas chemistry on tritium release behavior from wet orthosilicate are also investigated and the H_2 isotope exchange temperature and water formation temperature with H_2 gas are determined, which would deepen understanding of tritium behavior and be valuable to establish tritium release physical model and produce related data for engineering and design activities.

2. Experimental

Li_4SiO_4 powders were prepared by the reaction of lithium carbonate and silica, then kilogram scale Li_4SiO_4 pebbles were made by a freeze-drying method [13]. These pebbles were subsequently sintered over 1000 °C for several hours and then sealed in a dried container. Before packaging Li_4SiO_4 pebbles in a quartz capsule for irradiation, the samples were annealed again at about 200 °C for 2 h in vacuum by flushing with helium gas for several times to remove potential water adsorption during the transfer process. Then the samples were sealed up in quartz capsules under He gas atmosphere. Characteristics of the pebbles are summarized in Table 1. Impurities were measured before irradiation and the cation impurity levels <0.2 wt% that were determined by emission spectroscopy and activation analysis.

Irradiation conditions of the encapsulated Li_4SiO_4 pebbles were same to TRINPC-I (Tritium Release experiments in the Institute of Nuclear Physics and Chemistry), more experimental details had already been given previously [10]. After irradiation, out-of-pile tritium release experiments were performed under different water uptake on the sample and sweep gas conditions (pure He and

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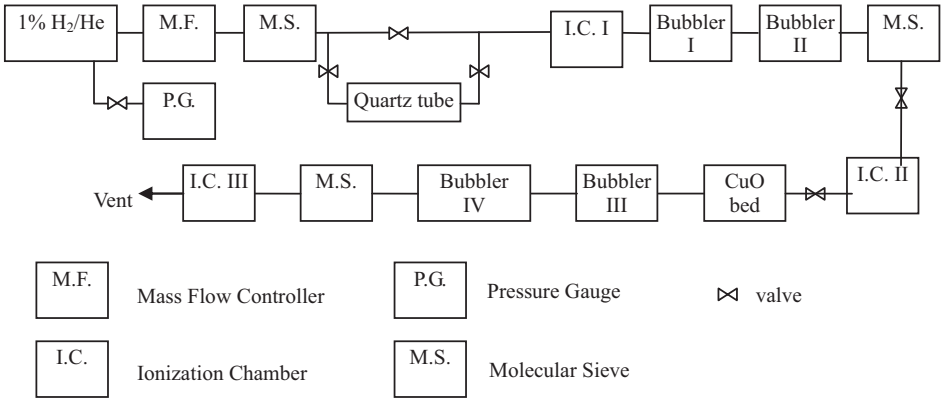

Fig. 1. Flow chart of out-of-pile tritium release experiments on Li_4SiO_4 pebbles.

He + 1% H_2). The purity of the sweep gas is higher than 99.999%, which means the residual water vapor would be lower than 0.001%, especially after the sweep gas passing through the MS5A adsorbent before reaching the samples. Gas flow rate was 50 ml/min and was controlled with conventional mass flow controllers. A flow chart of the experimental system is shown in Fig. 1. Ionization Chamber I (I.C. I) was used to measure the concentration of total tritium while Ionization Chamber II (I.C. II) measured the concentration of tritium gas. Accumulated amount of tritiated water in glycol bubblers was measured by a liquid scintillation counter. During Temperature Programmed Desorption (TPD) experiments, the quartz tube was heated at a constant rate from room temperature to 800 °C. Temperature of the quartz tube was controlled by a conventional electric furnace and a thermocouple was placed outside the quartz tube without contacting directly with pebble samples.

Table 1
Characteristics of batch B Li_4SiO_4 pebbles.

Characteristics	Li_4SiO_4 pebbles (batch B)
Density	80% TD[a]
Diameter	0.5–1.0 mm
Sphericity	≤1.02 (a.v.)[b]
Li enrichment	4.93%
Grain size	3.5 μm (a.v.)
Crush load[c]	15 N (a.v.)

[a] "TD" means theoretical density.
[b] "a.v." means average.
[c] The crush load of Li_4SiO_4 pebbles was measured using an MTS RT/5 Universal material Testing Machine. Maximum test force was 125 N and testing speed was 0.5 mm/min.

Since it is hard to measure directly water content on the sample during TPD experiment, water uptake was measured on Li_4SiO_4 pebbles that were treated at similar conditions to those irradiated samples by a modified 831KF Coulometer. A stainless steel (SS) cell (8 mm diameter) containing the sample was connected to the 831KF Coulometer. A copper mesh was used to fix the sample in the SS cell.

3. Results and discussion

3.1. Influence of water content on tritium release behavior

Three environmental moisture conditions were investigated. In case 1, the sample capsule was broken directly in a sealed quartz tube connecting to the TPD facility. Effects of environmental moisture on tritium release behavior could be neglected in this case, which was the case of sample A_3 in our previous experiment [10]. In case 2, the sample was transferred immediately to the quartz tube after the capsule was broken in a glove box. In this case, effects of adsorbed water during transfer process on tritium release behavior could be observed, samples B9-1 was operated in this way; In case 3, the sample was transferred and stored in a container after the capsule was broken in a glove box, thus, both of transfer and storage effects could be analyzed, our remaining samples used in this paper were handled as such. Table 2 shows treatment conditions of those irradiated samples.

Moisture measurement experiments were performed on parallel Li_4SiO_4 which were treated at similar conditions to those irradiated samples. Results show that the water contents are 87, 209 and 289 μg per gram sample (annealing at 200 °C for 4 h) respectively for the samples treated in similar conditions to those of cases 1–3 (35 days in a container dried by desiccant) mentioned

Table 2
Sample handling conditions and fraction of released tritium gas.

Samples	Weight (g)	Sweep gas	Storage time in a dried container	Storage time in a wet container[b]	Transferred in the glove box[c]	Ratio of tritium gas to total released tritium[d]
A_3	0.150	He + 1%H_2	–[a]	–	–	72%[e]
B9-1	0.041	He + 1%H_2	–	–	Yes	25%
B9-8	0.018	He + 1%H_2	12 months	–	Yes	7.5%
B9-9	0.014	He	12 months	–	Yes	~0
B9-6	0.023	He	12 months	2 days	Yes	~0
B9-4	0.021	He	12 months	10 days	Yes	~0

[a] "–" means no related action happened.
[b] Not dried by desiccating agent.
[c] Moisture content is about 0.2–1.0 μg/ml in the 15–20 L glove box.
[d] Tritium released at room temperature is excluded from calculating the ratio of tritium gas. This is because part of this tritium may lose during transfer and storage process and thus variable.
[e] The ratio is calculated through dividing total released tritium by tritium gas. Total tritium is calculated by making sum of tritium gas and tritiated water collected in the four glycol bubblers. Amount of tritium in the glycol bubblers are measured by a liquid scintillation counter.