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Tritium release from lithium orthosilicate pebbles deposited with palladium

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A B S T R A C T

Slightly overstoichiometric lithium orthosilicate pebbles are fabricated from lithium hydroxide and silica by a melting and spraying method in a semi-industrial scale facility. The authors performed out-of-pile annealing tests using the lithium orthosilicate pebbles irradiated in a research reactor. Moreover, the effect of the deposition of palladium in the lithium orthosilicate pebbles on the behavior of tritium release was investigated. The lithium orthosilicate pebbles were irradiated in a research reactor. In the out-of-pile annealing experiments, the temperature of lithium orthosilicate pebbles was raised from ambient temperature to 1173 K at a constant rate of 5 K/min under the stream of 0.1% hydrogen/nitrogen sweep gas. The experimental results indicate that almost all tritium was released as tritiated water vapor from the virgin lithium orthosilicate pebbles. It was also found that a lager amount of tritium was released as the molecular form (HT) from the lithium orthosilicate pebbles deposited with palladium.

1. Introduction

Slightly overstoichiometric lithium orthosilicate pebbles have been selected as one optional breeder material for the European Helium Cooled Pebble Bed blanket. The lithium orthosilicate pebbles are fabricated by a melting and spraying method in a semi-industrial scale facility [1,2]. Previously, the non-enriched pebbles were produced from a mixture of lithium orthosilicate and silica powders, whereas enriched lithium orthosilicate is not available on the market. Thus, highly enriched lithium carbonate powder was used for the production of the lithium orthosilicate pebbles, which resulted in unsatisfactory pebble characteristics as a solid breeder material. Enriched lithium hydroxide is commercially available as well, and thus a new production route of lithium orthosilicate pebbles with lithium hydroxide was pursued. As a result, the melting process was found to be applicable to the production of lithium orthosilicate pebbles from lithium hydroxide and silica. The lithium orthosilicate pebbles produced by the process contains one metastable high-temperature phase such as $Li_6Si_2O_7$, but it was also found that the oxide phases can be decomposed by annealing at high temperatures. The lithium orthosilicate pebbles produced in this new process possesses satisfactory pebble characteristics as a solid breeder material. Therefore, the authors performed out-of-pile annealing tests using the lithium orthosilicate pebble irradiated in a thermal reactor.

In most current designs of D–T fusion reactor blankets with ceramic breeder materials, tritium bred in breeders such as Li_2O, Li_4SiO_4, $LiAlO_2$, Li_2ZrO_3 and Li_2TiO_3 is to be extracted using helium sweep gases containing 0.1% of hydrogen. Hydrogen is added to the sweep gas to enhance the isotope exchange reaction on the surface of the breeder materials and to promote the tritium release as the chemical form of HT. However, the exchange reaction is considered to be slow even at higher temperatures. Thus, in this study, the authors investigated the effect of the deposition of palladium as a catalyst in the lithium orthosilicate pebble. Palladium was deposited in the lithium orthosilicate pebble by the incipient wet impregnation method. The lithium orthosilicate pebbles deposited with palladium were also irradiated in the thermal reactor, and out-of-pile tritium release experiments were performed.

2. Deposition of palladium in lithium silicate

Palladium was deposited in the Li_4SiO_4 pebbles by the incipient wet impregnation method that is generally used for the fabrication of catalysts. For this purpose, Li_4SiO_4 pebbles placed in a flask were first dried under air at 150 °C for 24 h. Then a solution of palladium tetra ammonium nitrate $Pd(NH_3)_4(NO_3)_2$ was pored dropwise onto the previously dried Li_4SiO_4 pebbles. After this treatment the wet Li_4SiO_4 pellets were dried in an oven first at 90 °C for 3 h and then at 150 °C for another 24 h. The obtained precursor was calcined in

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a quartz tube reactor under a He atmosphere containing 10% O_2 by raising the temperature stepwise up to 400 °C. Following the calcination, the noble metal impregnated ceramic breeder pebbles were reduced under a hydrogen atmosphere at 400 °C for several hours. The color of Li_4SiO_4 impregnated with palladium was found to be dark grey, indicating that palladium was successfully deposited on the pebbles.

3. Experimental

The lithium orthosilicate pebbles were irradiated in the Kyoto University Research Reactor. The breeder pebbles were first dried under a dry helium stream for 12 h by raising the temperature stepwise up to 500 °C. Then, the dried breeder pebbles were encapsulated in the quartz tubes with a small pressure of helium gas. The encapsulated lithium orthosilicate sample prepared in this way was irradiated in the thermal reactor with a neutron flux of $2.75 \times 10^{13}\,cm^{-2}\,s^{-1}$. The irradiation time of the breeders was 6 or 12 min. After irradiation, the quartz capsules were mechanically broken, and the breeder materials were removed and placed in a reactor tube made of quartz for the out-of-pile experiments. All these procedures were carried out in a glove box filled with dry argon gas (the dew point was lower than −90 °C), and thus the breeder materials were never exposed to the atmosphere before and during experiments.

The experimental flow diagram is shown in Fig. 1. The temperature of the reactor (containing breeder materials of 0.3 g) was controlled with a conventional electric furnace. Nitrogen gases containing 0.1% of hydrogen was used as the sweep gas, and the gas flow rate was controlled with conventional mass flow controllers. The gases employed were purified with a trap containing 5A molecular sieve to remove residual water vapor. The sweep gas containing water vapor was generated by introducing H_2/N_2 gases to a copper oxide bed maintained at 300 °C. In the out-of-pile experiments, the concentrations of tritium in the outlet streams of the reactor charged with the lithium orthosilicate pebbles were traced with two ionization chambers for the separative measurement of different chemical forms of tritium. The total tritium concentration (molecular form of tritium and tritiated water vapor) in the outlet stream of the reactor was measured with the first ionization chamber as shown in Fig. 1. Then the gas was introduced to a water bubbler, which removes tritiated water vapor from the process gas. After this procedure, the gas was again introduced to the second ionization chamber, which makes it possible to measure the concentration of only molecular form of tritium. In the out-of-pile annealing experiments, the reactor temperature was kept at ambient temperature before the sweep gas was introduced to the reactor. The sweep gas was introduced to the reactor with the flow rate of 100 ml/min. Even after the sweep gas began to flow into the reactor bed, the temperature of the breeder bed was kept at ambient temperature for several 10 min. Then, the reactor temperature was raised at the constant rate of 5 °C/min up to 900 °C. After the bed temperature reached 900 °C, the reactor temperature was held at 900 °C for several 10 min. The sweep gas was finally mixed with 1% H_2O/N_2 gas and introduced to the reactor with the flow rate of 200 ml/min to ensure the release of all the tritium bred in the breeder.

4. Results and discussion

Fig. 2 shows the result of out-of-pile annealing tests with Li_4SiO_4 irradiated for 6 min in the thermal reactor and with the 0.1% H_2/N_2 sweep gas. In this figure, the change in the total tritium concentration (denoted as HT + HTO and shown as a black line) in the outlet stream of the reactor and the change in the concentration of molecular form of tritium (denoted as HT and shown as a grey line) are shown. The dotted line shows the change in the reactor temperature. As seen in this figure, even at ambient temperature a small amount of tritium was released, which could be tritium that diffused to the grain surface of Li_4SiO_4 during irradiation, since the temperature of Li_4SiO_4 rose by irradiation in the thermal reactor. The main tritium release started at approximately 200 °C. The release curve appears to have two major peaks at the temperatures of 350 and 450 °C. At higher temperatures tritium was gradually released with increasing temperature. The change in the concentration of molecular form of tritium in Fig. 2 indicates that almost no molecular form of tritium was released. Thus, it can be said almost all the tritium bred in the Li_4SiO_4 pebble was released as tritiated water vapor though the 0.1% H_2/N_2 sweep gas was used. This result suggests that the isotope exchange reaction on the Li_4SiO_4 sample surface is quite slow. Even after the reactor temperature reached 900 °C, the tritium was continuously released. When the sweep gas was replaced by a (0.05% H_2 + 0.5% H_2O)/N_2 mixture gas, tritium release was once enhanced and the tritium release still continued for 3 h.

The same experiments was also carried out for the Li_4SiO_4 sample irradiated for 12 min. Fig. 3 shows the result of out-of-pile annealing tests with Li_4SiO_4 irradiated for 12 min in the thermal reactor and a 0.1% H_2/N_2 sweep gas. This experiment was performed to examine the effect of irradiation time to the tritium

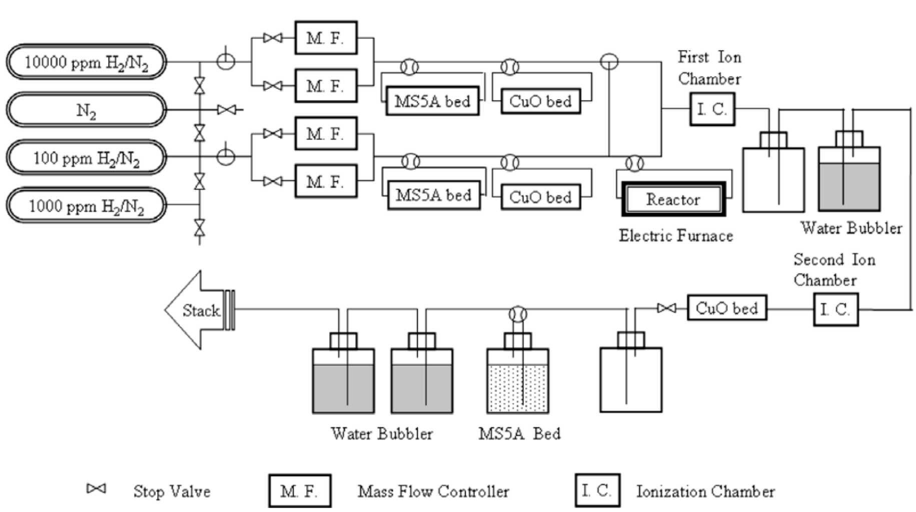

Fig. 1. Flow diagram of experimental apparatus.

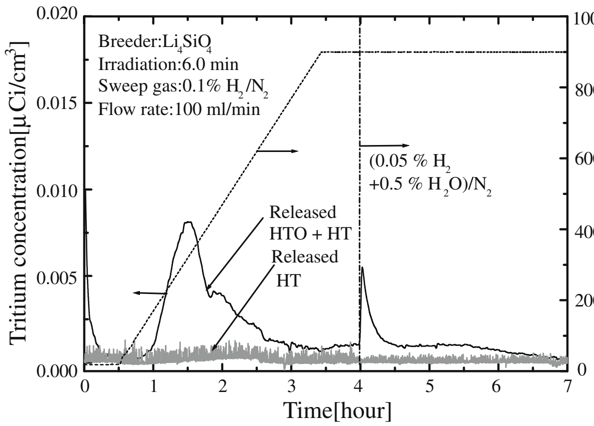

Fig. 2. Out-of-pile annealing experiment of Li_4SiO_4 irradiated for 6 min.

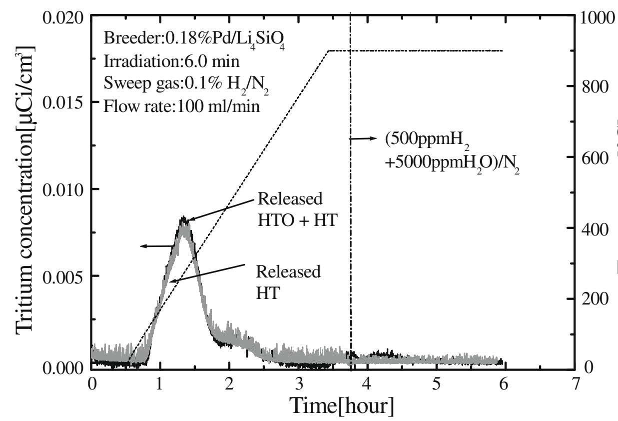

Fig. 4. Out-of-pile annealing experiment of 0.18% Pd/Li_4SiO_4 irradiated for 6 min.

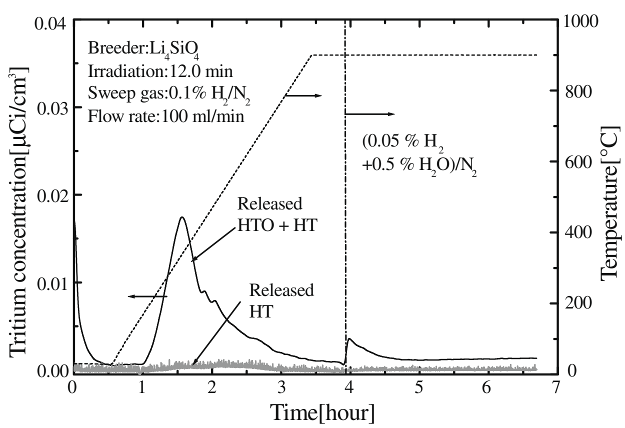

Fig. 3. Out-of-pile annealing experiment of Li_4SiO_4 irradiated for 12 min.

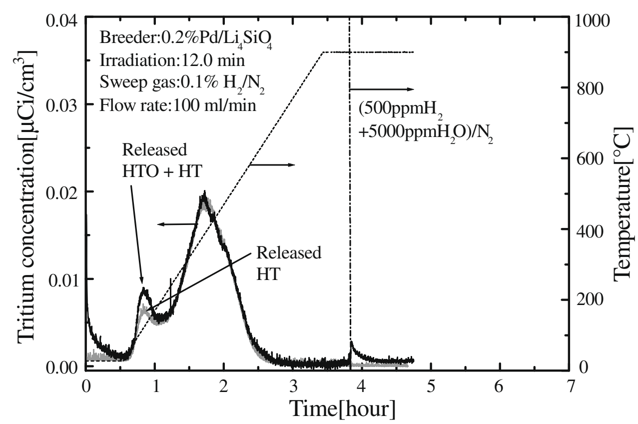

Fig. 5. Out-of-pile annealing experiment of 0.2% Pd/Li_4SiO_4 irradiated for 12 min.

release behavior. The release curves shown in Fig. 3 are similar to those shown in Fig. 2. Also in this case, almost no molecular form of tritium was released, and almost all the tritium bred in the Li_4SiO_4 pebble was released as tritiated water vapor. When the sweep gas was replaced by a (0.05% H_2 + 0.5% H_2O)/N_2 mixture gas, tritium release was once enhanced and the slow tritium release continued. The results shown Figs. 2 and 3 indicate that the addition of hydrogen to the sweep gas has little effect on the enhancement of tritium release. In our previous work, tritium release experiments on Li_4SiO_4 pebbles fabricated by an old different process were studied with a 0.1% H_2/N_2 sweep gas by the same experimental method described in this paper [3–5]. In terms of the Li_4SiO_4 pebbles prepared by the old process, the tritium release started at 300 °C and the release curve has two major peaks at the temperatures of 400 and 700 °C. The amount of tritium released at higher temperatures was considerably larger for that Li_4SiO_4 pebbles. Thus, comparison with this previous result suggests that tritium release performance was improved for the Li_4SiO_4 pebbles fabricated by the new process; more amounts of tritium were released at lower temperatures from the Li_4SiO_4 pebbles. One reason for this is probably the smaller grain size of the pebbles fabricated by the new process.

Next, the effect of deposition of palladium on the release behavior of tritium was investigated. Fig. 4 shows the result of out-of-pile annealing tests with the Li_4SiO_4 pebble deposited with 0.18 wt.% of Pd. The Li_4SiO_4 pebble was irradiated for 6 min in the thermal reactor and the experiment was also carried out using the 0.1% H_2/N_2 sweep gas. As shown in the figure, the main tritium release started at approximately 100 °C. The release curve appears to have one major peak at the temperatures of 250 °C. These results suggest that the tritium was released at lower temperatures in comparison with the case of Li_4SiO_4 with no catalyst (see Fig. 2). At higher temperatures tritium was gradually released with increasing temperature and tritium release finished at 600 °C. Comparison of the change in the concentration of molecular form of tritium (denoted as HT and shown as a grey line) with that of the total tritium concentration (denoted as HT + HTO and shown as a black line) in Fig. 4 indicates that almost all the tritium was released as the molecular form such as HT, which is one of the major differences compared with the case of the virgin Li_4SiO_4 pebble (see Fig. 2). This result suggests that the isotope exchange reaction on the surface of the Li_4SiO_4 pebble was substantially promoted and the release rate of tritium as the molecular form was enhanced by the deposition of palladium. When the sweep gas was replaced by a (0.05% H_2 + 0.5% H_2O)/N_2 mixture gas at the temperature of 900 °C, almost no tritium was released, whereas the slow tritium release continued in the case of the virgin Li_4SiO_4 pebble irradiated for 6 min.

The effect of irradiation time on the tritium release behavior was also examined with regard to the Li_4SiO_4 pebble deposited with palladium. Fig. 5 shows the result of out-of-pile annealing tests with the Li_4SiO_4 pebble deposited with 0.2% wt.% of Pd that was irradiated for 12 min in the thermal reactor. In this case, the main tritium release started just after the reactor temperature was raised. The release curve appears to have two major peaks at the temperatures of 100 and 350 °C. The main tritium release finished at the temperature of 600 °C. Comparison of the change in the concentration of molecular form of tritium with that of the

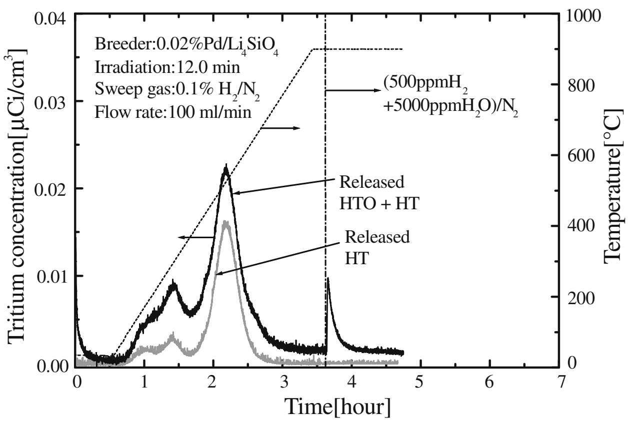

Fig. 6. Out-of-pile annealing experiment of 0.02% Pd/Li_4SiO_4 irradiated for 12 min.

total tritium concentration shown in Fig. 5 indicates that almost all the tritium was released as the molecular form such as HT. When the sweep gas was replaced by a (0.05% H_2 + 0.5% H_2O)/N_2 mixture gas at the temperature of 900 °C, a very small amount of tritium was released. In the case of the virgin Li_4SiO_4 pebble irradiated for 12 min (see Fig. 3), the slow tritium release continued for more than 2.5 h.

Fig. 6 shows the result of out-of-pile annealing test with the Li_4SiO_4 pebble deposited with 0.02% wt.% of Pd that was irradiated for 12 min in the thermal reactor. In this case, the amount of Pd deposited in the Li_4SiO_4 pebble was decreased. The main tritium release started at approximately 100 °C. The release curve has two major peaks at the temperatures of 300 and 500 °C. Comparison with the result shown in Fig. 5 indicates that the deposition of a smaller amount of Pd decreases the effect of the catalyst. As seen in Fig. 6, the fraction of tritium released as the molecular form was decreased, though a considerable amount of tritium was still released as the molecular form. The slow tritium release in the form of tritiated water vapor continued at higher temperatures; the slow tritium release continued even after the 0.1% H_2/N_2 sweep gas was replaced with the wet sweep gas.

The results shown above indicate that the deposition of catalyst like palladium in the Li_4SiO_4 pebble is effective to extract bred tritium as the molecular form at lower temperatures. However, the amount of palladium deposited appears to affect the promotion effect on the tritium release by catalytic metals. The authors are now in the process of investigating the effect of other catalyst metals such as platinum or nickel.

5. Conclusions

Slightly overstoichiometric lithium orthosilicate pebbles were fabricated from lithium hydroxide and silica by a melting and spraying method in a semi-industrial scale facility. Out-of-pile annealing tests were performed using the lithium orthosilicate pebbles irradiated in a research reactor. Moreover, the effect of the deposition of palladium in the lithium orthosilicate pebbles on the behavior of tritium release was investigated. Palladium was deposited in the lithium orthosilicate pebbles by the incipient wet impregnation method. The lithium orthosilicate pebbles were submitted to neutron irradiation in the Kyoto university research reactor. In the experiments, a 0.1% hydrogen/nitrogen sweep gas was used. The experimental results indicate that almost all tritium was released as tritiated water vapor from the virgin lithium orthosilicate pebbles and the slow tritium release takes place even at higher temperatures. In contrast, it was also found that a considerably larger amount of tritium was released as the molecular form (HT) from the lithium orthosilicate pebbles deposited with palladium at lower temperatures. Therefore, it can be said that the deposition of catalytic metal in the lithium orthosilicate pebble is effective to improve the tritium release from the breeder material.

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