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Tritium release kinetics from Li_2TiO_3 pebbles as prepared by soft-wet-chemistry

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Abstract

Lithium meta titanate pebbles has been prepared from agglomeration-sintering powders which were obtained by Li-Ti-peroxo-complex solution precursor (Li_2TiO_3 dissolved at room temperature in $H_2O + 40\%$ H_2O_2 and stabilized with citric acid). Through this wet route Li_2TiO_3 pebbles with high density(~92% of T.D.) has been obtained and the tritium release behavior has been tested 'in-pile' by the EXOTIC-8.9 experiment (~440 days of irradiation at full power in the high neutron flux of HFR-Petten). Tritium residence times (τ) in the pebbles has been measured during irradiation between 550 and 400 °C and $He + 0.1\%H_2$ purge gas composition. By a thermally activated process (activation energy = 111 kJ/mol) with 410 °C as minimum temperature the tritium residence time is found to be about 1 day, which places this specimen in a good ranking position among those tested by the EXOTIC-series. A clear increase of the tritium release rate has been observed by increased H_2 concentration (up to 1%) in the He purge. Out-of-pile ramp-annealing tritium desorption (TPD) tests on short-time irradiated pebbles has been also performed by various devices and conditions. The kinetic parameters from the TPD investigation gave consistent results with those characterizing the equilibrium times of tritium release rate after the gas composition and temperature transients imposed on the specimen during the in-pile experiment.
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1. Introduction

Lithium meta-titanate is a candidate for the European 'Helium Cooled Pebble Bed' (HCPB) Blanket design for a DEMO Fusion Reactor (long-term program) [1] in form of dense (>90% of T.D) ceramic pebbles with diameter ranging from 0.3 to 1.2 mm. These properties were met for Li_2TiO_3 pebbles as prepared by an original route described in Ref. [2] and in this work we report their testing in the EXOTIC-8.9 experiment in which their tritium release rate could be measured 'in-pile' into the $He + 0.1\%$ H_2 purge gas (R-gas) during irradiation.

Hence these pebbles were tested and qualified within the frame of the EXOTIC-series designed for the HCPBB program. The aim of this paper is to report and discuss the results with the objective of improving the data base supporting the lithium titanate pebble bed as breeder system.

Moreover, since tritium release rate from this kind of pebbles (as briefly irradiated) also has been measured in several out-of-pile ramp-annealing desorption (TPD) tests, an evaluation of these TPD spectra has been made to relate the results to those obtained in-pile [4]. Our objective is to get complementary information on the tritium removal mechanism from Li_2TiO_3 ceramics.

2. Li_2TiO_3 pebbles characteristics

A batch of Li_2TiO_3 pebbles (ENEA code FN5) has been prepared following the 'citrate' route among those described in Ref. [2]. A very soft microcrystalline Li_2TiO_3 powder (reaction completed at 650 °C, well below the normal solid state temperature reaction

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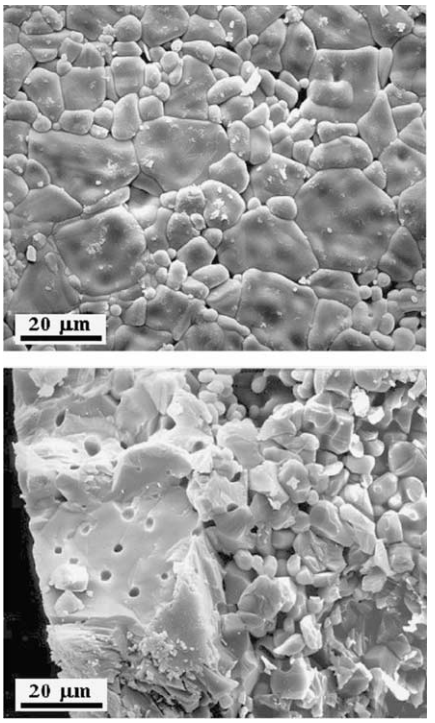

Fig. 1. SEM Images of the FN5 pebble surface (top) and of fractured section near the surface.

between TiO_2 and lithium salts) has been obtained and green pebbles have been formed (by tumbling the powder together with an organic binder solution in a planetary mill without grinding media) and have been sintered (1100 °C×2 h) up to a density of about 92% of TD. The pebbles size distribution is as follows: 16% in the size range 0.2–0.4 mm, 40% between 0.4 and 0.6 mm and 44% between 0.6 and 1 mm. The bed density is 1.91 g cm^{-3} and, assuming a packing factor of 60%, the density results 92.8 % of TD. The crystal density characterizing this compound (3.43 g cm^{-3}) is consistent with the density measured by helium pichnometry (3.37 ± 0.01 g cm^{-3}) with a closed porosity of 1.7 ± 0.2% and an open porosity of 5.5%. The grain size ranges between 3 and 20 μm as observed by SEM analysis (Fig. 1). The pebbles are covered by a compact surface layer (about 60 μm thick, see SEM images of Fig. 1). Monoclinic lithium metatitanate is the only phase detected by XRD analysis. Neutron Activation Analysis (NAA) has showed the presence of about 0.1% of total impurities in the irradiated pebbles, mainly Na, K, Al and Zr.

3. In-pile tritium release test: EXOTIC 8.9 experiment

EXOTIC-8.9 objectives, lay-out, capsule design and results after the first 100 days of this irradiation test has been reported in Ref. [3]. The vented capsule containing about 60 g of FN5 pebbles has been irradiated in HFR by 18 reactor cycles (about 440 days at full power). The average temperature of the specimen has been step-varied within the range 550–400 °C, the purge gas flow rate was 100 cm^3/min and its composition was mainly He + 0.1% H_2 gas (the'reference' gas, R). Some 'chemical' transients also have been performed by changing the purge gas composition from pure He to He + 1% H_2 under isothermal conditions. The steady-state tritium generation rate (G) was nearly constant during each cycle (~600 h) but fluctuated about a value of 21 mCi/h from cycle to cycle; the total generated tritium amount is about 200 Ci (Fig. 2).

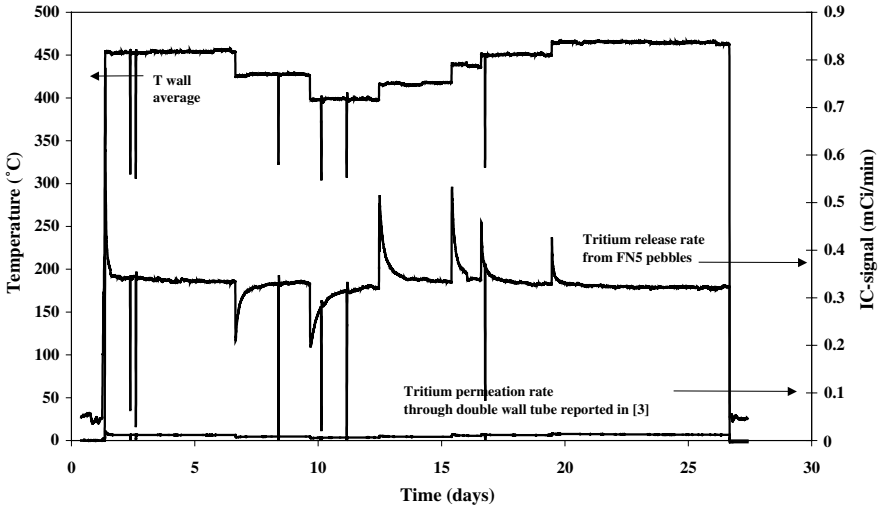

Fig. 2. FN5 specimen tritium release rate to the R-gas purge (IC signal on the right scale) during the EXOTIC-8.9, cycle 00–02 irradiation. The upper curve shows the temperature (°C on the left scale) measured outside the specimen on the capsule wall.

The tritium residence time (τ) has been obtained for each run (temperature) by evaluating the steady state tritium inventory (I) in the specimen at each averaged temperature (T) in the volume of the capsule and by using Eq. (1).

$$\tau = I/G. \tag{1}$$

The values are reported in the Arrhenius plot of Fig. 3. The characteristic temperature corresponding to $\tau = 24$ h was ~410 °C and the best fitting slope of $\ln\tau$ vs. $1/T$ gave the activation energy $E_a = 111 \pm 10$ kJ/mol.

The runs performed in He or He + 10 volume ppm H_2 showed a remarkable increase in tritium inventories. The beneficial effect of H_2 addition to the He purge was tested at 473 °C by step-changing the gas composition (P_{H_2}) as follows:

$R \rightarrow (1)\ P_{H_2} = 0.01\% \rightarrow (2)\ P_{H_2} = 0.05\% \rightarrow (3)$
$P_{H_2} = 0.5\% H_2 \rightarrow (4)\ P_{H_2} = 1\% H_2.$

The corresponding measured τ's are plotted in Fig. 4, the best fitting gave τ depending on $(P_{H_2})^{-0.34}$.

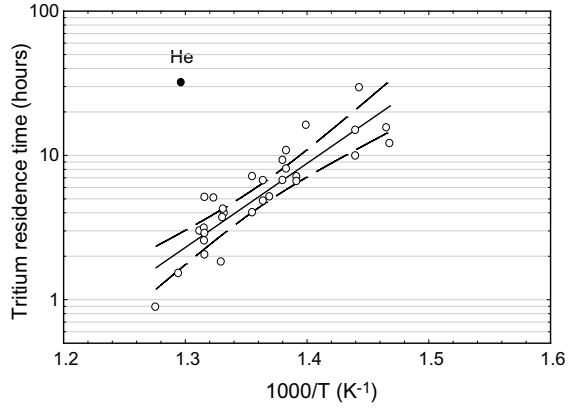

Fig. 3. Arrhenius plot of the tritium residence time for FN5 pebbles irradiated in EXOTIC 8.9 experiment for the runs with R-gas. The black point was obtained in pure He purge gas.

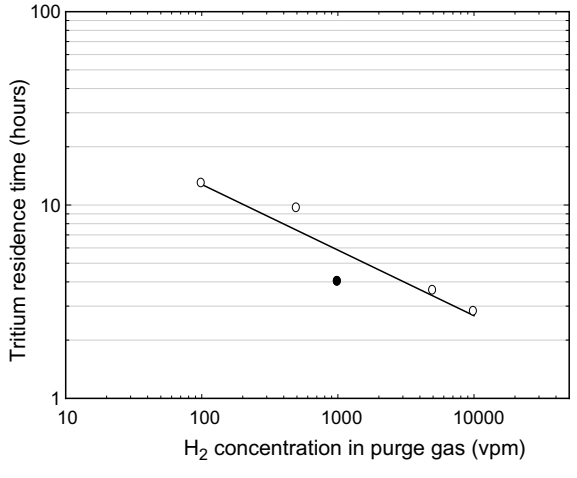

Fig. 4. Tritium residence time in the FN5 pebbles at 473 °C as a function of H_2 concentration in the He purge. The black point results from the best fitting line obtained for reference purge.

4. Out-of-pile TPD tests

Short irradiations and out of pile tritium release tests also have been performed to characterize the FN5 pebbles. A few tenths of grams has been irradiated in HFR (Rodeo device, E8-87/88 tests) and TRIGA (Lazy–Susan device) reactors at relatively low temperature <100 °C and for neutron doses typically used in NAA [4,6,7]. Tritium has been removed from the specimens by thermo-desorption ramps up to 800 °C in R-gas purged cells, the heating rate β has been varied from 0.5 to 5 K/min. The complex patterns of the resulting TPD spectra has not been influenced by the pebbles dimensions, providing evidence that the tritium release rate is mainly determined by the microstructure, which is the same for small and large pebble size.

According to the pioneering works on these kind of pebbles [7], the presence of multiple tritium energy-bonding sites has been observed. In the frame of first-order approximation, dimensionless 'fractional' concentration evolution may be considered, so that it is possible to use the data as considered independent from the initial tritium concentration. 'Each contribute to the rate was assumed to follow the simple thermally activated 'Arrhenius law' (2)

$$k = A\exp(-E/RT)\ [\mathrm{s}^{-1}]. \tag{2}$$

Since in one of the device used (Rodeo) instrumental signal distortion was observed for $\beta > 1$ K/min, only the TPD spectra for $\beta = 0.5$ K/min were evaluated by 'single peak' shape-analysis [4, and refs. therein]. This de-convolution fitting procedure also has been employed to study the pebbles irradiated in Lazy-Susan, which spectrum has been obtained at $\beta = 5$ K/min, an heating rate proven to give negligible signal distortion. The resulting kinetic parameters characterizing the three main peaks of tritium release rate for these two β values are reported in Table 1. They show that 'peak-shape' and 'β-variation' methods gave results in fair agreement.

By using Eq. (1) the rate constant $k_i = 1/\theta_i$ (where θ_i is the 'time constant' of the reaction step (i) can be evaluated with an uncertainty lower than those associated to the values of E and A due to a 'compensation effect' [8]. The tritium release rate transients $\Delta R_i(t)$ obtained in-pile (when the temperature perturbing steps are

Table 1
Kinetic parameters of the main tritium release desorption sites by TPD analysis for $\beta = 0.5$ (Rodeo E-8-87) and $\beta = 5$ (Lazy–Susan, Triga) tests

Step (peak)	β (K/min)	T_p (K)	A (s^{-1})	E (kJ/mol)
I	0.5	665	7.1	60
I	5	755	2.5	50
II	0.5	735	420	90
II	5	856	8.6	80
III	0.5	794	3.0×10^3	110
III	5	941	1.6×10^3	110

low enough to leave the steady state material conditions nearly unchanged) allow an evaluation based on the same assumptions made for the TPD analysis (simple pseudo-first order rate not dependent on initial conditions). In this case the $\Delta R_i(t)$ response goes exponentially to zero ($\Delta R_i(t \to \infty) = 0$) at T through the 'relaxation time' $\theta_i = 1/k_i$, and the corresponding 'fractional tritium inventory variation' ($\Delta I(t)/\Delta I(t \to \infty)$) in the pebbles can be well approximated by Eq. (3)

$$\begin{aligned}\pm\Delta Y(t) &= \pm\sum_i w_i \frac{\Delta I_i(t)}{\Delta I_i(t\to\infty)} \\ &= \pm\sum_i w_i \frac{\int_0^t \exp(-t/\theta_i)}{\int_0^\infty \exp(-t/\theta_i)} \\ &= \pm\sum_i w_i(1-\exp(-t/\theta_i)) \quad \text{with } \sum_i w_i = 1.\end{aligned} \tag{3}$$

To reconstruct $\Delta Y(t)$ the weighing factors w_i (that are function of the previous history of the specimen during irradiation) have to be known. For example in the case of EXOTIC-8.9 $w_1 \sim 0$ because the step-I is always very fast (see Table 2) and the corresponding site always void.

The calculated order of magnitude of θ_2 and θ_3 in Table 2 is in rough agreement with that corresponding to the measuredτ's at 400 and 500 °C. It suggests that an overlapping of the steps-II and III are controlling the tritium release rate within the temperature range and time scale of the EXOTIC-8.9 irradiation runs. This hypothesis is verified by the corresponding activation energies (80–110 kJ/mol for steps II–III (Table 1) vs. 111 kJ/mol for τ).

Table 2
Time constant of the main three tritium desorption sites from FN5 pebbles

β (K/min)	Temperature (°C)	θ_1 (h)	θ_2 (h)	θ_3 (h)
0.5	400	1.7	6.5	32.2
5.0	400	0.85	52.7	60.5
0.5	500	0.45	0.8	2.53
5.0	500	0.27	8.3	4.75

5. Conclusions

A Li_2TiO_3 pebble batch fabricated by an original method (suitable for reprocessing this kind of ceramic breeder [2]) showed tritium release properties, which are comparable to those obtained by classical routes [5].

The tritium release properties have been mainly tested in He + 0.1% H_2 purge gas. Pebble dimensions are not found to play a role in tritium release rate measured by out-of-pile TPD methods. The analysis of TPD spectra [4] has given the correct order of magnitude of the time constants characterizing the main desorption sites, in rough agreement with the residence times obtained by the in-pile step-perturbation methods performed during EXOTIC-8.9 experiment [3].

Pure He purge increases the tritium inventory; during the last cycle of this irradiation experiment variations of the H_2 concentration in the He purge showed an increase in tritium release rate from Li_2TiO_3 pebbles that was found to be proportional to $(P_{H_2})^{0.34}$ at 473 °C.

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