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Reactor experiments on irradiation of two-phase lithium ceramics Li_2TiO_3/Li_4SiO_4 of various ratios

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ABSTRACT

The design of future fusion reactors involves the production of tritium inside the breeder blanket. The most promising material for solid breeder blankets is a two-phase lithium ceramic containing orthosilicate Li_4SiO_4 (LOS) and metatitanate Li_2TiO_3 (LMT) of lithium in various proportions. Tritium is formed in lithium under neutron irradiation by the reaction ^{6}Li(n,α)T. Further, this tritium is extracted from the blanket with a purge gas and returned to the fusion zone, realizing the concept of a closed fusion cycle.

Irradiation under fission reactor conditions is still one of the few available methods for estimating the parameters of tritium generation and release from lithium-containing materials in the "in-situ" mode. This paper presents the results of experiments on neutron irradiation of two-phase lithium ceramics of various ratios (LOS + 35 mol. % LMT (pebble size 250–1250 μm), LOS + 35 mol. % LMT (pebble size 500–710 μm) and LOS + 25 mol. % LMT (pebble size 500–710 μm) at the WWR-K research reactor.

Irradiation of each batch of samples lasted from 5 to 22 days. The experiments were carried out by the vacuum extraction method. This paper describes the main methodological aspects of the studies, namely the technical features of four irradiation campaigns, the sequence and scope of the studies. A comparison is also made of the initial sections of reactor experiments for all campaigns, where the reactor was sequentially brought to power, according to which the parameters of the Arrhenius dependence of the effective tritium diffusion coefficients were estimated.

1. Introduction

The fusion reaction of deuterium and tritium, $D + T = He + n + 17.6$ MeV, is the most accessible and efficient reaction for use in fusion installations, taking into account the current level of technology development.

To implement a closed fuel cycle of a fusion reactor operating on DT-fuel, it is necessary to produce tritium within the facility itself. For these purposes, lithium-containing materials are used in the breeder blanket, and tritium is produced in lithium under neutron irradiation by the reaction ^{6}Li(n,α)T. The tritium formed is collected using a purge gas, and then, after extraction and purification, is fed into the fusion reactor chamber and used as a fuel.

Numerous studies showed that lithium-based ceramics are among the best candidates for use as breeder materials in solid breeder blankets of future fusion reactors [1,2]. Lithium ceramics, compared to other lithium-based materials, exhibit improved mechanical and thermal characteristics, are low activated, have good chemical stability, and have good tritium release parameters [3–6].

Recently, two-phase compounds containing lithium metatitanate Li_2TiO_3 and lithium orthosilicate Li_4SiO_4 in various proportions have attracted particular attention [7,8]. The idea of creating such a two-phase compound was proposed by scientists from KIT (Karlsruhe Institute of Technology) in 2013 [9].

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One of the most important tests for characterizing new types of ceramics are reactor experiments, which make it possible to estimate the parameters of tritium extraction directly under neutron irradiation. Interest in irradiation studies of two-phase lithium ceramics is confirmed both by a number of works carried out to date, for example, reactor experiments [10–12], and by future studies planned for various scientific programs for the development of controlled fusion.

The authors of this paper have been performing work on the irradiation of various lithium ceramics at the WWR-K reactor (Almaty, Kazakhstan) for many years. Since 2020, 4 reactor experiments have been carried out on the irradiation of two-phase lithium ceramics containing various ratios of LMT and LOS components (from 25 to 35 mol % of lithium metatitanate). Research was carried out sequentially with each type of ceramics. In experiments performed by the vacuum extraction method, the composition of gases released from lithium ceramic samples was recorded. The absence of a purge gas during the experiments eliminated the possibility of the appearance of such tritium compounds as T_2O and HTO, which significantly facilitated the processing of results and provided more opportunities for analyzing the results.

So far, the results of only the first campaign with ceramics containing 25 mol. % lithium metatitanate (with pebbles size from 250 to 1.250 μm and a total weight of 5.027 g) have been presented in [13–15].

This paper describes the main methodological aspects of the studies, namely the technical features of four irradiation campaigns, the sequence and scope of the studies. A comparison made of the initial sections of reactor experiments for all campaigns, where the reactor was sequentially brought to power, according to which the parameters of the Arrhenius dependence of the effective tritium diffusion coefficients were estimated.

2. Materials and method

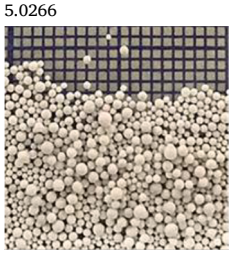
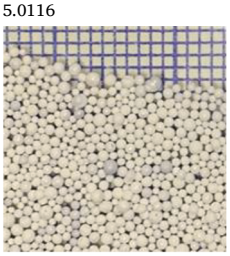
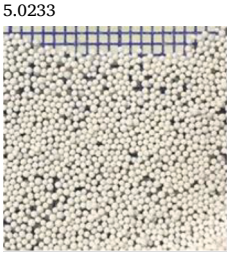
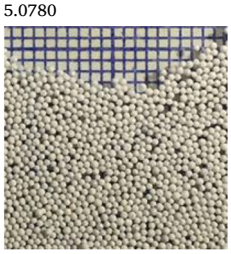
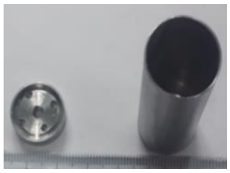
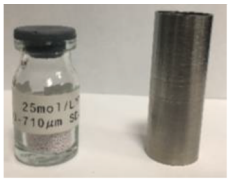
Four consecutive irradiation campaigns were carried out with spherical samples of lithium orthosilicate of various sizes, containing 25 and 35 mol % of lithium metatitanate, respectively.

The ceramic samples were fabricated at KIT by the KALOS process [16]. In this process first lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$), silicon dioxide (SiO_2) and titanium dioxide (TiO_2) were mixed and then subjected to heat treatment to remove residual water. The resulting composition was then poured into a platinum alloy melting crucible. The mixture was heated to a temperature of 1300–1400 °C (depending on the composition) and fed through a nozzle, forming drops. Then the droplets were cooled with liquid nitrogen to solidify.

The main parameters of the samples are given in Table 1 and Fig. 1, more detailed information on the method of making pebbles is given in [17]. It should be noted that batches of ceramic samples of the specified sizes were provided by the manufacturer. Irradiation of pebble beds of various sizes is due to the interest associated with the fact that for different pebble beds the packing factor will be different [18], and the kinetics of tritium release will be determined by a combination of parameters: the packing factor and the geometric dimensions of the pebbles themselves (and their quantitative distribution in the pebble bed).

Experiments on the irradiation of ceramic samples were carried out at the CIRRA (Complex of In-Reactor gas Release Analysis) facility [19–22], located at the WWR-K research reactor in Almaty, Kazakhstan. Fig. 2 shows a diagram of the facility with the main dimensions. Structurally, the facility can be divided into four main elements: a reactor ampoule device (AD) with samples; vacuum path and pumping system; mass spectrometer, as well as a system for supplying gas into the chamber with samples. Fig. 3 shows the part of facility in the experimental box. The experiments were carried out as follows: initially, an ampoule device was loaded into the dry channel of the reactor, which is a hermetically sealed stainless steel tube with an external heater and thermocouples installed in the sample irradiation area. During all four campaigns, the AD was not removed from the channel: samples were changed by reloading replaceable capsules. Further, through the upper open flange of the AD, the studied ceramic samples in a replaceable capsule were loaded, so that the samples were located at the core center level (Fig. 4).

Table 1
Main parameters of Li_2TiO_3-Li_4SiO_4 pebbles.

	1st campaign	2nd campaign	3rd campaign	4th campaign
Samples	25 LMT «Standard» (lithium orthosilicate with 25 mol % lithium metatitanate	35 LMT «Standard» (lithium orthosilicate with 35 mol % lithium metatitanate)	35 LMT «500 −710 μm» (lithium orthosilicate with 35 mol % lithium metatitanate)	25 LMT «500 −710 μm» (lithium orthosilicate with 25 mol % lithium metatitanate)
Pebble size, μm	250–1250	250–1250	500–710	500–710
Irradiation time, days	5	22	22	15
Weight, g	5.0266	5.0116	5.0233	5.0780
Appearence				
Irradiating capsule				

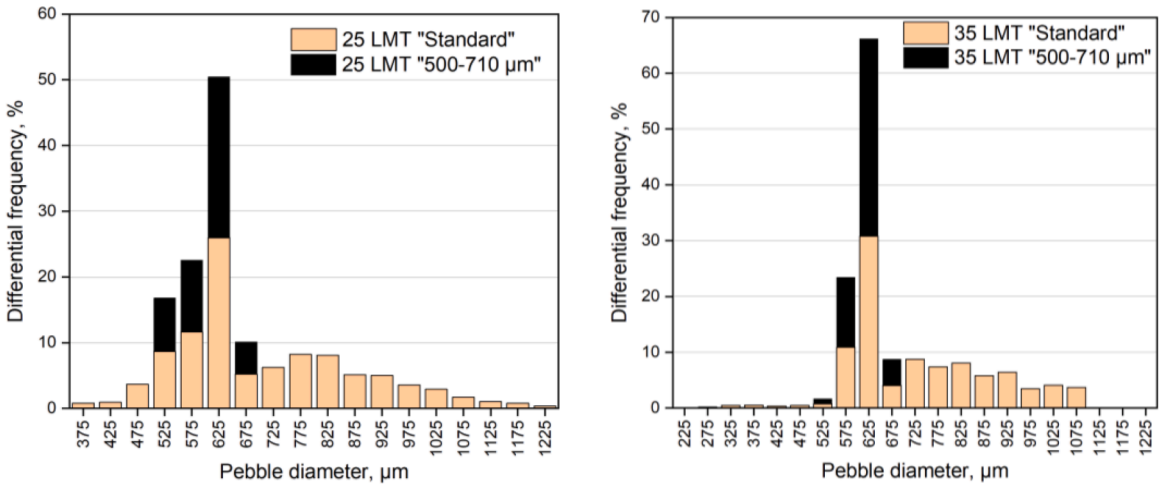


Fig. 1. The content of pebbles of different diameters in irradiated ceramic samples: a) 25 LMT; b) 35 LMT.

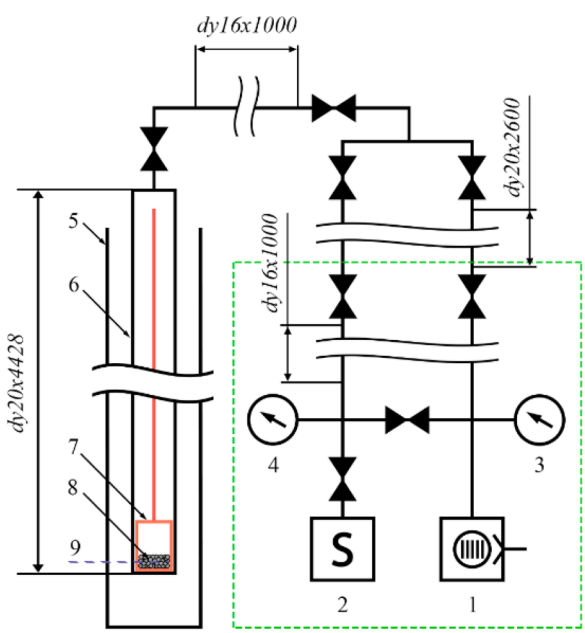


Fig. 2. Scheme of the CIRRA facility: 1 – pumping unit; 2 – mass spectrometer; 3, 4 – pressure sensors; 5 – reactor channel; 6 – ampoule device; 7 – capsule; 8 – sample; 9 – core center.

Fig. 3. The part of the CIRRA facility in the experimental box: 1 – pressure sensors; 2 – spiral pump; 3 – turbomolecular pump; 4 – controller of turbomolecular pump; 5 – mass spectrometer; 6 – heating tape.

Further, the AD was hermetically connected to the CIRRA facility and then the whole system with the pipelines was pumped out for several hours with heating to 100 °C.

Immediately before the reactor experiments, the registration of the pressure in the facility and AD's temperature, as well as mass spectrometric registration of the partial pressures of gases in the chamber was started, and continued until the end of irradiation.

At the initial stage of irradiation experiments, the reactor was gradually brought to the power levels 1, 3 and 4.8 MW (more than 1 h at each level). Further, long-term irradiation was carried out at a power of 6 MW, during which a number of experiments were carried out, associated with a change in the irradiation conditions (for example, the sample's temperature was changed, deuterium was supplied into the chamber).

A detailed description of such experiments is given for 1st campaign in [16]. The end of irradiation was carried out by a gradual decrease in the reactor power. On the 2nd (3rd) day after the end of the irradiation experiment, the AD was disconnected from the CIRRA facility (without being removed from the reactor channel) and the replaceable capsules were reloaded. Further, the AD was again connected to the facility and the next reactor experiment followed. Fig. 5 shows the above-described block diagram of experiments on the tritium vacuum extraction from lithium ceramics. The neutron spectrum of the WWR-K reactor is presented in Fig. 6.

3. Results and discussion

As mentioned above, the experiments performed dealt with various aspects of studying the tritium release from lithium ceramic samples under reactor irradiation. In particular, each experiment included sections in which the sample's temperature and gas composition in the chamber changed (for example, in the first experiment [19]). For a qualitative comparative analysis of all four experiments, this paper presents data on the tritium release in the initial sections of irradiation (for each experiment), where the reactor gradually reached power and changes in the tritium flux into the chamber and the samples temperature were recorded (Fig. 7).

As follows from the graphs, with an increase in the reactor power, an increase in the sample's temperature is observed (which quite quickly reached equilibrium values for each of the reactor power levels). An increase in the tritium flux from the samples was also observed, which also quite quickly (within several min) reached equilibrium values (for

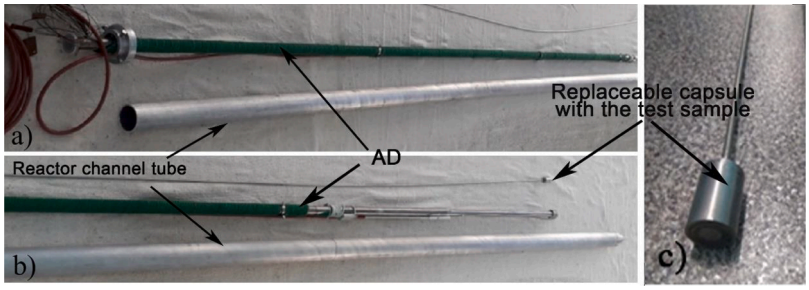


Fig. 4. View of the irradiation device: a) – the upper part of the AD and a tube of the reactor channel, b) – capsule with guide wire, bottom part of the AD and a tube of the reactor channel; c) capsule enlarged.

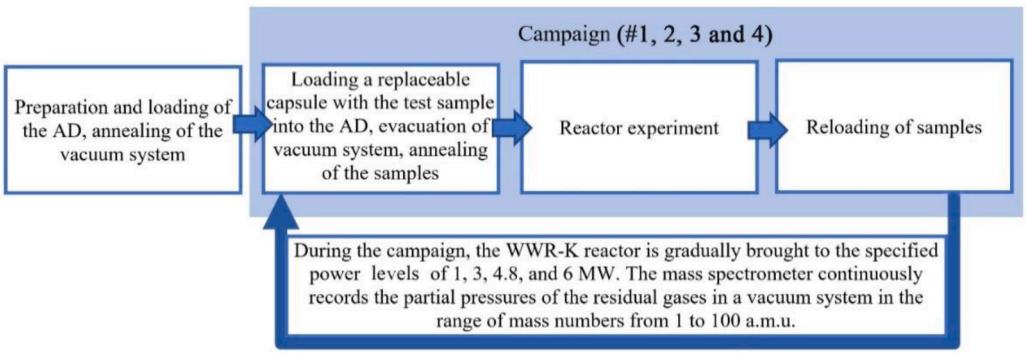


Fig. 5. Block diagram of a series of experiments on vacuum extraction of tritium from lithium ceramics under neutron irradiation.

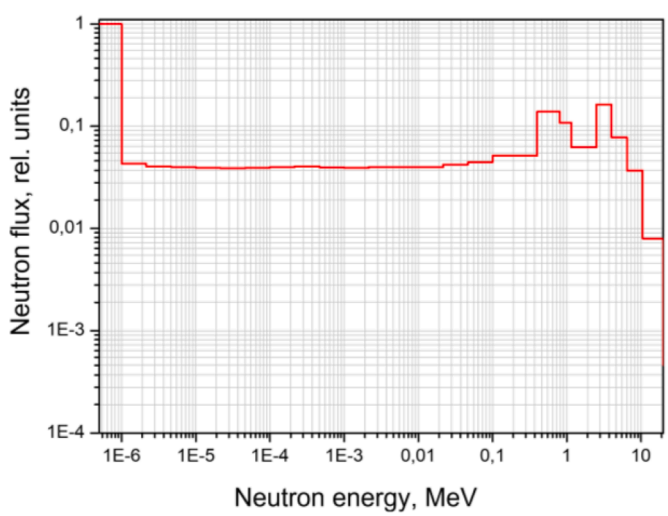


Fig. 6. Neutron spectrum of the WWR-K reactor.

reactor powers of 4.8 and 6 MW). It should be noted that the values of tritium release and sample temperature are comparable for different samples of two-phase lithium ceramics under study. The comparability of the equilibrium values of the samples temperatures and tritium fluxes is due to the fact that each experiment was carried out under similar conditions (in the same ampoule, the position of which was not changed between reactor runs) and for the same masses of lithium ceramics. According to the calculations, the difference in the pebble bed densities and, accordingly, in the total amount of lithium in the samples for different experiments did not exceed 10 %.

Slightly higher temperatures in the first campaign compared to the others (especially at the reactor power of 1 MW) are caused by the difference in the design of the capsules (Table 1). The capsule for the first campaign has a thickening in the upper part and a greater weight, which leads to its increased heating.

Some difference in the features of tritium release for the 3rd campaign at a reactor power of 1 MW (Fig. 7c) was caused by methodological reasons: in this section, the mass spectrometer worked for some time in the overload protection mode.

The insignificant difference in the equilibrium fluxes of tritium release (less than 10 %) at 6 MW is caused both by a slight difference in the number of ^{6}Li atoms in pebble bed for different campaigns and by a difference in the design of capsule caps for different campaigns (namely, the location, number and sizes of holes on capsule caps), which could lead to an error (less than 2 %) in the absolute measurements of the tritium flux from the samples.

One way or another, similar kinetics of tritium release were observed in experiments for various ceramic samples. Nevertheless, one can notice a difference in the release at low irradiation levels (for example, when the power changes from 1 to 3 MW) for campaigns 3 and 4 (where pebbles with sizes of 500 −710 μm were studied): the onset of equilibrium release of tritium for these samples occurs somewhat faster, due to the fact that there are no large pebbles in the pebble bed.

Also, a very good agreement between the values of the equilibrium tritium release from ceramics with the calculated value for the reactor power of 6 MW was achieved (Fig. 8).

Based on the experimental results, an attempt was made to describe the kinetics of tritium release from ceramics immediately after the start of irradiation (for the first section of all experiments, where the reactor reached power and 1 MW irradiation occurred).

For these sections of the experiments, it is easy to write down an analytical formula that describes the release of gas from a ball with a source of tritium, assuming that the initial concentration of tritium in the sample is zero, and the release of tritium is determined by diffusion in ceramics.

As is known, with a homogeneous initial $C_T(r,0) = 0$ and a zero boundary conditions $C_T(r_0,t) = 0$, $\left(\frac{\partial C_T}{\partial r}\right)_{r=0} = 0$, in the presence of a tritium source, the expression for the 2nd Fick's law in the spherical coordinate system (for a pebble of radius r_0) has the form:

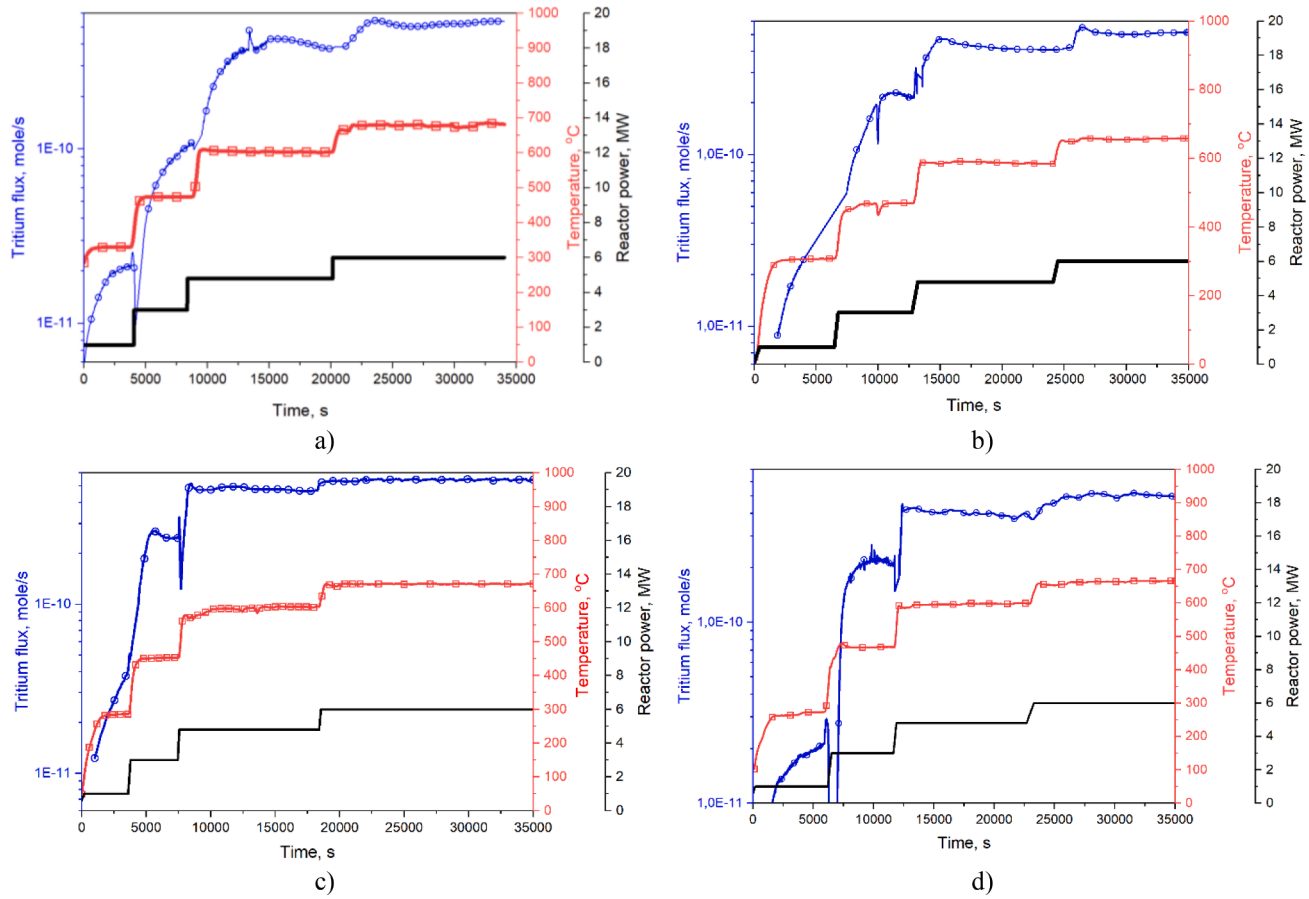


Fig. 7. Diagrams of reactor experiments with different samples: a) 25 LMT «Standard» (Pebble size 250–1250 μm); b) 35 LMT «Standard» (Pebble size 250 −1250 μm); c) 35 LMT «500 −710 μm» (Pebble size 500 −710 μm); d) 25 LMT «500 −710 μm» (Pebble size 500 −710 μm).

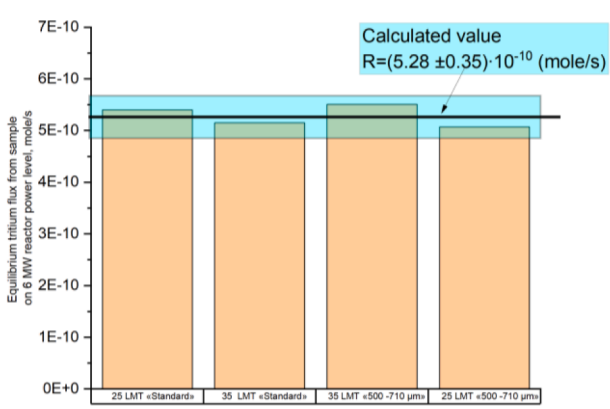


Fig. 8. The values of tritium equilibrium release from ceramics for various experiments in comparison with the calculated value.

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C_T}{\partial r^2} + \frac{2}{r}\frac{\partial C_T}{\partial r}\right) + Q, \tag{1}$$

where Q is the source power (tritium generation rate (mol/m^3·s)); C_T is the concentration of tritium, atom/(cm^3); $\left(\frac{\partial C_T}{\partial r}\right)_{r=r_0}$ is the tritium concentration gradient in the surface layer of the pebble; D is the diffusion coefficient of tritium, m^2/s.

For this problem, it is easy to obtain the dependence of the tritium flux from the pebble:

$$J(t) = \frac{Q \cdot V_0}{3}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-\frac{n^2\pi^2 Dt}{r_0^2}\right\}\right], \tag{2}$$

where V_0 is the pebble's volume.

Taking into account that there are pebbles of different radii in the pebble bed, the resulting flux (J_{sum}) will be determined by the sum of fluxes (J_i) for pebbles of different radii (r_i), taking into account their share δ_i of the total number of pebbles N_0:

$$J_{sum} = N_0 \cdot \sum_i \cdot \delta_i \cdot J_i \tag{3}$$

Moreover, the total number of pebbles in the pebble bed is estimated by the formula:

$$N_0 = m \Big/ \left(\rho \cdot \sum_i \cdot \delta_i \cdot V_i\right), \tag{4}$$

where m is the mass of the pebble bed; ρ is the ceramic density; V_i is the volume of the pebble with radius r_i.

Using the proposed approach to determining tritium flux from the sample and varying the diffusion coefficients, the curves of tritium release from lithium ceramic samples were simulated for all 4 campaigns. Typical simulation results for 25LMT in 1st and 35LMT in 2nd campaigns are shown in Figs. 9,10. The graphs show the calculated values of the tritium fluxes released from pebbles of various sizes in the pebble bed and their total release value in comparison with the experimental curve. As can be seen from the figures, when modeling, it is important to take into account all groups of pebbles (according to their sizes). The simulation performed for one group of pebbles with an

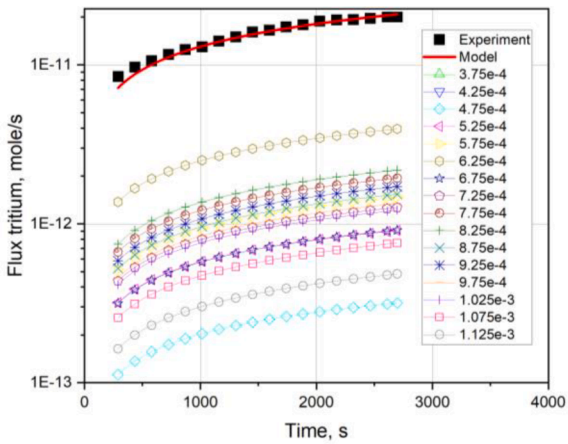


Fig. 9. Example of tritium release simulation the 1st campaign with 25 LMT "Standard" samples (Pebble size 250 −1250 μm).

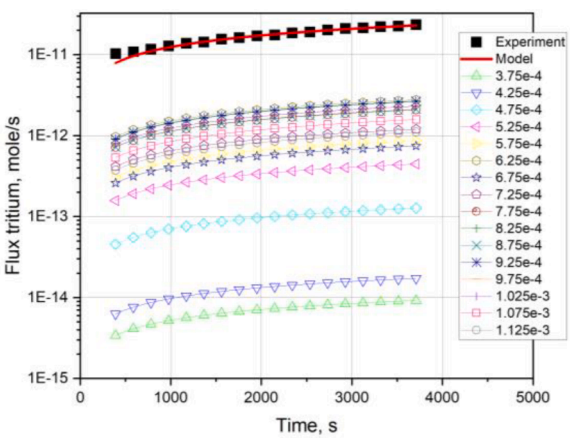


Fig. 10. Example of tritium release simulation for the 2nd campaign with 35 LMT "Standard" samples (Pebble size 250 −1250 μm).

averaged radius over all groups gave a significantly worse approximation of the model curve to the experimental one.

The interval of estimated diffusion coefficients of tritium in two-phase lithium ceramics for the temperature range from 260 to 350 °C is $3{\cdot}10^{-13}$ m^2/s. For lithium ceramic 25 LMT, the Arrhenius dependence of the effective diffusion coefficient has the form:

$$D = 8.5e-11\left(\frac{m^2}{s}\right)\cdot\exp\left(-\frac{31\left(\frac{kJ}{mole}\right)}{RT}\right). \quad (5)$$

The values of the effective diffusion coefficient of tritium in the 25 LMT ceramic turned out to be 15 % lower than in the 35 LMT ceramic. The obtained estimated values will be used later in the development of a tritium release model, which will be based on recurrent calculations of the tritium concentration in pebbles for the entire time of irradiation at 6 MW, that is, with a change in the power and samples temperature. Such modeling will make it possible to obtain the dependences of tritium release parameters from ceramics more correctly and in a wider temperature range from 100 to 700 °C.

4. Conclusions

The paper provides a description of a series of sequential reactor experiments with two-phase lithium ceramics of various types: the methodological procedures for conducting research are described in detail, as well as a number of technical features of the experimental facilities.

The kinetics of tritium release from two-phase lithium ceramics with different LMT/LOS ratios for 3 irradiation campaigns are presented. The calculated values of the tritium production rate in ceramic samples are compared with the tritium flux released in the experiment.

The study also reflects the results of the analysis of tritium release dependencies from samples of two-phase lithium ceramics at the initial stage of experiments: It was shown that the diffusion approximation can describe the release of tritium well, taking into account the real distribution of pebbles along the radius, and allow simulation of tritium release from at least 5 main groups.

The obtained simulation results and estimated values will be used later in the development of a tritium release model, which will be based on recurrent calculations of the tritium concentration in pebbles for the entire time of irradiation at 6 MW, that is, with a change in the power and samples temperature. Such modeling will make it possible to obtain the dependences of tritium release parameters from ceramics more correctly and in a wider temperature range from 100 to 700 °C.

It should also be said that differences in tritium release will most likely be seen in TDS experiments with irradiated samples, which are planned to be performed later. In TDS experiments, the kinetics of tritium release for different samples, as well as the amount of residual tritium in samples after irradiation, may differ.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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References

[1] G. Federici, R. Kemp, D. Ward, C. Bachmann, et al., Overview of EU DEMO design and R&D activities, Fusion Eng. Des. 89 (2014) 882–889.
[2] L. Boccaccini, L. Giancarli, G. Janeschitz, et al., Materials and design of the European DEMO blankets, J. Nucl. Mater. 329–333 (2004) 148–155.
[3] S. van Til, A.V. Fedorov, A.J. Magielsen, Study of ceramic pebble beds in post irradiation examination of the pebble bed assemblies irradiation experiment, Fusion Eng. Des. 87 (2012) 885–889.
[4] R. Knitter, P. Chaudhuri, Y.J. Feng, T. Hoshino, I.-K. Yu, Recent developments of solid breeder fabrication, J. Nucl. Mater. 442 (2013) s420–s424.
[5] L.M. Giancarli, et al., Overview of the ITER TBM Program, Fusion Eng. Des. 87 (2012) 395–402.
[6] K. Munakata, T. Shinozaki, K. Inoue, S. Kajii, Y. Shinozaki, R. Knitter, N. Bekris, T. Fujii, H. Yamana, K. Okuno, Tritium release from lithium silicate pebbles produced from lithium hydroxide, Fusion Eng. Des. 83 (2008) 1317–1320.
[7] Y. Wang, Q. Zhou, L. Xue, H. Li, Y. Yan, Synthesis of the biphasic mixture of Li2TiO3-Li4SiO4 and its irradiation performance, J. Eur. Ceram. Soc. 36 (2016) 4107–4113. V.
[8] M. Xiang, Y. Zhang, Y. Zhang, S. Liu, H. Liu, C. Wang, Fabrication and characterization of Li2TiO3eLi4SiO4 pebbles for tritium breeder, J. Fusion Energy 34 (2015) 1341–1347. V.
[9] R. Knitter, M.H.H. Kolb, U. Kaufmann, A.A. Goraieb, Fabrication of modified lithium orthosilicate pebbles by addition of titania, J. Nucl. Mater. 442 (2013) S433–S436.
[10] Q. Qi, J. Wang, Q. Zhou, Y. Zhang, M. Zhao, S. Gu, M. Nakata, H. Zhou, Y. Oya, G. Luo, Comparison of tritium release behavior in Li2TiO3 and promising core-shell Li2TiO3–Li4SiO4 biphasic ceramic pebbles, J. Nucl. Mater. 539 (2020), 152330.

[11] M. Yang, L. Zhao, Y. Qin, G. Ran, Y. Gong, H. Wang, C. Xiao, X. Chen, T. Lu, Tritium release property of Li2TiO3-Li4SiO4 biphasic ceramics, J. Nucl. Mater. 538 (2020), 152268.
[12] Q. Zhou, A. Togari, M. Nakata, M. Zhao, F. Sun, Q. Xu, Y. Oya, Release kinetics of tritium generation in neutron irradiated biphasic Li2TiO3–Li4SiO4 ceramic breeder, J. Nucl. Mater. 522 (2019) 286–293. V.
[13] T. Kulsartov, Z. Zaurbekova, R. Knitter, A. Shaimerdenov, Y. Chikhray, S. Askerbekov, A. Akhanov, I. Kenzhina, G. Kizane, Y. Kenzhin, M. Aitkulov, D. Sairanbayev, Studies of two-phase lithium ceramics Li4SiO4-Li2TiO3 under conditions of neutron irradiation, //, Nuclear Mater. Energy, ToM 30 (2022), 101129. March.
[14] I. Kenzhina, T. Kulsartov, Y. Chikhray, Y. Kenzhin, Z. Zaurbekova, A. Shaimerdenov, G. Kizane, A. Zarins, A. Kozlovskiy, M. Gabdullin, A. Tolenova, Analysis of the reactor experiments results on the study of gas evolution from two-phase Li2TiO3-Li4SiO4 lithium ceramics, //, Nuclear Mater. Energy, ToM 30 (2022), 101132. March.
[15] Y. Kenzhin, R. Knitter, G. Kizane, Y. Chikhray, A. Shaimerdenov, S. Askerbekov, A. Akhanov, I. Kenzhina, Z. Zaurbekova, A. Zarins, D. Sairanbayev, Investigation of hydrogen and deuterium impact on the release of tritium from two-phase lithium ceramics under reactor irradiation, //, Nuclear Mater. Energy, ToM 30 (2022), 101115. March.
[16] Oliver Leys, Julia M. Leys, Regina Knitter, Current status and future perspectives of EU ceramic breeder development, Fusion Eng. Des. 164 (2021), 112171.
[17] J.M. Heuser, M.H.H. Kolb, T. Bergfeldt, R. Knitter, Long-term thermal stability of two-phased lithum orthosilicate/metatitanate ceramics, J. Nucl. Mater. 507 (2018) 396–402.
[18] S. Pupeschi, M. Moscardini, Y. Gan, R. Knitter, M. Kamlah, Cyclic behavior of ceramic pebble beds under mechanical loading, Fusion Eng. Des. 134 (2018) 11–21.
[19] P. Blynskiy, et al., Experiments on tritium generation and yield from lithium ceramics during neutron irradiation, Int. J. Hydrogen Energy 46 (13) (2021) 9186–9192.
[20] T. Kulsartov, et al., Determination of the activation energy of tritium diffusion in ceramic breeders by reactor power variation, Fusion. Eng. Des. 172 (2021), 112783.
[21] T. Kulsartov, et al., Modeling of hydrogen isotopes release from lithium ceramics Li2TiO3 during in-situ experiments using vacuum extraction method, Fusion. Eng. Des. 170 (2021), 112705.
[22] Timur Kulsartov, et al., Features of the in-situ experiments on studying of tritium release from lithium ceramic Li2TiO3 using vacuum extraction method, Fusion. Eng. Des. 172 (2021), 112703.