

Mechanism of Tritium Accumulation and Release from Li_2TiO_3 during Long-Term Irradiation at WWR-K Reactor

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Abstract

Proposed mathematics and software of the reactor experiments allowed to interpret the experimental results of tritium release study. Tritium was continuously generated as a result of the nuclear reaction of lithium-6 and thermal neutrons under variable thermal impacts on lithium metatitanate Li_2TiO_3 . Main gas release parameters were calculated in order to assess acceptability to use lithium metatitanate in tritium breeders; the parameters are as follows: gas release rate, tritium retention in the materials, retention time, activation energy of thermal desorption HT , activation energy of volume diffusion T^+ , as well as corresponding pre-exponential (frequency) indexes.

Keywords: tritium diffusion coefficient, lithium metatitanate, retention time, gas release portion, blanket

Introduction

Preliminary we studied tritium generation and release from lithium ceramics Li_2TiO_3 ($\text{Li}_2\text{TiO}_3 + 5\text{mol}\% \text{TiO}_2$) with 96% enrichment by lithium-6 under long-term (5350 hours, 15 campaigns, 2-year experiment) irradiation by thermal neutrons in WWR-K reactor (Kazakhstan) [1]. At that, lithium burn-up was about 23%. Samples' temperature of and tritium release flow was automatically and continuously measured [2]. Characteristics of the samples, apparatus and experimental technique, as well as results of post-radiation studies of changes in physical-mechanical properties of lithium ceramics due to long-term reactor irradiation are given in the papers [3,4].

The present paper describes proposed mathematics for the experiments on measurement of tritium release processes under reactor irradiation. Main attention is paid on mathematical simulation of release processes of tritium, which is continuously generated in ceramics under stepped heating/ cooling of a sample. One of the tasks included processing of the results of diffusion experiment in order to calculate diffusion coefficient of tritium by lithium metatitanate lattice, as well as consideration of possible mechanisms of tritium migration and processes of its release under thermal cycling of lithium ceramics in neutron irradiation field.

2. Changes in Tritium Flux under Thermocycling the Lithium Ceramic Sample under Reactor Irradiation

Experiment showed that tritium flux apparently depends on temperature – temperature change (heating or cooling) is accompanied by changes in tritium flux from the sample. At that “peak-effect” can be observed under the heating mode when the temperature is changed from one to another – there is abrupt surge of tritium accumulated at previous temperature step. The “peak-effect” was not observed for the cooling mode. Data on release of continuously generated tritium during step-by-step heating (alternating stages of heating and cooling) allows to solve diffusion inverse problem and to calculate tritium diffusion coefficient.

Let's consider changes in gas flow from a sphere under stepped change of sample temperature (heating and cooling).

2.1. Stepped Heating of Ceramic Sample

Degassing of the pebble sample was considered in the framework of classical diffusion mechanism (that is, complying with Fick law (diffusion) and Henry law (solubility) taking into account presence of the sources and drains under boundary conditions of first type.

The following factors affecting tritium release were taking into account:

- 1) generation of tritium in the course of nuclear reaction (source);
- 2) Tritium radioactive decay (drain);
- 3) Tritium depletion of near-surface layer (layer's width is tritium atom recoil track) due to recoil effect;
- 4) Generation of tritium water due to ion exchange between H_2O and T^+ ;

5) Possible impact of helium-4 (second product of nuclear reaction) on tritium diffusion mechanism:



impact of ${}^3\text{He}$ (${}^3\text{H}$ decay product) was neglected;

6) Molization of atomic tritium at open surface of a sample.

Role of radiation effects related to irradiation with fast neutrons and gamma-irradiation will be considered in our future publications.

Preliminary analysis of abovementioned processes showed that main stage limiting tritium release is bulk diffusion of triton along material's crystal lattice. Thus, proposed mathematics was based on second Fick law taking into account presence of continuous source of diffusant evenly distributed along pebble volume. Solution of diffusion equation was carried out under boundary conditions of first type with initial conditions defined by history of thermal impacts at sample.

Let tritium to be continuously and evenly generated in ceramic pebble sample. The sample is kept at temperature T_1 during period of time t_1 . Then temperature is sharply increased up to value of T_2 and kept at this level during period of time t_2 , etc. Since diffusion coefficient is changed from value D_1 to value D_2 , then gas flux is sharply increased as well (here $T_1 < T_2$, and $D_1 < D_2$). It shall be noted that at new temperature T_2 tritium flux consists of two components:

“new” molecules, which are born at temperature T_2 ; their flux is controlled by diffusion coefficient D_2 :

$$J_2(t) = SQ \left[\frac{r_0}{3} - \frac{2r_0}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left\{-\frac{n^2 \pi^2 D_2 t}{r_0^2}\right\} \right] \quad (2)$$

where J_2 [atom/s] – complete flux of tritium atoms, generated under temperature T_2 , $S=4\pi r_0^2$ [cm²] – square of pebble surface, r_0 [cm] – sphere radius, Q [atm/(cm³×s)] – power of source (tritium generation rate).

and “old” molecules, which were born at temperature T_1 and were unable to leave during previous period t_1 (their release rate was controlled by diffusion coefficient D_1), but due to rise of temperature up to T_2 they actively leave sphere (tritium release rate is now controlled by diffusion coefficient D_2). Flux of these type molecules from the sphere is:

$$J_1(t) = \frac{2 \langle C_{T1} \rangle S D_2}{r_0} \sum_{n=1}^{\infty} \exp\left\{-\frac{n^2 \pi^2 D_2 t}{r_0^2}\right\} \quad (3)$$

Where as a first approximation $\langle C_{T1} \rangle$ [atom/cm³] is average concentration of tritium remained in a sphere after sample burnup at temperature T_1 within time t_1 :

$$\langle C_{T1} \rangle = \frac{r_0^2 Q}{D_1} \left(\frac{1}{15} - \frac{6}{\pi^4} \sum_{n=1}^{\infty} \frac{1}{n^4} \exp\left\{-\frac{n^2 \pi^2 D_1 t_1}{r_0^2}\right\} \right) \quad (4)$$

If the time t_1 during which temperature T_1 is held, is sufficient for establishment of stationary diffusion then

$$\langle C_{T1, \infty} \rangle = \frac{r_0^2 Q}{15 D_1}, \quad (5)$$

That significantly simplifies the calculations.

Let consider that tritium flux from sphere at temperature T_2 is described by the equation:

$$J(t) = J_1 + J_2 = SQ \left[2r_0 \frac{D_2}{D_1} \left(\frac{1}{15} - \frac{6}{\pi^4} \sum_{n=1}^{\infty} \frac{1}{n^4} \exp\left\{-\frac{n^2 \pi^2 D_1 t_1}{r_0^2}\right\} \right) \sum_{n=1}^{\infty} \exp\left\{-\frac{n^2 \pi^2 D_2 t}{r_0^2}\right\} + \left[\frac{r_0}{3} - \frac{2r_0}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left\{-\frac{n^2 \pi^2 D_2 t}{r_0^2}\right\} \right] \right] \quad (6)$$

(6)

where D_1 – gas diffusion coefficient at temperature T_1 , and D_2 – at temperature T_2 .

For great time t_1 :

$$J(t) = QV \left(1 + \frac{2 D_2}{5 D_1} \sum_{n=1}^{\infty} \exp\left\{-\frac{n^2 \pi^2 D_2 t}{r_0^2}\right\} - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left\{-\frac{n^2 \pi^2 D_2 t}{r_0^2}\right\} \right) \quad (7)$$

where $V=(4/3)\pi r_0^3$ – volume of spherical granule.

If time t_2 at temperature T_2 is rather big then the stationary gas flow is established

$$J = QV \quad (8)$$

Thus, during transfer from temperature T_1 to temperature T_2 we consider that gas flow from sphere is changed from the law at temperature T_1 :

$$J(T_1, t) = SQ \left[\frac{r_0}{3} - \frac{2r_0}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left\{ -\frac{n^2 \pi^2 D_1 t}{r_0^2} \right\} \right] \quad (9)$$

to the law at temperature T_2 :

$$J(t) = QV \left(1 + \frac{2}{5} \frac{D_2}{D_1} \sum_{n=1}^{\infty} \exp \left\{ -\frac{n^2 \pi^2 D_2 t}{r_0^2} \right\} - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left\{ -\frac{n^2 \pi^2 D_2 t}{r_0^2} \right\} \right) \quad (10)$$

Similar formulas describe behavior of stable gas flow (tritium decay during reactor experiment can be neglected because of its large half-decay period) under following stepped heating up to temperatures T_3 , T_4 , T_5 , etc.

It shall be noted that formula describing tritium flow at temperature T_2 doesn't include diffusion coefficient but ratio D_2/D_1 , so it is impossible to determine the values D_1 and D_2 from stepped heating experiment alone.

2.2. Stepped Cooling of Ceramic Sample during Irradiation

Let's consider behavior of tritium flow under stepped cooling of the sample. Here, $T_1 < T_2$, and $D_1 > D_2$, so difference in gas retention times is

$$\Delta\tau = \tau_2 - \tau_1 = \frac{\langle C_{T_2} \rangle - \langle C_{T_1} \rangle}{Q} \quad (11)$$

Mathematics apparatus is the same as above, but has one significant difference.

If temperature T_1 is rather high and time t_1 is rather long then there will practically be no gas in sphere, i.e. $\langle C_{T_1} \rangle = 0$ and correspondingly $\Delta\tau = \langle C_{T_2} \rangle / Q$. Hence, tritium flow at temperature T_2 is changed by the law:

$$J_2(t) = SQ \left[\frac{r_0}{3} - \frac{2r_0}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left\{ -\frac{n^2 \pi^2 D_2 t}{r_0^2} \right\} \right] \quad (12)$$

which allows to find diffusion coefficient D_2 .

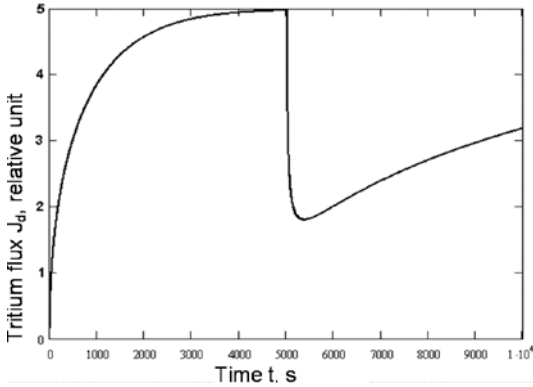


Figure 1 shows the example of change of tritium flow under stepped decrease of temperature. We can see abrupt practically vertical dip of the flow under abrupt change of temperature. Taking into account of partial degassing (i.e. presence of tritium in a sample under higher temperature step) results in more monotonous dip of the flow in temperature change area. However, dip time is very small and doesn't have sufficient effect on a form of the curve of following rise of tritium flux generated at new temperature step.

Figure 1. Release of tritium generated in a sphere taking into account tritium generated during previous temperature step (stepped cooling)

Thus, analysis of flux dependence from time allows to determine diffusion coefficient at low temperature under stepped cooling; and for stepped heating – firstly, ratio D_2/D_1 , then (using stepped heating curves) diffusion coefficient at higher temperature.

2. Determination of Tritium Diffusion Coefficient by Crystal Lattice of Lithium Titanate

Processing of data obtained during experiment in the framework of classical diffusion model showed that during one year irradiation of lithium ceramics in the reactor diffusion activation energy was significantly decreased – the evidence of decrease of depth of potential wells, along which tritium (T^+) diffusion and tritium release in a form of HT and T_2 is realized. At that, value of pre-exponential (entropic) factor is decreased as well, that is the evidence of decrease of diffusion paths available for diffusion probably due to creation of radiation defects acting as the traps of diffusing tritium.

Analysis of dependence of flow from time allows to determine diffusion coefficient at low temperature under stepped cooling; and to determine ratio D_2/D_1 under stepped heating and then to determine diffusion coefficient at high temperatures by using stepped heating curves. Data on HT and T_2 release

(data of stepped cooling from high temperatures, at which degassing of the granules were rather large) were converted in diffusion coefficient of triton (T^+) by crystal lattice of lithium metatitanate and then they were specified by stepped heating data.

As usually, we assumed that temperature dependence of tritium bulk diffusion can be described by Arrhenius law. Assessment of Arrhenius dependence of diffusion coefficient T^+ showed the following values: $D_{01}=0.1 \text{ cm}^2/\text{s}$ and $E_{D1}=130 \text{ kJ/mole}$ for initial stage of lithium burn-up and $D_{02}=0.006 \text{ cm}^2/\text{s}$ and $E_{D2}=69 \text{ kJ/mole}$ during last campaigns. Thus, long-term irradiation of lithium ceramics resulted in decrease of activation energy of tritium diffusion in two times and decrease of pre-exponential (entropic) factor of diffusion on more than one order of magnitude.

Some diffusion coefficients in lithium metatitanate under various temperatures and various times are given in Table 1.

Table 1. Diffusion coefficients in lithium metatitanate under various temperatures and various times

Irradiation initial stage		Irradiation final stage	
Temperatur e, °C	Diffusion coefficient t	Temperatur e, °C	Diffusion coefficient t
300	$1,35 \cdot 10^{-13}$	300	$3,0 \cdot 10^{-9}$
500	$1,59 \cdot 10^{-10}$	500	$1,28 \cdot 10^{-7}$
700	$1,02 \cdot 10^{-8}$	700	$1,17 \cdot 10^{-6}$

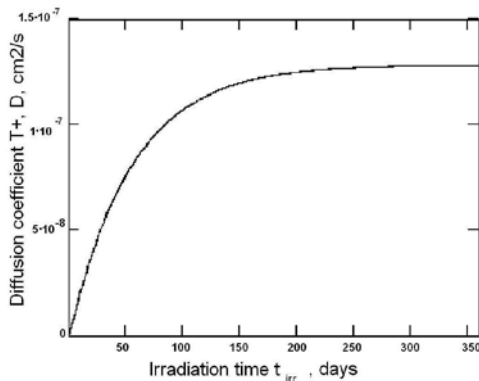
For semiquantitative estimation of diffusion coefficient changes under constant temperature during reactor irradiation we used empirical formula. For example, under temperature of 500°C this dependence to a first approximation can be described by:

$$D(t_r) = 1,59 \cdot 10^{-10} + 1,28 \cdot 10^{-7} \cdot [1 - e^{-0,018 \cdot t_r}] \quad (13)$$

where t_r – irradiation time.

Graphic of this function $D(t_r)$ is given at Figure 2. From this dependence we can conclude that diffusion coefficient actively increases only during first 10 months of reactor irradiation, the effective diffusion coefficient is stabilized on $1.3 \times 10^{-7} \text{ cm}^2/\text{s}$ and doesn't change or changes insignificantly. Reach of limit value of diffusion coefficient relates with opposed action of two factors – 1) lithium burnup resulting in disappearance of lithium ions from crystal lattice joints and following easing of diffusion process and 2) radiation defects appeared by influence of fast neutrons and external gamma-irradiation, which catch diffusing tritium into traps.

Figure 2. Example dependence describing change of tritium diffusion coefficient in lithium metatitanate during reaction experiment



3. Gas Release Rate and Tritium Retention Time

While estimating suitability of lithium ceramics as a breeder material the important parameter is gas release ratio – parameter having values in the range from 0 up to 1, where 1 corresponds stationary flow of tritium from granules.

Gas quantity $G(t)$ [atom] remaining in the sphere to the moment of time t :

$$G(t) = 4\pi \int_0^{r_0} C(r,t) r^2 dr - \frac{4\pi}{3} r_0^3 C_{(0)} = \frac{8}{\pi} r_0^3 C_{(0)} \left[\frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left\{ - \left(\frac{n\pi}{r_0} \right)^2 t \right\} \right] \quad (14)$$

Quantity of gas released from a sphere to the moment of time t :

$$M(t) = \frac{4}{3} \pi r_0^3 C_{(0)} \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(- \frac{n^2 \pi^2 D t}{r_0^2} \right) \right] \quad (15)$$

Average concentration of tritium in sphere:

$$\langle C \rangle = C_{(0)} \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{r_0^2}\right) \quad (16)$$

depends on diffusion coefficient, granule radius and the period passed from beginning of tritium generation in ceramics.

As a example, figure 3 shows time dependences of tritium release (portions from stationary flow) at temperature 700°C for initial and final stages of reactor experiment. We can see that beginning of tritium generation in lithium ceramics corresponds to a rise of tritium flow and the flow tends to stationary value with increase of irradiation duration. Flow reached stationary value faster at the final stage of irradiation in comparison with initial stage of the experiment.

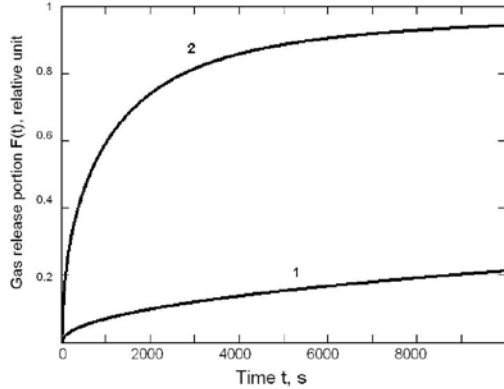


Figure 3. Time dependences of tritium release (portions from stationary flow) at temperature 700°C for initial (1) and final (2) stages of reactor experiment.

As was shown above for initial stage of lithium ceramic irradiation at temperature 700°C, tritium diffusion coefficient was $1.02 \times 10^{-8} \text{ cm}^2/\text{s}$, gas release portion was 13.1% after the period $t=1 \text{ h}$, whereas for final stage at the same temperature diffusion coefficient was $1.168 \times 10^{-6} \text{ cm}^2/\text{s}$, and gas release portion was 84.4% for the same period. Thus, in our reactor experiments at the temperature higher than 500°C tritium

stationary flow was reached after several hours after beginning of tritium generation.

Another important criterion is based on a notion of tritium retention time in ceramics, τ . The lesser generated tritium is stayed in ceramics, and therefore, the better are ceramics properties to its use as a breeder material.

Retention time was calculated by formula:

$$\tau(T) = \frac{r_0^2}{15 \cdot D(T) \cdot 3600 \cdot 24} [\text{days}] \quad (17)$$

For example, Table 2 includes some calculated retention times.

Table 2. Tritium retention times τ [days], at various temperatures and various stage of lithium-6 burnup in lithium metatitanate

Temperature, °C	Retention time τ [days], Burnup stage	
	Initial	Final
300	$5,7 \times 10^4$	2,6
500	48,7	0,06
700	0,76	$6,6 \times 10^{-3}$

Table 2 showed that tritium retention times (Li_2TiO_3 pebble, 1 mm diameter) are changed in wide range – from 57000 hours (initial burnup stage) to 10 minutes (burnup of lithium-6 is about 20%). Small retention times under high temperatures are the evidence of high perspectives to use lithium metatitanate-based ceramics as a breeder material in fusion facilities.

Conclusion

It was established that tritium release is mainly controlled by bulk diffusion, however, some role is played by capture by point defects and molization of tritium at the material surface.

There were calculated diffusion coefficients and activation energies of tritium release from irradiated ceramics. While lithium is burnt-up, activation energy of tritium release is decreased tending to constant value at high levels of lithium-6 burnup. The effect is explained by decrease of lithium ion concentration in lattice points appearing as additional diffusion barriers. Low values of retention levels and retention times, which provide sufficiently low tritium concentrations in pebbles under irradiation at rather moderate temperatures, allow us to recommend ceramics on the basis of lithium metatitanate as a breeder material for fusion facilities provided conservation of physical-mechanical properties.