Chemical Forms of Tritium in Be Pebbles after Different Treatments

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Abstract. Chemical forms of tritium in two types of neutron-irradiated beryllium pebbles - BERYLLIUM and EXOTIC-8-3/13 were investigated before and after their annealing under action of 5 MeV fast-electrons of the dose rate 14 MGy/h and in magnetic field of 1.7 T separately and simultaneously in order to evaluate possible effects of these factors. Chemical forms of tritium were analyzed using chemical scavenger's method. In both types of pebbles, BERYLLIUM and EXOTIC-8/3-13, three forms of tritium – ionic T^+, atomic T^o and molecular T_2 were determined, but their contents were different. In the untreated BERYLLIUM pebbles, tritium was in an ionic form – 5-6 %, in an atomic form 10-13 % and in a molecular form 80-85 %. The untreated EXOTIC 8-3/13 pebbles have different values of these abundance ratios: the tritium in molecular form – 60-70 %, the atomic form of tritium – 20-25 %, and the ionic form – 10-15 %. The abundance ratios of chemical forms of the tritium accumulated in the neutron irradiated beryllium pebbles depend on the irradiation temperature, the neutron fluencies, the contents of structural defects and impurities. After tritium release at annealing the pebbles under action of radiation and magnetic field separately and simultaneously, the abundance ratio of separate chemical forms in the pebbles changes. It is related to radiolysis of localized T_2 into pairs of radicals of T^0 and MF-induced spin transformation S→T in pairs of radicals resulting in an increase of concentration of T^0 – main diffusing particles in beryllium metal.

1. Introduction

Beryllium in the form of pebbles is foreseen as a neutron multiplier in the Test Blanket Module for ITER and also in DEMO fusion devices [1, 2]. Beryllium is needed as neutron multiplier to maintain a sufficiently high neutron flux for tritium breeding in the reactors blanket zone. Advantages of beryllium are its low Z number, high melting point and low absorption cross section for thermal neutrons. The beryllium pebbles in the blanket zone will be under action not only of a high temperature of 900-1100 K and an intense fast neutron radiation of 2.4 $MW \cdot m^{-2}$ or 10^{18} $n \cdot m^{-2} \cdot s^{-1}$ but also under action of a high magnetic field (MF) of 7-10 T during operation time. Considerable amounts of tritium may accumulate in the beryllium under the operation conditions in the blanket zone at the end of life of the reactors. The accumulation and retention of tritium in the beryllium pebbles is a very important issue for the ensuring of the fuel cycle, for the mechanical stability under swelling and cracking processes of the pebbles and also for the radioactive waste management at the decommissioning process. Neutron radiation effectively causes changes in the structure of beryllium (dislocations, vacancies) and generates tritium, initially, as a dynamic solution of separate tritium atoms in beryllium lattice, but, consequently, new forms of tritium arise in beryllium under influence of irradiation, temperature, and precipitation. Tritium could accumulate in beryllium in different chemical forms (T_2, T^+, T^o, T^-) and each of them has different mobility. Tritium release from beryllium materials depends on its thermal diffusion velocity in beryllium crystal lattice [3]. The main diffusion form for tritium in beryllium is T^o which migrates by interstices of crystal lattice. Considerable increase of the tritium release under the simultaneous action of high temperature, ionizing radiation and intense magnetic field was observed in our previous investigations [4]. The synergetic effect of tritium release is also connected with chemical forms of localized tritium and could be explained that the under simultaneous action of temperature, radiation and MF abundance ratio of chemical

forms of tritium changes and MF causes the spin transformation in pairs of radicals $T^0 \cdots T^0$. Such transformation reduces recombination of atomic tritium into molecular tritium. In order to understand the features of tritium release from the pebbles under the operational conditions, it is very important to know chemical forms of the localized tritium as they have different mechanisms of diffusion. This paper focuses both on the previous and latest results achieved on analysis of chemical forms of tritium in two types of neutron-irradiated beryllium pebbles - EXOTIC-8-3/13 and BERYLLIUM before and after their treatment under different conditions.

2. Experimental

2.1. Materials investigated

Both the types of pebbles were irradiated in the High Flux Reactor, Petten, the Netherlands with fast fission neutrons. Pebbles were manufactured by Brush Wellman by the following methods: the BERYLLIUM pebbles – by the fluoride reduction process, while the EXOTIC 8-3/13 pebbles – by the inert gas atomization method. Both the types of pebbles have the same range of the grain size 40-200 μm, but they have different size and content of impurities. The BERYLIUM pebbles have diameters of 1.6-2.1 mm; contain 3125 ppm BeO, 1200 ppm Mg. The EXOTIC 8-3/13 pebbles have size of 0.1-0.2 mm; contain 3400 ppm BeO, 28 ppm Mg. The irradiation conditions also were different. The BERYLIUM pebbles were irradiated only for 97.4 days with the fluence $1.24\ 10^{25}$ n m^{-2} at 780 K, while EXOTIC 8-3/13 – 449.8 days with the fluence $2.70\ 10^{25}$ n m^{-2} at temperature 800-900K, the energy of fission neutrons larger than 0.1 MeV [3]. The total activity of tritium in 1 g of beryllium is not uniform (in the BERYLLIUM pebbles – 0.6 – 1.5 GBq g^{-1}, in the EXOTIC-8-3/13 pebbles – 2-9 MBq g^{-1}). The EXOTIC8-3/13 pebbles contained also some coarse agglomerates of the pebbles with larger content of tritium - 10-19 MBq/g. This non-uniformity could be explained by different content of tritium and impurities in Be pebbles caused by different temperatures and neutron fluxes of separate pebbles.

2.2. Treatment of samples at thermo-annealing

Annealing of the pebbles was performed in a special radiation thermo magnetic rig based on a linear electron accelerator [4] under action of temperature, radiation (irradiation with fast electrons 5MeV, dose rate 14 MGy.h^{-1}), magnetic field (1.7 T) separately or simultaneously. Annealing of Be pebbles within 3-13 mg was performed in a continuous flow of the purge gas He + 0.1 % H_2. The Be pebbles were annealed at a temperature ramp of 5 K/min to 553K, 773K, 1073K or 1123K and then at a given constant temperature from 0.5-3 h with or without magnetic field 1.7-2.35 T. The tritium released was measured continuously with a gas flow-through proportional meter TEM 2102A with a detector DDH 32 of the operating volume 300 cm^3.

2.3. Determination of chemical forms of tritium in beryllium pebbles with chemical scavenger method

The chemical forms of tritium were analyzed using a chemical scavenger (dissolution) method. This method does not change the content of chemically active particles in a solid matrix since at the dissolution process the particles transfer into a dissolution layer and reacts with a scavenger. The dissolution of samples was performed in a special setup [4]. In order to determine the total tritium in the gaseous phase (T_2, T^o) and in the liquid phase (T^+), the

pebbles were dissolved in 2 M sulphuric acid. The T_2 and T^o localized in Be pebbles transfers as T_2+HT in gaseous phase, but tritium in ionic stays in liquid phase.
Dissolution of sample of beryllium in the presence of the scavenger of T^o was used in order to determine the chemical forms T^o and T_2 separately. Chemically active particles of atomic tritium T^o were determined by dissolution of the pebbles in 2 M sulphuric acid with 0.5 M sodium dichromate. In such solvent, 90% of the T^o localized in Be transform into T^+ and 10 % into HT [4]. The content of chemical forms of tritium (T_2, T^o, T^+) in the beryllium pebbles was calculated from the tritium activities in gaseous and liquid phase respectively [4].
Beryllium pebbles from BERYLLIUM irradiation experiment were investigated as separate pebble (2-4 mg) in each experiment while in the case of EXOTIC8-3/13 numerous pebbles were used. Tritium in the gaseous phase was detected with a proportional gas flow detector. Tritium in liquid phase was detected using a liquid scintillation method. The solution with tritium was distilled in order to prevent the influence of radiochemical impurities of Co-60, Zn-65 etc.

3. Results and discussion

In order to understand the features of tritium release from the pebbles under the operational conditions, it is very important to know chemical forms of the localized tritium as they have different mechanisms of diffusion.
In both the types of pebbles, BERYLLIUM and EXOTIC-8/3-13, the three forms of tritium – ionic T^+, atomic T^o and molecular T_2 were determined, but their contents were different. In the untreated BERYLLIUM pebbles, tritium was in an ionic form – 5-6 %, in an atomic form 10-13 % and in a molecular form 80-85 % [5]. The untreated EXOTIC 8-3/13 pebbles have different values of these abundance ratios: the tritium in molecular form – 60-70 %, the atomic form of tritium – 20-25 %, and the ionic form – 10-15 % (*see FIG. 1.*). A larger abundance ratio of the ionic form of tritium in the EXOTIC 8-3/13 could be explained by the fact that a larger amount of beryllium oxide is present in the pebbles. A larger ratio of atomic tritium in the EXOTIC 8-3/13 pebbles could be related to the differences in the irradiation conditions and the different surface to volume ratio of both the types of pebbles.

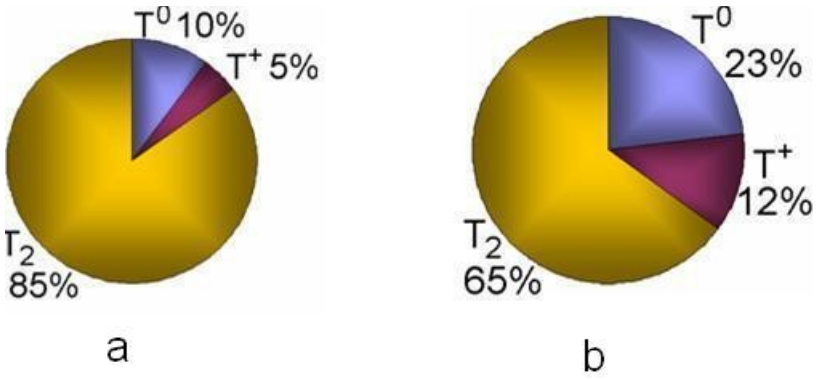

FIG. 1. Chemical forms of tritium for untreated pebbles: a- BERYLLIUM, b- EXOTIC8-3/13

In this study, the pebbles were investigated a relatively long time after their irradiation in the BERYLLIUM (1994) and EXOTIC 8-3/13 (2000) experiments, but nevertheless the results obtained allow us to conclude that the abundance ratios of the chemical forms of the tritium accumulated in the neutron irradiated beryllium pebbles depend on the irradiation

circumstances - temperature, the neutron fluence and the contents of structural defects and impurities (see Section 2.1.).
After tritium release at annealing the pebbles under action of radiation and magnetic field separately and simultaneously, the abundance ratio of separate chemical forms in the pebbles changes.
In the presence of radiation and magnetic field, at annealing of the EXOTIC 8-3/13 pebbles at relatively low temperature 553K for 3h, 20-29 % of the localised tritium was released, in the presence of ionizing radiation of fast electrons, up to 20 % of tritium was released, but at temperature only 10-15%. After such treatment in the presence of magnetic field and radiation, the abundances of the chemical forms of the residual tritium had the following values - the amount of molecular tritium in the pebbles decreased to 30-35 %, the atomic tritium to 20-30 %, but the amount of tritium in the ionic form did not change in comparison with initial amount of tritium. At such low thermo-annealing temperature 553K the amount of residual molecular tritium did not change and release only of atomic tritium was observed (*see FIG. 2.*). In the case of thermo-annealing under action of radiation (R, T) we can observe that the fast electron radiation in experiments can cause radiolysis of part of T_2 in bubbles ($T_2 \rightarrow T^o + T^o$), but temperature is too low for more considerable release of tritium. In the case of tritium thermo-annealing under action of all three factors simultaneously (R, MF, T) residual amount of molecular tritium reduces much more because the magnetic field can cause spin transformation (S→T) of a pair of radicals generated by radiolysis; the efficiency of recombination decreases and diffusion of tritium in form of atomic tritium T^o increases.

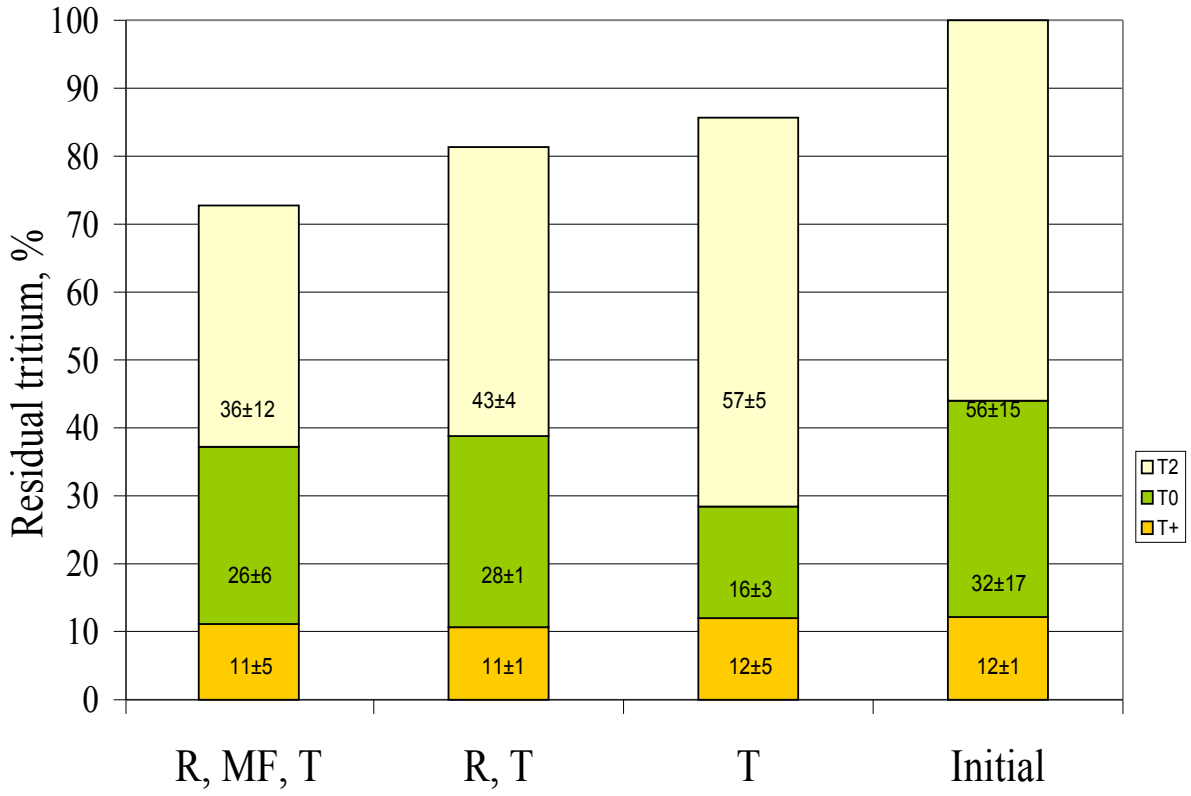

FIG. 2. Chemical forms of tritium in EXOTIC8-3/13 beryllium pebbles after treatment - 1) R, MF, T-radiation, magnetic field and temperature; 2) R, T –radiation and temperature; 3) only at temperature T 553 K and 4)initial - without treatment. Radiation – accelerated 5 MeV electrons 14 MGy.h^{-1}, MF-1.7 T, temperature 553 K, time - 3 h.

Annealing the EXOTIC 8-3/13 pebbles at a higher temperature 770 K for 1h, 17 – 24 % of localized tritium was released in the gaseous phase. The abundance ratios of the chemical forms of the residual tritium change to the following values – the molecular tritium – 30-55 %, atomic - 40-45 %, ionic form 10-14 %. After thermo-annealing EXOTIC8-3/13 pebbles at 770 K in the simultaneous presence of magnetic field and radiation, the abundances of the chemical forms of the residual tritium changes with the same trend as at 553 K - the amount of molecular tritium in the pebbles decreases considerably up to 30-40 %, the atomic tritium decreases to 20 - 30 %, but the tritium in the ionic form does not change substantially. The changes of chemical forms after treatment of EXOTIC8-3/13 pebbles are more considerable in comparison with changes in abundance ratio of tritium forms in BERYLLIUM pebbles as shown in previous investigations [4].

4. Conclusions

The main forms of tritium localized in the Be pebbles irradiated in the BERYLLIUM and EXOTIC8-3/13 experiment are molecular tritium, atomic tritium and tritium in ionic form. At thermo-annealing process under simultaneous action of radiation and MF, the chemical forms of residual tritium change. Radiation stimulates a formation of faster diffusing particle of tritium - atomic tritium, while magnetic field affect chemical reactions of tritium chemical forms in beryllium pebbles. MF changes the spin state of pairs of radicals and further reactions of radicals with molecules. MF may cause singlet-triplet transformation (S↔T).
As a pair of radicals in a singlet state for the most part recombines, but in the triplet state does not react, MF changes kinetics of high-energy chemical reactions.
As a result of this study we can conclude that additional exposure to radiation and MF simultaneously at thermo-annealing accelerates formation of atomic tritium from molecular tritium localized in the pebbles.

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