

# Ceramic Breeder Material with Catalytic Function

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## 1. Introduction

In most current designs of D-T fusion reactor blankets employing ceramic breeder materials such as  $\text{Li}_2\text{O}$ ,  $\text{LiAlO}_2$ ,  $\text{Li}_2\text{ZrO}_3$  and  $\text{Li}_4\text{SiO}_4$ , the use of a helium sweep gas containing 0.1 % of hydrogen is contemplated to extract tritium efficiently via isotopic exchange reactions. However, at lower temperatures, the release process of tritium from the breeders is dominated by the desorption of tritiated water and are therefore rather slow. For this reason, there is still a need to develop techniques that contribute to the acceleration of the recovery of bred tritium.

In our previous studies, the isotope exchange reactions and water adsorption on the surface of several solid blanket materials were investigated [1-3]. The results revealed that these isotope exchange reactions proceed fast only at more elevated temperatures. Because of the strong temperature dependence of the exchange reactions, a considerable decrease in the reaction rate takes place as temperature is lowered. Taking into consideration that there is a broad temperature distribution within a blanket module [2], it is anticipated that the tritium bred in the regions of lower temperature will presumably be poorly recovered. The result could be an increased overall steady state tritium inventory in the blanket module.

In order to obtain an improved recovery of tritium from a blanket over a broad range of temperatures, the effect of catalytic active metal additives, such as platinum and palladium, on the heterogeneous isotope exchange reactions at the breeder-sweep gas interface was examined.

These catalytic additives are irradiated in the 14 MeV neutron field during the operation of fusion reactors, which could lead to the nuclear transmutation of Pd and Pt and thus change in the chemical properties of these noble metals. Moreover, there is a possibility that nuclear reactions cause induced radioactivity related to additive metals. The authors also investigate these aspects using cross sections of the nuclear reactions.

## 2. Experimental

Platinum and palladium were deposited on solid breeder material pebbles ( $\text{Li}_4\text{SiO}_4$ , 0.51-0.94 mm (av. 0.68 mm) in diameter, >98 %TD) by the incipient wet impregnation method generally used for the fabrication of catalysts. The exact content of the deposited Pt or Pd has not yet been determined, but according to the mass balance in the fabrication process the concentrations can be estimated being within a range of 0.7 to 2 weight %; the contents never exceed 2 weight %.

A schematic diagram of the experimental apparatus is shown in Fig. 1. For a run between 2.5 and 20.0 g of Pt/Li<sub>4</sub>SiO<sub>4</sub>, Pd/Li<sub>4</sub>SiO<sub>4</sub> or Li<sub>4</sub>SiO<sub>4</sub> pebbles were placed in reactors made of quartz. The gaseous compositions of inlet and outlet streams of the reactor were analyzed with respect to H<sub>2</sub>, HD and D<sub>2</sub> by gas chromatography. A hygrometer was used to determine the water vapor content in these streams. The gas flow rate was controlled with conventional mass flow controllers. The gases employed were purified with a cold trap containing 5A molecular sieve that was cooled with an ice/water mixture to remove residual water vapor. To achieve controlled concentrations of deuterated water in the carrier gas molecular deuterium was quantitatively oxidized with a CuO bed held at 350 °C.

During runs, which were carried out under steady state conditions, the reactor temperature was stepwise decreased from the maximum experimental temperature. The experimental conditions employed are summarized in Table 1. The space velocity (*SV*) in Table 1 is defined as

$$SV = \frac{Q}{V}, \quad (1)$$

where *Q* and *V* are the volumetric velocity of the gas introduced to the reactor and the bed volume of the breeder materials, respectively. As seen in the above equation, *SV* is the reciprocal of the residence time of the process gas. Thus, the higher *SV* corresponds to the lower residence time. As shown in Table 2, the experiments on Pt/Li<sub>4</sub>SiO<sub>4</sub> and Pd/Li<sub>4</sub>SiO<sub>4</sub> were performed under higher *SV* conditions than that for the virgin material Li<sub>4</sub>SiO<sub>4</sub>. A blank test was also performed with an empty reactor, and it was confirmed that no exchange reactions take place within the experimental condition of this work.

### 3. Experimental Results and Discussion

In each experiment a gaseous mixture of helium containing H<sub>2</sub> (3500–4300 ppm) and D<sub>2</sub>O (260–300 ppm) was passed through the reactor packed with the breeder pebbles. The extent of the exchange reactions taking place on the surface of the breeder materials was obtained from the composition of the exhaust stream of the reactor measured by gas chromatography.

The ratio of conversion *R* is defined as

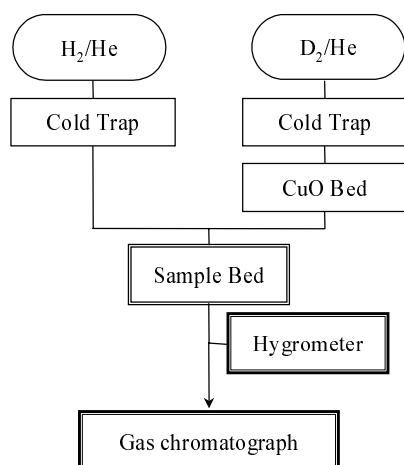


Table 1 Experimental conditions

	Li <sub>4</sub> SiO <sub>4</sub>	Pt/Li <sub>4</sub> SiO <sub>4</sub>	Pd/Li <sub>4</sub> SiO <sub>4</sub>
Amount [g]	30	2.4	2.5
Gas velocity [ml/min]	955	326	320
Bed diameter [mm]	22	16.2	16.2
Space velocity [h <sup>-1</sup> ]	2700	5500	5200
Temperature [°C]	200 – 600	25 – 400	25 – 400
Inlet gas composition			
H <sub>2</sub> [ppm]	3500	3900	4300
D <sub>2</sub> O [ppm]	300	260	260

Fig.1 Experimental flow diagram

$$R = \frac{C_{D,out}}{C_{D,in}}, \quad (2)$$

where  $C_{D,in}$  and  $C_{D,out}$  are the molar concentration of D-atoms in  $D_2O$  in the inlet stream and the molar concentration of D-atoms in HD and  $D_2$  in the outlet stream, respectively.

Figure 2 shows conversion ratios as function of temperature for the investigated breeder materials. In the case of  $Li_4SiO_4$  (without noble metals), a conversion ratio of only 33 % was attained even at 400 °C. On the contrary, on the surface of the lithium silicate containing dispersed platinum ( $Pt/Li_4SiO_4$ ), conversion ratios of nearly 90 % (almost corresponding to the equilibrium condition of the isotope exchange reaction) were obtained at temperatures of only little over 200 °C. This higher degree of conversion was attained in spite of employing a much higher space velocity than in the experiment with  $Li_4SiO_4$  (virgin material). Even at 25 °C a conversion ratio of 28 % was obtained over the  $Li_4SiO_4$  pebbles impregnated with platinum. Similar results were obtained in experiment with  $Pd/Li_4SiO_4$  pebbles, which indicates that palladium is also an effective catalyst for the enhancement of the exchange reaction. For comparison, experimental results for other ceramic breeders ( $LiAlO_2$  and  $Li_2ZrO_3$ ) are also shown in Fig. 2, which indicates poor conversions even at higher temperatures. By these results it can be concluded that isotope exchange reactions proceed at very fast rates even at temperatures below 400 °C when lithium silicate pebbles contain dispersed catalytic active noble metals. The improved solid breeder materials are here designated as catalytic breeder material. Thus, a considerable enhancement effect for the release of tritium from catalytic breeder materials is expected. One could consider the use of the insoluble residues from nuclear reprocessing of spent nuclear fuel that is known to contain large amounts of metals like Pt, Pd or Rh. While these materials cannot be utilized by conventional industries, a use for the fabrication of catalytic breeder materials is thought to become their practical application.

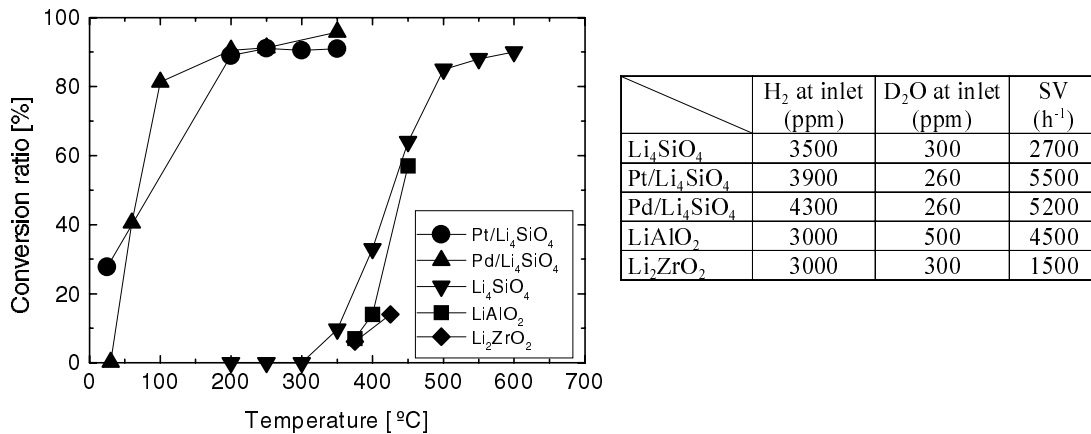
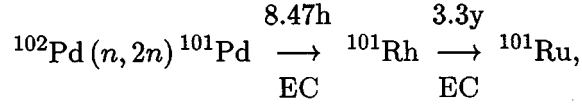


Fig. 2 Conversion ratio of  $D_2O$  into HD or  $D_2$  over various breeders

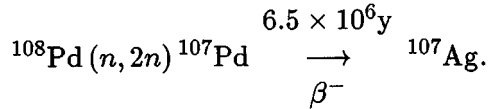
#### 4. Need for Nuclear Data of Catalytic Breeder Materials

Nuclear data of the catalytic metals are required for two aspects, the evaluation of induced radioactivity and nuclear transmutation. To estimate the induced radioactivity of Pd and Pt, we surveyed long-lived nuclei in the decay chain of the nuclear reactions. A particle

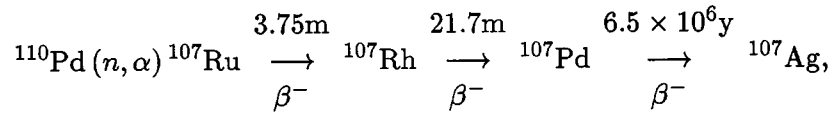
emission process is dominant in the 14 MeV neutron-induced reactions, and thus residual nuclei produced via  $(n,2n)$ ,  $(n,p)$ , and  $(n,\alpha)$  reactions are the parents of the decay chains. For Pd the important nuclear decay processes, which produce long-lived nuclei, are ( $T_{1/2}$  data taken from Ref. [4]),



and

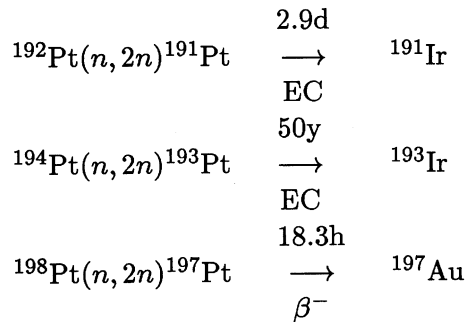


The first process produce only a small amount of radioactive nuclei ( $^{101}\text{Pd}$ ) because the natural abundance of  $^{102}\text{Pd}$  is only 1.02 %, and the half life of  $^{101}\text{Rh}$  is not so long in comparison with the duration of operation of the fusion blanket modules. The second process yields a long-lived product  $^{107}\text{Pd}$ . The natural abundance of  $^{108}\text{Pd}$  is 26.5 % and therefore an accurate cross section of the  $^{108}\text{Pd}(n,2n)$  reaction is required to estimate the induced radioactivity of the catalytic breeder materials. This nucleus is also produced by the chain



but its yield is expected to be small since the  $(n,\alpha)$  reaction cross section at 14 MeV is  $<1$  mb in JENDL-3.2.

In the case of 14 MeV neutron-induced reactions on Pt, the charged particle emission processes is thought to be ignorable, and the  $(n,2n)$  reaction could be an important process for the production of long-lived nuclei. The decay schemes of the residual nuclei are as follows:

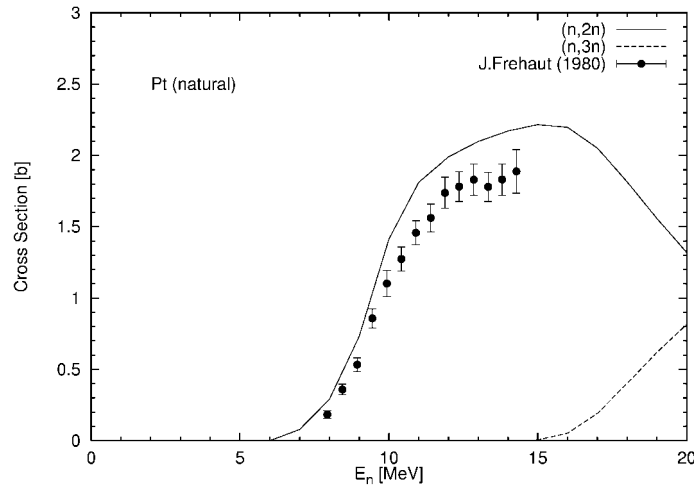


Residual nuclei of the  $^{195,196}\text{Pt}(n,2n)$  reaction are stable. Therefore, a  $(n,2n)$  reaction on  $^{194}\text{Pt}$ , of which natural abundance is 32.9 %, is a major process with regard to induced radioactivity.

The evaluated nuclear data of Pd are available in JENDL-3.2, whereas no data on Pt are given so far. Accordingly we calculated the cross sections of  $^{\text{nat}}\text{Pt}(n,2n)$  and  $(n,3n)$  reactions with the GNASH code[5]. The model parameters used were the Walter and Guss' global optical potential[6], and the level density parameters proposed by Yamamuro[7]. The calculated cross sections of  $(n,2n)$  and  $(n,3n)$  reactions are compared with the experimental data[8] in Fig. 3. No attempt was made to improve the accuracy of fitting in this calculation, and thus the calculated cross section is about 15 % larger than the experimental values.

With these nuclear data, one can estimate transmutation rates of noble metals in the fusion blanket. A rough estimation of the transmutation rate  $R \text{ s}^{-1}$  is given by  $R = \Phi \sigma$ ,

where  $\Phi$  is a flux of 14-MeV neutrons, and  $\sigma$  is a cross section of the reaction in which the residual nucleus changes into other atoms with different chemical property. The neutron flux for the ITER design is about  $10^{13} \text{ cm}^{-2} \text{ s}^{-1}$  at just outer side of the first wall, then the estimated  $R$  is less than 1 % per 10 years for both Pt and Pd. Therefore, transmutation of noble metals is a minor problem for a design of the catalytic breeder materials.



**Fig.3 Comparison of the calculated  $^{nat}\text{Pt}(n,2n)$  and  $(n,3n)$  reaction cross section with the experimental data**

## 5. Conclusions

Catalytic breeder materials were produced by impregnating lithium silicate with either platinum or palladium. The isotope exchange reactions between molecular protium and gaseous perdeuterated water over these new breeder materials were found to be very fast even at temperatures far below 400 °C. Nuclear data of noble metals were surveyed to estimate the induced radioactivity and the transmutation rate. It was found that the  $(n,2n)$  reaction produces  $^{107}\text{Pd}$  and  $^{194}\text{Pt}$  which have long half-life, and that less than 1 % of noble metals will be transmuted during 10-year-operation of a fusion reactor of ITER-class design.

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