

# Design of a System for Hydrogen isotopes Injection into Lead-Lithium

Belit Garcinuño<sup>a,b</sup>, David Rapisarda<sup>a</sup>, Carlos Moreno<sup>a</sup>, Javier Sanz<sup>b</sup> and Ángel Ibarra<sup>a</sup>

<sup>a</sup> CIEMAT, Fusion Technology Division, Avda. Complutense 40, 28040 Madrid, Spain

<sup>b</sup> UNED, Dept. of Energy Engineering, C/Juan del Rosal 12, 28040 Madrid, Spain

corresponding author: belit.garcinuno@ciemat.es

In a fusion reactor based on liquid breeding blankets, tritium is generated due to the neutron irradiation of lithium based alloy, such as eutectic lead-lithium (PbLi). Then, tritium is extracted from the liquid metal by means of technologies that are presently under development such as the vacuum sieve tray, the permeation against vacuum or the gas liquid contactors. Nevertheless, for the experimental validation of these technologies at laboratory scale, hydrogen isotopes cannot be generated in situ in the liquid metal as in the breeding blanket. Hence, a system able to inject the gas in the flowing liquid at desired concentrations is required, avoiding the formation of bubbles as a consequence of the low solubility of hydrogen/deuterium in PbLi. The system should be capable of solubilizing the hydrogen to replicate as close as possible the conditions of a breeding blanket.

A design of an injector based on a permeable membrane is here presented, being the driving force the gradient of concentrations existing between the two surfaces of the membrane. A hydrogen transport model for a tube-in-tube injector has been developed, showing that the injected hydrogen flux is proportional to the tube radius. However, the change on this parameter, that affects the velocity of the liquid and thus the mass transport coefficient, has opposite consequences on the rate of injection whose final impact relays on the properties of the employed membrane.

An evaluation of the physical and geometrical aspects of a conceptual injector is depicted with the aim of optimizing the design to obtain adequate injection rate depending on the facility where the injector is installed. Finally, a conceptual design of a system to be implemented in an experimental PbLi loop for the validation of the permeation against vacuum technique for tritium extraction from PbLi is presented. The injector is based on a multi-tube component made of niobium able to inject hydrogen at the same rate as it is extracted under relevant conditions for a Dual Coolant Lithium Lead breeding blanket.

Keywords: hydrogen injection, permeation, tritium extraction

## 1. Introduction

In future fusion plants, due to the  $\text{Li}^6(n,\alpha)\text{T}$  reaction tritium would be generated in the breeding blanket (BB) to be further extracted in dedicated systems to accomplish with the plant tritium self-sufficiency [1]. Blankets currently considered in EUROfusion using a liquid metal as breeder material employs the eutectic lead lithium (PbLi) alloy as tritium breeder, tritium carrier and neutron multiplier and, in the case of the Dual Coolant Lithium Lead (DCLL [2], [3]) it is also used as primary coolant. The other two concepts are based on helium (Helium Coolant Lithium Lead, HCLL [4]) and water (Water Coolant Lithium Lead, WCLL [5]) as primary coolant.

One of the main issues regarding the mentioned self-sufficiency is the recovery of tritium from the PbLi, since the system has to be capable of managing huge amounts of material with adequate extraction efficiency [6], [7]. Thus, large R&D activities are being performed within the field of tritium extraction from liquid metal technologies. The main objective is focused on designing components devoted to hydrogen isotopes removal from PbLi based on different techniques such as the vacuum sieve tray [8], the permeation against vacuum [9] or the gas liquid contactors [10]. In addition, some efforts are put on the development of sensors to measure the hydrogen content in the PbLi, but they are still on a recent grade of maturity since the stabilization times are large and the measurement takes several hours ([11], [12]). The experimental validation of these technologies is performed in dedicated PbLi loops aiming to reproduce conditions as close as possible to those of a fusion reactor but working with other hydrogen species (hydrogen, deuterium) due to the limitations in managing tritium. As an example, the Melodie loop is an experimental facility dedicated to the assessment of gas liquid contactors [13]. In this facility the behaviour of a packed column was investigated with the aim to develop the tritium recovery process for a WCLL. By varying the operational conditions, an extraction efficiency for hydrogen up to 30% was obtained. More recently, a loop called TRIEX [14] was built in ENEA to test the same technique but working under HCLL conditions. The main components of the loop are the recirculation tank, the saturator tank, the injector and the extraction column. Different experiments were carried out to experimentally determine the efficiency of the extraction system which was in the range between 10 and 30% [15], showing a good agreement with the previous reported results [13]. On the other side, the recovery of hydrogen by means of a bubbling tower is explored in [16]. Not focused on the efficiency of the system, the purpose of the work is to determine the mass transfer coefficient under conditions of wide temperature and wide hydrogen partial pressure. In CIEMAT, a PbLi loop

for the validation of the permeation against vacuum technique is under development [17]. The loop, called CLIPPER, is designed to demonstrate the extraction technology under DCLL conditions of high PbLi temperature, PbLi velocity and hydrogen concentration [18].

However, the experimental validation of the above technologies requires a system for hydrogen isotopes injection into the liquid metal, since hydrogen cannot be generated in situ in PbLi as it is originated inside the BB. The most extended technique is based on hydrogen bubbling into the liquid either in static [16] or dynamic conditions [13], [14]. The system is based on the injection of a mixture of a small percentage of hydrogen in argon carrier gas leaving it to saturate the liquid metal prior starting the extraction process. Following this methodology, the reported hydrogen pressures in PbLi are between 1.0 and  $10^4$  Pa to simulate WCLL [13] or HCLL [15] conditions.

Some basic requirements must be followed for an injector to be suitable for this application and to help to experimentally demonstrate the validity of the associated technologies. It should:

- Solubilize hydrogen into the liquid metal
- Procure an uniform distribution of the hydrogen within the liquid

In the present work a completely different approach of hydrogen/deuterium injection into PbLi, based on forced permeation, is presented. It consists on a permeable membrane in a tube-in-tube component; the inner tube containing the flowing liquid metal and the outer tube a constant gas pressure. Therefore, the material of the inner tube, in contact both with the PbLi and the gas, has to be selected with the aim of facilitate the permeation. The advantages of this kind of system are that the liquid metal flow is not perturbed since there are no parts in the path of the flow; the gas injected is distributed uniformly along the surface in contact with the liquid; the possibility of bubbles formation is reduced and the solubilisation is enhanced because isotopes are injected in atomic form.

A model of gas injection that relates the physical and geometrical aspects of the system is presented (section 2). It tries to guide the optimization of a design able to introduce a certain concentration of hydrogen in the PbLi. The parameters affecting the behaviour of the transport are evaluated and analysed in order to obtain the better conditions for the design of an injector (section 3) and its applicability to an experimental loop (section 4).

## 2. Model of Forced Permeation

The development of a model that correlates all the parameters of the permeation process of injection is presented. The principle is based on the difference of pressure existing between the two sides of a permeable membrane. The inner surface is in direct contact with the liquid metal. In the outer surface, a controlled gas pressure is applied. The effectiveness of the gas injection into the liquid metal depends on the properties and geometry of such membrane.

A model of a tube-in-tube injector is proposed, where the liquid metal flows across the inner tube, which is connected to the main PbLi loop (Figure 1). An external case contains pressurized hydrogen (or deuterium, depending on the experiment) at a given pressure (Figure 1). To guarantee the hydrogen flux to the PbLi, the outer tube should avoid any gas leakage to the exterior and materials with low permeability are preferable.

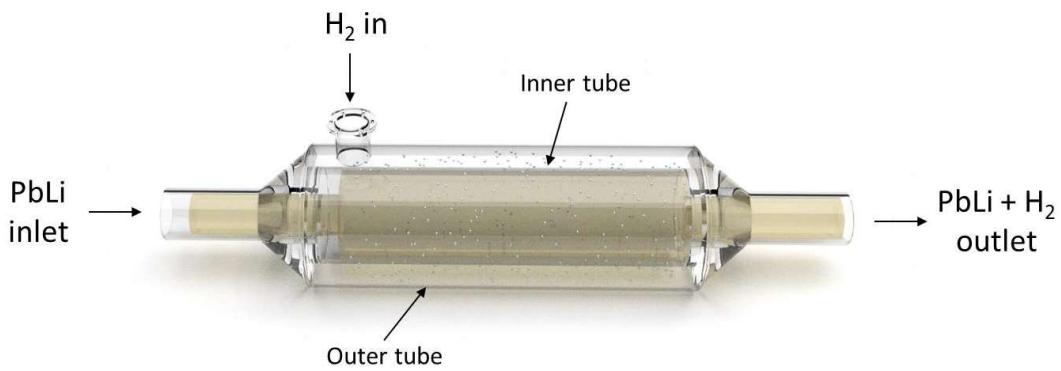


Figure 1. Artistic view of a tube-in-tube injection system

In order to obtain a relation between the hydrogen pressure to be applied in the injector and the desired concentration in the PbLi, a model of transport based on diffusive-limited [19] permeation for this kind of geometry has been developed.

To start with, a mathematical analysis of hydrogen diffusion from the inner tube to the bulk of the PbLi has been made. A pressure of hydrogen is applied to the outer face of the inner tube where, according to Sieverts' law, it is

solubilized. Then, hydrogen diffuses from the outside with a flux ( $J$ ) that depends on the concentration gradient and the diffusivity of the membrane ( $D$ ) according to Fick's law (eq. 1):

$$J = -D \frac{dC}{dr} \quad \text{eq. 1}$$

The concentration in the solid (eq. 2) is given by the solution to the diffusion equation in a cylinder as seen in [20], where  $r_i$  and  $r_o$  are the inner and outer radius of the cylinder, respectively, and  $C_s$  and  $C_h$  are the concentration in the membrane at  $r_i$  and  $r_o$ .

$$C(r) = \frac{C_s \cdot \ln \frac{r_o}{r} + C_h \cdot \ln \frac{r}{r_i}}{\ln \frac{r_o}{r_i}} \quad \text{eq. 2}$$

The concentration in the liquid-membrane surface ( $C_L$ ) is related with that from the solid-membrane interface ( $C_s$ ) via the solubility coefficients, eq. 3, being  $K_L$  and  $K_s$  the liquid and solid solubilities, respectively.

$$\frac{C_L}{C_s} = \frac{K_L}{K_s} \quad \text{eq. 3}$$

Substituting the concentration in the solid with that from the interface condition, and given that the flux is positive in the direction of the radius decrease, the equation for the radial flux variation across the membrane is obtained, eq. 4:

$$J_{\text{membrane}} = D \cdot \frac{C_h - \frac{K_s}{K_L} C_L}{r_i \ln \frac{r_o}{r_i}} \quad \text{eq. 4}$$

The flux through the membrane, eq. 4, is equal to the flux from the membrane to the bulk ( $J_{\text{liquid}}$ ) which depends on the mass transport coefficient ( $K_T$ ) and the concentration in the liquid ( $C_{\text{PbLi}}$ ):

$$J_{\text{liquid}} = K_T \cdot (C_L - C_{\text{PbLi}}) \quad \text{eq. 5}$$

Where the mass transport coefficient depends on the PbLi diffusivity ( $D_{\text{PbLi}}$ ), the Sherwood number [21] and the diameter of the tube [22], eq. 6

$$K_T = \frac{D_{\text{PbLi}} \cdot Sh}{2 \cdot r_i} \quad \text{eq. 6}$$

To obtain  $C_L$ , both equations (eq. 4 and eq. 5) are equalled. In eq. 7, the permeability ( $\phi$ ) of the membrane is introduced as the product between solubility ( $K_s$ ) and diffusivity ( $D$ ):

$$C_L = \frac{D \cdot K_L \cdot C_h}{K_T \cdot K_L \cdot r_i \ln \frac{r_o}{r_i} + \phi} + \frac{C_{\text{PbLi}}}{1 + \frac{\phi}{K_T \cdot K_L \cdot r_i \cdot \ln \frac{r_o}{r_i}}} \quad \text{eq. 7}$$

Substituting eq. 7 in eq. 5 the entering hydrogen flux is obtained as a function of the geometrical and physical parameters of the system:

$$J' = K_T \cdot \left( \frac{K_L \cdot D \cdot C_H}{K_T \cdot K_L \cdot r_i \cdot \ln \frac{r_o}{r_i} + \emptyset} + C_{PbLi} \cdot \left[ \frac{1}{1 + \frac{\emptyset}{K_T \cdot K_L \cdot r_i \cdot \ln \frac{r_o}{r_i}}} - 1 \right] \right)$$

eq. 8

As during the operation of the facility the liquid metal is flowing through the gas injector system, the hydrogen transport in the axial direction (x) has to be also analysed. Thus, the evaluation of the flow rate over a fluid element of length  $\Delta x$  is performed. The flow entering the injection system ( $\dot{m}_{in}$ ) depends on the cross section area, the liquid velocity (v) and the concentration, through the following equation

$$\dot{m}_{in} = \pi \cdot r_i^2 \cdot v \cdot C_{PbLi}(x)$$

eq. 9

In the same way, the flow rate exiting ( $\dot{m}_{out}$ ) the system is

$$\dot{m}_{out} = \pi \cdot r_i^2 \cdot v \cdot C_{PbLi}(x + \Delta x)$$

eq. 10

The difference between these flows is due to hydrogen permeation through the wall ( $\dot{m}_{per}$ ) which depends on the surface of permeation and the flux ( $J'$ , eq. 8),

$$\dot{m}_{per} = 2 \cdot \pi \cdot r_i \cdot \Delta x \cdot K_T \cdot \left( \frac{K_L \cdot D \cdot C_H}{K_T \cdot K_L \cdot r_i \cdot \ln \frac{r_o}{r_i} + \emptyset} + C_{PbLi}(x) \cdot \left[ \frac{1}{1 + \frac{\emptyset}{K_T \cdot K_L \cdot r_i \cdot \ln \frac{r_o}{r_i}}} - 1 \right] \right)$$

eq. 11

A balance of the fluxes gives the differential equation of the concentration over the length of the tube.

$$\frac{dC_{PbLi}(x)}{dx} + C_{PbLi}(x) \left[ \frac{2 \cdot K_T \cdot \emptyset}{v \cdot r_i \cdot (K_T \cdot K_L \cdot r_i \cdot \ln \frac{r_o}{r_i} + \emptyset)} \right] - \left[ \frac{2 \cdot K_T \cdot K_L \cdot D \cdot C_H}{v \cdot r_i \cdot (K_T \cdot K_L \cdot r_i \cdot \ln \frac{r_o}{r_i} + \emptyset)} \right] = 0$$

eq. 12

Resolving the non-homogenous differential equation, the concentration variation over the length (L) of the tube is,

$$C_{PbLi}(x) = \left( C_o - \frac{K_L \cdot D \cdot C_H}{\emptyset} \right) e^{\left[ -\frac{2 \cdot K_T \cdot \emptyset}{v \cdot r_i \cdot (K_T \cdot K_L \cdot r_i \cdot \ln \frac{r_o}{r_i} + \emptyset)} x \right]} + \frac{K_L \cdot D \cdot C_H}{\emptyset}$$

eq. 13

Substituting into eq. 8 and integrating over the surface of the injector, the entering flux is finally obtained as a function of the initial concentration in the PbLi,  $C_o$ , and the concentration in the membrane,  $C_H$ , resulting from the applied pressure in the outer tube,

$$J = \pi \cdot r_i^2 \cdot v \cdot N \cdot \left[ \left( \frac{K_L \cdot D \cdot C_H}{\emptyset} - C_o \right) \cdot \left( 1 - e^{\left[ -\frac{2 \cdot K_T \cdot \emptyset \cdot L}{v \cdot r_i \cdot (K_T \cdot K_L \cdot r_i \cdot \ln \frac{r_o}{r_i} + \emptyset)} \right]} \right) \right]$$

eq. 14

Here,  $N$  denotes the number of inner tubes used for the injection, i.e. the number of tubes in where the PbLi flow is spread. This parameter comes as an element that directly affects the surface of permeation.

This equation, eq. 14, correlates geometrical parameters of the injector such as its length, radii, membrane thickness (through the logarithm of the relation  $r_o$  and  $r_i$ ) and number of tubes with physical aspects of the material used as membrane (i.e. the permeability). It also considers the transport process inside the liquid metal; therefore it is dependent on the solubility, diffusivity and mass transport of the gas injected.

An evaluation of the influence of some of those coefficients has to be assessed prior to design an injection system; the solubility and diffusivity of the gas in the liquid metal increase, may enhance the flux; the radius and number of tubes and velocity of liquid metal may improve the injection. Nevertheless, as will be described in the next section, there are opposite effects when these parameters change that must be analysed to optimize the behaviour of the injector.

### 3. Conceptual design of the Injection System

The model developed in the previous section has been used to evaluate the influence of each of the injector parameters on the design of the injection system. For this aim, operational limits typically useful in experimental PbLi loops have to be used (PbLi temperature, tritium concentration). Table 1 summarizes the main data for the three liquid metal-based BB considered in the EUROfusion project [1]. It is worth noting that there is an important difference in the PbLi temperature for the DCLL when comparing with the other two BB concepts. The reason is that, as previously stated, the DCLL extracts most of the reactor power thanks to the liquid metal, implying a higher temperature of the coolant [2].

Table 1. Parameters from different breeding blanket concepts of interest for the design of the gas injector

Breeding Blanket Concept	Temperature at PbLi loop	Total PbLi flow rate	Tritium concentration
DCLL	535 °C	26466.8 kg/s	5.56 E-4 mol/m <sup>3</sup>
WCLL	311.5 °C	956.3 kg/s	1.41 E-2 mol/m <sup>3</sup>
HCLL	300 °C	1040-2080 kg/s	6.61 E-3 - 1.32 E-2 mol/m <sup>3</sup>

The material of the inner tube has to follow requirements of high permeability to hydrogen/deuterium; compatibility with PbLi; withstand high temperatures. The use of elements such as aluminium, copper, nickel, titanium and zirconium should be avoided since they have a low hydrogen diffusivity and bad compatibility with PbLi [23], [24]. There are several possibilities, as shown in a previous dissertation about available and proper materials with application in this field [9]. Pure materials such as palladium, platinum, iron (Fe), vanadium are compared with alloys and composite compounds (Pd/Ag; VCo; NbTiCo; SS316) showing that the most promising materials for their application as a permeable membrane are vanadium (V), niobium (Nb) and tantalum (Ta) due to their good permeability [25] and tested compatibility with PbLi [26]. In this work, Nb and Fe are compared as possible materials for the membrane of the injector. In spite of the low permeability of Fe, [27], this material may lead to enough injection capability in order to demonstrate the permeation technique. With regard to the outer tube, it constitutes a cover case for the inner injecting tubes (see Figure 1). This outer tube contains the gas at the required pressure. As mentioned, to avoid a loss of pressure, the material should have a low hydrogen permeability. Thus, a case of stainless steel 316L has been selected due to its low permeability ( $\phi$  (535 °C) = 1.50E-11 mol/m·s·Pa<sup>0.5</sup>) [28]. A thickness of 2 mm is enough to withstand the operation pressures of the injection system.

Special concern requires the solubility of hydrogen in PbLi. It has been previously reported the existence of dispersion in the measured solubility coefficients ([29], [30]). This may be caused by the technique applied for its obtainment, the purity of the liquid metal or the eutectic grade of the alloy. As a consequence, there is a large uncertainty in the expected behaviour of PbLi systems depending on this parameter [31]. For this reason, two limit values are considered for the study, Reiter's [32] and Aiello's [33] solubility. As an example and following Table 1, at 535 °C the tritium partial pressure would vary between 2.52E-4 Pa (Aiello) and 2.91E-1 Pa (Reiter).

An evaluation of eq. 14 shows the importance of the different parameters on the injection process. Some of them have an influence on the hydrogen flux which can be directly deduced, for the others a more careful analysis is required, as will be shown in this section (Figures 2 to 5). In the first group of parameters is the length of the tube. According to eq. 14, as the tube is lengthened, the process is enhanced as a consequence of the increase on the surface of injection in contact with the liquid metal. In parallel, with regard to the thickness of the membrane, it is deduced that as the relation between outer

and inner radii is reduced, the permeation through the membrane becomes more favoured and, consequently, the process is enhanced.

The behaviour of the injected hydrogen flux as a function of the radius of the tube is presented in Figure 2, considering different radii of tubes commercially available. Results have been obtained for the case of a DCLL (see Table 1) where the PbLi temperature and mass flow are considerably high and there is a low hydrogen concentration. In parallel, a first approximation of the length and number of tubes ( $L = 0.5$  m;  $N = 1$ ) is chosen considering an easy implementation at laboratory scale. According to eq. 14, as the radius is increased, the flux would be enhanced. Nevertheless, there are two opposite factors affecting this behaviour. First of all, the surface becomes larger; therefore, the PbLi is more exposed to the hydrogen income facilitating the injection. On the other side, the increase on  $r_i$  causes a decrease in the mass transport coefficient requiring a higher pressure applied on the gas side. Hence, the two consequences of increasing the radius are contrary. Moreover, the PbLi velocity also depends on the tube radius through the mass flow rate. Hence, for a fixed flow, the consequent decrease on velocity with the increase on radius causes the mass transport coefficient to diminish even more.

For a Nb based tube, as can be observed in Figure 2 (solid line), when the radius of the tube increases the flux of hydrogen entering into the liquid metal to achieve a certain concentration is lower. The permeability of this material ( $\phi_{Nb}$  (535 °C) = 2.6032E-7 mol/m·s·Pa<sup>0.5</sup>) is so high that the process is governed by the transport in the liquid, from the wall of the membrane to the bulk. At higher radii the distance from the wall to the centre of the tube is larger and therefore this process becomes difficult, as a consequence of the faster permeation through the membrane versus the transport in the liquid. When considering a Fe membrane (dotted line in Figure 2), the permeation of hydrogen through the membrane ( $\phi_{Fe}$  (535 °C) = 1.6038E-11 mol/m·s·Pa<sup>0.5</sup>) is slower than the transport in the liquid due to the lower permeability of this material. Thus, the hydrogen flux is higher as the radius increases because the surface of permeation is being enlarged and this factor has more impact on the injection process than the transport itself.

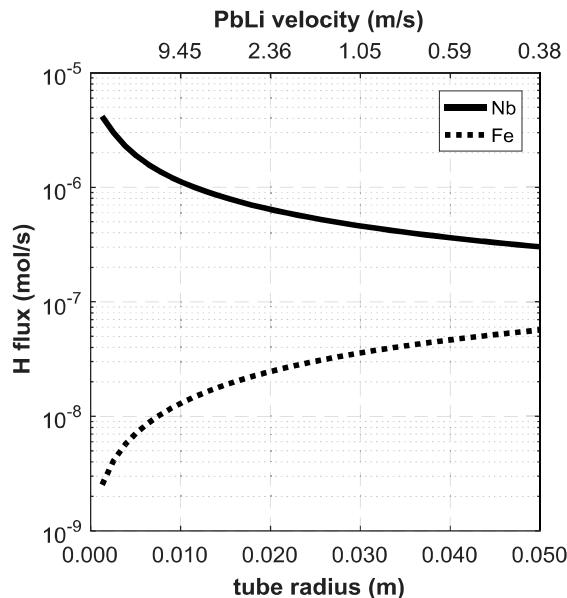


Figure 2. H flux vs. tube radius. ( $P_{H_2} = 100$  Pa;  $C_{PbLi} = 5.56E-4$  mol/m<sup>3</sup>;  $T_{PbLi} = 535^\circ\text{C}$ ;  $L = 0.5$  m;  $N = 1$ ; PbLi mass flow = 28 kg/s; Reiter's solubility;  $\phi_{Nb} = 2.60E-7$  mol/m·s·Pa<sup>0.5</sup>;  $\phi_{Fe} = 1.60E-11$  mol/m·s·Pa<sup>0.5</sup>)

Regarding the number of tubes to be used for the injection of hydrogen into the PbLi, it is straightforward that with more tubes, the hydrogen flux would be higher (Figure 3) due to the increase of the surface exposed to the liquid metal. Nevertheless, it is found here a similar effect on the velocity as the caused by the increase on the radius. For a fixed mass flow rate in the loop, the velocity diminishes with the increase of the number of tubes and therefore the mass transport coefficient decreases. At the end, as shown in Figure 3, the global effect is to improve the process although it is not linear as in principle one can deduct from eq. 14.

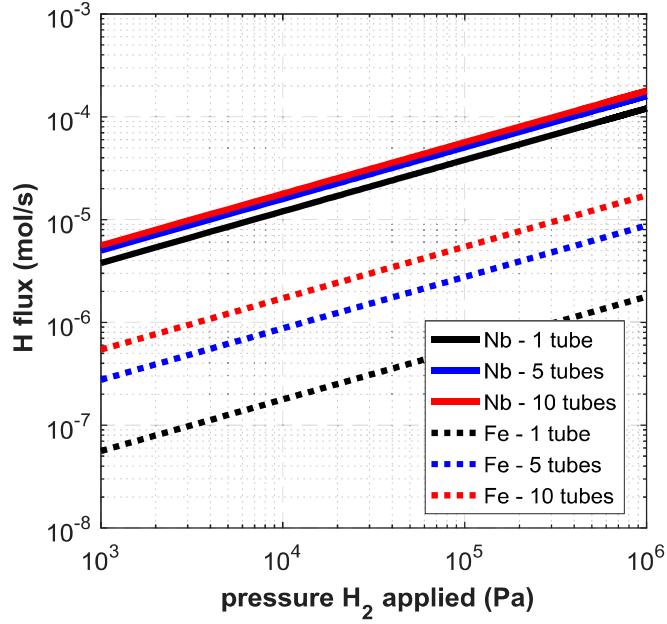


Figure 3. Influence of the number of tubes on the hydrogen injection versus the gas pressure applied ( $C_{\text{PbLi}} = 5.56\text{E-}4 \text{ mol/m}^3$ ;  $T_{\text{PbLi}} = 535^\circ\text{C}$ ;  $L = 0.5 \text{ m}$ ;  $r_i = 0.0127 \text{ m}$ ; PbLi mass flow = 28 kg/s; Reiter's solubility;  $\phi_{\text{Nb}} = 2.60\text{E-}7 \text{ mol/m}\cdot\text{s}\cdot\text{Pa}^{0.5}$ ;  $\phi_{\text{Fe}} = 1.60\text{E-}11 \text{ mol/m}\cdot\text{s}\cdot\text{Pa}^{0.5}$ ).

Figure 4 shows how the solubility of hydrogen in the liquid metal affects the injection process. It can be seen that, when comparing the two values considered for the solubility of hydrogen in PbLi, a substantial difference is observed in the obtained hydrogen flux. The solubility constant for Reiter is lower in comparison with Aiello's one. This means that for the same pressure, the concentration of hydrogen solubilized in the liquid metal is higher when Aiello's constant is considered. Hence, the flux is higher and therefore the required pressure to reach a certain concentration in the liquid is lower (Figure 4). The difference between the two coefficients is more accentuated in the case of Nb due to the higher dependence on liquid transport processes when compared with Fe, as seen previously.

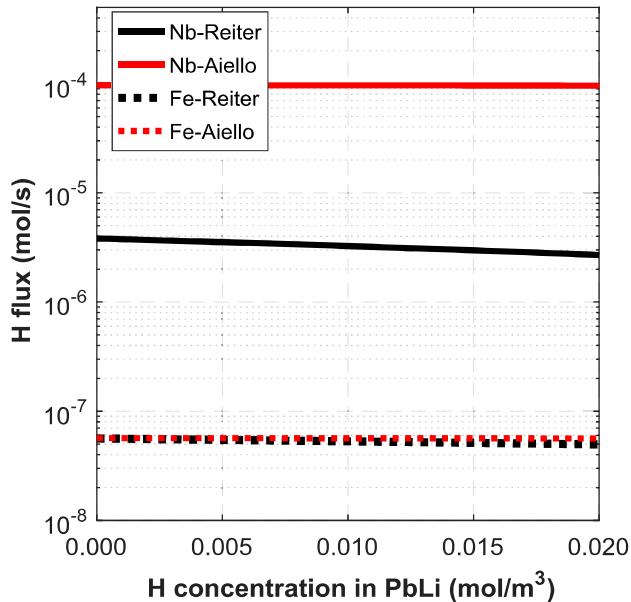


Figure 4. Hydrogen flux variation with the solubility of H in PbLi. ( $P_{\text{H}_2} = 100 \text{ Pa}$ ;  $C_{\text{PbLi}} = 5.56\text{E-}4 \text{ mol/m}^3$ ;  $T_{\text{PbLi}} = 535^\circ\text{C}$ ;  $L = 0.5 \text{ m}$ ;  $r_i = 0.0127 \text{ m}$ ;  $N = 1$ ;  $v_{\text{PbLi}} = 1.5 \text{ m/s}$ ;  $\phi_{\text{Nb}} = 2.60\text{E-}7 \text{ mol/m}\cdot\text{s}\cdot\text{Pa}^{0.5}$ ;  $\phi_{\text{Fe}} = 1.60\text{E-}11 \text{ mol/m}\cdot\text{s}\cdot\text{Pa}^{0.5}$ )

Finally, the influence of the PbLi temperature on the hydrogen flux needed to reach a certain concentration in PbLi (in this case that for the DCLL) is presented in Figure 5. Calculations have been performed both for Nb (solid line) and Fe (dotted line) to see the impact of the material permeability (note that the black Fe line is below the red one). As the temperature increases, the flux is enhanced due to the increase of the different parameters defining the liquid transport processes (mass transport, diffusion, solubility). Although for Nb the permeability decreases with temperature [23], it does not have a negative impact on the flux, as can be seen in Figure 5. This is explained by the fact that the other factors affecting the global process are being improved faster with regard to the injection than the decrease on the permeability.

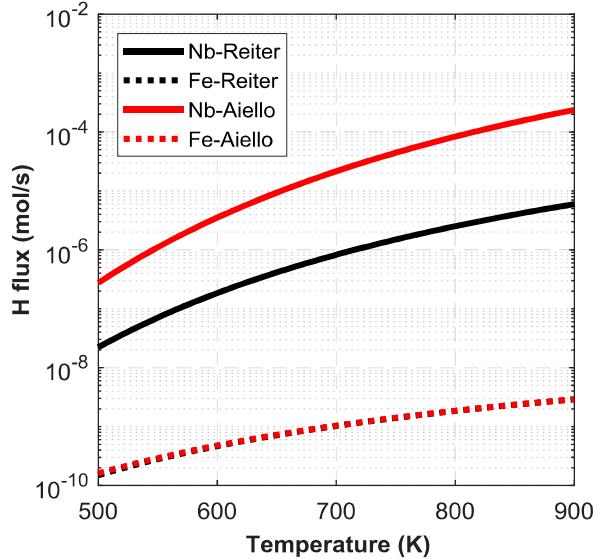


Figure 5. Influence of PbLi temperature on the entering flux of hydrogen for two different membrane materials. ( $P_{H_2} = 100 \text{ Pa}$ ;  $C_{PbLi} = 5.56E-4 \text{ mol/m}^3$ ;  $L = 0.5 \text{ m}$ ;  $r_i = 0.0127 \text{ m}$ ;  $N = 1$ ;  $v_{PbLi} = 1.5 \text{ m/s}$ ;  $\phi_{Nb} = 6.3E-9 \cdot \exp(25 \text{ kJ/RT}) \text{ mol/m} \cdot \text{s} \cdot \text{Pa}^{0.5}$ ;  $\phi_{Fe} = 1.77E-9 \cdot \exp(-31.6 \text{ kJ/RT}) \text{ mol/m} \cdot \text{s} \cdot \text{Pa}^{0.5}$ )

From all these results it can be concluded that Nb presents a better performance for its application on the construction of an injector system than Fe. As previously mentioned, other materials could also be used, but Nb presents good compatibility to work in contact with the PbLi and owns the highest permeability of the group V metals. In the range of temperatures and concentrations evaluated, this material provides better operational conditions in terms of required gas pressure and sizing of the system, facilitating the implementation in an experimental facility.

#### 4. Application to an experimental PbLi loop.

As presented in [17] and described in [18], a new PbLi loop to test the permeation against vacuum technique is being constructed, CLIPPER (CIEMAT Lithium Lead loop for Permeation exPERiments). The objectives of the loop are focused on the validation of the technique based on permeation against vacuum for hydrogen extraction from PbLi, although other techniques could be also validated in future. The design of the loop will allow the experiments to be performed at different temperatures and PbLi flow rates, but mainly to test the technology at DCLL relevant conditions of PbLi temperature, velocity and tritium concentration (Table 1). The main parameters of the loop are depicted in Table 2.

Table 2. CLIPPER main operational parameters

Parameter	Value
Temperature	300-550 °C
PbLi mass flow rate	2-39 kg/s
PbLi pressure	1-3 bar
PbLi volume	0.03 m <sup>3</sup>
Pipes length	12 m

The extraction system, consisting on a permeator against vacuum, is based on a multi-channel component with alternated channels for PbLi and vacuum made of a vanadium membrane [18]. This small prototype of PAV, called TRITON (TRITium permeatiON) has been developed conditioned by the PbLi loop parameters (Table 2) and based on a

design which could be extrapolated for a DCLL DEMO reactor [9]. The design is based on the efficiency optimization, defined as the ratio between the difference of the inlet and outlet hydrogen concentrations and the concentration at the inlet. For this aim, an equation which relates physical and geometrical properties of a permeator against vacuum was developed [9], being possible to adjust the design according to the operational parameters of the loop. The range of efficiencies expected for TRITON in CLIPPER is between 21 and 39%, depending on the selected mass flow rate via de electromagnetic pump. When working at relevant conditions for a DCLL BB (Table 1) the permeator should provide an efficiency of 22%.

Based on the operational conditions of the extractor, a conceptual design for an injection system and its integration in CLIPPER has been performed. With the objective of optimizing the performance of the injector in the loop, a condition has been established for injecting hydrogen at the same rate as it is being extracted in the permeator, i.e. the flux of hydrogen entering into the PbLi ( $J_{INJ}$ ) should be the same as the flux exiting the liquid ( $J_{EXT}$ ), Figure 6.

The operational parameters have been fixed to DCLL relevant conditions of temperature, velocity and hydrogen concentration, the same as in the case of TRITON design. Hence, applying eq. 14 and following the conclusions obtained in section 3, the final dimensions of the system are obtained. It is worth noting that the injector could be applied for the validation of other extraction techniques adjusting the performances of the system (dimensions, number of tubes, membranes...). Selecting Nb as the membrane material, the rest of geometrical parameters are summarized in Table 3. Note that, as explained in the previous section, when Reiter's solubility is considered the requirements of pressure applied in the injector are more demanding, therefore this scenario has been selected in the optimization procedure to assure that the established conditions are reached.

The area of the PAV membrane is  $1.12 \text{ m}^2$  [18] while the area of the injection system is  $0.46 \text{ m}^2$ . Even though the principle of operation is based on the permeability through a membrane, the conditions of each system are different. In the PAV, the pressure gradient is established by performing vacuum in the free side of the membrane and the tritium concentration is rather low (see Table 1). In contrast, the injector is based on the application of a high pressure to force the permeation, reaching a huge gradient of hydrogen. Thanks to this, the membrane area required for the injector system is much lower than the PAV system.

Table 3. Parameters of an injection system to work in CLIPPER

Parameter	Value
Material	Niobium
Inner radius	$0.0127 \text{ m}$
Wall thickness	$0.002 \text{ m}$
Length	$0.2 \text{ m}$
Tubes	5
Total membrane area	$0.46 \text{ m}^2$

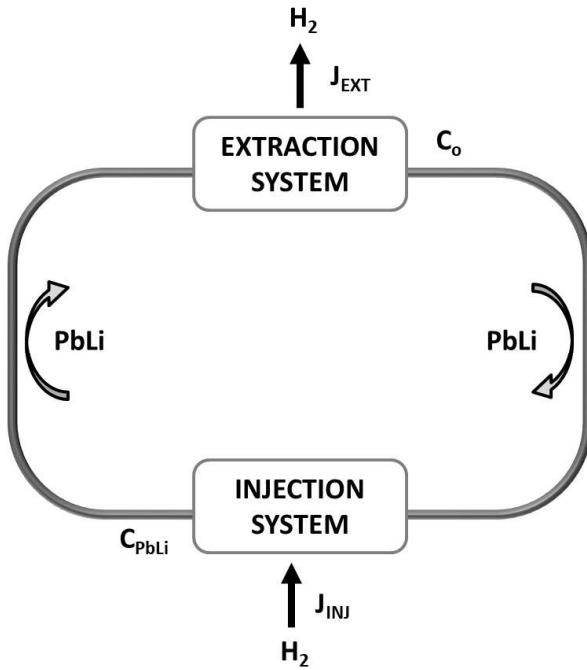


Figure 6. Simplified scheme of PbLi loop CLIPPER

Following Figure 7 it is straightforward to see the variation on the equilibrium concentration that can be fixed in the loop as a function of the applied pressure of hydrogen in the injector. As the desired concentration increases, the required pressure is higher. Thus, for the required hydrogen concentration of 5.56E-4 mol/m<sup>3</sup> (Table 1), an applied pressure of 207 Pa is needed to keep the equilibrium between entering and exiting fluxes in the loop.

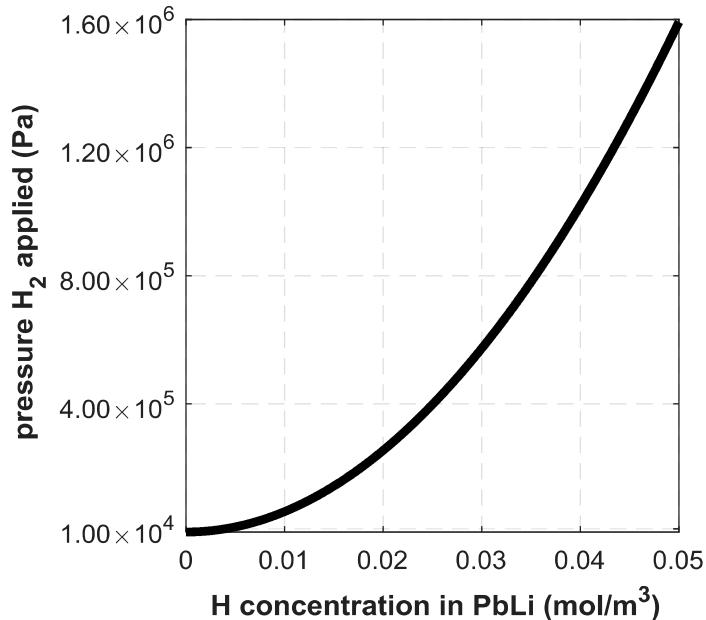


Figure 7. Concentration of hydrogen in the PbLi vs pressure of hydrogen applied in the injector ( $T = 500^\circ\text{C}$ ;  $L = 0.2\text{ m}$ ;  $r_i = 0.0127\text{ m}$ ;  $N = 5$  tubes;  $v_{\text{PbLi}} = 1.16\text{ m/s}$ ;  $\phi_{\text{Nb}} = 3.08\text{E-}7\text{ mol/m}\cdot\text{s}\cdot\text{Pa}^{0.5}$ )

Figure 8-a shows a simulation of the variation of the inventory of hydrogen with time along the loop when the concentration to reach is fixed to 5.56E-4 mol/m<sup>3</sup>. Initially, the extraction system is switched off, then, concentrations at the exit both of the injector and the extractor ( $C_{\text{PbLi}}$  and  $C_o$ , see Figure 6) are equal and increase with time according to eq. 14. After 2 hours of operation at the nominal operational conditions of the loop (500 °C, 28.4 kg/s) a steady state is reached, with the DCLL hydrogen concentration in PbLi. At this moment the hydrogen pressure in the entire loop and the injector are equal and the extraction system starts working. As can be seen, both concentrations drop to reach the

equilibrium established by the design. An amplification of the scale is presented in Figure 8-b to see in detail the difference between the concentrations  $C_{\text{PbLi}}$  ( $5.56 \times 10^{-4} \text{ mol/m}^3$ ) and  $C_o$  ( $4.34 \times 10^{-4} \text{ mol/m}^3$ ). As it has been fixed, the injected flux of hydrogen is the same as the extracted because concentrations remain stable and the difference between them is the efficiency of the extractor (22%).

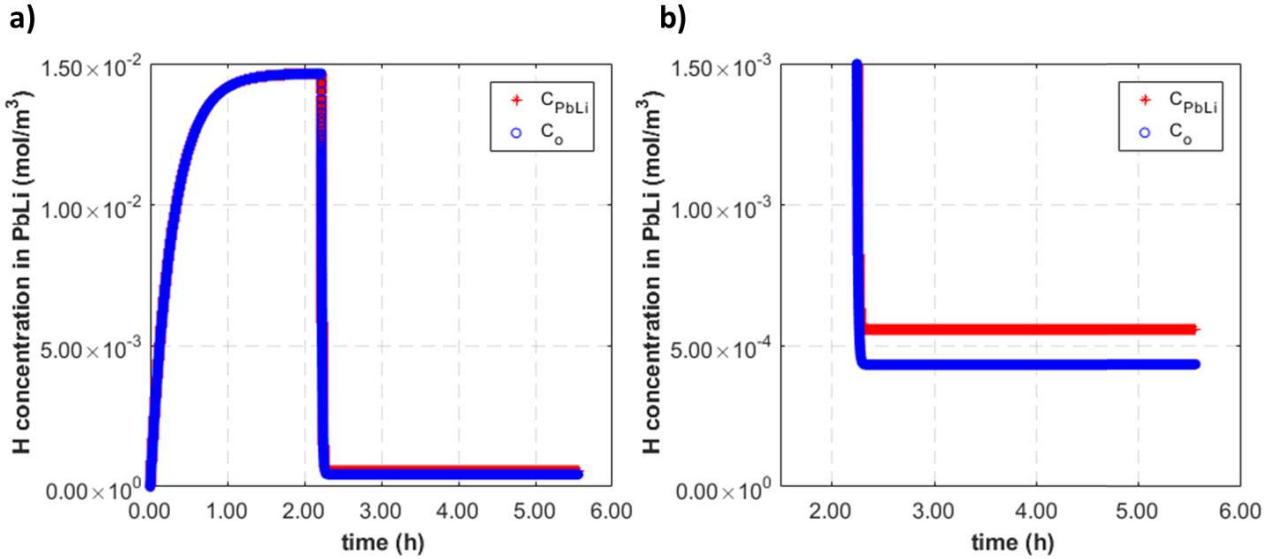


Figure 8. Variation of hydrogen concentration in the liquid metal with time: a) 8 hours of operation showing the stationary and the beginning of the PAV operation; b) detailed view of the difference on concentrations after the start of the extraction( $P_{\text{H}_2} = 207 \text{ Pa}$ ;  $T_{\text{PbLi}} = 500 \text{ }^{\circ}\text{C}$ ;  $L = 0.2 \text{ m}$ ;  $r_i = 0.0127 \text{ m}$ ;  $N = 5$  tubes; PbLi mass flow =  $28.4 \text{ kg/s}$ )

The flux variation with time, both for the injection and the extraction systems in CLIPPER, is presented in Figure 9 in the same conditions and time scale than Figure 8. As the concentration in the PbLi increases, the inlet flux ( $J_{\text{INY}}$ ) decreases according to eq. 14, until the steady state is reached, while the outlet flux ( $J_{\text{EXT}}$ ) is zero since the permeator remains inoperative. Then, after 2 hours of operation, the concentration of hydrogen in the liquid metal reaches the bullet point and the extractor starts to operate. It is seen that injection and extraction fluxes increase to the point where both are equal, being the rate of hydrogen injected the same as the extracted and equal to  $3.56 \times 10^{-7} \text{ mol/s}$ . It is worth noticing that, to keep these conditions of operation, the pressure in the outer tube has to remain constant in order to assure a continuous injection of gas into the PbLi. Otherwise the pressure would decrease with the subsequent reduction on the hydrogen concentration in the liquid.

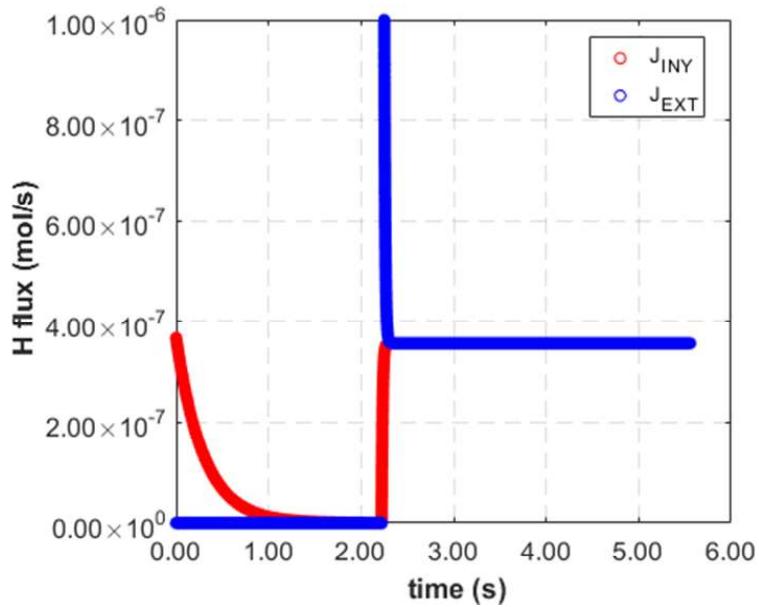


Figure 9. Variation of injected flux of hydrogen with time ( $P_{H_2} = 207$  Pa;  $T_{PbLi} = 500$  °C;  $L = 0.2$  m;  $r_i = 0.0127$  m;  $N = 5$  tubes; PbLi mass flow = 28.4 kg/s)

## 5. Conclusions

In order to experimentally validate different PbLi technologies within the field of nuclear fusion, especially those associated with tritium detection and extraction, solubilization of hydrogen isotopes in the liquid metal is a basic requirement. Thus, there is a need of designing systems able to inject hydrogen into the liquid metal.

In this paper, a novel idea for injecting hydrogen isotopes in a flowing liquid metal is presented. A conceptual design of a system based on a cylindrical geometry is depicted. This new approach is based on the forced permeation of hydrogen into the liquid metal through a permeable membrane using a tube-in-tube configuration. The liquid metal flows through an inner tube and a controlled gas pressure is applied on it. Materials for both the inner and outer tubes are chosen accordingly to its function, i.e. the inner tube has to present high permeability to hydrogen and compatibility with the liquid metal; the outer tube has to act as a permeation barrier to avoid losses to the environment. The design is optimized according to an analytical model of the present tritium transport processes. It relates physical and geometrical aspects of the system with the tritium concentration in the liquid metal and the concentration in the membrane.

Following the operational conditions of different breeding blankets, an evaluation of the influence of geometrical aspects of the injector, the liquid metal parameters, as well as the material used as membrane on the overall performance of the injector are depicted. It is shown that the capability of injection is directly proportional to the inner tube radius and length, as their increase enlarges the surface of permeation. However, the change to higher radii affects the velocity of the liquid and thus the mass transport coefficient, lowering their value and diminishing the rate of injection. The global effect is that the injection becomes favoured at increasing radii. Another important conclusion is that the number of inner tubes speeds up the injection process, although it is not linear, and that the temperature effect is to improve the injection due to the increase of the different parameters defining tritium transport processes within the liquid. Finally, the high dependence with the hydrogen solubility in PbLi is presented. Due to the high dispersion of the solubility value found in the literature, two limit values have been considered. The result is that the injection rate at fixed conditions can vary up to two orders of magnitude, which causes a high impact on the design.

The design of an injection system to be installed in CLIPPER, a PbLi loop devoted to tritium extraction experiments, is presented. It takes as inputs the operational characteristics of the loop in terms of mass flow rate and temperature and the condition of being able to inject hydrogen at the same rate as is being extracted. The result is a multi-tube component composed of 5 tubes of 0.2 m length and 1 inch diameter made of niobium and covered by a stainless steel case pressurized with hydrogen. The simulation of the behaviour of CLIPPER under DCLL conditions shows that 2 hours are needed to saturate the liquid metal prior to start with the extraction process. Later, the relation of concentrations of hydrogen in PbLi at the entrance and exit of the PAV provides an expected efficiency of 22%.

## List of symbols and abbreviations

$C_H$	hydrogen concentration in membrane in gas surface
$C_L$	hydrogen concentration in liquid in membrane surface
$C_o$	initial hydrogen concentration in liquid (before entering the injector)
$C_{PbLi}$	final hydrogen concentration in liquid (after exiting the injector)
$C_S$	hydrogen concentration in membrane in liquid surface
$D$	diffusion coefficient in membrane
$D_{PbLi}$	diffusion coefficient in PbLi
$J$	hydrogen flux
$K_L$	solubility coefficient in liquid
$K_S$	solubility coefficient in membrane
$K_T$	mass transport coefficient
$L$	tube length
$\dot{m}_{in}$	hydrogen mass flow entering the injector
$\dot{m}_{out}$	hydrogen mass flow exiting the injector
$\dot{m}_{per}$	hydrogen mass flow permeating through the injector
$N$	number of tubes
$\phi$	membrane permeability coefficient
$r_i$	inner radius of tube
$r_o$	outer radius of tube
$v$	velocity of liquid
$x$	position along the length of the tube
$\Delta x$	increment of length of the tube

## Acknowledgments

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission. This work has been partially funded by the MINECO Ministry under project ENE2013-43650-R. B. Garcinuño acknowledges a pre-PhD contract of the Spanish MINECO.

## References

- [1] L. V. Boccaccini, et al., Objectives and status of EUROfusion DEMO blanket studies, *Fusion Eng. Des.* 109-111 (2016) 1199–1206
- [2] D. Rapisarda et al., Conceptual design of the EU-DEMO Dual Coolant Lithium Lead equatorial module, *IEEE Trans. Plasma Sci.* 44 (2016) 1603-1612
- [3] D. Rapisarda et al., Status of the engineering activities carried out on the European DCLL, *Fusion Eng. Des.* 124 (2017) 876-881
- [4] G. Aiello et al., Design of the helium cooled lithium lead breeding blanket in CEA: from TBM to DEMO, *Nucl. Fusion* 57 (2017) 046022
- [5] A. Del Nevo et al., WCLL breeding blanket design and integration for DEMO 2015: status and perspectives, *Fusion Eng. Des.* 124 (2017) 682-686
- [6] B.J. Merrill, et al., Normal operation and maintenance safety lessons from the ITER US PbLi test blanket module program for a US FNSF and DEMO, *Fusion Eng. Des.* 89 (2014) 1989–1994

- [7] O. Gastaldi, et al., Tritium transfers and main operating parameters impact for demo lithium lead breeding blanket (HCLL), *Fusion Eng. Des.* 83 (2008)1340–1347
- [8] F. Okino et al., Vacuum sieve tray for tritium extraction from liquid Pb-17Li, *Fusion Eng. Des.* 87 (2012) 1014-1018
- [9] B. Garcinuño et al., Design of a Permeator against vacuum for tritium extraction from eutectic lithium-lead in a DCLL DEMO, *Fusion Eng. Des.* 117 (2016) 226-231
- [10] E. H. Lee et al., Progress of tritium extraction and measurement methods development from liquid breeder blanket in Korea, *Fusion Sci. Technol.* 62 (2012) 77-82
- [11] L. Livina et al., Development of a hydrogen permeation sensor for future tritium applications, *Fusion Eng. Des.* 89 (2014) 1209-1212
- [12] A. Ciampichetti et al., Performance of a hydrogen sensor in Pb-16Li, *J. Nucl. Mater.* 367-370 (2007) 1090-1095
- [13] N. Alpy et al., Hydrogen extraction from Pb-17Li: tests with a packed column, *Fusion Eng. Des.* 39-40 (1998) 787-792
- [14] A. Aiello et al., TRIEX facility: an experimental loop to test tritium extraction systems from lead lithium, *Fusion Eng. Des.* 82 (2007) 2294-2302
- [15] M. Utili et al., Investigation on efficiency of gas liquid contactor used as tritium extraction unit for HCLL-TBM Pb-16Li loop, *Fusion Eng. Des.* 109-111 (2016) 1-6
- [16] M. Kinjo et al., Experiment on recovery of hydrogen isotopes from Li17-Pb83 blanket by liquid-gas contact, *Fusion Sci. Technol.* 71 (2017) 520-526
- [17] I. Fernández-Berceruelo et al., Conceptual Design of a Lithium-Lead Loop for Testing the Permeator Against Vacuum Technique at High Velocity Flows, ISFNT-12 P1.074, Jeju, Korea
- [18] B. Garcinuño et al., Design and fabrication of a Permeator Against Vacuum prototype for small scale testing at Lead-Lithium facility, *Fusion Eng. Des.* 124 (2017) 871-875
- [19] A. Pisarev et al., Hydrogen gas driven permeation through asymmetric membranes in diffusion limited and surface limited regimes: interplay between analytical and numerical calculations, *Phys. Scripta* T108 (2004) 124-128
- [20] J. Crank, *The mathematics of diffusion*. Oxford Science Publications, 1975
- [21] W.H. Linton, et al., Mass transfer from solid shapes to water in streamline and turbulent flow, *Chem. Eng. Prog.* 46 (1950) 258.
- [22] D.R. Heldman, *Encyclopedia of Agricultural, Food, and Biological Engineering*. Marcel Dekker Inc. 2003
- [23] T. Gnanasekaran, et al., Liquid metal corrosion in nuclear reactor and accelerator driven systems, *Nucl. Corros. Sci. Eng.* (2012) 301–328
- [24] H. Glasbrenner, et al., Corrosion behaviour of Al based tritium permeation barriers in flowing Pb-17Li, *J. Nucl. Mater.* 307–311 (307) (2002) 1360–1363
- [25] A. Basile, *Handbook of membrane reactors*, Woodhead Publishing Series in Energy, 2013
- [26] H. Feuerstein, et al., Compatibility of refractory metals and beryllium withmolten Pb-17Li, *J. Nucl. Mater.* 233–237 (1996) 1383
- [27] A. Tahara, et al., Measurements of permeation of hydrogen isotopes through  $\alpha$ -iron by pressure modulation and ion bombarding, *Trans. Jap. Inst.* 26 (1985)869.
- [28] H. Katsuta, et al., Hydrogen and deuterium transport through type 304stainless steel at elevated temperatures, *J. Nucl. Sci. Technol.* 18 (2) (1981)143–151
- [29] M. Caorlin et al., The impact of tritium solubility and diffusivity on inventory and permeation in liquid breeder blanket, *Fusion Technol.* 14 (1988) 663-674
- [30] A. Pozio et al., Behaviour of hydrogenated lead-lithium alloy, *Int. J. Hydr. Energy* 42 (2017) 1053-1062
- [31] B. Garcinuño et al., Design and fabrication of a Permeator Against Vacuum prototype for small scale testing at Lead-Lithium facility, *Fusion Eng. Des.* 124 (2017) 871-875
- [32] F. Reiter, Solubility and diffusivity of hydrogen isotopes in liquid Pb-17Li, *Fusion Eng. Des.* 14 (1991) 207-211
- [33] A. Aiello et al., Determination of hydrogen solubility in lead lithium using sole device, *Fusion Eng. Des.* 81 (2006) 639-644