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# Hydrogen isotope separation by permeation through palladium membranes

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**Abstract**

An inverse isotope effect is observed for both the solubility and the diffusivity of hydrogen in palladium, i.e., the lightest isotope has the highest solubility and lowest diffusivity. For permeation of hydrogen isotopes through palladium alloy membranes when diffusion is the rate determining step tritium is the least permeating isotope. Since the absolute values of hydrogen, deuterium and tritium permeabilities in palladium differ considerably, the effect could be employed as a basis for technical isotope separation. Using an experimentally verified mathematical model, a parametric computational study was performed to show the net isotope effects in permeate and bleed flows when feeding a technical permeator with various hydrogen isotope mixtures under different feed and permeate pressures. The technical feasibility of hydrogen isotope permeation as a method for separation is discussed with regard to the necessary process control for either a single permeator or a cascade.


## 1. Introduction

The different aspects of hydrogen isotope effects in palladium and in the more technically practical Pd–Ag alloys have been studied abundantly in the past. Large relative mass differences for hydrogen isotopes give rise to significant thermodynamic and kinetic isotope effects for chemical reactions and physicochemical processes which can be advantageously used and applied for the isotope separation in case of either isotopically labeled water or mixtures of gaseous hydrogen species.

Permeation through membranes, especially those made of palladium alloys such as Pd–Ag, is also mentioned and sometimes proposed as a potential process for the separation of hydrogen isotopes as required in future fusion plants [1,2]. Two primary techniques can be distinguished for this process: large total pressure differences (A) or only partial pressure differences across the permeation membrane (B) as shown in Fig. 1. In both cases, a pumping system must be considered to overcome pressure drops. For the present study, only the total pressure difference case will be discussed.

The consequences of the isotope effect during operation of a permeation unit have been analyzed. Based on a simple model [3,1] that describes the permeation of hydrogen isotopes, the separation factor

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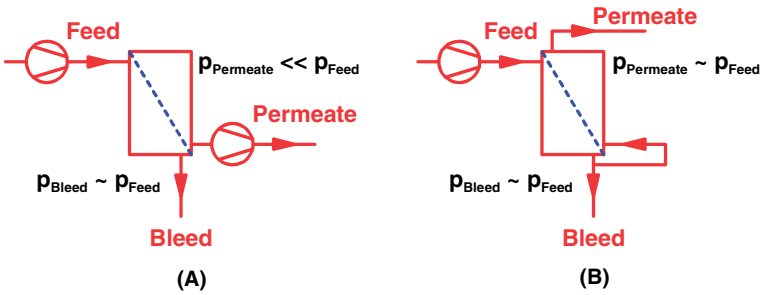


Fig. 1. Large total pressure difference (A) across the membrane and only partial pressure difference (B) as principal techniques for isotope separation.

and the separation efficiencies have been calculated. The results reveal that numerical studies are highly useful to set appropriate working regimes for a permeator so that highest separation factors are achieved. The results presented allow discussion of the technical feasibility of permeation as a separation process for hydrogen isotopes.

## 2. Theoretical background

The behavior of hydrogen isotopes in Pd–Ag membranes in terms of solubility, diffusion and permeation is known to follow an inverse isotope effect: It was observed that protium is consistently more soluble than deuterium [4], and the diffusion coefficients increase with the mass of the isotope [5].

At sufficient hydrogen pressures on the upstream side of the membrane, above about $10^3$ Pa, diffusion is the rate determining step for permeation. In this regime, the multi-step permeation process is governed by solubility. The permeability coefficients are therefore decreasing with increasing isotope masses.

In the model employed the solubility of hydrogen isotopes for the case of a multi-component mixture is assumed to follow Raoult's law, i.e., ideal solution. This means that hydrogen isotopes do not act independently but as a single chemical species and that specific interactions are neglected. Under these assumptions the concentration of hydrogen isotopes in the metal ${}^{Q}c$ with Q = H, D or T at the feed or permeate side can be simply written taking into account the atomic fractions in the gas phase ${}^{Q}x$, the Sievert's constant for each isotope ${}^{Q}S$ and the overall pressure of hydrogen isotopes $\sum {}^{Q}p$ [6]:

$$ {}^{Q}c = ({}^{Q}S \cdot {}^{Q}x)\sqrt{\sum_{Q} {}^{Q}p}. \tag{1} $$

Afterwards the permeation flux of each hydrogen isotope ${}^{Q}j$ can be written considering the area ($A$) and the thickness ($t$) of the membrane, the permeability coefficient ${}^{Q}P$, the isotope fraction in the gas phase ${}^{Q}x$ and overall hydrogen isotope pressure $\sum {}^{Q}p$ at the feed and permeate side:

$$ {}^{Q}j = \frac{A}{t}{}^{Q}P \cdot \left( {}^{Q}x_{\mathrm{Feed}}\sqrt{\sum_{Q} {}^{Q}p_{\mathrm{Feed}}} - {}^{Q}x_{\mathrm{Permeate}}\sqrt{\sum_{Q} {}^{Q}p_{\mathrm{Permeate}}} \right). \tag{2} $$

The permeability coefficients used in this study are taken from literature for protium and deuterium [7] and for tritium [8]. The following data have been employed at the operating temperature of 673 K:

$$ \begin{aligned} {}^{H}P &= 1.4 \times 10^{-8}\ \mathrm{mol/m\,s\,Pa^{1/2}}, \\ {}^{D}P &= 8.3 \times 10^{-9}\ \mathrm{mol/m\,s\,Pa^{1/2}}, \\ {}^{T}P &= 6.6 \times 10^{-9}\ \mathrm{mol/m\,s\,Pa^{1/2}}. \end{aligned} \tag{3} $$

Basic assumptions for the model are that the temperature along the permeator membrane is constant, that the gas is radially well mixed, that the membrane is only permeable for hydrogen isotopes ($I_0 = I_N$ in Fig. 2) and that impurities have no effect on the hydrogen permeabilities. The numerical approach is illustrated in Fig. 2 and can be briefly described as follows: The permeation membrane area is divided into $n$ elements and is fed with a mixture of hydrogen isotopes Q containing impurities at flow rates $Q_0$ and $I_0$, respectively. Then for each element $i$ along the membrane ($i$ varying from 1 to $n$) the permeation flow rate ${}^{Q}j$ is computed using Eq. (2), and the mass balance provides the flow rate in the next element ($i + 1$). Eventually the bleed flow rates $Q_n$ for hydrogen isotopes and the total permeated flow rates are obtained. The model only consid-

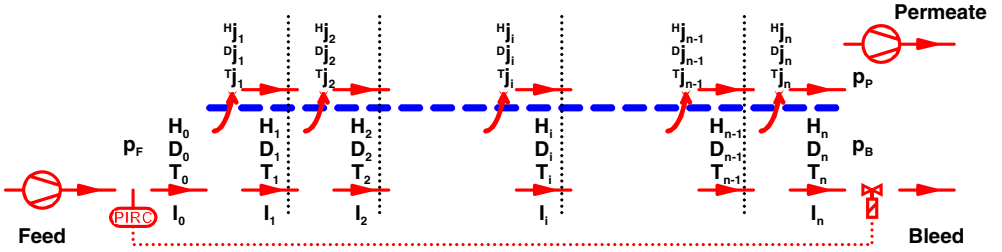


Fig. 2. Illustration of the mathematical model describing the flow of hydrogen isotopes and impurities in a permeator.

ers variation of the gas composition with position but not with time (steady state).

## 3. Numerical simulations

Numerical simulations are performed considering a 1 $m^2$ area Pd–Ag membrane with a thickness of 100 μm. In the calculation code the membrane area was divided into $n = 2000$ elements. The gas mixture that is permeating through contains D and T mixed in equal proportions as major components, but also a small amount of H (0.01%) and a given impurity concentration (mol.% or atomic fractions are used as concentration units).

A parametric study was performed by varying the following parameters within the respective ranges:

- feed flow rate ranging from 20 to 200 mol/h,
- feed pressure varying from 200 to 600 kPa,
- pressure at the permeate side ranging from 0.2 to 20 kPa,
- impurity concentration ranging from 1.99% to 19.99%.

In order to evaluate and characterize the performances of the permeator non-dimensional parameters are defined as follows:

- Yield, corresponding to the ratio between the total flow rate of hydrogen isotopes in the bleed ($Q_n$) and the total flow rate of hydrogen isotopes in the feed ($Q_0$):

$$\text{Yield} = \frac{Q_n}{Q_0}. \tag{4}$$

- Efficiency, corresponding to the ratio between the total flow rate of hydrogen isotopes in the outlet flow (permeate or bleed) and the flow rate of hydrogen isotopes in the feed ($Q_0$) and taking into account the T/D ratio variation:

$$\text{Efficiency}_{\text{Permeate}} = \frac{\sum_Q \sum_{i=1}^{n} {}^{Q}j_i}{Q_0} \cdot \frac{[\text{T/D}]_{\text{Feed}} - [\text{T/D}]_{\text{Permeate}}}{[\text{T/D}]_{\text{Feed}}}, \tag{5}$$

$$\text{Efficiency}_{\text{Bleed}} = \frac{Q_n}{Q_0} \cdot \frac{[\text{T/D}]_{\text{Feed}} - [\text{T/D}]_{\text{Bleed}}}{[\text{T/D}]_{\text{Feed}}}. \tag{6}$$

## 4. Results and discussion

In Fig. 3, the total bleed flow rate is shown as a function of the total feed flow rate when feed and permeate pressures are set to 250 kPa and 10 kPa, respectively. Calculations were performed for different impurity concentrations. These curves are the well-known breakthrough curves that characterize the permeator behavior. In such curves two regions can be distinguished. At low feed flow rates almost

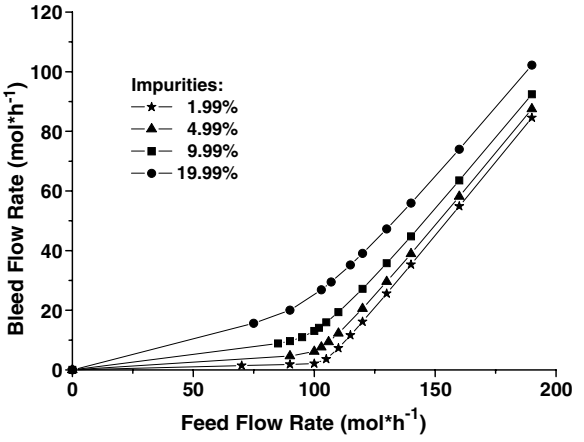


Fig. 3. Breakthrough curves of a D–T mixture (1:1) permeating through a Pd–Ag membrane (1 $m^2$ area, 100 μm thickness) operating at 673 K; calculated for different impurity concentrations ranging from 2% to 20% when feed and permeate pressures are 250 kPa and 10 kPa, respectively.

all hydrogen isotopes permeate proportionally to the feed flow rate; the bleed flow remains low and contains mainly impurities. At higher feed flow rates the permeator is operated beyond its capacity and the additional feed appears in the bleed. It can be seen that increasing the impurity concentration tends to smoothen the breakthrough phenomenon and to shift it towards lower feed flow rates. Taking into account the dimensions of the membrane and the pressure regime chosen, calculations reveal that breakthrough occurs at feed flow rates of about 100 mol/h.

To further illustrate the phenomena the calculated partial pressures of deuterium, tritium and impurities on the feed side for element $i = 1$ to element $i = n$ are plotted in Fig. 4 for feed flow rates below (A) and beyond (B) breakthrough. As tritium is the least permeating isotope its partial pressure on the feed side remains higher than the partial pressure of deuterium towards the bleed outlet. The partial pressure of impurities increases and the extracted bleed contains impurities with deuterium and tritium only at partial pressures equal to their permeate pressures at low feed flow rates (A) or at elevated partial pressures for feed flow rates beyond breakthrough (B). If the task of a permeator is to separate impurities from hydrogen isotopes the specific membrane area should be sized such that no breakthrough occurs under the given operating conditions.

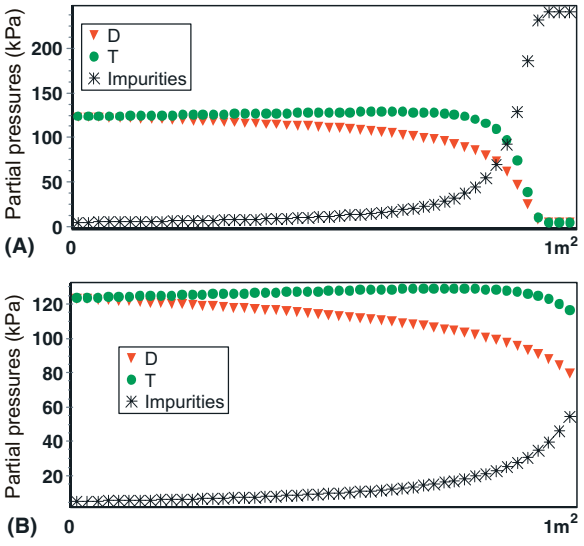


Fig. 4. Calculated deuterium, tritium and impurities partial pressures along a permeator membrane from element $i = 1$ to $i = n$ on the feed side: (A) at feed flow rates below breakthrough and (B) at feed flow rates beyond breakthrough.

### 4.1. Isotope effects in the bleed

When feeding a permeator at a T/D ratio of one the bleed flow is expected to be enriched in tritium and T/D ratio is greater than unity. Fig. 5 gives the T/D ratio in the bleed flow versus the total feed flow rate plotted for the different impurity concentrations. Calculations were performed with feed and permeate pressure of 250 kPa and 10 kPa, respectively. Each of these curves presents a peak appearing when the feed flow rate corresponds to the breakthrough phenomenon. In accordance with the breakthrough curves it is observed that increasing the impurity concentration gives smoother and broader peaks that are shifted towards lower feed flow rates. Under these conditions and depending on the impurity concentration, maximal T/D ratios between 1.3 and 1.6 are predicted. These results clearly demonstrate that operating the permeator at this particular regime maximizes the tritium enrichment in the bleed flow.

For technical reasons it is of great importance not only to have high enrichment factors but also to have high throughputs or recovery rates, and the enrichment factors and the yields of the process need to be considered simultaneously. In Fig. 6, these two characteristic values are superimposed and plotted against the permeate pressure. It shall be noted that for these calculations the feed flow rate was set at the breakthrough in order to give the maximum enrichment factor in the bleed. The general behavior observed for all impurity contents is that high enrichment goes along with low yield at

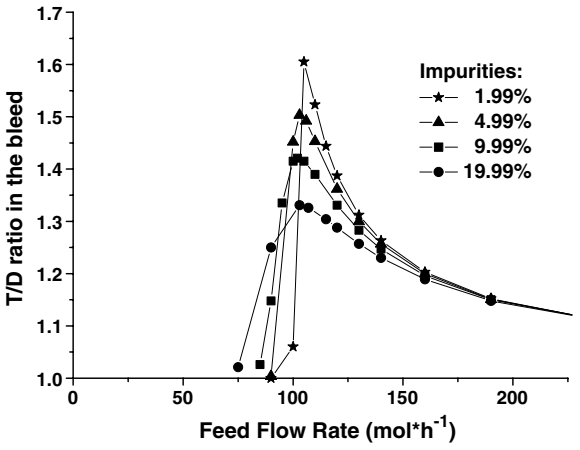


Fig. 5. T/D ratio in the bleed flow versus the total feed flow rate calculated for different impurity concentrations at feed and permeate pressures of 250 kPa and 10 kPa, respectively.

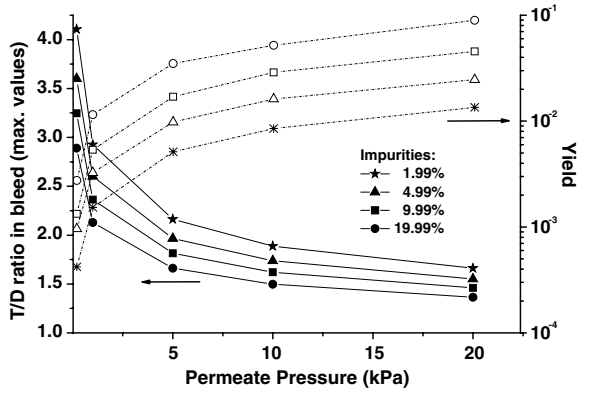


Fig. 6. Superposition of the T/D ratio in the bleed flow (filled symbols) and the yield as defined by Eq. (4) (empty symbols) plotted versus the permeate pressure for different impurity concentrations and a feed pressure of 600 kPa; for each point the feed flow rate is set at the breakthrough so that it maximizes the T/D ratio.

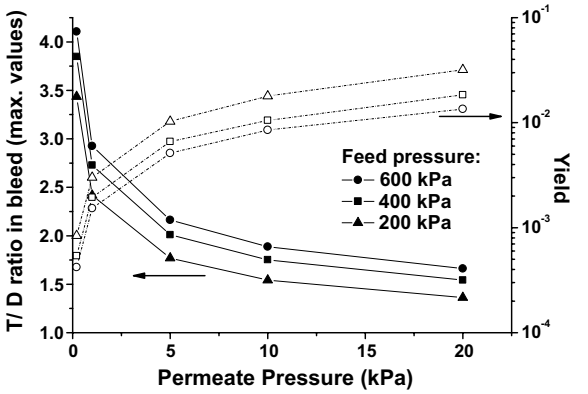


Fig. 7. Superposition of the maximum values of T/D ratio in the bleed flow (filled symbols) and the yield as defined by Eq. (4) (empty symbols) plotted versus the permeate pressure for different feed pressures of a mixture containing 1.99% impurity; for each point the feed flow rate is set at the breakthrough so that it maximizes the T/D ratio.

low permeate pressures or poor separation with high recovery at high permeate pressures. By considering a mixture containing 1.99% impurity a very high enrichment factor up to 4.1 is calculated for the lowest permeate pressure. However, at the same time the yield is extremely low and does not exceed 0.001, which means that the recovery rate is lower than 0.1%. Increasing the permeate pressures the yield can be enhanced, but on the expense of the enrichment factor. With a mixture containing 19.99% impurity the yield is close to 0.1 at highest permeate pressure, which means that about 10% of the D–T mixture could be recovered in the bleed flow, but the enrichment factor does not exceed 1.4 under these conditions.

In Fig. 7, the influence of the feed pressure on the enrichment factor and the yield of the process is shown when the bleed flow is considered. Both characteristics are plotted versus the permeate pressure, and the same general tendency previously reported is observed: high enrichment factors with poor yields at low permeate pressure are calculated, while low enrichments and high yields are expected at high permeate pressures. It should also be pointed out that increasing the feed pressure is favorable in terms of enrichment factors but unfavorable from the yield point of view.

### 4.2. Isotope effect in the permeate flow

For separation purposes the permeate flow could also be used. The T/D ratio in the permeate flow versus the total feed flow rate for different impurity concentrations is plotted in Fig. 8. It is clear from these curves that the isotope effect in permeability causes only a small separation factor on the permeate side; obviously, the impurity content in the feed has no significant effect. At feed flow rates below the breakthrough no separation takes place (T/D equal to unity), despite of the difference in the permeability coefficient for D and T. Beyond breakthrough the T/D ratio gradually decreases when increasing the feed flow rate, however, the separation remains rather limited. For the actual conditions, a maximum reciprocal separation factor of about 0.9 was calculated for feed flow rates of 200 mol/h or higher.

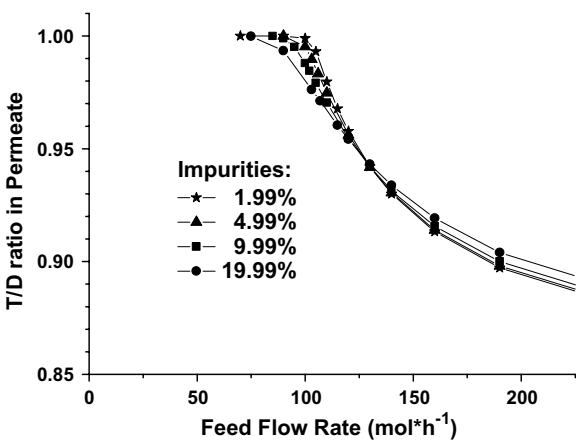


Fig. 8. T/D ratio in the permeate flow plotted versus the feed flow rate for different impurity concentrations at feed and permeate pressures of 250 kPa and 10 kPa, respectively.

### 4.3. Combined effects in the bleed and permeate flows

For a technical application of a permeator unit in a separation process not only high separation factors but also large yields must be simultaneously achieved. In Fig. 9, the T/D ratios in the permeate and bleed flows and the efficiency of the process as defined by Eqs. (5) and (6) are shown. It should be noticed that the efficiencies of both permeate and bleed flow exhibit an optimum when the feed flow rate is about 1.7 times the breakthrough feed flow rate. However, both efficiencies are limited to 5% and 7% for the permeate and for the bleed flow, respectively.

### 4.4. Initial evaluations of employing a permeator cascade for ITER tokamak exhaust processing

The main function of the torus exhaust processing (TEP) system of ITER [9] is to recover unspent D–T fuel yielding to a product stream suitable for transfer either to the isotope separation system (ISS) or to the storage and delivery system of ITER. Currently the front-end stage of TEP consists of 4 $m^2$ surface area permeators to process a 320 mol/h feed stream with a typical plasma exhaust composition of 4% protium, 39% deuterium, 39% tritium and 18% non-permeable impurities.

In order to reduce the separation duty of the ISS (and the associated tritium inventory) it would be desirable to enrich tritium in an upstream system to the highest extent. A cascade of permeators could hypothetically be a solution for such a system. Based on the above considerations a cascade of five permeators, each with 1 $m^2$ surface area, have been considered. In this configuration, for the optimized working regime determined in Section 4.3, it was found that about 30 mol/h of tokamak exhaust gas (T/D = 1) could be fed into the system and would be enriched to 9 mol/h with 68% tritium and 32% deuterium on the heavy product side, and correspondingly depleted to 21 mol/h with 40% tritium and 60% deuterium on the light product side. However, the high nominal protium content of the plasma exhaust gas was neglected in this case study. As for the ITER-like permeators, 250 kPa pressure on the feed side and 10 kPa pressure on the permeate side have been considered.

Besides the large permeator surface area and the significant number of pumps needed, the variable torus exhaust composition (particularly related to the protium content) would raise additional problems in the control system of such a cascade. It is therefore not considered advantageous to employ the front-end permeators of the ITER TEP system for isotope separation purposes.

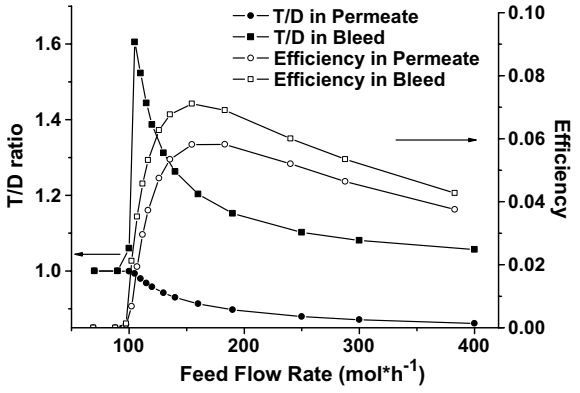


Fig. 9. Superposition of the T/D ratio in the permeate and bleed flows (filled symbols) and the efficiencies of the processes as defined by Eqs. (5) and (6) (empty symbols) versus the total feed flow rate calculated for an impurity concentration of 1.99% and for feed and permeate pressures of 250 kPa and 10 kPa, respectively.

## 5. Conclusions

By considering permeation involving palladium membranes for hydrogen isotopes separation purposes, calculations on the separation performances of such a process have been performed. For a separation process, a control of the working regime of the permeator is of great importance to ensure the best performances. Despite the difference in permeability coefficients for H, D and T, no change in the isotope T/D ratio in bleed and permeate appears at flow rates below breakthrough.

Isotope separation takes place at feed flow rates beyond breakthrough. On one hand, high separation factors can be achieved in the bleed flow when operating the permeator just beyond the breakthrough. On the other hand, conditions that maximize the separation factor in the bleed flow (low impurity contents, high feed pressures and low permeate pressures) are always at the expense of the yield in the process. When considering the permeate flow, the separation factors gradually increases beyond breakthrough, however, the effect remains small. The maximal efficiency in separation for both permeate and bleed flow is observed at

about 1.7 times the breakthrough feed flow rate and does not exceed few percent.

Moreover, it has also been demonstrated that the separation significantly depends on the operating conditions (feed flow rates, feed and permeate pressures and feed gas compositions). If a permeator cascade would be foreseen in a separation process these operating conditions will vary along the process so that it will be very difficult to operate each single unit such that the efficiency is optimized. Furthermore, the requirements on compressors, vacuum pumps and process control associated with a technical facility are significant and have not been quantified yet in detail. It therefore appears that separation of hydrogen isotopes using permeation through membranes is quite complicated compared with the other foreseen processes.

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