

## Experimental study of the isotope effect of the permeability in structural steels for fusion reactors: Eurofer and SS316

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### ABSTRACT

The transport of hydrogen isotopes through the elements that make up a fusion reactor, and their corresponding interaction with these materials, have a direct impact on its operation. Consequently, it is essential to master in advance their transport parameters in the different materials proposed to constitute the elements that will compound the fusion reactors, and, consequently, this is one of the main lines of fusion investigation. For reasons of technology, safety and viability, it would be desirable to have the possibility of experimenting only with protium and, from these values, to extrapolate those of deuterium and, above all, tritium. To do so, the classical atomic theory establishes that the ratio of these parameters is inversely proportional to square root of their mass ratio. However, discrepancies have been detected, so its verification has become fundamental. For this reason, this study presents the analysis of a series of tests of permeability carried out at the Fusion Materials Laboratory (UPV/EHU) using protium and deuterium with some samples of SS316 and EUROFER steels, in order to contrast the isotope effect, as well as the variables that could influence its adjustment. The results show that 316 steels present an isotope effect much closer to the theoretical one, while EUROFER steels differ more, increasing their isotopic ratio of permeabilities with temperature. In both cases, the trends are in line with published results.

### Introduction

Nuclear fusion is a promising alternative for energy generation in the medium term [1], being ideal to complement the variable contribution of renewables due to their climate dependence.

However, its development presents many challenges, one of the main ones being related to the high-temperature processes that materials under the influence of hydrogen isotopes (protium (H), deuterium (D), and tritium (T)) have to face. In fact, this interaction has different effects. On the one hand, isotopes can easily permeate into metals, which may result in a significant structural degradation [2–4]. In addition, it is also important to take into consideration that the permeation of tritium to the outside could be dangerous, due to its radioactivity [5–8].

In this context, the study of the interaction of hydrogen isotopes with the various materials that will make up the elements of fusion reactors is indispensable. To this end, there is an interesting way of reducing the difficulty and cost of experimental studies: to achieve an accurate isotope ratio, so that it would not be necessary to experiment with all

three isotopes, but it would be possible to test only protium and deuterium, or even only protium, and extrapolate the results for tritium from the results.

For many years, it was believed that the transport parameters of hydrogen isotopes were related by classical atomic theory [9], relating diffusivity to atomic vibrational frequencies and establishing these frequencies as inversely proportional to masses, and doing so with permeability rates [10].

However, discrepancies have been detected, and these differences have been attributed to numerous reasons, such as the quantum effect [10–13] or trapping, although, in theory, it does not affect the permeability [14]. In any case, it has been found that the difference with respect to this classical value is strongly related to the type of material [15], and therefore it is not possible to draw general all-encompassing conclusions and it is necessary to carry out independent studies for each one.

In the present study, an experimental study of the permeability of protium and deuterium in different steels of interest for fusion reactors is

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carried out. On the one hand, reduced activation ferritic/martensitic steel samples of the EUROFER type have been analysed. On the other hand, 316 type steels have also been analysed, i.e. an austenitic alloy.

## Materials and methods

Experimental permeation tests have been carried out in the permeation facility located at the Fusion Materials Laboratory of the University of the Basque Country between 2015 and 2022, following exactly the same process and mathematical model. A total of 13 samples have been tested, all of them were polished between P600 and P1200 and their characteristics are shown in Table 1. It is relevant to take into account that all EUROFER samples tested belong to batch 3.

The gas evolution permeation technique has been chosen to characterize the materials and obtain their permeability equations. The mentioned method is a well established experimental method when analysing fusion materials, and it is based on recording the pressure increase resulting from the gas passing through the samples from a high pressure region, that remains constant, to a low pressure region, that starts from an ultra-high vacuum situation [16].

It consists of the following (see Fig. 1). To begin with, an ultra-high vacuum situation is generated, pumping out all the gas that may be present inside the facility by the three UHV pumping units (until at least  $10^{-5}$ - $10^{-6}$  Pa) to ensure the absence of any species that could superficially oxidise the sample (S) or cause any type of inaccuracy in the measurements. As different isotopes have been tested for this work, this process takes on special relevance and is carried out before each of the tests, so that the vacuum at the beginning of each test is so good that the partial pressure of whatever is in the background can be neglected. It can be therefore assumed that the total pressure measured corresponds to the amount of the isotope that has permeated. In addition, a blank test has always been carried out for each temperature, in order to determine that the desorption of the elements of the installation itself is low enough to be negligible.

Starting from this UHV situation, the bottom side of the sample (the “high pressure region”) is immediately exposed to the chosen gas (protium or deuterium for this study) at a fixed pressure set by the pressure controller (PC) (usually between 100 and 150000 Pa). The gas will pass through the sample to the other side (the “low pressure region”), where it will cause a pressure rise which will be measured continuously by two Baratron capacitance manometers, with full scale of 1000 Pa and 13.33 Pa, respectively. Two gold O-rings guarantee the tightness of the sample during the whole process, so that the entire pressure increase measured in the low pressure region results from the gas from high pressure region and not from outside and vice versa, all gas leaving the high pressure region passes through to the low pressure region and there are no leaks. After completing a test, the permeated gas is evacuated to a volume, which is calibrated. As a result of this process, the rate of pressure increase can be converted into a flow rate, that is, the amount of gas in moles permeating through the unit area of the sample per second ( $J(t)$ ).

**Table 1**  
Characteristics of the samples (shape/size, thickness and mass).

Name	Shape and size	Thickness [mm]	Mass [g]
EUROFER_A	Ø = 15 mm (circle)	0.07	0.0817
EUROFER_B	Ø = 15 mm (circle)	0.081	0.0939
EUROFER_C	□ = 25 mm (square)	0.47	2.0362
EUROFER_D	□ = 25 mm (square)	0.23	1.0726
EUROFER_E	□ = 25 mm (square)	0.34	1.4685
EUROFER_F	□ = 25 mm (square)	0.43	1.7908
EUROFER_G	Ø = 15 mm (circle)	0.098	0.1318
EUROFER_H	Ø = 15 mm (circle)	0.052	0.0669
EUROFER_I	Ø = 15 mm (circle)	0.56	0.7707
SS316_A	Ø = 20 mm (circle)	0.5	1.2725
SS316_B	Ø = 25 mm (circle)	0.1	0.3683
SS316_C	Ø = 15 mm (circle)	1	1.2355
SS316_D	□ = 25 mm (square)	0.5	2.378

The temperature at which the test is carried out can be set by means of an electric furnace with PID controller. And, for more accurate calculations, during the process, it is possible to know the exact temperature of the sample due to a thermocouple inserted in the permeation column. A quadrupole mass spectrometer (QMS) is also available to check the purity of the gas and the vacuum level if necessary.

The process followed during the test results in a typical experimental curve as shown in Fig. 2. Based on this curve and the corresponding mathematical analysis of the steady state zone, it is possible to obtain an accurate permeability value in diffusion-limited regimes.

## Theory

### Classical theory

To begin with, it is important to note the origin of the classical theory, which states that the transport parameters of protium and deuterium isotopes are related by the square root of two. The basic equation relating the diffusivities of any isotope of the same element ( $D_\alpha$ ,  $D_\beta$ ) is the following [11]:

$$\left(\frac{D_\alpha}{D_\beta} - 1\right) = f \left(\frac{w_\alpha}{w_\beta} - 1\right) \quad (1)$$

where  $w_\beta$  and  $w_\alpha$  correspond to the frequency of a jump to an interstitial or vacancy site in the metal lattice, and  $f$  represents the correlation coefficient, which, in the basic case, in which the transport is arbitrary, as stated, takes the value of unity.

Classical theory also states that the ratio of the jump frequencies of two isotopes is related to their atomic masses ( $m_\beta$  and  $m_\alpha$ ) as long as there is no interaction between the vibrations of the atom being transported and the vibrations of the atoms of the remaining metal:

$$\frac{w_\alpha}{w_\beta} = \left(\frac{m_\beta}{m_\alpha}\right)^{1/2} \quad (2)$$

Consequently, the following relationship between protium and deuterium is obtained for the specific context of this work:

$$\frac{D_H}{D_D} = \left(\frac{m_D}{m_H}\right)^{1/2} = \left(\frac{2}{1}\right)^{1/2} = \sqrt{2} \quad (3)$$

On the other hand, since the solubility of the isotopes of an element, according to this same theory, is independent of their masses, and therefore so is the Sievert constant ( $K_s$ ), then the isotopic ratio of permeabilities ( $\Phi$ ) must fulfil the same relation as that of diffusivities in order for it to be satisfied that:

$$\Phi = DK_s \quad (4)$$

Consequently:

$$\frac{\Phi_H}{\Phi_D} = \left(\frac{m_D}{m_H}\right)^{1/2} = \sqrt{2} \quad (5)$$

Therefore, according to the theory explained, the value that should be obtained when relating the permeabilities of H and D, as has been done in this work, is  $\sqrt{2}$ .

### Equations and model

The theory and model used in this study are developed as follows.

When the gas transport through the sample is limited by interstitial diffusion through the bulk of the material, the process is defined as diffusion-limited. In this case, the following transport parameters are used to define the transport of isotopes through materials: effective diffusivity ( $D_{\text{eff}}$ ), permeability ( $\Phi$ ) and Sieverts' constant ( $K_{s\text{eff}}$ ) [17]. However, in this study only permeability has been analysed, and therefore the development and explanation will focus on this parameter.

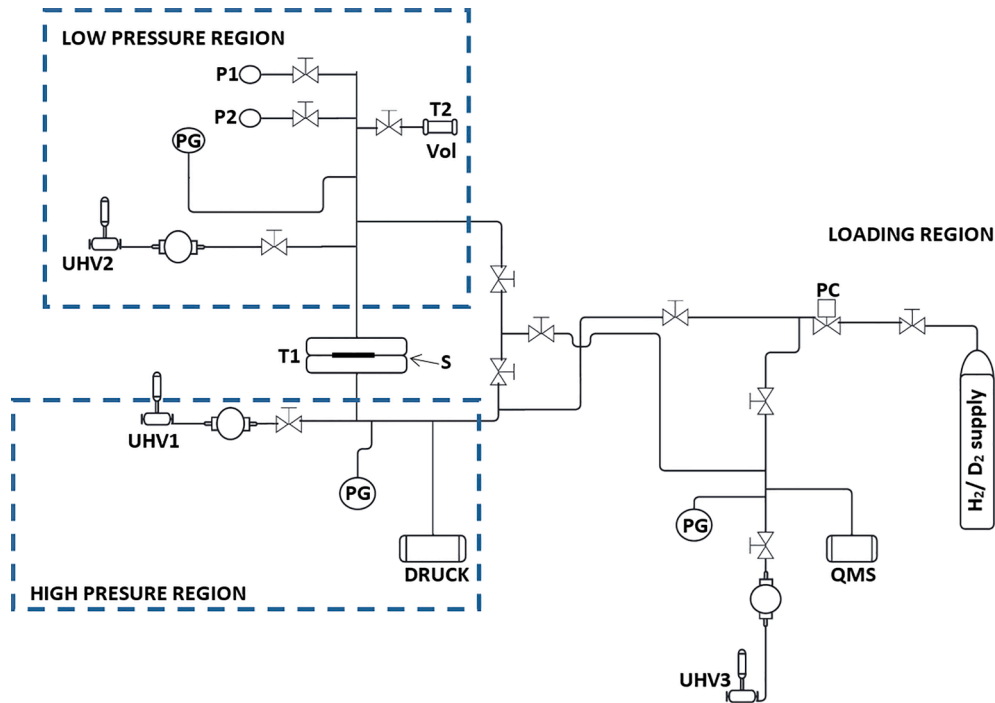


Fig. 1. Schematic view of the permeation facility. UHV: ultra-high vacuum pumping units; S: sample; T1, T2: nickel/chromium–nickel thermocouples; P1, P2: capacitance Baratron manometers; Vol: calibrated volume PG: penning gauges, PC: pressure controller, QMS: quadruple mass spectrometer, DRUCK: Absolute pressure transducer.

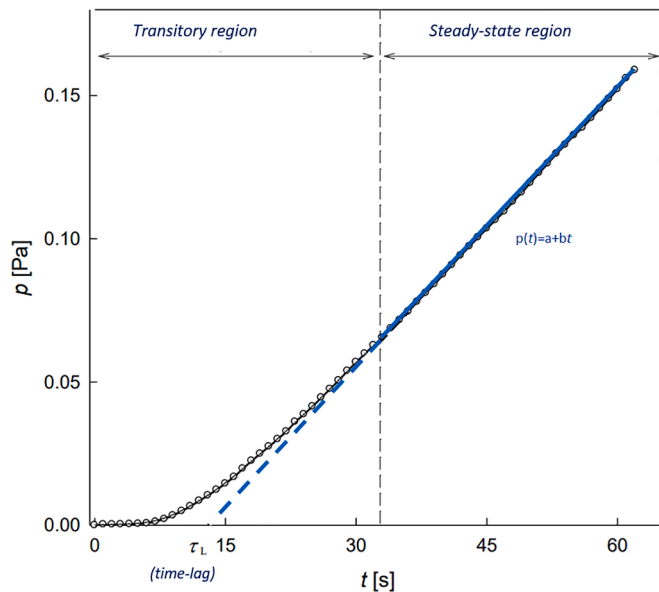


Fig. 2. Experimental  $p(t)$  curve example.

Permeability is known to relate the steady state gas flow ( $J$ ) through a slice of material of known thickness ( $d$ ), i.e. the sample to be tested, based on the pressure difference between each face of the slice (“high-pressure region” and “low-pressure region”). For a steady state process, the diffusion-limited flow is described by Richardson’s law:

$$J = \frac{\Phi}{d} (p_{\text{high}}^{1/2} - p_{\text{low}}^{1/2}) \quad (6)$$

Because the second surface is under ultra-high vacuum conditions, and therefore at a much lower pressure than the first surface, it can be simplified as follows:

$$J \approx \frac{\Phi}{d} p_{\text{high}}^{1/2} = \frac{\Phi}{d} p_{\text{load}}^{1/2} \quad (7)$$

In each permeation test, these parameters are estimated for a previously established loading pressure ( $p_{\text{load}}$ ) and temperature, as explained in the previous section. During the process, the pressure  $p(t)$  is recorded as it increases in the low-pressure region by means of the two mentioned Baratron.

This pressure increase will be a direct consequence of the permeate gas flow, and its expression is defined by Fick’s second law [8,18]:

$$p(t) = \frac{RT_{\text{eff}}}{V_{\text{eff}}} \left[ \frac{\Phi p_{\text{load}}^{1/2}}{d} A t - \frac{\Phi p_{\text{load}}^{1/2} d}{6D_{\text{eff}}} A - \frac{2\Phi p_{\text{load}}^{1/2} d}{\pi^2 D_{\text{eff}}} A \sum_{n=1}^{\infty} \exp\left(-D_{\text{eff}} \frac{n^2 \pi^2}{d^2} t\right) \right] \quad (8)$$

$A$  refers to the permeation area, i.e. the area of the sample in direct contact with the gas flow;  $d$  relates to its thickness;  $V_{\text{eff}}$  corresponds to the effective volume where the permeated gas gets retained which, in the case of the UPV/EHU facility, refers to the calibrated volume where the gas expands at the end of the test (Vol in Fig. 1) and  $T_{\text{eff}}$  is the temperature of the volume, which is measured using the T2 thermocouple in Fig. 1.

For a very long time period ( $t \rightarrow \infty$ ) in steady state conditions, and in the terminology of the facility used, this expression can be simplified resulting in Equation (9).

$$p(t) = \frac{RT_2}{\text{Vol}} \left[ \frac{\Phi p_{\text{load}}^{1/2}}{d} A t - \frac{\Phi p_{\text{load}}^{1/2} d}{6D_{\text{eff}}} A \right] \quad (9)$$

Therefore, to obtain the values of diffusivity ( $D_{\text{eff}}$ ) and permeability ( $\Phi$ ), a linear least squares fit is made to the experimental curve, such as the one shown in Fig. 2, by means of the line  $p(t) = a + bt$  [8]. Thus, the value of the permeability, which is the one analysed in the present study, would be given directly by the slope of the straight zone in the steady-state permeation regime.

$$\Phi = \frac{b \text{ Vol d}}{RT_2 A p_{\text{load}}^{1/2}} \quad (10)$$

For diffusivity, it would be necessary to introduce a further concept: as expression (9) would correspond directly to the linear zone in Fig. 2, by extending this straight line until it crosses the X axis (time), a characteristic time known as time-lag is obtained (Eq. (11), thanks to which  $D_{\text{eff}}$  would be solved [19]:

$$\tau_L = \frac{d^2}{6D_{\text{eff}}} \quad (11)$$

Finally, the Sieverts' constant ( $K_{S,\text{eff}}$ ), on the other hand, would be obtained from the equation (4). However, these two parameters will not be further detailed here.

Going back to the permeability, thanks to the adjustment explained above, one value would be obtained for each of the tests.

On the other hand, it is known that the permeability shows an Arrhenius-type dependence on the absolute temperature (Eq. (12), since so do diffusivity and Sieverts' constant:

$$\Phi(T) = \Phi_0 \exp\left(\frac{-E_\Phi}{RT}\right) \quad (12)$$

where  $\Phi_0$  corresponds to the pre-exponential permeability constant and  $E_\Phi$  to the activation energy of permeability.

Therefore, by performing different tests varying the experimental temperature, it is possible to define different points for the same sample and gas, and thus the Arrhenius-type permeability equation.

Finally, by repeating this process with each of the loading gases to be compared, the permeability equations for each isotope will be obtained for the same sample. Therefore, by relating both expressions, the experimental isotopic ratio of permeabilities for a particular sample between H and D will be derived.

$$\frac{\Phi_H}{\Phi_D} = \frac{\Phi_{0H} \exp(-E_{\Phi H}/RT)}{\Phi_{0D} \exp(-E_{\Phi D}/RT)} = \frac{\Phi_{0H}}{\Phi_{0D}} \exp(-(E_{\Phi H} - E_{\Phi D})/RT) \quad (13)$$

## Results and discussion

A total of 513 permeability tests have been performed with the 13 samples listed in Table 1. To this end, temperatures between 250 °C and 550 °C were combined with different loading pressures, depending on the needs at that moment, normally using values of 0.5, 1 and 1.5 bar. Tests were performed with both protium and deuterium.

Taking into account that the experimental tests have been carried out in other contexts and not exclusively for the purpose of this study, it has not been possible to select the conditions in advance. This is why a previous analysis and selection of the data has been made, considering the circumstances.

First of all, for each of the samples, tests using different loading gas but at the same temperatures and pressures have been selected, so that the resulting Arrhenius equations for each of the samples only differ in the isotope used but not in any other factor. In this way, if both expressions are divided as explained before, the isotopic permeability ratio between protium and deuterium is directly obtained for this material.

Apart of that, to ensure reliable results, before treating the data in the context of the isotope effect, the average  $J$ - $p_{\text{load}}$  ratios obtained have been analysed to corroborate the predominantly diffusive regime assumed in the mathematical development, according to Equation (2) [20]. By analysing the results, it has been decided to exclude a case in which the average exponent value is 0.44 (EUROFER\_H), which is physically impossible. On the other hand, it has also been decided to discard for the study those samples in which the  $J$ - $p_{\text{load}}$  ratio takes an average value higher than 0.7, setting this value as the limit between the predominantly diffusive regime and the diffusive/surface intermediate regime (EUROFER\_C, EUROFER\_E and SS316\_B).

However, the verification of the diffusion-limited regime does not

imply that surface effects do not appear [21]. Therefore, taking into account that at higher loading pressures surface phenomena have lower influence, for the study of the isotope effect, the Arrhenius equations constructed for the highest pressures tested with each sample (1.5 bar in most cases) have been used. In this way, the effects of surface phenomena during permeation are minimised and the parameters corresponding to the diffusive regime within the sample are more accurately characterised.

Once the data have been selected according to the chosen criteria, the resulting values for all the samples with each of the two isotopes are shown in Table 2. The pre-exponential factor is given together with the permeability activation energy for each case.

Having compiled the equations suitable for the study, in order to evaluate the isotope effect, it was decided to divide the Arrhenius expressions for each sample. The resulting expressions for each of the samples are shown in the following:

$$\text{EUROFER\_A} : \frac{\Phi_H}{\Phi_D} = 5.04 \exp(-8147.72/RT)$$

$$\text{EUROFER\_B} : \frac{\Phi_H}{\Phi_D} = 4.9 \exp(-7399.46/RT)$$

$$\text{EUROFER\_D} : \frac{\Phi_H}{\Phi_D} = 8.27 \exp(-10309.36/RT)$$

$$\text{EUROFER\_F} : \frac{\Phi_H}{\Phi_D} = 23.42 \exp(-14632.64/RT)$$

$$\text{EUROFER\_G} : \frac{\Phi_H}{\Phi_D} = 1.35 \exp(166.28/RT)$$

$$\text{EUROFER\_I} : \frac{\Phi_H}{\Phi_D} = 2.48 \exp(-3741.3/RT)$$

$$\text{SS316\_A} : \frac{\Phi_H}{\Phi_D} = 1.69 \exp(-1080.82/RT)$$

$$\text{SS316\_C} : \frac{\Phi_H}{\Phi_D} = 1.17 \exp(997.68/RT)$$

$$\text{SS316\_D} : \frac{\Phi_H}{\Phi_D} = 0.961 \exp(2161.6/RT)$$

For a more visual comparison of the isotope effect, the Arrhenius equations of isotopic permeability ratios are shown in Fig. 3. It has been decided to represent all the lines corresponding to the EUROFER

**Table 2**  
Conditions and results of the experimental tests.

Sample	$p_{\text{load}}$ [bar]	Temperature range [°C]	Protium/Deuterium	$\Phi_0$ [mol m <sup>-1</sup> Pa <sup>-1/2</sup> s <sup>-1</sup> ]	$E_\Phi$ [J/mol]
EUROFER_A	1.5	350-550	H	3.31E-10	33837.98
EUROFER_A	1.5	350-550	D	6.57E-11	25690.26
EUROFER_B	1.5	350-550	H	7.89E-09	55537.52
EUROFER_B	1.5	350-550	D	1.61E-09	48138.06
EUROFER_D	0.5	250-550	H	1.15E-09	41154.3
EUROFER_D	0.5	250-550	D	1.39E-10	30844.94
EUROFER_F	1.5	325-550	H	8.34E-09	31593.2
EUROFER_F	1.5	325-550	D	3.1E-09	28433.88
EUROFER_G	1.5	350-550	H	5.37E-09	51047.96
EUROFER_G	1.5	350-550	D	3.99E-09	51214.24
EUROFER_I	1.5	400-550	H	2.16E-07	71832.96
EUROFER_I	1.5	400-550	D	8.70E-08	68091.66
SS316_A	1.5	350-550	H	7.09E-07	66096.3
SS316_A	1.5	350-550	D	4.19E-07	65015.48
SS316_C	1.5	325-550	H	1.88E-07	64932.34
SS316_C	1.5	325-550	D	1.61E-07	65930.02
SS316_D	1.5	325-550	H	9.33E-07	74576.58
SS316_D	1.5	325-550	D	9.71E-07	76738.22

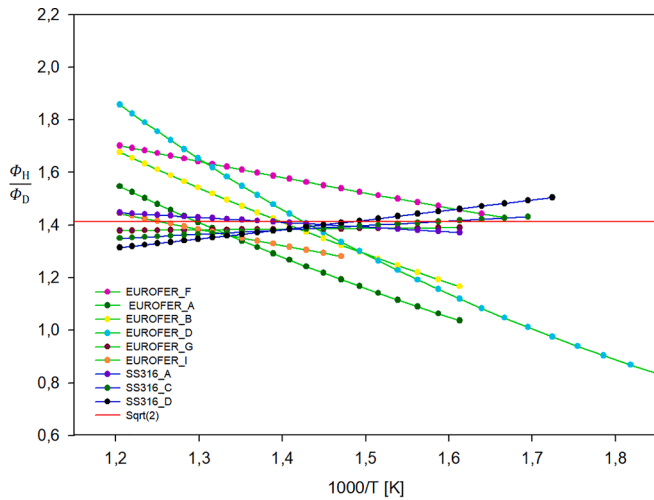


Fig. 3. Arrhenius plot of the isotope ratios obtained.

samples in green, and all the lines corresponding to the 316 steels in blue. In addition, the maximum errors between the experimental and the theoretical results, average errors and the slope of the linear trendline to which the 9 isotopic ratios approximate have been plotted in Table 3. For the calculation of these errors, the absolute value of the difference between the classical value and the value obtained from the Arrhenius ratios for each temperature has been calculated. In this way, it has been indicated the error at the point that permeability ratio differs the most from the classical value, as well as the average of the absolute errors for all temperatures in each case.

This study clearly shows the coinciding trends between the same sample types, and consequently it confirms more precisely what had already been studied [15]: the isotope effect and its difference with respect to the classical value are directly related to the type of material.

The three 316 samples take values very close to the classical isotope ratio, with a maximum error of 9.1 % for SS316\_D, a maximum error of 6.4 % for SS316\_C and a maximum error of 4.2 % for SS316\_A. In terms of their average errors, these are 5.0 % in the case of SS316\_D, 3.1 % in the case of SS316\_C and 1.9 % in the case of SS316\_A. All the values of the ratio curves obtained for the three samples are concentrated within the range of 1.31–1.46. Taking into account the great variability of published values for the isotopic effect [15], it can be stated that the three SS316 analysed are fairly close to the classical value, and that the errors, since they are quite low, could perhaps be attributed to the human factor.

In addition, it is worth noting their tendency to horizontality. Despite the fact that two of the lines are upward and a third one downward, the slope shown in the three cases is very small, taking values of  $-0.18$  (K) for SS316\_A,  $0.37$  (K) for SS316\_C and  $0.17$  (K) for SS316\_D. All these values are shown in Table 3.

The concept of horizontality is to be emphasised, since classical

Table 3

Maximum error and average error comparing to the classical value, and slope of each of the protium/deuterium ratio.

Sample	Max. error (%)	Avg. error (%)	Slope (K)
EUROFER A	37.7	15.6	-1.25
EUROFER B	26.3	13.4	-1.26
EUROFER D	44.3	29.3	-1.54
EUROFER F	28.7	15.5	-0.71
EUROFER G	3.5	3.0	0.03
EUROFER I	14.6	6.1	-0.60
SS316_A	4.2	1.9	-0.18
SS316_C	6.4	3.1	0.16
SS316_D	9.1	5.0	0.37

theory establishes that the activation energies should be independent of the mass of the isotope tested, and therefore should not present an isotope effect. Consequently, when dividing the expressions of two isotopes, this term should disappear, leaving only an absolute ratio of the pre-exponential factors of permeability, which therefore remains constant with temperature. It can be said, after this study, that the 316 samples are closer to this trend.

Regarding the EUROFER samples, the isotopic permeability ratios show a higher error with respect to  $\sqrt{2}$  in most cases, increasing their range to values between 1.04 and 1.85. It is true that the EUROFER\_G and EUROFER\_I cases have a smaller error, but in the latter case the range of temperatures tested is also much smaller, and it seems that if the line were extrapolated the trend would be similar to those of the other cases. In fact, this is reflected when analyzing the case of EUROFER\_D, which presents the highest average error, but the tests have been carried out in a higher range of temperatures, so its line is the longest. The others, however, have a similar pattern. As for EUROFER\_G, the smaller error, apart from the pre-exponential factors' relation found for the deuterium and protium equations (similar to  $\sqrt{2}$ ), is due to the horizontality of the curve, and therefore to the similarity between the activation energies, as mentioned above.

Continuing with the concept of the slope, all the rest of the EUROFERs present a descending shape, with such a parallel trend, as can be seen in Fig. 3. That is, it can be established that the isotopic ratio in the case of the EUROFERs has a general trend to increase with temperature, taking values above the theoretical value at the highest temperatures, and doing so in a quite proportional way. In addition, the four samples EUROFER\_A, EUROFER\_B, EUROFER\_D, EUROFER\_I cross the limit of the theoretical value in a very close range of temperatures, between  $440$  °C and  $500$  °C.

On the other hand, trying to analyse the influence of other factors involved in the isotope effect by means of this study, it is complicated to obtain other types of conclusions. In fact, the most similar isotope-ratios have been obtained for quite different conditions. For example, EUROFER\_A and EUROFER\_I, which are precisely the samples with almost the lowest and highest thickness, respectively, are very similar. As for the testing-pressure, the limits are 0.5 bar and 1.5 bar, pressures used for EUROFER\_D and EUROFER\_B, respectively, which curiously take very close values. On the other hand, samples that are physically very similar, such as EUROFER\_B and EUROFER\_G (same form, 15 mm diameter, about 0.08–0.1 mm thick and about 0.094–0.14 g mass), tested in both cases under the same conditions (temperatures of  $350$ – $550$  °C and 1.5 bar), show a quite different tendency. Therefore, no proved statement can be made about other factors, so the only conclusions that can be affirmed through this study are the similarity to the classical ratio in the case of the 316 samples both in value and horizontality, and the tendency for the ratio to increase with temperature in the case of the EUROFERs, in a quite parallel way although shifted on the y-axis.

To confirm the conclusion about the coinciding trends in each material, their results have been compared with some isotopic studies in the literature.

Regarding the isotope effects studies selected for SS316, the following isotope ratios are found: [22] (T. Shiraishi, 1999), [23] (S.K. Lee, 2014), [24] (W.J. Byeon, 2020).

$$\frac{\Phi_H}{\Phi_D} = 1.17 \exp(1400/RT)$$

$$\frac{\Phi_H}{\Phi_D} = 1.15 \exp(2300/RT)$$

$$\frac{\Phi_H}{\Phi_D} = 1.28 \exp(900/RT)$$

These isotopic ratios between protium and deuterium permeabilities, obtained with the same methodology as the one used in this work are shown in Fig. 4, together with those corresponding to the 316 steel samples analysed.

The results of this work and the isotope ratios obtained by Byeon, Lee and Shiraishi show a similar trend (upward, but not very pronounced). Furthermore, it can be said that the values obtained in this study are in very good agreement with those of Byeon and Shiraishi, which are

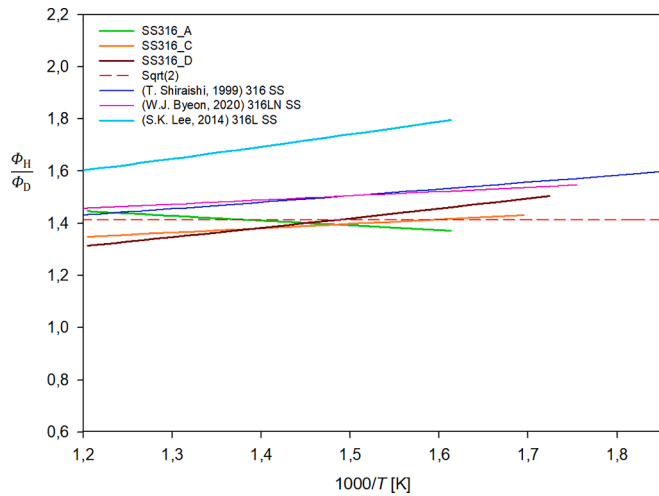


Fig. 4. Arrhenius plots of the isotope effect ratios of 316 samples. Comparison with literature.

somewhat displaced upwards, but still close to the theoretical value (in the present case being closer to the theoretical ratio). The ratio of Lee takes higher values, although it respects the tendency of having a quite light slope. It is also true that in the study of Byeon, it is stated that the permeability of protium achieved is somewhat higher than in other studies [25] and that of deuterium somewhat lower [26], which could be the reason why the ratio ( $\frac{\Phi_H}{\Phi_D}$ ) may be shifted upwards in the graph. This could also be happening in the other two studies. Moreover, in the three studies used for comparison, lower testing pressures than in this study have been used, which could perhaps affect the fact that they were not in a fully diffusive regime and consequently lead to some errors in the results, taking into account the model used.

Regarding the EUROFER tests, they have been compared with another isotopic study of the same material type (Fig. 5). [27] (A. Aiello, 2002)

$$\frac{\Phi_H}{\Phi_D} = 3.62 \exp(-3500/RT)$$

It is difficult to achieve complete isotopic studies in order to compare the real isotope effect in EUROFER alloys.

There are different permeability studies with only protium [28–30] or only deuterium [26,31–34], but hardly with both isotopes under the

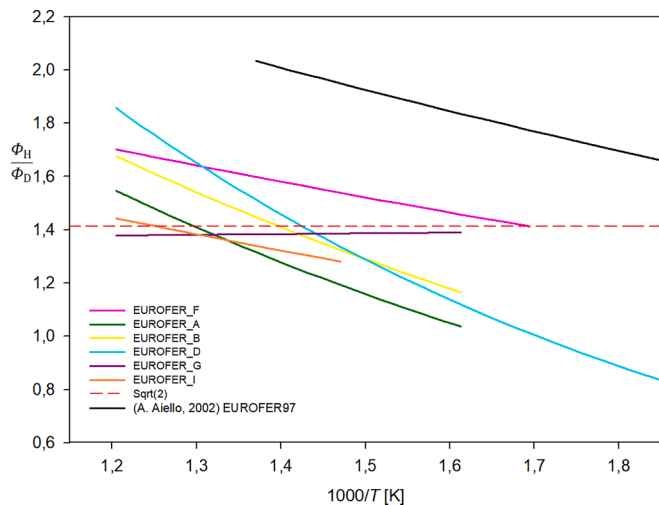


Fig. 5. Arrhenius plots of the isotope effect ratios of EUROFER samples. Comparison with literature.

same circumstances and same samples in the same facility.

Therefore, it is difficult to analyse the isotope effect as such, because if results from different authors were mixed to relate the curves of both isotopes, there might be other factors that actually mask the strictly isotope effect.

It can be seen that the trend of the isotope ratio is maintained when comparing the EUROFERs analysed in this study with the study published by Aiello, so it increases with temperature, with a fairly steep slope. However, the latter curve is shifted upwards even more, confirming the higher variability between the EUROFER studies, where the results show much lower repeatability.

It should be noted that in that study the same type of facility was used, as well as the same model, but lower temperatures (200–450 °C) and lower pressures (0.75 bar) were used.

## Conclusions

The isotope effect is a phenomenon of special interest in the development of nuclear fusion, in order to obtain the relationship between the isotope parameters and therefore to be able to predict the behaviour of tritium in a more feasible way.

Having deduced that the difference with respect to the classical ratio is highly varied and depends strongly on each type of material, it has been deduced that it is impossible to find an explanation for this phenomenon for all materials, so that this study must be carried out individually. In this context, the isotopic ratio of protium and deuterium permeabilities in different samples of EUROFER and 316 steel has been analysed. From the 13 samples tested, the results of 9 of them were finally used, while 4 were discarded because the diffusive regime could not be ensured.

The permeability equations of the resulting samples have been successfully obtained for the two gases and their isotope ratios have been plotted. The permeability ratios obtained for SS316 are in good agreement with the classical ratio, being at all times within the limits of 1.31 and 1.46, which are very good values. It can be said, in this case, that the classical theory is largely fulfilled both in value and horizontality and that the low error could perhaps be due to the human factor. Furthermore, comparing the results with other isotopic studies with 316 steel, the trends are quite consistent, taking higher values for lower temperatures, but in a slight way, not too pronouncedly sloping. The lines of Byeon and Shiraishi are also very close to the theoretical value, although slightly shifted upwards. The ratio of Lee is the most different, taking higher values than both this study and other publications. Nevertheless, the slope and the trend coincide and the results in better agreement with the theory are those obtained in this work.

With regard to the EUROFER results, the values are further away from the theoretical value than in the case of the 316 analysed. The ratios increase with increasing temperature, and do so more abruptly, reaching higher and lower values in the same temperature range. However, they do so in a fairly parallel way with each other, although shifted on the y-axis. Comparing them with another published permeability ratio, it has been observed that the results of this study present values closer to the theory than those of Aiello, although his line is also quite parallel to the present ones. It should be noted that in that case, lower temperatures and pressures were tested, which could lead to a less diffusive regime.

Regarding the existence of other factors affecting the isotope effect within the same type of material, it has not been possible to reach any relevant conclusion in this study, as they do not seem to have any correlation with its thickness, temperatures or pressures, finding similar ratios for different circumstances and different ratios for similar circumstances. Therefore, it has not been possible to explain the reason for so much variability in the results, especially in the case of EUROFER, which leads to the fact that, repeating the test circumstances, only the tendency to increase with temperature can be affirmed, but not the exact value, since their ratio curves are quite displaced. In the case of SS316,

however, it can be stated that, independent of other factors, the isotopic ratios of this work are very similar to each other and tend to the classical theory.

Whatever the case may be, the added value of this study is that the isotope effect of 9 samples has been analysed using exactly the same process, and the same facility. Consequently, even if there were any source of uncertainty in the process, it is repeated in all the samples and would therefore be ruled out. This means that it can really be stated that 316 steels show a much higher repeatability in the results and that there is some factor in the EUROfer that makes this material not only not present a classical isotope effect, but also that its results vary considerably even when they are equal samples from the same batch.

#### CRedit authorship contribution statement

**María Urrestizala:** . **Jon Azkurreta:** . **Natalia Alegría:** . **Igor Peñalva:** . **Marta Malo:** . **Carlos Moreno:** Funding acquisition, Resources, Writing – review & editing. **David Rapisarda:** Funding acquisition, Resources, Writing – review & editing.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Igor reports financial support was provided by European Consortium for the Development of Fusion Energy. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

The data that has been used is confidential.

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