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D. Matveev[*], M. Wensing, S. Möller, A. Kreter, S. Brezinsek and Ch. Linsmeier

Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung – Plasmaphysik, Partner of the Trilateral Euregio Cluster (TEC), 52425 Jülich, Germany

Abstract

The time evolution of the release of the dynamically retained deuterium from tungsten after plasma exposure is investigated. Possible analytical dependencies in fully de-trapping-, diffusion- and recombination-limited regimes are reviewed. Detailed parameter studies with respect to various parameters, such as the material temperature during exposure and release, the exposure flux and fluence, the binding energy and the depth distribution of traps, as well as the diffusivity and recombination properties of deuterium, are performed using reaction-diffusion modelling without pre-imposed limitations on the rate limiting process. To judge the conformity of the time evolution of the released flux F to the power law decay $F(t) \sim t^{\alpha}$, the time dependent parameter $\alpha(t)$, namely the local slope of the $\log_{10}F$-$\log_{10}t$ dependence, is introduced. It is demonstrated that a good power law fit of the outgassing flux with average parameter α in the range of experimental observations is possible even in a fully diffusion-limited regime for non-uniform initial depth profiles when the actual time evolution $\alpha(t)$ demonstrates an oscillatory behavior. For conditions of plasma exposures in the linear plasma device PSI-2 where a power law flux decay with α varying in the range of 0.8 – 1.2 depending on exposure conditions in a pure deuterium plasma was observed, none of the investigated parameter combinations result in a strict power law decay of the outgassing flux (α does not remain constant over time). It is demonstrated, however, that in some cases and for certain time intervals, the flux decay can be reasonably well fitted by a power law with values of α in the range of experimental observations. It is indicated that also experimental data from JET and PSI-2 exhibit deviations from a power law.

Keywords: dynamic retention; outgassing; power law; reaction-diffusion; CRDS

[*]Corresponding author: d.matveev@fz-juelich.de

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1. Introduction

The tritium retention of future fusion devices such as ITER or DEMO is a critical issue due to safety reasons. The release of the dynamically retained deuterium and tritium from wall components after plasma exposure will strongly influence the resulting retention, as well as the residual gas pressure in the main chamber between plasma operations. The deuterium outgassing from plasma-exposed surfaces in present tokamaks with different wall materials and loading

conditions is usually well described by a power law decay of the flux F being released with time after exposure: $F(t) \sim t^{\alpha}$, with $\alpha = -0.8 \pm 0.2$ [1, 2]. A power law decay of the outgassing flux with $\alpha \sim -1$ was also observed in the PSI-2 linear plasma device [3] for a bulk tungsten (W) target [4]. In contrast, the retention in specially prepared recrystallized W samples in an ultra-high vacuum setup after low-flux ion beam exposures was suggested to follow an exponential decay with the decay time constant of several hours [5]. The release of hydrogen from plasma or ion beam irradiated materials is governed in general by the interplay of the processes of diffusion, trapping, de-trapping and re-trapping at intrinsic and irradiation-induced defects, as well as surface recombination and desorption. An analytical description of the outgassing is possible in special cases when only a single process dominates, leading to either a power law ($\alpha = -0.5$, $\alpha = -1.5$ or $\alpha = -2.0$) or exponential flux decay [1]. Guterl [6] provided a detailed mathematical and numerical analysis of the release in diffusion-limited and surface-limited regimes in the context of equilibrium between trapping and de-trapping processes reconciling the models of Grisolia [7] and Andrew [8]. The authors demonstrated that both models are equivalent under conditions of trapping-detrapping equilibrium in a surface-limited regime and both can predict a power law decay of the outgassing flux with parameter α between -2/3 and -0.9. It was also suggested that complex surface processes with a recombination order different from 2 may induce a power law decay. In [9-11] it has been shown that release from traps with a continuous distribution of trap energies may also result in a power law decay of the outgassing flux.

In this work, we review the possible simple analytical expectations and perform numerically detailed parameter studies with respect to exposure conditions (flux and temperature), retention properties (binding energy and trap density), and release behavior (diffusion and recombination) in a general case using a rate equation approach implemented in the coupled reaction-diffusion systems (CRDS) modelling tool [12, 13] adopted to calculations of deuterium (D) in tungsten (W).

It must be noted that a power law decay is usually detected by fitting the $\log_{10}$-$\log_{10}$ $F(t)$ dependence (see e.g. figures 1 and 3 in [6]). We find such a comparison not sufficient since small deviations from the linearity of the actual log-log plot are often obscured, e.g. due to axes scales. Instead, we propose to use the time dependent parameter $\alpha(t)$, namely the local slope of the $\log_{10}F$-$\log_{10}t$ dependence, as a measure of the conformity to true power law, for which α must remain constant:

$$\alpha(t) = d(\log_{10}F) / d(\log_{10}t) = (t/F)(dF/dt) \tag{1}$$

In the following, results from both analytical and numerical analysis are presented and discussed with respect to the time dependence of α.

2. Analytical models

At least in three cases when only one process is the rate-limiting (de-trapping, diffusion or surface recombination), it is possible to deduce analytical solutions for $F(t)$.

2.1. De-trapping limited outgassing

Assuming that hydrogen diffusion through the material and recombination at both, plasma exposed and opposite, surfaces of a wall element are infinitely fast compared to de-trapping from material defects, the outgassing flux can be written as release from traps:

$$F(t) = \frac{dc_{tot}(t)}{dt} = c_{tot}(t) \cdot v e^{-E_a/kT} = c_{tot}(t) \cdot K(T) \xrightarrow{T=const} F(t) \sim e^{-K(T)t}, \tag{2}$$

where $c_{tot}(t)$ is the total concentration of trapped hydrogen in the material, which decreases due to de-trapping with a rate defined by an Arrhenius-type equation, where v stands for the de-trapping attempt frequency and E_a is the de-trapping energy barrier. A solution at a constant temperature results in an exponential decay of the outgassing flux with time.

2.2. Diffusion-limited outgassing

Assuming that all hydrogen being released resides as interstitial atoms distributed throughout the material and that recombination is instantaneous, the time evolution of hydrogen concentration at each given depth $c(x, t)$ will be controlled by diffusion with zero Dirichlet boundary conditions at surfaces:

$$\frac{dc(x,t)}{dt} = D \cdot \frac{\partial^2 c(x,t)}{dx^2}, \quad c(x,t)|_{x=0,L} = 0, \tag{3}$$

where D is the temperature dependent diffusion coefficient (considering a homogeneous media where D does not depend on x), and boundaries $x = 0$ and $x = L$ correspond to plasma exposed and opposite surfaces of the material.

By separation of variables, a solution for equation (3) can be obtained for the arbitrary initial profile $f(x)$ in the following form [14]:

$$c(x,t) = \sum_{n=1}^{\infty} C_n \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{n^2\pi^2 Dt}{L^2}}, \quad C_n = \frac{2}{L} \int_0^L f(x) \sin\left(\frac{n\pi x}{L}\right) dx, \tag{4}$$

The diffusive flux through $x = 0$ and $x = L$ defines then the hydrogen release:

$$F(t) = -D \frac{\partial c(x,t)}{dx}\bigg|_{x=0,L} = -D \cdot \sum_{n=1}^{\infty} C_n \frac{n\pi}{L} \cos\left(\frac{n\pi x}{L}\right) e^{-\frac{n^2\pi^2 Dt}{L^2}} \tag{5}$$

One rather straightforward conclusion from equation (5) is that for times

$$t_{crit} \gg L^2/(\pi^2 D) \tag{6}$$

the exponential term with $n = 1$ will dominate the decay of the outgassing flux.

Figure 1 illustrates some numerical solutions of equation (5) at room temperature. In all cases, the summation over n is truncated at $n_{max} = 1000$, which was proven to be sufficient. The outgassing flux $F(t)$ (figure 1a) and the parameter $\alpha(t)$ (figure 1b) are shown. Frauenfelder diffusion [15] isotope-corrected for deuterium by factor $1/\sqrt{2}$ was used for a 1 mm thick W sample with 1 at% uniform trap density in the layer of thickness d that was varied from *1 μm* to *1 mm* (entire sample) defining the initial deuterium depth profile $f(x)$. One can clearly distinguish several different outgassing regimes. Figure 1c shows depth profiles $c(x, t)$ for the case of $d = 20$ *μm* for different times, thus giving the qualitative explanation of the observed time evolution of

outgassing. Outgassing starts with $\alpha = -0.5$ when the edges of the initial depth profile start to diffuse. After some time the depth profile acquires a smooth shape with a single maximum that moves deeper into the material, which results in transition to $\alpha = -1.5$. As soon as the diffusion front reaches the opposite side of the sample, the onset of hydrogen release there leads to a reduction of the decay rate (α increases). Finally, when the depth profile and outgassing become symmetric, a fast exponential flux decay can be observed (α tends to infinity). The exponential decay happens absolutely the same way in all cases, being defined by the critical time t_{crit}, which according to equation (6) depends only on the hydrogen diffusion coefficient (thus temperature) and sample thickness. In case of conditions selected above, $t_{crit} \approx 1.25 \times 10^6$ s, in agreement with figure 1b.

In many cases when outgassing is studied analytically or numerically, an assumption of a uniform initial distribution of hydrogen is imposed, as in the cases addressed above. In the case of a non-uniform initial depth distribution (figure 2c), the time evolution of the release becomes more complex even in a fully diffusion-limited regime, and more variations of parameter α can be seen (figure 2b), although the flux itself still can be fitted by a power law reasonably well (figure 2a). The step-like distribution with higher density in the first 10 μm and 10 times lower density in the next 90 μm that is assumed here reflects somehow the experimental observations and expectations that plasma-induced defects in the near-surface layer and intrinsic material defects in the bulk layer of the material act as trapping sites for hydrogen (we consider pure diffusion though!). The power law fit of the outgassing flux shown in figure 2a results in parameter $\alpha \sim -1$, which is comparable to experimentally observed values. Modifying the initial density distribution, e.g. number of steps, step heights and widths, other power law fits with average values of α between -0.5 and -1.5 can be expected, despite strongly varying $\alpha(t)$.
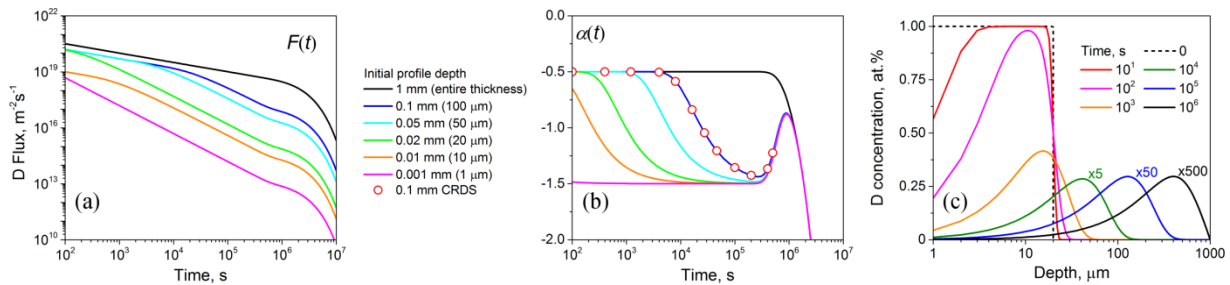

Figure 1. Numerical solutions of equation (5) for the outgassing flux $F(t)$ (a) and the parameter $\alpha(t)$ (b) as functions of time for different initial profiles of deuterium $f(x)$ representing single step functions with deuterium concentration of 1 at% up to a given depth (see the plot legend) and zero concentration through the rest of the material. Open circles in figure (b) show results of equivalent simulations with the CRDS code (see section 3) as a benchmark example. Evolution of the deuterium depth profile with time for the initial profile up to the depth of 20 μm is shown in figure (c). Evolution of the profile can be associated with changes in the value of parameter α. Details are given in the text.
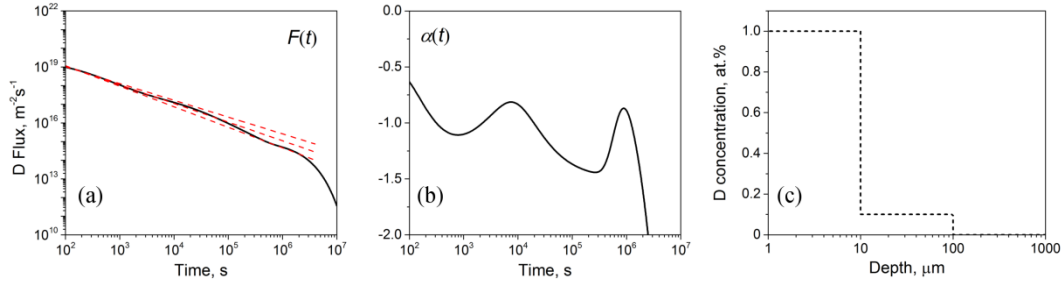
Figure 2. Numerical solution of equation (5) for the outgassing flux $F(t)$ (a) and the parameter $\alpha(t)$ (b) as functions of time for the initial profile of deuterium $f(x)$ (c) representing a double-step function with deuterium concentration of 1 at% up to a depth of 10 μm and 0.1 at% up to a depth of 100 μm. The dashed lines in figure (a) show power law dependencies $F(t) = A \cdot t^{\alpha}$ in the time interval from 10^2 to 10^6 seconds with α values of -0.9, -1.0 and -1.1.

It has to be noted that the initial assumption that hydrogen resides as interstitial atoms in the bulk is not unphysical, since especially at high plasma fluxes strong oversaturation of the near surface layer can be expected and was observed experimentally [16, 17]. The amount of retained hydrogen atoms exceeds the hydrogen solubility in the material under normal conditions by orders of magnitude. It can also be expected that during plasma exposure the amount of intrinsic and induced defects is not sufficient to instantaneously accommodate all implanted hydrogen atoms, therefore the population of interstitial and thus mobile atoms should be significant, leading to H release during exposure (recycling almost equal to unity) and H diffusion into the bulk. After plasma irradiation the out-diffusion of these mobile atoms may contribute at least some fraction to the hydrogen release referred to as dynamic retention.

2.3. Recombination-limited outgassing

Assuming that de-trapping and diffusion are fast and that hydrogen release is limited by surface recombination, a uniform hydrogen profile in the sample decreasing with time can be expected:

$$F(t) = K_r(T)c^2(t) = -\frac{dc(t)}{dt}L \xrightarrow{T=const} F(t) = K_r C_0^2 \left(1 + \frac{K_r C_0}{L}t\right)^{-2}, \qquad (7)$$

where $c(t)$ is the uniform density of hydrogen in the bulk locked between two surfaces $x = 0$ and $x = L$ due to limited recombination rate constant $K_r(T)$. A solution at a constant temperature results in a slow onset of outgassing that approaches power law with $\alpha = -2$ for times $t_0 \gg L/K_r C_0$, where C_0 is the initial uniform density of hydrogen in the bulk. For a W sample with $L = 1\ mm$ and $C_0 = 1$ at%, assuming K_r according to Anderl [18], the transition time t_0 at room temperature is about 15200 s (Figure 3).

3. Methods and tools

In intermediate regimes when neither process is dominating, an analytical analysis of hydrogen release behavior becomes rather complicated and, in the most general case, impossible. To be able to address such general cases, reaction-diffusion modelling is employed. For parameter

studies presented in the next section, the coupled reaction-diffusion systems (CRDS) code is used [12, 13]. The code was initially applied for hydrogen in beryllium. In this work, however, we adopted the code to simulations of hydrogen in tungsten. In the code, multiple species can be introduced that all may be mobile and undergo transformation reactions. For the purpose of simulation of hydrogen outgassing in tungsten, only three species were used, namely mobile hydrogen atoms, immobile traps and immobile (trapped) hydrogen atoms. These assumptions were used to simplify the picture and are not limitations of the model.

The general master equation for the time evolution of concentrations of each species can be written as follows:

$$\frac{\partial c_i(x,t)}{\partial t} = D_i(T)\frac{\partial^2 c_i(x,t)}{\partial x^2} + S_i(x,t) + R_i(x,t); \quad R_i(x,t) = \sum_j \gamma_j(T)c_k(x,t)c_m(x,t), \qquad (8)$$

where $D_i(T)$ and $S_i(x,t)$ are the temperature dependent diffusion coefficient and the spatially distributed time dependent source term for species of type i. The reaction term $R_i(x,t)$ describes the sum of all the transformation reactions which lead to creation or destruction of that type of species. Each reaction rate in its general form is proportional to local densities of interacting species, and the reaction rate coefficient $\gamma_j(T)$ that has an Arrhenius temperature dependence.

Surface desorption is accounted for by Neumann boundary conditions at material surfaces equating the diffusive flux from the bulk to the second order desorption flux from equation 7:

$$K_r(T)c^2(x,t)|_{x=0,L} = -D(T)\frac{dc(x,t)}{dx}\Big|_{x=0,L}, \qquad (9)$$

For N species or states under consideration, such a description results in a system of N coupled partial differential equations that is constructed and solved numerically in *Wolfram Mathematica* [19] software. The main benefit of such a description in comparison with common codes as TMAP [20] is the flexibility for the system extension with respect to new species and reactions, as well as the possibility of dynamic creation and mobilization of all species in the system. However, the code does not ensure that for a given particular case the numerical system obtained will be easily resolvable. This implies scrupulous code tuning for each particular system and scenario.

4. Results and discussion

4.1 CRDS Simulations

The CRDS tool was applied to a W system similar to one described in section 2.2. The reference case was chosen to be the following:

- W sample of 1 mm thickness kept at 500 K during exposure and outgassing;
- Only one type of traps with de-trapping energy of 1 eV uniformly distributed through the entire material thickness, atomic density of traps equal to 10^{-4} atomic fractions;
- Exposure to a pure D^+ plasma given by a Gaussian source term with a mean depth of 3 nm and a standard deviation of 2 nm, using plasma flux 10^{22} m^{-2}s^{-1} up to fluence of 10^{26} m^{-2} (10^4 seconds exposure);

- Deuterium diffusion according to Frauenfelder [15] (isotope-corrected), surface recombination according to Anderl [18].

From the reference case specified above, over 100 parameter variations were performed in several series when only one parameter at a time was modified: exposure temperature, trap density, de-trapping energy, plasma flux, etc. It has to be noted that by no means can the performed parameter variations be considered as sufficient to cover the full parameter space. There may be combinations of parameters that lead to results essentially different from those presented here.

Each simulation consists of the plasma exposure phase with the implantation source switched on for the total exposure time defined by the chosen flux and fluence, and the outgassing phase, when the source term was deactivated. The material temperature during outgassing was either kept constant or allowed to cool down to room temperature. During the implantation phase deuterium diffuses deeper into material populating the available traps. During the outgassing phase, the mobile deuterium with densities well above the solubility limit starts to diffuse in and out, and, depending on the temperature, the trapped deuterium atoms get released. The transport of deuterium through the material at all times is not solely classical diffusion, since trapping, de-trapping and re-trapping processes take place. Figure 3 shows time evolution of the outgassing flux $F(t)$ and parameter $\alpha(t)$ for some of the simulation series. In most cases, parameter α shows a complex oscillatory behavior. In particular cases, some of which are shown in figure 3 (upper right set) and in figure 4, reasonable power law fit of the outgassing flux evolution over long time intervals can be obtained, despite strong variations of $\alpha(t)$.
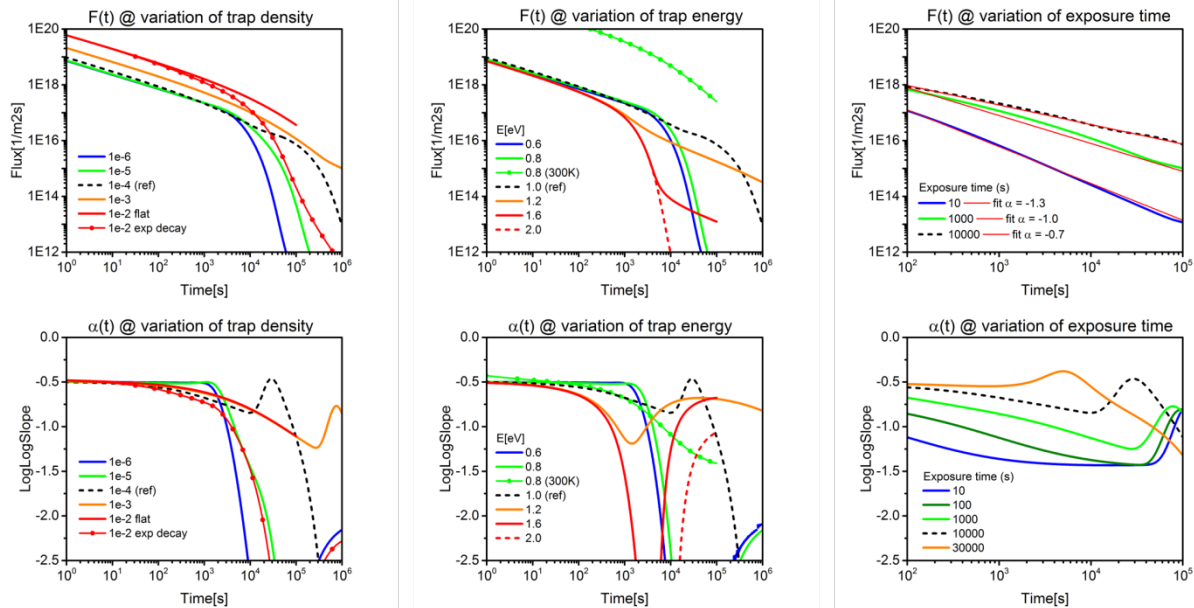

Figure 3. Time evolution of the outgassing flux $F(t)$ and parameter $a(t)$ simulated with the CRDS code for variations of the trap density (left), trap energy (middle), and exposure time (right). All variations are performed with respect to the reference case described in the text and shown as black dashed line. For the variation of the exposure time also power law fits of the outgassing

flux in the time interval from 10^2 to 10^5 seconds are shown (upper right) with values of α between -0.7 and -1.3.
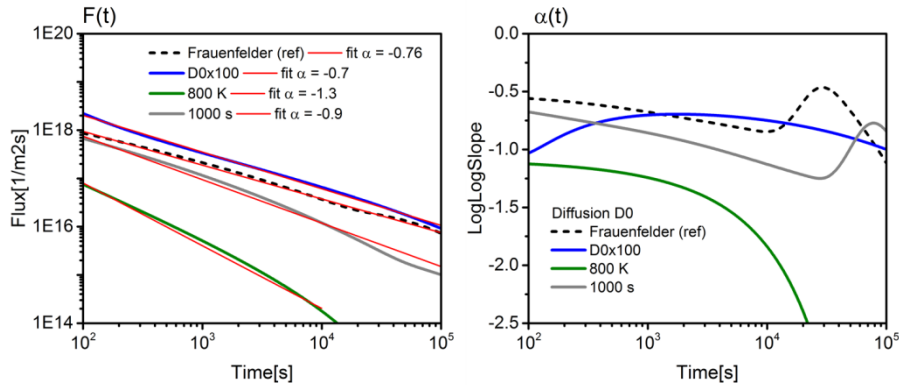

Figure 4. Time evolution of the outgassing flux $F(t)$ and parameter $a(t)$ simulated with the CRDS code for variations of different parameters (single change with respect to the reference case shown as black dashed line). D0x100 – factor 100 increased pre-exponential factor in the diffusion coefficient as compared to the Frauenfelder value [15]; 800 K – exposure and outgassing at increased temperature; 1000 s – 10 times shorter exposure up to the fluence of 10^{25} m^{-2}.

4.2 Comparison with experiments

The most recent result on hydrogen outgassing in a large-scale tokamak comes from JET with the ITER-like Wall (ILW) (figure [2]. Decimating the data and taking the proper derivative, one can extract some information about the experimentally measured evolution of $\alpha(t)$ (Figure 5). Despite unavoidable artificial numerical noise in $\alpha(t)$ computed this way deviations from a pure power law decay can be seen in both $F(t)$ and $\alpha(t)$ evolution. The parameter α changes from about -0.6 to about -0.8 and then continues to fluctuate.
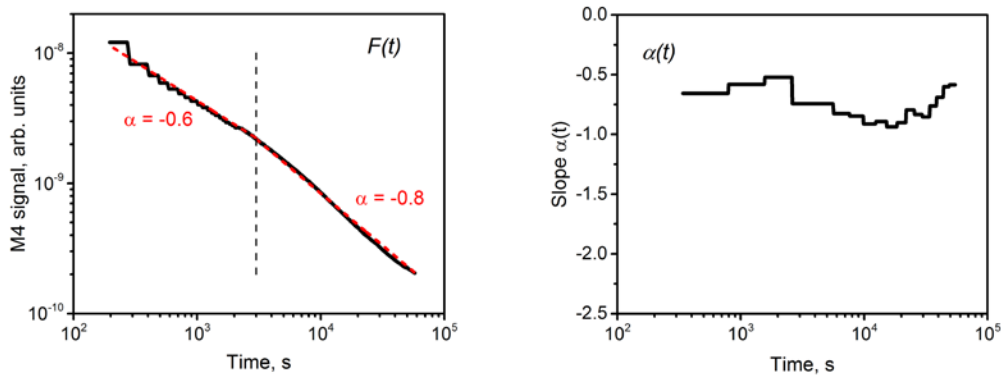

Figure 5. $F(t)$, $\alpha(t)$ for long-term outgassing data of mass 4 in JET-ILW from [2].

It is clear that comparison with outgassing experiments in tokamaks is complicated due to strong variation of many parameters over plasma-exposed surfaces: exposure surface temperature, plasma flux, material mixing and surface conditions, etc. Recently, experiments on the dynamic outgassing from bulk W exposed to high flux pure D_2 and mixed D_2+N_2 and D_2+N_2+He plasmas

up to the peak fluence of 10^{27} m^{-2} have been performed [4] in the linear plasma device PSI-2 [3]. The target was pre-heated up to 550 K and reached about 1000 K during exposures to reflect the DEMO wall coolant and operation temperatures, respectively. Details of exposure conditions and measuring procedures can be found in [4]. Characteristic for exposures in PSI-2 is the hollow plasma profile resulting in non-uniform flux distribution over the exposed surface. A similar analysis as above with smoothing/decimating the data and taking the proper derivative results in experimentally measured evolution of $\alpha(t)$ shown figure 6. Despite numerical noise, deviation from a pure power law can be clearly seen that shows similar trends as in simulations (a decrease from values equal or below -0.5 with some intermediate increases and an exponential decay in long-term).
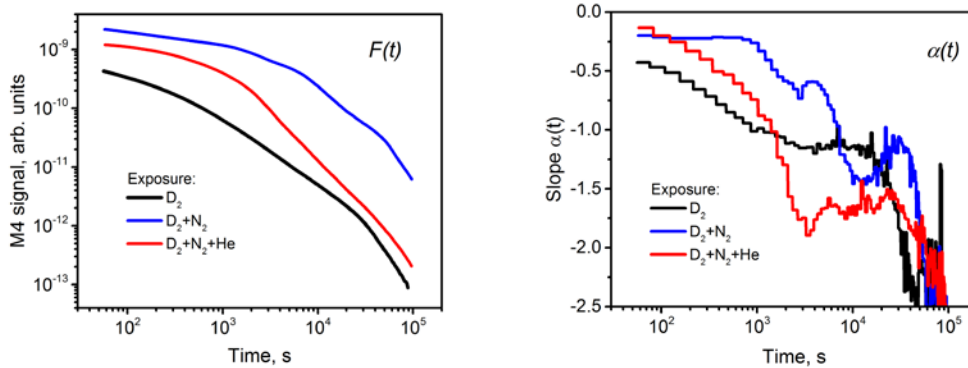

Figure 6. $F(t)$, $\alpha(t)$ for long-term outgassing data of mass 4 for bulk W exposed in PSI-2 to high flux high fluence pure D_2 and mixed D_2+N_2 and D_2+N_2+He plasmas [4].

5. Conclusions

Several analytical and computational models have been presented in the literature to describe the hydrogen outgassing from plasma exposed materials. Simple analytical models have been reviewed here and indications were given that a satisfactory power law scaling of the outgassing flux can be attributed even to solely diffusion processes under the assumption of a non-uniform initial density distribution. Furthermore, simulations with the reaction-diffusion code CRDS have been performed for general cases without pre-imposed limitations on the dominating process with over 100 parameter variations from the selected reference case. The local slope $\alpha(t)$ of the $log_{10}(F)$-$log_{10}(t)$ dependence was introduced as a measure of conformity of the outgassing flux to a power law decay. Complex time evolution of the parameter $\alpha(t)$ has been demonstrated both in the case of analytical solutions in the diffusion-limited regime and in the case of CRDS simulations. Despite that, several cases of satisfactory power law scaling have been obtained in good comparison with experimental observations. Analysis of the experimental data on long-term outgassing from the JET tokamak with the ITER-Like Wall and from the linear plasma device PSI-2 indicated that real outgassing also deviates from pure power law scaling with $\alpha(t)$ varying in time, recalling the trends corresponding to the diffusion-limited regime. Although observed experimentally, the power law scaling results from the interplay of different processes and does not correspond to pure power law dependence. A better understanding of the processes involved can be obtained in experiments under well-defined conditions, both in terms of

exposure and material characterization, by analyzing the actual time evolution of $\alpha(t)$ depending on controllable parameters in comparison to reaction-diffusion simulations. Ideal conditions for that would be exposures at different well-controlled surface temperatures, when the temperature is kept constant and the same during exposure and outgassing.

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