

Towards an Integrated Scenario for Tritium Inventory Control during ITER Operation under Carbon PFCs by Nitrogen-Based Chemistry

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Abstract.

In spite of being highly suited for advanced plasma performance operation of tokamaks, as demonstrated during at least two decades of fusion plasma research, carbon is not presently considered as an integrating component of the PFCs in the active phase of ITER. The main reason preventing its use under the very challenging scenarios foreseen in this phase, with ELMs delivering several tens of MW/m² to the divertor target every second or less, is the existing concern about reaching the tritium inventory value of 1Kg used in safety assessments in a time shorter than the projected lifetime of the divertor materials eroded by the plasma, set at 3000 shots. Although several mechanisms of tritium trapping in carbon components have been identified, co-deposition of the carbon radicals arising from chemically eroded CFCs in remote areas appears as the most threatening one. Several possible ways to keep control of the tritium build up during the full operation of ITER have been put forward, mostly based on the periodic removal of the co-deposits by chemical (thermo oxidation, plasma chemistry) or physical (laser, flash lamps,) means. In this work we propose a combination of techniques for the inhibition and removal of tritium rich co-deposits based on the strong chemical reactivity of some N-bearing molecules with carbon. These techniques can be used in a sequential scheme thus providing an integrated scenario for T inventory control in the active phase of ITER.

1. Introduction

The use of carbon materials in a fusion reactor is strongly hampered by the chemical erosion processes leading to a large in-vessel tritium inventory hard to recover. Although several proposals exist about how to remove tritium from their carbon co-deposits [1], very few of them are able to prevent the retention during plasma operation, as the concept of high wall temperature operation. Since its proposal in 2002 [2], the scavenger technique for the inhibition of tritium rich co-deposit formation in hidden areas of carbon-based Fusion Reactor has been tested in several tokamak devices, divertor simulators and laboratory cold plasmas [3]. Although successful application of the technique was achieved upon nitrogen injection in the sub-divertor region of the Asdex-Upgrade tokamak [4], the concern about a possible enhancement of carbon erosion by the injected scavenger ionic species at the divertor plasma still exists [5], so that alternative injection schemes must be developed. However, experiments performed in the PSI-2 divertor simulator showed that ion chemistry may play a negligible role in the scavenger mechanism, and that a clear correlation exists between the inhibition effect and some molecular species, such as ammonia, produced in the plasma [6]. In the

experiments here reported, ammonia has been tested as a possible candidate for the use of the scavenger concept in a non-perturbative way i.e., injected away from the plasma-wall interaction area.

Plasma assisted cleaning methods are in principle highly suited for carbon film removal from plasma exposed surfaces. Although their intrinsic efficiency is higher than other, time consuming alternatives, their main drawback comes from a limited access of the plasma to the areas of main co-deposit accumulation. To date, either pure D₂ or He/O₂ mixtures are the main plasma species to be used, depending on their aim, isotope exchange of full carbon removal, respectively [1]. In the presence of strong getters, as it will be the case of ITER with its main wall fully covered by Be, the application of oxidizing plasmas can lead to long-term deleterious effects. Not only the getter has to be de-oxidised with devoted plasma discharges but also the formation of thick oxide layers can lead to enhanced fuel retention during normal operation. For that reason, glow discharges having nitrogen as the active gas have been proposed as alternative [7,8]. Laboratory test by DC [7] or low-pressure ECR [8] plasmas in H₂/N₂ mixtures on carbon films have shown that high etching rates can also be achieved in the absence of oxygen. More recently, ammonia plasmas were tested in DC and RF plasmas [9]. It was shown that the efficiency of a He/NH₃ plasma on open surfaces could be as high as that of the conventional He/O₂ mixture, leading to the formation of HCN as a main product. In this work we present the first results of carbon removal in gaps by ammonia plasmas. For the removal of carbon films from difficult-to-reach, remote areas, thermo-oxidation in pure O₂ at high (50 torr) pressure and high temperature, (up to 350 C under the present divertor design) seems to be the most efficient method to be used during long operation breaks. However, a big concern exists about re-processing the T₂O created during the oxidation process. Recent experiments in our labs have shown that NO₂ can remove carbon deposits at a much higher rate than O₂ under the specific conditions of temperature and pressure foreseen in ITER [10]. Moreover, a different mechanism for the oxidation exists, as demonstrated from the mass spectrometric recordings. In this paper, experiments oriented at the optimization of the technique in terms of absolute removal efficiency and minimum water formation are also described.

Finally, the implications of all these findings, and some other possible methods under consideration, on the design of an integrated T control scenario during ITER operation under carbon-based PFC are addressed.

2. Film Inhibition by nitrogen and ammonia seeding in remote areas.

The possibility of inhibiting the formation of tritium rich carbon films by scavenger reactions during plasma operation was put forward several years ago [2]. Several possible molecules were proposed for the task but, since molecular nitrogen is a candidate for the enhancement of local radiation in divertors, its injection into the area (not directly exposed to the plasma) where chemical processes lead to the formation of the tritium-rich co-deposits was proposed. Up to date, nitrogen has been extensively tested as a possible radical scavenger in cold plasmas, divertor simulator and Fusion plasma devices with different success [3,4]. However, the high carbon erosion rate observed under ionic nitrogenised species, with an anomalously low energy threshold [5] raises concern of enhanced erosion of the divertor plates when nitrogen is injected into the plasma periphery. Therefore, the injection of scavengers in carbon-radical rich areas, well away from the main plasma and prone to co-deposit and dust formation would be desirable. Recent experiments of nitrogen seeding at the PSI-2 linear plasma device [6] indicated that radical, as opposed to ion, chemistry plays the main role in the scavenger effect. Moreover, a possible direct reaction between ammonia, formed as a chemical product from the recombination of N and H atoms at the walls, and carbon radicals was deduced from mass spectrometric recordings. Compared with nitrogen, a well-known

inert gas in its molecular form, ammonia shows high reactivity against radical species, and no need for plasma activation should exist. In this work, recent experiments of direct injection of ammonia as a carbon-radical scavenger in a, divertor-type plasma are described [11]. Scavenger experiments were performed at the PILOT-PSI linear plasma device [12] and in an inductively-coupled RF plasma.

The most important modification made in the PILOT-PSI for these experiments was the insertion a hot stainless steel liner, coaxial to the plasma and with an inner diameter of 25 cm. The temperature of the liner was kept at $\sim 300^\circ\text{C}$ in order to minimize local deposition of carbon and thus to enhance the transport of plasma-borne radicals to the deposition sample [13]. Two different pumping systems were used for the cylindrical zones produced. The sample consists of two polished silicon wafers, located downstream of the plasma and ~ 7 cm behind the target. No direct line of sight was allowed between the plasma and the samples. Figure 1 shows a sketch of the set-up. Carbon deposition was monitored in situ by laser interferometry [14] through a view port and a hole made in the liner. One of the samples was used as a reference of the naked Si reflectivity, and the other one was pre-coated with a 50 nm film layer in order to match the part of interference pattern most sensitive to the film growth. The technique was calibrated by ex-situ ellipsometry.

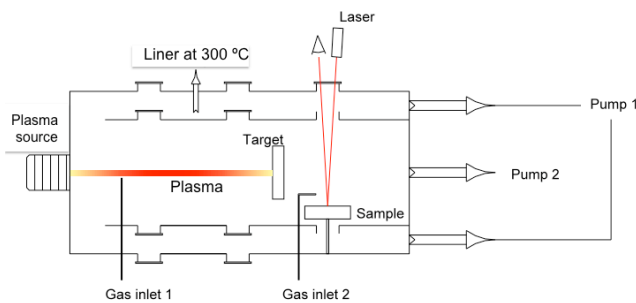


Figure 1. Sketch of the set up used in PSI-2

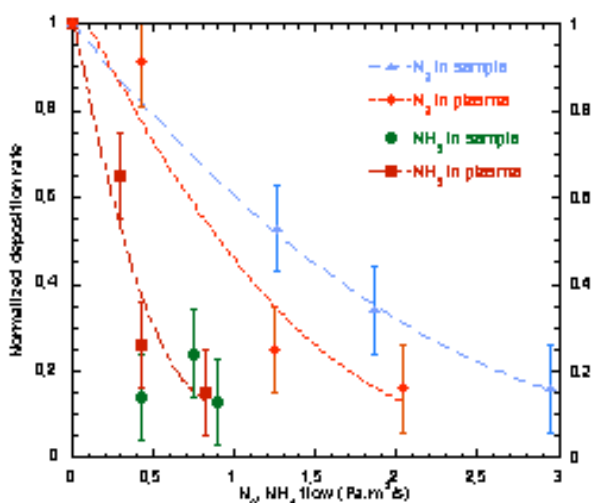


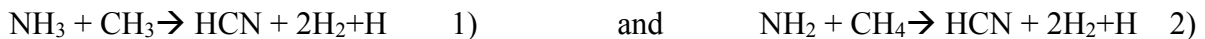
Figure 2. Impact of gas flow and injection location on the scavenger effect for ammonia and nitrogen in PILOT-PSI

Hydrogen plasmas were run with a flow of $Q = 3.66 \text{ Pa}\cdot\text{m}^3\cdot\text{s}^{-1}$. Methane was added to the hydrogen plasma at $Q = 0.27 \text{ Pa}\cdot\text{m}^3\cdot\text{s}^{-1}$ and the total pressure in the deposition mode was $P \sim 4 \text{ Pa}$. Nitrogen and ammonia were used as scavengers. They were injected either into the plasma region or at the location of the deposition sample with different flows. The plasma duration was kept constant at 100 s, at a magnetic field of 0.4 T. Typical deposition rates at the Si sample, in the absence of a scavenger, were up to 4 nm/min.

Under initial constant H_2/CH_4 plasma composition, current and total pressure conditions, the deposition rate at the sample was strongly modified by the addition of nitrogen or ammonia to the plasma. Some blank experiments were eventually run during the sweep to check for reproducibility. Under some conditions, a net deposition in the sample was found for pure H plasmas. This is attributed to a memory effect, the erosion of carbon at the walls from previous depositions, which must be taken into account when comparing runs well separated in time. In any case, a systematic decrease of the deposition rate upon increasing the ammonia concentration in the plasma was systematically recorded in consecutive shots.

The influence of ammonia and nitrogen injection location on the film inhibition

effect was tested by using the gas pipe located in front of the deposition monitor for the scavenger inlet. The results are shown in Figure 2. The injected fluxes shown in the abscissa were evaluated from the partial pressure recordings in the MS. The peak at amu 17, for ammonia, was used for reference. As seen, no significant difference in the flux of ammonia required for a given film inhibition effect was recorded, regardless of inlet locations. This is not the case for nitrogen, also shown in figure 2, where a factor of 2 to 3 higher flows were required if the gas is injected near the sample. However, nitrogen injection in a H₂ plasma typically leads to ammonia formation if a metallic state of walls is dominant [15]. As displayed in figure 3, a linear dependence of hydrogen cyanide (HCN), detected at amu 27 in the mass spectrometer, upon ammonia feeding was found, but only in the presence of methane. Based on these findings, we postulate the following scavenger mechanism for the inhibition of film formation in the presence of ammonia, either externally injected or plasma produced:



While reaction 2 would require the decomposition of the injected ammonia in the plasma, reaction 1 wouldn't.

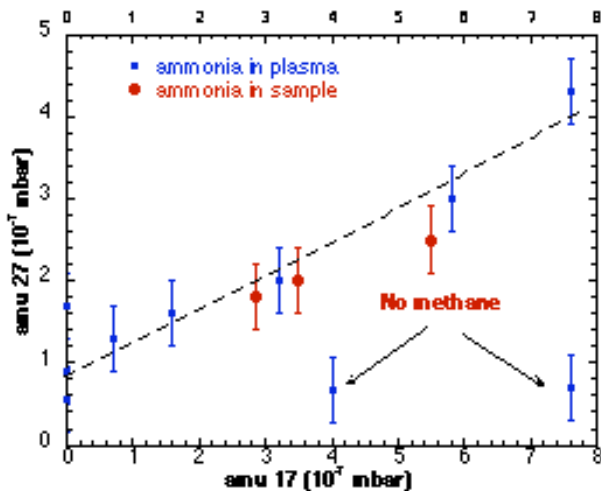


Figure 3. Formation of HCN by ammonia injection in H₂/CH₄ plasmas in PILOT-PS

plasma conditions, the pressure of ammonia was swept and the MS peaks at amu 25-30 were recorded. No carbon deposits were observed in the plasma chamber during the reported experiments.

Contrary to the Pilot-PSI experiments, a significant production of C₂ hydrocarbons was detected in the absence of ammonia, created by the recombination of C₁ radicals from the cracking of methane into the plasma, therefore complicating the mass spectra interpretation. Nevertheless, the reconstruction of the reaction product composition from the recorded mass spectra was possible due to the lack of contribution of HCN to mass 25 and the known intensities of the MS peaks from the ionization of C₂ hydrocarbons into the mass spectrometer [16], experimentally verified for the analysis here reported.

The results of the scan in ammonia pressure, referred to the intensity of amu 17 in the MS, are displayed in Figure 5. The direct contribution to amu 27 by pure ammonia (plasma off) is also

In order to directly assess the presence of reaction 1 under much better defined conditions, a different experiment, in which no ammonia was dissociated into the plasma, was envisaged (fig.4). An inductively coupled RF plasmas with a high dissociation efficiency for methane were created in a Pyrex chamber at P= 20 Pa and P_{in}= 120 W. This chamber was connected through a narrow tube (l= 40 mm, φ= 3 mm) to a downstream region where ammonia was directly seeded. OES was used to verify the absence of back

diffusion into the methane plasma. A differentially pumped mass spectrometer was again used for the monitoring of

shown for comparison. The data displayed support the presence of two competing processes: C_1 recombination to yield C_2 hydrocarbons and scavenging of C_1 radicals by ammonia to yield HCN. The larger extent of reaction 1, as ammonia is increased, leads also to a continuous drop of the ratio 25/26, as shown in figure 5.

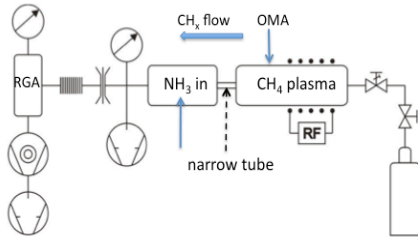


Figure 4. Sketch of the set-up used for the RF plasma experiments with remote

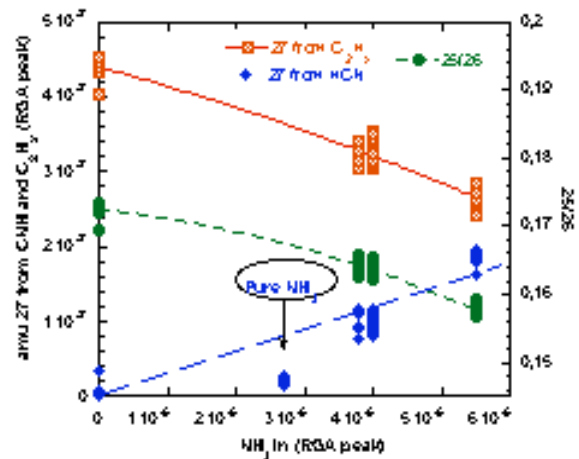


Figure 5. HCN and ethylene formation under the injection of ammonia in the afterglow of RF

3. Cleaning plasmas in N_2 and NH_3

When considering the use of etching plasmas for film removal in ITER, there are two aspects of the plasma facing components of particular concern: the extensive coverage of the first wall by Be and the presence of narrow gaps. Experiments specifically oriented to these issues were performed at CIEMAT, and described in previous works [7,10]. In summary, He/O_2 mixtures (at several ratios) and H_2/N_2 mixtures (20:80) were used in a DC glow discharge plasma in order to remove pure and metal and B-doped a-C:H films. The films were either fully exposed to the plasmas or lying on the sides of a gap (0.2-1mm wide x25mm deep). The maximum attained rate for a He/O_2 mixture on a fully exposed plasma was 12 nm/min. More recently [9], it was shown that He/NH_3 plasmas were highly suited for carbon film removal at open surfaces, its efficiency being comparable to that of the He/O_2 mixtures. The same conclusion was drawn from experiment in a RF, inductively coupled discharge [17]. In a previous work we addressed the possible cleaning of deposits in narrow gaps by these plasmas. Experiments similar to those described in ref 10 were then performed. The temperature of the structure used for the 1 mm gap simulation was raised up to 150 °C. The results for different times of exposure and two temperatures are shown in figure 6. Also shown is the effect of a He/O_2 GD at 150°C under the same experimental conditions. As seen in figure 6a (top), no significant decrease of the recorded film thickness was detected even at the longest exposure times. Moreover, some kind of structure seems to develop at the very entrance of the gap, corresponding to the larger values of the x-axis in the figure. Since laser interferometry is highly sensitive to the optical constants of the film, these maxima could be directly associated to changes in such parameters upon chemical reaction of the deposited carbon films and the active species from the plasma. This would be consistent with the lack of such patterns when the sample is exposed at high temperatures, (6b, bottom) and points to the creation of easily evaporable compounds, as it would be the case of some sort of polymeric CNH films.

Only the very top of the gap, a few millimeters long, seems to be removed by $He/ammonia$ plasmas at 150 °C. Therefore, the possibility of the requirement of ion assisted processes for

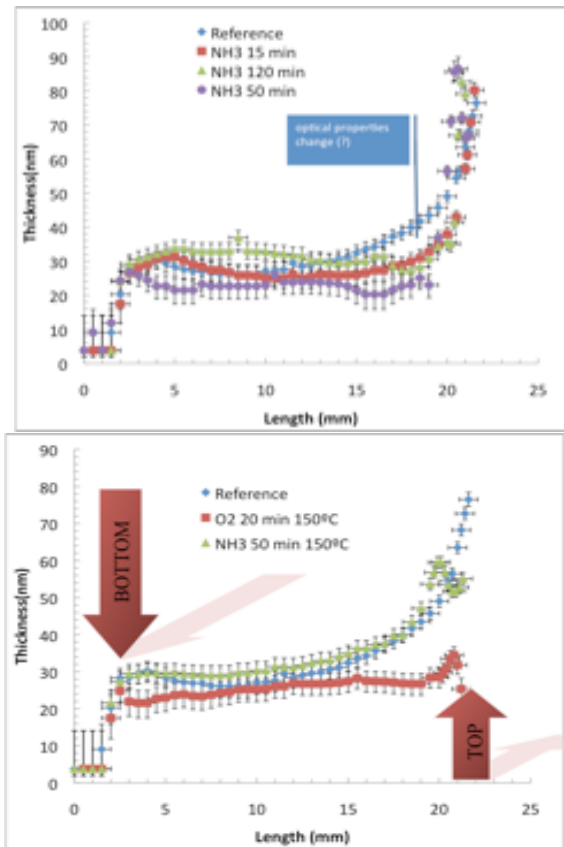


Figure 6. Profile of film thickness into a gap upon exposure to an ammonia/He plasma. Top, room temperature, bottom, 150 °C.

the cleaning mechanism in these plasmas cannot be ruled out. This point was very recently addressed in CIEMAT. The structure holding the Si sample, in which a hard a-C:H film had been previously deposited, was biased respect to the GD, He/ammonia plasma at +10 V. Laser interferometry together with mass spectrometric recording of the released HCN were used to follow the erosion process. While erosion rates of > 12 nm/min were deduced for the grounded sample, very weak erosion by the plasma was seen at V=+10V, thus confirming the need of ion bombardment for the etching of the film in ammonia plasmas. The possibility of recovering the good cleaning characteristics of these plasmas in gaps by further increase of the exposure temperature (and perhaps decomposing the passivated layer) is still under investigation. Metal (Li and Mg) mixing into the a-C:H layer did not prevent their cleaning by He/O₂ discharges. Only when a stratified structure was developed by alternating the exposure of the sample to the He/CH₄ deposition plasma and to an effusive Li oven, a highly decreased erosion rate was observed [18]. To date, no information on the impact of metal inclusion into the carbon film respect to their etching characteristics by

nitrogen-containing plasmas is available.

Finally, boron-containing films have been exposed to O₂ and N₂ cleaning plasmas. Either of the two reactive species, N and O, produced much lower etching rates. This fact has also been observed in boronized machines as in AUG and TEXTOR [19], and rather than to the oxygen uptake by the B in the film, it could be due to conversion from sp² to sp³ hybridization in the presence of B, which leads to a lower reactivity.

4. Thermo-oxidation by NO₂

In a previous work [10], it was found that NO₂ is able to remove carbon films, regardless of their location, at a significantly faster rate than O₂ at the pressures foreseen for the thermo-oxidation of ITER deposits. Thus, for the plasma generated, hard, amorphous carbon films with a typical H content of H:C of 0.4, an erosion rate of < 100 nm/h was measured, while values of 120nm/h at 300°C were recorded when a 1:1 mixture of NO₂ and N₂ is used instead. Mass spectrometric data taken during the oxidation process indicate that NO₂ will spontaneously decompose into NO and O₂ on metallic wall at T> 300 °C. However, the oxidizing reaction of the film



inhibits the formation of molecular oxygen. In fact, the ratio 2:1 found for the CO_2/CO production under NO_2 oxidation is much larger than the typical values of 0.2 found when molecular oxygen is used [ref], thus revealing a different mechanism for the film oxidation. The question remains as in which form the hydrogen retained into the film is released during the film disintegration. Although water is typically seen during thermo-oxidation with oxygen and, in some instances, in the etching by He/O_2 GD,

molecular hydrogen release has been documented when hard a-C:H films are chemically etched in oxidizing plasmas [20]. Moreover, the fact that NO molecules, created during the oxidizing process according to reaction 3, are prone to recombine with atomic H to produce HNO, opens the possibility of recovering tritium from the carbon films in the form of molecular T_2 , instead of its, more cumbersome, oxide form when the technique is applied in a fusion reactor. Therefore, special care was devoted to the assessment of water production during the film oxidation by NO_2 . While neither H_2 , nor H_2O were detected at high-pressure exposure (50 torr), a clear indication of water formation was seen at 0.5 torr and 300°C oxidizing conditions. The experiment was first carried out in pure Ar in order to account for any other possible sources of water from colder parts of the reactor. The results are shown in figure 7. Unfortunately no absolute calibration of the mass spectrometer respect to the reaction products was possible, so that no estimate of the actual yield for water generation was obtained. The possible change in the reaction kinetics at higher pressures or in plasma discharges of NO_2 , to produce H_2 instead of water, is presently investigated at CIEMAT.

5. Integrated scenario in ITER

The combined use of the chemical techniques here addressed during ITER operation could provide an integrated scheme for tritium inventory control if carbon materials are used as PFCs. First, a systematic injection of ammonia in the region between the bottom of the vessel, below the divertor structure, and the cryopumps should be provided in order to prevent for tritium rich carbon co-deposits in that preferred area. Although a detailed calculation remains to be done and large uncertainties of the expected carbon fluxes to the hidden parts of the divertor still exist [21], maximum ammonia fluxes of the order of those used for radiative cooling of divertor plasmas [22] are foreseen. As noted above, all C atoms leaving the confined plasma as hydrocarbon radicals will eventually be converted into D(T)CN, readily trapped at LN_2 temperatures. A periodic removal of such deposits, from an independent, devoted cryotrap, could be performed when required. Furthermore, thermal decomposition of D(T)CN and tritiated ammonia to recover the fuel are well established techniques [9].

In addition to carbon migration to the lower divertor structure and duct regions, deposition in gaps can account for up to half the total tritium inventory in ITER [20]. Although the removal of metal containing, carbon deposits from gaps remains challenging, He/O_2 GD at elevated temperatures has been proven quite effective [23]. However, the production of water by this technique still represents a problem for the tritium reprocessing plant. Efforts oriented at non-

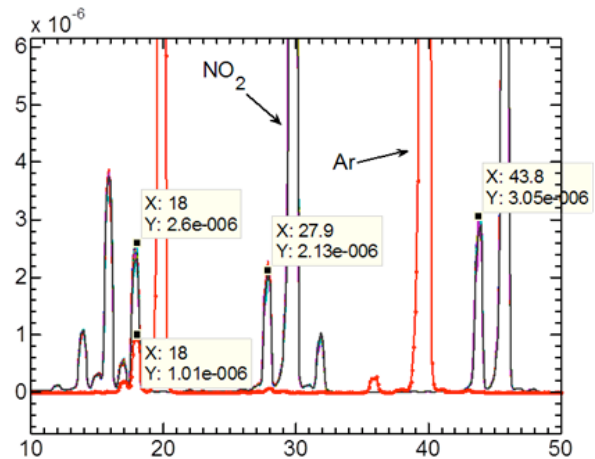


Figure 7. Mass spectrum of the reaction products during thermo-oxidation of a C:H film in NO_2 and Ar at 0.5 torr and 300°C

oxidative plasma or high-pressure high-temperature gas exposure of the full vessel in the lines here addressed are still needed, in particular, and for the sake of economy of resources, those sharing the kind of chemistry involved in the scavenger reactions.

In conclusion, it is shown in this work that two species alone, ammonia and NO₂, could perform the integrated task of T control in ITER with CFC target if water production by thermo-oxidation can be prevented. Even more interesting could be the use on only ammonia for radical scavenger and for the plasma etching of the co-deposits if gaps could be cleaned in the absence of ionic species. Work in these directions, mostly supported by the EFDA PWI Task Force, are presently in progress in several Associations.

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