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Influence of He and Ar injection on ammonia production in N_2/D_2 plasma in the medium flux GyM device.

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Abstract

Nitrogen used to reduce the power load to the divertor in tokamak fusion devices (JET, AUG) has the drawback of ammonia formation. Also non-negligible quantity of tritiated ammonia could be a serious concern for ITER, since it cannot be reduced through the presently designed fuel cycle loop. To study the ammonia production in nitrogen seeding plasma, a dedicated laboratory experiment was carried out, in which surface catalytic reactions have been proved to be the principal responsible for ammonia formation. The influence of the introduction of noble gases, like He or Ar, on the ammonia formation was also investigated.

In this paper we report a study of the production of ND_3 as a function of the electron temperature (T_e) and neutral pressure in a N_2/D_2 plasma mixture in the linear machine GyM for 60 min of cw plasma. The nitrogenized compounds were monitored by Optical Emission Spectroscopy (OES) and Mass Spectrometry (MS). Measurements were performed at different values of T_e ranging from 3 eV to 6 eV by varying the microwave power (2.45 GHz, up to 1.5 kW cw) that sustains the plasma, and for different neutral pressure at a constant ratio of nitrogen and deuterium partial pressures. The effect of introduction of He or Ar in the N_2/D_2 mixtures has been also investigated.

The ND_3 produced during plasma experiments has been quantified with a dedicated setup based on an in-line LN_2 trap and a Liquid Ion Chromatography (LIC).

Mass-spectrometry results showed that ND_3 is formed only during the plasma phase of the experiment while LIC showed that ammonia production increases with T_e and with the total neutral pressure. Optical Emission Spectroscopy confirms the presence of ND species in all cases studied with the intensity of the relative bandhead (at 335.7 nm) increasing with T_e, in agreement with the amount of ammonia measured by LIC. These results indicate ND compounds as a necessary precursor for ammonia formation. The addition of 17% of He in the N_2/D_2 plasma does not change the intensity of the ND line, although LIC measurements resulted in a reduction of 80% of ammonia. This suggests that He does not affect the interaction between nitrogen and deuterium inside the plasma, while modifying the physical chemical process occurring at the wall, where the adsorbed He inhibit the catalytic reactions leading to ammonia formation at the metallic surface of the vessel. These results confirm the active role of a metallic surface in ammonia production and indicate He injection as a promising solution to limit formation of the tritiated ammonia in the N seeded plasma of ITER.

Keywords: Nitrogen seeding, Ammonia, Optical Spectroscopy, Chromatography, Mass Spectrometer

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1. Introduction

The high expected power on the ITER divertor targets requires the use of the impurity seeding to mitigate the heat load by radiative dissipation. Nitrogen is a leading candidate for edge-seeding as it allows a substantial reduction of the heat flux while maintaining high core confinement. Being chemically reactive, N_2 interacts with the Plasma Facing Components (PFCs) to form nitrides but the more important issue is its chemical reaction with hydrogen isotopes to form ammonia (ND_3) [1]. The plasma-assisted ammonia formation is well-documented in the low-temperature plasma physics literature [2] and it is not surprising to occur in tokamak scrape-off layer. Both in ASDEX-Upgrade [3] and JET [4] ammonia has been found as a consequence of experiments with nitrogen-seeded plasmas.

The concern arises since experiments on ASDEX-Upgrade [3] have shown that the 8% of injected nitrogen is converted to ammonia. This percentage is significant and could have serious implications on the ITER tritium plant, currently designed to tolerate low levels (1-10 ppm) of ammonia in the exhaust gas.

In addition, tritiated ammonia could be adsorbed in the ITER cryo pumps, based on active charcoal, whose desorption, which requires a high temperature cryo-pumps regeneration, could have a significant impact on the operation duty cycle of the plant.

In spite of there being different methods to process tritiated ammonia like isotopic exchange, oxidation and catalytic decomposition, it would be also useful to identify a process that reduces ammonia production without modifying the positive effects of nitrogen seeding on plasma performance.

The purpose of this paper is to report results obtained in our laboratory during the 2015 experimental campaign, carried on in the framework of the Work Package Plasma Facing Component (WPPFC) of EUROfusion Consortium, and devoted to quantify ammonia production in medium flux ($< 10^{20}$ m^{-2} s^{-1}) N admixed D plasma as a function of neutral pressure and electron temperature and to investigate the influence of helium (He) and argon (Ar) addition on ammonia production. Ammonia quantification in the experiments was based on exhaust collection in a Liquid Nitrogen (LN_2) trap and a subsequent inventory by Liquid Chromatography (LIC) [5]. Ammonia formation was also controlled by *in situ* Mass Spectroscopy (QMS) and the results were compared with absolute ammonia values derived from chromatography. During the experiments, Optical Emission Spectroscopy (OES) was used to monitor for ND-radicals, which can reveal information about ammonia formation in plasma phase operations.

2. Experiment set-up

2.1 GyM device

GyM [6] consists of a cylindrical vacuum chamber (with radius 0.125 m and length 2.11 m) mounted in a solenoid (magnetic field equal to 0.09 T in the experiments). Plasma is produced at low pressure (0.8×10^{-3} Pa - 6×10^{-2} Pa) and steadily sustained by microwave power (up to 4.5 kW cw) at the electron cyclotron frequency (2.45 GHz), injected perpendicularly to the magnetic field lines, in O-mode polarization. The resonance at 0.0875 T is a vertical layer close to one end of the vessel, opposite to the RF power launcher.

During the experiments, N_2/D_2 partial pressure ratio was kept constant at 4%. To study the influence of plasma parameters on ammonia formation, the total pressure was varied between 0.015 Pa to 0.065 Pa, at constant RF power (150 W). Within this range, T_e and n_e accordingly change between 4-5 eV and 10^{16}-10^{17} m^{-3}, as measured by a Langmuir probe placed in the center of the plasma column. Moreover, plasmas at different T_e (from 3.5 to 6.5 eV) were made varying the RF power from 150 W to 600 W. The effect of noble gases on ammonia production was investigated adding He and Ar to the N-D gas mixture separately, in such a way that He/D_2 and Ar/D_2 partial pressure ratios were 17% and 3%, respectively. In this case the total pressure of $N_2/D_2/Ar$ and $N_2/D_2/He$ mixtures was 5.0×10^{-2} Pa. All the experiments lasted 60 min, in order to have a fluence of the order of 10^{24} m^{-2}.

2.2 Diagnostics for ammonia detection

The diagnostics used to study the conditions of ammonia formation are basically four. A Langmuir probe to measure T_e and n_e at the center of the plasma column; OES, based on a Horiba Jobin-Yvon iHR550 spectrometer (spectral resolution 0.06 nm), with the line of sight perpendicular to the plasma axis and a wavelength interval from 300 nm to 850 nm to detect the species in the plasma phase; a differentially pumped QMS to analyze neutral gas composition, connected to the vessel via a 4 mm ID pipe. The latter assures a gas transfer in molecular flow regime during all the phases of the experiment so that the temporal evolution of the chemical species can be monitored continuously. During experiments, the signals from the following molecules were recorded: H, D, He, ND_3 and H_2O (AMU 15-20) N_2 and CO (AMU 38), O_2, Ar and CO_2. Since the mass spectrometer system was not calibrated, the intensities of the signals cannot be translated to absolute quantities of the detected species. The cracking patterns used to analyze the MS spectra are those provided by the factory.

Absolute quantification of deuterated ammonia was performed by the insertion of a by-pass with a liquid nitrogen trap between the turbo and the background pump. In figure 1 the scheme of the pumping system is reported.

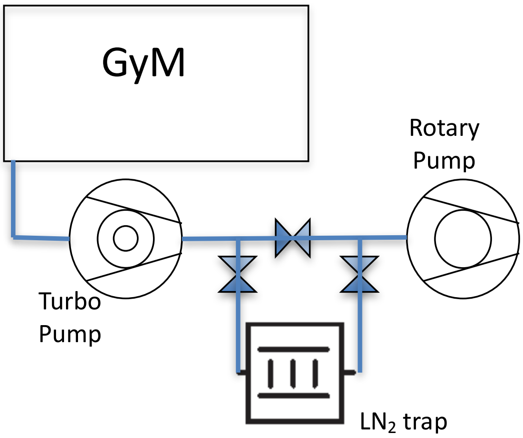

Figure 1. A sketch of the vacuum system of GyM properly modified for the LN_2 trap

Gaseous species in GyM exhaust with temperature condensation point above 77 K as ND_3 and CO_2 (240 K and 110 K, respectively), can be condensed on the LN_2 trap surfaces. After one hour of steady-state plasma the LN_2 trap (at maximum pressure of 10 Pa to guarantee a high condensation efficiency) was removed from the vacuum line and waiting that the room temperature was restored. In a separate ventilated atmosphere box the trap was inserted in a line where an Ar carrier forces the released gas from the trap through a bubbler, filled with demineralized water. The ND_3 possibly present is dissolved in the water according to the reaction $ND_3 + H_2O = ND_3H^+ + OH^-$. The solution is then sampled and analyzed by a LIC, Dionex DX100, to count the NH_4^+ concentration [5]. Providing that bubbling was done in the same conditions, the results obtained, even without an absolute calibration, can be used for relative comparisons and analysis.

3. Results

3.1 Base process characterization

The exact mechanism that leads to ammonia formation during N seeded D plasma experiments is not yet completely understood, even if one of the most accredited hypotheses [7] focuses on the interaction between nitrogen and deuterium occurring in the plasma phase and on the surface of the wall. In order to discriminate between the two processes we initially saturated (at room temperature) GyM's wall with deuterium injecting lately nitrogen (at 4% N_2/D_2 partial pressure ratio) in order to reach a total pressure of the 3.0×10^{-2} Pa. This neutral gas phase was monitored by QMS and the exhaust collected, bubbled in water and analyzed by LIC. The same setup was used to check the presence of ammonia or other impurity (like CD_4 and D_2O) during non-seeded deuterium plasmas. For both experiments the test lasted for one hour, in order to reveal a possible wall memory effect.

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The QMS spectra reported in figure 2 do not show the presence of ammonia (at M/Z=20), and moreover no molecules of ammonia were counted by LIC in the exhaust.

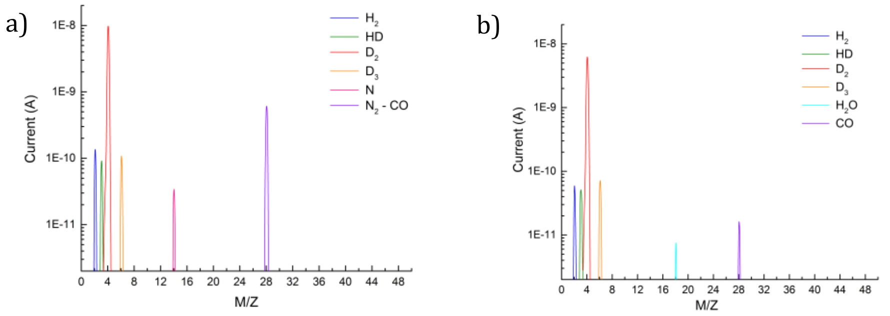

Figure 2. Mass spectrum acquired during saturation of GyM's wall with deuterium and subsequent nitrogen injection, at room temperature and a 3.0×10^{-2} Pa (a). Mass spectrum acquired during a non-seeded D plasma at 3.0×10^{-2} Pa, 5 eV and density of 10^{17} m^{-3} (b).

After the two experiments described above, we performed a reference experiment at $5.5x0^{-2}$ Pa, at 5.5 eV in which the N_2/D_2 partial pressure ratio was fixed at 4%. This experiment was accurately charaterized by OES and QMS, and ammonia was quantified by LIC.

The OES spectrum is shown in figure 3. The emission bands of ND radicals at 335.7 nm and 336.4 nm are visible. The presence of these radicals is a fingerprint of the chemical reactions occurring either in the plasma or at the wall.

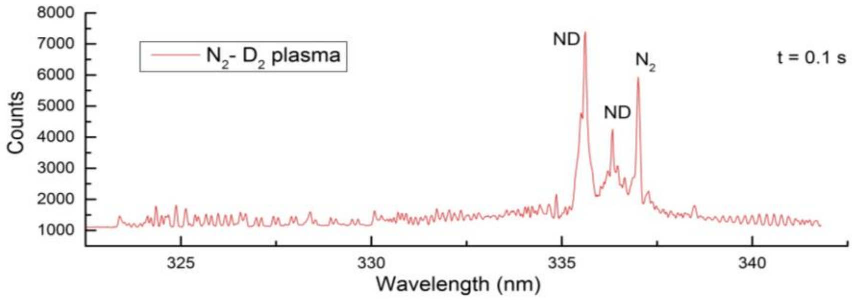

Figure 3. OES of the reference D plasma seeded with 3,75% of $N_{2,}$ at 5x10^{-2} Pa. RF power was fixed at 400W. In these conditions T_e=5.5eV.

To study the evolution of the chemical species during the different phases of the reference experiment (background vacuum, gas injection, plasma and exhaust), QMS measurements were acquired as intensity versus time for each mass to charge ratio of interest (figure 4).

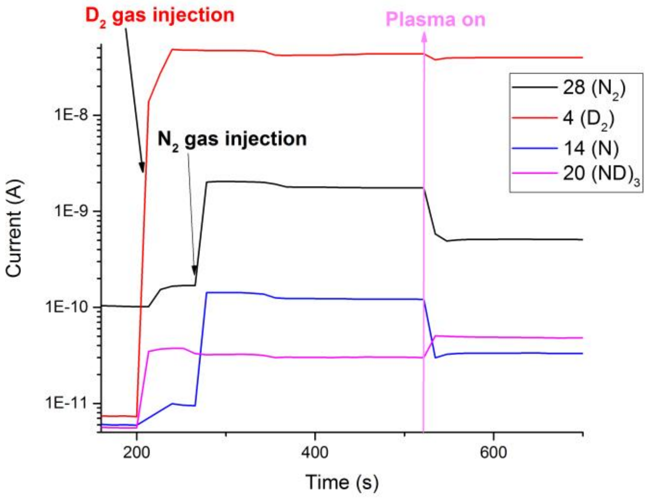

Figure 4. Mass to charge signals versus time during reference D plasma seeded with 3,75% of N_2. This sequence was repeated in the 3 identical experiments, not shown for clarity, with identical results. Total neutral pressure was 5.5 x10^{-4} mbar, and T_e=5.5eV. The increase of all the signals at D_2 injection is artifact due to a wrong acquisition setting (OFFSET off).

During the gas injection phase the signal of 20 AMU which corresponds only to ND_3 (no water was detected in GyM during the control experiments, see figure 2) does not increase, while it grows up at the plasma switch-on while at the same time intensity of 14 and 28 AMU of N and N_2 decreases, highlighting that ammonia is formed only during the plasma phase.

3.2 Effect of the neutral total pressure

The experiment devoted to study the influence of the total pressure on ammonia formation was conducted increasing the partial pressure of N_2 and D_2 at constant N_2/D_2 partial pressure ratio. The T_e dependence with the total pressure, as measured with a Langmuir probe, is reported in figure 5. T_e varies less than 1eV for in the whole pressure range.

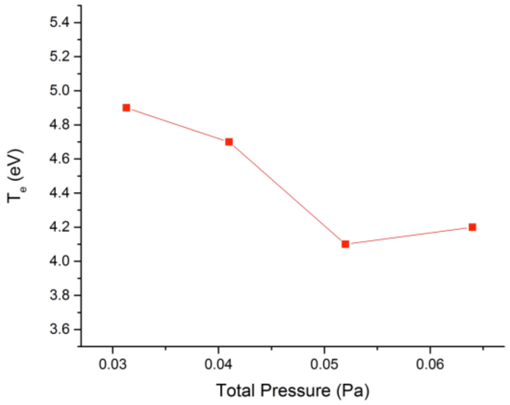

Figure 5. Electron temperature, measured in the center of GyM vessel by Langmuir probe, as a function of total neutral pressure of the D-N plasma.

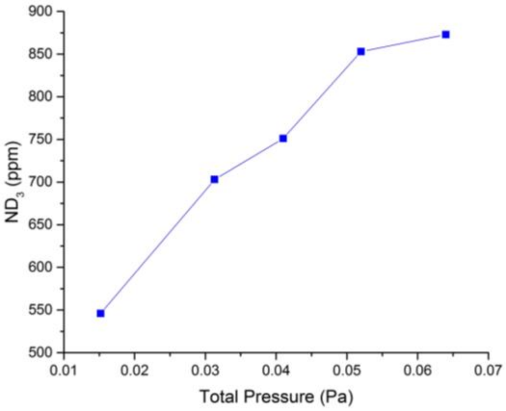

Figure 6. Ammonia collected in the LN_2 trap, quantified by LIC, as a function of the total neutral pressure of D-N plasma.

As reported in figure 6, varying the total pressure from 2.0×10^{-2} Pa to 6.0×10^{-2} Pa, an increase of 60% of ammonia content in the mixture collected by the LN_2 trap was measured by LIC. This trend can be ascribed to the increased density of nitrogen species that influence ammonia formation [8-9].

3.3 Effect of electron temperature

The electron temperature was varied, using reference experiment as initial point, increasing the RF power at constant total pressure and N_2/D_2 partial pressure ratio. The influence of the T_e on the ND_3 production is shown in figure 7.

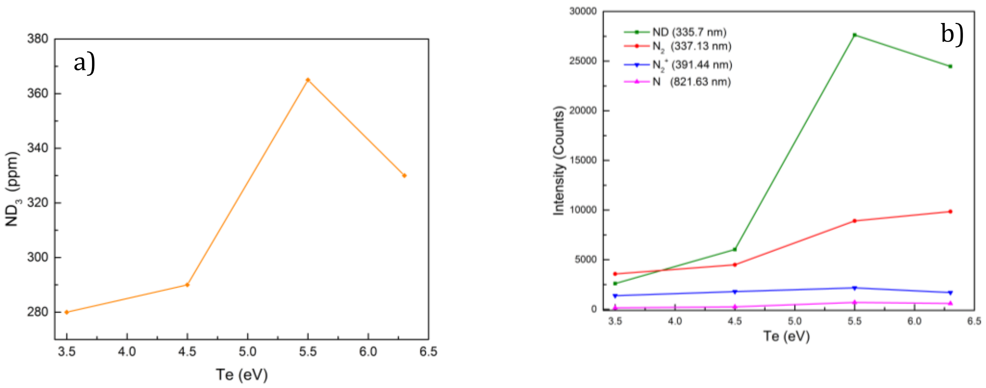

Figure 7. Ammonia quantification by LIC as a function of the electron temperature (a) and intensity of nitrogen related emission lines from plasma measured by OES. Total pressure was 2.0 x 10^{-2} Pa, RF power was varied from 150 W to 600W, N_2/D_2 ratio was maintained constant at 0.04.

Ammonia production increases of 28% with T_e in the range 3.5-6.5 eV as evaluated by LIC (figure 7a). The N_2 and ND emissions intensity also increases with T_e, as shown in figure 7b. Though both the lines are affected by the increase of T_e, from the LIC results, the increase of the ND intensity might be due to the increasing interactions between nitrogen and deuterium.
If the N_2 direct dissociation by electron impact is the limiting step for ammonia formation in the plasma and the threshold for this reaction is at 9.8 eV, an increasing of T_e increases the fraction of electrons above the threshold and thus the reaction rate.
The processes involved in ammonia formation during experiments of plasma wall interaction involve, in addition of the dissociation of molecules, also the adsorption of the molecules on the surface of the wall. An increase in Te increases the likelihood of N_2 and ND adsorption on the surface of the wall, (where at the end take place the reactions that lead the ammonia formation) and then an increase in ammonia production.

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3.4 Effect of noble gases addition

To study the influence of the noble gases on ammonia formation, low concentration of argon or helium was admixed at nitrogen seeded deuterium plasmas. In the same conditions of reference experiment, Ar and He were added to N_2/D_2 mixture. Each of these two experiments was characterized by Langmuir probe, OES, QMS to measure plasma T_e and n_e, plasma composition, neutral gas composition, respectively, and finally by LIC to determine the composition of the exhaust.
Each experiment was performed three times. The variation in ammonia quantification was of the order of ±5%. Figure 8 shows ammonia production measured by LIC in the following conditions (expressed in terms of molar concentrations): (i) 96.3% D_2 + 3,7% N_2, (ii) 79.8%

D_2 + 3,2% N_2 + 17% He and (iii) 93.4% D_2 + 3,2% N_2 + 3,1 % Ar. Although it would be more appropriate to work with the same percentage of helium and argon, we had to use the concentrations indicated because the only ones that allow us to perform experiments under the same conditions of pressure, ratio of N_2/D_2 and Te.

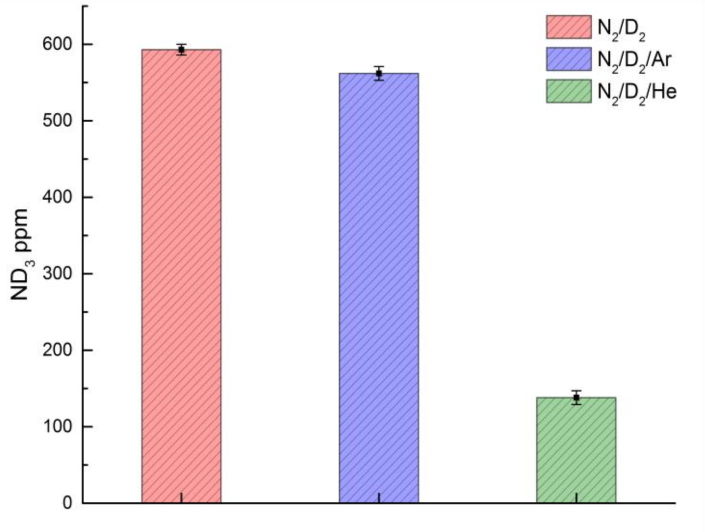

Figure 8. Ammonia counted by LIC during N_2/D_2, $N_2/D_2/Ar$, $N_2/D_2/He$ plasmas. Total pressure ws 5x10^{-2}Pa, T_e= 3.5 eV and n_e= 6.0x10^{16} m^{-3} in all the cases.

It is worth to notice that 17% of He reduces ammonia of 80% while Ar, although in lower concentration than helium, seems to be practically not effective. The comprehension of this difference is not straightforward and requires more dedicated experiments, foreseen in the near future on GyM.

In figure 9 the comparison of OES measurements for the three experiments is shown. The content of nitrogenized species and the deuterium dissociation is unchanged adding Ar or He, indicating that the interaction between nitrogen and deuterium in the plasma phase is not modified by noble gases addition.

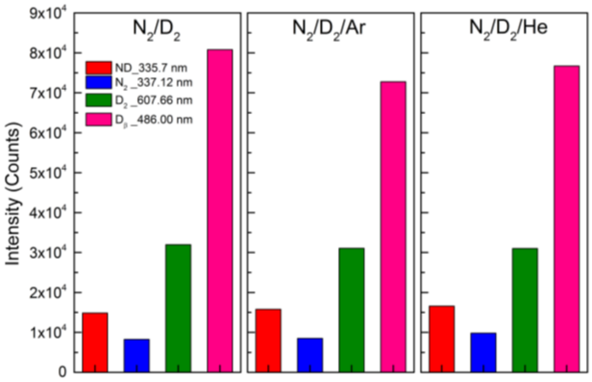

Figure 9. Spectroscopic intensity of the nitrogenized and deuterated species in N_2/D_2, $N_2/D_2/Ar$, $N_2/D_2/He$ plasmas.

At the present it is not fully understood the key process that causes the reduction observed with the addiction of He. The overall analysis of the LIC and OES measurements suggests that this phenomenon could be ascribed to a variation in the reaction rate of the chemical-physical processes likely occurring on the surface of the wall.

The observed reduction of ammonia in presence of He seems to be very promising for ITER, where He will be naturally present and the T_e range in the divertor is foreseen to be of the same order of that of the experiments here described. A deep understanding of the surface reaction involved and further experimental confirmations are therefore necessary.

4. Conclusions

Experiments on ammonia formation in conditions relevant for the ITER divertor region (in terms of the electron temperature) were been carried in GyM. The dependence of total pressure, plasma temperature and the effect of the addition of noble gases to the deuterium nitrogen plasma were investigated.

A technique to evaluate the amount of ammonia formed during the experiments was developed and it is based on: the collection of GyM exhaust in a LN_2 trap, the bubbling in water of the collected gas in a controlled volume and a subsequent off-line analysis of the sample by LIC.

Ammonia was formed only during plasma phase, as demonstrated by QMS measurements and its quantity clearly depends on total pressure and electron temperature. These observations based on LIC are confirmed also by OES analysis of the plasmas, where two bands from ND radicals were detected and their intensity follows the increase of ammonia production with total pressure and T_e.

Electron temperature increases the rate of the dissociation in plasma phase of the different species and that of the interactions between nitrogen and deuterium. Both effect can be invoked to take in account the observed increase in ammonia production.

We observed that He addition to the N_2-seeded D plasma reduces ammonia of 80%. Helium addition did not modify plasma with respect to the only nitrogen seeded D scenario. It seems therefore that He acts as an inhibitor of chemical - physical processes for ammonia formation likely occurring on the surface of the wall. Ammonia is likely produced at the wall by interaction between ND and N radicals, formed in the plasma, and D species, adsorbed on the surface of the GyM wall. More detailed experiments devoted to study processes occurring at the wall surface and the chemical processes involved in ammonia formation are required to confirm this first observation. If these results will be confirmed, the He ashes produced during ITER's active phase, can have a positive role in minimizing ND_3 formation in the N_2 seeded plasmas.

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