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Influence of residence time and Helium addition in the ammonia formation on Tungsten walls in N_2-H_2 Glow Discharge Plasmas

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Abstract

The influence of the residence time for the active species and of the helium addition to the plasma in the ammonia formation in N_2-H_2-(He) Glow Discharge plasmas has been studied using differential pumped mass spectrometry. Three different residence times for the N_2 molecule were studied: 25, 50 and 100 ms. Other experiments scanning the helium plasma content (0-8%) were performed with a residence time of 100 ms. While no difference in the ammonia formation yields was found between the cases of 25 ms and 50 ms, the ammonia yields were increased by a 25% in the case of 100 ms. Additionally, an increasing helium plasma content enhances the ammonia formation yields up to 45%. Three different effects induced by the presence of helium in the plasma were analyzed: effects in the pumping speed associated to the He addition, changes in the electron temperature and modification of the surface chemistry. The analyzes pointed out to an improved N-H recombination on tungsten walls induced by helium presence as the key factor that could explain the higher ammonia yields experimentally found for the highest helium content in the plasma.

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1. Introduction

The use of carbon based materials as a suitable election for the Plasma Facing Materials (PFM's) in fusion devices has been ruled out due to the associated enhanced hydrogen retention and codeposition [1]. The use of tungsten (W) on the divertor tiles and beryllium (Be) on the first wall is now the current design for ITER. This change in the PFM's has reduced the long term hydrogen retention in one order of magnitude [2] on the ILW JET operation in comparison with the previous operation based on carbon PFC's (JET-C). On the contrary the intrinsic radiation of carbon impurities in the divertor region has been suppressed and the injection of extrinsic impurities has become necessary to achieve good plasma performance.

Nitrogen is commonly considered as the best candidate for radiator in impurity seeded plasma operation [3, 4]. Its extended use in the JET-ILW operation has re-established the confinement level achieved in JET-C operation [5]. However, the associated interaction between nitrogen and hydrogen isotopes leads to a significant ammonia production. Neuwirth et al. found in AUG [6] that up to 8% of the injected nitrogen was converted into ammonia. The formation of ammonia has also been observed in JET [7, 8]. The last studies and observations show that with a 5% conversion into ammonia, 0.2 grams of associated tritium could be trapped per pulse in the future ITER D-T operation [9].

Furthermore, the strong affinity of ammonia with water makes its removal difficult and the sticking of tritiated ammonia on PFC's and vacuum ducts can induce corrosion problems. With this problematic, more frequent cryopump regeneration would be necessary, limiting in this way the ITER operational cycle. For all these reasons the study of ammonia

formation and its mitigation strategy has been given priority for the future ITER operation [9, 10].

Despite the recent studies on this topic, the effects of a fusion reactor environment with a long residence time for the seeded species and the presence of Helium as an intrinsic plasma impurity on the ammonia formation is uncertain. Under such scenario, the comprehension of the induced effects by the reactor conditions is clearly necessary in order to estimate and try to mitigate its generation. In this study, several experiments have been performed to measure the ammonia formation in N_2-H_2 (He) direct-current Glow Discharge (DC-GD) plasmas on a W wall device, at different and increasing residence times for the active species and focusing in the understanding of the effects induced by the helium addition in the underlying plasma-surface processes that determine the ammonia generation.

2. Experimental setup

The used setup and the experimental procedure is the same that was used in previous experiments prepared to measure the ammonia formation on tungsten, stainless steel and aluminum by using DC-GD plasmas [11] (see the figure attached in the previous reference). Briefly, it consists on a cylindrical stainless steel vacuum chamber for the plasma operation (grounded cathode of the Glow Discharge) connected to an analysis chamber through a differential pumped vacuum system. In this analysis chamber a Mass Spectrometer (SRS 200 Residual Gas Analyzer) is situated. Inside the plasma chamber a cylindrical and concentric stainless steel liner (V=5.4 L), whose inner wall (A=0.14 m^2) is totally covered with a cold-rolled tungsten sheet, is placed. This inner tungsten sheet is heated with a

thermocoax wire rolled in the external wall of the liner. The W wall temperature is measured with a type K thermocouple inserted on the liner. The annular space between the liner and the plasma chamber walls is isolated to avoid plasma exposition with boron nitride elements. The whole system is pumped out by using two turbomolecular-rough pump sets. The base pressure, (ionization gauge measurements) is kept around 10^{-7} Pa in the analysis chamber and 10^{-5} Pa in the plasma chamber. The gases with a purity of 99.999 % are introduced in the setup by using flowmeters and the working pressure (2 Pa for all the experiments) is measured with a capacitance manometer.

The DC-GD plasma is built up by providing the necessary voltage to an anode. The discharge characteristics during the experiments were: discharge voltage between 300-400 V, plasma current of 200-350 mA and hydrogen/nitrogen fluences up to 10^{23} m^{-2}. Additionally, Optical Emission Spectroscopy measurements were performed to estimate the electron temperature (T_e) and its changes during the helium addition to the plasmas, performing a 400-750 nm wavelength scan. The surface temperature of the tungsten wall was kept constant at 200ºC in all instances.

A complete wall conditioning, that assures a good reproducibility, was carried out before the experiments including: irradiation of the W wall with pure Argon DC-GD plasma and wall baking up to 200ºC. Two different types of experiments were performed:

- Experiments with N_2-H_2 DC-GD plasmas with different residence times for the plasma species. The pumping speed of the system was decreased by changing (reducing) the vacuum conductance of the pumping duct. Three different residence times for N_2 molecules (τ_{N_2}) were studied: 25, 50 and 100 ms.

- Experiments with N_2-H_2-He DC-GD plasmas using a τ_{N_2}=100 ms, scanning the helium plasma content from 0 to 8%.

All the experiments were performed following the same strategy previously used and explained in [11]. Finally, absolute calibration works to correlate the single mass spectrometry recorded signals (28, 2, 17 and 4 Amu) with the associated partial pressures of N_2, H_2, NH_3 and He was also performed. The effects of the gas addition and mixture were also taken into account. In most of the experiments the residual water levels were low enough to ignore the contribution of residual water molecules to 17 Amu. Anyway these levels were checked, in order to subtract these contributions when they were not negligible.

3. Results and discussion

3.1. Influence of τ_{N_2} in the ammonia formation on W walls

In Figure 1 absolute ammonia formation yields deduced from the experiments for different nitrogen residence time values (τ_{N_2} of 25, 50 and 100 ms), are shown depending on the N_2 cracking efficiency parameter (calculated as $\Delta N_2/N_2^{inj}$). This efficiency represents the fraction of nitrogen molecules that are depleted from the gas phase during the plasma. Two different formation yields have been calculated: one of them is normalized to the injected nitrogen (calculated from the N_2 inlet puffing, NH_3/N_2^{inj} yield), and the other one is the yield normalized to the amount of nitrogen molecules that disappear in the plasma (calculated as the difference between the 28 Amu signal with only gas flux and the subsequent lower signal during the plasma, NH_3 / $2\Delta N_2$ yield). The different pumping speeds and residence times for N_2 used in the experiments are shown in Table 1.

As can be seen in Figure 1, there are no significant differences between the ammonia formation yields for τ_{N_2} =25 ms and 50 ms. For all τ_{N_2}, the yields normalized to the injected nitrogen present a linear dependence with nitrogen cracking efficiency while the $NH_3/2\Delta N_2$ yields are approximately constant and independent of this parameter. These yields are also very similar compared to previous findings [11] obtained for an intermediate residence time (approximately 40 ms). On the other hand, both yields for a reactor configuration with τ_{N_2} =100 ms are a 25% larger than those of the other two reactor configurations, for similar values of $\Delta N_2/N_2^{inj}$.

From the gas phase balance at steady state for a given molecule (A) the dependence of its concentration (expressed as [A]), with the residence time can be deduced:

$$1)\quad V\frac{d[A]}{dt} = [A]_0 \cdot S - K_{dis} \cdot n_e \cdot [A] \cdot V - [A] \cdot S = 0 \rightarrow [A] = \frac{[A]_0}{1+K_{dis} \cdot n_e \cdot \tau}$$

In this expression V is the reactor volume, S the pumping speed for the gaseous specie, K_{dis} is the dissociation constant of the molecule in the plasma that depends on the electron temperature (T_e) [12], n_e the electron density of the plasma, and τ is the residence time in the reactor (calculated as V/S). Applying this balance to ammonia and nitrogen the general expression, that is also applicable to different plasma devices, is obtained. It gives the dependence of the NH_3/N_2 ratio with the plasma parameters (T_e, n_e) and the reactor conditions (τ):

$$2)\quad \frac{[NH_3]}{[N_2]} = \frac{[NH_3]_0}{[N_2]_0} \cdot \frac{1+K_{dis}^{NH_3} \cdot n_e \cdot \tau_{NH_3}}{1+K_{dis}^{N_2} \cdot n_e \cdot \tau_{N_2}}$$

Unfortunately measurements of plasma parameters (T_e, n_e), for the different reactor conditions, that could enable a complete analysis of the residence time effect in the ammonia formation, are not available for these experiments. Previous estimations using a simple Langmuir probe gave electron temperatures around 1.5-3 eV and densities of 1-$3 \cdot 10^{10}$ cm^{-3} for an intermediate residence time of 40 ms but it is important to note that the uncertainties of these measurements are high due to the significant error associated to plasmas with low electron temperatures. These effects together with an exhaustive analysis of the electron temperature changes in the plasma (T_e estimations using Helium line emission measurements) will be analyzed in the following chapter about the ammonia formation in N_2-H_2-He DC-GD plasmas.

3.2. Ammonia formation in N_2-H_2-He plasmas

The presence of helium as an intrinsic impurity that will be produced from D-T nuclear reactions in the plasma core of a fusion reactor can also affect to the ammonia formation in a hypothetic future ITER nitrogen-seeded plasma operation. The intense surface bombardment with energetic helium ions can modify the surface on the PFC's and the chemistry that determines the ammonia formation. Furthermore, important plasma parameters in the SOL region can be also affected, and the associated effect in the ammonia formation is difficult to predict. Several experiments involving N_2-H_2-He plasmas have been performed at different helium plasma contents in order to study the modification of the ammonia formation induced by the presence of helium.

In Figure 2 the ammonia formation yields (for a τ_{N_2} of 100 ms) is presented for the case of N_2-H_2 plasma and three different N_2-H_2-He plasmas (He contents ≈ 1.5, 3 and 8 %). Both

yields are increased up to a 45% factor for increasing helium plasma content by comparing values with similar nitrogen cracking efficiency. As it was commented previously, the improved ammonia formation could be affected by changes in the plasma parameters (T_e mainly) as well as modifications on the surface chemistry. Moreover, helium addition in the plasma can decrease the pumping speed of the system, modifying the RGA measured signals and the concomitant ammonia formation yields. This effect will be analyzed in the next subsection.

3.2.1. Effects of helium addition in the pumping speed

Helium can decrease the effective pumping speed of turbopumps when is injected in a gas mixture, thus increasing the associated residence time of the reactants. Pumping speeds for the species of a mixture can be affected differently by this gas addition/mixture effect, changing the measured signal ratio obtained with mass spectrometry measurements. Although in ITER no change in the pumping speed is expected due to the presence of helium inside the vacuum vessel, this effect can be important and must be evaluated in our experiments. Following this assumption the addition of helium can suppose simply a change in the pumping speed that could explain the results.

To analyze this effect, the changes in RGA signals in a NH_3-N_2-H_2 gas mixture at constant pressure (2 Pa) were measured by injecting helium (keeping approximately constant the N_2 and NH_3 contents and decreasing the H_2 inlet at the same time that the He content is increased) in the reactor and monitoring the evolution of the 17 Amu/ 28 Amu ratio. The composition of the gas mixture was similar to the plasma experiments: N_2 fixed content around 3%, being NH_3 content approximately 7-8 times lower than N_2 content. The helium

content in the gas mixture was varied from 0 to 8%. In Figure 3 the evolution of the 17/28 Amu ratio ($F_{17/28}$) normalized to the value with no helium content is presented. The injection of helium increases the parameter $F_{17/28}$ up to 7% for helium concentrations in the gas mixture close to 8%, but the enhanced ammonia yields (45% higher) observed in the experiments cannot be totally explained by this effect.

3.2.2. The general plasma-surface chemistry in the ammonia formation and the influence of T_e in the process.

The formation of ammonia takes place on metal walls that act as a heterogeneous catalyst. Surface recombination between nitrogen and hydrogen neutrals produces N-H radicals that are hydrogenated in consecutive steps until the formation of ammonia molecules that are finally desorbed from the walls [13]. Ions coming from the plasma can be also dissociated on actives sites of the walls providing actives species for the formation process and NH_x radicals present in the gas phase may recombine on the surface producing ammonia. The desorbed ammonia molecules can be also destroyed in the plasma before leaving the plasma chamber (dissociation reactions that depends on T_e). The recombination reactions can happen following two mechanisms: Langmuir-Hinshelwood (L-H) reactions between two adsorbed species or Eley-Rideal (E-R) reactions between and adsorbed specie and an impinging neutral. From previous results with N_2-D_2 DC-GD plasmas the E-R recombination between adsorbed hydrogen and impinging nitrogen can be excluded [14]. Hence, in our plasmas the generation of ammonia is supposed to be produced by a mixture of L-H recombination between N and H atoms adsorbed on the W surface and E-R recombination between adsorbed N atoms and impinging H atoms, being these surface processes supposed to be independent on the electron temperature. Before these surface

steps, the presence of the active species (neutrals, radicals and ions) on the W wall is necessary to start the process. These active species are generated in the plasma (ionization and dissociation) by means of electron impact processes [12].

Changes of the electron temperature can modify the ionization-dissociation of N_2 and H_2 molecules increasing or decreasing the content of the active species on the walls, and finally affecting the amount of produced ammonia. Moreover, these changes may affect to the dissociation of the produced ammonia molecules. Taking into account the rate coefficient expressions for the ionization/dissociation of nitrogen (source terms for ammonia formation) and for the dissociation of ammonia (sink terms) and their dependences with T_e [12], an estimation of the possible effect of the electron temperature in the global process, can be done. In Figure 4 the ratio between the sum of ionization and dissociation rate coefficients for the N_2 molecule over the sum of the dissociation rate coefficients for the ammonia molecule is presented. This ratio gives an idea about the net effect of the electron temperature changes in the ammonia formation process and is defined as:

$$3) \quad R = \frac{D_{N_2} + I_{N_2}}{D_{1_{NH_3}} + D_{2_{NH_3}}}$$

In this expression D_{N_2} is the rate coefficient for the electron impact dissociation of nitrogen, I_{N_2} is the rate coefficient for the electron impact ionization of nitrogen to produce N_2^+ ions, $D_{1_{NH_3}}$ and $D_{2_{NH_3}}$ are the rate coefficients for the two possible routes for the electron impact dissociation of the ammonia molecules [12]. Only one electron impact ionization reaction (to produce molecular N_2^+ ions that are the dominant in our plasmas [15]) for the N_2 molecule has been taken into account. The amount of N^+ ions is supposed to very low in

DC-GD plasmas, so this ionization process can be considered as negligible. Supposing that wall chemistry parameters are not affected by changes in the electron temperature, then Figure 4 shows that in the range of 2-12 eV an increasing electron temperature can enhance the ammonia formation because ionization/dissociation of nitrogen are more favored than dissociation of ammonia molecules.

3.2.3. Evaluation of T_e in N_2-H_2-He plasmas using helium spectroscopy

To analyze if the enhanced ammonia yields obtained from the experiments can be attributed to changes in the electron temperature, estimations of this parameter have been performed by using helium spectroscopy. In order to estimate the electron temperature in our plasmas a theoretical calculation of several He lines ratios ($R_{728/667}$, $R_{706/667}$ and $R_{504/471}$) has been done taking into account the T_e dependence of the cross sections for the different He excited levels [16] in the case of a low density plasma ($n_e = 2 \cdot 10^{10}$ cm^{-3}, similar density compared to our plasmas). With these values the line ratio can be calculated by correcting the theoretical population levels with the corresponding atomic transition probabilities [17]. Finally comparing the experimental values with the theoretical ones, the electron temperature in our plasmas for the different helium contents can be estimated.

In Figure 5a the theoretical dependence of the selected line ratios with the electron temperature is presented and the Figure 5b shows the corresponding estimations of this parameter from the He line emission in the N_2-H_2-He DC-GD plasmas. According to the experimental data the electron temperature would be in the range of 2-5 eV depending on the used line ratio. He lines are weak when He content in the plasma is low and consequently the associated error in the T_e calculation increases. Hence, only at the highest

He content the T_e estimation is reliable enough, being the evolution of this parameter with the helium addition uncertain. As explained previously, an increase in the electron temperature in this range would lead to a higher ammonia formation in our DC-GD plasmas, although is necessary to have into account that in ITER the electron temperature along the divertor region is not expected to be modified by the presence of helium in the plasma. Nonetheless according with these estimations, the influence of this effect in the enhanced ammonia formation observed in the experiments with increasing helium plasma contents cannot be confirmed.

3.2.4. Possible modification of the surface chemistry induced by the helium bombardment

Wall bombardment with imping helium ions or metastables from plasma can alter the chemistry between N and H on the W surfaces, then modifying the active surface centers where the L-H and E-R recombination reactions take place. Particle induced desorption with impinging helium particles could also increase the number of free centers as well as the impact of chemically inert projectiles (He) can affect the activation of these centers (plasma activation). These effects might increase the rate coefficients for the recombination into ammonia. In Table 2 the nitrogen (N_{ret}) and hydrogen retention (H_{ret}) on the W wall after reaching the steady state (calculated by particle balance, as in [11]) and the hydrogen flux (H_{imp}) calculated from the depleted hydrogen in the plasma are presented depending on the helium plasma content (f_{He}).

Assuming that L-H recombination takes place between adsorbed N and H atoms and E-R recombination occurs between adsorbed N and impinging H the normalized products

$(N_{ret}*H_{ret})_{norm}$ and $(N_{ret}*H_{imp})_{norm}$ gives an idea about the amount of active species available to produce ammonia. These values are presented for the different helium plasma contents in Figure 6. In general, both parameters decrease with increasing helium content. Hence, the quantity of the species present on the surface does not increase with the helium content, but the obtained ammonia formation yields are higher, pointing to enhanced N-H recombination induced by the helium bombardment as the key factor behind the higher ammonia formation. It is important to note that with these calculations is not possible to distinguish if the proportion of chemically active species (not implanted) is changing. To analyze the underlying chemistry in a more accurate way, experiments able to discern among these factors and with suitable diagnostics to analyze the ion/neutral composition of the plasma are necessary.

4. Conclusions

The effects of increasing residence time for nitrogen (τ_{N_2}) and the presence of helium in the ammonia formation in N_2-H_2-(He) DC-GD plasmas has been analyzed. While a change of τ_{N_2} from 25 to 50 ms has no measurable effect on the ammonia formation yields, a value of 100 ms increases them up to a 25%.

The presence of helium enhances the ammonia formation yields up to 45% factor for increasing helium content in the plasma. Three possible factors have been analyzed to explain this higher ammonia formation: 1) changes in the pumping speed of the system, 2) increasing electron temperature of the plasma and 3) modification of the surface chemistry induced by the helium surface bombardment.

The increasing residence time for nitrogen in helium containing plasmas cannot explain totally the enhanced ammonia formation. Increasing T_e (between 2-12 eV) can determine a more efficient ammonia production but our estimations do not assure that this parameter is increased with the helium addition.

The surface modification induced by the helium bombardment seems to play a key role that modifies the net ammonia formation. Although the amounts of adsorbed and impinging species that determines L-H and E-R recombination reactions would not increase with the helium plasma content, other factors as the rate coefficients for these reactions, the effective W wall surface for the N-H recombination or the proportion of active/free surface centers could be enhanced by the helium bombardment. This effect together with the changes in the pumping speed might explain the enhanced ammonia yields obtained in the N_2-H_2-He DC-GD plasmas.

Anyway to understand these effects a further investigation involving neutral and ions analyzers is necessary for a better comprehension and quantification of the involved surface chemistry parameters. These results represent an approximation to the complex chemistry that determines the ammonia formation in a future ITER N_2-seeded plasma operation but is necessary to keep in mind that their extrapolation to the conditions of a hot and fully ionized plasma existing in a fusion reactor may be not straight forward.

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Table captions:

Table 1. Pumping speeds and associated N_2 residence time for the different reactor conditions studied.

Table 2. Nitrogen and hydrogen retention on the W wall and impinging H flux (steady state) for the different helium plasma contents.

Table 1.

N_2 pumping speed (S_{N_2}), L/s	N_2 residence time (τ_{N_2}), ms
210	25
120	50
55	100

Table 2.

f_{He}, %	N_{ret}, m^{-2}	H_{ret}, m^{-2}	H_{imp}, $m^{-2}s^{-1}$
0	$1.5 \cdot 10^{21}$	$6.3 \cdot 10^{20}$	$1.1 \cdot 10^{19}$
1.6	$9.5 \cdot 10^{20}$	$4.2 \cdot 10^{20}$	$1.3 \cdot 10^{19}$
3.3	$1.2 \cdot 10^{21}$	$3.7 \cdot 10^{20}$	$1.2 \cdot 10^{19}$
8.2	$7.5 \cdot 10^{20}$	$3.1 \cdot 10^{20}$	$1.1 \cdot 10^{19}$

Figure captions.

Figure 1. Deduced ammonia formation yields related to N_2 cracking efficiency for the 3 different reactor conditions defined by τ_{N_2}. The yields are similar for τ_{N_2} of 25 and 50 ms, however for 100 ms the ammonia formation yields are a factor 25 % higher.

Figure 2. Ammonia formation yields related to N_2 cracking efficiency in N_2-H_2-He plasmas with different helium content. The yields increase up to a 45% factor with a higher helium plasma content. Reactor configuration with τ_{N_2} = 100 ms.

Figure 3. Evolution of the 17/28 Amu ratio normalized to the value with no helium content ($F_{17/28}$) for the helium plasma content covered in the experiments. These changes in the pumping speed are not able to explain totally the enhanced ammonia yields obtained in N_2-H_2-He DC-GD plasmas.

Figure 4. Electron temperature dependence of the ratio between the sum of dissociation and ionization rates coefficients for N_2 over the sum of the rate coefficients for NH_3 dissociation.

Figure 5. 5a: theoretical dependence of selected He line ratios with T_e. 5b: corresponding estimations of Te for the He emission from N_2-H_2-He DC-GD plasmas with different helium content.

Figure 6. Normalized surface chemistry parameters for the different helium plasma contents. Dotted lines are just a guide for the eye.

Figure 1.

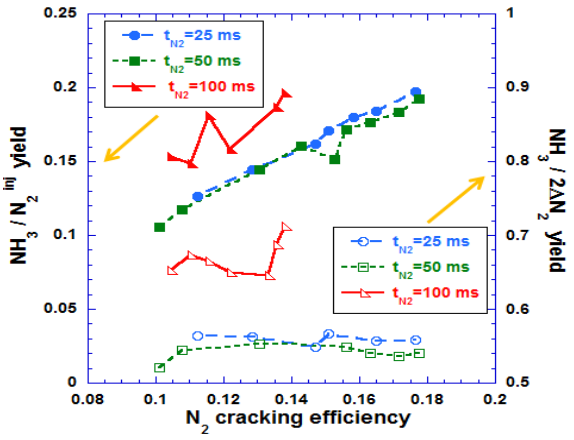

t_{N2}=25 ms
t_{N2}=50 ms
t_{N2}=100 ms
t_{N2}=25 ms
t_{N2}=50 ms
t_{N2}=100 ms
NH_3 / N_2 ^{inj} yield
NH_3 / $2\Delta N_2$ yield
N_2 cracking efficiency
0.25
0.2
0.15
0.1
0.05
0
1
0.9
0.8
0.7
0.6
0.5
0.08
0.1
0.12
0.14
0.16
0.18
0.2

Figure 2.

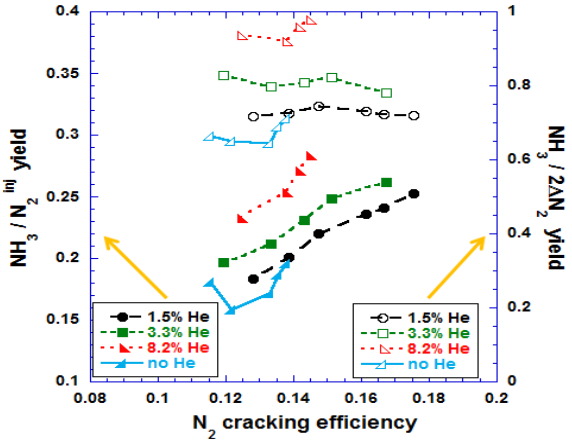

0.4
0.35
0.3
0.25
0.2
0.15
0.1
1
0.8
0.6
0.4
0.2
0
0.08
0.1
0.12
0.14
0.16
0.18
0.2
NH3 / N2 inj yield
NH3 / 2AN2 yield
N2 cracking efficiency
1.5% He
3.3% He
8.2% He
no He
1.5% He
3.3% He
8.2% He
no He

Figure 3.

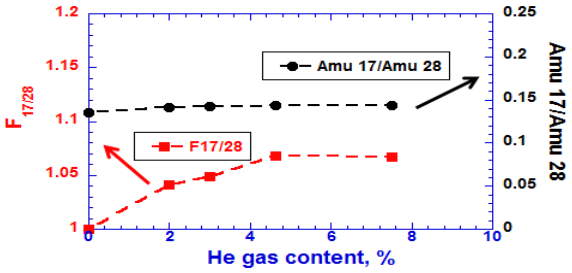

1.2
1.15
1.1
1.05
1
F17/28
0.25
0.2
0.15
0.1
0.05
0
Amu 17/Amu 28
Amu 17/Amu 28
F17/28
0
2
4
6
8
10
He gas content, %

Figure 4.

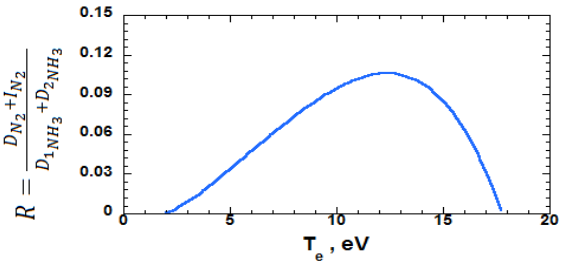


Figure 5.

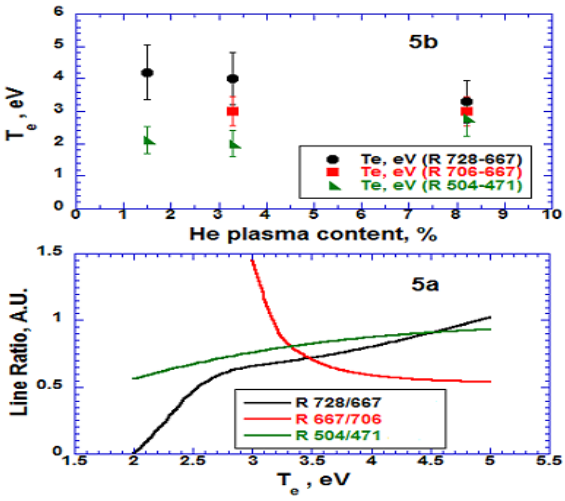
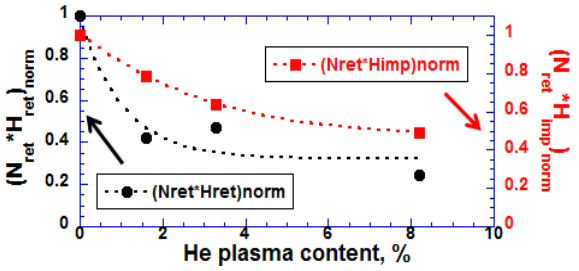

5b
T_e, eV
He plasma content, %
Te, eV (R 728-667)
Te, eV (R 706-667)
Te, eV (R 504-471)
5a
Line Ratio, A.U.
T_e, eV
R 728/667
R 667/706
R 504/471

Figure 6.


(Nret*Himp)norm
(Nret*Hret)norm
(N ret *H ret)norm
(N ret *H imp)norm
He plasma content, %
0
0.2
0.4
0.6
0.8
1
2
4
6
8
10