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Physisorption of ammonia on AISI 304 L stainless steel at different surface temperature under high vacuum conditions

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Abstract

The physisorption of ammonia molecules (sticking) on the walls of a stainless steel pipe (AISI 304 L) has been studied at different wall temperatures (323-473 K). The total amount of ammonia that is retained on the walls, once equilibrium is reached, has been measured by differentially-pumped mass spectrometry in gas exposure laboratory experiments. The results show ammonia retentions in the range of $\mu\text{g}/\text{cm}^2$ resulting in a multilayer adsorption with lower amounts of stuck ammonia at higher temperatures of the stainless steel surface. The sticking coefficient follows an exponential decay evolution with time. The activation energy of the process has been estimated by an Arrhenius fit, assuming that the characteristic time for this decay is inversely proportional to the kinetic adsorption constant. A value of 0.15 eV per ammonia molecule has been obtained, being in agreement with nominal values for the physisorption of small molecules or atoms (CO, N₂, Ar...) that can be found in the specialized literature. The implication of these results in the possible extrapolation to the ITER vacuum system under nitrogen seeded plasma operation is also addressed.

Keywords: **Nitrogen Seeding, Ammonia, Physisorption, AISI 304 L SS**

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1. Introduction

Nitrogen impurity seeding operation has been essential to develop an acceptable plasma performance in relevant magnetic fusion devices (JET, ASDEX Upgrade) [1-3], with the ITER-based plasma facing material scenario characterized by a full W divertor. The use of nitrogen as radiator is motivated to control the electron temperature in the plasma edge and to limit the plasma contamination due to W sputtering. Consequently the nitrogen impurity seeding enhances the radiation in the divertor region, decreasing the associated plasma contamination by tungsten and improving the confinement [4]. Despite these advantages in the plasma performance, the interaction between N and H isotopes on the surfaces leads to a significant production of ammonia as it has been experimentally found [5-10]. Therefore, the hypothetical use of nitrogen impurity seeding in ITER with D-T operation would produce significant amounts of tritiated ammonia. This associated tritium retention could pose a serious risk for ITER operation and maintenance. According to recent estimations, 0.2 grams of associated tritium per discharge will be trapped in ITER if the 5% of the injected nitrogen is converted into ammonia [9, 11, 12].

The high solubility of the ammonia molecules in water and its relative high decomposition temperature ($>500^{\circ}\text{C}$) [13-15] makes its removal in the liquid nitrogen cryopump panels even more difficult. This complex and mandatory operation would limit the operational cycles in ITER due to the necessity to regenerate these vacuum system modules [11, 12]. Furthermore the ammonia sticking on recessed areas and pumping ducts beyond the cryopump units could also represent an important issue, increasing the associated tritium retention in remote parts of the vacuum system. Although strong evidences of this sticking process have been observed [7, 8] the total amount of ammonia that could be retained by

sticking in these parts of a fusion device is still uncertain [10]. The purpose of this work is to try to quantify the amounts of ammonia retained by physisorption on the AISI 304 L SS surface at different temperatures in gas exposure experiments to have an approximate estimation of this problematic and to minimize it as much as possible.

2. Experimental setup and procedure

The basic idea of the experiments is the equilibrium that is reached in a gas-solid interface. In this case the equilibrium between ammonia gas molecules and the AISI 304 L stainless steel surface has been studied in several experiments by flowing ammonia gas (at constant temperature and pressure) and monitoring the time evolution of the 17 Amu signal (directly related to ammonia) with a Residual Gas Analyzer (RGA) Mass Spectrometer for different surface temperatures.

The experimental setup consists on an AISI 304 L stainless steel (SS) (a material frequently used for vacuum technology components under magnetic fields) pipe pumped out by a turbomolecular-rotary pump set (base pressure of 10^{-4} Pa measured with an Ionization Gauge). At the beginning of the pipe, the high purity (99.999 %) gases (NH_3 for the experiments and Argon (Ar) for the blank test and cleaning procedure) are separately introduced into the pipe by using two different MKS mass flow controllers. At the end of this pipe a SRS 200 Quadrupole Mass Spectrometer is connected to the pipe (using an AISI 304 L stainless steel connector) to monitor the experiments following the evolution of the 17 Amu. The dimensions of the pipe with the total surface exposed to ammonia flow and the main composition of the experimental material are given in Table 1. The mass spectrometer is differentially pumped by another turbomolecular-rotary pump set until a

base pressure of 10^{-6} Pa. To restrict the flow and do not saturate the mass spectrometer, a Teflon disc with a 1 mm diameter hole is placed between the pipe and the RGA port connection. This disc acts as a collimator to provide a differential vacuum environment. With this configuration the ammonia pressure in the RGA chamber during the experiments is at least two orders of magnitude lower compared to the nominal pressure on the pipe and consequently the amount of adsorbed ammonia in this part of the setup can be considered as negligible. The collimator is made of Teflon (instead of usually used copper or stainless steel) to avoid changes in the conductance (and the concomitant gas RGA signal) related with possible thermal gradients between a metal collimator and the stainless steel walls of the setup. These changes in the RGA signals due to thermal gradients and conductance changes have been observed in preliminary experiments and have disturbed the mass spectrometry analysis. A Teflon collimator (due to its low thermal conductivity), prevents the temperature increase of a metal collimator that could change the conductance and the RGA signal measured by the mass spectrometer. The ammonia adsorption in the Teflon collimator and other parts of the system, as in the mass flow controller inlet, can be considered negligible compared to the adsorption on the rest of the setup due to their much smaller area (2 orders of magnitude lower). Moreover the physical interaction between the Teflon and the ammonia molecules is supposed to be lighter compared to the case of the sticking of ammonia on stainless steel. With this strategy more accurate mass spectrometry measurements are possible due to the presence of very low water (its contribution to 17 Amu can be considered as negligible) and impurity content in the RGA proximity.

All the equipment (included RGA chamber) is heated homogeneously until its nominal experimental temperature (from 323 to 473 K) by using a thermal blanket fed by a power

supply. The system is isolated with several layers of mineral wool and isolating blankets. The temperature is measured with two type K thermocouples at different and distant points of the system. The control of the temperature is carried out by a PID controller installed inside the power supply. It is of paramount importance to maintain the temperature homogeneous along the system to reduce ammonia condensation on cold parts in order to avoid systematic error in the experiments.

To assure their reproducibility, the experiments were carried out after a conditioning procedure that consists on the heating of the whole pipe until 473 K to desorb the ammonia residual content and water, reducing in this way its mutual and strong chemical interaction. Then a continuous and constant Argon flow ($p=0.75$ Pa) is introduced into the pipe during 1 hour to clean it by dragging the possible rest of adsorbed ammonia and to assure the consistency in the RGA signal over the time. After this, the temperature is kept constant at this nominal value (from 323 to 473 K, depending on the experiment) and a constant flow (≈ 3.5 sccm) of ammonia gas is introduced. A total pressure of 0.75 Pa (measured with a capacitance manometer) was used in all instances. No significant ammonia decomposition into N_2-H_2 molecules was observed in the RGA spectra (no changes in the Amu 28 and 2 signals) during the experiments, excluding in this way the possibility of ammonia chemisorption or dissociation on the SS surface.

Then the increase of the mass 17 signal with time is monitored by mass spectrometry until it reaches a constant value, i.e. the system is in equilibrium. At this moment the total amount of ammonia molecules that can be retained on the walls is adsorbed. An absolute calibration work that relates single RGA peak (17 Amu) with NH_3 total pressure was carried out. With this calibration work, and using a simple particle balance calculation

taking into account the difference between the equilibrium values for 17 Amu obtained in the final part of the experiment and the measured values during it, the total amount of retained ammonia by sticking (physisorption) can be obtained.

3. Experimental results and discussion

In the Figure 2 the evolution of the 17 Amu signal for different surface temperatures, until its saturation, is represented. A clear trend is visible: the characteristic time for the wall saturation with NH₃ molecules (t_{sat}) is lower for higher surface temperatures. The dependence of t_{sat} and the concomitant amount of adsorbed ammonia, obtained by particle balance, with the surface temperature are presented in Figure 3. The amount of stuck ammonia decreases clearly with surface temperature except in the range of 373-423 K. For these temperatures the estimated amount of retained ammonia is very similar (around 17 $\mu\text{g}/\text{cm}^2$). The obtained results give total ammonia retentions on the SS surface among 5 and 40 $\mu\text{g}/\text{cm}^2$, depending on the surface temperature.

Defining the sticking coefficient as:

$$Y_{sticking} = \frac{n_{ret}}{n_{tot}} \quad (1)$$

Being n_{tot} the total number of incident ammonia molecules, and n_{ret} the number of retained (stuck) molecules estimated as the difference between the value of 17 Amu when the equilibrium takes place and the value of this parameter in a given time. The equation to calculate the evolution of the sticking coefficient for ammonia over time can be expressed in this form:

$$Y_{sticking} = \frac{17Amu(equilibrium) - 17Amu(t)}{17Amu(equilibrium)} = 1 - \frac{17Amu(t)}{17Amu(equilibrium)} \quad (2)$$

In the Figure 4 the time dependence of the sticking coefficient for the different surface temperatures and the subsequent exponential fit is shown. These plots show a sticking coefficient strongly dependent on time with maximum values between 0.04 and 0.08. The curves fit with reasonable accuracy to an exponential decay evolution that can be expressed in this form:

$$Y_{sticking} = Y_0 \cdot e^{-\frac{t}{\tau}} \quad (3)$$

From the exponential fit, the experimental parameter τ can be estimated. This value is the characteristic time for the sticking exponential decay observed in the experiments. Assuming that this parameter is inversely proportional to the kinetic constant for the physisorption of the ammonia molecules, and using an Arrhenius fit:

$$K_{ads} = A \cdot e^{-\frac{E_a}{RT}}; \tau \propto \frac{1}{K_{ads}} \rightarrow \tau = A' \cdot e^{\frac{E_a}{RT}} \quad (4)$$

The estimation of the activation energy for the process can be deduced as in Figure 6, resulting in a value of: $E_{activation} = 0.15 \text{ eV / molecule} \equiv 14.3 \text{ kJ / mol}$. This experimental value is lower compared to the latent heat of vaporization for pure ammonia (23.3 kJ / mol) and is in agreement with the energy range for the physisorption of small molecules on metal walls [16].

On the other hand, using a nominal value for the number of ammonia molecules that are adsorbed in a monolayer (assuming one Langmuir $\equiv 10^{-6} \text{ Torr's} \equiv 6.2 \cdot 10^{14} \text{ molecules/cm}^2$ per monolayer [17]), the total number of ammonia monolayers adsorbed on the SS surface, can be calculated. A summary of the experimental results and calculated parameters

including the number of monolayers and the associated hydrogen retention depending on the surface temperature can be found in the Table 2.

Finally it is important to note that the experimental parameter τ gives an idea about the velocity of the physisorption of ammonia on the AISI 304 L stainless steel surface for a given wall temperature, T. The extrapolation of the obtained $\tau(T)$ values for each wall temperature, to higher flux conditions can be an approximation for the saturation of the surface in pumping lines of relevant fusion devices. By multiplying this time by the nominal flow of ammonia (at steady state conditions, after the saturation of the SS surface with ammonia) that was used in the experiments ($\Gamma_{\text{NH}_3} \approx 7.2 \cdot 10^{15}$ NH₃ molecules/cm²·s) a normalized value of the τ parameter is obtained for each temperature, $\tau(T) \cdot \Gamma_{\text{NH}_3}$. This normalized parameter could be extrapolated to devices with a higher particle flux as ITER, to estimate the necessary time to produce a total coverage of the surface with the physisorbed NH₃ molecules at a given ammonia flow (Γ_x) and surface temperature:

$$\tau_x = \tau(T) \cdot \frac{\Gamma_{\text{NH}_3}}{\Gamma_x} \quad (5)$$

The characteristic regime of the ammonia flow can be defined using the Knudsen number:

$$Kn = \frac{\lambda}{d} = \frac{\eta}{p \cdot d} \cdot \sqrt{\frac{\pi \cdot R \cdot T}{2 \cdot M_m}} \quad (6)$$

This number determines the nature of the gas flow and takes into account the molecular mean free path (λ) and the characteristic dimension (diameter, d) of the pipe. Using our experimental parameters:

$p = 0.75$ Pa, $d = 35$ mm, $M_m = 17$ g/mol and $\eta \approx 10^{-6}$ Pa·s (average value for all temperature estimated using the Chapman-Enskog equation [18]), a value of $Kn = 0.02$ - 0.025 is obtained depending on the different experimental temperatures, indicating a transitional regime flow for our experiments. For different Knudsen numbers and regime flows (molecular and continuum), additional experiments at different flow/pressure conditions would be necessary to extrapolate the results of this work.

4. Conclusions

The quantification of the physisorption (sticking) of ammonia molecules on AISI 304 L stainless steel surface, under high vacuum conditions relevant for future fusion devices as ITER, has been carried out. The results show a total retention in the range of 5 - 40 $\mu\text{g}/\text{cm}^2$ that decrease clearly with the surface temperature, except at 373 and 423 K where the total amount of physisorbed ammonia was very similar (approximately 17 $\mu\text{g}/\text{cm}^2$).

The sticking coefficient can be adjusted to an exponential decay with reasonably accuracy. The experimental parameter obtained from this fit (τ) allows the estimation of the activation energy for the multilayer adsorption. According to the experiments a value of 0.15 eV per molecule is obtained for the activation energy of the process.

The normalization of the τ parameter to the incident molecular flow on the surface would give an applicable approximation for the sticking of ammonia molecules on stainless steel surfaces on the ITER vacuum lines with higher and more relevant particle fluxes.

Experiments to investigate the sticking process on tungsten, at higher surface temperatures (beyond 473 K) and to study the thermal decomposition of the adsorbed ammonia on hot

metal surfaces ($T_{\text{surface}} > 750 \text{ K}$) are necessary to understand and mitigate the ammonia retention and the associated tritium inventory in a hypothetical ITER N_2 -seeded operation.

5. Acknowledgements

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References

- [1] R. Neu et al., Plasma Phys. Control. Fus. **49 (12B)**, (2007) **B59–B70**
- [2] A. Kallenbach, M. Balden, R. Dux et al. J. Nucl. Mater. **415**, (2011) **S19**
- [3] C. Giroud, G.P. Maddison, S. Jachmich, et al. Nucl. Fusion **53** (2013) **113025**
- [4] R. Neu et al., J. Nucl. Mater. **438**, (2013) **S34-S41**
- [5] D. Neuwirth, V. Rohde et al. Plasma Phys. Controlled Fusion **54** (2012) **085008**
- [6] M. Oberkofler, D. Douai, S. Brezinsek et al. J. Nucl. Mater. **438** (2013) **S258-S261**
- [7] V. Rohde and M. Oberkofler, J. Nucl. Mater. **463** (2015) **672-675**
- [8] A. Drenik, M. Oberkofler, D. Alegre et al. J. Nucl. Mater. **463** (2015) **684-687**
- [9] M. Oberkofler, D. Alegre, F. Aumayr et al. Fus. Eng. Des. (2015)
- [10] A de Castro, D Alegre and F L Tabares. J Nucl Mater **463** (2015) **676–679**
- [11] G. De Temmerman, R. A. Pitts et al., 21st ITPA SOL and Divertor TG Meeting **(2015)**, Princeton, USA
- [12] G. De Temmerman and R. A. Pitts, Joint WPJET 2 and WPPFC EUROfusion Annual Meeting **(2015)**, Culham, UK
- [13] E. Wilhelm, R. Battino and R. J. Wilcock, Chem. Rev. **77 (2)** (1977) **219–262**
- [14] J.M. Hales and D.R. Drewes, Atmos. Environ. **13 I6** (1979) **1133-1147**
- [15] C.H. Kunsman, J. Am. Chem. Soc. **50 (8)**, (1928) **2100–2113**

[16] J.M. Lafferty, “Foundations of vacuum science and technology”, Wiley-Interscience Publication (1998)

[17] J.L. Gland, B.A. Sexton and G.E. Mitchell, Surf. Sci. **115** (1982) **623-632**

[18] S. Chapman and T.G. Cowling, “The mathematical theory of non-uniform gases”, Cambridge University Press (1939)

Table captions:

Table 1. Total dimensions of the pipe including the total surface exposed to ammonia flow and the AISI 304 L SS main composition.

Table 2. Sticking experimental parameters and estimated NH_3 and hydrogen retention for the different surface temperatures.

Table 1.

Dimensions of the AISI 304 L SS pipe exposed to NH₃ flow			
\varnothing_{in} , mm	L, mm	S _{in} , cm ²	\varnothing_{in}/L
35	400	440	0.09
AISI 304 L SS composition			
% Fe	% Cr	% Ni	ρ , g / cm ³
Balance	18-20	8-12	8.03
% Mn	% Si	% N	% C
2.00 max.	0.75 max.	0.10 max.	0.03 max.

Table 2

T, K	t_{sat}, s	τ, s	τ_{norm}, cm⁻²	NH₃ ret, cm⁻²	Monolayers	NH₃ ret, μg/cm²	H ret, μg/cm²
323	3,468	2,003	1.44E+19	1.41E+18	2,280	39.9	7.04
373	1,678	851	6.13E+18	5.84E+17	942	16.5	2.91
423	1,347	767	5.52E+18	6.20E+17	1,001	17.5	3.09
473	820	314	2.26E+18	2.00E+17	322	5.6	1.00

Figure captions

Figure 1: General view of the setup: 1. Capacitance manometer, 2. Mass-Flow controller (gas inlet), 3. Isolation elements, 4. Temperature sensor (thermocouple), 5. Heating element, 6. Teflon collimator (differential pumping), 7. Mass spectrometer, 8. Ionization Gauge (Bayard Alpert), 9. Pumping units, 10. Power supply (heating)

Figure 2: Evolution of the 17 Amu signal for different surface temperatures. Beyond the saturation time (t_{sat}) the signal keeps constant and indicates that the equilibrium between the gas and the adsorbed layer on the surface is reached.

Figure 3: Wall temperature dependence of the saturation time and the total amount of retained ammonia. For higher surface temperatures both parameters decrease.

Figure 4: Time evolution of the sticking coefficient for the ammonia retention on SS for the studied surface temperatures. The experimental data can be fit to an exponential decay with reasonably accuracy.

Figure 5: Arrhenius Fit of the τ parameter for the estimation of the activation energy. An estimate value of 0.15 eV per molecule is obtained from the experimental data.

Figure 1

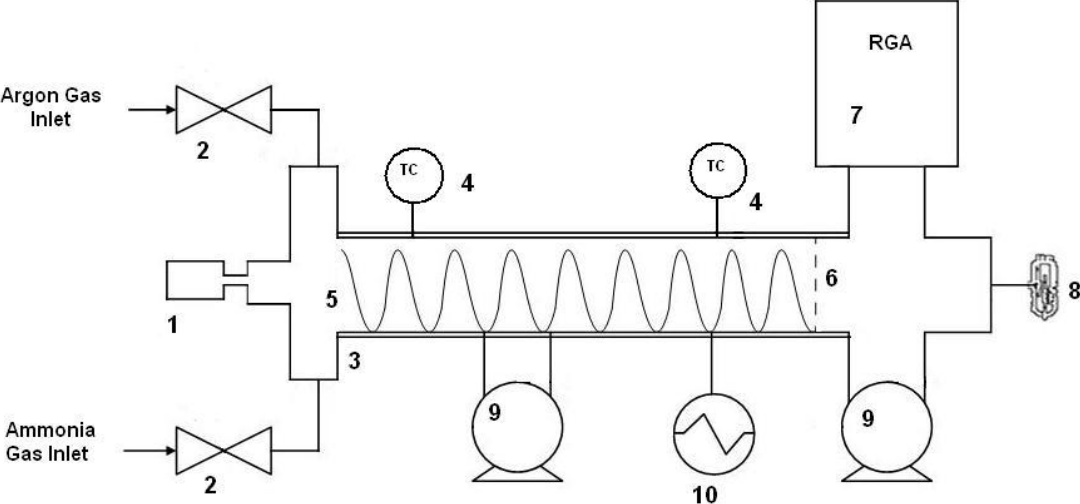


Figure 2

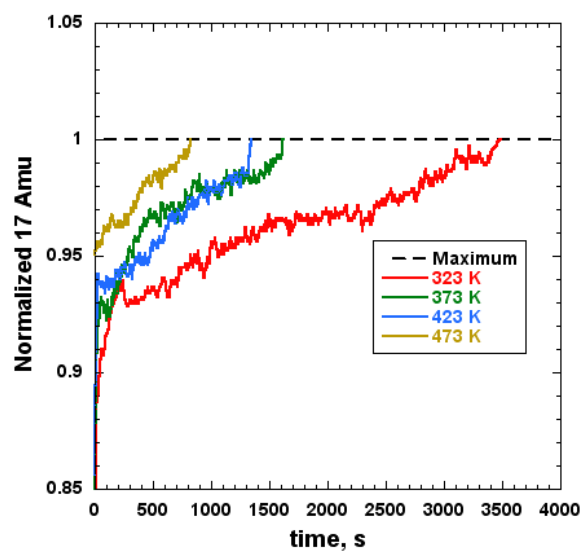


Figure 3

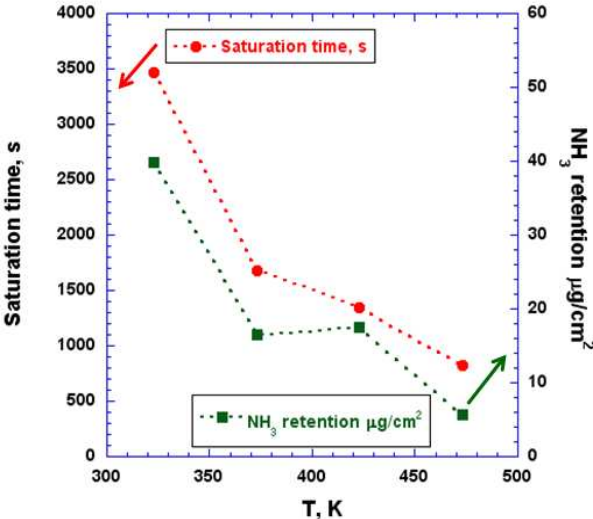


Figure 4

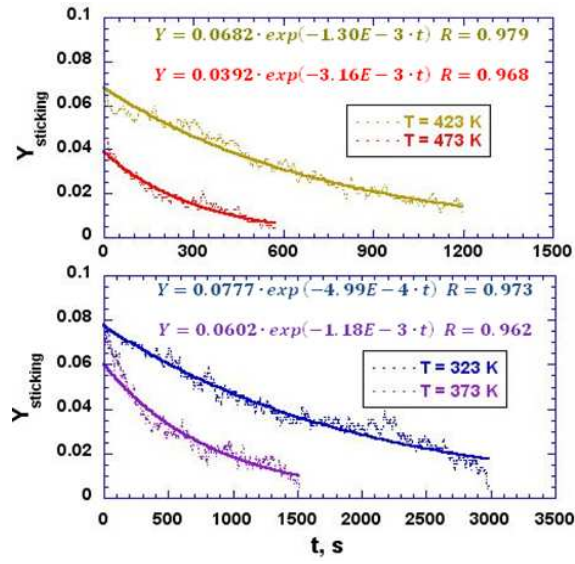


Figure 5

