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Contributions to the study of plasmas used for neutralization of gaseous pollutants

- PhD thesis summary -

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INTRODUCTION

This paper contains topical elements treated in many research labs in the world to which are added a few original results obtained in the laboratory for plasma physics of the Faculty of Physics, with direct reference to the techniques of diagnosis and characterization of microwave plasmas used in techniques of decontamination with plasma. Currently are being studied and largely used, including on industrial scale, different techniques and methods for destruction or modification of environmental pollutants. This is the priority at this stage of social evolution, fact determined by the idea that the harmonious development of society cannot neglect the environmental factor and the implications of its destruction. In this respect, major efforts are being made in all countries in order to ensure, at the local level, of a certain level of pollution. Thus, air quality is monitored continuously and, particularly in technologically advanced countries, research groups search for effective destruction techniques of emissions of polluting gases into the atmosphere. Of the categories of pollutants emitted into the air, volatile organic compounds (VOCs) and greenhouse gases present a raised danger, the vast majority of substances included in this class are generally toxic and some of them carcinogenic.

In this paper we propose studying and investigating a microwave plasma discharge used for decomposition of gaseous pollutants from the category of oxides such as CO_2, CO, NO.

The paper is structured around four well-defined chapters completed by an introduction and conclusions. In the first chapter are described the contaminants monitored in the framework of the national network for monitoring air quality and also those that are not subject to this monitoring, following, in the final part of the chapter, to be the described the non-thermal and thermal plasma discharges used for decomposition of gaseous pollutants. The second chapter describes the electrical and optical methods of diagnosis of low temperature plasma. In terms of chapters three and four, they include the experimental results obtained with the methods described in the second chapter, in microwave plasma used to dissociate carbon dioxide at low pressure, medium pressure and atmospheric pressure, and also to dissociate nitrogen monoxide.

Chapter I: Air quality monitoring and the methods and techniques of flue gases reduction

With the increase of pollution and greenhouse effect raised the issue of flue gases reduction through various techniques and methods of depollution. To apply these methods and techniques of depollution, it is necessary to know the pollutants and their concentrations, and also the effects they can produce on human health and ecosystems. If we confine ourselves to the gaseous pollutants, these are monitored at national level by the National Network of Air Quality Monitoring within the National Environmental Protection Agency, or are subjects to systems with a local or zonal monitoring area, or even at the source of their production. The national network for monitoring air quality is monitoring of immission gases. These are the gases that have a very wide range of propagation and their concentrations are in the range of those tolerated by man. The network's goal is to evaluate and be familiar with the air quality levels and also to inform the public, the authorities and also institutions interested on it [1].

Fig.1.1. Regional monitoring station

Fig.1.2. Urban monitoring station

The network comprises 142 automatic monitoring stations that provide air quality data representative for a particular area surrounding each station. The pollutants studied by these stations are: ozone, nitrogen oxides, sulphur dioxide, particulate matter PM10, PM 2.5, carbon monoxide and benzene. Following, there will be highlighted the main features of each pollutant.

Ozone is a gas very reactive oxidizer, with stifling smell of garlic and naturally he is present in the stratosphere and protects against UV radiation. It

is produced at ground level from reactions which include nitrogen oxides and it is it is included in the “photochemical smog” [1]. Exposure at low concentrations can cause irritation of the eyes and respiratory system while exposure to high concentrations can cause the reducing of the respiratory function [1].

Nitrogen oxides are toxic gases, very reactive oxidizer, formed from nitrogen and oxygen, highly reactive, and contribute, like we early sawn, to the production of ozone at ground level. Among the nitrogen oxides being monitored by the national network, we remember the nitrogen oxide NO (colourless and odourless gas) and nitrogen dioxide NO_2 (reddish-brown in colour with a strong, stifling smell) [1]. Because in sunlight nitrogen oxides can react with hydrocarbons and can form photochemical oxidants, they can be declared responsible for smog and greenhouse effect and also for the acid rain, affecting both terrestrial ecosystem and water through the accumulation of nitrates to ground level. Due to his training especially in urban areas where road traffic is the major problem, the population exposed to this type of pollutants may have respiratory difficulties manifested through irritation of the airways and lungs dysfunction. Exposure to high concentrations of this pollutant can cause death due to lung tissue damage and suspension of respiratory function of the person concerned [1].

Sulphur dioxide is a pollutant, whose importance has declined in recent years because of the low level of its concentration. In nature this pollutant concentration increase is due to volcanic eruptions, phytoplankton, marine bacterial fermentation in the marshy areas and gas oxidation of sulphur-containing result from the decomposition of biomass [1]. Anthropogenic sulphur dioxide occurs mainly in areas where heating systems are used. Inhalation by the population of this type of pollutant affects the respiratory system severe and children, individuals with respiratory diseases and the elders are part of the people with sensitivity to the major pollutant [1].

Particulate matter poses an acute problem at European Union level and few countries fall within the limits imposed by European directives. PM10 and PM2.5 are classifications of particulate matter depending on size, these representing particles with aerodynamic diameter less than 10 micrometers respectively 2.5 micrometers. In the wild they can be produced by: volcanic eruptions, erosion of rocks, sand storms and pollen dispersion, and among the anthropogenic sources which can give rise to particulate matter are included: industrial activity, the heating system, thermal power plants [1].

Carbon monoxide is a gas of natural and anthropological origin, which has no colour, smell or taste [1]. Its concentration is high in traffic areas, thus having a positive correlation (concentrations are directly proportional) with other pollutants from traffic, benzene and nitrogen oxides NO_X. As the sulphur dioxide, the segment of the population most affected by exposure to carbon monoxide it is represented by the children, the elderly and people with a high

degree of sensitivity of the respiratory system (people with respiratory disease, smokers) [1].

Benzene is an aromatic compound, volatile and toxic, insoluble in water, renowned for the fact that it can cause cancer and harmful effects on the central nervous system. In the roadside monitoring stations the concentration of benzene entered is about three times higher than other stations, a sign that the multiplicity of existing cars is mainly responsible for the existence of this pollutant in the atmosphere, and only a tiny fraction of the up to 10% comes from the evaporation of fuel during storage and distribution processes [1].

If we give credence to the reports of the European Union, few countries in the EU are on schedule with the concentrations of atmospheric pollutants. Most countries recorded overrun at concentrations of particulate matter PM10. If in the 1970s-1980s the most watched pollutant was the sulphur dioxide, because it was a determining factor in the occurrence of acid rain, now its concentration has lowered due to the occurrence of the filters from the exhaust flues of heating systems. At present, in the first line of the most intensely monitored pollutants we find particulate matter, ozone and nitrogen oxides. For this reason researchers are seeking new methods of destruction of these flue gases, following a total destruction or total transformation of flue gases dangerous for human health in non toxic compounds or radicals that can be used in various activities.

In reality there are many other atmospheric pollutants which, as I said in the previous section, either are not monitored or are subject to other systems for tracking and evaluation. Among these are the vapours of organic compounds, appointed through generic VOC (volatile organic compounds), organic compounds of biogases and last but not least the carbon dioxide.

Volatile organic compounds are organic chemical compounds that have low boiling point and high vapour pressure at ambient temperature. These features make them to either evaporate or sublimate very quickly in the environment. Their origin can be due to both natural and human action. They can be divided into several categories: i) the alcohol-based solvents, phenolphthalein, acetone; ii) the chlorine-based products, in particular chlorocarbons and chlorofluorocarbons and iii) aromatic compounds which have in their composition the benzene radical.

Biogas is obtained as a result of decomposition of organic matter in the absence of oxygen and is composed mainly of methane CH_4, and carbon dioxide, but also from small percentages of hydrogen sulphide H_2S, water vapours and sometimes the compounds of the group of siloxane Si-O-Si [2]. Through its compounds combustion or oxidation with oxygen it liberates a large amount of energy which allows the biogas to be used as an alternative source of energy. The production and storage of biogas can have harmful environmental influences. Biogas is detrimental to the environment due to the volatile organic compounds in its composition that participate in the production

of photochemical smog. As stated above, the gas composition of biogas is not monitored by the national network for monitoring air quality because they are not part of the imission gases.

In this thesis we have focused on the investigation of microwave plasma in the destruction of various pollutants, such as carbon dioxide [2-6], carbon monoxide and nitric oxide [7-16]. Though about the origin and toxicity of the nitrogen monoxide we talked about in the above section, about carbon dioxide can be written many things concerning the manner in which it can be produced, but also neutralized, and also the efforts that are being made in order to decrease its concentration in the environment. Carbon dioxide is an emission gas, being evicted on the cart as a result of incomplete combustion, and thus it is subject to other tracking systems and monitoring. Carbon dioxide is the main gas causing the greenhouse effect, and its concentration has increased substantially in recent years.

Through depollution we can understand the action to reduce or eliminate pollutants or their sources, i.e. to purify the environment. Currently there are numerous depollution methods and techniques used in industry or research: photocatalitic oxidation [17-19], UV oxidation [20], membrane separation, absorption in carbon [18] and condensation. Lately a new method began to be increasingly used in pollution control. This method consists in using discharge plasma in the dissociation processes of gaseous pollutants. For this are used or a low temperature plasma, in which pollutants are dissociated into radicals and then turn, in the plasma discharge, into less toxic compounds than those incident, or a high-temperature plasma in which pollutants are completely dissociated, resulting sometimes just the elements that compose them.

Amongst low-temperature plasma discharges used in pollution control we can mention: the dielectric barrier discharge (DBD) [21], Corona discharge or microwave plasma [22]. Low temperature plasma in combination with catalyst is a great way to increase energy efficiency, and this symbiosis is found in many systems, one of these being the PAC system (Catalysis-assisted Plasma-Plasma-Enhanced (Assisted) Catalysis). The role of plasma into such system is twofold: helps produce ozone and partially reduces the reactant that then, with the help of some reducing agents (NH_3 and hydrocarbons) placed at the entrance of the catalyst, it been helped to turn into non-toxic compound or less toxic than the original.

High-temperature plasma is used in large-scale purification not only in the case of gaseous pollutants but also those solid and liquid, and the methods that use this type of plasma we can specify gasification in plasma, pyrolysis in plasma [38] and the electric arc. Through the plasma gasification we understand the incomplete oxidation of organic compounds of pollutants and production of gas (Syn-gas) that can be used as alternative sources of energy. Pyrolysis in plasma means the complete dissociation (destruction) of organic compounds, but, the process of oxidation is not present. As advantages of these

methods, that use high temperature plasma, we include the fact that they have a high temperature and energy density, which allows them to have high rates of heat transfer and reactants, as well as the chance to reach out effectively to the melting temperature of the material in question. Another advantage is that it uses electricity as energy source which allows much better control over the processing environment and the chemical processes that take place, fact that can lead to obtaining reaction products which can be valued later [39-40]. These benefits added to the fact that it takes up a small space, it follows that these methods can be included in a production chain. The methods also have disadvantages – the high electricity consumption and low safety in operating them [38].

Chapter II: Methods and techniques for diagnosis of low temperature plasma used in depollution processes

Microwave discharge, as I said in the second chapter, it is an electrode less discharge, with the help of which one we can produce non-thermal plasma, where electron temperature is higher than the gas temperature. In microwave discharge plasma (MPD) electron temperature is much higher compared to those of the plasma discharges are produced in alternate or direct current, so energetic electrons form have the property of excite and ionize atoms and dissociate gas molecules through inelastic collisions. Due to these properties, the MPDs are used in pollution control because they can dissociate certain gaseous pollutants introduced into plasma discharge [75]. Microwave discharge plasma can also be used to deposit thin layers [76-78] or as radical or ion source [79-81] of molecules or atoms [42].

Electrons play an essential role in elementary processes balance in which is defined as low temperature plasma and plasma with medium or low degree of ionization [32]. Electron-atom collisions, respectively the electron-molecule collisions are responsible for producing ions, their excited states, dissociations and other processes that cause the plasma to be a very active environment that could lead to the free radicals production, flue gases neutralization or thin layers deposition. The elementary processes mentioned above depend, through the potential energy of their interaction, on the nature of the particles which collide and also the collision type: ionization, dissociation, excitement or recombination. The generation of electronic excited states of vibration and rotation of molecules, of free radicals and ions thereof is, in fact, the result of electron energy collision with heavy particles. These processes are described by the reactions that may have a probability of achieving higher or lower depending on the size of the effective impact and EDF of electrons. These probabilities are expressed quantitatively by reaction constants. Reaction constants expresses the probability that CO_2 to disassociate in CO and O or that

the degradation products of the reaction to recombine and form carbon dioxide again. The simplest model which is used in describing the speed of variation of the concentrations of various species of particles in such a system is the so-called kinetic model, which uses speed rate equations [35]. The model applies to a uniform and isotropic system where edge processes are neglected. In this case the speed of variation of the concentration *n* of a species of particles in the system may be expressed by the equation:

$$\frac{\partial n}{\partial t} = \Gamma_{prod} - \Gamma_{dis} \qquad (1)$$

where Γprod and Γdis are respectively terms expressing the “generation” and "destruction" of those particles per time unit. It is noted that, in the volume of plasma, the most likely reaction are carbon dioxide dissociation and recombination of atomic oxygen, which, being highly reactive, is converted into molecular oxygen. Thus, according to these reactions, the concentration of carbon dioxide will fall with a fairly high yield, and concentration of the stable reaction products can be considered through specific techniques downstream of the discharge. In the case of stationary plasma, in which appears the stationary condition given by $\frac{\partial n}{\partial t} = 0$, we obtain the equality of the members on the right, and of this equality we can acquire a prerequisite for the concentrations of the species involved in this balance, i.e. the concentration of carbon dioxide will be equal to the sum of the concentrations of the two reaction products: carbon monoxide and oxygen.

The electrical methods and techniques of microwave plasma discharge diagnosis were introduced to determine the temperature and density of the electrons in the plasma. To determine these parameters, the method of the simple probe requires placing an electrode in the plasma, electrode which in the following will be called Langmuir probe, whose surface is active and can have multiple geometries: cylinder, flat or spherical. This electrode, acting as probe, is polarized at different potentials from that of the plasma, and the analysis of flows of charged particles captured by the probe, which determine the electronic currents intensities, respectively ionic ones, by the electric circuit of polarization of the probe can provide quantitative information on the plasma parameters.

Triple probe is an ensemble of three identical cylindrical probes. The system thus established is placed in homogeneous and isotropic plasma in order to determine plasma parameters and ensures direct display having generally a very low response time [42]. This method ensures the direct display of the plasma parameters, generally having a very low response time. The theoretical model of the triple probe was proposed by Sekiguchi [43] and is based upon a system that consists of the insertion in the plasma of a set of three identical probes, P_1, P_2, P_3, with a very small distance between them, a few millimetres. The studies used a simplified version of the triple probe which uses only a

single voltage source for negative polarization of probe P_3 in relation to probe P_1, considered as the reference probe, and probe P_2 remains floating. If the power supply U_3 provides sufficient polarization so that the intensity I of the current in the circuit made up of P_1 and P_3 probes corresponds to the ionic saturation, then a voltmeter, with large entering impedance, connected between the probe P_2 and the reference probe P_1 allows the measurement of the U_2 value with which the potential of the probe P_1 rises in comparison to the floating potential of probe P_2 [42].

The methods and techniques of spectral diagnostics of microwave plasma discharge may use the emission or absorption spectra. The emission spectra can be used to determine the species of particles present in microwave discharge plasma and also to the plasma electron temperature determination from measurements of the relative intensities of the spectral lines. From the absorption spectrum of laser diode radiation we can determine the temperature and the concentration of atoms in the microwave plasma discharge.

Mass spectrometry is used for investigating stable products resulting from the microwave plasma discharge. The method can be used in a wide range of pressure, the mass spectrometer used in the experiments being a cutting-edge device that allowed carrying out of specific measurements for samples of material taken from the systems at atmospheric pressure or, through a direct coupling, allowed the analysis of samples from an experimental chamber where pressure can vary up to 10-6-10-7 Torr. For finding out the partial pressure of each gas introduced into or produced by the discharge it is necessary to trace calibration curves that allow finding the partial pressures of each compound or element introduced into the discharge, depending on the number of counts registered in the mass spectrum.

Chapter III: Electrical and optical diagnostics of microwave plasma at low and high pressure used to neutralize carbon dioxide. Experimental results

The experimental device used in microwave plasma characterisation is presented in Figure 1. For the measurement of microwave plasma parameters, electric probes were used, and to determine the concentration of the final products resulting from the action of plasma over the gas mixtures involved was used a mass spectrometer.

The electrical probes employed were: i) the cylindrical probe and ii) respectively, a triple probe. For the construction of the cylindrical Langmuir probe has been used a wire of Tungsten of 0.5 mm in diameter. The wire has been inserted in a ceramic protection tube resulting in a 3 mm tip out of the ceramic coating which may be exposed to the plasma. For the construction of the triple probe were used three identical cylindrical probes, with the same

diameter and the same length, placed parallel to one another, being placed in the peaks of an equilateral triangle of side 2 mm.

The simple probe was inserted into the plasma in the direction of the axis of the discharge tube at a distance of 6 cm from the centre of the applicator. For marking the volt-ampere I(V) characteristic of the cylindrical probe, in the discharge tube were introduced two reference electrodes placed

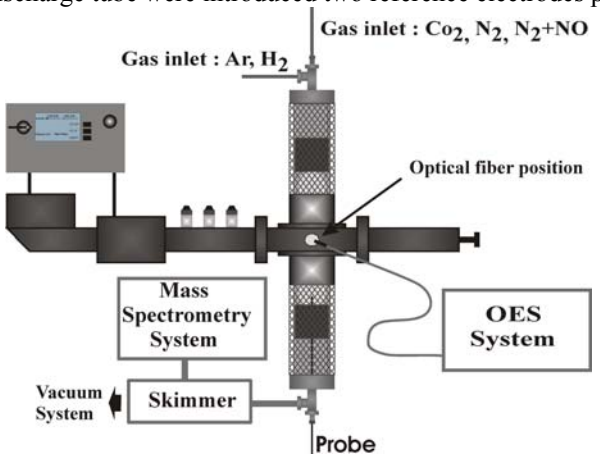

Fig.1. The experimental device

symmetrically on either side of the applicator into the outside. The reference electrodes have been made of stainless steel sheet and have a cylindrical shape with a diameter of 4.5 cm and a length of 5 cm. The reference electrodes were connected either to the overall mass of the measurement system or were kept at a floating potential in other measurements. The probe characteristic was achieved by varying the external voltage applied between the probe and the reference electrodes, and by gathering a probe stream in proportion to the potential loss of a resistor R = 33 Ω connected in series on the circuit. The probe characteristic was acquired with a Tektronix oscilloscope TDS5034B and then smoothed and processed using standard analysis software to be able to determine temperature and electron density.

In the case of triple probe, the probe system was introduced also in the direction of the axis of the discharge tube, and plasma parameters have been obtained in real time using only an ongoing source of polarization of two probes and measuring the current in that circuit, respectively the potential value of the third probe in relation to the probe connected to the positive voltage source mentioned above.

To analyze the CO_2 gas dissociation in a microwave discharge, downstream was attached a mass spectrometer Hiden Analytical quadrupolar

filter HPR60 used in the RGA mode. The mass spectrometer is investigating stable chemical compounds resulting from the discharge using a 30μm in diameter skimmer.

To control and to decrease as much as possible the electromagnetic radiation dissipated outside the device, the quartz tube was shielded with a wire mesh. This operation helps protect laboratory personnel against the incident electromagnetic field dissipated by the microwave generator. From the measurements performed with NARDA 300 for registered power density at 10 cm from the applicator, in the Fraunhofer area, and also at 55 cm from the device, in the Fresnel area, the results are almost two orders of magnitude lower than the maximum limit of exposure of laboratory personnel.

One of the methods of microwave plasma diagnosis, used in this thesis, was optical emission spectrometry. Optical emission spectrometry was performed with a high resolution spectrophotometer TRIAX 550 equipped with a detector ICCD and an optic fibre (0.4 mm). Optical fibre collected plasma radiation in the central zone of the plasma [64]. In the spectrum of radiation emitted by the plasma discharge produced only in CO_2, as seen in Figure 2, are clearly stated the main components of plasma. These are: i) atomic oxygen represented by the atomic spectral lines at 777 nm and 844 nm, ii) carbon monoxide with more spectral bands $B^1\Sigma^+ \rightarrow A^1\Pi$ present in two specific areas of wave lengths 290-325 nm and 400-650 nm, and iii) CO_2 represented by continuous spectrum due to the superposition of many spectral bands in the area 400-750 nm [65].

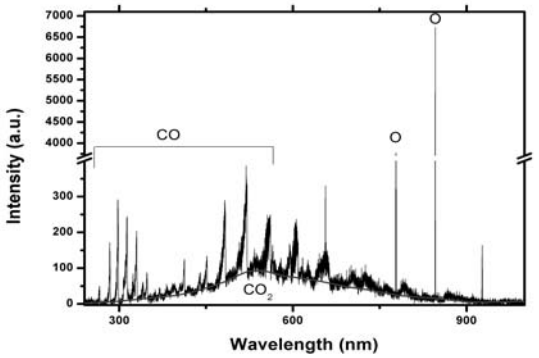

Fig.2. The emission spectrum of a CO_2 microwave plasma discharge

If the initial pressure, for all gas flow rates used in experimental works, was 2.1 Torr, during molecular gas dissociation, the pressure of the gas mixture obtained in the discharge tube increased, being included in the range 2.7-3.44

Torr. This increase is the result of dissociation and creating new gases such as carbon monoxide CO and molecular oxygen O_2, after the following reactions:

$$CO_2 + e^- \rightarrow CO + O \qquad (1)$$

$$CO_2 + O \rightarrow CO + O_2 \qquad (2)$$

These new components resulting from the CO_2 dissociation are clearly highlighted in the emission spectrum of microwave plasma radiation as shown in Figure 2.

In the series of experiments in which microwave discharge consisted of a mixture of carbon dioxide and hydrogen was found that along with the specific discharge reactions in carbon dioxide described above, add up three new reactions: i) dissociation of hydrogen molecule and atomic hydrogen forming, ii) recombination of oxygen and hydrogen atoms and hydroxyl radical formation, and iii) recombination of the hydroxyl radical with the hydrogen atom such as:

$$H_2 + e^- \rightarrow H + H \qquad (3)$$

$$H + O \rightarrow OH^* \xrightarrow{H} H_2O \qquad (4)$$

Regarding the points obtained for the logarithm of the intensity of the spectral lines of hydrogen depending on the corresponding excited states energies, it is observed that their linear fitting gives us the information of distribution on the energy levels of atoms excited is a Boltzmann distribution, which leads to the hypothesis that plasma is at thermodynamic equilibrium.

From the ratio of the spectral line intensities of the spectral lines of argon in accordance with the model shown in the previous chapter, for a variation of the CO_2 flow between 25 and 100 ml / min and a pressure of the discharge tube that ranged from 1 to 5 Torr, the electrons temperature determined by this method has a value of 0.13 eV. Given that, for a pressure of 0.6 Torr, the electron temperature determined by triple probe is about 6 eV, the value obtained from spectral line intensity ratio raises several questions. A first question is whether this method is feasible for such gas mixtures. The second question is whether the temperature obtained is actually a temperature of vibration, due to a balance that may be formed between the electron population and the vibrational - rotation excitation processes of the gas molecules.

Using optical absorption spectrometry to determine both temperature of metastable oxygen atoms and their density, in relation to the increasing flow of carbon dioxide and hence the corresponding pressure. Laser diode radiation was set to a wavelength of 777.194 nm, corresponding to the transition $3^5S_2 \rightarrow 3^5P_3$.

Microwave radiation power was varied in the range 300W and 600W and working gas pressure ranged from 0.55 Torr CO_2 - 2.1 Torr. The temperature determined for metastable oxygen atoms was 420 K. In many cases, one being that which admits the idea that the plasma is at local

thermodynamic balance, this temperature can be approximated as the gas temperature [68]. Monotonous increases the density of atoms of metastable oxygen atoms, shown in Figure 4, together with the increasing power of microwave radiation from the plasma generator can be explained by the fact that with the increasing power of the microwave radiation and plasma density increases, which leads to an increase of the probability of the electron collision with neutral atoms and molecules in plasma resulting in an increase in the number of elementary processes that lead to dissociation of carbon dioxide [68] The more carbon dioxide dissociates, the more atomic oxygen is formed and, of course, the density of metastable oxygen atoms grows. In Figure 4 is noted that with increase of the carbon dioxide flow and its corresponding pressure, which increases from 0.55 Torr to 2.1 Torr, the density of metastable atoms decreases by almost an order of magnitude: from 10^{16} m^{-3} to 10^{15} m^{-3}. This can be explained by the enhanced probability of recombination of carbon dioxide with increasing pressure, which leads to a diminishing in the density of metastable atoms [68].

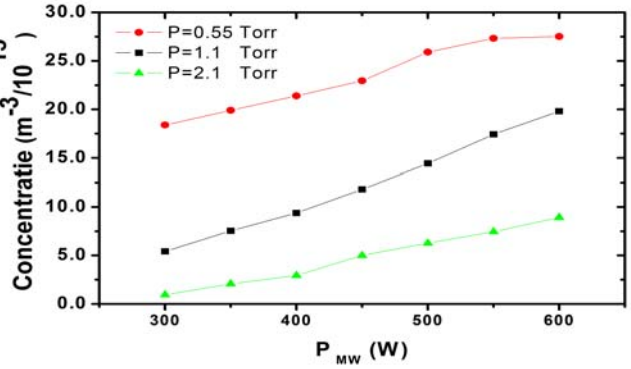

Fig.4. Changes in the concentrations of metastable oxygen atoms in relation to the microwave radiation power and the working gas pressure

The following are the main results obtained using mass spectrometry. There were performed two sets of experiments. A first category is that where plasma was produced by carbon dioxide, and in it, in some experiments, were placed varying percentages of argon or hydrogen. In the second type of measurements, plasma was produced in a buffer gas, in this case argon, in which were introduced relatively low percentages of molecular compounds of CO_2, N_2, CO, NO and mixtures thereof. Dissociation of carbon dioxide was investigated in two directions: the first direction is when carbon dioxide was introduced into the discharge with and without H_2 to see how the presence of

hydrogen affects the dissociation of carbon dioxide. Both gases flows ranged from 7.4 ml/min - 200 ml/min, ratio 1:1, for a pressure of the discharge tube that varied between $3x10^{-1}$ Torr to 16 Torr, and a microwave radiation power that varied between 200W and 600W. The second direction was that when the gas pressure in the discharge tube was set at 2.1 Torr and we studied the dissociation of carbon dioxide by changing its residence time in the applicator. CO_2 flows ranged from 25 ml / min and 150 ml / min, and the power of the microwave radiation varied between 200W and 600W.

Dissociation efficiency η of carbon dioxide in the microwave plasma discharge is expressed as percentages and was calculated according to the equation below, by using the numbers of counts C_i and C_f measured with the mass spectrometer before and after plasma ignition at different powers. Also, in the relation below can be seen the yields of formation of CO and O_2, where in addition to C_i, already stated, are used the measures C_{CO} and C_{O2}, which represent the numbers of counts of CO_2 to CO and O_2 recorded with the mass spectrometer during CO_2 dissociation:

$$\eta = \frac{Ci - Cf}{Ci} * 100\,, \quad R_{co} = \frac{C_{CO}}{C_i} \text{ and } R_{O_2} = \frac{C_{O_2}}{C_i}$$

The experimental results obtained are shown in Figure 5. For the first part of the experiment can be observed that the dissociation of carbon dioxide decreased from 90% for a flow rate of 7.4 ml / min and a power of 600 W, down to 68% on a CO_2 flow rate of 200 ml/min and a power of 600W, and respectively below 20% at the same rate but a microwave power of 200W.

For relatively large flows of carbon dioxide, its dissociation tends to rise with the increasing of microwave power, but for low flows, the system is saturated from the microwave discharge power of 200W. The efficiency of

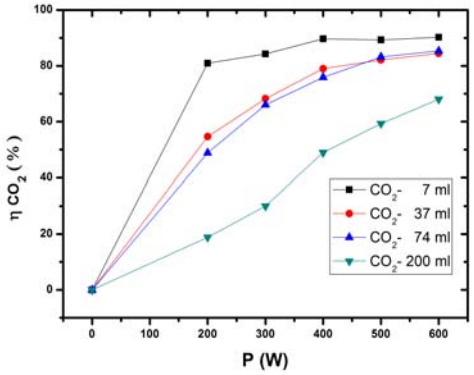

Fig.5. The yield of CO_2 dissociation in a microwave plasma where the microwave radiation power and the flow of CO_2 introduced varied

carbon monoxide and molecular oxygen formation significantly increase with the increase of CO_2 flow.

The results obtained supplement very well the details shown in Figure 4, i.e. there is very good correlation between the quantity of carbon dioxide dissociated and the quantity of carbon monoxide and oxygen formed, fact confirming the mechanism and chemical reactions that take place in the microwave plasma (reactions 1 and 2).

In another series of measurements, together with carbon dioxide, in microwave plasma discharge was introduced hydrogen, in controlled percentages. In order to have a complete cycle of carbon dioxide destruction was desirable for carbon monoxide resulted from dissociation to enter at high temperature hydrogen-rich atmosphere and form Syn-gas. Since the formation of this Syn-gas requires special facilities in our laboratory, we have only limited to observe how carbon dioxide dissociation efficiency changes when hydrogen is inserted in the microwave plasma discharge.

When introducing hydrogen in microwave plasma discharge produced in a steady stream and a constant partial pressure of carbon dioxide dissociation, the efficiency of it, as shown in Figure 6, drops from 78% calculated in the absence of hydrogen to 53%.

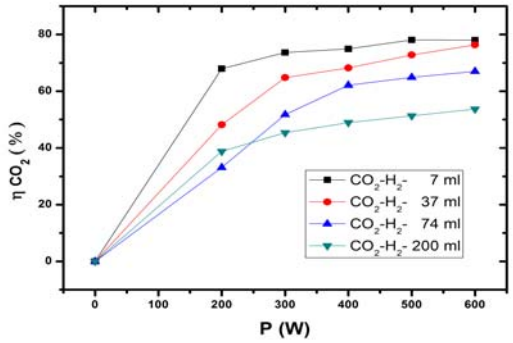

Fig.6. The yield of CO_2 dissociation in a microwave plasma where the microwave radiation power and the flow of CO_2 and H_2 introduced varied

In this case was brought a steady stream of hydrogen equal to that of carbon dioxide. At the same time it is found that the efficiency of carbon monoxide formation decreases with increasing flow rate of CO_2 and H_2 mixture, meanwhile the molecular oxygen generation tends to 0. This is due to the fact that the presence of hydrogen to the system leads to the water formation according to reaction (3) and (4).

As regards the second part of the experiment, when the pressure was set at 2.1 Torr and residence time of the gas in the applicator was modified, we can

observe in Figure 7 that the efficiency of carbon dioxide dissociation is more than 50% if the power is more than 300W and CO_2 flow is greater than 75 ml/min. The results show clearly that for a high residence time of the pollutant in the applicator, the dissociation is high, over 50%, and it grows with the increasing of the microwave radiation power. Yields for the formation of CO and O_2 also increase with higher residence time of carbon dioxide into the applicator. The augmentation of gas flow causes a decrease of the residence time of carbon dioxide into the applicator and microwave discharge area. This lowers the number of CO_2 dissociated molecules, and also the number of CO and O_2 produced molecules, thus explaining the lowering of the dissociation efficiency.

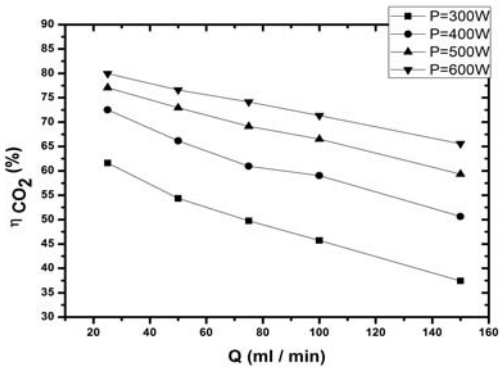

Fig.7. The yield of CO_2 dissociation in a microwave plasma where the microwave radiation power and the flow of CO_2 introduced varied, for a stable pressure of 2.1 Torr

In order to investigate the dissociation of carbon dioxide at atmospheric pressure, in place of the applicator and the quartz tube was placed a special device designed to generate a microwave plasma torch [69-72]. If for a low pressure in the plasma discharge were visible carbon monoxide and atomic oxygen because carbon dioxide was separated in these two compounds, at atmospheric pressure carbon monoxide vanishes from the emission spectra. In the plasma discharge at atmospheric pressure, there is the atomic oxygen and instead of carbon monoxide atomic carbon emerges, being visible spectral lines of atomic carbon from 248 nm and of atomic oxygen from 777 nm and 844 nm. The efficiency of the carbon dioxide dissociation, according to the microwave radiation power introduced in the discharge, is very small compared to that at low pressure. This yield does not change even with increasing flow rate of carbon dioxide introduced into the discharge. As seen from mass spectrometry experiments at low pressure, with increasing pressure decreases the dissociation

yield, so that, as expected, at atmospheric pressure, it is very small, less than 10%.

Chapter IV: Electrical and optical diagnostics of microwave plasma produced in nitrogen and nitrogen monoxide. Experimental results

The results achieved and which will be presented in this chapter relate to the determination of plasma parameters with a cylindrical Langmuir probe and a triple probe. The experiments were performed in argon microwave plasma in which have been introduced certain concentrations of nitrogen or mixtures of nitrogen monoxide (NO) and nitrogen (N_2). The use of the two types of probes was primarily motivated by the need to highlight the advantages but also of the sensitive elements of using the triple probe against the simple Langmuir probe.

Plasma was produced in gases at a pressure of 0.5 Torr and the microwave radiation power varied from 100W to 500W. As has already been stated, both types of probes were mounted axially in the discharge tube and were mainly used for determination of electron temperature and density in the plasma. As I mentioned in the description of the experimental device for use in Langmuir probe microwave discharge plasma, which is a download without electrodes, we need to introduce a reference electrode at discharge which is a disadvantage of this method due to the mismatch produced in plasma due to the measuring probe circuit. The mismatch manifests itself through the determination of an adjustment rather difficult between microwave radiation power ceded to the plasma and reflected. Introduction into discharge of a floating probe [82] as triple probe, which produces a minimal perturbation in plasma diagnostics, can provide a viable method of microwave plasma parameters determination [42].

In a first experiment, electron temperature and density were measured using the simple probe in argon plasma. In semi-logarithmic plots of probe characteristics are highlighted two groups of electrons. For the first group, the low energy or “slow” electrons, the majority of electrons in the plasma, there was determined, with the help of simple probe, a temperature between 1 eV and 3 eV and a density of order 10^{13} cm^{-3}. For the second group of electrons, the “fast” ones, constituting a small fraction of the total population of electrons, the temperature determined with simple probe is almost double, from 4 eV to 8 eV, but the density is lower by almost two orders of magnitude than the electrons in the first group [42]. Because we wanted a comparison between the data provided by the both methods, the triple probe was inserted in the discharge to measure plasma parameters in similar conditions.

In Figure 8 you can see the temperatures of the two electron groups determined with the simple probe, but also the temperatures registered with the triple probe. When the electrons distribution function of in the plasma is

maxwellian, simple and the triple probe shows comparable values of the plasma parameters. When EEDF is bi-maxwellian, triple probe displays the

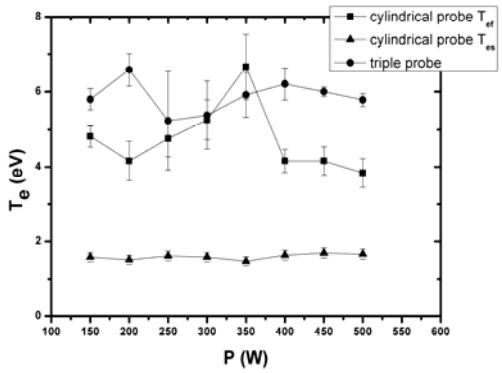

Fig.8. Electron temperatures measured with a simple probe and triple probe in Ar microwave plasma [42]

temperature of a single group of electrons that depends on the ratio of the densities of these two groups present [42]. If the argon plasma molecular nitrogen is introduced or a mixture thereof with another gas, the plasma volume shrinks [85], the probe remaining, however inside the plasma volume, but the connection between the reference electrode and microwave generator reference connection gets very low. In this situation, to be able to make simple probe characteristics, it is necessary to increase the power of the microwave radiation, in this case over a 300 W.

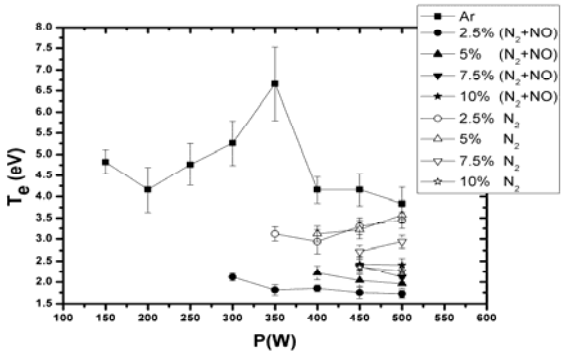

Fig.9. Changes in power of electron temperature measured with the single probe in Ar plasma in which different concentrations of N_2 and N_2 + NO were added [42]

As shown in Figure 9, electron temperature decreases when nitrogen is inserted in the discharge but increases when nitric oxide is introduced. Electron temperature reduction is made on account of the discharge 'cooling' phenomenon do to nitrogen inlet, often put in evidence in the literature [86], and given the explanation that this effect is caused by enhanced ionization of nitrogen and by the electron energy loss in a molecular gas excitation, vibration, dissociation [42]. Instead, the advent of negative ions of oxygen in the plasma [86], thanks NO dissociation, maybe leading to their recombination with less energetic plasma electrons and thus remain the majority population of high-energy electrons and electron temperature will grow [42].

Figure 10 shows the evolution of electron temperature when determined with the triple probe in Ar plasma, where we have introduced different concentrations of N_2 or N_2+NO, the conditions being the same as those from the measurements with the simple probe. In this graph you can see that the electron temperature measured with the triple probe is situated in the same range as the one measured with the simple probe, but its evolution with increasing of the percentage of molecular gas introduced in the discharge is different.

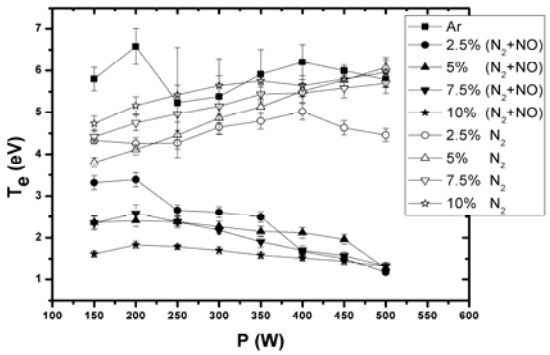

Fig.10. Changes in power of electron temperature measured with the triple probe in Ar plasma in which different concentrations of N_2 and N_2 + NO were added [33]

This behaviour shows a sensitivity of the method of elementary processes in molecular gases complexes which have a strong influence and lead to a decrease in the average kinetic energy of the electrons involved in these processes [42].

Although it seems like the Langmuir probe has an advantage over triple probe because the data provided by this method are more conclusive than those offered by the triple probe, due to the phenomena explained above and which are so much better tracked by this method, the Langmuir probe has the

disadvantage that it is much more sensitive to the measure circuit because it requires the introduction of a reference electrode in to the discharge which induces a fairly difficult adjustment between the power radiation of microwave plasma and reflected outward. Also, due to the coupling with the reference electrode, errors may appear in determination of plasma density and temperature. Another disadvantage of the method is that it requires much more time for data acquisition and processing, so that there should be a thorough analysis before opting for one of the two methods of monitoring and diagnostics of plasma parameters in a microwave discharge [42].

The electrons densities obtained with the two methods are shown in figures 11a and 11b. Plasma density was determined using either the standard model of the simple probe or was calculated using ionic saturation current like is proposed by the Sekiguchi method. This method introduces in the determination of electron density the mass of all ions in the plasma, but in our case, because further analysis is needed to learn the mass of the other ions, we got as a first approximation the presence of a single ion species Ar+, argon being the dominant gas in the plasma. The differences in the measurement of

a) b)

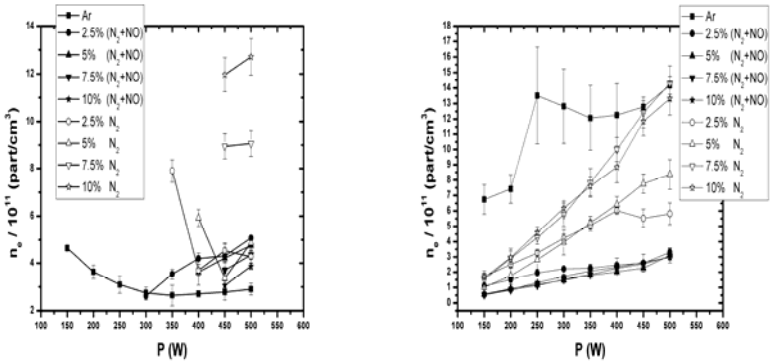

Fig.11. Changes in power of electron temperature measured with a) the simple probe and b) the triple probe, in Ar plasma in which different concentrations of N_2 and N_2 + NO were added [33]

plasma density with the two methods know more categories and can have several causes.

A first difference in the density measurement with the two methods is that the plasma density measured with simple probe is lower than the one determined with the triple probe. This can be explained by the fact that the simple probe measures the electron density, while the triple probe uses the ionic stream of the probe to calculate plasma density [42].

In the second category of differences we can observe a trend contrary to plasma density measured by the two methods yet to nitrogen or N2/NO mixture in argon is produced. These behaviours makes it clear that the introduction in the argon discharge molecular gases that have a low energy of ionization, leads, as shown above, both to a decrease electron temperature and density and also to their growth. This trend is highlighted by the simple probe only, due to the fact that seeks far better elementary processes occurring in the plasma, while triple probe method, used in the calculation of the density of the plasma ionic saturation, should be limited to only be used to confirm other methods [42]. Another cause of the differences between the measured densities by the two methods in microwave plasma alight in pure argon can be, as has been highlighted when temperature was measured, due to errors induced by coupling the probe with the reference electrodes inserted in the discharge. Having a determination of electron temperature using Langmuir probe and triple probe, we determined the electron temperature also from measurements of the relative intensity of spectral lines. The results are consistent with those obtained with the simple probe into microwave plasma obtained in Ar at a pressure of 0.5 Torr.

CONCLUSIONS

In this paper we intend to study and investigation of plasma microwave downloads used for decomposition of gaseous pollutants in category of carbon and nitrogen oxides. For this we conducted work in which the contributions were made in three different directions: i) building the experimental devices, ii) microwave plasma diagnosis iii) dissociation kinetics of gaseous oxides in microwave plasma.

Building the experimental devices

1. During this thesis we built two experimental plants, one of which was used to produce microwave plasma at low and medium pressure to streams controlled by gas and the other was used for the production of microwave torch at atmospheric pressure.

2. We manufactured Langmuir and triple probes with which I performed microwave plasma electric diagnosis. In terms of optic diagnosis, I configured and performed laboratory facilities for spectral measurements that were obtained and registered with the absorption and emission spectra of microwave plasma produced in molecular gases. For obtaining the absorption spectra I used radiation emitted from a laser diode.

3. I installed for the first time in plasma physics laboratory, a quadrupolar mass spectrometer which allows sampling directly from the discharge, including a pressure equal to atmospheric pressure.

Microwave plasma diagnosis

4. Using optical emission spectrometry I have investigated the existing species in microwave discharge plasma and I pointed out that, for low and medium pressure, carbon dioxide dissociates into carbon monoxide and oxygen, which is confirmed by mass spectrometry. At atmospheric pressure, in plasma discharge are found in species such as atomic and atomic oxygen and carbon, a sign that the carbon dioxide it dissociates into these products but this has not been confirmed by other methods.

5. In the local thermodynamic equilibrium hypothesis and using the method of spectral lines ratio we measured plasma electron temperature of microwave plasma produced at low and high pressure. The measured electron temperature corresponds to the majority group who have a low average kinetic energy. At the introduction of carbon dioxide in microwave plasma discharge, the results are no longer accurate but fitting with a straight four the four points indicate that plasma is local thermodynamic equilibrium and the distribution of energy levels of atoms excited is Boltzmann.

6. Using TDLAS method, we have measured the temperature and concentration of oxygen atoms of microwave plasma discharge produced into carbon dioxide. Through this method I found a temperature of 420 K for oxygen atoms metastables (777.194 nm) and that, under certain conditions, can be approximated with the gas temperature. Also was showed that the density of atoms metastables of oxygen decreases with increasing pressure which indicates a drop in yields of dissociation with increasing pressure, the measurements been confirmed by mass spectrometry.

7. The results obtained with the simple probe showed that the electron distribution function of microwave plasma can be approximated by the presence of two electron termalized groups, but the reference electrode, which is required in obtaining simple probe characteristics produce powerful plasma disruption so it can be used only in a narrow range of parameters. Disturbance due to the introduction of triple probe in microwave discharge is negligible, but this method makes it possible to measure the temperature of the energetic electrons.

Dissociation kinetics of gaseous oxides in microwave plasma

8. Through the experiments, we have achieved a systematic study on the yields of dissociation of carbon dioxide in microwave discharge plasma at different flow rates of gas and corresponding pressures and different powers of microwave radiation. The studied case was when plasma discharge was produced in carbon dioxide but investigated also the adding effects of H_2 in the discharge over these yields. At low pressures, defined under 0.1 Torr, and the average pressure in the range 0.1 to 10 Torr, microwave plasma produces carbon dioxide dissociation and contributes to the formation of a mixture of carbon dioxide, carbon monoxide and oxygen both in atomic and molecular state.

9. I have obtained higher yields of dissociation of carbon dioxide that can be over 78% when plasma is switched directly into the pollutant gas and decrease up to 53% if the hydrogen is introduced in constant flow equal to that of carbon dioxide. The presence of hydrogen in the discharge decrease yields of dissociation of carbon dioxide but the proportion of carbon dioxide and carbon monoxide dissociated format remains the same. The introduction of hydrogen in the plasma produced in carbon dioxide leads to a decrease in the fraction of carbon dioxide and the formation of the dissociated, as the final product, and, without a decrease in the fraction of carbon monoxide results from dissociation of carbon dioxide.

10. I have made it clear that, for high residence time of pollutant in microwave applicator area disassociation yield is high, over 50%, and it grows with the increasing of microwave radiation power.

11. The results obtained following dissociation of carbon dioxide in a microwave plasma torch ignited at atmospheric pressure have highlighted that a small fraction of the carbon dioxide is dissociated, less than 20%, the remainder being undissociated, and the resulting products in plasma, highlighted by optical emission spectrometry, are essentially atomic oxygen and carbon, which are then highlighted in different molecular structures by mass spectrometry.

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