Purification Processes in Heterogeneous Non -Equilibrium Plasma.

Boris V.Potapkin , Maxim A. Deminski, and Alexander A. Fridman.

RRC "Kurchatov Institute" Moscow, 123182, Russia

Environmental application of the technologies based on discharges and electron beam stimulation of oxidation and reduction process strongly depends on the possibility to reduce oxidation and reduction energy cost, to get high degree of conversion at the low energy consumption, and to avoid generation of toxic or undesirable intermediate substances[1]. One of the way to solve these problems and to improve the efficiency is related with the heterogeneous discharges and electron beam systems were water or other liquid is present in form of droplets or film on the surface of discharge chamber. The avantages of heterogenious systems are related with the several factors.

First of all water or other polar liquid can be considered as a kind of plasma because water as a polar liquid can generate and stabilize ions, at a very high concentration level, even at room temperature. That is why in many cases in the water long chain reactions can occur and at the same time these reactions are very slow or do not proceed in gas phase at all. SO_2 oxidation reaction, which can have, in water, chain length more then one million and does not occur in the gas phase at all can be mentioned as one of the most expressive example [2]. Nevertheless in many cases to start chain oxidation in liquid the initiation i.e. the generation of the active species which can be chain carrier is required. For example chain SO_2 oxidation can be initiated by OH radical or positive ion. That is why heterogeneous plasma with water droplets, where active species generated by plasma in the gas initiate long length chain reactions in the droplets, can be very effective catalytic media.

Ion generation in polar liquids also can lead to the effective utilization of ozone which can be generated in non-thermal plasma with the high efficiency. Ozone in alkali solution converts in extremely chemically active OH radical (O3 + OH- = O3- + OH) hence becomes more suitable for reaction stimulation. The second reason of effective ozone utilization in heterogeneous system is that toxic compound itself can exist in liquid in ion form and reaction rate between ozone and ion form of toxic compound increases significantly (in one million times for definite types of VOC[2])

Let us mentioned finally that water can be effective media for spontaneous reactions of substances which are relatively stable with respect to gas phase oxidation and reduction reactions. For example hydrolysis reactions of COCl2 or disproportional reactions of high nitrogen oxides in water with nitrous acid formation. Taking into account that these compounds appear as an intermediate ones during oxidation and reduction processes in non-thermal plasma the addition of water droplets to the system can lead to quenching of the intermediate products and hence to the process efficiency enhancement.

The kinetics and mechanisms of heterogeneous oxidation and reduction reactions are very complicated and are determined by various physicochemical processes: chemical reactions in gas and droplets or water film, dissolution of the components involved in the chemical reactions transfer processes in the gas and liquid, and the dynamics the formation and decay of droplets and aerosol particles. Thus to have effective heterogeneous plasma processes it's quit important to reveal general kinetics features of oxidation and reduction in heterogeneous media and to find optimum conditions for such processes. The review of the experimental and theoretical works made in this field by other authors is presented too.

Let us consider as an example the kinetics peculiarities of chain oxidation in heterogeneous non- equilibrium plasma and conditions which must be fulfilled to have real catalytic effect. Ions or radicals generated by plasma in the gas must get the droplets without essential losses in recombination and other undesirable reactions. The initiation rate and acidity of the liquid must be appropriate to the long chain oxidation. Transport phenomena in gas and in the droplets have not limit the chemical reaction and others. Thus for effective catalysis in fog plasma the optimization of the system parameters like droplets radius , droplets number density, acidity of liquid and ea. is required.

In general the conditions of effective plasma catalysis can be written as follows:

$$\gamma >> 1 \quad \omega^l >> \omega^g \quad \omega^l >> \omega_{e,c} \qquad (1)$$

Here γ chain length in liquid; ω^g, ω^l-reactions frequencies in the gas (non chain reaction) and in the liquid (chain oxidation) respectively; $\omega_{e,c}$ is evaporation for coagulation frequencies. The third condition means that fog must exist during a period of time much longer them characteristic time of the chemical reaction.

To specify the conditions we will assume that chemical reaction (for example SO2 oxidation) stimulated by electron beam proceeds in matrix gas (nitrogen and oxygen) with liquid droplets of definite radius. Analysis of oxidation process kinetic will be performed under the following simplified assumption: droplet can have an effect on the concentrations profiles only at the distance of several droplet radiuses and this size is significantly less than the average distance between droplets; the characteristic times of

diffusion, chemical reactions and dissolution are less than the characteristic times of coagulation and nucleation processes; the acidity of droplets is constant; the reactions frequencies of matrix gas components are much less than those for active components (ions, radicals etc.); solvatation is not limiting process. In this case the physical chemical kinetics of oxidation process in water cloud can be described by the following master equations and appropriate boundary conditions for the limiting component I (active species initiated chain process in our case with the concentration $n_I^{l,g}$ in the liquid and in the gas respectively):

$$\frac{dn_I^l}{dt} = \frac{D_I^l}{r^2} \cdot \frac{d}{dr}\left(r^2 \frac{dn_I^l}{dr}\right) - \omega_r^l \cdot n_I^l + \omega_i^l \cdot n^l \cdot G_I^l \qquad (2)$$

$$\frac{dn_I^g}{dt} = \omega_I^g \cdot n^g \cdot G_I^g - \omega_I^g \cdot n_I^g - \frac{3D_I^g}{a^2} \cdot \theta \cdot \left(n_I^g - n_I^g(r=a)\right) \qquad (3)$$

boundary conditions at the droplet surface:

$$J_I^l(r=a) = J_I^g(r=a); \qquad n_I^g(r=a) \cdot H_I = n_I^g(r=a) \qquad (4)$$

The criterion (29) can be rewritten in this case too:

$$\gamma \cdot \omega_I^l >> \omega_I^g \qquad (5)$$

Here $\omega_i^{l,g}$ - frequencies of initiating species generation in gas and in liquid which is directly proportional to current density of an electron beam; $G_I^{l,g}$ - radiation yields of initiating species generation; $D_I^{l,g}$ - diffusion coefficients; θ - volume liquid water concentration; H_I - Henry constant; $J_I^{l,g}$ - fluxes of component I in the gas and liquid.

In steady - state conditions and neglecting recombination processes it's possible to solve this system analytically [5] and reaction frequency in liquid can be written as:

$$\omega^l = \cdot\gamma_{\max} \cdot \left(\frac{\gamma}{\gamma_{\max}}\right) \cdot \theta \cdot \varpi \qquad (6)$$

where $\gamma_{\max}$ maximum value of the chain length of the oxidation process at the optimum conditions; γ - average value of the chain length in droplet at definite conditions; and ϖ - efficient frequency:

$$\varpi = \frac{3D_I^g / a^2}{1 + \dfrac{D_I^g}{H_I \cdot D_I^l \cdot (q \cdot cth(q) - 1)}} \qquad (7)$$

and $$q = \sqrt{\frac{\omega_r^l}{\omega_{dl}^l}} = a\sqrt{\frac{\omega_r^l}{D_I^l}}$$

It's clear that efficient frequency (7) is oxidation frequency in droplet for heterogeneous conditions. Indeed, depending on system parameters this frequency is equals to certain frequencies of physical - chemical processes which can determine the rate of oxidation process. For example, in the case when oxidation is limited by reaction in liquid:

$$\tilde{\omega} = H_I \cdot \omega_r^l \qquad (8)$$

On the contrary when diffusion from the gas on the droplet is limiting process (the droplet size is sufficiently large and reaction frequency in liquid is very quick):

$$\tilde{\omega} = \omega_{dl}^g = {}^{3 \cdot D_I^g}\!/_{a^2} \qquad (9)$$

And finally, in intermediate case, when liquid diffusion is limitation process

$$\tilde{\omega} = H_I \cdot \left(\omega_r^l \cdot \omega_{rl}^l\right)^{1/2} = H_I \cdot \left(\omega_r^l \cdot \frac{3D_I^l}{a^2}\right)^{1/2} \qquad (10)$$

These simple analytical formulas (7-10) permit to find the optimum conditions for effective plasma catalysis process in the cloud system. Thus for the case when diffusion in the droplet is limiting process the critical droplet size (the boundary value of size, when the efficient chain oxidation in liquid is possible) does not depend on chemical reaction rate in liquid and is determined as:

$$a < a_{cr} = \sqrt{3D_I^g \cdot \frac{\theta \cdot \tilde{\gamma}}{\omega_r^g}} \qquad (11)$$

If liquid diffusion is limiting process criteria (2,6) can be written in the form:

$$a < a_{cr} = H_I \cdot \tilde{\gamma} \cdot \theta \sqrt{3 \cdot D_I^l \cdot \frac{\omega_r^l}{\left(\omega_r^g\right)^2}} \qquad (12)$$

At last if chemical reaction in liquid is a limiting process the dependence on droplet size is absent , and equation (2) can be rewritten as a condition on the reaction frequency in liquid:

$$\omega_r^l > \left(\omega_r^l\right)_{cr} = \frac{1}{H_I \cdot \gamma \cdot \theta} \cdot \omega_r^g \qquad (13)$$

These formulas (11-13) permit to describe the necessary (for effective catalysis by plasma) parameters range. One can see that at a definite liquid water content, chain length has maximum value if droplets radius and current density are less than the critical value. In this case all active species generated in the gas will initiate the long chain oxidation process in the liquid and effective plasma catalysis can occur. The restriction on the size can be weakened with the increase of the liquid water content (12). Let us mention, that too low current density can be unprofitable for the process because of coagulation effect.

In general the developed approach and formulas obtained can be easily adopted to the other types of kinetic mechanisms and for other cases of heterogeneous system geometry (for example gas - water film casein corona discharge) and can be used for the estimation of the heterogeneous effects and process optimization.

As an example, let us consider SO2 oxidation in heterogeneous air stream by the relativistic electron beam. The ion-molecule mechanism of the SO_2 chain oxidation has been investigated in numerous works [2]. In the result of analysis of these works the liquid-phase SO2 chain oxidation mechanism was proposed for the wide range of the liquid acidity and SO2 concentration. In this case SO2 dissolved in water exists in the form of SO_3^{2-} and oxidation starts from the formation of SO_3^- in the reaction with OH radicals. Let us mention that OH radical and hence positive ions are the only active species generated by plasma which can initiate chain oxidation. In the excess of O_2 ion radical SO_3^- forms SO_5^- ion which can oxidize SO_3^{2-}. The last reaction is relatively slow (~5 10^{-14} cm^3/s) and is a limiting stage of this mechanism. In acid solution dissolved SO_2 exist in the form of HSO_3^- and in spite of the same chain carriers SO2 oxidation proceeds at the significantly low rate (rate coefficient of limiting stage is here about 1.6 10^{-16} cm^3/s) The reactions of chain termination are recombination ones in the case of high concentration of the chain carriers and are reactions with the admixture for the low initiation rate. The simulation of radiation yield of SO2 liquid-phase oxidation have shown that at the low current density range ($J < 10^{-6}$ A/cm^2) in the basic solution (pH>7) chain length can be in the range 10^3 - 10^6 .Simultaneously the strong decrease of the chain length with the increase of the acidity and current density was found (up to 3-10 at the pH<2 and $J>10^{-3}$ A/cm^2). The dependence of the chain length on acidity is related both with the decrease of concentration of dissolved SO2 and, as we mentioned above, with the diminishing of oxidation rate when acidity increase. The dependence on current density is provide by squared character of chain termination (recombination reaction). These results are in good agreement with the experimental data on photochemical SO2 oxidation in the liquid [6] (chain length up to 10^5) and are very promising from the point of effective SO2 oxidation in heterogeneous condition too.

Computer simulations have been done with the help of especially elaborated code "ELENA" [2] to verify the possibility of plasma catalysis of the SO2 oxidation in the water fog. The results of calculation shown that even addition of neutral droplets with a radius of about 1μm can lead to the strong catalytic effect. Energy cost of SO2 oxidation can fall in three hundred times with respect to conventional price in plasma. This effect as it was mentioned above is realized at low current density level. At a higher acidity and bigger droplets (r ~10μm) the catalytic effect becomes not so essential. Nevertheless at relatively high liquid water content ($\theta=10^{-3}$) energy cost according to calculation can decrease in ten times in a good agreement with experimental results [3]. In this work air stream with the water aerosol was irradiated by elecron beam. Oxidation energy cost measurements (SO2 oxidation energy cost was below 1eV per molecular) confirmed chain character of SO2 oxidation in this case.

Based on developed approach and computer simulation a possibilities to realize heterogeneous effects were investigated for other substances like NOx, H2S, CS2, phenol too. It was shown that heterogeneous media can be profitable for the discharges and electron beam treatment of these toxic compounds. The analysis of the experimental work on heterogeneous corona, barrier discharge and electron beam gas cleaning have confirmed these conclusions

References.

1. Penetrante B M 1993 Non-Thermal Plasma Techniques for Pollution Control ed Penetrante B M and Schultheis S E (Berlin: Springer-Verlag) NATO ASI Series vol. G 34 Part A pp 65-89.

2. Potapkin B V, Deminsky M A, Fridman A A and Rusanov V D 1993 Non-Thermal Plasma Techniques for Pollution Control ed. Penetrante B M and Schultheis S E (Berlin: Springer-Verlag) NATO ASI Series vol. G 34 Part A pp 91-106.

3. Yermakov A N, Zhitomirsky B M and Poskrebyshev G A Radiat. Phys. and Chem. 39 pp 455-61.

4. Abolentsev A, Korobtsev S, Medvedev D, Rusanov V and Shiryaevski V 1994 Abstracts 1st Int. Conf. Advanced Oxidation Technologies for Water and Air Remediation (London, Canada) pp 70-1.

5. Deminski M., Potapkin B., Rusanov V. , Fridman 1994 High Energy Chemistry 28, pp 304 -314.

6. Martin L.R. Kinetic Studies of SO2, NO and NO2 oxidation mechanisms: Atmospheric Consideration. Ed. by Calvert G.J., London: Butterwoaths. vol. 3, 1984