

IMPACT OF THE ANTHROPIC ELECTROMAGNETIC FIELDS ON ELECTROCHEMICAL REACTIONS FROM THE BIOSPHERE

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The theoretical and practical aspects concern influence of electromagnetic field on the electrolytic systems in biosphere has been studied. A few theoretical aspects concern A.C. polarization of electrolytic systems are presented.

1. INTRODUCTION

The majority processes from nature (in biosphere) take place in wet environments. These processes, in majority situations, are developing by an electrochemical mechanism (for example, the redox processes from the cytoplasm interface/cellular membrane, metals corrosion in various electrolytic media etc.).

Kinetics and electrochemical processes mechanism are determined by the electric signals superposed on the reaction media, respectively electrode system (metal or membrane)/electrolyte. In this way, we can consider that any electric signal, which is superposed on the natural electrolytic environments from biosphere, can perturb the developing of the natural electrolytic processes and consequently is a pollutant signal [1].

The electromagnetic pollution consequences on the environment are various. Pollutant electromagnetic fields disturb natural processes, both by heat effect generated in various environments, and by its electric and magnetic components. The electric component disturbs the developing of the natural electrochemical reactions, like the transit of Ca^{++} by human cellular membranes, and implicit, the calcium homeostasis (the cause of the high frequency of leukemia at the children systematic exposed to the electromagnetic field [2]), accelerates the corrosion reactions [3], etc. Magnetic component disturbs the biomagnetic systems, like the orientation system of the bees, which was discovered that at signals of 500 V/m become very aggressive and are killing each other [4], and in electromagnetic field of 0.6 ÷ 3.2 GHz, by 0.5 ÷ 1 V/m

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order, get lost and they can not return to the beehouse. The cancer generating effect of mobile phone systems was demonstrated by more research reports [5–7].

The study of signals influence in alternative current (A.C.) superposed on the electrochemical systems represents a complex theoretical problem, with especially practical importance.

The theoretical complexity of the problem results, firstly, diversity of the kinetic ways (partial reactions) for the electrode processes, but also from complexity of the electromagnetic field influence – especially of the electric component – upon the ionic atmosphere [8].

In the actual conditions of technological and industrial development, characterized, firstly, by increasing both of the production, and of the electric energy consumption, and implicit the enhancement of the electromagnetic pollution of natural and industrial environment with signals in A.C., very complex, it imposed the profoundly study of the signals influence in A.C. superposed on the electrochemical processes and reactions which take place in nature (photosynthesis, redox processes from the cytoplasm interface/cellular membrane, metals corrosion etc.) [1].

The acceleration effect of corrosion of the A.C. stray currents in was been demonstrated both theoretically, and experimentally [9, 10].

Assessment of the signals in A.C. on the electrode processes in industrial conditions – electrolysis in sinuous current – can presents an especially interest to performances increasing of some galvanic deposition, the galvanic obtaining of some alloys, reduction of the overvoltages, and implicit, of the voltage drops on electrolyze – so energetically optimization of the industrial electrochemical processes [11].

The purpose of this paper consists both in influence study upon the developing of electrochemical reactions of the disturbing signals in A.C. superposed on the reaction environment, and in study of nature and origin of these disturbing signals.

2. INFLUENCE OF SIGNALS IN A.C. SUPERPOSED ON THE ELECTROCHEMICAL SYSTEMS

2.1. IONIC ATMOSPHERE AND THIS DEFORMATION IN ELECTRIC FIELD

Electrolytes are electroconducting environments of second species and carry on the electric current by the ions with negative charge (anions – migrate to anode) and with positive charge (cations – migrate to cathode) that are forming after dissolution in water of the substances with ionic bonds, of electrolytic dissociation. The solvent (water) having polar molecule (the center of positive charges is not the

same with the center of negative charges), in electrolytic environments, the ions are surrounded by the oriented water molecules-ionic atmosphere (Fig. 1).

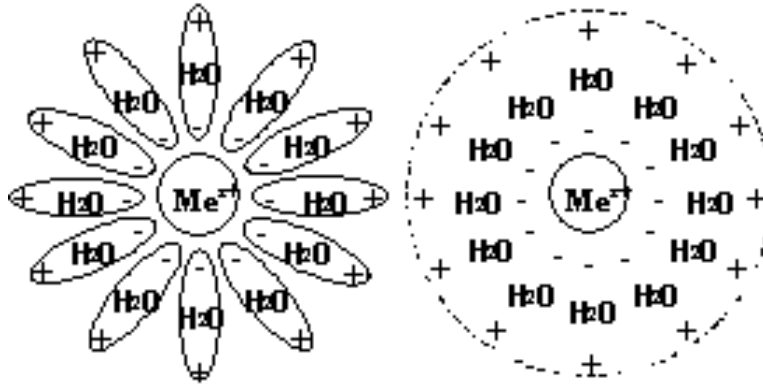


Fig. 1 – Ionic atmosphere of a metallic ion with z^+ valence.

The ionic atmosphere – the sphere of ions hydration – remains unchanged only when the electrolyte is in balance hence upon him not operate external forces, for example, an electric field which induces the ion motion by solvent [8].

In the case of overlapping of a continuous electric field with electrolytic system, the ion moves and, due to the friction force, the sphere of ion hydration cripples, modifying, firstly, the distribution of electric charges, and implicit, localization of the ion in hydration sphere (Fig. 2).

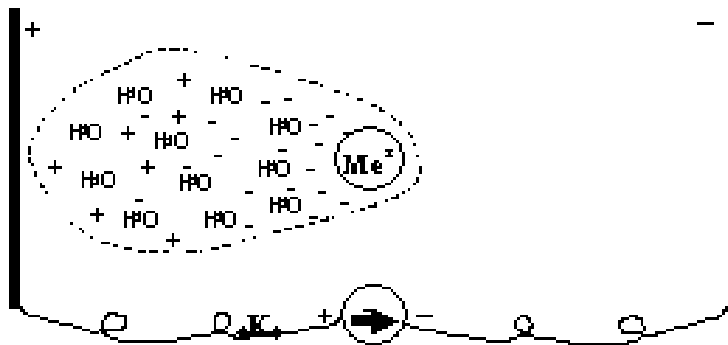


Fig. 2 – Deformation of the ionic atmosphere on action of a continuous electric field (the K switcher is closed).

Obviously, to discontinuance of the electric filed action (opening of K from Fig. 2), the ion inclines to remake its ionic atmosphere, reverting to initial spherical shape (Fig. 1).

In the case of overlapping of an alternative electric field with electrolytic system, deformations of the ionic atmosphere follow the periodicity of the disturbing signal (Fig. 3).

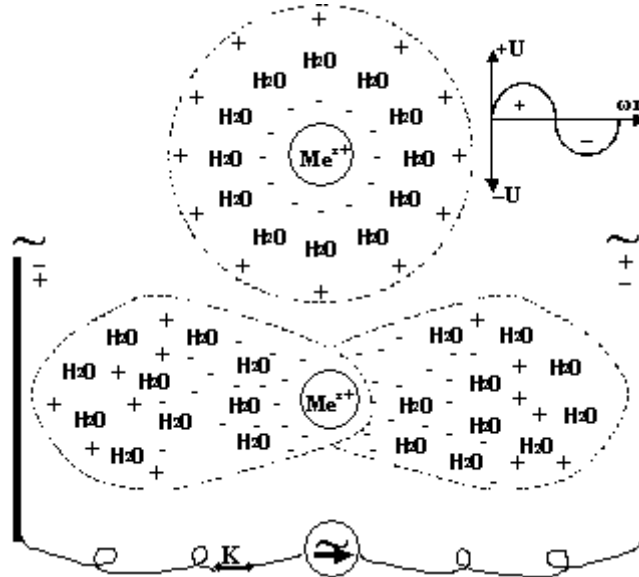


Fig. 3 – Evolution of ionic atmosphere deformations upon the action of an alternative electric field.

Deformation and rehabilitation of ionic atmosphere is developing with different speeds (determined, firstly, by ion nature and size of hydration sphere), hence the rehabilitation is achieved staggered in time, named relaxation time. The relaxation time t of a hydrated ion [8] is inverse proportional with concentration and equivalent conductivity of the electrolyte, respectively with ion valence, namely (1):

$$t = k_r / c \cdot z \cdot A, \quad (1)$$

where: k_r – proportionality constant; c – molar concentration of the ion; z – ion valence; A – equivalent conductivity of the electrolyte.

2.2. POLARIZATION OVERVOLTAGE IN ALTERNATIVE CURRENT. POLARIZATION IMPEDANCE

Electrodes polarization takes place not only to the passing of the continuous current, but also by electrode/electrolyte resistances of an alternative current. In case of a linear sinusoidal alternative current signal, polarization overvoltage η fluctuates in time [12] by relation (2):

$$\eta = Z_p \cdot I_v \cdot \sin(\omega t - \delta), \quad (2)$$

where: Z_p – polarization impedance (Fig. 4), parameter determined by the capacity of the double electric layer and by the series resistances (ohmic polarization) and parallel resistances (Faraday polarization) from equivalent circuit of electrode / electrolyte system; I_v – peak intensity of the overposed current; δ – difference of phase determined by the capacitive component of the electrolytic system.

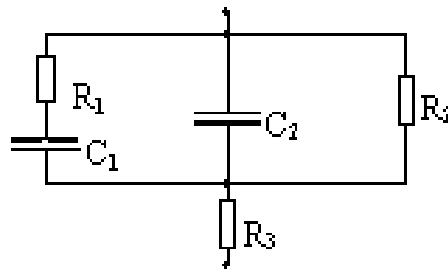


Fig. 4 – Equivalent circuit of the polarization impedance: R_1 and C_1 – capacity and resistance that characterizes a partial stage (for example, ion dehydrating); C_2 – capacity of the double electric layer of the electrode; R_2 – electrolyte resistance; R_3 – resistance of the charge transfer.

In the case of overlapping with the electrolytic system of an electromagnetic field, due– firstly – to the electric component (which is an alternative electric field), this will disturb the ionic atmosphere only if the vibration period (the frequency inverse) is bigger than the relaxation time, the perturbation measure being determined by the superposed signal frequency.

At small vibration periods (high frequencies of the superposed electric signal), deformation of the ionic atmosphere no more occurred, in consequence appears a increasing of the equivalent conductivity (Debye–Falkenhagen effect [8]). In these conditions, it can determine that the minimum limit frequency f at which takes place the disappearing of the ionic atmosphere deformation, is (3):

$$f = l/t = c \cdot z \cdot \Lambda / k_r. \quad (3)$$

In conclusion, it can affirm that:

- deformation of the ionic atmosphere carry on to the decreasing of the equivalent conductivity of the solutions;
- deformation is so much bigger, so the electric signal frequency is lower and relaxation time is bigger;
- at frequencies sufficiently high, when a period duration of electric signal in A.C. is smaller than the relaxation time of the ionic atmosphere or equally, the equivalent conductivity of the electrolyte trends towards a maximum value.

2.3. DIFFUSION OVERVOLTAGE IN PRESENCE OF THE SIGNALS IN A.C. SUPERPOSED ON THE ELECTROLYTIC SYSTEM

Under the influence of the alternative electric field, near to the electrode, the concentration of the ionic species, which maintain the electrode reactions, is changed periodically. Due to the periodic variations of the concentration produced by the variable electric field, the concentration gradient, which it establishes, generally, is much smaller than that due to a polarization in continuous current. In the presence of signals in A.C. superposed on the electrochemical systems, it produces a modification of the ionic species concentration, which assist in electrode process, fact that can modifies the kinetics of the respective electrochemical reactions. In these conditions, it can affirm that, in case of the natural electrochemical processes, the electromagnetic fields superposed on the reaction environment, can disturb the natural developing of these, therefore are pollutant.

For analyses of an A.C. signal influence superposed on the electrolytic system upon the diffusion overvoltage, are proposed two limit cases, respectively:

- *Limit case I – the current in A.C. that passes by system and it consumes integral in the electrode process.* It is the case of the supervoltages lower than $R \cdot T / z \cdot F$, when the current that passes by system produces almost integral the Faraday processes (and, implicit, produces the modification of the concentrations at the electrode surface), all partial processes and charge transfer are rapidly – the only slow stage (determined by the speed) being the diffusion.

In this case, the diffusion flow of the charge carriers to the electrode surface is equally with the current, which passes by system. In the case of a current in A.C. sinusoidal (linear), the current density i_{\sim} will be:

$$i_{\sim} = i_{v_{\sim}} \cdot \sin \omega \cdot t, \quad (4)$$

where $i_{v_{\sim}}$ represents the peak value of the current density.

In conditions of a linear diffusion, we have:

$$i_{v_{\sim}} \cdot \sin \omega \cdot t = z \cdot F \cdot D \left(\frac{\partial c}{\partial x} \right)_{x=0}, \quad (5)$$

where: z – valence; F – Faraday number; D – diffusion coefficient; c – concentration; x – distance.

In these conditions, the concentration gradient near to the electrode becomes:

$$\left(\frac{\partial c}{\partial x} \right)_{x=0} = \frac{i_{v_{\sim}}}{z \cdot F \cdot D} \cdot \sin \omega \cdot t. \quad (6)$$

In the established limit conditions, solving the differential equation afferent to the second law of Fick for a linear diffusion, it computes the evolution of the diffusion overvoltage in time $\eta_{d(t)}$ as being:

$$\eta_{d(t)} = \frac{R \cdot T}{z^2 \cdot F^2 \cdot c_0 \sqrt{D \cdot \omega}} \sin\left(\omega \cdot t - \frac{\pi}{4}\right), \quad (7)$$

where: c_0 – represents the concentration of the ionic species which participates in process at the electrode surface.

From the analyses of the (7) relation, it results that, in the presence of a signal in A.C. superposed, the diffusion overvoltage is determined both of the maximum density value of the alternative current which passes by system, and of this frequency. The diffusion supervoltage is dephased with $-\pi/4$ towards the A.C. superposed – capacitive difference of phase for diffusion – difference of phase, which is due firstly to the modifications (due to the superposed A.C.) in the charges distribution of the species which participate in process and not due to the capacity of the double electric layer.

In these conditions, the peak value of the diffusion overvoltage $\eta_{d\sim}$ corresponding to the peak current $i_{v\sim}$ is:

$$\eta_{d\sim} = i_{v\sim} \cdot \frac{R \cdot T}{z^2 \cdot F^2 \cdot c_0 \sqrt{D \cdot \omega}}. \quad (8)$$

From the analyses of relation (8), it determine that, at a known density of the peak current for superposed A.C., the diffusion overvoltage due to this decreases to increasing of the superposed signal frequency.

By comparison of the overvoltage value produced by the passing by electrochemical system of an alternative current ($\eta_{d\sim}$) with the adequate value of the overvoltage $\eta_{d=}$ produced by the passing of a continuous current of the same density ($i_{v\sim} = i_{=}$), it obtain:

$$\frac{\eta_{d\sim}}{\eta_{d=}} = \frac{i_{dl}}{z \cdot F \cdot c_0 \sqrt{D \cdot \omega}} = \frac{\sqrt{D}}{\delta_c \sqrt{\omega}}, \quad (9)$$

where: i_{dl} – limit current of diffusion; δ_c – limit layer of diffusion.

It determined that the diffusion overvoltage produced of an A.C. is much smaller than that produced by a continuous current of same density, thing that is explained by the fact that, due to the cyclic variations (produced by the A.C. passing) of the ionic species concentration which participates in the electrode process, these diffusion is limited al small distances towards the electrode surface.

● *Limit case II the current in A.C. which passes by system it consumes integral at the charging of double electric layer*, when it considers an electrode perfect polarizable at which the current that passes by system change only the charging of the double electric layer, and not participates in the Faraday processes. In these conditions, the charge transfer is strongly slow down (slow stage,

determined by the speed), and electrode/electrolyte system can be assimilated with an capacitor – C – at whom terminals the passing of an alternative current $i_{\sim cap}$ produces a voltage drop $\Delta\eta_{\sim cap}$ in accordance with relation:

$$\Delta\eta_{\sim cap} = -\frac{i_{\sim cap}}{\omega C} \cdot \cos\omega \cdot t. \quad (10)$$

The limit cases I and II represent extreme cases, which are not found in practice. In the real cases, the current that passes by system produced both Faraday processes (charge transfer between electrode and electrolyte), and modification of the double electric layer charging. In these conditions, the total alternative current – i_t – that passes by system is the sum of the partial currents which produce the charging of the double electric layer – $i_{\sim cap}$ – and – $i_{\sim cc}$ – current which participates in the Faraday process, therefore produces the modification of the ionic species concentration which participates in process, respectively:

$$i_t = i_{\sim cap} + i_{\sim cc}. \quad (11)$$

By comparison of the (8) and (10) equations, it obtains:

$$\frac{i_{\sim cap}}{i_{\sim cc}} = \frac{R \cdot T \cdot C \sqrt{\omega}}{z^2 \cdot F^2 \cdot c_0 \cdot \sqrt{D}}. \quad (12)$$

From (11) and (12) relations, results that in the diluted electrolytes (c_0 has small values), the weigh of the capacitive current is relatively high and increases with the increasing of the alternative current frequency which passes by system, and inverse, at signals in A.C. superposed on the system, the weigh of the Faraday current increases to the increasing of the ionic species concentration which participates in process and to decreasing of the frequency of the applied A.C.

3. CONCLUSIONS

It were analyzed the main aspects regarding the electromagnetic pollution impact of environment on the natural electrochemical reactions. From the made researches resulted that, the electromagnetic fields superposed on the electrochemical environments from biosphere produce modifications both in charge transport phenomena from electrolytes and in the mechanism and/or kinetics of the electrochemical reactions which are developed both in the biological electrochemical systems (like cytoplasm/cellular membrane system), and in natural electrolytes (soil, phreatic waters etc.). In these conditions it determines that the electromagnetic fields rise from various disturbing sources modify the natural

development of the natural electrochemical processes from biosphere – so are pollutant signals.

From theoretical analysis of the signals influence in A.C. superposed on the electrolytic environments resulted that the main effect of the pollutant signals in A.C. consist of modification of kinetics parameters for electrochemical reactions that are developing in these – especially the increasing of the change current. In these conditions, we can affirm that, in case of the natural electrochemical processes, the electromagnetic fields superposed on the reaction media can disturb the natural performing of the reactions, so they are disturbing (pollutants).

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