

Physico-chemical Processes in Electric Discharges in Liquid Media

J.I. Kornev, N.A. Yavorovsky, G.G. Saveliev, A.I. Galanov, S.M. Zaharchenko*,
A.E. Perekos**, N.B. Danilenko, and T.A. Yurmazova

High Voltage Research Institute, Tomsk, Russia

**Electrodynamics Institute of NASU, Kiev, Ukraine*

***G.V. Kurdyumov Institute for Metal Physics of NASU, Kiev, Ukraine*

Abstract – The paper analyses factors determining the pathways and mechanisms of chemical reactions induced by pulsed electrical discharges in a layer of metallic pieces immersed in water or dilute salt solutions. The main factors influencing the process are local heating, components of discharge plasma in water and dispersed metal particles.

The major features of the process are pulsed mode of energy delivery and high excitation level of initially kinetically “frozen” system. Studies of the products and kinetics of their formation has shown that chemical reactions in this system can proceed in several directions, including inverse reactions. Reactions take place not only on the surface of metal particles at the moment of their formation, but also as a result of the discharge action on the previously formed metal particles.

1. Introduction

In the present work, we consider pulsed electrical discharge in liquid media as a complicated phenomenon characterized by a number of factors that induce various physicochemical processes. The major factors are pulsed electric current, high temperature, plasma with high-energy electrons and ions, electromagnetic irradiation and shock waves.

As a result of this complex action several processes may take place, such as electrolysis, thermal and mechanical erosion of electrodes, physical dispersion and mechanical decomposition of the medium, as well as the interaction of the electrodes erosion products with the products of medium decomposition. Physicochemical results of electric discharge treatment depend on chemical and aggregative states of the electrodes and the medium; electrical, energetic, geometrical and temporal characteristics of electrical discharge.

In the work [1], the first variant of multiple spark discharges in solutions has been proposed. A layer of metal (alloy) pieces was immersed in a liquid medium. Voltage was fed to the metal charge layer via massive solid electrodes. At relatively low voltages (usually more than 30 V but more often 250–300 V) multiple sparks and spark chains between metal pieces were formed. Metallic parts were heated and dispersed changing the composition of the solution.

This principle was further explored for the purification of water from impurities and production of

composite materials [2–7]. Parameters of the discharge and dispersity of the discharge products were optimized [2, 8, 9].

In the present work, we discuss the results of our studies and formulate some physicochemical properties of electric discharges at the interphase boundary of the solution and metallic electrodes (pieces). Some of these dependences have more general meaning and can be observed in other types of electrical discharges.

2. Analysis of the influencing factors of the discharge

The authors [10] identify five stages of electric discharge development – initiation; electron avalanche formation and propagation; primary channels (streamers); leader process and arc. Each of these stages consists of a number of elementary processes. Moreover, during the formation and propagation of pulsed discharges in liquids, formation and evolution of gas bubbles is of particular importance. Gases are present in the liquid and the electrode material in dissolved and adsorbed states, or may be formed as a result of electrolysis or radiolysis of water molecules. Further development of electrical discharge occurs via the processes in bubbles. Elementary processes mainly occur in the gas phase and that is why the mechanism of gas discharges can be applied to the processes in solutions.

Using [10], we have made estimations of a number of parameters for a model discharge in 1 cm³ of water. The discharge duration (ϕ), concentration of electrons (N_e), energy of ions (E_i), energy of electrons (E_e), ionization rate (σ), typical radius (r), and typical volume of the process (V) were used as characteristic parameters of these stages. The estimation was used to compare the efficiency of several discharge stages for the propagation of chemical reactions and dispersion of the electrode material.

Electron avalanches are not efficient for chemical reactions and electrodes erosion due to small ionization rate ($< 10^{-6}$) and low concentration of electrons.

Primary channels (streamers) are efficient for the reactions typical for radiation chemistry, since the channels can fill up the whole interelectrode area. The electron energy and density are high (1–10 eV and 10^{13} – 10^{14} cm⁻³, respectively), and the energy of ions is relatively small (0.1–1 eV), $\tau < 10^{-6}$ s.

Leader process has a small characteristic size ($r = 50$ – 150 μm , $V = 10^4$ – 10^8 μm^3) but the electron

density and ionization rate are high. That is why leader process can be efficient for electrical erosion and production of fine powders.

Arc process is efficient for thermal treatment of surfaces. It is not optimal for selective reactions (e.g. radiation chemistry) since it creates nearly equilibrium conditions and high temperature at high surface area and in a large volume. The arc process can be avoided at relatively short pulse durations ($\tau \leq 100 \mu\text{s}$).

Electric discharge at micrometer interelectrode distances more often propagates as one channel changing from an electron avalanche to an arc. But the arc stage is usually avoided by using short voltage pulses. High concentration of energy in one short channel results in the absorption of energy by the electrodes and dispersion of the electrode material. The channel is also a source of thermal irradiation and accelerated electrons and ions. The latter produce strong oxidizers (hydroxyl radicals—OH) and reducers (atomic oxygen—H). The same processes occur under the action of electric discharge on a layer of metallic charge pieces in liquid [1–3]. Experimental setup for this process is shown in Fig. 1. Typical size of charge pieces is 10–20 mm. Energy is delivered to the charge layer through massive outer electrodes. Under the action of voltage pulses chains of electrical discharges between the metal pieces are formed. The use of pulsed voltage helps to avoid heating of the system [6, 7], at $\tau_i < 10 \mu\text{s}$ the discharge develops only to the beginning of the leader stage.

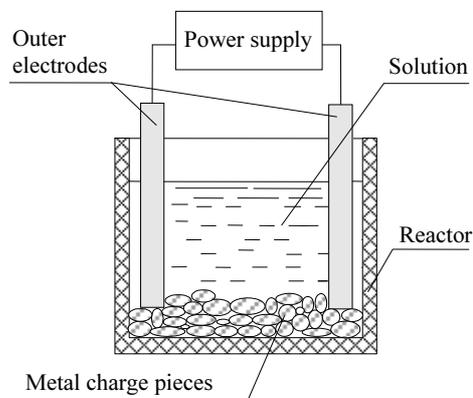


Fig. 1. Electric discharge in a layer of metal pieces (experimental setup)

Further considerations, experimental data and mechanisms are applicable to electrical discharges in a layer of metallic charge under the action of voltage pulses with a duration of 15–20 μs , voltage amplitude of 300–400 V and pulse repetition rates of 300–600 s^{-1} .

The temperature of particles, formed as a result of electrical erosion, is more than 2000 K, the temperatures of cathode and anode spots are 3000 and 4000–5000 K respectively [9]. Particles of the dispersed metal have typical diameters from 5 nm to 10 μm (depending on a type of metal). The rate of cooling for metallic particles is 10^5 – 10^6 deg/s.

That is why it can be expected that the action of spark electric discharges in a layer of metallic pieces can be accompanied by simultaneous heating of the metal and the medium, chemical reactions of the heated metal, irradiation of the medium with accelerated electrons and ions (action of discharge plasma).

3. Dispersion of metal and chemical interaction of the eroded metal with water

The biggest part of studies of metal dispersion and chemical reactions were carried out for aluminum, iron and titanium charge. Studies of accumulation kinetics of the dispersed metal have shown that at constant discharge power, the rate of electrical erosion is also constant or slightly decreasing. The dependence of the amount of eroded metal on time is given by the general equation

$$C = At^n, \quad (1)$$

where $n \leq 1$.

In the case of Al and Ti charge $n = 1$, for Fe charge $n = 0.72$.

Our investigations with the use of transmissive electron microscopy show that electrical erosion products are usually spherical particles with a characteristic size from 20 nm to 1 μm (for Al charge), from 1 nm to 5 μm (for Fe charge) and from 3 to 150 nm (for Ti charge). This is an evidence of particles formation from melt and only minor influence of mechanical fragmentation.

Summarizing, we can conclude that the erosion of electrodes under the action of short ($< 20 \mu\text{s}$) voltage pulses occurs through the dispersion of melted metal.

Studies of phase composition using X-ray phase analysis, electron transmissive spectroscopy and IR-spectroscopy of the dispersed particles, stabilized in water, has revealed the formation of the following phases: for aluminum charge – $\text{Al}(\text{OH})_3$ (bayerite), for iron charge – Fe, FeO, Fe_2O_3 , for titanium charge – Ti_2O_3 and TiO .

The composition of the dispersed phase originates from the chemical interaction of metallic particles during their cooling in the dispersion medium. The content of the metal phase in the discharge products is primarily determined by the nature (activity) of the metal and medium, as well as particle size. It also strongly depends on the temperature of the medium – the yield of dispersed metal grows at lower temperatures which is an evidence of metal oxidation by water at low temperatures, after cooling of the formed particles.

4. Chemical reactions of the dissolved substances

Considering thermodynamics of the electric discharge systems shows that these systems are usually far from equilibrium and reactions in these systems are kinetically inhibited. On the other hand, electric discharge creates highly non-equilibrium conditions that may

cause various chemical reactions, such as chemical decomposition, thermal hydrolysis, reduction of water and dissolved substances with the droplets of heated metal and atomic hydrogen, oxidation of the dissolved substances with water and products of water decomposition. The secondary processes, such as adsorption of the dissolved substances on the products of metal oxidation, chemical reactions between them, co-crystallization of various solid products are also possible.

Studies of chemical reactions during discharge in a layer of metallic pieces were carried out mainly for iron and aluminum charge. These metals feature high chemical activity, low price and relatively small toxicity. That is why the use of iron and aluminum is perspective for water treatment, synthesis of adsorbents, catalysts, and other materials. Various salts were used as dissolved substances to study different types of reactions – redox, ion exchange, hydrolysis, co-crystallization, and adsorption. Removal of these salts is also of practical importance in water purification technologies.

Experimental dependencies of purification degree on the amount of eroded metal are shown in Fig. 2.

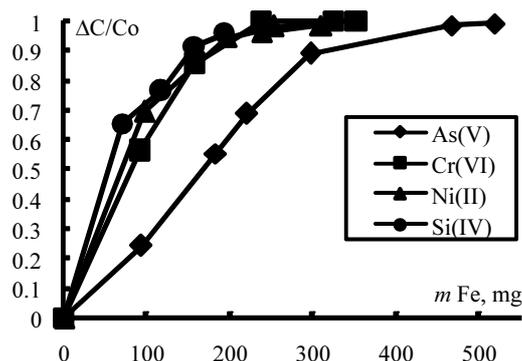


Fig. 2. Dependence of water purification degree on the mass of eroded iron (mg) during action of electrical discharges on As(V), Cr(VI), Ni(II), Si(IV) water solutions

Kinetics studies have shown that kinetics is determined by electrical erosion and reactions of the eroded metal with dissolved substances according to the first order reaction:

$$\lg C_i = -k_i' t^{1+\nu} + \lg C_0. \quad (2)$$

In this case, the diffusion of a dissolved substance to an eroded metal particle does not limit the process. Since the stages of erosion and chemical reaction are consecutive and the rate of electrical erosion is high, the overall rate of the process depends on both rates and it is proportional to the number of the eroded metal. At small concentrations of impurities in the microvolume, occupied by the discharge channel, all impurities react with metal particles, radicals OH, H and water (hydrolysis). Between the sequential discharges, concentration becomes equal in the reactor volume due to solution mixing. And the transforma-

tion is mainly caused by the action of the discharge on previously eroded metal.

To study the reactions of *thermal hydrolysis* we took the solution of sodium silicate. In this case, ions of HSiO_3^- which do not participate in redox reactions were present in the solution. This ions may be removed by hydrolysis, ion-exchange reactions with the eroded metal and adsorption on metal particles. Iron and aluminum were used as charge materials. Studies of solid products with the method of IR spectroscopy identified SiO_2 and silicates of the charge material.

The highest removal efficiency was observed for the combined Al-Fe charge. Efficiency of Si removal was 1.2 mole/kW · hr. The composition of the reaction products shows that the most probable initial stage of the reaction is high-temperature hydrolysis.

Oxidative action of the discharge products was investigated for the systems Fe + MnSO_4 and Fe + NaH_2AsO_3 . Chemical analysis of the solutions and IR-spectroscopy of solid products showed that in the first system MnO_2 , $\text{Mn}(\text{OH})_4$, and MnOOH were formed, in the second system H_2AsO_4^- ions were formed. These findings are the evidence of oxidative action of electrical discharges. Energy efficiency of MnSO_4 removal was 1.2 mole(Mn)/kW · hr.

Reducing action of electrical discharges was demonstrated for iron charge and solutions of potassium chromate and sodium arsenate. Chromium (VI) anions can be removed by direct reduction by metal in the discharge or without it. Hydrolysis and exchange reactions are also possible. Experiments show the decrease of concentration for Cr(VI) ions in the solution and formation of Cr(III) in solid products. Studies using IR-spectroscopy detected Cr_2O_3 , $\text{Cr}(\text{OH})_3$, and structural elements of CrO_4 in the reaction products.

The discharge action in Cr(VI) solutions occurs due to metal dispersion and destruction of passivating films on metal surface. Then metal is oxidized to hydroxides by water, oxygen, and dissolved impurities.

The yield of chromium (VI) removal was about 1.2 mole (atoms of Cr)/kW · hr, making the method perspective for industrial applications.

After the discharge treatment of sodium arsenate, arsenite ions were detected in the solution and solid products of the reaction. This is the evidence of the reduction process. It was also shown that hydro- and dihydroarsenate ions were adsorbed on the surfaces of iron hydroxides at the moment of their formation. Energy efficiency of treatment was 0.43 mole (As)/kW · hr.

It was also shown that during pulsed electrical discharges in sulphate solutions, removal of SO_4^{2-} ions is observed, which is also an evidence of the reduction process.

Summarizing, our studies have shown that the discharge in thermodynamically non-equilibrium systems, like metal + water and metal + salt solution, promotes chemical reactions and brings the system to equilibrium at elevated temperatures. Under these

conditions, we observed thermal hydrolysis of dissolved substances, as well as oxidative or reducing interaction with the products of medium decomposition and dispersed metal. The yields of all the reactions with dissolved substances are nearly equal. This is an evidence of comparable rates even for different reaction pathways.

5. Conclusion

1. It has been shown that the most important factors of electric discharge action in water and water solutions are the products of water decomposition (OH, H), highly dispersed metal particles and local heating of the solution.

2. Kinetics of electrical erosion of metal pieces and chemical reactions has been studied. It was shown that erosion goes with nearly constant rate, chemical reactions proceed not only on the surface of particles at the moment of their formation, but also as a result of discharge action on the dispersed metal particles.

3. It has been shown that under the action of electrical discharges in a layer of metal pieces several reaction types can occur simultaneously – oxidation, reduction, hydrolysis, adsorption, combination. This is connected with the composition of the medium and electrodes, and with the propagation mode of chemical reactions: high excitation and cooling rates. As a re-

sult, the state of the system shifts towards thermodynamical equilibrium at elevated temperatures.

References

- [1] W. Ishibashi, *Patent U.S. 3355279*, 1967.
- [2] A.E. Berkowitz and J.L. Walter, *J. Mater. Res.* **2/2**, 277 (1987).
- [3] A.R. Shidlovkii, A.A. Shcherba, and S.N. Zakharchenko, *Water and water treatment technologies* (Ukr. Woda i wodoochisnii tehnologii) **2**, 26 (2003).
- [4] V.F. Levchenko and A.N. Gupak, *Problems of machine building engineering* (Ukr. Problemi mashinostroeniya) **1/3–4**, 138 (1998).
- [5] V.M. Turin and L.P. Fominskii, *Patent of Russian Federation RU 2049733 C02*, 1995.
- [6] N.B. Danilenko, N.A. Yavorovsky, G.G. Saveliev, T.A. Yurmazova, A.I. Galanov, and P.V. Balukhtin, *Zh. Prikl. Khim.* **78/9**, 1463 (2005).
- [7] N.B. Danilenko, A.I. Galanov, J.I. Kornev et. al., *Nanotekhnika* **4(8)**, 81 (2006).
- [8] R.A. Valiev, F.M. Gaisin, and U.I. Shakirov, *Elektr. Obrab. Mater.* **3**, 32 (1991).
- [9] C. Descoedres, C. Hollenstein, G. Walder, and R. Perez, *J. Phys. D: Appl. Phys.* **38/22**, 4066 (2005).
- [10] V.Ya. Ushakov, V.F. Klimkin, and S.M. Korobeynikov, *Impulse Breakdown of Liquid*, Berlin, Springer-Verlag Berlin Heidelberg, 2007, 398 pp.