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APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

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Composition and Formation Kinetics of Erosion Products of the Metallic Charge in an Electric-Discharge Reactor

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Abstract—The composition and formation kinetics of erosion products of the metallic charge (aluminum, iron) in an electric-discharge reactor operating at an open-circuit voltage of 500–1000 V, peak pulse current of 250 A, and pulse energy of 0.5–1 J were studied. Dispersion products of the charge were subjected to electron-microscopic and X-ray phase analyses. The energy yield of erosion products was determined by chemical analysis to be hundreds of times the calculated yields of electrolysis. The erosion kinetics was studied and the mechanism of erosion was considered.

Electric-discharge methods for purification of wastewater, based on electroerosion of electrodes [1, 2], find use because a wider variety of chemical processes can be provided by substances constituting the electrode. If, however, the discharge occurs in water, the erosion yield of the electrodes is low, and the energy expenditure is high. For example, it was found in [3, 4] that the energy expenditure for erosion of metals in this mode is 2.8×10^6 to 5.6×10^6 kJ mol⁻¹ (~104 kW h kg⁻¹).

In electric-discharge erosion treatment, the energy expenditure is 1.2–12 kW h kg⁻¹ [5–10]. In this case, a reactor with bulky electrodes is used, with metal in the form of grains or shavings more or less insulated from one another by oxide films or having point contacts charged in between. When an electric current is passed through the reactor, a breakdown occurs in the multitude of insulating gaps, with electric explosions at these gaps or at conducting microcontacts.

In the opinion of Fominskii [5] and Zubenko and Yushchishina [6], the electroerosion of metals in water occurred via breakdown of the oxide layer at the electrode surface and the subsequent melting and spraying of the metal. The efficiency of such a process was rather high, 3–4 kW h kg⁻¹. Similar results were obtained in [9, 10]. In [7], a system with an active charge in the form of metal shavings was tested. In this case, the curvature of the contacting surfaces is markedly higher and each current pulse gives rise to multiple discharges at randomly arranged contacts. In

this case, electroerosion occurs via disintegration of contacts by the current, and purification of water is associated not only with discharges in water, but also with chemical reactions involving the charge. Preliminary experiments demonstrated that the energy efficiency of erosion may be in this case as high as 1.2 kW h kg⁻¹ [7]. This indicates that the method in question is promising both for purification of potable water and wastewater and for synthesis of various materials.

This study is concerned with the energetics, chemical mechanism, and formation kinetics of erosion products of the metallic (aluminum, iron) charge of an electric-discharge reactor.

EXPERIMENTAL

The experimental setup comprised a vessel into which 200 g of metal shavings used as a chemically active charge was placed. Electrodes were lowered into the vessel and 950 ml of distilled water was poured in. The electrodes were connected to a two-circuit source of pulsed current with the following parameters: pulse width $\epsilon_p = 10$ μ s; pulse repetition rate 100 Hz; voltage U 500–1000V; and current in the first half-period of the pulse, $I = 250$ –400 A.

The concentration of iron ions was determined colorimetrically [11]: Fe²⁺, with 2,2'-bipyridine; Σ Fe, with sulfosalicylic acid in an alkaline medium; and Fe³⁺, as the difference $c(\text{Fe}^{3+}) = c(\Sigma \text{Fe}) - c(\text{Fe}^{2+})$.

The specific surface area of the forming precipitate was measured by BET from thermal desorption of argon.

Electron-microscopic studies were carried out on a JEM-100 CXII electron microscope, and X-ray phase analysis, on a Shimadzu XRD 6000 diffractometer.

The energy expenditure for water purification was determined by obtaining current and voltage pulse oscillograms with an S8-17 oscilloscope. The pulse energy was calculated by integrating current and voltage oscillograms, to give values E 0.5–1.0 J pulse⁻¹. In addition, we measured the temperature of water in which an iron charge is subjected to the action of an electric discharge: at $E = 0.5$ J pulse⁻¹ its rise was 0.53 deg min⁻¹.

When electric pulses act upon a charge poured-over with water, electric discharges are observed in the form of sparks all over the visible volume. After the iron charge is treated for several tens of seconds, a black suspension becomes noticeable, which partly turns brown in storage. In the case of an aluminum charge, a light gray suspension is formed, which becomes white in storage.

Spectral studies and X-ray phase analysis of products formed in dispersion of the charge demonstrated that the reaction of metal particles with water yields both hydroxides and oxides, which have a developed surface and fibrous structure for aluminum (Fig. 1a), and are of different shapes (plates, needles, and isometric crystals; Fig. 1b) for iron. The diameter of fibers of aluminum erosion products is 5–10 nm, and the diagonal dimensions of iron plates, about 100 nm. These structures have a large specific surface area (105 ± 5 m² g⁻¹ for an iron charge dried at 110°C, and 293 ± 5 m² g⁻¹ for an aluminum charge).

An X-ray phase analysis of products formed in erosion of the electrodes demonstrated that the products obtained mainly contain a crystalline substance with a structure close to that of Fe₃O₄ in the case of an iron charge, and boehmite AlOOH in the case of the aluminum charge.

To study the dynamics of accumulation of erosion products of an iron charge in various forms in water, both the forming suspension as a whole and, separately, the filtrate were analyzed after a certain time of treatment with electric discharges. The data on iron accumulation in various forms in solid erosion products are listed in the table.

The experimental data obtained were processed and dependences were plotted in the log–log coordinates (Figs. 2, 3). The total amount of iron (mg s⁻¹) re-

Data on accumulation of erosion products of the iron charge in various forms (Fe⁰, Fe²⁺, Fe³⁺) in water

| t, s | Fe ⁰ , | Fe ²⁺ , | Fe ³⁺ |
|--------|--------------------|--------------------|------------------|
| | mg l ⁻¹ | | |
| 0 | 0 | 0 | 0 |
| 10 | 47 | 18 | 65 |
| 30 | 109 | 37 | 146 |
| 60 | 252 | 78 | 330 |
| 180 | 441 | 130 | 571 |
| 360 | 699 | 299 | 998 |
| 600 | 1086 | 445 | 1531 |
| 1800 | 1454 | 1221 | 2675 |

moved from the electrodes (charge) is described as a function of the time of action of the discharge by the following empirical relations:

$$\log c_{\text{Fe}} = 0.72 \log t + 1.1331 \text{ or } c_{\text{Fe}} = 13.6t^{0.72}. \quad (I)$$

The relative amount of Fe³⁺ in the suspension is

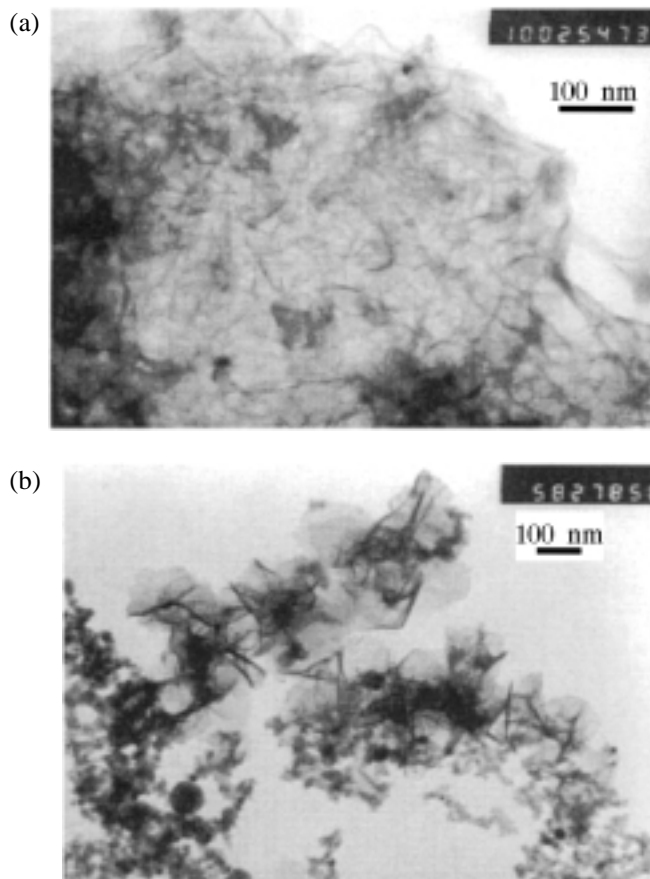


Fig. 1. Typical electron micrographs of solid products formed by electric discharges in water. Charge: (a) aluminum and (b) iron.

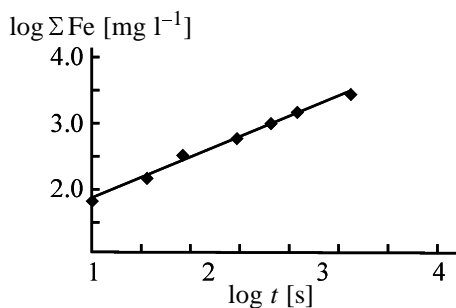


Fig. 2. Concentration ΣFe of iron ions in erosion products (in suspension) vs. the treatment time t .

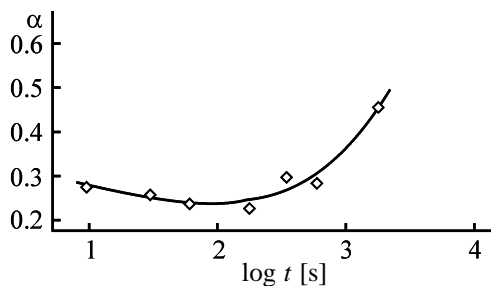


Fig. 3. Fraction of completely oxidized iron, $\alpha_{\text{Fe}^{3+}} = c_{\text{Fe}^{3+}}/c_{\Sigma\text{Fe}}$, vs. the erosion time t .

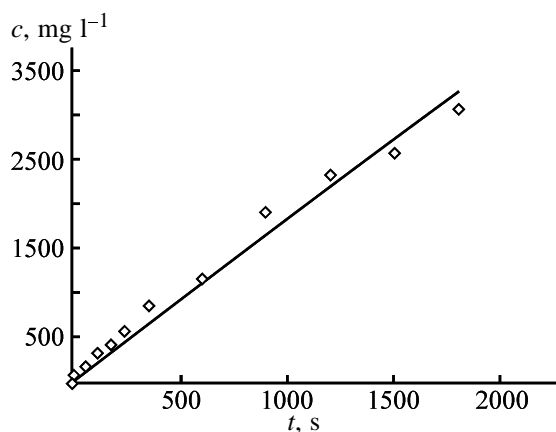


Fig. 4. Concentration c of aluminum ions in erosion products (in suspension) vs. the time t of action of an electric discharge.

shown in Fig. 3, whence follows that it passes through a minimum.

The variation of the concentration of Fe^{3+} and Fe^{2+} ions in the filtrate in electric-discharge treatment of water with an iron charge does not follow any regular pattern, and their concentration is approximately 1000 times less than that in the solid product, 0.187 to 2.347 mg l^{-1} .

The electroerosion kinetics of an aluminum charge was studied (Fig. 4). In contrast to the case of an iron charge, the dependence of the concentrations in the suspension and filtrate on the treatment time is

linearized in the c - t coordinates [Al^{3+} concentration (mg l^{-1}) against the time of an electric-discharge treatment (s)].

The amount of aluminum removed from the electrodes (charge) is described as a function of the time of action of the discharge by the following empirical relation:

$$c_{\text{Al}^{3+}} = 1.82t. \quad (\text{II})$$

The installation used in the study shows a wide scatter of working characteristics, which is due to the structure and composition of the charge and to the dimensions and configuration of the reaction zone. Below, the results obtained in determining the energy expenditure in one of the runs are presented as an example.

In this run, the pulse repetition frequency was 100 Hz; energy released in a pulse, $E = 0.5$ J; mass of water, 950 g; mass of iron charge, 200 g; and mass of iron passing into suspension (in the form of oxide), 0.33 g min^{-1} . Hence, it can be calculated that the energy yield of iron was 7.0 mol (kW h)^{-1} , and the energy expenditure, 2.54 kW h kg^{-1} (0.142 kW h mol^{-1}) dispersed iron.

In this case, the balance of the electric and thermal energy has in this case the following form: with the loss of heat disregarded, a temperature rise by 0.714 deg min^{-1} corresponds to the experimentally determined uptake of electric energy equal to 3 kJ min^{-1} . In addition, chemical reaction may yield 16.5 kJ mol^{-1} in oxidation of iron with water, which may lead to a temperature rise by 0.01 deg min^{-1} , but more probable is oxidation of Fe with dissolved oxygen to give 376 kJ mol^{-1} (0.297 deg min^{-1}). The overall rise in temperature may constitute 1.0 deg min^{-1} . This value exceeds that found in the experiment (0.53 deg min^{-1}), which may be due both to thermal loss and to incomplete oxidation of iron to Fe^{3+} .

The energy expenditure obtained in this study markedly exceeds that reported previously (0.067 kW h mol^{-1} [7]), which is due to different geometric and other parameters of the experimental setup.

The energy expenditure in electroerosion of aluminum under comparable conditions was 0.046 kW h mol^{-1} . If the electroerosion mechanism consists in melting and spraying of the melt, the lower expenditure for heating to the melting point (30 and 9 kJ mol^{-1}) and for detachment of particles from the support (atomization heats 354 and 302 kJ mol^{-1})

may be responsible for the decrease in the energy expenditure.

It is of interest to compare the energy yield of the electroerosion product with the radiation-chemical and electrochemical yields of reactions in solutions and in an electric explosion of a wire [12–14].

For example, the energy yield of a product in non-chain radiation-chemical processes is commonly within 0.01–10 molecules per 100 eV. The above value of the yield for iron, $7.0 \text{ mol (kW h)}^{-1}$, corresponds to 19 molecules per 100 eV, and a value of 40 was obtained in [7].

In the case of a purely electrochemical oxidation of iron, the energy expenditure

$$W = znUF = 3 \times 1 \times 500 \times 97500 = 1.4 \times 10^8 \text{ J mol}^{-1} \text{ or } 714 \text{ kW h kh}^{-1}, \quad (\text{III})$$

where z is the ion charge; n , number of metal equivalents; F , Faraday constant; and U , potential difference.

If 2.54 kW h is expended for oxidation of iron, only 3.6 g of the metal can be oxidized at a voltage of 500 V. As 1 kg is actually oxidized in this case, the amplification factor is more than 275, and even 550 according to [7].

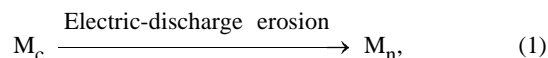
A comparison with the process of metal dispersion by an electric explosion of a wire [12] can be made in the ratio of the supplied energy to the sublimation energy of the corresponding metal. In the given set of experiments, this value was 0.68 to 1.44 for electroerosion of iron, and 0.27 to 0.55 for aluminum. Commonly, metal powders are obtained by electric explosion of a wire at $E/E_c \approx 0.8\text{--}2.5$. If this procedure is carried out in the atmosphere of chemically active gases, the relative energy contribution may be ~ 0.6 and less.

Thus, the efficiency of electroerosion considerably exceeds that of processes in which each atom (molecule) of a reagent is subjected to an external action. This is evidence in favor of a collective or chain mechanism, in which energy is consumed for dispersion of the material via detachment of particles containing a large number of bound atoms, rather than by its evaporation. Alternatively, the process uses the energy of oxidation of the material with water or oxygen. The electroerosion resembles to the greatest extent the electric explosion of a metallic wire in an oxygen atmosphere [13, 14].

In the case when current pulses are passed through

the metallic charge, the pulse energy probably mostly acts upon the metal, with the metal heated and small metal particles detached from the support. A particular detachment mechanism and the size of these particles will depend on the specific energy supplied and the rate of the energy supply. This may be evaporation of the metal, its melting and spraying, or mechanical detachment of nanoparticles. At the electric discharge parameters used in the study, the most probable in the primary process is formation of metal particles via spraying and detachment.

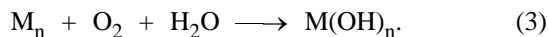
Apparently, the main stages of the process can be represented as the following scheme (M_c , compact metal; M_n , metal nanoparticles):



reduction of water with the metal:



and oxidation of metallic particles with dissolved oxygen:



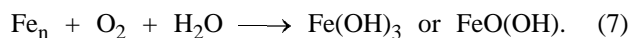
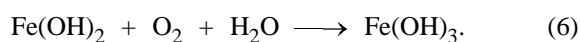
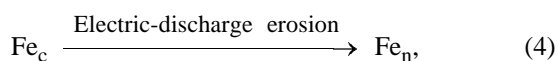
The local temperature may be high because of the energy released by the electric discharge or by the exothermic oxidation [8]. Therefore, the resulting hydroxides may decompose partly (to oxohydroxides) or completely (to oxides). These are Fe(OH)_2 , Fe(OH)_3 , FeO , Fe_2O_3 , Fe_3O_4 , and FeO(OH) in the case of Fe, and Al(OH)_3 , AlOOH , and Al_2O_3 for Al.

It is noteworthy that, in the mechanism described, the electric discharge acts upon the metallic electrode (charge), rather than upon water. In an alternative mechanism, the action of the electric discharge upon water is considered. This mechanism includes reactions in which O and OH radicals and H_2O_2 and O_3 molecules are formed in the electric discharge, with the subsequent oxidation of the compact material with these species. In this case, OH and O radicals presumably do not have enough time to react with M_n before their recombination to give H_2O_2 , O_3 , and O_2 , and, therefore, the most probable pathway in this case is oxidation of the compact material with hydrogen peroxide and ozone, e.g., $\text{Fe}_c + \text{H}_2\text{O}_2 = \text{Fe(OH)}_2$.

The energy yield of reactions (1)–(3) under the action of an electric discharge on the metal should theoretically considerably exceed that for decomposition of water under the action of an electric discharge to give O_3 and H_2O_2 (without formation or involve-

ment of iron particles). This is due to the fact that, in the latter case, electric energy is expended for formation of each molecule of the product, whereas in the case of an electric discharge with electrode erosion, it is consumed for formation of a metal particle containing 107–108 atoms. At a particle size of 30–50 nm, only less than 1% of its bonds with the matrix are to be ruptured; further, nanoparticles react spontaneously to give the final product with energy release. The role of the electric discharge is reduced in this case to activation (depassivation) of the metal both via formation of nanoparticles and because of self-heating, with the amplification factor (per energy expended for detachment of a particle) exceeding 100. This estimate is made without regard for melting of the metal; taking this factor into account will make the amplification factor lower. The value calculated from the experimental data exceeds that expected on the basis of the above considerations by a factor of 2–3. This may be due to activation of the interaction between water and the metal matrix at the place of particle detachment or to a lower energy expenditure for dispersion of the metal by spraying.

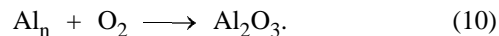
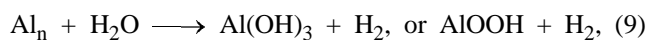
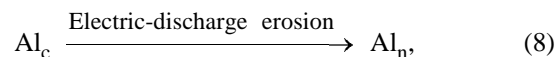
The energy expenditure in electropulse erosion of iron, 0.067–0.142 kW h mol⁻¹ (Fe), is markedly lower than that for electric-discharge synthesis of H₂O₂ molecules and OH radicals in water (0.12 molecule per 100 eV corresponds to 22.34 kW h mol⁻¹ [15]), and, therefore, reactions of the type (1)–(3) are more probable; in the case of an iron charge, these reactions can be specified:



The fraction of completely oxidized iron passes through a minimum (Fig. 3), which may be due to consumption of dissolved oxygen by reactions (6) and (7), with the subsequent increase in this fraction through diffusion of oxygen to incompletely oxidized particles.

In the case of an aluminum charge, the occurring processes are simpler: aluminum particles formed in the electric discharge react with water and oxygen by reactions (2) and (3) to give a hydroxide, which can decompose to an oxhydroxide and oxide.

The main stages of the process for the aluminum charge can be represented as the following scheme:



Complex ions, e.g., [Al(H₂O)₅(OH)]²⁺ and [Al(H₂O)₄(OH)₂]⁺, may be formed in solution.

Three mechanisms are possible for the erosion kinetics. The first consists in that erosion occurs via microscopic explosions of the material of the electrode (charge) at places of contacts, with the nature and number of these contacts remaining unchanged during erosion. This mechanism may become operative for a charge in the form of spheres or particles of other shapes, with surfaces of low curvature. This may be promoted by presence on the metal surface of thin dense films whose breakdown causes erosion, as well as by a low melting point of the metal and its low hardness. This is presumably the case for the aluminum charge, for which the erosion rate is constant (Fig. 4).

The second mechanism, which is characteristic of an iron charge, consists in that erosion occurs at irregularities with a high surface curvature (small radii of curvature). Electric discharge leads to a decrease in the height of projections and in the number of irregularities, and this decrease makes the resistance of breakdown gaps higher and the fraction of energy expended for spraying of the material lower.

The time dependence of the erosion rate can be represented in this case in the general form as

$$dc/dt = kc^{1/n}, \quad (\text{IV})$$

where c is the concentration of the dispersed metal in the suspension, and n is the exponent dependent on the electrode configuration: $n = 3$ if the projections are eroded so that the volume of the metal being dispersed is proportional to the projection heights; $n = 2$ if the erosion products insulate or somehow diminish the active area of the electrodes; and $n = 1$ if the degree of erosion depends on the volume of the material removed in erosion (e.g., in the case of a decrease in the conductivity of the liquid, which is hardly probable).

Integration gives

$$c_{\text{Fe}} = \frac{n+1}{n} kt^{n/(n+1)} = k_n t^n. \quad (\text{V})$$

Comparison of the experimentally obtained time dependences of the erosion yield [Fig. 2, formula (I)] shows that $\nu = 0.72$. This value corresponds to $1/n = 0.38$, which somewhat exceeds the theoretical value $1/n = 0.33$ for the case of erosion of projections.

The third mechanism consists in that, after primary erosion by, e.g., the second mechanism, a spontaneous topochemical reaction is initiated at damaged places. If this reaction is rapidly terminated (by fast formation of a protective film), the overall kinetics may correspond to formula (V). If, however, the specific rate of the reaction remains constant at the place of particle detachment, the kinetic equation becomes more complex:

$$dc/dt = k_1c^{1/n} - k_2c^m, \quad (\text{VI})$$

where n is the configuration index for primary erosion; m , the index of the topochemical reaction, which is dependent on the configuration of the reaction zone; and k_1 and k_2 , effective rate constants of the primary erosion and topochemical reaction, respectively.

Integration of this expression in the general form gives rather complex formulas inconvenient for analysis. However, rather simple expressions are obtained in certain particular cases, e.g., for $n = 3$ and $m = 1$:

$$t = 3(k_1 + k_2c^{4/3})/4k_2. \quad (\text{VII})$$

Such a mechanism is possible, e.g., in the presence of a catalyst.

CONCLUSIONS

(1) The action of pulsed electric discharges on a metallic charge causes its erosion with the subsequent oxidation of the forming micro- and nanoparticles. This gives precipitates with varied morphology: fibrous for Al and mixed (films, needles, nanocrystals) for Fe.

(2) The energy expenditure is $0.142 \text{ kW h mol}^{-1}$ for Fe atoms, which is by a factor of 275 lower than that in electrolytic erosion. For the aluminum charge, the energy expenditure is approximately three times lower, which is due to the lower melting point of aluminum.

(3) A kinetic analysis demonstrated that, in electroerosion of a charge in the form of iron shavings, the erosion is hindered by dispersion of projections (points) and their resulting gradual smoothing. The

electroerosion of aluminum occurs under similar conditions at a constant rate, at least during a time of about 30 min. This is probably due to higher plasticity and lower melting point of aluminum and to specific properties of the surface oxide film.

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