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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Chemical Reactions in Electric Pulse Dispersion of Iron in Aqueous Solutions

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Abstract—IR spectroscopy, X-ray phase, chemical, kinetic, and thermodynamic analyses were used to determine the nature of chemical reactions occurring in electric pulse dispersion of a metal (Fe) in aqueous solutions of inorganic substances ($MnSO_4$, NaH_2AsO_4, H_3AsO_3, $K_2Cr_2O_7$).

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Electric discharges (ED) in solutions find practical application in water treatment to remove impurities and in synthesis of highly dispersed materials. Therefore, problems associated with determining the composition of the products formed, raising the yield, and controlling the process parameters are topical. A rather interesting area in this field is application of pulsed electric discharges (PED) in a layer of metallic grains placed in an aqueous solution [1–6]. The energy introduced acts upon the electrodes, whose part is played by metallic grains, and leads to their erosion and formation of highly dispersed particles. In a system of this kind, not only the output capacity becomes higher, but also the temperature and dispersity of the material are easily controlled. However, the composition of the products formed and chemical mechanisms of these processes remain insufficiently understood.

It has been shown [7] that, at least in the case of ED between electrodes with insulating sheaths (barrier ED) or those spaced far apart, the prevalent effect is the oxidizing action on solutes. This effect is mostly attributed [7, 8] to formation of $OH^{\cdot}$ radicals under the action of the ED plasma. The reducing effect of barrier ED in aqueous solutions is, as a rule, insignificant and is less understood [7, 9]. It may be associated with such primary products of water decomposition as hydrated electrons e_{aq} and H atoms. The oxidation by $OH^{\cdot}$ radicals is also assumed to occur under the action of ED on metallic grains (zero-barrier ED) [10]. For example, it has been shown [5] that the oxidizing action of zero-barrier ED is observed in water treatment to remove As(III), with at least part of arsenic converted to As(V). However, the metal is dispersed in this case and, if it is active, this must lead to a reducing effect of PED on a solution. This has been confirmed experimentally for the example of water treatment to remove the Cr(VI) impurity [4]. However, the role of redox reactions and the extent to which products formed in water decomposition and metal particles are involved in these processes cannot be considered well understood because the composition of the products removed from solution has been insufficiently studied.

This study was aimed to determine the composition of the products and the type of reactions occurring in PED treatment of a layer of iron grains in solutions containing oxidizing ($Cr_2O_7^{2-}$, $H_2AsO_4^-$) and reducing agents (Mn^{2+} and As^{3+}). The kinetics of water treatment to remove impurities with oxidizing and reducing properties were compared.

EXPERIMENTAL

The experimental setup comprised a 1.5-l reactor and a pulsed power source. Iron shavings ($10 \times 5 \times 2$ mm) were placed in an amount of 200 g on the bottom of the reactor fabricated from a dielectric material. A pulsed voltage (pulse amplitude 500 V, repetition frequency 300 s^{-1}, width 15 μs) was applied to two external feeding electrodes submerged into the shavings to a depth of 3 cm. The maximum discharge current was 250 A. The pulse energy was 0.5 J per pulse. St.3 served as the material of iron

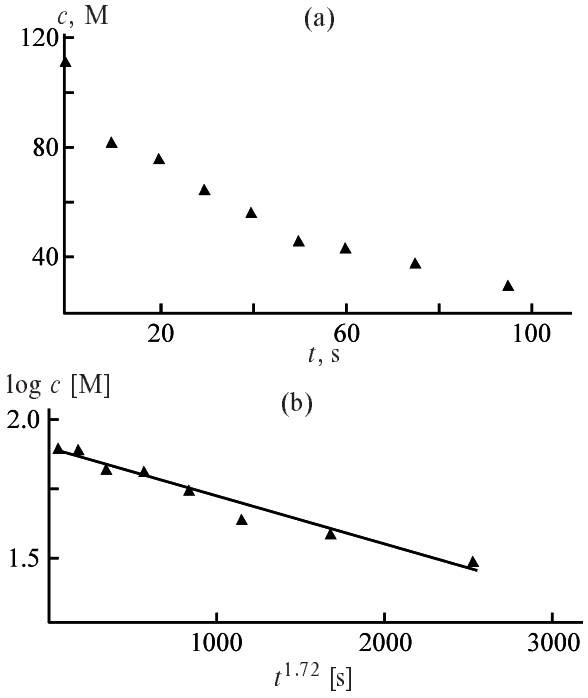

Fig. 1. (a) Concentration c of Mn^{2+} cations vs. the PED treatment time t and (b) $\log c$–$t^{1.72}$ dependence for PED treatment of iron grains in a salt solution containing Mn^{2+} cations. $c_0(Mn^{2+})$ = 110 mg l^{-1}, solution volume 100 ml.

shavings and feeding electrodes. Working solutions containing $H_2AsO_4^-$, Mn^{2+}, and $Cr_2O_7^{2-}$ ions of various concentrations were prepared from distilled water and $MnSO_4 \cdot 5H_2O$, NaH_2AsO_4, and $K_2Cr_2O_7$. Solutions containing As(III) were prepared from GSO (State Reference Sample) 7264–96 standards by dissolving As_2O_3 in HCl at pH 2.

A PED treatment of metallic grains submerged in a working solution leads to formation of a suspension composed of eroded metal particles and a solution. To obtain dry electroerosion powders, the suspension was passed through a "blue ribbon" filter and the resulting solid product was dried at room temperature. The content of Fe^{2+}, Fe^{3+}, As^{5+}, and Mn^{2+} in the filtrate was found by photocolorimetry [11]. The concentration of As^{3+} was determined by voltammetry [12].

The dry electroerosion powders were subjected to an X-ray phase analysis on a DRON-3.0 diffractometer (powder method). The X-ray diffraction patterns were interpreted using the Powder Diffraction File (PDF) compiled by Joint Committee on Powder Diffraction Standards (JCPDS). The dispersity and morphology of the particles were determined by analysis of carbon replicas with extraction on an EM-125 transmission electron microscope. The chemical composition and the structure of the compounds formed in electroerosion of metallic grains in water and aqueous solutions were found by IR spectroscopy on a Nicolet IR Fourier spectrometer in the range 4000–400 cm^{-1} with an attachment for diffuse reflection in KBr (spectral resolution 4 cm^{-1}).

It has been shown previously [6] that the electroerosion of iron grains in water and solutions under the action of PED occurs to give nano- and microparticles by the law

$$[Fe_s] = k_e t^{0.72}, \quad \text{(I)}$$

where $[Fe_s]$ is the concentration of the eroded metal in the suspension (mg l^{-1}); t, time of PED action (s); and k_e, empirical constant dependent on the PED parameters and properties of the electrodes and the medium [mg $(l\,s^{0.72})^{-1}$], with the exponent 0.72 accounting for the variation of the PED conditions in the course of electroerosion.

For dilute [$(0–5) \times 10^{-3}$ M] solutions of $H_2AsO_4^-$ and $Cr_2O_7^{2-}$ anions, the impurity is removed from the solution in accordance with the equation [4, 5]

$$\log c_i = k_i^{1+0.72} + \log c_0, \quad \text{(II)}$$

where c_0 and c_i are the initial and running concentrations of an ion in solution (mg l^{-1}), and k_i' is the effective rate constant including k_e.

Equation (II) was derived by integration of Eq. (III) with account of Eq. (I) under the condition that the concentration of the dispersed metal in the suspension changes only via erosion, i.e., increases.

$$dc_i/dt = k_i [Fe_s] c_i, \quad \text{(III)}$$

Consequently, the reaction of dispersed iron with the impurity is of partial first order with respect to both the reactants. This means that all Fe_s particles are activated and react in the discharge zone. The adequacy of the description was verified by experiments in which the PED was terminated and the initial concentration of the impurity was varied and by calculations in terms of other equations, which demonstrated a considerably poorer agreement with the experiment.

Similar experiments were carried out with a $MnSO_4$ salt solution. Figures 1a and 1b show raw data on removal of Mn^{2+} ions from water and the

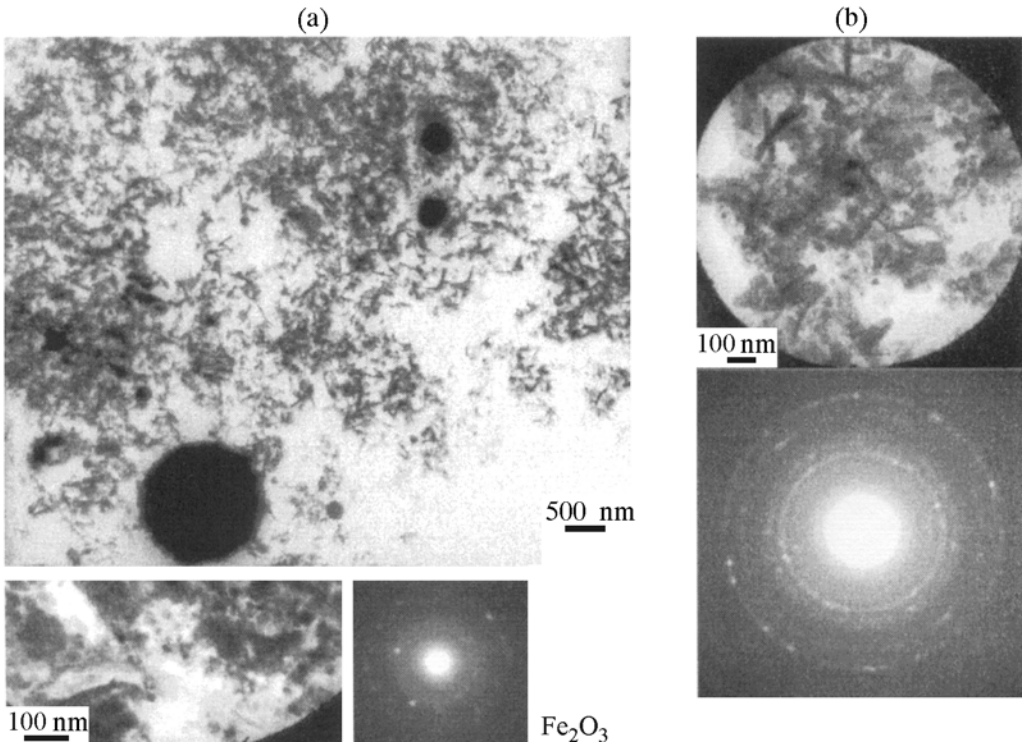

Fig. 2. Electron micrograph of (a) Fe_2O_3 and (b) Fe_3O_4 particles in a sample produced by a PED treatment of iron grains in water. PED treatment time 10 min.

same data plotted in the coordinates of Eq. (II). It can be seen that the experimental data are described by the same relations as those for $H_2AsO_4^-$ and $Cr_2O_7^{2-}$ anions [4, 5], i.e., Mn^{2+} ions are removed in accordance with the same laws, despite the possibly different chemical mechanisms.

In the next stage of the study, we determined by XPA and IR spectroscopy the composition of the products formed under the action of PED on a bed of iron grains in water and salt solutions containing $H_2AsO_4^-$, $Cr_2O_7^{2-}$, and Mn^{2+} ions and examined the occurring reactions with account of the necessary condition $\Delta G_{298} < 0$.

Fe–distilled water. A study of electroerosion powders and the suspension by transmission electron microscopy demonstrated that they contain particles with sizes ranging from several nanometers to several micrometers (largest size 5–10 μm). Two maxima are observed in the particle size distribution: at 1–30 nm and 0.2–10 μm. Particles of regular (spheres) and irregular (faceted particles, plates, rods, fibers) shapes can be found (Figs. 2a, 2b).

It can be seen from the electron micrographs that crystalline particles are observed together with those of amorphous structure, as follows from the appearance of rings constituted by point reflections. A calculation of interplanar spacings and their comparison with reference data demonstrated that, in sample produced by a PED treatment of iron grains, all fine particles (<100 nm) are composed of oxides: Fe_2O_3, Fe_3O_4, FeO. Coarse particles cannot be identified by electron diffraction analysis and are probably composed of Fe, which follows from XPA data and results of a chemical analysis, according to which the suspension produced by PED contains, immediately after the treatment, 85–90% Fe^0. This content decreases in the course of time, to become 20–40% in dry powders, which is due to oxidation of iron by atmospheric oxygen in storage, filtration, and powder drying. XPA data demonstrated that the products formed in electroerosion of iron grains mainly contain α-Fe^0, FeO, and Fe_2O_3 phases (see table). A comparison of the IR spectra obtained in this study (Figs. 3–5) with those reported in the literature [13, 14] demonstrated that the following compounds are formed in PED of a bed of iron grains in distilled water (stretching vibration frequencies are given in parentheses): Fe_2O_3 (560 and 1480 cm^{-1}), $FeFe_2O_4$ (415 cm^{-1}), FeOOH (485 cm^{-1}), and $FeOOH \cdot nH_2O$ (700, 1030, 1650 cm^{-1}). The whole body of data furnished by chemical analysis, XPA,

Diffraction angles and intensities of the main reflections for products formed in electrolysis of iron grains

Reflection no.	Experimental values				JCPDS data		Phase
	2θ, deg	H, rel. units	d, Å	I_{rel}, %	d, Å	I_{rel}, %	
1	35.318	1836	2.951	7	2.950	30	Fe_2O_3 (maghemite-Q)
2	41.766	6083	2.511	24	2.514	100	Fe_2O_3 (maghemite-Q)
3	47.079	625	2.241	2	–	–	–
4	49.274	3628	2.147	14	2.153	100	FeO (wustite)
5	50.884	1981	2.084	8	2.086	15	Fe_2O_3 (maghemite-Q)
6	52.489	25238	2.024	100	2.027	100	α-Fe
7	67.698	1417	1.607	6	1.607	24	Fe_2O_3 (maghemite-C)
8	72.245	1487	1.518	6	1.523	60	FeO (wustite)
9	74.548	2487	1.478	10	1.476	34	Fe_2O_3 (maghemite-C)
10	77.399	3980	1.432	16	1.433	20	α-Fe
11	99.892	6886	1.169	27	1.170	30	α-Fe

and IR spectroscopy shows that the main solid products formed in iron dispersion by PED in distilled water are α-Fe, α-FeO, Fe_2O_3, Fe_3O_4, FeOOH, and $FeOOH \cdot nH_2O$.

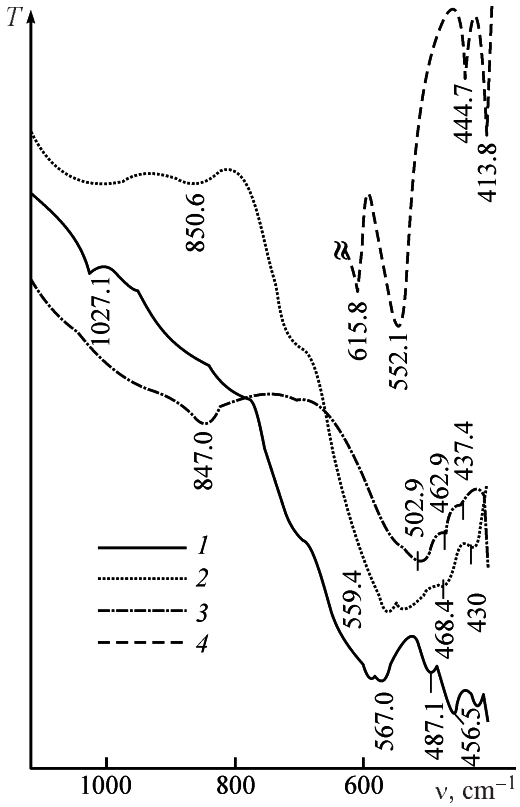

Fig. 3. IR spectra of samples produced by PED in a reactor with iron grains in (*1*) distilled water and (*2*) salt solution containing $Cr_2O_7^{2-}$ ions. (*3, 4*) Spectra of $Cr(OH)_3$ and Cr_2O_3 produced by a chemical method. (*T*) Transmission and (ν) wavenumber; the same for Figs. 4 and 5.

Thus, the results of the study suggest that, in a PED treatment of a bed of Fe grains in water, exclusively its oxidizing action is manifested. The PED energy is mostly expended for heating and dispersion of the metal, rather than for chemical reactions [1, 3, 6, 15]. Further, the dispersed iron is oxidized by water and atmospheric oxygen by the reactions

$$Fe^0 + H_2O = FeO + H_2, \quad (1)$$

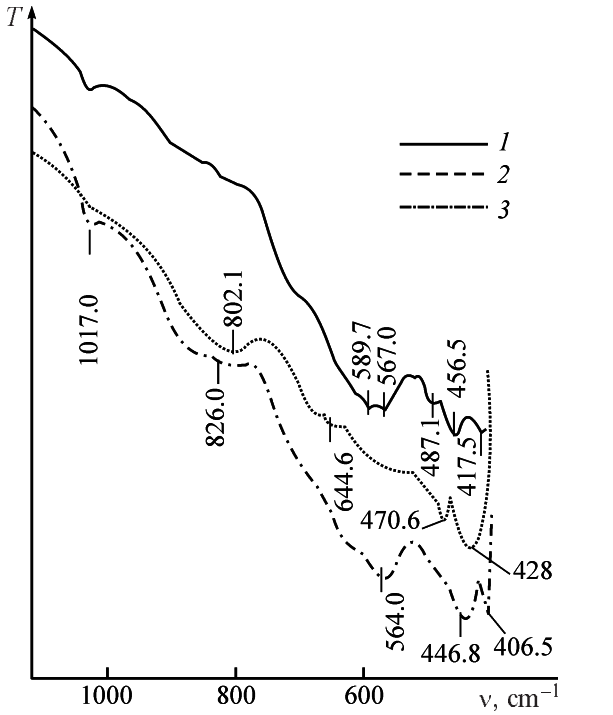

Fig. 4. IR spectra of samples produced by PED in a reactor with iron grains in (*1*) distilled water and (*2*) salt solution containing $H_2AsO_4^-$ ions. (*3*) Spectrum measured after sorption of $H_2AsO_4^-$ ions from solution on the product of electroerosion of Fe grains.

$$4FeO + O_2 + 2H_2O = 4FeOOH, \quad (2)$$

$$FeO + Fe_2O_3 = Fe_3O_4. \quad (3)$$

FeO is probably formed via $Fe(OH)_2$ decomposing because of the high local temperature in the discharge channel [15]. Also possible is oxidation of the metal by products of water decomposition. These are mainly OH radicals [8]:

$$H_2O \xrightarrow{PED} OH^{\cdot} + H^{\cdot}. \quad (4)$$

However, the steep decrease in the yield of the oxidized metal, observed as the solution temperature is lowered [1], indicates that radicals make only a small contribution to formation of the electroerosion products.

Fe–$K_2Cr_2O_7$ solution. The following vibration bands appear in the IR spectrum of a sample obtained by PED in a salt solution containing $Cr_2O_7^{2-}$ ions: band at 559 cm^{-1}, which belongs to Cr_2O_3 (552.1 cm^{-1}); bands at 430 and 850.6 cm^{-1}, which correspond to those associated with $Cr(OH)_3$ (437 and 847.0 cm^{-1}); and also a band at 846 cm^{-1}, which can be attributed to $[CrO_4]^{2-}$. Thus, it can be suggested that, as a result of PED treatment of a salt solution containing $Cr_2O_7^{2-}$ ions, the compounds Cr_2O_3, $Cr(OH)_3$, $Fe[CrO_4]$, and $Fe_2[CrO_4]_3$ are formed. Apparently, heated drops of dispersed iron reduce bichromate ions by the reactions

$$Cr_2O_7^{2-} + 3Fe + 7H_2O = 2Cr(OH)_3 + 3Fe(OH)_2 + 2OH^-, \quad (5)$$

$$Cr_2O_7^{2-} + 2Fe + 7H_2O = 2Cr(OH)_3 + 2Fe(OH)_3 + 2OH^-. \quad (6)$$

Further, Cr(III) hydroxide decomposes to give the oxide. It is also possible that insoluble chromates are formed because "superequilibrium" iron ions and an exchange interaction of $Cr_2O_7^{2-}$ with iron hydroxide occur at high temperatures:

$$2Fe^{2+} + Cr_2O_7^{2-} + H_2O = 2FeCrO_4 + 2H^+, \quad (7)$$

$$2Fe(OH)_2 + Cr_2O_7^{2-} = 2FeCrO_4 + 2OH^- + H_2O. \quad (8)$$

Fe–NaH_2AsO_4 and H_3AsO_3 solutions. The IR spectrum of a sample obtained by PED in a salt solution containing $H_2AsO_4^-$ ions shows bands associated with this ion adsorbed on erosion products (bands at 470.6 and 802 cm^{-1}) and with compounds $FeAsO_4$ or $FeAsO_3$ (band at 644.6 cm^{-1}). According to the data of [16], the presence of bands at 784–805 cm^{-1} clearly points to partial reduction of As(V) to As(III) (Fig. 4). Special-purpose experiments with an $H_3AsO_3^-$ containing solution demonstrated that, under the action of PED, the recovery of As(III) ions is incomplete and As(III) is oxidized to As(V), with the fraction of As(V) in solution constituting 7.5% relative to the initial concentration of As(III). The presence of bands associated with adsorbed anions is in agreement with published data on water treatment to remove arsenic impurities via adsorption on Fe and Al hydroxides [16]. In the case under consideration, inner-sphere complexes XH_2AsO_4 and XH_2AsO_3 (X is the goethite matrix) [16] are formed:

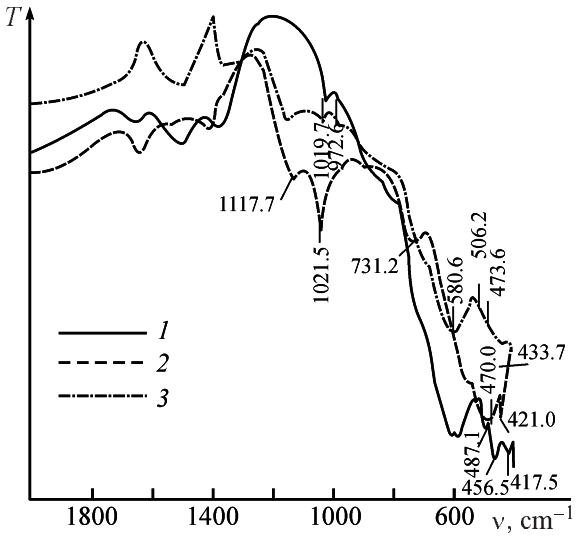

Fig. 5. IR spectra of samples produced by PED in a reactor with iron grains in (*1*) distilled water and (*2*) salt solution containing Mn^{2+} ions. (*3*) Spectrum measured after sorption of Mn^{2+} ions from solution on the product of electroerosion of Fe grains.

$$XOH + H_3AsO_4 \rightleftarrows XH_2AsO_4 + H_2O, \quad (9)$$

$$XOH + H_3AsO_3 \rightleftarrows XH_2AsO_3 + H_2O. \quad (10)$$

The transformation $As^{3+} \rightarrow As^{5+}$ in solution has been confirmed by chemical analysis [5]. This transformation virtually does not occur under the action of dissolved oxygen under ordinary conditions, even though it is thermodynamically possible. This process can occur in particular conditions because of heating or formation of $OH^{\cdot}$ radicals:

$$2H_3AsO_3 + O_2 \xrightarrow{T} 2H^+ + 2H_2AsO_4^-, \quad (11)$$

$$H_3AsO_3 + OH^{\cdot} = H^+ + H_2AsO_4^-. \quad (12)$$

As can be seen from the composition of the products, back transformation $As^{5+} \rightarrow As^{3+}$ is also possible and can occur in accordance with the equations

$$2H_2AsO_4^- + 2Fe = 2FeAsO_3 + 2OH^- + H_2O, \quad (13)$$

$$H_2AsO_4^- + 2H = H_3AsO_3 + OH^-, \quad (14)$$

$$H_2AsO_4^- + 2e_{aq} = H_3AsO_3 + 3OH^-. \quad (15)$$

However, a kinetic analysis demonstrated that both the redox reactions (11), (12) and the adsorption (9), (10) are described under PED conditions by Eq. (II), according to which the rate is proportional to the suspension concentration [Fe_s]. Hence follows that the main channel involves reactions initiated by repeated activation by the discharge of the steadily increasing number of suspension particles, i.e., reactions (11) and (13). Thus, in the case of As compounds, there may occur adsorption on erosion products [reactions (9), (10)], oxidation of As(III) by dissolved oxygen [reaction (11)], and reduction of As(V) by the discharge-dispersed metal [reaction (13)].

Fe–$MnSO_4$ solution. The IR spectrum of a sample obtained by PED in a salt solution containing Mn^{2+} ions shows absorption bands at 972.6, 731.2, 470.0, and 420.1 cm^{-1} (Fig. 5), associated with MnO_2 (characteristic bands at 970, 720, and 420 cm^{-1}) and MnOOH compounds (740, 550, and 485 cm^{-1}). The increase in the intensity of the absorption band at 1021 cm^{-1}, compared with the absorption band in the IR spectrum of a sample obtained by PED in H_2O, shows that the content of hydroxy groups in the sample increases. Thus, the following products are found experimentally: MnO_2, $Mn(OH)_4$, and MnOOH. The reduction of Mn^{2+} by iron is impossible because Mn is a more active metal than Fe. The removal of Mn^{2+} from solution may be due either to its oxidation to insoluble oxides and hydroxides of Mn^{3+} and Mn^{4+} or to precipitation of $Mn(OH)_2$. Also possible is reduction of the sulfate ion to SO_2 or to sulfide ion. Because no sulfides were found in the precipitate, the following reaction is more probable:

$$SO_4^{2-} + 2H_2O + Fe = SO_2 + Fe(OH)_2 + 2OH^-. \quad (16)$$

At the same time, oxidation of Mn^{2+} by the sulfate ion is thermodynamically impossible.

Because the removal of this ion from water is described by Eq. (II), it cannot be governed by the oxidation with the $OH^{\cdot}$ radical, which is a primary product of ED in water. The proportionality of the reaction rate to the concentration of dispersed iron may be associated with precipitation of $Mn(OH)_2$ by the hydroxide after reaction (16) and with the hydrolysis of Mn^{2+}, initiated by heated particles of the suspension and followed by oxidation of the hydroxide being formed:

$$Mn^{2+} + 2H_2O \xrightarrow{T} Mn(OH)_2 + 2H^+, \quad (17)$$

$$Mn(OH)_2 + 1/2O_2 + H_2O \xrightarrow{T} Mn(OH)_4. \quad (18)$$

Thus, the analysis of the reactions occurring under the action of PED on a bed of Fe grains in solution demonstrated that, in solutions of typical oxidizing agents (SO_4^{2-}, $Cr_2O_7^{2-}$, $H_2AsO_4^-$), these oxidants are reduced, whereas in solutions that contain reducing agents (H_3AsO_3, Mn^{2+}), these latter are oxidized. Also, to explain the results obtained, it is necessary to assume that there occur hydrolysis reactions and secondary reactions involving primary highly dispersed solid products. Such a multichannel behavior is accounted for both by the composition of the reagents and by the occurrence of the reactions under conditions of rapid temperature rises and falls.

CONCLUSIONS

(1) The products formed in chemical reactions that occur under the action of a pulsed electric discharge on a bed of iron grains in solutions of inorganic substances ($MnSO_4$, NaH_2AsO_4, H_3AsO_3, $K_2Cr_2O_7$) were identified. The composition of the products indicates that the reactions proceed in several thermodynamically possible, including opposite (oxidation and reduction), directions.

(2) The rate of recovery of a dissolved substance from water under the action of pulsed electric discharge is proportional both to the concentration of the substance and to that of dispersed iron, which points to a secondary activation of particles in subsequent discharges.

(3) The products of water decomposition in a discharge ($H^{\cdot}$ and $OH^{\cdot}$) do not contribute noticeably to the reactions with dissolved substances.

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