



16th International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov, CCE 2015

Pulsed Electric Discharge in Active Metallic Grains for Water Purification Processes

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Abstract

Chemical reactions in electric metal pulse dispersion in the aqueous solutions of inorganic substance (HSiO_3^- , Ni^{2+} , H_2AsO_4^- , Mn^{2+} , $\text{Cr}_2\text{O}_7^{2-}$) were determined through IR spectroscopy, X-ray phase, chemical, kinetic, and thermodynamic analyses. Under such conditions, both reduction and oxidation reactions occur, as well as, locally initiated by heating, hydrolysis and exchange reactions without changing the oxidation rate of the dissolved substance itself. Reduction and oxidation of dissolved substances is determined by the generation and activation of high dispersed Fe in an electric discharge. Physical and chemical processes which take place under the action of pulse electric discharges upon the layer of metallic grains in salt solution, containing HSiO_3^- , Ni^{2+} , H_2AsO_4^- , Mn^{2+} , $\text{Cr}_2\text{O}_7^{2-}$ ions were determined on the basis of product composition, obtained experimentally and the thermodynamic data. It was shown, that PED discharge in heterogeneous mediums can be used for waste and natural water purification.

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Peer-review under responsibility of Tomsk Polytechnic University

Keywords: pulse electric discharge, electroerosion, electric metal pulse dispersion, chemical reactions, water purification.

1. Introduction

Electric discharges in solutions find practical application in water treatment to remove impurities and in synthesis of highly dispersed materials¹⁻⁴. 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 aqueous solution⁵⁻¹⁰. The

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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 mechanism of these processes remain insufficiently understood.

The scientific interest in this field is due to the particular conditions of occurrence of chemical reactions in a PED, their kinetics and mechanism. It is apparent, in particular, that different kinds of impurities are involved in different types of reactions: redox, acid-base, ion-exchange, chemisorption, coprecipitation, etc. On the other hand, the type and behavior of reactions can depend on the type of PED and the chemical nature of electrode.

The aims of the study are: (i) the study of the chemical mechanism and erosion kinetics of the iron charge of an electric-discharge reactor under the PED action; (ii) the study of chemical reactions in the case of PED treatment of metallic charges in dissolved solutions of salt, containing H_2AsO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, HSiO_3^- , Ni^{2+} , Mn^{2+} ions and determination the physic-chemical regularities of occurring processes.

2. Experimental

The experimental setup^{8,9,10} comprised a 1.5 l reactor and pulsed power source. Iron grains ($10 \times 5 \times 2$ 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 grains 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 grains and feeding electrodes.

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. Sparks may occur at several gaps simultaneously for a single voltage pulse. 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.

For model solutions to be prepared, salts $\text{Na}_2\text{SiO}_3 \times 9\text{H}_2\text{O}$, $\text{NiSO}_4 \times 7\text{H}_2\text{O}$, $\text{MnSO}_4 \times 5\text{H}_2\text{O}$, NaH_2AsO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ were used. These salts were selected because they contain H_2AsO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, HSiO_3^- , Ni^{2+} , Mn^{2+} ions and can demonstrate the possibility of reactions of different types: redox reactions, ion-exchange reaction, hydrolysis, cocrystallization, adsorption. Metal nanoparticles formed as a result of electroerosion react with water or salt solution with the reaction product formation, which were investigated with the use of chemical and physic-chemical methods.

The dry electroerosion powders were subjected to an X-ray phase analysis on a Shimadzu XRD-6000 diffractometer (powder method). 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 5700 IR Fourier spectrometer in the range $4000 - 400 \text{ cm}^{-1}$ with an attachment for diffuse reflection in KBr (spectral resolution 4 cm^{-1})^{11,12}.

3. Results and discussion

An X-ray phase analysis of products formed in erosion of the iron grains in water (Fig. 1) demonstrated that the products obtained mainly contain $\alpha - \text{Fe}$, FeO , Fe_2O_3 phases.

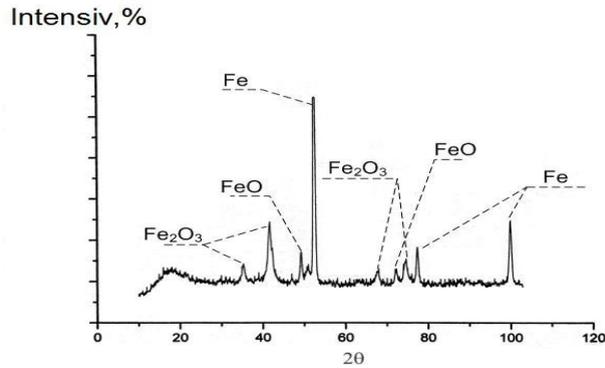


Fig. 1. X-ray pattern of products formed in erosion of the iron grains.

Transmission electron microscopy (Fig. 2) of products formed in erosion of the iron grains demonstrated that the reaction product have a regular (spheric) and irregular (plates, needles, and isometric crystals) shape. Particle size is from several nanometers to several microns. The maximum size is 5-10 μm .

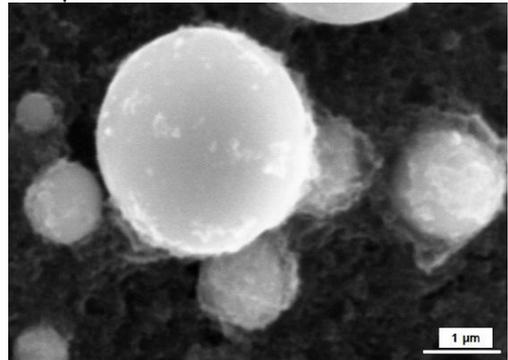
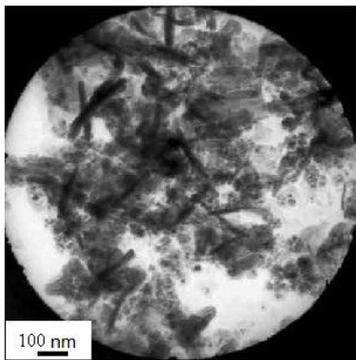


Fig. 2. Transmission electron microscopy of products formed in erosion of the iron grains in water.

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 shown on Fig. 3.

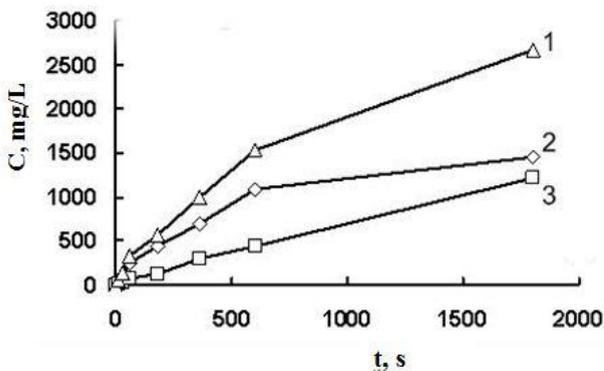


Fig. 3. Data on accumulation of erosion products of the iron grains in various forms (1) – ΣFe , (2) – Fe^{2+} и Fe^0 , (3) – Fe^{3+} in water

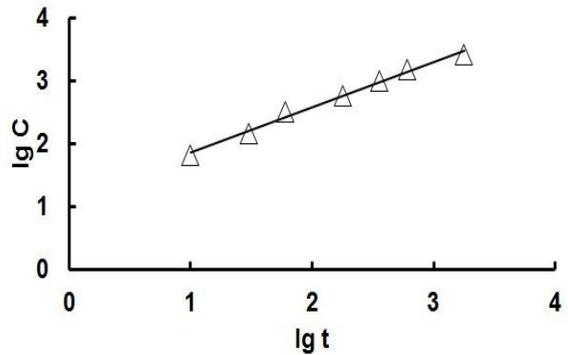


Fig. 4. Concentration ΣFe of iron ions in erosion products (in suspension) versus the treatment time t.

The experimental data obtained were processed and dependences were plotted in the log-log coordinates (Fig. 4). The total amount of iron (mg/l) removed from the electrodes (charge) is described as a function of the time of action of the discharge by the following empirical relations:

$$\lg C_{Fe} = 0.72 \lg t + 1.1331 \tag{1}$$

$$\text{or } C_{Fe} = 13.6 \cdot t^{0.72} \tag{2}$$

Thus, the kinetic equation describing the spark-erosion process of iron grains in water can be represented as a general formula:

$$[M_n] = k_e \cdot t^\nu, \text{ where } \nu \leq 1 \tag{3}$$

The index ν was determined experimentally and is likely to be connected with the change of contact geometry in a layer of iron grains and electrophysical characteristics of medium.

The value k_e – is an empirical constant which depends on intensity and other characteristics of discharge, properties of electrodes and medium $\text{mg}/(\text{l}\cdot\text{s}^\nu)$.

To receive the kinetic equation, describing the process of H_2AsO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, HSiO_3^- anions and Ni^{2+} , Mn^{2+} cations removal from salt solution under the action of PED in a reactor with iron grains, kinetic dependences which are given in Fig. 5 (a, b) were received.

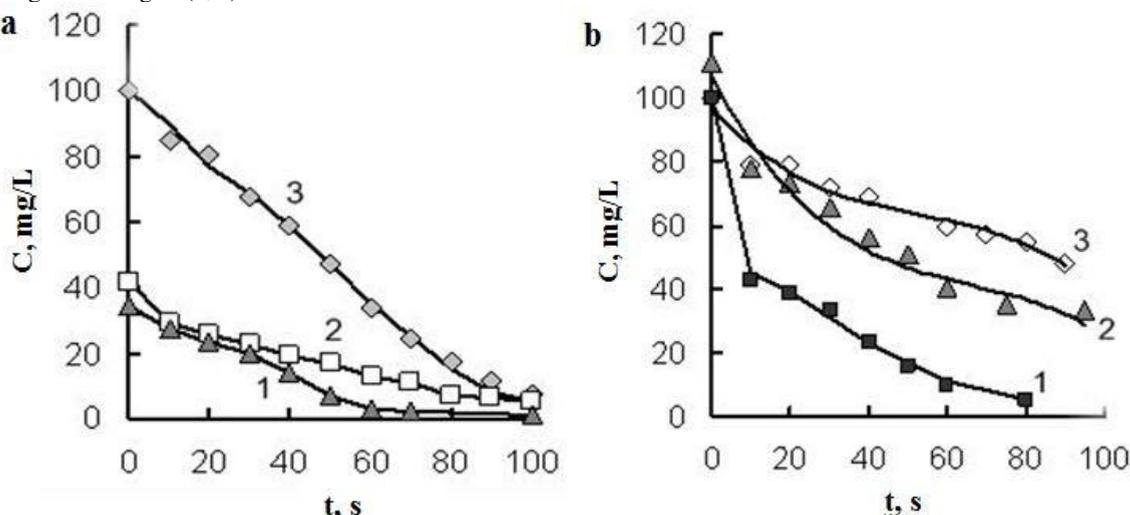


Fig. 5. (a) Concentration of anions (1) – H_2AsO_4^- , (2) – $\text{Cr}_2\text{O}_7^{2-}$, (3) – HSiO_3^- versus the processing time. The volume of solution 600 ml, (b) concentration of cations, (1) – Ni^{2+} (2) – Mn^{2+} , (the volume of solution 100 ml.); (3) – Ni^{2+} (the volume of solution 600 ml.) versus the processing time.

Fig.5 (a, b) shows the removal of H_2AsO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, HSiO_3^- , Ni^{2+} , Mn^{2+} ions from of solutions to occur with a gradually decreased rate. Qualitatively the reaction of salt cations or salt anions with dispersed iron can be shown as a scheme:



where Fe – is iron grains; Fe_n – is dispersed iron particles; B – is removed ion or molecule, P – is reaction product of dispersed iron with ion or molecule. The equation of reaction rate of ion or molecule with dispersed iron:

$$\frac{dC_i}{dt} = k_i \cdot [Fe_n] \cdot C_i \quad (6)$$

where k_i – is constant, including characteristics of electric discharge and constants of chemical reaction rate, C_i – is ion concentration in a solution, mg/l.

If order of the reaction (5) according to salt concentration is actually equal to one, and Fe_n constantly adds into solution according to the equation $[Fe_n] = k_{Fe} t^{0.72}$ (2), then on substituting of a equation (2) into the equation (6) and integrating we receive the equation, which describes the reaction process of salt cation or salt anion with dispersed iron.

$$\lg C_i = -k_i' \cdot t^{0.72} + \lg C_0 \quad (7)$$

where k_i' – is effective constant, including characteristics of PED, reactor geometry as well as constants of chemical reaction rate.

To examine the compliance of kinetic dependences given above with the semi-empirical equation obtained, dependences were plotted in $(\lg C; t^{1.72})$ coordinates (Fig. 6).

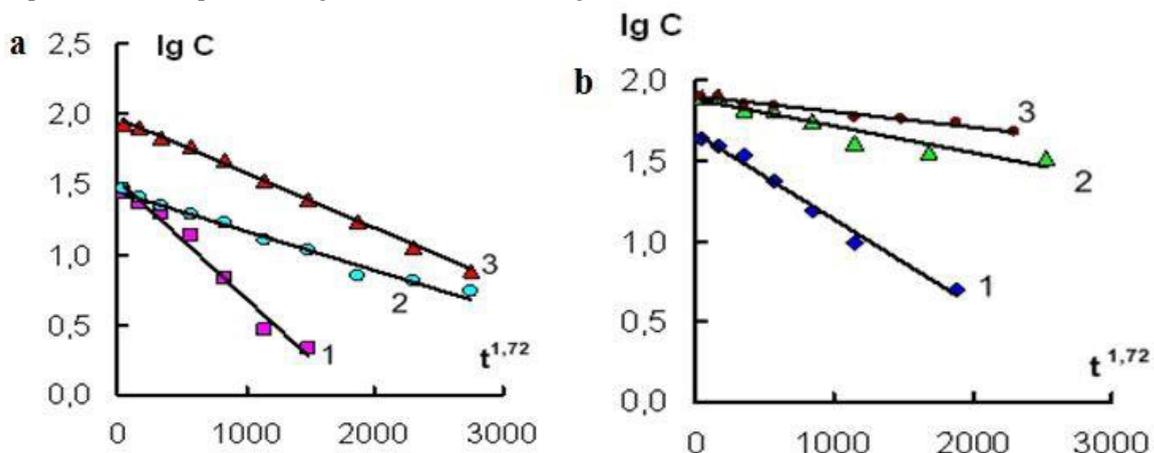


Fig. 6. (a) Dependence $\lg C - t^{1.72}$ under the PED treatment of iron grains poured - over with salt solution, containing anions (1) – $H_2AsO_4^-$, (2) – $Cr_2O_7^{2-}$, (3) – $HSiO_3^-$ ions. The volume of solution 600 ml; (b) Dependence $\lg C - t^{1.72}$ under the PED treatment of iron grains poured-over with salt solution, containing cations (1) – Ni^{2+} (2) – Mn^{2+} , (the volume of solution 100 ml.); (3) – Ni^{2+} (the volume of solution 600 ml.)

Fig.6 (a,b) shows, that experimental dependences show correlation with the equation obtained (7). It is necessary to mention, that the kinetic equation describing the removal of ions $H_2AsO_4^-$, $Cr_2O_7^{2-}$, $HSiO_3^-$, Ni^{2+} , Mn^{2+} from solutions proved to be equal both for cations and anions. The calculated values of coefficient of determination for all kinetic curves $R^2 \geq 0.98$.

Table 1. Effective constant for cations and anions

ion	$H_2AsO_4^-$	$HSiO_3^-$	$Cr_2O_7^{2-}$	Ni^{2+}	Mn^{2+}
k_i'	$8 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$9 \cdot 10^{-5}$	$3 \cdot 10^{-5}$

To determine the composition and structure of spark-erosion products in salt solutions, method of IR spectrometry was used. Interpretation of spectra showed composition of product formed in erosion of the iron grains in salt solution, containing:

1. anions $\mathbf{H_2AsO_4^-}$: $\text{FeO-H}_2\text{AsO}_4$, $\text{FeO-H}_2\text{AsO}_3$, FeAsO_4
2. anions $\mathbf{Cr_2O_7^{2-}}$: Cr_2O_3 , Cr(OH)_3 , FeCrO_4 .
3. anions $\mathbf{HSiO_3^-}$: FeSiO_3 , $\text{Fe}_2(\text{SiO}_3)_3$, SiO_2 , $\text{mSiO}_2 \cdot n\text{H}_2\text{O}$
4. cations $\mathbf{Ni^{2+}}$: Ni(OH)_2 , NiFe_2O_4 .
5. cations $\mathbf{Mn^{2+}}$: MnO_2 , Mn(OH)_4 , MnOOH .

Physical and chemical processes which take place under the action of pulse electric discharges upon the layer of metallic grains in salt solution, containing H_2AsO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, HSiO_3^- , Ni^{2+} , Mn^{2+} ions were determined on the basis of product composition, obtained experimentally and the thermodynamic data.

Physical processes are:

1. The process of metal dispersion under the action of PED, which can be represented as a following scheme (M_c – compact metal, M_n nanoparticles of metal):

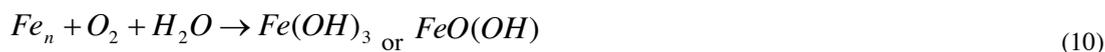


2. The formation of aquated ions, ions and active radicals, UV radiation formation.

Chemical processes taking place in the given conditions are divided into primary and secondary processes.

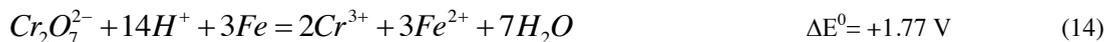
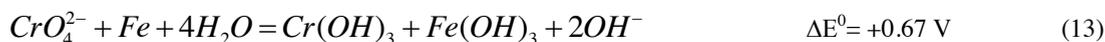
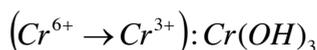
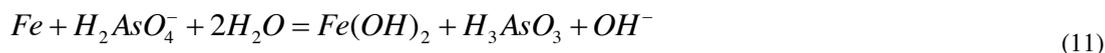
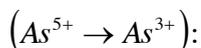
Primary chemical processes.

Water and oxygen oxidation of dispersed iron with Fe(OH)_2 , Fe(OH)_3 , FeO , Fe_2O_3 , Fe_3O_4 , FeOOH formation according to reactions:



As a result of high temperature in a discharge channel, hydroxides formed are partially decomposed to oxides and oxohydroxides, which can be confirmed by transmission electron microscopy, IR, X-ray phase analysis data.

Dispersed iron reduction of ions



High- temperature hydrolysis of ions with formation of oxides and hydroxides.

Processes under PED are supposed to take place due to discharge products of dispersed metal (Fe), OH^\cdot , O^\cdot and as a rule other processes are not taken into consideration, but it is shown that in case of silicon ions high-temperature hydrolysis is the primary chemical process, because direct oxidation-reduction reaction in the case of silicon ions doesn't take place. As in discharge zone there are high temperatures, the hydrolysis can go up to the end according to a second stage.



As a result of this reaction polysilicon acid is formed, which at high temperature is changed into silica gel SiO_2 according to reaction:



As a result of high local temperature in the discharge zone, reaction can take place:



High-temperature hydrolysis can take place in the case of ions Mn^{2+} and Ni^{2+}



Water decomposition under the action of the pulse electric discharge with $OH\cdot$, $O\cdot$ formation.



Secondary chemical processes.

hydroxide oxidation by dissolved oxygen ($Fe(OH)_2 \rightarrow Fe(OH)_3$; $Mn(OH)_2 \rightarrow Mn(OH)_4$)

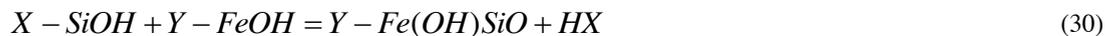


Hydroxide reactions



Ion adsorption ($H_2AsO_4^-$, $HSiO_3^-$) on the surface of dispersed iron oxidation product with $FeO - H_2AsO_4$, $FeO - H_2AsO_3$, ($\cdot SiOFeOH$) formation.





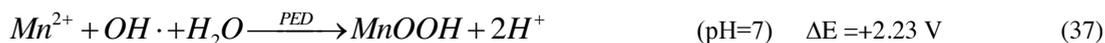
“Superequilibrium” ion formation



Superequilibrium metal ion deposition



Salt oxidation by water decomposition products ($OH\cdot$, $O\cdot$)



However the yield of these products is 0.1 molecule per 100 eV (energy expenditure is 10^8 J/mol)^{3,13}, then experimentally observable yield of oxidation product - about 1 molecule per 100 eV can be due to Mn(OH)₂ oxidation by dissolved oxygen.

Thus, summary scheme of physico-chemical processes was established:

1. Electrical breakdown of intergrain gap, as a result dispersion of metal occurs. At the same time plasma components ($O\cdot$, $OH\cdot$) in a small concentration are formed as it was established.

2. Heated metal particles $T_{\text{initial}} \sim 2000 \text{ K}$ react with water and dissolved oxygen with the formation of higher and lower hydroxides¹³. At the same time, interaction processes of metal particles with admixture take place according to reactions, which depend on nature of admixture and metal (admixture reduction or hydrolysis due to heating, as well as due to the heat of chemical reaction of dispersed metal particle reaction with water).

3. Secondary chemical processes: admixture adsorption on metal hydroxides, hydroxide reaction, hydroxide oxidation, “superequilibrium” ion formation, insoluble salt deposition, salt oxidation.

4. Conclusion

1. On the basis of experiment chemical composition, morphology and size distribution of iron erosion products were determined.

2. Kinetics of physico-chemical processes taking place in water solutions by PED was studied. Empirical equations, describing this process were obtained.

3. The possibility of occurring of different types of reactions by PED action in a layer of iron grains upon water solutions of salts was experimentally determined and theoretically proved.

4. Physical and chemical processes which take place under the action of pulse electric discharges upon the layer of metallic grains in salt solution, containing HSiO_3^- , Ni^{2+} , H_2AsO_4^- , Mn^{2+} , $\text{Cr}_2\text{O}_7^{2-}$ ions were determined on the basis of product composition, obtained experimentally and the thermodynamic data.

5. It was shown, that PED discharge in heterogeneous mediums (e.g. between metal grains in water and water solution) can be used for production of metal nanoparticles and their compounds and for waste and natural water purification, because a wider variety of chemical processes can be provided by substances constituting the electrode.

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