

=====

APPLIED ELECTROCHEMISTRY  
AND CORROSION PROTECTION OF METALS

=====

## Chemical Reactions in Treatment with Pulsed Electric Discharges of an Active Metallic Charge in a Solution of a Chromium(VI) Salt

N. B. Danilenko, G. G. Savel'ev, N. A. Yavorovskii, and T. A. Yurmazova

*Research Institute of High Voltages, Tomsk, Russia  
Tomsk Polytechnic University, Tomsk, Russia*

Received May 4, 2006

**Abstract**—Effect of pulsed electric discharges on aqueous solutions of chromium(VI) in a reactor with an aluminum or iron charge was studied. A mechanism of the occurring processes was suggested. Changes in the pH values of the aqueous solutions of chromium(VI) and the composition and yield of the products formed were determined. The possibility of water treatment to remove chromium by this method was demonstrated.

**DOI:** 10.1134/S1070427207010181

Recently, publications have appeared devoted to the electric-discharge method for water treatment in reactors with a metallic charge in the form of grains or shavings [1–10]. The experimental conditions used in these studies differed in the reactor design, in the position, shape, and composition of electrodes, and in the composition and concentration of solutions. All these factors affect the composition of dispersion products and efficiency of impurity removal, and, therefore, no adequate model of the occurring processes has been developed. The scientific interest in this issue is due to the particular conditions of occurrence of chemical reactions in a pulsed electric discharge (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. At the same time, the type and parameters of discharges predetermine both the reaction conditions and the kind of reactants. For example, the electrode material can be involved in the reaction in the case of a zero-barrier discharge, and the fraction of PED energy expended for electric erosion (EE) of the electrode and heating, evaporation, and ionization of the medium may vary as the electrical parameters change.

Previously, we studied the removal of As(V) impurity from water [2] and demonstrated that the results obtained can be understood in terms of a mechanism including stages of oxidation of the eroded metal with water and oxygen, with sorption of arsenate ions by the forming iron hydroxide.

This study is a continuation of [1, 2] and is devoted to analysis of chemical reactions and of the dependence of the yields of the products formed in these reactions on pH and Cr(VI) concentration in the case of PED treatment of metallic charges in aqueous solutions.

### EXPERIMENTAL

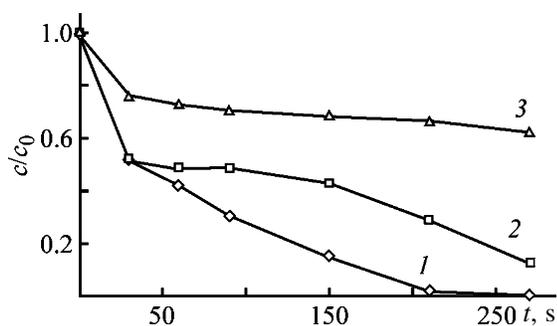
The study was performed on the experimental installation described in [1]. The electrical parameters used were as follows: voltage pulse width  $\tau_p = 10 \mu\text{s}$ ; pulse repetition frequency  $f = 300 \text{ Hz}$ ; voltage  $U = 500 \text{ V}$  for iron charge and  $U = 1000 \text{ V}$ ; maximum current  $I = 250\text{--}400 \text{ A}$ ; pulse energy  $E = 0.5 \text{ J}$ .

The solution was treated in a reactor of  $10 \times 10 \text{ cm}^2$  area and 20 cm height. The reactor was filled with a charge to a height of 2.5–3 cm. Model  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions of various concentrations (10 to  $400 \text{ mg l}^{-1}$ ) in distilled water were used in the study. The suspension produced upon the PED treatment of the solution was analyzed for the total content of dispersed iron,  $\text{Fe}_{\text{tot}}$ , and in particular for Fe(II) and Fe(III) by dissolving an aliquot in hydrochloric acid [11]. The content of Fe(0) in the suspension was determined by volumetry, and the concentration of Cr(VI) in the filtrate was found after separating the solid precipitate [11]. The composition of the solid precipitate was determined by X-ray phase analysis (XPA). The XPA data were interpreted using the JCPDS (International Centre for Diffraction Data) database.

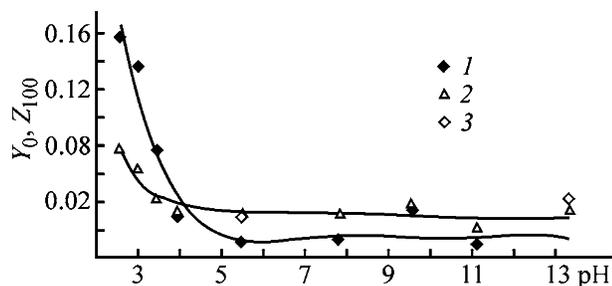
**Table 1.** Content of iron in various forms in the suspension produced in EE of shavings in water and Cr(VI) solution. Initial chromium(VI) concentration in model solutions,  $c_{\text{Cr(VI)}} = 50 \text{ mg l}^{-1}$ ; PED treatment time 60 s

System	pH	Content, wt %		
		Fe(0)	Fe(II)	Fe(III)
Fe + water	2.5	44	3	53
	5.5	87	3.7	9.3
Fe + Cr(VI) solution	2.5	32	28	40
	5.5	51	35.5	13.5

Table 1 lists data on the content of Fe(0), Fe(II), and Fe(III) in the suspension. It can be seen that the presence and involvement of Cr(VI) leads to oxidation of a large amount of iron. As the pH value decreases, the fraction of oxidized iron in the suspension grows. The extent of iron oxidation by chromium(VI) to



**Fig. 1.** Degree of Cr(VI) extraction from water vs. time  $t$  of PED treatment of various charges at  $c_0 = 25 \text{ mg l}^{-1}$ . ( $c_0$ ,  $c$ ) Initial and running Cr(VI) concentrations. Charge: (1) iron shavings, (2) iron grains, and (3) aluminum shavings.



**Fig. 2.** Fraction of reduced Cr(VI) vs. the solution pH. ( $Y_0$ ) Fraction of chromium(VI) that reacted before PED treatment and ( $Z_{100}$ ) relative yield of chromium(VI) reduced during the PED treatment for  $t = 100 \text{ s}$  and  $c_0 = 50 \text{ mg l}^{-1}$ . (1)  $Y_0$ , extrapolation of the equation  $Y(t) = Y_0 + \beta t$ ; (2)  $Z_{100}$ , after PED treatment for 100 s; and (3)  $Y_0$ , experiment (without PED).

Fe(II) exceeds that to Fe(III). The PED treatment of an iron charge in distilled water gives a black solid precipitate. A study of the precipitate by XPA demonstrated that it contains Fe(0) and Fe(II) and Fe(III) oxides.

Figure 1 shows curves describing the decrease in the Cr(VI) concentration in solution under PED treatment for different charges: Al and Fe shavings and Fe grains. The process is the most efficient with Fe shavings. The reduction yield per unit mass of eroded metal is the same for iron shavings and grains. In contrast to the case of spherical grains, use of shavings leads to enhanced erosion, which, in turn, accelerates chemical reactions of Cr(VI) reduction. Although aluminum is more thermodynamically active than iron, it is less efficient in the reaction with the solution.

There exists an initial region of fast Cr(VI) reduction by the metal (Fig. 1), which occurs via a reaction without any discharge. After the initial interaction, the reaction stops. The extent of this region can be found both in experiments without RED and from curves measured under EE conditions. In doing so, the following circumstance can be used for taking into account the oxidation before the PED treatment: after the initial interaction, the chromium(VI) concentration in solution varies virtually linearly, so that the fraction of reacted chromium(VI) is given by

$$Y = 1 - c_{\text{Cr(VI)}}/c_{0\text{Cr(VI)}} = Y_0 + \beta t. \quad (1)$$

Figure 2 (curve 1) shows the dependence of the fraction of chromium(VI),  $Y_0$ , reduced by iron without PED on the pH value. The fraction of chromium(VI) reacted before the PED treatment is independent of pH in the range 4–13.5. At pH values lower than 4, this fraction sharply increases. The points obtained directly in the experiment are close to those found by extrapolation.

Measurements of  $c_{\text{Cr(VI)}}$  on switching off PED also demonstrated that further reduction of Cr(VI) is terminated, i.e., the iron surface formed upon erosion is rapidly passivated.

Because it is assumed that reactions involving  $\text{H}^+$  and  $\text{OH}^-$  ions occur in the course of iron erosion in water (Table 2), changes in the pH value were measured in the course of the experiment (Table 3). It can be seen that, in the case of iron erosion in water, pH increases to approximately 9.0 (Table 3). It follows from Table 3 that the pH value increases upon PED treatment of acid and neutral solutions of Cr(VI) salts, and this effect becomes insignificant in the case of PED treatment of alkaline solutions ( $\text{pH} \geq 11$ ).

**Table 2.** Chemical reactions in EE of an iron charge in water and Cr(VI) solution

Reaction		$\Delta\varphi^{0,*}$ V
pH > 3.5		
$\text{Fe} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + \text{H}_2$	(1)	+0.9
$2\text{Fe} + 6\text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3 + 3\text{H}_2$	(2)	+0.8
$2\text{Fe} + 2\text{H}_2\text{O} + \text{O}_2 = 2\text{Fe}(\text{OH})_2$	(3)	+1.2
$4\text{Fe} + 6\text{H}_2\text{O} + 3\text{O}_2 = 4\text{Fe}(\text{OH})_3$	(4)	+0.85
$2\text{CrO}_4^{2-} + 3\text{Fe} + 8\text{H}_2\text{O} = 2\text{Cr}(\text{OH})_3 + 3\text{Fe}(\text{OH})_2 + 4\text{OH}^-$	(5)	+0.81
$\text{CrO}_4^{2-} + \text{Fe} + 4\text{H}_2\text{O} = \text{Cr}(\text{OH})_3 + \text{Fe}(\text{OH})_3 + 2\text{OH}^-$	(6)	+0.70
pH < 3.5		
$\text{Fe} + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2$	(7)	+0.44
$2\text{Fe} + 6\text{H}^+ = 2\text{Fe}^{3+} + 3\text{H}_2$	(8)	+0.06
$4\text{Fe} + 4\text{H}^+ + \text{O}_2 = 4\text{Fe}^{2+} + 2\text{H}_2\text{O}$	(9)	+1.67
$4\text{Fe} + 12\text{H}^+ + 3\text{O}_2 = 4\text{Fe}^{3+} + 6\text{H}_2\text{O}$	(10)	+1.3
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 3\text{Fe} = 2\text{Cr}^{3+} + 3\text{Fe}^{2+} + 7\text{H}_2\text{O}$	(11)	+2.23
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 2\text{Fe} = 2\text{Cr}^{3+} + 2\text{Fe}^{3+} + 7\text{H}_2\text{O}$	(12)	+2.12
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} = 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$	(13)	+0.61

\*  $\Delta\varphi^0$ , standard change in the potential.

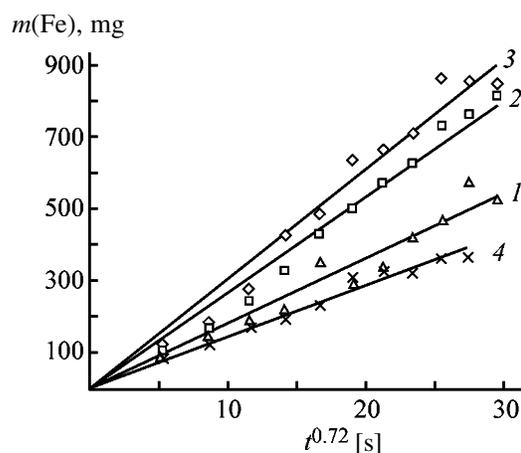
**Table 3.** Changes in the pH value in extraction of Cr(VI) from model solutions by PED with an iron charge. Initial chromium(VI) concentration  $c_{\text{Cr(VI)}} = 50 \text{ mg l}^{-1}$ , time of PED treatment 110 s

Solution	Solution pH							
	$\text{K}_2\text{CrO}_4$			$\text{K}_2\text{Cr}_2\text{O}_7$				$\text{H}_2\text{O}$
Before PED treatment	7.84	9.6	11.15	2.55	3	3.47	3.95	5.5
After PED treatment:								
suspension	11.5	11.26	11.25	4.43	5.1	6.94	8.5	9.13
filtrate	11.1	10.82	11	5.48	5.8	6.95	8.2	8.95

The effect of pH on the erosion of iron and reduction of chromium(VI) under a PED treatment is illustrated by Figs. 3 and 4.

In accordance with the previously obtained results [1], the mass of eroded iron is proportional to  $t^{0.72}$  (Fig. 3). The linearization was made using the equation  $m = k_2 t^{0.72}$  [1]. The pH dependence of the effective erosion constant  $k_2$  is shown in Fig. 4.

The yield of Fe erosion as a function of pH passes through a maximum at pH  $\sim 7$ . This circumstance was taken into account when studying the effect of pH on the reaction of Cr(VI) with eroded iron: for comparison we took masses of reacted chromium(VI) per unit mass of eroded iron. Figure 5 shows examples of how the pH value affects the kinetics of interaction between Cr(VI) and iron. It can be seen that the relative yield of chromium(VI) reduction,  $Z_t = (m_0 - m)_{\text{Cr}}/m_{\text{Fe}} =$


**Fig. 3.** Amount of eroded Fe,  $m(\text{Fe})$ , vs. treatment time  $t^{0.72}$  under PED at different pH values. pH: (1) 3.95, (2) 5.5, (3) 7.84, and (4) 13.33.

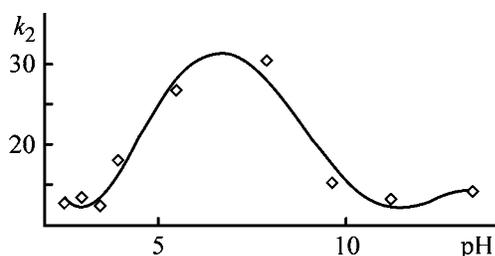


Fig. 4. Specific erosion constant of iron shavings,  $k_2$ , vs. pH.

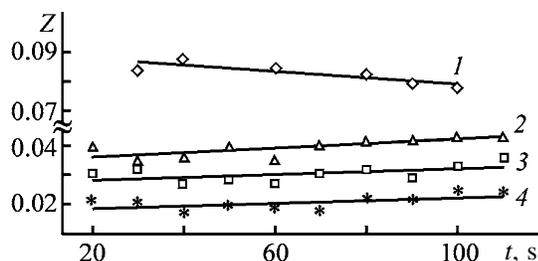


Fig. 5. Relative yield of the reaction,  $Z = (m_0 - m)_{\text{Cr}}/m_{\text{Fe}} = Z_0 + \alpha t$ , vs. the PED treatment time  $t$  at different pH values. Initial chromium(VI) concentration  $c_0 = 50 \text{ mg l}^{-1}$ . pH: (1) 2.55, (2) 3.47, (3) 7.84, and (4) 11.15.

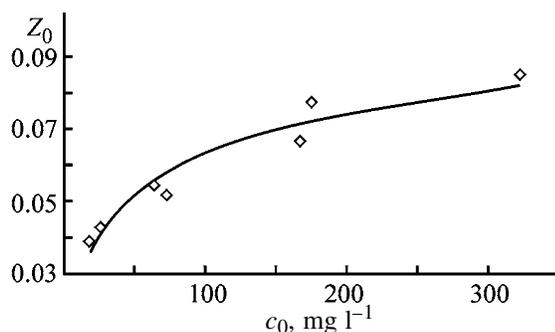


Fig. 6. Relative initial yield of Cr(VI) reduction,  $Z_0$ , vs. the initial chromium(VI) concentration  $c_0$  in solution.

$Z_0 + \alpha t$ , weakly and nearly linearly varies as the time of PED treatment increases (the coefficient  $\alpha$  at  $t$  is small).

The pH dependences of the relative yield  $Z_t$  at different treatment times are qualitatively the same and similar to that of the yield  $Y_0$  before the PED treatment (Fig. 2). In Fig. 5, a dependence of this kind is shown for  $t = 100 \text{ s}$ . It can be seen that the yield  $Z_{100}$  is weakly dependent on pH in the range 3.5–13.5 and steeply increases at  $\text{pH} < 3.5$ .

Figure 6 shows how the initial relative yield  $Z_0$  depends on the starting concentration of the Cr(VI) solution at pH 5.5. In the absence of PED, the surface of iron and aluminum is covered with oxhydroxide films. In the case of Al, the films are thinner and

denser. In the presence of oxidizing ions,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$ , the film may become thicker and denser via formation of oxhydroxides and other Cr(III) compounds. This hinders and terminates the reaction, i.e., additional passivation of the metal may occur. For Al this effect is more pronounced, which can be seen in Fig. 1. At pH 5.5, the initial yield of Cr(VI) reduction is approximately 0.06 mol of Cr per mole of Fe in the case of iron and 0.05 for aluminum. Outside the range of the initial steep rise, this difference is considerably stronger: the yields are 0.02 and 0.005, respectively. These differences are apparently due to the thickness and density of passivating films and to the fact that the film is formed faster in the case of Al. It can also be seen that the fraction of a utilized metal is small because of the passivation. If it is assumed that the specific surface area of the eroded metal is about  $10.0 \text{ m}^2 \text{ g}^{-1}$ , which is characteristic of electric-explosion-produced powders, about 0.1% of atoms will lie on the particle surface and, consequently, several tens of iron monolayers and several aluminum monolayers will react with chromium(VI). Thus, two processes noticeably contribute to the formation of a passivating film: interaction of surface metal atoms with Cr(VI) and water.

In a PED treatment of metallic charges in water or aqueous solutions, the metal is heated at places of discharges to a high temperature and its micro- and nanoparticles are ejected into the liquid. The particles are rapidly cooled and, in the process, react with neighboring molecules and ions. Also reacts the metal situated at places of particle detachment. As a result, the reaction surface of the metal strongly increases, compared with its initial value (by a factor of  $\geq 10^4$ ), and just this circumstance leads to an increase in the fraction of reacted impurity, compared with the case of a reaction without discharges. Because of the change in the configuration of discharge gaps, the amount of eroded iron varies with time in proportion to  $t^{0.72}$ , rather than linearly. For the aluminum charge, this dependence is linear [1], which was taken into account in experimental data processing (Figs. 3, 4). In this case, the fraction of the eroded metal that enters into the reaction is determined by the thickness and density of the passivating film, both intrinsic, formed in interaction with water and oxygen dissolved in the liquid, and that constituted by products of impurity reduction. Upon a PED treatment of an iron charge in distilled water, the pH value increases to approximately 9. It should be noted that pH 9.0 is the equilibrium value for a  $\text{Fe}(\text{OH})_2$  solution in water, saturated at 298 K [12]. Although iron(II) and (III) hydroxides are formed in erosion according to the data

presented, the concentration of dissolved iron is determined by the more soluble component,  $\text{Fe}(\text{OH})_2$ .

Thus, the experimental data obtained indicate that reactions (1)–(4) occur simultaneously in EE in distilled water (Table 2). In accordance with the potential presented, iron is predominantly oxidized to  $\text{Fe}(\text{OH})_2$  in the experiment. Upon acidification of water, the advantageousness of iron oxidation to Fe(II) becomes even more pronounced, which is due to a decrease in the potential of reaction (8). The high pH-independent potential of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple ( $\varphi^0 = 0.77$  V) precludes additional oxidation of  $\text{Fe}^{2+}$  with such oxidizing agents as  $\text{H}^+$  and  $\text{H}_2\text{O}$ . As a result, there occurs gradual oxidation with  $\text{O}_2$  as it is dissolved in water from the atmosphere. It can be seen that, as pH varies (Figs. 3, 4), the yield of Fe erosion passes through a maximum at about pH 7. The erosion is a physical process related to conductivity of intergrain spaces, and, therefore, such a behavior of the erosion yield can be attributed to the apparent change in the solution conductivity, which must pass through a minimum at pH 7. Apparently, the fraction of PED energy released into the solution will increase with the solution conductivity, whereas the energy expenditure for heating and dispersion of the metal will decrease.

The degree of iron oxidation in the reaction products and their composition are determined by both thermodynamic and kinetic factors. The former can be evaluated by the standard electrode potentials  $\varphi^0$  [13] for electrodes in an alkaline medium (V):  $\text{Fe}(\text{OH})_2/\text{Fe} = -0.896$ ,  $\text{Fe}(\text{OH})_3/\text{Fe} = -0.79$ ,  $\text{Fe}(\text{OH})_3/\text{Fe}(\text{OH})_2 = -0.58$ , and  $\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3 = -0.086$ . Here, the potential for a freshly precipitated chromium(VI) hydroxide is used. These values point to a somewhat higher thermodynamic probability of iron oxidation to Fe(II) by Eq. (5). At a chromium(VI) concentration in solution of  $50 \text{ mg l}^{-1}$ , the potentials of reactions (5) and (6) decrease by 0.22 V at pH 7 and remain virtually unchanged at pH 13, so that both reactions are thermodynamically probable for freshly formed precipitates. And even a decrease in the chromium(VI) concentration by additional three orders of magnitude does not change the sign of the difference of these potentials, which indicates that deep purification of water is possible. The oxidation to Fe(II) is also kinetically advantageous, because transfer of a smaller number of electrons is necessary in this case. The existence of this pathway is also evidenced by the above pH value of 9, established after the PED treatment.

In the acid medium, the  $\varphi^0$  values for the electrodes are important (V):  $\text{Fe}^{2+}/\text{Fe} = -0.44$ ,  $\text{Fe}^{3+}/\text{Fe} = -0.062$ ,

and  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+} = +1.33$ . These data indicate that two alternative pathways of interaction are possible: reactions (11) and (12). As in the alkaline medium, oxidation to Fe(II) is kinetically advantageous. However, reaction (11) can be followed by additional oxidation of Fe(II) by reaction (13). This liquid-phase reaction is kinetically more probable than oxidation of  $\text{Fe}(\text{OH})_2$  to  $\text{Fe}(\text{OH})_3$  by reaction (5) in an alkaline medium, because the latter occurs in the solid phase. It was experimentally demonstrated (Table 1) that the contribution from these reactions depends on pH of the starting solution: as pH becomes lower, the yield of Fe(III) increases from 13.5 to 40%, whereas that of Fe(II), contrariwise, decreases from 35 to 28% because of the occurrence of reaction (13).

It can also be seen that the yield of oxidation of eroded iron in the presence of Cr(VI) exceeds that in the case of erosion in pure water. This indicates that reactions (5), (6), and (10)–(13) occur, with reactions (5), (6), and (11) predominant. Measurements of the solution pH in PED (Table 3) demonstrated that, in accordance with reactions (5), (6), and (10)–(13), pH increases upon discharge treatment of Cr(VI)-containing solutions. The yield of the reduction of Cr(VI), based on metal unit mass, under PED for 100 s (Fig. 2, curve 2; Fig. 5) is virtually independent of pH in the range 3.5–13.5. The steep rise in the yield at  $\text{pH} < 3.5$  is due to a change of the reaction mechanism from that described by Eqs. (5) and (6) to that by (11). The independence of the yield from pH in the range 3.5–13.5 indicates that reaction (5) is irreversible under the experimental conditions. Some information about iron passivation in PED in a solution of a chromium(VI) salt was obtained by determining the dependence of the relative yield of the reaction on the initial concentration of the salt (Fig. 6). This dependence is weak, described by a flattening-out curve, which confirms that a passivating film is formed, because a linear or superlinear dependence would be expected in its absence. At the same time, the yield somewhat increases as the concentration becomes higher, which points to a low, but still noticeable permeability of the passivating film and to involvement of chromium(VI) compounds in its formation.

In conclusion, the energy expenditure for treatment of wastewater to remove the chromium(VI) impurity will be calculated. Let the energy expenditure for iron erosion be  $0.067 \text{ kW h mol}^{-1}$  [1], and the yield of chromium(VI) removal, 0.02 mol Cr per mole of Fe, as shown above. Then, 0.4 kW h of electric energy will be necessary for removal of  $300 \text{ mg l}^{-1}$  of chro-

mium(VI) from 1 m<sup>3</sup> of wastewater at pH > 3.5. This value is tens of times lower than that consumed in treatment of a grained iron charge with high-voltage (3–15 kV) electric discharges [3, 4]: 90 MJ m<sup>-3</sup> at  $c = 100 \text{ mg l}^{-1}$ . This difference is possibly due to expenditure of the PED energy both for metal erosion and for evaporation and ionization of the solution in intergrain spaces. In this case, in accordance with the mechanism suggested, the expenditure for erosion purifies water by removing impurities and that for evaporation and ionization either does not lead to purification, or purification occurs by a less efficient mechanism.

### CONCLUSIONS

(1) In treatment of Cr(VI) solutions with pulsed electric discharges in a reactor with an aluminum or iron charge, the eroded metal directly interacts with the impurity via dispersion of a metal, disintegration of the passivating film, and oxidation of the metal to the corresponding hydroxides.

(2) The efficiency of the interaction with Cr(VI) depends on the rate of formation of the passivating film, pH value, and initial concentration of the solution: it is 0.02–0.03 mol Cr(VI) per mole of eroded Fe.

(3) The yield of chromium(VI) reduction is virtually independent of pH in the range 3.5–13.5 and sharply increases at pH < 3.5. This is due to a change of the reaction mechanism: from oxidation of iron to give solid hydroxides to its oxidation to simple ions, Fe(II) and Fe(III), in solution.

(4) The possible energy expenditure for wastewater treatment to remove Cr(VI) ions at  $c = 300 \text{ mg l}^{-1}$  is

about 1.5 MJ m<sup>-3</sup>, which makes this method promising for practical use.

### REFERENCES

1. Danilenko, N.B., Savel'ev, G.G., Yavorovskii, N.A., et al., *Zh. Prikl. Khim.*, 2005, vol. 78, no. 9, pp. 1463–1468.
2. Danilenko, N.B., Savel'ev, G.G., Yavorovskii, N.A., et al., *Zh. Prikl. Khim.*, 2005, vol. 78, no. 10, pp. 1659–1663.
3. Khainatskii, S.A., Zubenko, A.A., Petrichenko, L.A., et al., *Elektronn. Obrab. Mater.*, 2005, no. 6, pp. 47–52.
4. Khainatskii, S.A., Zubenko, A.A., Smal'ko, A.A., et al., *Elektronn. Obrab. Mater.*, 2005, no. 6, pp. 53–58.
5. RF Patent 2220110.
6. RF Patent 2049733.
7. RF Patent 1353743.
8. Kul'skii, L.A., Grebenyuk, V.D., and Savchuk, O.S., *Elektrokhimiya v protsessakh ochistki vody* (Electrochemistry in Water Treatment), Kiev: Tekhnika, 1987.
9. Fominskii, L.P., *Elektronn. Obrab. Mater.*, 1980, no. 1, pp. 46–49.
10. Bairamov, R.K., Vedernikova, N.R., and Ermakov, A.I., *Zh. Prikl. Khim.*, 2001, vol. 74, no. 10, pp. 1703–1705.
11. *Unifitsirovannye metody analiza vod* (Unified Methods for Water Analysis), Lur'e, Yu. Yu., Ed., Moscow: Khimiya, 1973.
12. Shkol'nikov, E.V., *Zh. Prikl. Khim.*, 2005, vol. 78, no. 11, pp. 1819–1823.
13. *Kratkii spravochnik fiziko-khimicheskikh velichin* (Concise Handbook of Physicochemical Quantities), Ravdel', A.A. and Ponomareva, A.M., Eds., Leningrad: Khimiya, 1983.