

Radiation-Chemical Mechanism of the Metal Valence Increase During of the Radiolysis of Sulfuric Acid Water Solution

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Abstract – The paper is devoted to research of radiation-chemical of the electron beam induced increase of metal valence (on an example of iron) at an sulfuric acid water solutions. For this purpose we generalize the solely chemical mechanism of iron valence increase, well known in metallurgy: $Me^{n+} + (H-OH)^+ = Me^{(n+1)+} + H_2O$.

A system of the differential equations with unknown function and three parameters corresponds to this mechanism. The parameters of model as $k_7=10.956$ [ml / (g*s)] and $\tau_4=5425$ [s], $\tau_{11}=50.2$ [s] (at energy of an electronic beam 7 [MeV] and its power 175 [W]) were determined from our experimental data. A form of unknown function was also determined as inverse problem solution.

1. Introduction

Recently, we succeeded with research on radiation-chemical influence of high energy electrons on reactions rates increase of hydrometallurgical processes in technology of processing uranium and rare metals materials proceeded. The basic attention was given to investigations of an oxidizing from iron II to iron III state into sulfuric acid solutions and search of an optimum power mode, which could be a basis for designing skilled installation of uranium lixiviation, less power-intensive, without application chemical reactants and, hence, by more economical and ecologically safe.

2. Experimental

The irradiation was carried out of mostly by electrons at energy of 7 MeV and current 25 μ A. The solutions (or pulp) with various initial concentration of iron (II and III) and acid H₂SO₄ were exposed to the irradiation. The schematic of experiment was optimized. Like the earlier experiments, the water solutions were irradiated in polyethylene vessels installed on a rotating small table, while the pulp was irradiated in the module of radiation-chemical reactor with hashing speed 180 turns per minute. During the irradiation, the module or the vessel with a solution was installed on a place of a small table that was preliminarily removed. The parameters of the accelerator (electrons current and energy) were measured by the induction gauges, Faraday cup and magnetic spectrometer.

The procedure of the beam parameters measurement and their control during an irradiation was as the following. A constant thermal mode was delayed for approximately 1–2 hours with respect to switching on of the accelerator. When all systems of the accelerator were operated into a normal thermal mode, i.e. mode, when temperature of systems does not vary any more during work of the accelerator, the electronic gun was switched on. Thus the electrons current was measured by the induction gauge, the signal which was of monitored by oscilloscope and by the Faraday cup. Afterwards, the Faraday cup was removed from an axis of the accelerator, and the electron beam was directed to magnetic spectrometer. The accelerator was adjusted to the given parameters (current and energy) by using of the variation of gun filament current and accelerating field phase. After the accelerator was adjusted to the given parameters, magnetic spectrometer was switched off, and the Faraday cup was located to the former place. At given parameters of the electron beam, the absorbed dose in an irradiated sample was determined as product of dose rate and irradiation time:

$$D = \dot{D} t = \frac{3IE}{m} t.$$

Where η – operating ratio of a beam;

I – average electrons current;

m – weight of irradiated substance.

The time of an irradiation was determined by means of stop-watch. The accuracy of accelerator operations modes reproduction and absorbed doses was determined by accuracy of beam parameters measurement, their stability and accuracy of irradiation time measurement. The total error in reproduction of irradiation modes did not exceed 10 %. In our experiments on an irradiation of water solutions samples with the given concentration of iron and sulfuric acid, and also pulp, the electrons energy losses in walls of polyethylene vessels and in walls of the reactor module were taken into account. In the first case, an energy loss was approximately 400 keV, and in second case that was near 1 MeV. It should be noted, also, that introduced in this paper operational ratio of a beam η was assumed to be of 0.99 for water solutions, as before, and 0.95 for pulp.

3. Experimental results

The results of our experiments are given in the

N ⁰	Fe, g/l	C ₀ , g/l	T, s	E, MeV	dC, g/l
16	1	2.3	30	7	0.3
18	5	5.7	240	7	2.8
19	5	5.7	180	7	2.8
20	5	5.7	120	7	1.9
21	5	5.7	60	7	1.7
22	5	5.7	210	6	2.6
23	5	5.7	360	4	1.9
24	5	5.7	660	2	1.5
26	10	9.8	210	6	4.0
27	10	9.8	360	4	2.9
28	10	9.8	660	2	1.7
130	5	2.2	180	7	2.2
131	5	5.7	180	7	2.3
132	5	10.7	180	7	4.9
133	5	15.8	180	7	3.6
134	10	2.8	180	7	2.8
135	10	5.0	180	7	1.3
136	10	9.8	180	7	4.5
137	10	15.8	180	7	6.7
138	1	2.9	180	7	0.1
139	1	5.1	180	7	0.4
140	1	10.6	180	7	1.5
141	1	14.7	180	7	1.8

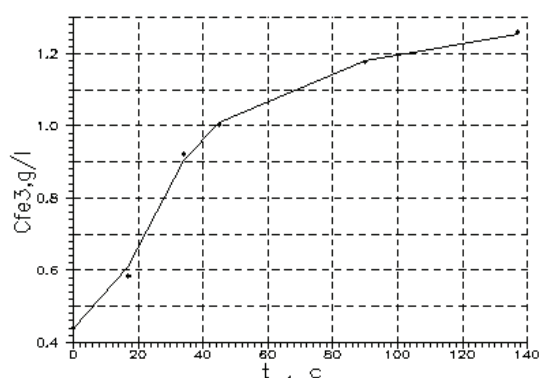


Fig. 1. Experimental points and fit (140 s it 400 kGy)

Table and in Fig. 1. Here dC is an experimental expenditure of a sulfuric acid. Initial kinetics equation for concentration H₂SO₄ looks like:

$$dC(t)/dt = -k_1 * C_{Fe} * C(t) - C(t)/\tau_2 + k_8 * C_{H_2} * C_{SO_4}$$

where $k_1 = 1.565 \text{ ml}/(\text{g} \cdot \text{s})$ and $\tau_2 (E = 7 \text{ MeV}) = 226 \text{ s}$. Approached solution of the above equation was defined as: $C(t) = C_0 - C_\tau * (1 - \exp(-t/\tau))$, where two parameters – $C_\tau(C_0)$ and τ – depends basically only on concentration of iron and electron beam energy. In according to limited experimental data (see Table), we find dependence of these two parameters on electron energy only in area $C_{Fe}(0) = 10 \text{ g/l}$. In Fig. 2 the de-

pendences of the H₂SO₄ charge $dC = C(t) - C_0$ on its initial concentration C_0 for $t = 30, 60, 120, 180 \text{ s}$ and $E = 1 \text{ MeV}$ are given. In Fig. 3 the dependences of the H₂SO₄ charge on its initial concentration for $t = 1, 5, 10, 20 \text{ s}$ and $E = 14 \text{ MeV}$ are given. At electron energy higher than 14 MeV a fast increase of reaction rate appears. A constant power of an electron beam 175 W was assumed in our calculations.

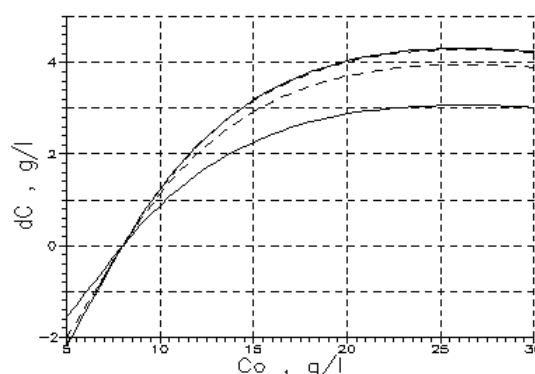


Fig.2. Irradiation times 30,60,120=180 s, E=1 MeV.

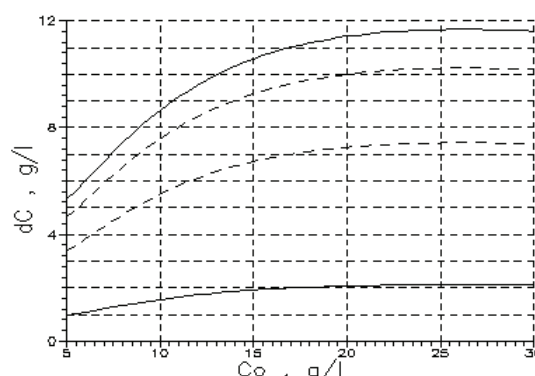


Fig.3. Irradiation times 1,5,10,20 s, E=14 MeV.

4. Model of experiments on the irradiation of iron (II) sulfate solutions by a electron beam

The proposed simplified kinetics model (with radiating catalysis) can be described by the following reactions:

- (1) $\text{Fe} + \text{H}_2\text{SO}_4 = \text{H}_2 + \text{FeSO}_4$
- (2) $\text{H}_2\text{SO}_4 = \text{H}_2 + \text{SO}_4$
- (3) $\text{H}_2\text{O} = \text{H}_2 + \text{O}$
- (4) $\text{H}_2\text{O} = (\text{H} + \text{OH})$
- (5) $\text{Fe} + \text{SO}_4 = \text{FeSO}_4$
- (6) $\text{Fe} + \text{O} = \text{FeO}$
- (7) $\text{Fe} + (\text{H} + \text{OH}) = \text{Fe}^{3+} + \text{H}_2\text{O}$

At the first stage the definition of unknown parameters (4 reaction rates and 3 decay times) based on experimental data, and also obtaining of its dependences (in the basic decay times) from electron energy and beam current is assumed. The modeling of iron (III) accumulation kinetics from iron (II) according to the following system of differential equations is carried out:

$$dC_{\text{Fe}^{3+}}/dt = k_7 * C_{\text{Fe}}(t) * C_{(\text{H} + \text{OH})}(t) + C_{\text{Fe}}(t)/\tau_{10}$$

$$dC_{Fe}/dt = -k_7 * C_{Fe}(t) * C_{(H+OH)}(t) - C_{Fe}(t)/\tau_{10}$$

$$dC_{(H+OH)}/dt = C_{H_2O}(t)/\tau_4 - (1/\tau_{11} + k_7 * C_{Fe}(t)) * C_{(H+OH)}(t)$$

$$C_{H_2O}(t) = 1000 * (1 - \psi(t)).$$

As a result, the values of model parameters $k_7=10.956 \text{ ml} / (\text{g} \cdot \text{s})$, $\tau_4=5425 \text{ s}$, $\tau_{11}=50.2 \text{ s}$ are defined, and the value $\tau_{10}=3.3 \cdot 10^8 \text{ s}$ shows that direct positron transition $2 +$ in $3 +$ state is negligible for the given experiment. The adjusted rough form of function $\psi(t)$ is given in Fig. 4. The behavior of three basic components concentration in time is given in Fig. 5. From Fig. 4 one can see that in an interval of irradiation times approximately from 40 up to 55 s (at energy 7 MeV) the value of $C_{H_2O}(t)$ became negative. We consider a behavior of model parameters as a function of electron energy (or beam current) in such a way that electron beam power is equal to 175 W. It is predicted, that at energy change from 7 MeV to 1 MeV the optimal time of iron 3+ concentration on equilibrium value decrease from 110 s to 39 s. In Fig. 1 experimental kinetics of iron 3+ accumulation which has served with a basis of our calculations is shown.

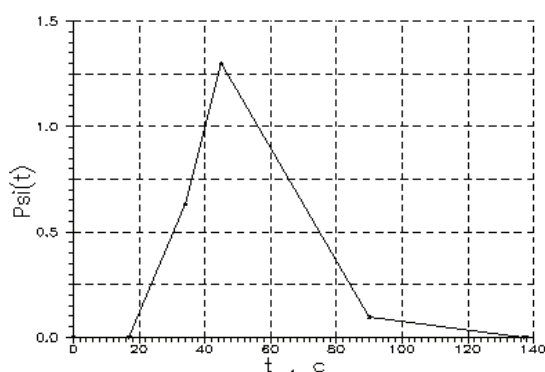


Fig. 4. A rough kind of unfolded modeling function $\psi(t)$

5. Conclusion

The main results of the presented research can be summarized as the following:

1. The analysis theoretical and experimental data on fast electrons interaction with substance is carried out. The mechanisms rendering the basic influence on substance are found and the beam parameters (sizes and length of penetration, beam current, electronic energy etc.) are appreciated.
2. The plenty of samples and tests of various solutions with different concentration of an acid and iron is irradiated.

3. The technique of electrons parameters measurement based on such devices, as induction gauges, Faraday cup and magnetic spectrometer is developed.

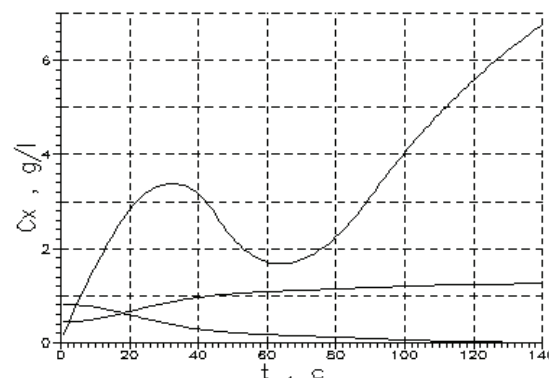


Fig. 5. Dependences of complexes (H-OH), iron (III) and iron (II) concentrations from irradiation time

4. The methods of energy deep adjustment based on absorption of accelerated electrons in water are tested.
5. During researches, some effects (for example, crisis phenomena are revealed during heating a liquid by a electron beam), which still wait for the explanation.
6. The advantages of a radiation-chemical oxidizer can be summarized as follows:
 - The essential decrease (in near 10 times) of energy consumption;
 - In a technological line of processing of uranium raw material in the future oxidizer such operations, as a purge pulp by air under pressure, pulp heating, expensive catalysts etc. will be eliminated;
 - The essential increase of ecological safety owing to exception chemical reactants from lixiviation process, and also that fact, that regeneration of an oxidizer will occur in the closed cycle;
 - On our deep belief, the including in a technological lixiviation line of the completely automated oxidizer (accelerator) will allow to automate all uranium (and other rare metals) lixiviation process.
7. The present researches will be carried out at the border of two sciences: physics and chemistry. Any infringement of these links results in to delay in researches only.