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Electrochemical Method of Discharged Waters Cleaning with of Alternating Current

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High power consumption, equipment unhandiness, and need for consumable materials prevent wide introduction of electrochemical methods of water and water solutions cleaning. This article presents the results of tests of industrial discharged water cleaning applying electrochemical method and shows the mechanism of this process.

Keywords: discharged water, electrochemical method, mechanism of the process, alternating current.

Introduction

Insufficient knowledge of the processes related to water resources, misuse of water and inefficient management methods in various regions of the world make problems of water resources, which are necessary to maintain sustainable welfare of a human society and functioning of ecological systems, very complicated [1].

Problems of clean water resources are universal. Rivers and lakes, underground sources are polluted (in particular across Russia: over 70 % of rivers and lakes, and 30 % of underground sources are polluted and cannot be used for drinking). To a great extent the reason for that are the discharged waters of galvanic production lines containing a variety of metal ions harmful for human health and environment. Attempts to create installations for neutralization of discharged waters of galvanic production do not give positive results because the mixed flows of discharged waters containing a whole «bouquet» of particularly harmful heavy metals are sent for neutralization. As the level of pollution in natural water sources is high the traditionally applied technologies of water cleaning are not sufficiently effective [1-3].

Electrochemical methods of water cleaning in general and electrochemical methods of water cleaning using alternating current of industrial frequency in particular belong to the most advanced directions of water cleaning process development. However, studies carried out in this area are still far

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from being completed, and available data about the processes occurring in water under the influence of alternating electric current are limited and insufficient to be used in proved scientific reports. The mechanism of alternating electric field effect on metal ions in water requires further development and more accurate definition. New data establishing qualitative and quantitative correlations between the cleaning process parameters are needed.

Among other things the solution of this scientific problem is urgent because industrial enterprises need installations to neutralize discharged waters. Therefore, this study devoted to the development of an effective electrochemical method of water cleaning from metal ions using quasistationary electric field on alternating current of industrial frequency, is rather actual.

Therefore the target of the performed study is to increase the efficiency of an electrochemical method of water cleaning from metal ions using quasistationary electric field on alternating current of industrial frequency.

Offered mechanism of cleaning process

At present the processes applying alternating current are not well studied. Thus, it is necessary to investigate the mechanism and give scientific explanation to the electrochemical processes applying alternating current, which as a consequence improves the efficiency of the cleaning process.

In order to obtain preliminary data the experimental research of electrochemical method of cleaning discharged waters from some enterprises was carried out.

After the results of the experiments were processed, a characteristic dependence of current change on time was observed (Fig. 1).

During anode semi-cycle the major amount of current is consumed for metal dissolution, and the rest (due to the electrochemical properties of metals) is used for formation of immunizing oxide film. As titanium is electrochemically active metal, mainly the latter process takes place. The immunizing film formation in a certain period of time t after voltage is switched on (Fig. 1) causes an abrupt drop in the operating current value. It can be explained by titanium catalytic activity against hydrogen, determined by the fact that titanium has a significant affinity with hydrogen, so hydrogen is consumed by titanium and dissolved in the surface layer. At titanium cathode polarization the release of hydrogen occurs slightly before than that from hydrogen inert materials, such as mercury or lead. The generated hydrogen is adsorbed by the titanium surface layer and desorbed during the «forced pause» period. The hydrogen on titanium is in active state, and it plays a significant role in ion electroreduction mechanism [4].

After the abrupt current drop the period of the «forced pause» t_{FP} begins (Fig. 1). The «forced pause» (FP) is the time constant for the electrode-electrolyte system, determined by nature of the electrode material and the electrolyte composition. During the «forced pause» period concentration of metal cations is fully or partially equalized due to their movement in the solution volume. The electrode-electrolyte system potential decreases slowly, which is typical for the processes when an electrode has high capacity and small partial exchange current, consequently large quantities of electropositive component precipitate (metal hydroxides formation).

In the process of soluble metal complexes transition into insoluble complexes the following fundamental points can be highlighted:

1. Electrons and protons play a specific role in electrical and chemical reactions. Chemical properties of hydrated proton and free proton do not have much in common. The same is characteristic

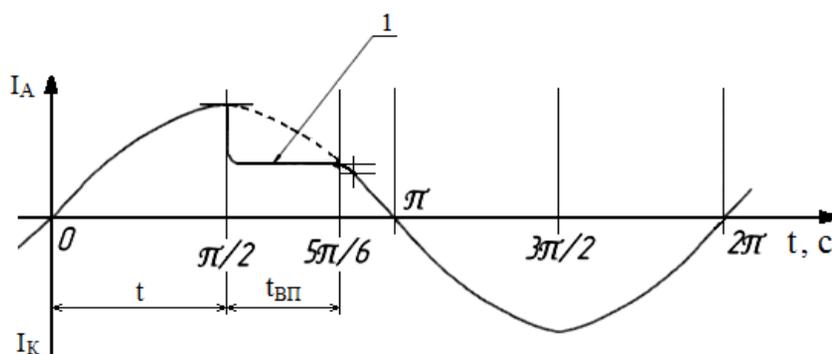


Fig. 1. Oscillogram of current-time curve 1 – actual current

for electrons. Partially hydrated electrons are available on the metal surface. As the degree of hydration, concentration of the hydrated ions and their mobility on various metals differs, and this is one of the reasons of electrode material influence on the electrochemical reactions.

Valence electrons participate in elementary reaction acts. In metals they are partly localized near atoms, and partly found in the form of Fermi electron gas (or Fermi electron liquid), that is, these are localized and collective electrons.

Concentration values of the collective electrons expressed as a function of metal atomic numbers, show periodicity, bearing some resemblance to periodic dependence of material electroreduction potentials.

In the course of cleaning process the most negative potentials were reached on s-p metals. When potentials shift in negative direction, emission of the hydrated electrons from the electrode increases, as well as emission of hydrogen atoms and their forming due to interaction of hydrated electrons and water molecules.

A cloud of such hydrated electrons near the electrode surface can affect structure of the double layer formed by alternating current. Participation of the hydrated electrons in oxidizing and reducing reactions in solutions is following: during the anode semi-cycle these electrons can easily participate in electrode reaction, and during the cathode semi-cycle ions reduction will occur. Finally, the reaction will result in the material recovery process [4].

It can be assumed that hydroxyl groups present in ion pairs near electrode and adsorbed hydrogen are donors for electrons.

At the same time, rapid change in current direction makes it difficult for hydroxyl ions OH^* (active unstable radicals) to discharge and favors their participation in reactions resulting in appearance of metal intermediate compounds with lower valence (their role is rather significant) [5].

One or more adsorbed hydrogen atoms contribute to transfer of electrons. Recombination of the hydrogen atoms slows down, and this favors the processes occurring on the titanium electrode in which the adsorbed atoms participate.

2. Hydrated electrons play an important role in the cleaning process. They interact with soluble metal complexes (associates) during the «forced pause» [4]. This interaction results in reduction of metal ions to lower valences, and finally, as a consequence metal hydroxides are formed. It should be noted:

- electrode material defines hydrated electrons activity and their concentration;
- alternating electric field increases the role of the hydrated electrons in the cleaning process.

3. Presumably different ions present in the solution provide for forming associates not uniform in their structure. Non-uniformity appears because water molecules are electrically neutral, and they can be present both in inner and outer spheres of the associate. Their quantity is determined by the central ion. Also, water molecules can attach to the outer-sphere ion. The key feature is that water molecules can be attracted to each other, thus, water molecules probably attract associates with different central ions to each other (published sources confirm the existence of associates consisting of more than two ions and having a common shell). By deforming an associate hydrated shell the alternating electric field favors separation of the solvent molecules [4]. Probably, associate nonuniformity means that instead of affecting the associate along the entire outer hydrated «shell», the alternating electric field affects it only along the part which has water molecules in its outer sphere. Different ion concentrations in the solution provide for different associate structural nonuniformity, therefore purification efficiency will differ, and this is proved by the experiments.

4. The cleaning process starts in the upper portion of the solution due to boundary layer, so called, surface or boundary phase that can be separated on the boundary between two phases (air and solution). It has some excess of free energy as compared to each of the neighboring phases. This energy-to-area ratio is related to surface tension force. The content of components in the surface phase can considerably differ from that in the volume of phases.

It is well known that simple metal ion complexes are better hydrolyzed than more complicated ones. It is assumed that simple metal ion complexes (the hydrates containing minimum of water molecules in both outer and inner spheres) are in the upper portion of the solution, and that different kinds of complexes are present in other zones of the solution volume. The above mentioned makes us assume that the environment – the ambient air – has a significant influence on the cleaning process.

Let us assume (similarly to the influence of electrical conduction distribution in the interelectrode gap on dissolution velocity in the source [6]) that in the upper layers the process increases rapidly, and then it goes out slowly (decelerates for a long time); in the bottom layers the process increases slowly but it runs more efficiently than in the upper zone.

This mechanism is proposed based on different structures of metal ion complexes.

5. The following figures illustrate the assumed mechanism.

Fig. 2 shows the initial moment of time. Heavy metal ions (HMI) are present in the form of complexes having hydrated shell and solvent molecules.

In the course of the process deformation of hydrated shell and detachment of solvent molecules occur caused by asymmetrical alternating electric field (Fig. 3).

During the «forced pause» equalizing of the metal ion associates concentration (complexes) occurs, and the hydrated electrons interact with associates (Fig. 4).

Fig. 5 presents the mechanism of hydroxide formation (specifically, the ferric hydroxide $\text{Fe}(\text{OH})_2$). Influenced by the alternating electric field, the hydrated electrons interact with the associate. This process comprises many stages; Fig. 5 shows stage 1 and the result.

The process of hydrated electrons interaction with soluble metal complexes can be explained in the following way. It is known that hydroxyl and hydrogen ions have much higher mobility in

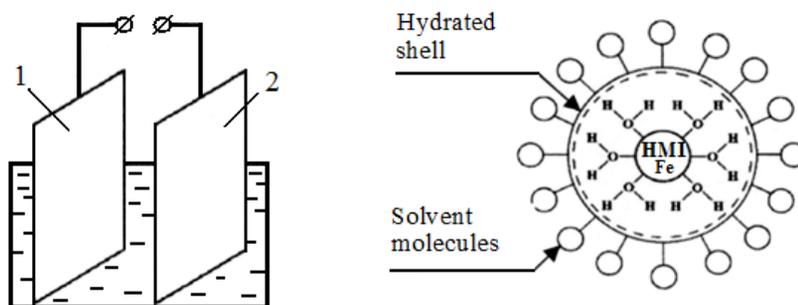


Fig. 2. Cleaning process layout at the initial moment (1 – titanium electrode, 2 – steel electrode)

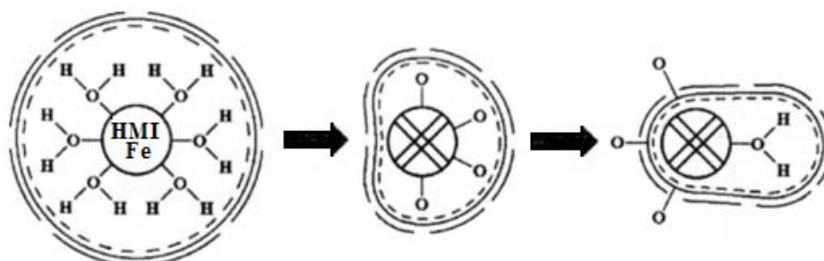


Fig. 3. Influence of alternating electric field on metal ion complexes

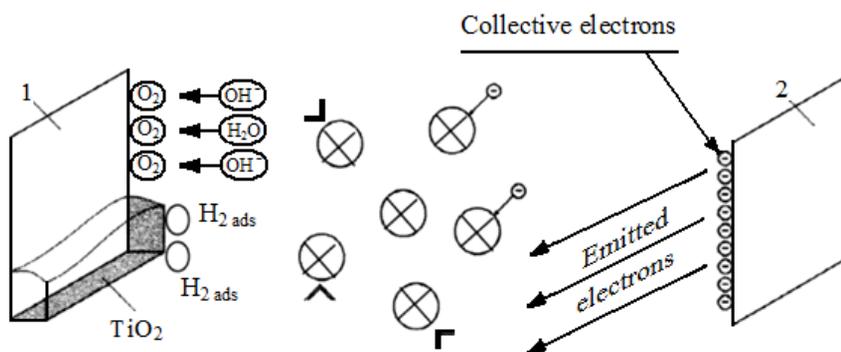
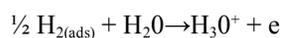


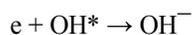
Fig. 4. Cleaning process scheme during the «forced pause»

water solutions than other ions. This phenomenon is explained through the relay-race or Grotthuss mechanism of hydrogen and hydroxyl ions motion.

A hydrated electron is formed by interaction between hydrogen atom ($H_{2(ads)}$) adsorbed on titanium and water molecule:



A hydroxyl ion is formed at interaction between hydrated electron and active unstable radical:



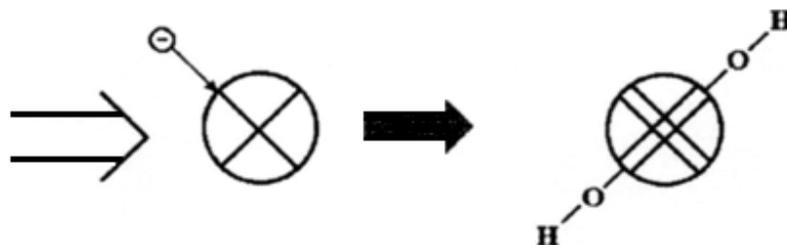
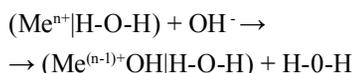


Fig. 5. Result of the hydrated electrons influence on the associate

As well as in the unified J. Lowell's model of charge transfer in polymers from one place of a chain segment to a «trap» of another chain with further tunneling, the metal ion hydroxide formation undergoes several stages, depending on valence of the complex-forming-ion (the number of stages equals to charge of the complex-forming-cation):



Initially a hydroxyl ion and water molecule in the inner sphere of the complex-forming-cation attract each other electrostatically. After they approach each other the process of proton jump from the water molecule to the hydroxyl ion occurs in compliance with the above presented scheme (probability of tunneling transfer strongly depends on distance). Then another hydroxyl ion approaches associate and similar interaction takes place. As a result hydroxyl cation is formed, and water molecules remained in the inner sphere are pushed out in the water solution.

Based on the statements of theoretical electrochemistry, chemistry of complex compounds and obtained current-time oscillogram (Fig.1), the transition mechanism of soluble complexes of metal ions into insoluble complexes (hydroxides) under the influence of alternating electric field is offered.

Experiment technique

In the Siberian State Aerospace University the method of water and water solutions cleaning from anions and cations by electrochemical process applying insoluble electrodes and alternating current was developed, besides an installation not requiring high operating and maintenance costs was designed [7-9].

In order to obtain some preliminary data the electrochemical method of discharged waters cleaning from some enterprises was tested.

A laboratory installation, which includes an electrolytic cell containing cells from plexiglass with alternating plates, was designed and manufactured for cleaning [9]. The volume of filled in liquid was 1 – 1.5 l.

Electrodes were 1 mm thick plates made from stainless steel 12X18H10T and titanium alloy OT4-0. The plates were installed alternately, the total number of plates varied from two to seven. The distance between plates was 10-12 mm. Electrodes were connected in parallel to a source of alternating current with frequency 50 Hz. The water temperature was 20-25 °C. Voltage was alternating of industrial frequency. After cleaning during 2-6 hours residue as metal hydroxide precipitated, then

atomic adsorption analysis of ions contained in water solutions was performed on spectrometer Thermo Scientific Solar M5 using the standard techniques.

These tests were performed using power supply source that permitted to receive alternating current voltage in the range from 1.6 to 120 V stepwise. To register the process parameters standard devices were used – voltmeters and amperemeters, to measure temperature – mercury thermometers and thermocouples (XK).

This method was applied to clean discharged waters of Federal State Unitary Enterprise Central Construction Department «Geophysics» and Ufa motor-building production association. The results of cleaning are presented in Table 1 and published in article [10].

Conclusions:

- experimental data prove the offered mechanism of soluble complexes of metal ions transition into insoluble complexes under the influence of alternating electric field;
- reactor for cleaning should be designed on the electrode pair 12X18H10T/OT4-0 because the oxide film on the titanium electrode has partially semiconductor properties and adds to the process required quasistationary state.
- current pulsing nature increases the role of hydrated electrons in the cleaning process which is a favourable condition for metal ions reduction.

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Электрохимический метод очистки сточных вод переменным током

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Широкому внедрению электрохимических методов обработки воды и водных растворов препятствуют энергозатраты, громоздкость оборудования и необходимость расходных материалов. В статье представлены результаты испытаний электрохимического способа очистки сточных вод промышленных предприятий и механизм этого процесса.

Ключевые слова: сточная вода, электрохимический способ, механизм процесса, переменный ток.
