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### SYNTHESIS AND STUDY OF NEW COMPLEX IRON-ALUMINUM REAGENT FOR WATER TREATMENT

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A reagent on the basis of the Fe(II),(III), Al(III),  $Cl^- - H_2O - OH^-$  system was synthesized. The synthesized reagent isn't a mixture of salts, but contains one or more poliheteronuclear iron-aluminum complexes. It possesses a number of improved characteristics in comparison with popular aluminum and iron-containing coagulants. On the basis of theoretical information and unique experimental data it has been proven that kinetics of reagent synthesis depends on a number of factors: aluminum surface nature, the initial concentration of iron(III) ions, the pH-value and the temperature of reactive media.

Key words: aluminum, iron, heteronuclear complexes, treatment, water

#### INTRODUCTION

The compounds of polyvalent metals, mainly those of iron and aluminum, are the effective coagulants for water treatment. There are inorganic coagulants which are widely used, e.g. aluminum sulphate and aluminum oxychloride, as well as iron salts, mainly sulfate and chloride.

Mixed coagulants on the basis of aluminum and iron compounds are the most efficient for water treatment. According to literature data (Rahna, 2003; Mamchenko, 2007, 2008; Lee, 2008; Sujana, 2009, 2010; Krishna Biswas, 2010; Rogachev, 2010; Chen, 2011), iron-aluminum coagulants in comparison with the coagulants, which contain only one ingredient, possess a number of advantages, such as reduction of residual Al(III) in water, acceleration of coagulated particles sedimentation, coagulation improvement at low temperatures, and coloration decrease. Raw material availability and a reliable technology to provide production of reagents with steady structure and characteristics necessary for water purification are the main requirements. Range expansion of the optimal pH-values due to a wide variety of hydrolysis products with individual properties can be observed during the application of this type of reagents.

Iron-containing waste which is hard to recycle are continuously generated, e.g. carbon steel pickling baths containing up to 100 g/l of iron ions and free acid at higher concentrations, or solid iron-containing waste as a scale, i.e. the dust from the metallurgy (Kumar, 2006). This kind of waste can be used in the production of reagents for water treatment.

Therefore, the problem of developing methods and technology for production of an efficient reagent on the basis of iron and aluminum from industrial iron-containing waste for water treatment is an urgent one.

The purpose of the work is to design a new route of obtaining new ironaluminum reagent from the solid and liquid industrial iron-containing waste and to study its chemical compound and physico-chemical properties.

The novelty of the work is not only a new route of obtaining ironaluminum coagulant, but also its chemical structure and physico-chemical properties. Therefore, an important aspect is an investigation of chemical structure, the existence region of complexes and their behavior in processes of natural water purification.

#### MATERIALS AND METHODS

The experiment was performed both with compact and narrowly fractionated samples of dispersed aluminum (purity was not less than 99.0 %), surface areas range were from 63.5 sm<sup>2</sup>/g (fraction of particles was 350 ± 55 microns) to 1000 sm<sup>2</sup>/g (25 ± 15 microns). FeCl<sub>3</sub>·6H<sub>2</sub>O (iron(III) concentration 0.1-2.0 mol/l) was as the main agent without further treatment. Industrial waste, contained iron-etching solutions, for example: FeCl<sub>3</sub> – 600-700 g/l, HCl – 20 g/l ( $\rho = 1.19$  g/sm<sup>3</sup>), 50 g/l Fe(II), was diluted in water in the ratio of 1:2.5. The solution was prepared by dissolving the metallurgical waste in hydrochloric acid in the ratio of 1:3 by weight.

### **Preparation of a water treatment reagent**

To obtain iron-aluminum coagulant the ingredients, such as ferric chloride(III) hexahydrate, aluminum foil and aluminum powder with particle sized between 20 and 200 microns, were used. Metallic aluminum was dissolved in 100 sm<sup>3</sup> iron chloride(III) solution with iron ion concentration 0.1-1.5 mol/l at room temperature and stirred for 10-15 minutes until the end of intensive gas generation and precipitation. Obtained precipitation was separated from the solution by magnetic separation. Hydrogen peroxide was used for the oxidation of Fe(II) to Fe(III) in the solution. The mixture was heated up to a temperature of 70-80°C for 0.5-1 hour. The concentration of iron(III) in the solution was determined by photometric method (ISO 6353-1:1982 Reagents for chemical analysis. Part 1: General test methods).

#### Methodology of kinetic studies

The kinetics of aluminum dissolution and the synthesis of the reagent were studied using thermostatic glass vessel equipped with a magnetic stirrer. Stirring rate was chosen so that aluminum microparticles were in a suspended state in the solution ( $\approx 250$  rpm).

Kinetics was studied by sampling at fixed time intervals. Then potentiometric titration was used for the determining iron(II) (dihromatometric method), and iron(III) (complexometric method) in samples according to the methods described in (Settle, 1997).

The kinetic curves were given in coordinates: C (Fe<sup>3+</sup>)-t, C (Fe<sup>2+</sup>)-t, W (Fe)-t.

Total iron content in solution was controlled by X-ray fluorescence analysis by universal Energy-dispersive X-ray spectrometer TXRF S2 PICOFOX with High Efficiency Module (Bruker, Germany). Measuring mode: crystal analyzer LiF 200, voltage 55 kV, current 35 mA, X-ray tube with tungsten anode, collimator 2, the counter SZ, discriminator 1.0 V, sensitivity  $3 \cdot 10^4 - 1 \cdot 10^5$  pulses/(s · sm<sup>2</sup>).

#### **Potentiometric studies**

The study of ionic equilibrium in solution were carried out in the M - $H_2O - OH^-$  system, where M = Fe(II), Fe(III), Al(III), by potentiometric titration according to (Sorokina, 2008). The pH-value was measured using high-resistance mV (pH Seven Multi S80-K, Mettler Toledo, Switzerland). pHmeter was checked against the standard buffer solutions with the pH-values are equal to 9.18 and 1.68. The measurement procedure was as follows: 25.0 sm<sup>3</sup> of 0.010 M salt solution was added to a glass beaker of 100 sm<sup>3</sup> and mixed with a magnetic stirrer. An indicating glass electrode was used for potentiometric studies grade, the reference electrode was the silver chloride electrode. At the established rate of mixing the solution was titrated by NaOH solution. At the end of each interval between drops - from 30 to 180 seconds - the titrated volume of NaOH and the corresponding pH-value were recorded. The pHvalue was adjusted by adding an appropriate quantity of hydrochloric acid in the stock solution. A solution of ferric chloride(III) passed previously through purified argon to remove dissolved oxygen. As the experiments were carried out in solution blown off by inert gas and under natural aeration conditions, it was showed that the presence of oxygen virtually did not influence the rate of reduction of iron(III) aluminum. Some investigations were carried out without deoxygenation of reaction mixture. During the titration the pH-values were observed to be corresponding to the beginning of precipitation. Precipitation bound was determined visually by the time of solution turbidity. After the appearance of sediment the large time interval between drops was kept, since heterogeneous process required more time for equilibrium state. According to the experiment the potentiometric titration curves of iron(II), aluminum(III) and their mixtures were given in coordinates  $pH = f (V_{NaOH})$ . Obtained experimental curves were converted into the curves of formation functions: n = f (pH), where  $n_{OH} = C_{NaOH} \cdot V_{NaOH} / C_M \cdot V_M$ , (C<sub>M</sub> and V<sub>M</sub> are the concentration and the initial volume of a salt solution).

#### **Proton-magnetic relaxation**

Measurements of the spin-lattice  $T_1$  and spin-spin relaxation time  $T_2$  were carried out by small-sized pulsed NMR relaxometer «Minispec MQ20» (Bruker, Germany) with working frequency 19.75 MHz (measurement error was up to 1%).

#### The methodology of the test coagulation

Coagulation test was performed by adding solutions of natural water obtained by adding a fixed amount of kaolin to distilled water, as well as to samples of natural water. The probe coagulation method was used for the investigating technological parameters of coagulation: the rate of flocculation, kinetics of discoloration. Kinetics of discoloration and the rate of flocculation were studied by monitoring water quality over time.

#### **RESULTS AND DISCUSSION**

#### **Dynamics of Iron-Aluminum Reagent Production Process**

This section provides data of kinetics study of aluminum dissolution in iron(III) chloride solutions and optimum conditions of this process. The dependence of coagulant synthesis process mechanism on aluminum surface nature and conditions, on the initial concentration of iron(III) ions, the pH-value, and the temperature of the solution was studied.

Thermal conditions of redox-process  $Fe(III) \rightarrow Fe(0)$  on aluminum microparticles were studied and characterized using thermodynamic characteristics.

Fig. 1 a presents the dependence of the reaction mixture temperature change on the size of aluminum particles.

In case of small size aluminum particles (10-40  $\mu$ m), a long induction period (up to 5 minutes) was observed. This can be explained by the tendency of small particles to aggregate and also by composition and properties of surface of oxide and hydroxide layers on aluminum particles (including the presence of organic constituent, i.e. a protective isolating lubricant on the surface of fine grained aluminum powder). Then there was a sharp increase of temperature with a short-term slowdown and further growth in the mode similar to thermal explosion, the development of which was limited only by the boiling temperature of the solution. The process was similar to the dependencies of temperature changes on time for particles of 70-100  $\mu m$  size; they are, however, characterized by a smaller induction period. In case of large size aluminum particles (195-305  $\mu m$ ), only a little smooth temperature increase, up to 318-323 K, and absence of bending were observed on the  $T - \tau$ curve. A considerable amount of heat emitted in this process was generated due to the aluminum ionization reaction. The warm-up started after a long induction period; the curve did not have steady section in the area of increase, which took place during the interaction between disperse aluminum and iron(III) chloride solutions.

Due to the considerable thermal effect of the reaction in case of small average size of aluminum particles and high transformation velocities, selfheating can occur, i.e. there is an essential increase of oxidized particles temperature and liquid phase period during redox-process relating to ambient temperature.

The concentration of iron(III) chloride has a considerable influence on the nature of temperature change of reaction mixture (Fig. 1 *b*). At low concentration (0.1 mol/l), the reaction mixture temperature practically does not increase, at average concentration (0.5 mol/l), a warm-up of suspension can be observed, and temperature dependence is characterized by a slight increase. At

high concentration of iron(III) ( $\geq 1.0 \text{ mol/l}$ ), a steady section is observed on the T –  $\tau$  curve, the reaction mixture temperature increases considerably in comparison with the previous cases. At average and high concentrations, the heating rate of solution grows; the highest value of temperature, however, does not change as it is limited by the boiling temperature of the liquid.



**Fig. 1.** Temperature change in reaction mixture during redox-process: *a) the* initial concentration of FeCl<sub>3</sub> 1.0 mol/l with various sizes of aluminum particles, μm: 1 – 10-40; 2 – 70-100; 3 – 195-305; *b)* aluminum (70-100 μm) with concentrations of FeCl<sub>3</sub>, mol/l: 1 – 0.1; 2 – 0.5; 3 – 1.0

Fig. 1 shows that a progressive heating of the reaction mixture, which reaches a steady value at 333-338 K, occurs while the Fe(III)  $\rightarrow$  Fe(II) reaction is transferring to the diffusion area. Active release of hydrogen is likely to occur at this temperature, which leads to the separation of oxide-hydroxide layer from the surface of aluminum particles. On the other hand, hydronium ions recovery on aluminum particles (and iron separation in case of the two-stage process) leads to strong alkalization of near cathode space at the interphase boundary. This, in its turn, causes corrosive destruction of protective oxide layer of aluminum particles, its ionization, and contributes to further growth of temperature which stops practically only after the full aluminum dissolution.

Fig. 2 illustrates that the nature of pH-value change during the process depends on the initial concentration of iron(III) chloride in the solution and, therefore, it influences the formation of heteronuclear iron and aluminum complexes. The rate of hydrogen evolution in this case is more than three orders of magnitude less than the rate of release of iron(0) Dresvyannikov, 2002). Such a difference from those presented in the literature data can be explained by the difference nature of the metal of base, the evolution of hydrogen only from deposited metal due to significant differences surge release of this gas on aluminum and iron (Sukhotin, 1981), and a high rate of deposition of the metal, caused the developed surface of the aluminum surface. In this case the pH-value of the solution significantly increases (the increment is about 2 units).



**Fig. 2.** Change of pH suspension and the evolution of hydrogen during redox-process of Fe(III) reduction from solution FeCl<sub>3</sub> (298 K; [Fe(III)] – 1.0 mol/l)

For the purpose of assessing the influence of temperature on kinetics of iron(III) reduction by aluminum particles, the experiments were carried out at the initial solution temperatures within the range of 278-338 K. The temperature was found to influence not only the velocity of separate phases, but also the mechanism of the process as a whole. Fig. 3 represents the typical kinetics curves of Fe(III) reduction by disperse aluminum at various temperatures of reactive media.



**Fig. 3.** Influence of temperature on mechanism of iron(III) ions reduction in aqueous solution on powder 70-100 μm at: *a*) 278 K, *b*) 293 K. 1 –Fe(III); 2 – Fe(II); 3 – Fe(0)

At low temperatures (278 K) the Fe(III)  $\rightarrow$  Fe(II) phase dominates, i.e. iron(0) is not released. With the increase of temperature, the process velocity increases and elemental iron release decreases.

Graphic method and the Ostwald-Noyes method showed that in case of aluminum surplus, decrease of the iron(III) ions concentration in the solution is described by the first order equation (or pseudo-first order). On the basis of experimental results, it can be assumed that the redox-process has the following stages (Dresvyannikov, 2002):

$$Fe(III) \xrightarrow{k_1} Fe(II) \xrightarrow{k_3} Fe(0)$$
(1)

For this scheme:

$$C(Fe(II)) = \frac{C_0(Fe(III)) \cdot k_1}{k_3 - k_1} \cdot (\exp(-k_1 \cdot \tau) - \exp(-k_3 \cdot \tau))$$
(2)

where  $k_1$ ,  $k_3$  – the rate constant of the respective stages, s<sup>-1</sup>.

Thus, the change of Fe(III) and Fe(II) concentration ratio is determined by velocity constants of consistent process stages; this was proven by the experimental kinetic dependencies.

# Chemical Balances in Aqueous Solutions of Fe (II), Fe (III), Al (III) Cations

In order to identify the composition of Fe and Al hydroxo-aqua complexes, which can be formed during the interaction of elemental Al with  $FeCl_3$  solution, a number of experiments were carried out using NMR relaxation and potentiometric titration methods.

Until present, polynuclear and heteronuclear compounds formed in the Fe(II), Al(III),  $SO_4^{2-}$ ,  $CI^- - H_2O - OH^-$ ,  $NH_3$  (A); Fe(II),(III), Al(III),  $CI^- - H_2O - OH^-$  (B) systems have not been identified completely, and description of their properties have been of a contradictory nature (Belousov, 1997; Dresvyannikov, 2008, 2010; El-Sharkawy, 2000; Luísa Durães, 2007; Mujika, 2011; Shinde, 2010).

Fig. 4 shows the distribution curves of different forms in the Fe(II), (III) –  $Al(III) - H_2O - OH^-$  system. The diagram shows that up to the pH-value 2.5 aluminum is in the form of aqua ions. In the range of the pH-value 2.5-3.6 gomopolinuclear aqua ions pass into the form  $[Al_2(OH)_2]^{4+}$  and  $[Al_2(OH)_3]^{3+}$ . At the pH-value of 3.6 gomopolinuclear begins forming the  $[Al_6(OH)_{12}]^{6+}$  complex, which share rapidly increases and reaches 93 mol.% at the pH-value 5.0, then its concentration also sharply reduces. Formed at the pH-value 4.0 the  $[Al(OH)_2Fe(OH)_2]^{2+}$  heteropolynuclear compound, which share up to 14 mol.% at the pH-value 5.0 and its concentration sharply increases with increasing the pH-value and reaches 100 mol.% at the pH-value 9.0.

So, in the Fe(II), (III) – Al(III) –  $H_2O$  –  $OH^-$  system (mother liquor after the interaction between FeCl<sub>3</sub> solution and elemental aluminum of the relative concentration  $C_{Al} = 1.64$ ,  $C_{Fe(II)} = 0.21$  mol/l) it is possible to mark out two heteronuclear compounds in the areas with the pH-value 4 and 9, with presumable stoichiometric composition [FeAl<sub>2</sub>(OH)<sub>5</sub>]Cl<sub>3</sub> and [Fe<sub>2</sub>Al<sub>4</sub>(OH)<sub>15</sub>]Cl<sub>3</sub> (Sorokina, 2010).



**Fig. 4.** Allocation diagram of ionic and molecular forms in the Fe(II),(III), Al(III),  $Cl^- - H_2O - OH^-$  system

The coefficients of spin-lattice relaxation efficiency (CRE) for three solutions were determined: A) Mohr salt solution with  $C_{Fe(II)} = 0.2133 \text{ mol/l}$ , pH 2.2; B) Mohr salt solution with  $C_{Fe(II)} = 0.2133 \text{ mol/l}$  in the presence of sodium chloride ( $C_{NaCl} = 3.0 \text{ mol/l}$ ), pH 2.2; C) mother liquor of coagulant with  $C_{Al(III)} = 1.6383 \text{ mol/l}$ ,  $C_{Fe(II)} = 0.2133 \text{ mol/l}$ ,  $C_{NaCl} = 3.0 \text{ mol/l}$ , pH 2.2.

The A solution shows the value of 390 l/mol s, and it corresponds to iron(II) aqua-ion, and the B solution has the value of 110 l/mol s. As water concentration (and protons concentration) decreased at such high content of NaCl (3.0 mol/l), the solution density was measured (1.1165 g/sm<sup>3</sup>), and water concentration was calculated ( $C_{water} = 49.1 \text{ mol/l}$ ). Such a low value of  $K_{E1}^{0}$  completely corresponds to the aggregation of iron(II) ions into FeCl<sup>+</sup> and the FeCl<sub>2</sub> chloride complexes (Shukla, 2009). The C solution shows a high value of  $K_{E1}^{0}$ =1100 l/mol s (solution density 1.1672 g/sm<sup>3</sup>, water concentration  $C_{water} = 48.2 \text{ mol/l}$ , appropriate correction into CRE was made). The increase of CRE during complex formation is possible in case of heteronuclear complexes with bridge water molecules and OH<sup>-</sup>-groups formation.

## Performance Properties of Reagent based on the Fe(II),(III), Al(III), $CI^- - H_2O - OH^-$ System

In order to test the functionality and to optimize a natural water treatment mode by the introduction of a reagent, a fixed amount of river water was taken and a dosed amount of reagent was supplied. The water quality was controlled in accordance with standard techniques ISO TC 147 «Water Quality». The pH-value of a coagulant is equal to be  $1.81 \pm 0.1$ . At the same time, the quality of treated water by the coagulant on the basis of aluminum sulphate (pH =  $2.5 \pm 0.5$ ) was also controlled.

The experimental results obtained during the coagulation test in natural water (the Volga river), showed that the iron-aluminum coagulant can get water with lower values of aluminum content and color, compared with a known aluminum-coagulant (Aluminum sulphate). Other indicators do not go beyond

the regulatory requirements ISO TC 147 «Water Quality». Technical indicators are comparable with ones for the proposed coagulant used in practice and an industrially produced sample.

The use of synthesized coagulant for drinking water treatment at a dosage of 10 to 120 mg/l is not dangerous for human health, the MPC in water aluminum and iron a few times less what is important in terms of increasing efficiency of water treatment.

It should be noted that the aspect of reducing the content of Al(III) during the treatment of natural water and preventing them from falling into the drinking water is very important in view of the latest views on the toxicity of Al(III) compounds. The proposed coagulant is approaching the international standards established for this type of water, which is associated with the tightening of requirements for the content of Al(III) compounds in water. Unlike other aluminum-containing coagulants, residual aluminum content in water after the treatment with the proposed reagent is less than 0.005 mg/liter. Low residual aluminum content in treated water after using an iron-aluminum coagulant showed that aluminum is in the poliheteronuclear complexes form.

Coagulation efficiency at various temperatures and process duration was investigated. The results are presented in Fig. 5. The ratio of iron to aluminum after re-calculation into  $Fe_2O_3$  and  $Al_2O_3$  in synthesized coagulant is 1:10.

In Russia, during winter, the efficiency of coagulation can decrease due to low temperatures, so coagulation efficiency can be increased using these new coagulants. It was estimated that at 5-15°C, aluminum sulphate and iron(III) chloride slow down both aggregation and sedimentation velocities. It can be explained by the increase of aluminum hydroxide stability under these conditions. The results of comparison of coagulation abilities showed that at 5-10°C, the coagulation efficiency of the synthesized coagulant is higher than that of the traditionally used aluminum and iron containing coagulants.

#### CONCLUSIONS

1. The scientific fundamentals of a new iron-aluminum reagent synthesis in aqueous media were developed. The process for obtaining the complex reagent for water treatment based on chemical interaction of iron-containing liquid medium and elemental aluminum was proposed.

2. The methods of formal and electrochemical kinetics were used for system analysis of processes in chloride-containing media during the contact of iron ions with elemental aluminum; the mechanism of iron redox-forms transformation was proposed.

3. It was established that mechanism of interaction between elemental aluminum and  $FeCl_3$  solution considerably depends on aluminum surface conditions, the initial concentration of iron (III) ions, the pH-value and the temperature of the solution. Self-heating effects of the reaction mixture, which accompany the recovery of iron (III) on an aluminum base, were observed. On the basis of kinetic investigation results, optimum conditions for the interaction of elemental aluminum and concentrated solutions of iron (III) chloride were specified.

4. The methods of potentiometry, NMR spectroscopy were used to specify chemical and phase compositions of the Fe(II),(III), Al(III), Cl<sup>-</sup> – H<sub>2</sub>O – OH<sup>-</sup> systems and to determine the conditions of heteronuclear complexes formation. It was revealed that the interaction between elemental aluminum and iron(III) chloride solution leads to the creation of heteronuclear coordination compounds of iron and aluminum in the solution, the general formula of substance is  $[Fe_mAl_nCl_k(OH)_q]^{2m+3n-k-q}$ , where the m, n, k, and q values depend on the concentrations of components and the pH-value of a solution. These substances seem to be the effective coagulants in comparison with the all-known iron and aluminum-containing reagents for water treatment.



Fig. 5. Dependency of natural water purification degree on: a) temperature; b) process duration

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#### REFERENCES

- Belousov V.M., Chertov V.M., Rozhkova É.V., Litvin V.I., Zazhigalov V.A., A sol-gel method for synthesizing porous iron-aluminum oxide substances and regulating their physicochemical characteristics, Theoretical and Experimental Chemistry, 1997, 33 (2), 103-105.
- Chen N., Zhang Z., Feng C., Zhu D., Yang Y., Sugiura N. Preparation and characterization of porous granular ceramic containing dispersed aluminum and iron oxides as adsorbents for fluoride removal from aqueous solution, Journal of Hazardous Materials, 2011, 186 (1), 863-868.
- 3. Dresvyannikov A.F., Kolpakov M.E. Kinetics of recovery Fe(III)→Fe(0) on aluminum in aqueous solutions, Russian Journal of Applied Chemistry, 2002, 75 (10), 1602-1607.
- Dresvyannikov A.F., Kolpakov M.E., Pronina E.V. Joint Reduction of Fe(III), Ni(II), and Co(II) Ions in Solution in Contact with Aluminum, Russian Journal of Applied Chemistry, 2008, 81 (11), 1879-1884.
- Dresvyannikov A.F., Kolpakov M.E., Pronina E.V. Synthesis of Nanoparticles of Iron Triade Metals in Water Solutions, Russian Journal of General Chemistry, 2010, 80 (10), 1901-1907.
- 6. El-Sharkawy E.A., El-Hakam S.A., Samra S.E. Effect of thermal treatment on the various properties of iron(III)-aluminum(III) coprecipitated hydroxide system, Materials Letters, 2000, 42 (№ 5), 331-338.
- Krishna Biswas, Kaushik Gupta, Arijit Goswami, Uday Chand Ghosh Fluoride removal efficiency from aqueous solution by synthetic iron(III)–aluminum(III)–chromium(III) ternary mixed oxide, Desalination, 2010, 255 (1-3), 44-51.
- 8. Kumar S., Kumar R., Bandopadhyay A. Innovative methodologies for the utilisation of wastes from metallurgical and allied industries, Resources, Conservation and Recycling, 2006, 48, 301-314.
- 9. Lee Sun-Jong, Lee Yoon-Jin, Nam Sang-ho Improvement in the coagulation performance by combining Al and Fe coagulants in water purification, Korean J. Chem. Eng., 2008, 25 (3), 505-512.
- Luísa Durães, Benilde F.O. Costa, Regina Santos, António Correia, José Campos, António Portugal – Fe<sub>2</sub>O<sub>3</sub>/aluminum thermite reaction intermediate and final products characterization, Materials Science and Engineering: A, 2007, 465 (1-2), 199-210.
- Mamchenko A.V., Gerasimenko N.G., Deshko I.I., Pakhar T.A. Efficiency of Aluminum-Iron Coagulants When Purifying Water of Clayey and Humic Matter, Journal of Water Chemistry and Technology, 2007, 29 (5), 238-245.
- Mamchenko A.V., Gerasimenko N.G., Deshko I.I., Pustovit V.M., Pakhar T.A. A mixed Chlorine-Containing Coagulant-Reagent for Purifying Natural and Waste Waters, Journal of Water Chemistry and Technology, 2008, 30 (3), 180-186.
- Mujika J.I, Lopez X., Rezabal E., Castillo R., Marti S., Moliner V., Ugalde J.M. A QM/MM study of the complexes formed by aluminum and iron with serum transferrin at neutral and acidic pH, J. Inorg Biochem., 2011, 105 (11), 1446-56.
- 14. Rahna K. Shamsudeen, Nisha K., Sugunan S. Acidity and aniline alkylation activity of mixed Fe-Al pillared montmorillonites, React. Kinet. Catal. Lett., 2003, 79 (1), 19-26.
- 15. Rogachev A.S., Mukasyan A.S. Combustion of Heterogeneous Nanostructural systems (Review), Combustion, Explosion, and Shock Waves, 2010, 46 (3), 243-266.
- 16. Settle A. Frank Handbook of Instrumental Techniques for Analytical Chemistry, Prentice Hall, 1997.
- 17. Shinde S.S., Rajpure K.Y. Investigation of structural, morphological, luminescent and thermal properties of combusted aluminium-based iron oxide, *Journal of Solid State Chemistry*, 2010, 183 (12), 2886-2894.

- 18. Shukla A.K., Hariprakash B. Chemistry, electrochemistry, and electrochemical applications, Iron, Encyclopedia of Electrochemical Power Sources, 2009, 744-750.
- Sorokina I.D., Dresvyannikov A.F., and Yusupov R.A. Mathematical Modeling of equilibria in the systems of Fe(II), SO<sub>4</sub><sup>2-</sup> H<sub>2</sub>O OH<sup>-</sup> (I); Fe(II), SO<sub>4</sub><sup>2-</sup> H<sub>2</sub>O OH<sup>-</sup>, and NH<sub>3</sub> (II); Fe(II) Al(III) H<sub>2</sub>O OH<sup>-</sup> (III) for optimization of synthesis heteronuclear compounds, Vestn. Kaz. Tekhol. Univ., 2008, 6 (part 1), 17-24.
- Sorokina I.D., Dresvyannikov A.F., Yusupov R.A., Devyatov F.V. Heteronuclear compounds formed in the systems based on Fe(II), Fe(III), Al(III), SO<sub>4</sub><sup>2−</sup>, Cl<sup>−</sup> – H<sub>2</sub>O – OH<sup>−</sup>, and NH<sub>3</sub>, Russian Journal of Applied Chemistry, 2010, 83 (4), 593-597.
- Sujana M.G., Anand S. Iron and aluminium based mixed hydroxides: A novel sorbent for fluoride removal from aqueous solutions, Applied Surface Science, 2010, 256 (23), 6956-6962.
- Sujana M.G., Soma G., Vasumathi N., Anand S. Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides from aqueous solutions, Journal of fluorine Chemistry, 2009, 130 (8), 749-754.
- 23. Sukhotin A.M. Handbook of Electrochemistry, Leningrad, Khimia, 1981.