

Investigation of aluminosilicic reagent interaction with iron in water by Mössbauer spectroscopy

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Abstract. Mössbauer spectroscopy is a required analytical technique in the investigations of water treatment process mechanism for purification from iron. In this paper the new-made aluminosilicic reagent for purification of water was described. This reagent was used for water purification from iron dissolved complexes. The precipitated sediment is obtained and investigated. The iron valence state and relative concentrations of these states were detected in sediment. The presence of superparamagnetic particles is established.

1. Introduction

Environmental human safety depends on the quality of the used water. Currently, the present problem is the treatment of man-made and waste waters everywhere. The sources of water for household needs are: surface waters and artesian waters. Artesian waters contain a complex of minerals which are various forms of ion-molecules, colloidal states, organic substances and iron compounds. The surface waters are still more vulnerable to anthropogenic pollution. In general, water under treatment contains inorganic salts, organic substances, dissolved and hydrated gases, aquatic organisms such as plankton, bacteria and viruses.

Today, there are no technological scheme of natural and wastewater treatment which works without using coagulants and flocculants [1]. This is proved due to the fact that the majority of natural and waste water in addition to suspended allocated solids released by devices of mechanical treatment (grit chamber and others) containing fine-grained pollutions, which removal is effectively possible after consolidation with coagulants and flocculants only.

It is widely known that artesian waters of Moscow and Moscow region are contaminated with iron. Sometimes the contamination index is higher than several times of the maximum permissible concentration which is 0.3 mg per liter. This scientific and applied research work is aimed to study the properties of a new reagent in aluminosilicic reagent (flocculant-coagulant) [3] containing aluminium sulfate and active silicic acid on example of removal of iron compounds. Create the physico-chemical model of the sorption artesian water from high iron content is the main purpose. Also it is needed to say that the excess iron ions are toxic for the organism, they react with the hemoglobin in the blood, cause of which decreases in blood oxygen levels also form insoluble compounds contaminating blood.

In this paper exactly there is a special interest of is the analysis of sediment water after reaction with reagent and the study of the valence state of iron of this sediment which contain last and its



mechanism of sorption in the process of interaction with the reagent. Iron interact with the natural waters which contains there as mineral and organic substances present in the water dissolved, colloidal and suspended which form a complex set of compounds. The main form of iron in artesian waters is complexes of ferrous iron in divalent state with dissolved inorganic and organic compounds.

The most effective and direct method to determine the chemical state of iron and its correlation between formation of nanostructure matrix and follow adsorption iron is the method of nuclear gamma-resonance Mössbauer spectrometer which supplies information about the isomer shift, quadrupole splitting. Research precipitated reagent (pellet) carried out by Mössbauer spectroscopy in transmission mode.

Nuclear gamma resonance method is able to detect the magnetic state of the valence iron in the reactants before and after reaction with water and to determine the quantity of iron (less than 0.1%) in the test sample also. Therefore, this method is suitable for analysis of substances with a low content of iron atoms. The aim of this work is to reveal the results of the interaction of the aluminosilicate coagulant-flocculant with the iron contained in the water. Mossbauer spectroscopy is used to study the process of interaction of the contaminated water with reagent.

2. Experimental technique

2.1. Method of preparation of sorption-coagulation-flocculation reagents and reaction process during cleaning

The aluminosilic reagent used in this paper, refers to a group of binary composites, acting simultaneously as a coagulant-flocculant. This reagent is produced from cheap aluminosilicate raw materials is of mining waste containing nepheline, syenite minerals [3]. The interaction nepheline with dilute sulfuric acid thus formed a mixture with potassium alum $KAl(SO_4)_2 \cdot 12H_2O$ and $NaAl(SO_4)_2 \cdot 12H_2O$ and hydrated silicic acid (nanoparticles)

$$(Na, K)_2SO_4Al_2(SO_4)_3 \cdot mH_2O + 2SiO_2 \cdot nH_2O.$$

This active reagent is applied as an aqueous solution with different concentrations of the main components which are nepheline and syenite. The addition of this made reagent in a weakly acidic, neutral or alkaline (pH range of the reagent of 5 or higher) causes hydrolysis processes occur, resulting in the formation of aluminum hydroxide having coagulation properties and hydrated silicic acid as is an inorganic flocculant. As a result of their chemical interaction is an association and formation of silico-supramolecular structures with high rate adsorption. Then self-organization of these structures is performed, possibly forming macrocomplexes such zeolite matrix (flocculation). Dynamics of synergetic effect in the aluminosilic reagent is poorly studied. The studies of reagent particle sizes carry out using the laser particle size analyzer Nanotrac Ultra (ISO 13321). In our case the particle size range is 40-200 nm.

The last resulting macrocomplexes adsorb pollutants as impurities contaminated water and consequently increase in size and in weight as result. In this process, there were an intense flocculation and a formation of flocs which are dropped to the bottom of the container. Then flocs are taken and dried and thus the obtained sediment takes the form of the little crystals which are used for investigations.

3. Mössbauer spectroscopy sample preparation.

These crystals of the sediment may have the size up to several mm. The crystal density is 2.0 g cm^{-3} . These crystals of the sediment are pulverized with using of a porcelain mortar for obtain the same-dimension crystals in form of a powder. The resulting powder filled in the molten paraffin and then mixed until a homogeneous mass. This mixture contains a known amount of paraffin and a known amount of the test material. The mixture warmed to the viscous state and placed in a cuvette with known parameters such as the area of a circle. After the cooling the obtained mixture can be used as a Mössbauer absorber. Paraffin is used for a Mössbauer absorber preparation as it is neutral substance

and it does not entail the reaction with the powder. The Mössbauer absorbers have prepared, their thickness is equal to $98 \pm 2 \text{ mg cm}^{-2}$.

The Mössbauer spectrometer (named YAGRS-6 "Persey") operating in the mode of constant velocities is used $^{57}\text{Co}(\text{Rh})$ was used as a source of resonant radiation. Isomer shifts are given relating to metallic iron. Mossbauer radiation detector is a scintillation detector with a thin NaJ (Tl) crystal (250 microns). The spectrometer is calibrated using the standard thin absorber of alpha-iron. The fitting of spectra is carried out using programme Univem MS.

The total iron content in the powder was determined by x-ray fluorescence spectrometry (RF-spectrometry). X-ray fluorescence spectrometer of system INNOV-X Series ALPHA SERIES TM was used.

RF spectrometry is used to identify elements in the substance, an element is identified by his characteristic wavelength (λ) or energy (E) of X-rays. The concentration of the identified element is determined by measuring the intensity of the line of its characteristics. RF-spectrometry ultimately determine the elemental composition of the material.

The selected powder pellet with weight of 100 mg has been used for analysis. The analysis had showed that the powder contains elements such as Fe, Zn, Zr, Cu and other heavy elements. Heavy elements are in very small quantities. The iron content in the powder is approximately 2% of a total weight. The content of the Mössbauer isotope ^{57}Fe will be $0.02 \times 0.0214 = 0.000428$, where 0.0214 is the percentage of ^{57}Fe in natural iron. The ^{57}Fe iron density in the absorber is $0.000428 \times 98 \text{ (mg cm}^{-2}\text{)} = 0.04 \text{ mg cm}^{-2}$. This low content of the ^{57}Fe requires much time to obtain a Mössbauer spectrum.

4. Results and discussion.

The results of Mössbauer investigations are shown in Figures 1, 2 and tables 1, 2. Figure 1 shows the Mössbauer spectrum of ^{57}Fe in the sediment produced from reaction of the aluminosilicic with water. The spectrum is recoded at 293 K. The shape of the spectrum is the superposition of lines of hyperfine magnetic splitting of the magnetic phases and lines of quadrupole splitting of the paramagnetic phases. The Mössbauer spectra parameters obtained in paper [4] were used for fitting. The Mössbauer spectra parameters such as values of the hyperfine magnetic field H_{eff} , quadrupole splitting Q_s , isomers shift IS and areas of spectra lines are used for phases and compounds identifications. One could see that the lines of magnetic phases have low intensities.

The Mössbauer spectrum (Fig.1) is fitted using the model of two paramagnetic phases. The obtained Mössbauer spectrum parameters are presented in Table 1. The main share of the iron ($\sim 86\%$) is in the trivalent paramagnetic state ($IS=0.34 \pm 0.02 \text{ mm s}^{-1}$, $Q_s=0.78 \pm 0.02 \text{ mm s}^{-1}$) and another part ($\sim 14\%$) is in the paramagnetic phase in divalent state ($IS=1.14 \pm 0.02 \text{ mm s}^{-1}$, $Q_s=2.38 \pm 0.02 \text{ mm s}^{-1}$).

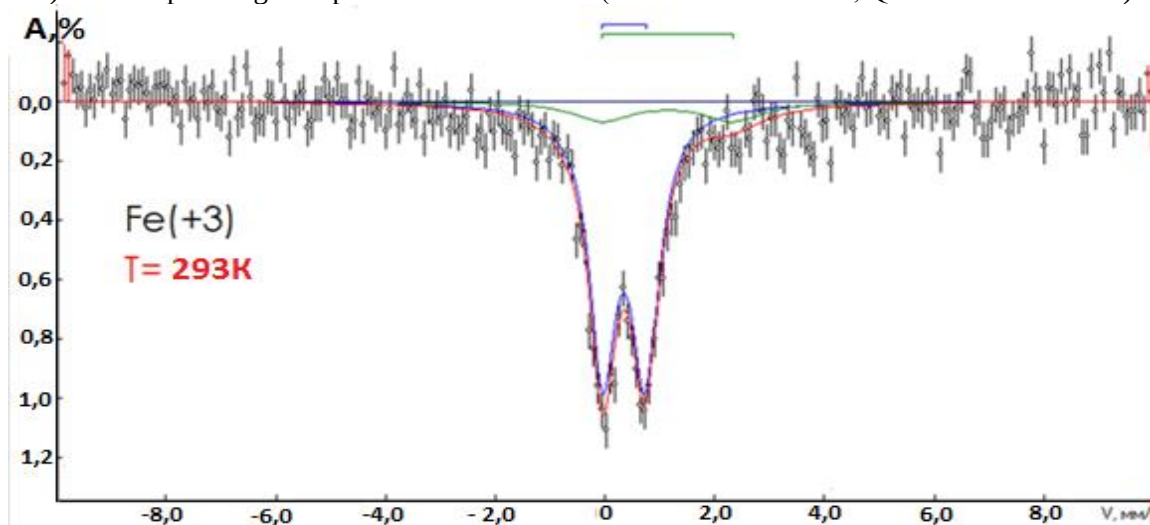


Figure 1. Mössbauer spectrum of ^{57}Fe in the sediment. Spectrum is obtained at 293K.

It is supposed that in initial water the iron is in divalent state than one can concludes that during reaction with reagent (alumosilicate coagulant-flocculant) the main share of the iron transforms in to the trivalent state. The rest iron reacts with reagent too and it is found in sediment in the divalent state. For identification of the obtained phases the spectrum is registries at liquid nitrogen temperature.

Table 1. Mössbauer spectrum parameters at 293 K of the sediment produced from alumosilicic reagent.

Phase	IS, mm/s	QS, mm/s	S,rel.,%
Fe ³⁺ doublet 1	0.35±0.02	0.78±0.02	88±1
Fe ²⁺ doublet 2	1.14±0.02	2.38±0.02	12±1

Figure 2 shows the Mössbauer spectrum of ⁵⁷Fe in the sediment. The spectrum is recoded at temperature of liquid nitrogen. This Mössbauer parameters are presented in Table 2. Mössbauer spectrum obtained at 77 K shows the superposition of lines of hyperfine magnetic splitting of the magnetic phases and lines of quadrupole splitting of the paramagnetic phases. The intensities of magnetic phase lines are increased. This indicates the existence of superparamagnetic particles in the sediment. It follows from knowledge that with decreasing of temperature the part of superparamagnetic particles shows hyperfine magnetic splitting.

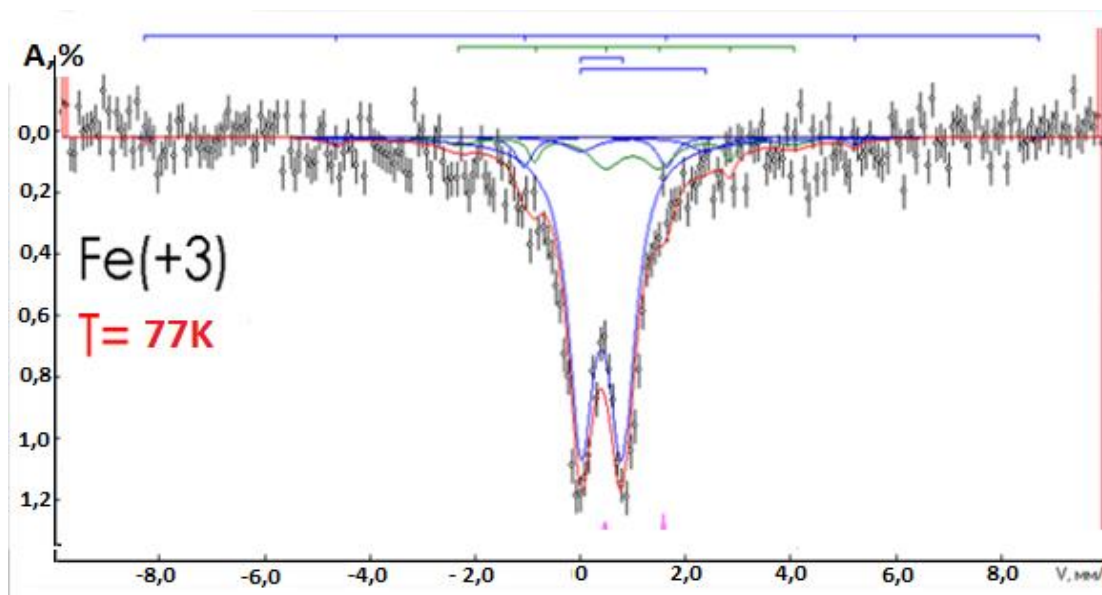


Figure 2. Mössbauer spectra of ⁵⁷Fe in the sediment at 77K.

Table 2. Mössbauer parameters if the sediment produced from alumosilicic reagent at 77 K.

Phase	IS, mm/s	QS, mm/s	H _{eff} , T	S,rel.,%
Fe ³⁺ doublet 1	0.45±0.05	0.89±0.05	----	77 ±1
Fe ²⁺ doublet 2	1.21±0.05	2.43±0.05	----	4±1
Fe ³⁺ sextet 1	0.34±0.05	0.02±0.05	51.8±0.3	14±2
Fe ²⁺ sextet 2	0.93±0.05	0.02±0.05	19.2±0.6	5±2

The Mössbauer spectrum parameters of the paramagnetic phase with trivalent iron state ($IS=0.34\pm0.02$ mm s⁻¹, $QS=0.78\pm0.02$ mm s⁻¹, $S=88\pm2$) at room temperature and magnetic phase with trivalent iron state ($IS=0.34\pm0.02$ mm s⁻¹, $QS=0.02\pm0.05$ mm s⁻¹, $H_{\text{eff}}=51.8$ T, $S=14\pm2$) at liquid nitrogen temperature present the same iron composition in superparamagnetic state. The iron composition as $\alpha\text{-Fe}_2\text{O}_3$ at the same temperatures has approximately the same Mössbauer [4] spectra parameters.

5. Conclusion

1. The aluminosilicic reagent is prepared and its reactions with water is carried out, and products of the reaction such as sediment are investigated.
2. The product contains elements such as Fe, Zn, Zr, Cu and other heavy elements in small concentrations.
3. It has been shown that main part of iron (88%) is in trivalent state, another part (~12%) is in divalent state.
- 4 The existence of superparamagnetic iron containing particle in the sediment are established.

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