

Mössbauer spectroscopy research of interaction of aluminosilicic reagent and iron dissolved in water

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Abstract. The aim of this work is to reveal the results of aluminosilicic reagent interaction with iron compounds contained in the water. This reagent is simultaneously coagulant-flocculant and adsorbent. The iron atoms state is studied in the reagent and in reacted sediment. The valence state of iron atoms are determined in the reagents and sediments. The existence of iron containing superparamagnetic particles in the sediment is shown.

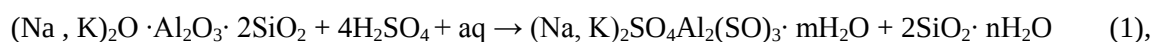
1. Introduction

Artesian waters contain complexes of iron compounds. The surface waters are vulnerable to anthropogenic pollution. People's health depends on water purity, for example, consumption of water with the high iron content could develop the blood disease. Therefore the process of water treatment from dissolved iron is necessary. In modern technological scheme of natural and wastewater treatment coagulants and flocculants are used. To purify water from all contaminants the aluminosilicic reagent has been used [1]. This reagent is a coagulant-flocculant and simultaneously an adsorbent [2,3]. Water was purified from iron and the precipitates or sediment were obtained with coloured rust. The main form of iron in the artesian waters taken from Moscow region is complexes of ferrous iron in divalent state with dissolved inorganic and organic compounds. The most effective and direct method to determine the iron chemical state and to detect iron nanoparticles is the Mössbauer spectroscopy which supplies an information about the isomer shift and quadrupole splitting.

2. Experimental

2.1. Method of preparation of sorption-coagulation-flocculation reagent

The sorption-coagulation-flocculation reagent is produced from cheap aluminosilicate raw which is the nepheline [3]. The model formula of the reaction is:



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which includes hydrated silicic acid (nanoparticles).

The active reagent such as $(\text{Na, K})_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot m\text{H}_2\text{O}$ with different concentrations of the main components is introduced into the aqueous solution. Its chemical interaction in water leads to an association and formation of silico-supramolecular structures with high rate adsorption. Then the self-organization of these structures forms macrocomplexes, such as zeolite matrix. Dynamics of synergetic effect in the aluminosilicic reagent is not well studied. Size of the reagent particles in the range 40-200 nm was determined, in our case, using the laser particle size analyzer Nanotrak Ultra (ISO 13321).

The resulting matrix molecules adsorb pollutants such as impurities in contaminated water and as a result increase in size and weight. During this process an intense flocculation occurs and nascent flocs drop to the bottom of the container. The flocs were picked out and dried. Thus, obtained little crystals of sediment were used for investigations.

2.2. Sample preparation for Mössbauer spectroscopy.

The Mössbauer absorbers were prepared from the reagent before interaction with water and from sediments. The crystals of the sediment and initial reagent were pulverized using a porcelain mortar to obtain a powder of same-dimension crystals. The crystal density was 2.0 g cm^{-3} . The resulting powder filled in the molten paraffin and then mixed until a homogeneous mass. The thickness of absorbers were $40\text{-}100 \text{ mg cm}^{-2}$. The content of the Mössbauer isotope ^{57}Fe was approximately 0.012 mg cm^{-2} . The used Mössbauer spectrometer operated in the mode of constant acceleration. Mössbauer radiation detector with a thin NaJ (Tl) crystal (200 microns) was used. The spectrometer was calibrated using the standard thin absorber of alpha-iron. ^{57}Co (Cr) was used as a source of resonant radiation. The isomer shifts are given relatively a-Fe. Mössbauer spectra were obtained at room temperature and 77 K. The fitting of spectra is carried out using Univem MS.

3. Results and discussion

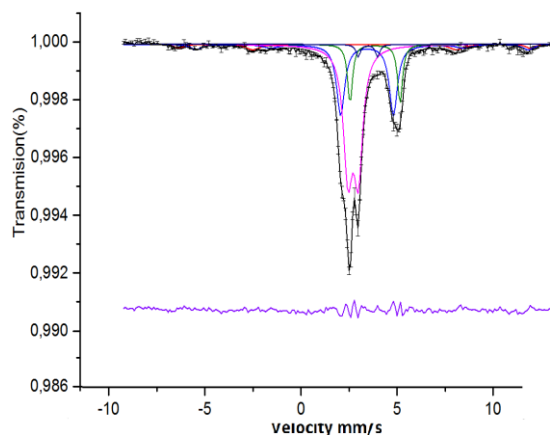


Figure 1. Room temperature Mössbauer spectra of nepheline minerals.

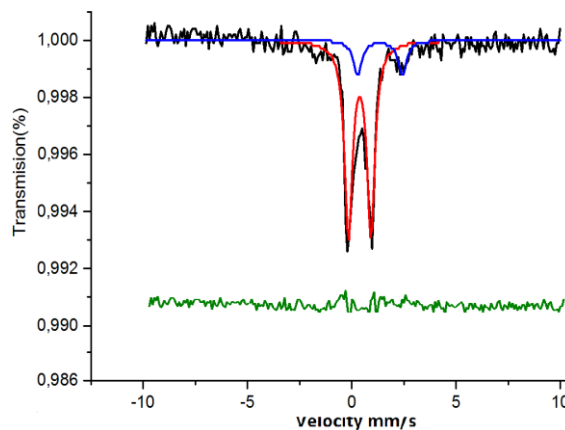


Figure 2. Room temperature Mössbauer spectra of dried reagent

In Figure 1 the room temperature Mössbauer spectra and fitting for nepheline minerals before reaction with sulfuric acid are shown. The spectra were fitted with two magnetic components and two or three paramagnetic components. The main subspectra of the iron ($\sim 60\%$) is in trivalent paramagnetic state ($\text{IS} = 0.36 \pm 0.02 \text{ mm s}^{-1}$, $\text{QS} = 0.46 \pm 0.02 \text{ mm s}^{-1}$). All parameters of this spectra are presented in Table 1. Results of the fitting and analysis of the experimental spectra of nepheline shown that $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles with sizes approximately of 30 – 70 nm are contained in nepheline [6]. The room

temperature Mössbauer spectra of the dried reagent are shown in Figure 2 as an addition. Main part (~90%) of these spectra is doublet with $IS = 0.37 \pm 0.02 \text{ mm s}^{-1}$, $QS = 1.01 \pm 0.02 \text{ mm s}^{-1}$.

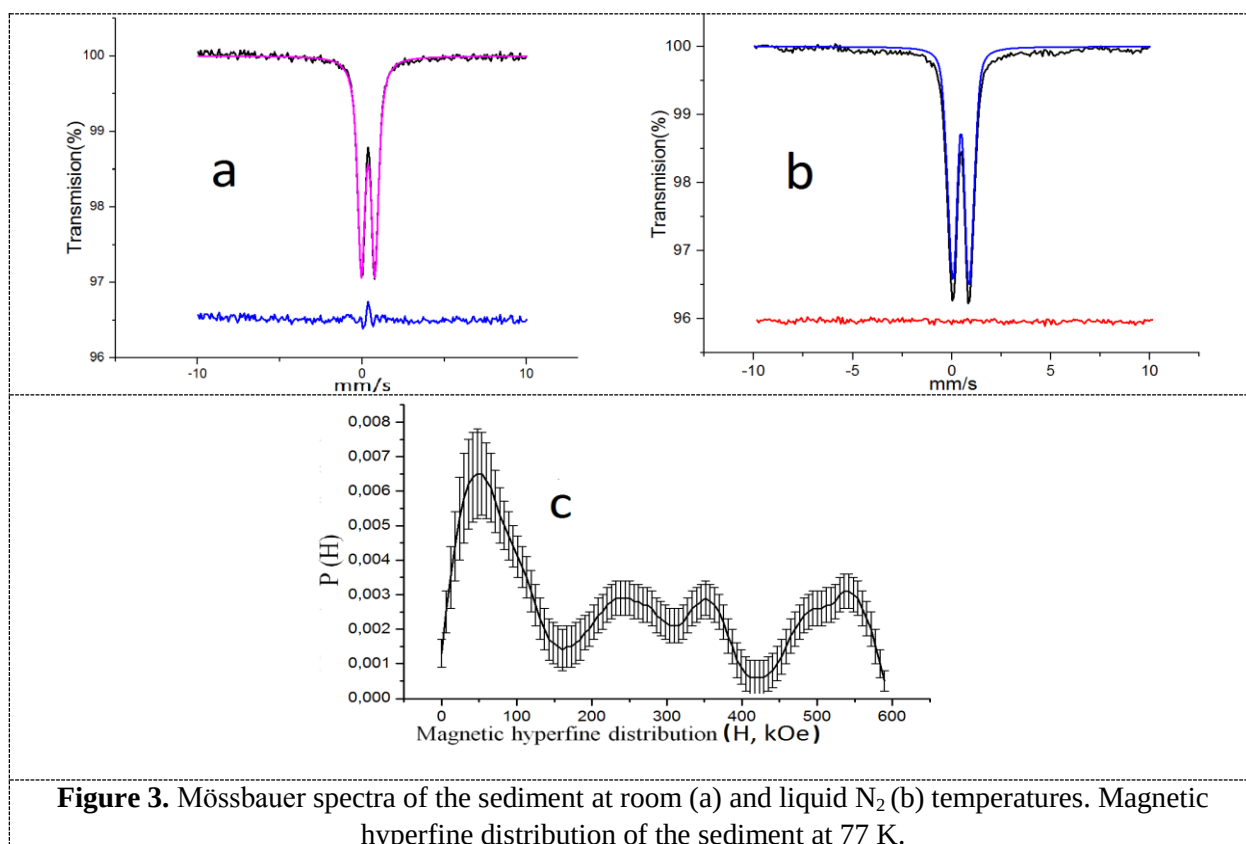
Table 1. Mössbauer parameters of the nepheline minerals used for synthesis aluminosilicic reagent $T = 293 \text{ K}$.

Phase	IS, mm/s	QS, mm/s	H_{eff} , T	G, mm/s
Sextet 1	0.43 ± 0.05	0.00 ± 0.05	49.1	0.4242
Sextet 2	0.88 ± 0.05	-0.21 ± 0.05	46.3	0.5826
Doublet 1	0.36 ± 0.05	0.46 ± 0.05		0.4884
Doublet 2	1.34 ± 0.05	2.24 ± 0.05		0.2609
Doublet 3	1.02 ± 0.05	0.87 ± 0.05		0.2328

The result spectra of the reaction of reagent with dissolved iron in the water are shown in Figure 3. The spectra were obtained at 293 K (a) and 77 K (b). The shape of the spectra corresponds to lines of hyperfine quadrupole splitting of paramagnetic phases. The main share of 90% of the iron is in the paramagnetic phase in the trivalent state (isomer shift $IS = 0.35 \pm 0.02 \text{ mm/s}$, quadrupole splitting $QS = 0.82 \pm 0.02 \text{ mm/s}$). The fitting of the spectra at 77 K gives doublet with paramagnetic phase ($IS=0.45 \pm 0.02 \text{ mm/s}$, $QS = 0.87 \pm 0.02 \text{ mm/s}$). The measurements at $T = 77 \text{ K}$ showed that, along with the existence of the paramagnetic phase, a small amount of magnetic phases are contained in the sample. In this phase the iron is in trivalent and divalent states. This indicates there are the iron superparamagnetic particles in precipitates. Calculated size of these particles is $d \sim 3.7 \text{ nm}$ [5]. The distribution of hyperfine magnetic fields of the sediment at 77 K was obtained (Figure 3c). This distribution allows distinguishing four magnetic phases. Fitting of the spectrum obtained at 77 K by one doublet and four sextets gives precise results for IS, QS, H_{eff} in these magnetic phases (Table 2). As the lines of these phases are not visible in spectra measured at room temperature, we conclude that these phases are in superparamagnetic state. So, the process of water treatment by reagent gives sediment in which the iron is in the form of nanoparticles. Using known data [6], the phase with lines of quadrupole splitting (doublet 1, Table2) can be identified as paramagnetic $\gamma\text{-Fe}_2\text{O}_3$ compound. The sextets 3 and 4 may be caused by presence of $\gamma\text{-Fe}_2\text{O}_3$ $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles in the superparamagnetic state. The magnetic phases with $H_{\text{eff}} = 24.9 \pm 0.2 \text{ T}$ and $H_{\text{eff}} = 34.5 \pm 0.2 \text{ T}$ (sextets 1 and 2 Table2) were not identified at this step of investigations.

Table 2. Mössbauer parameters of the sediment at liquid N_2 temperature.

Phase	IS, mm/s	QS, mm/s	H_{eff} , T	G, mm/s
Doublet 1	0.45 ± 0.05	0.86 ± 0.05		0.55 ± 0.05
Sextet 1	0.16 ± 0.05	0.02 ± 0.05	24.9 ± 0.2	0.77 ± 0.05
Sextet 2	0.18 ± 0.05	-0.21 ± 0.05	34.5 ± 0.2	0.26 ± 0.05
Sextet 3	0.60 ± 0.05	-0.48 ± 0.05	49.9 ± 0.2	0.76 ± 0.05
Sextet 4	0.28 ± 0.05	0.19 ± 0.05	54.9 ± 0.2	0.39 ± 0.052



4. Conclusion

Mössbauer spectroscopy was applied to investigate nepheline minerals, initial component for reagent preparation, reagent itself and product of its reaction with water, sediment.

The following was shown.

a) In the nepheline minerals the iron forms several complex paramagnetic and magnetic phases with Fe²⁺ and Fe³⁺ ions. Size of nanoparticles in magnetic state was estimated as 30–70 nm.

b) The sediment contains one paramagnetic and four superparamagnetic phases of iron in Fe²⁺ or Fe³⁺ valance state. One of these phases was identified as γ -Fe₂O₃ in magnetic and paramagnetic states. One of the magnetic phases was identified as α -Fe₂O₃ nanoparticles.

Acknowledgements

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