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

D Y Feklistov¹, V P Filippov¹,², I M Kurchatov¹, N I Laguntsov¹, V A Salomasov² and Yu V Permyakov³

¹ National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, 115409 Moscow, Russia
² JSC Aquaservice, Kashirskoe shosse 31, 115409 Moscow, Russia
³ VNIIFTRI, 141570, Mendeleevo, Solnechnogorskiy district, Moscow region, Russia

E-mail: vpfilippov@mephi.ru

Abstract. The aim of this work is to reveal the results of alumosilicic 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 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 alumosilicic 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-floccilation reagent is produced from cheap aluminosilicate raw which is the nepheline [3]. The model formula of the reaction is:

\[(Na, K)_2O \cdot Al_2O_3 \cdot 2SiO_2 + 4H_2SO_4 + \text{aq} \rightarrow (Na, K)_2SO_4 \cdot Al_2(SO)_4 \cdot mH_2O + 2SiO_2 \cdot nH_2O \quad (1)\]

¹ To whom any correspondence should be addressed.
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 alumosilicic 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 Nanotrac 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 40-100 mg cm\(^{-2}\). The content of the Mössbauer isotope \(^{57}\text{Fe}\) 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. \(^{57}\text{Co}\) (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 (~60%) is in trivalent paramagnetic state (\(IS = 0.36 \pm 0.02\) mm s\(^{-1}\), \(QS = 0.46 \pm 0.02\) 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].
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 ± 0.02 mm s\(^{-1}\), QS = 1.01 ± 0.02 mm s\(^{-1}\).

Table 1. Mössbauer parameters of the nepheline minerals used for synthesis aluminosilicic reagent \(T = 293\) K.

| Phase   | IS, mm/s   | QS, mm/s   | \(H_{\text{eff}}\), 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 ± 0.02 mm/s, quadrupole splitting QS = 0.82 ± 0.02 mm/s). The fitting of the spectra at 77 K gives doublet with paramagnetic phase (IS=0.45 ± 0.02 mm/s, QS =0.87 ± 0.02 mm/s). The measurements at \(T = 77\) 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 \(d \sim 3.7\) 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, \(H_{\text{eff}}\) 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 \(\gamma\)-Fe\(_2\)O\(_3\) compound. The sextets 3 and 4 may be caused by presence of \(\gamma\)-Fe\(_2\)O\(_3\) \(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles in the superparamagnetic state. The magnetic phases with \(H_{\text{eff}} = 24.9 \pm 0.2\) T and \(H_{\text{eff}} = 34.5 \pm 0.2\) 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   | \(H_{\text{eff}}\), 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 Fe$^{2+}$ and Fe$^{3+}$ 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 Fe$^{2+}$ or Fe$^{3+}$ valance state. One of these phases was identified as $\gamma$-Fe$_2$O$_3$ in magnetic and paramagnetic states. One of the magnetic phases was identified as $\alpha$-Fe$_3$O$_4$ nanoparticles.

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References

[1] Laguntsov N I, Neschimenko Y P, Feklistov D Y 2008 Nanotechnology in water treatment processes Proceedings of Nanotechnology International Forum «Rusnanotech 08» (Moscow) 609-611
[2] Kim V E, Laguntsov N I, Karpukhin V F, Lisujk B S 1998 The method of water purification. Patent RU № 2114787 B.I. № 19
[3] Kurchatov I M, Laguntsov N I, Neschimenko Y P, Feklistov D Y 2015 The reagent-sorption technology of water treatment Physics Procedia 72 89-92
[4] Brent Fultz  2011 Mössbauer Spectrometry in Characterization of Materials ed. Elton Kaufmann (John Wiley, New York)

[5] Morup S, Frandsen C, Hansen M F, 2010 Uniform excitations in magnetic nanoparticles Belstein J. Nanotechnol. 1, 48-54

[6] Skryarova A, 2010 Mössbauer spectra of iron oxides in the bulk and nanocrystalline states, Lapeeranta university of technology Faculty of Technology Master’s Degree Programme in Technomathematics and Technical Physic