

Mössbauer investigation of a nepheline substrate used for preparing a water treatment reagent

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Abstract The aim of this work is to reveal the results of the reaction of nepheline mineral with concentrated sulfuric acid. The valence states of iron atoms are determined in the nepheline and the reacted nepheline. The existence of iron containing magnetic particles in the sediment is shown. The differences in the lineshape are discussed also and are associated with a transfer from one phase to another of the magnetic particles.

Keywords Mossbauer spectroscopy · Zeolite · Superparamagnetic iron oxide · Alumosilicic coagulant-flocculant

1 Introduction

In the technology of water treatment it is proposed to use a alumosilicic reagent which simultaneously is coagulant, flocculant and adsorbent [1, 2]. This reagent can also be used for iron compounds isolated from water. The reagent is the result of the mixing of nepheline with concentrated sulfuric acid. During the synthesis process of this reagent some part of the iron can transform and stays in the reagent. We know that consumption of water with a high iron content could develop blood disease, and also that this water has a bad smell

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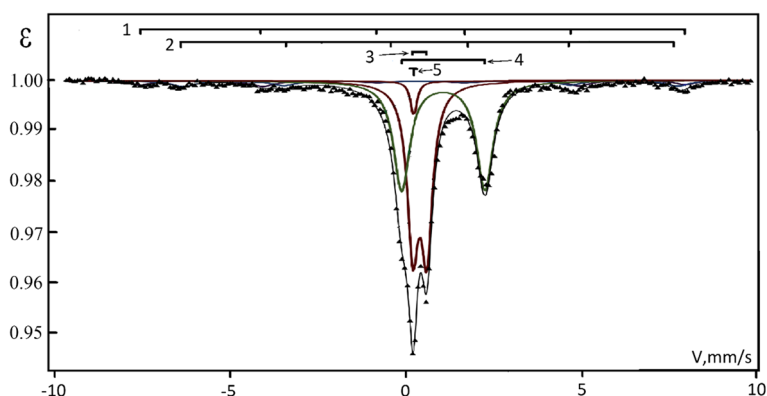


Fig. 1 Room temperature Mössbauer spectrum of nepheline minerals

and taste. Referring to the standards on the quality of water intended for human consumption (The European Drinking Water Directive), the iron concentration in water intended for human consumption should be less than 0.2 mg/l. It is therefore necessary to purify the water from dissolved iron. It is important also to show the initial iron content in nepheline used in the reagent preparation. This information can be useful for preparation of the model reagent where nepheline is used. The most effective and direct method to determine the iron chemical state and to detect iron nanoparticles is Mössbauer spectroscopy.

2 Experimental

2.1 Sample preparation for Mössbauer spectroscopy

The first Mössbauer absorbers have been prepared from the nepheline before interaction with concentrated sulfuric acid takes place. The second set of Mössbauer absorbers were prepared from the product of the nepheline interaction with concentrated sulfuric acid (redox reaction). The initial nepheline and reaction products densities were 2.6 g cm^{-3} . The content of the Mössbauer isotope ^{57}Fe was approximately 0.012 mg cm^{-2} . The Mössbauer spectrometer was operated in constant acceleration mode. A Mössbauer radiation detector with a thin NaI(Tl) crystal (200 microns) was used. The spectrometer was calibrated using a standard thin absorber of alpha-iron. ^{57}Co (Cr) was used as a source of resonant radiation. The isomer shifts are given relatively $\alpha\text{-Fe}$. The Mössbauer spectra were obtained at room temperature. Spectra were fitted using the program UNIVEM MS [3].

2.2 Results and discussion

The Mössbauer spectrum of nepheline minerals before reaction with concentrated sulfuric acid is shown in Fig. 1. The spectrum was fitted using a model of two sextets of magnetic phases, two doublets of paramagnetic phases and one singlet of paramagnetic phase. The sextet 1 and 2 are described by lines of hyperfine magnetic field $H_{\text{eff}1} = 49.2 \text{ T}$, $IS_1 = 0.30 \pm 0.05 \text{ mm s}^{-1}$, $QS_1 = 0.10 \pm 0.05 \text{ mm s}^{-1}$ (iron is in trivalent magnetic state) and $H_{\text{eff}2} = 44.5 \text{ T}$, $IS_2 = 0.39 \pm 0.05 \text{ mm s}^{-1}$, $QS_2 = 0.41 \pm 0.05 \text{ mm s}^{-1}$ (iron is in divalent paramagnetic state). The magnetic phase with these two sextets can be identified

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

Phase	IS, mm/s	QS, mm/s	H_{eff} , T	S_{rel} , %
Sextet 1	0.30 ± 0.05	-0.25 ± 0.05	49.2 ± 0.3	5.59
Sextet 2	0.65 ± 0.05	0.10 ± 0.05	44.5 ± 0.3	8.40
Doublet 1	0.39 ± 0.05	0.41 ± 0.05		42.36
Doublet 2	1.07 ± 0.05	2.42 ± 0.05		41.97
Singlet 1	0.21 ± 0.05			2.68

as the compound Fe_3O_4 . The doublet 1 ($\text{IS} = 0.39 \pm 0.05\text{ mm s}^{-1}$, $\text{QS} = 0.41 \pm 0.05\text{ mm s}^{-1}$, $S \sim 42\%$) represents iron which is in a trivalent paramagnetic state and the doublet 2 ($\text{IS} = 1.07 \pm 0.05\text{ mm s}^{-1}$, $\text{QS} = 2.42 \pm 0.05\text{ mm s}^{-1}$, $S \sim 42\%$) represents iron which is in a divalent paramagnetic state. The parameter S represents the relative spectral line area of the given phase. A paramagnetic phase characterized by a singlet line ($\text{IS} = 0.21 \pm 0.05\text{ mm s}^{-1}$, $S \sim 2.68\%$) represents iron which is in trivalent paramagnetic state. The obtained parameters of the Mössbauer spectrum components are given in a Table 1.

The paramagnetic phase described with lines of quadrupole splitting $\text{IS} = 0.39 \pm 0.05\text{ mm s}^{-1}$, $\text{QS} = 0.41 \pm 0.05\text{ mm s}^{-1}$ (doublet 1 Table 1) can be identified as nanoparticles of $\gamma\text{-Fe}_2\text{O}_3$ [4, 5]. The paramagnetic phase, described with lines of the doublet 2 ($\text{IS} = 1.07 \pm 0.05\text{ mm s}^{-1}$, $\text{QS} = 2.42 \pm 0.05\text{ mm s}^{-1}$, Table 1) with quite large IS and QS, can be identified as Fe oxide compound with the structure where iron atoms are substituted by Al or Si atoms [6]. The main part of iron is in paramagnetic state.

The spectrum of the product of the nepheline interaction with concentrated sulfuric acid (redox reaction) is shown in Fig. 2. The spectrum was obtained at 293 K. This spectrum is also fitted in the assumption of the existence of two magnetic phases characterized by the lines of sextets, two paramagnetic phases characterized by the lines of doublets and one paramagnetic phase characterized by the line singlet. The results of the fitting are given in Table 2. The paramagnetic lines of the initial nepheline and the lines of the reaction product are compared and are found to be different.

The sextet 1 with hyperfine magnetic field $H_{\text{eff}1} = 48.4\text{ T}$, $\text{IS}_1 = 0.27 \pm 0.05\text{ mm s}^{-1}$, $\text{QS}_1 = -0.01 \pm 0.05\text{ mm s}^{-1}$ differs from sextet 1 of nepheline (Table 1) by its QS. The magnetic phase with those spectrum parameters can be identified as $\gamma\text{-Fe}_2\text{O}_3$ [5, 6] where iron is in a trivalent magnetic state. The second sextet with hyperfine magnetic field $H_{\text{eff}2} = 39.0\text{ T}$, $\text{IS}_2 = 0.89 \pm 0.05\text{ mm s}^{-1}$, $\text{QS}_2 = 0.00 \pm 0.05\text{ mm s}^{-1}$) represents iron, which is in a divalent magnetic state. The magnetic phase described by sextet 2 is not identified. The main area part ($S \sim 87\%$) of the spectrum consists of the lines of the hyperfine quadrupole splitting of paramagnetic phases, which are in the trivalent state ($\text{IS} = 0.36 \pm 0.05\text{ mm s}^{-1}$, $\text{QS} = 0.41 \pm 0.05\text{ mm s}^{-1}$, $S \sim 42\%$) and the lines of the hyperfine quadrupole splitting of paramagnetic phases, which are in the trivalent state ($\text{IS} = 1.08 \pm 0.05\text{ mm s}^{-1}$, $\text{QS} = 2.49 \pm 0.05\text{ mm s}^{-1}$, $S \sim 42\%$). The phase described by doublet 1 can also be identified as compound $\gamma\text{-Fe}_2\text{O}_3$ which is in the paramagnetic state as in the case of the initial nepheline. The spectrum parameters of doublet 2 of the reacted nepheline differ from the parameters of doublet 2 of nepheline only in the area of the spectrum lines (42 % for nepheline vs. 32 % for the reaction product). These last compounds are described by doublet 2 and contain iron in valence state Fe^{2+} . These last paramagnetic phases in nepheline and in the reaction product have similar Mössbauer spectra parameters and they may be complex iron oxide compounds containing Al or Si atoms [7].

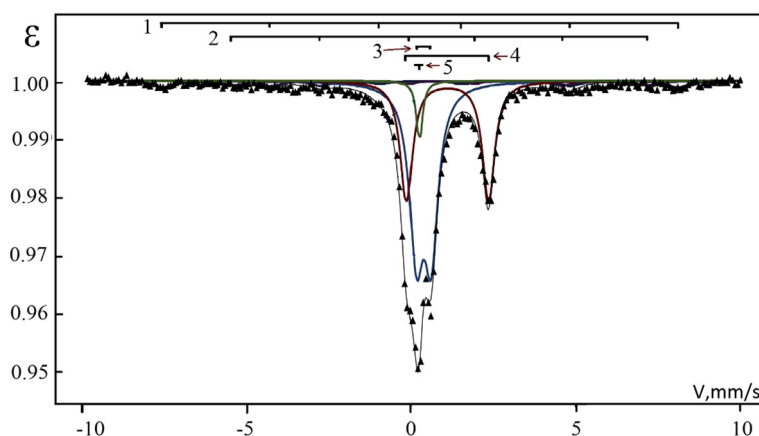


Fig. 2 Mössbauer spectrum of the sediment of reacted nepheline with concentrated sulfuric acid at room temperatures

Table 2 Mössbauer parameters of the sediment of reacted nepheline with concentrated sulfuric acid at room temperatures

Phase	IS, mm/s	QS, mm/s	H_{eff} , T	S_{rel} , %
Sextet 1	0.27 ± 0.05	-0.01 ± 0.05	48.4 ± 0.2	6.28
Sextet 2	0.89 ± 0.05	0.00 ± 0.05	39.0 ± 0.2	7.56
Doublet 1	0.36 ± 0.05	0.44 ± 0.05		49.52
Doublet 2	1.08 ± 0.05	2.49 ± 0.05		32.34
Singlet 1	0.29 ± 0.05			4.29

We thus observe that some quantity of the compounds in nepheline during this redox reaction transform into another phases, such as $\gamma\text{-Fe}_2\text{O}_3$ and the quantity decreases from 42 % to 32 %.

In discussing these results we propose a model where a part of Fe^{2+} in the nepheline minerals with $\text{IS} = 1.07 \text{ mm s}^{-1}$ $\text{QS} = 2.42 \text{ mm s}^{-1}$ (Table 1 Doublet 2) may be contained inside pores of the aluminosilicate mineral in our case the nepheline minerals. Then after reaction of the nepheline with the sulfuric acid the part of the Fe^{2+} outside the pores is transformed into Fe^{3+} with $\text{IS} = 0.36 \text{ mm s}^{-1}$ $\text{QS} = 0.44 \text{ mm s}^{-1}$ (Table 2 Doublet 1).

3 Conclusion

Nepheline and its reaction product with sulphuric acid are investigated by Mössbauer spectroscopy.

It is shown that:

- Iron contained in nepheline minerals is in different and complex paramagnetic and magnetic phases with Fe^{2+} and Fe^{3+} . One of the magnetic states is the compound Fe_3O_4 . For all phases the Mössbauer spectra parameters are determined;

- b) The reaction product of nepheline with concentrated sulfuric acid contains iron in paramagnetic and magnetic phases. One part of iron is dominating and has valence state Fe^{+2} and another part has valence state Fe^{3+} in magnetic phase. Some quantity of iron atoms in the Fe^{2+} state transform to the Fe^{3+} state as the result of the redox reaction. One of the magnetic phase is identified as $\gamma\text{-Fe}_2\text{O}_3$.

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