

Mössbauer spectroscopy and X-ray diffraction of oxide precipitates formed from FeSO₄ solution

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Chemical and structural properties of oxide precipitates formed from FeSO₄ solution were investigated using X-ray diffraction and ⁵⁷Fe Mössbauer spectroscopy. The hydrolysis of urea at elevated temperature was used for the generation of OH⁻ ions during the precipitation process. The formation of particular oxide phase in the precipitate is strongly dependent on the concentrations of FeSO₄ and urea, as well as on the rate of oxygenation. The phase analysis of precipitates showed the presence of different oxide phases, such as goethite, lepidocrocite, hematite and magnetite, and in one sample of a small amount of siderite. Only substoichiometric magnetite, Fe_{3-x}O₄, was detected. Significant differences in the Mössbauer spectrum of goethite were observed, due to a very small particle size, the degree of crystallinity and/or different content of structurally bonded water. The correlation between the Mössbauer spectra of precipitated goethite and goethite formed during the atmospheric corrosion of steel is discussed.

1. Introduction

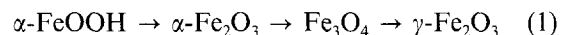
Iron oxides have important applications in the industry and engineering (pigments, catalysts, gas sensors, magnetic materials, etc.). For this reason, many researchers have investigated extensively different methods of their preparation and characterization. The precipitation from FeSO₄ solutions can be used for the preparation of various Fe-oxides, such as α-FeOOH, γ-FeOOH, δ-FeOOH, α-Fe₂O₃ and Fe₃O₄. However, the phase composition and physico-chemical properties of oxide precipitates formed from FeSO₄ solution are strongly dependent on the precipitation conditions.

Musić *et al.* [1, 2] studied the phase composition, crystallinity, stoichiometry and nuclear magnetic properties of oxide precipitates formed from FeSO₄ solutions. They found that the chemical and structural properties of the formed Fe-oxides were strongly dependent on the [Fe²⁺]/[OH⁻] concentration ratio at the beginning of the precipitation process, on the rate of oxygenation, the time of precipitation, the temperature and the kind of alkali (NH₄OH or NaOH).

Lorenz *et al.* [3] investigated the phase composition of precipitates formed from FeSO₄, FeCl₂ or FeBr₂ solution by O₂ oxidation in alkaline medium. Goethite, α-FeOOH, was the dominant component in the precipitates. Also, it was shown [4] that the size of the α-FeOOH crystals, produced from Fe(OH)₂ suspension by air oxidation, depended strongly on the reaction time (measured up to 8.3 h).

The growth of the needle-like α-FeOOH particles,

formed from FeSO₄ solution by air oxidation at 40° C, was followed by Kiyama *et al.* [5]. α-FeOOH particles were used as the starting material for the preparation of ferromagnetic particles, F₃O₄ and γ-Fe₂O₃. The preparation of maghemite, γ-Fe₂O₃, from goethite, α-FeOOH, was based on the sequence of reactions:



Optimum conditions and experimental details for the formation of γ-Fe₂O₃ from α-FeOOH were worked out by Anantharaman *et al.* [6]. In the same work, this method was compared with the method of solid state preparation of γ-Fe₂O₃ (thermal decomposition of ferrous oxalate, FeC₂O₄ · 2H₂O).

Lepidocrocite, γ-FeOOH, can be obtained [7] from 0.36M FeSO₄ solution at 293 K and pH 7. On the other hand, δ-FeOOH can be prepared [8, 9] by (a) very rapid bubbling of oxygen through a suspension of Fe(OH)₂, (b) rapid oxidation of Fe(OH)₂ with H₂O₂, other peroxides or persulphates, and (c) exposure of dried Fe(OH)₂ to oxygen. The method (b) is by far the most commonly used.

The preparation of hematite, α-Fe₂O₃, from FeSO₄ solution was investigated by Šubrt *et al.* [10, 11]. The analysis of hematite showed the presence of structurally bonded water (~5%). The water was assumed to be bonded in the form of OH⁻ groups replacing a part of the O²⁻ in the α-Fe₂O₃ structure.

Kiyama [12] investigated conditions for the formation of Fe₃O₄ by the air oxidation of Fe(OH)₂ suspensions. Matsuda [13] synthesized magnetite, Fe₃O₄,

TABLE I Experimental conditions for the preparation of samples

Sample	Volume of solution (ml)	FeSO ₄ (M/l)	Urea (M/l)	Time of precipitation (h)	Time of aeration (h)	Flow rate (l min ⁻¹)	Speed of stirrer (r.p.m)	Temperature of oil bath (°C)	Final pH
S-1	200	0.1	0.5	6	6	0.4	250	90	3.20
S-2	200	0.1	1.5	6	6	0.4	250	90	5.38
S-3	200	0.1	3	6	6	0.4	250	90	7.80
S-4	200	0.1	6	6	6	0.4	250	90	8.20
S-5	200	0.1	10	6	6	0.4	250	90	8.45
S-6	200	0.1	0.5	6	–	–	250	90	4.30
S-7	200	0.1	1.5	6	–	–	250	90	5.67
S-8	200	0.1	3	6	–	–	250	90	5.98
S-9	200	0.1	6	6	–	–	250	90	6.28
S-10	200	0.3	0.5	6	6	0.4	250	90	2.25
S-11	200	0.3	1.5	6	6	0.4	250	90	4.00
S-12	200	0.3	6	6	6	4	250	90	4.10

applying the reactions between β -FeOOH and FeSO₄ in aqueous solution containing urea at 98°C.

The purpose of the present study is to obtain the information about the chemical and structural properties of Fe-oxides, which precipitate in the system FeSO₄-urea. In previous studies [1, 2], during the precipitation of Fe-oxides from FeSO₄ solution (without the urea addition) the pH value decreased with the time of precipitation. The addition of urea suppresses the pH-decrease, because the hydrolysis of urea at elevated temperature generates OH⁻ ions during the precipitation process. In the present experiments the number of parameters, which affect the precipitation process, is restricted in order to simplify the investigated systems.

The phase analysis of oxide precipitates was performed using ⁵⁷Fe Mössbauer spectroscopy and X-ray diffraction. The combination of these techniques makes possible, not only the determination of phase composition of the precipitates, but also the investigation of their structural properties, such as crystallinity, stoichiometry, etc.

2. Experimental details

Analar grade FeSO₄ · 7H₂O and urea were used. Water was twice distilled. During the experimental work the finely grained FeSO₄ · 7H₂O salt was kept in O₂-free atmosphere to prevent the Fe²⁺ oxidation into Fe³⁺. Experimental conditions for the precipitation of iron oxides are given in Table I. The reaction cell was made of glass and fitted with five inlet necks. Reflux condenser, cooled with water, was mounted onto the reaction cell. Glass stirrer was movable with an electromotor and the angular speed of the stirrer was measured. The isolation between the reaction cell and the glass mixer was performed with a specially designed adapter, which was filled with silicon oil. The air was cleaned with filters in the line between the compressor and the reaction cell. Flow rates of the air were adjusted with commercial devices. A very careful purification of precipitates was performed. Samples were dried under vacuum.

Mössbauer spectra were recorded using Mössbauer spectrometer produced by Wissenschaftliche Elektronik GmbH (D-8130 Starnberg, West Germany). A ⁵⁷Co/Rh source, as well as ⁵⁷Fe/Rh, α -Fe and α -Fe₂O₃ absorbers were used. In the interpretation of the Möss-

bauer spectra the results and observations of other researchers were used [14–19].

X-ray powder diffraction measurements were performed at room temperature using a counter diffractometer with monochromatized CuK α radiation.

3. Results and discussion

Samples S-1 to S-5 were precipitated from 0.1M FeSO₄ solutions containing urea in the concentration range from 0.5 to 10M. After the precipitation of samples S-1 to S-5 the pH values of the mother liquors, in the 3.20 to 8.45 pH range, were measured. Fig. 1 shows the Mössbauer spectra of samples S-1 to S-5 recorded at room temperature. Mössbauer spectrum of sample S-1 ($H_{s/2} = 378$ kOe) can be ascribed to α -FeOOH. This spectrum also shows the central quadrupole doublet (Q) of a small intensity, due to the

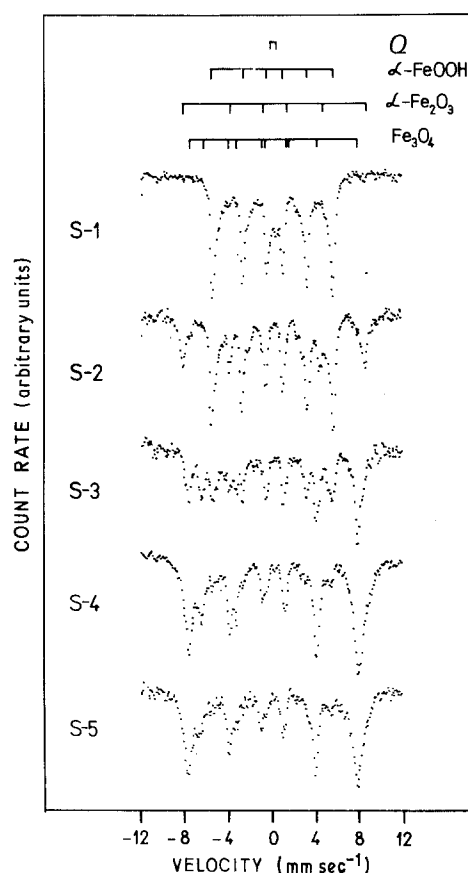


Figure 1 Mössbauer spectra of samples S-1, S-2, S-3, S-4 and S-5 recorded at room temperature.

TABLE II X-ray diffraction phase analysis

Sample	Phase composition* (Molar fraction, approx.)
S-1	α -FeOOH
S-2	α -FeOOH + α -Fe ₂ O ₃ (0.7) (0.3)
S-3	Fe ₃ O ₄ + α -FeOOH (0.5) (0.5)
S-4	Fe ₃ O ₄ + α -FeOOH (0.9) (0.1)
S-5	Fe ₃ O ₄ + α -FeOOH (0.95) (0.05)
S-6	α -FeOOH + α -Fe ₂ O ₃ (0.8) (0.2)
S-7	α -FeOOH + Fe ₃ O ₄ (0.6) (0.4)
S-8	Fe ₃ O ₄ + α -FeOOH (0.8) (0.02)
S-9	Fe ₃ O ₄ + α -FeOOH + FeCO ₃ (0.80) (0.15) (0.05)
S-10	α -FeOOH
S-11	α -FeOOH
S-12	α -FeOOH + α -FeOOH (0.85) (0.15)

*The actual stoichiometry of magnetite, Fe₃O₄, is discussed in the text.

presence of superparamagnetic particles. The Mössbauer spectrum of sample S-2 is characterized with two sextets of lines. The value of the hyperfine magnetic field ($H_{5/2} = 508$ kOe) of the outer sextet is lower than the $H_{5/2}$ value of well-crystallized hematite ($H_{5/2} = 517$ kOe). The inner sextet ($H_{5/2} = 382$ kOe) corresponds to goethite. In this spectrum the presence of central quadrupole doublet is not observed. The Mössbauer of sample S-3 indicates the presence of goethite and magnetite in equivalent amounts.

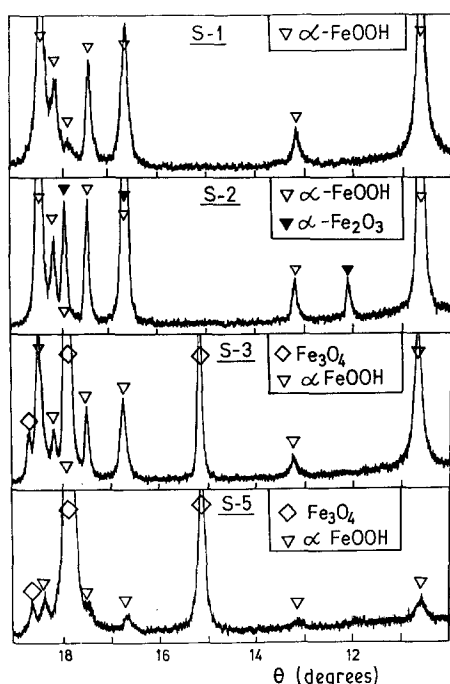


Figure 2 Characteristic parts of the X-ray diffraction powder patterns of samples S-1, S-2, S-3 and S-5.

In samples S-4 and S-5 the molar fraction of goethite is significantly decreased. Mössbauer spectroscopy also indicates differences in the stoichiometry of magnetite in samples S-3 to S-5. For instance, in sample S-3 the stoichiometry of magnetite is Fe_{2.95}O₄, and in sample S-4 it is Fe_{2.91}O₄. The Mössbauer spectrum of sample S-5 indicates a further decrease of the Fe²⁺ content in the magnetite structure.

The results of the X-ray diffraction phase analysis of the samples investigated are shown in Table II. Fig. 2 shows characteristic parts of the X-ray diffraction patterns of samples S-1, S-2, S-3 and S-5 recorded at room temperature. The X-ray diffraction analysis of sample S-1 confirmed the presence of goethite as a single phase. The X-ray diffraction pattern of sample S-2 indicates the presence of α -FeOOH and α -Fe₂O₃. Diffraction lines of α -FeOOH are sharper than those recorded for sample S-1. This observation is in agreement with the Mössbauer spectroscopic results. The X-ray diffraction analysis of sample S-3 indicates that magnetite in this sample has the composition close to the stoichiometric. Also, the broadening of the diffraction lines of magnetite increases from sample S-3 to sample S-5.

Fig. 3 shows the Mössbauer spectra of samples S-6 to S-9 recorded at room temperature. The Mössbauer spectrum of sample S-6 is characterized with two sextets of lines which can be ascribed to α -Fe₂O₃ ($H_{5/2} = 503$ kOe) of decreased crystallinity and α -FeOOH ($H_{5/2} = 382$ kOe).

Samples S-6 to S-9 were precipitated from 0.1 M FeSO₄ solution containing urea in the concentration range from 0.5 to 6 M. The precipitation of these samples was performed under more reductive conditions (no bubbling of air).

The Mössbauer spectra of samples S-7 to S-8 indicate the presence of goethite and substoichiometric magnetite, Fe_{3-x}O₄. The spectrum of samples S-7

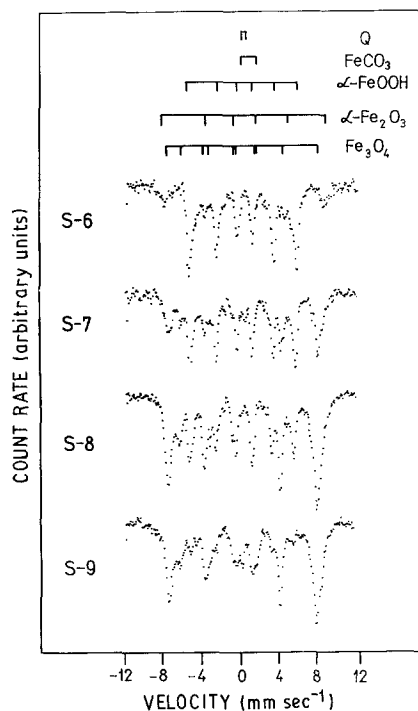


Figure 3 Mössbauer spectra of samples S-6, S-7, S-8 and S-9 recorded at room temperature.

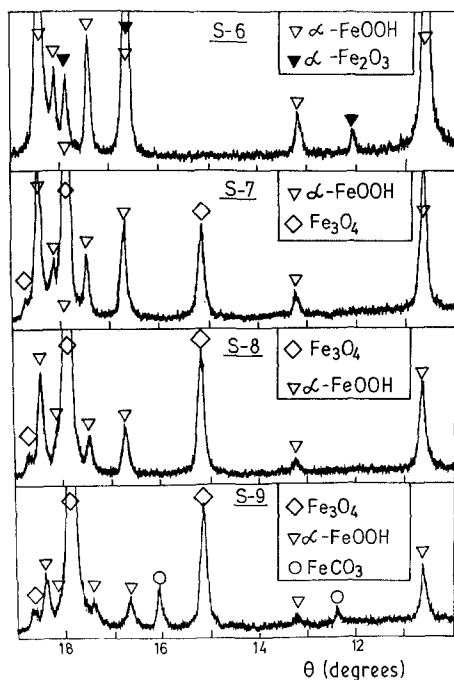
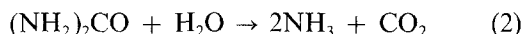


Figure 4 Characteristic parts of the X-ray diffracton powder patterns of samples S-6, S-7, S-8 and S-9.

shows the central quadrupole doublet (Q) of a very small intensity, due to the presence of superparamagnetic particles. Also, the hyperfine magnetic fields of goethite in sample S-7 ($H_{5/2} = 376$ kOe) and in sample S-8 ($H_{5/2} = 372$ kOe) are reduced. In sample S-9 a small amount ($\sim 5\%$) of iron(II) carbonate ($\delta_{Fe} = 1.27$ mm sec $^{-1}$ and $\Delta = 1.80$ mm sec $^{-1}$ at room temperature) is additionally detected.

Urea undergoes hydrolysis at elevated temperature in accordance with the chemical reaction:



This chemical reaction is responsible for the formation of small amount of FeCO_3 in sample S-9.

Fig. 4 shows characteristic parts of the X-ray diffraction patterns of samples S-6 to S-9. Diffraction lines of α -FeOOH in sample S-6 are sharp, similarly

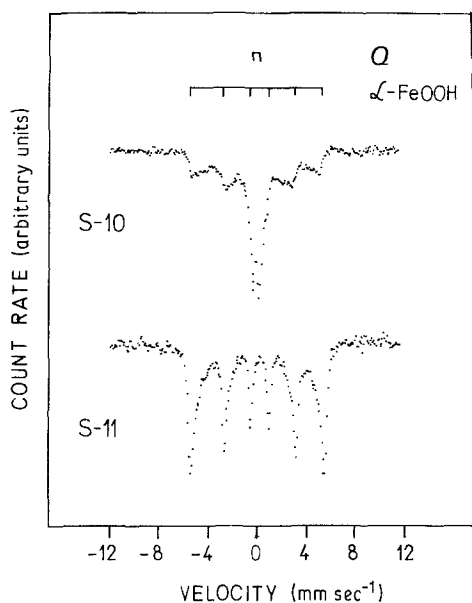


Figure 5 Mössbauer spectra of samples S-10 and S-11 recorded at room temperature.

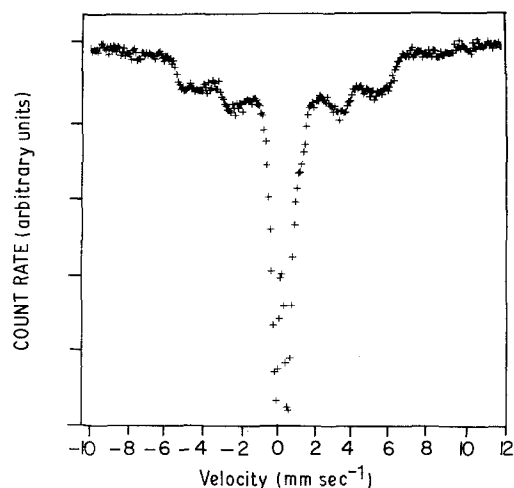


Figure 6 Mössbauer spectrum of the rust generated by the atmospheric corrosion of raw steel (2 years) in Bethlehem, Pa.

as for sample S-2. The X-ray diffraction patterns of samples S-2, S-8 and S-9 indicate the presence of substoichiometric magnetite, $\text{Fe}_{3-x}\text{O}_4$, and α -FeOOH. The diffraction lines of α -FeOOH in samples S-7, S-8 and S-9 are somewhat broadened, similarly as for sample S-1. Also, the X-ray diffraction lines, corresponding to $\text{Fe}_{3-x}\text{O}_4$ in samples S-7, S-8 and S-9, show a broadening similar to that for sample S-5.

Fig. 5 shows the Mössbauer spectra recorded for samples S-10 and S-11. The Mössbauer spectrum of sample S-10 is very similar (in shape) to the spectrum of the rust generated by the atmospheric corrosion of raw steel (2 years) in Bethlehem, Pennsylvania (Fig. 6). The rust was delaminated (vertical position) from the corroded surface with scotch tape. The central quadrupole doublet in the Mössbauer spectrum of the

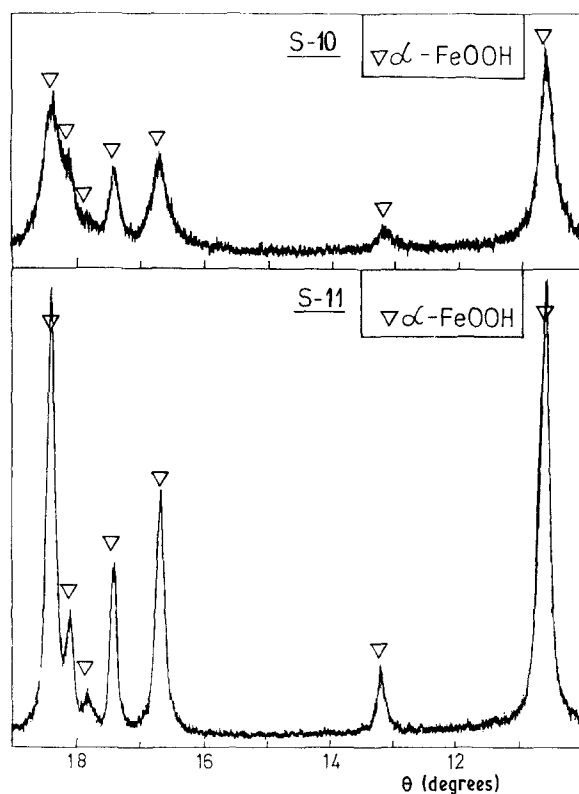


Figure 7 Characteristic parts of the X-ray diffraction powder patterns of samples S-10 and S-11.

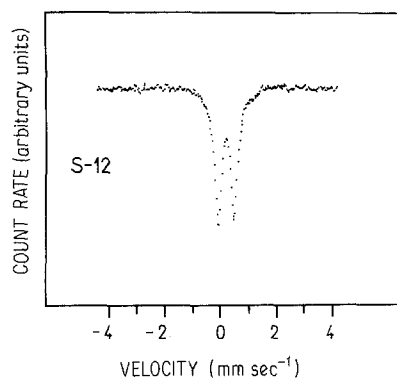


Figure 8 Mössbauer spectrum of sample S-12 recorded at room temperature.

atmospheric rust represents γ -FeOOH and the superparamagnetic α -FeOOH. This is confirmed by Mössbauer measurements at low temperatures. The formation of Fe-oxides during the atmospheric corrosion of steel and their Mössbauer spectra are discussed in the paper by Leidheiser and Musić [20]. The Mössbauer spectrum of sample S-11 corresponds to α -FeOOH ($H_{5/2} = 378$ kOe).

Generally, well-crystallized goethite [21] exhibits a typical six-line hyperfine magnetic spectrum with peak intensity ratios approximating to 3:2:1:1:2:3. Goethite samples precipitated from aqueous solutions show, as a rule, significant differences in their Mössbauer spectra. These differences are influenced by very small particle size, degree of crystallinity and/or different content of structurally bonded water. The superparamagnetic behaviour of goethite particles can be used to determine their size. However, due to the combined effects (not only the effect of particle size) it is difficult to use the values of the hyperfine magnetic field ($H_{5/2}$) to measure the particle size of goethite samples. At room temperature, Mössbauer spectrum of the precipitated goethite can vary from well defined sextet up to quadrupole doublet. The Mössbauer spectrum of sample S-11 shows asymmetric broadening of lines, which is primarily influenced by decreased crystallinity of goethite. This type of Mössbauer spectrum can be deconvoluted assuming the presence of two sextets. The outer sextet can be ascribed to better defined goethite particles, while the inner sextet

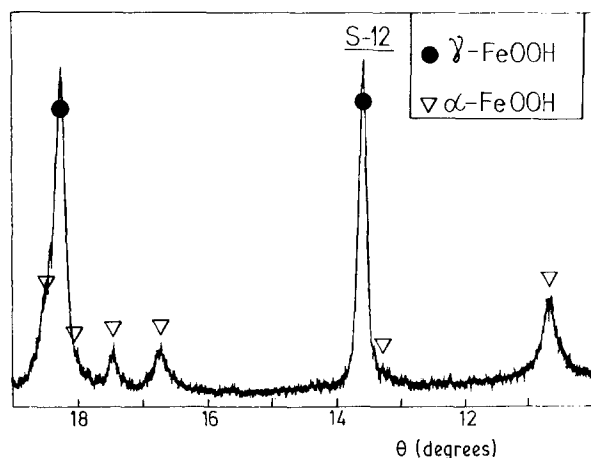


Figure 9 Characteristic parts of the X-ray diffraction powder patterns of sample S-12.

deviates very much from the Lorentzian profile. In the present paper, the values of hyperfine magnetic field of goethite are given only for the outer sextet.

Fig. 7 shows characteristic parts of the X-ray diffraction patterns of samples S-10 and S-11. The X-ray diffraction pattern of sample S-10 shows very broad diffraction lines of α -FeOOH, due to small crystallite size. This is in accordance with the Mössbauer spectroscopic results. Diffraction lines obtained for sample S-11 are sharp as for sample S-2.

The Mössbauer spectrum of sample S-12 is characterized by quadrupole doublet (Fig. 8), and Mössbauer parameters of this spectrum are in very good agreement with those obtained for γ -FeOOH standard. The X-ray diffraction analysis of sample S-12 (Fig. 9) indicates that lepidocrocite, γ -FeOOH, is a dominant component in this sample. Sample S-12 also contains 15% of α -FeOOH (superparamagnetic particles).

References

1. S. MUSIĆ, I. NAGY-CZAKÓ, S. POPOVIĆ, A. VÉRTES and M. TONKOVIĆ, *Croat. Chem. Acta* **59** (1986) 833.
2. S. MUSIĆ, S. POPOVIĆ and M. GOTIĆ, *ibid.* **60** (1987) 661.
3. M. LORENZ, S. KNAKE and K. STOPPERKA, *J. Signal AM* **10** (1982) 449.
4. M. FEIGE, M. LORENZ and K. STOPPERKA, *ibid.* **8** (1980) 357.
5. M. KIYAMA, S.-I. SHAMOTO, N. HORIISHI, Y. OKUDA and T. TAKADA, *Bull. Inst. Chem. Res., Kyoto Univ.* **64** (1986) 150.
6. M. R. ANANTHARAMAN, S. SESHAN, S. N. SHRINGI and H. V. KEER, *Bull. Mater. Sci.* **6** (1984) 59.
7. A. ŠOLCOVA, A. ŠUBRT, F. HANOUSEK, P. HOLBA, V. ZAPLETAL and J. LIPKA, *Silikaty* **24** (1980) 133.
8. W. FEITKNECHT, *Z. Electrochem.* **63** (1959) 34.
9. O. MULLER, R. WILSON and W. KRAKOW, *J. Mater. Sci.* **14** (1979) 2929.
10. J. ŠUBRT, A. ŠOLCOVA, F. HANOUSEK, A. PETRINA and V. ZAPLETAL, *Coll. Czech. Chem. Commun.* **49** (1984) 2478.
11. J. ŠUBRT, F. HANOUSEK, V. ZAPLETAL and H. ŠTEPANKOVA, *J. Mater. Sci.* **17** (1982) 215.
12. M. KIYAMA, *Bull. Chem. Soc. Jpn* **47** (1974) 1646.
13. K. MATSUDA, *Nippon Kagaku Kaishi*, (11) (1983) 1589.
14. G. W. SIMMONS and H. LEIDHEISER Jr, "Corrosion and Interfacial Reactions", in "Application of Mössbauer Spectroscopy", Vol. 1, (Bell Telephone Laboratories, Inc., 1976) p. 85.
15. F. J. BERRY, *Trans. Met. Chem.* **4** (1979) 209.
16. L. H. BOWEN, "Mössbauer Spectroscopy of Ferric Oxides and Hydroxides", in "Mössbauer Effect Data Index - 1979", (Plenum, New York, 1979) p. 76.
17. W. MEISEL, *Kemai Közlemenyek* **48** (1977) 41.
18. I. DEZSI and M. FODOR, *Phys. Status Solidi* **15** (1966) 247.
19. E. MURAD, "Properties and Behaviour of Iron Oxides as Determined by Mössbauer Spectroscopy, in Iron and Soils and Clay Minerals" edited by J. W. Stucki *et al.* (D. Reidel Publications Co., 1988) p. 309.
20. H. LEIDHEISER Jr and S. MUSIĆ, *Corrosion Sci.* **22** (1982) 1089.
21. E. de GRAVE and R. E. VANDENBERGHE, *Hyperfine Interact.* **28** (1986) 643.

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