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Mössbauer Spectroscopy and X-Ray Diffraction of Oxide Precipitates Formed from $FeSO_4$ Solution. Part II*

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The chemical and structural properties of Fe-oxides formed from $FeSO_4$ solutions are strongly dependent on the $[Fe^{2+}]/[OH^-]$ 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 (NH_4OH or NaOH). Goethite (α-FeOOH) of varying crystallinity and/or substoichiometric magnetite ($Fe_{3-x}O_4$) were precipitated at 90 °C. Differences in the crystallinity of α-FeOOH were revealed by Mössbauer spectroscopy, as well as by X-ray diffraction. The stoichiometry of $Fe_{3-x}O_4$ varied from $Fe_{2.91}O_4$ to the one close to $Fe_{2.67}O_4$. The X-ray diffraction showed only the presence of $Fe_{3-x}O_4$, but not of maghemite (γ-Fe_2O_3). The formation of hematite (α-Fe_2O_3), under specific experimental conditions, was also observed. Amorphous iron(III) hydroxyde precipitated at room temperature. The mechanism of precipitation of Fe-oxides from $FeSO_4$ solution is discussed.

INTRODUCTION

In a recent study[1] we investigated the composition, stoichiometry and particle size of Fe-oxides precipitated from $FeSO_4$ solutions at a low O_2 content. The magnetic properties of Fe-oxides, via the magnetic hyperfine interaction of ^{57}Fe nucleus, were also investigated. The Mössbauer spectroscopy, X-ray diffraction and IR spectroscopy were used as experimental techniques. The results of this study[1] can be summarized briefly as follows.

The chemical composition and structure of Fe-oxides precipitated from $FeSO_4$ solutions depend strongly on the $[FeSO_4]/[NaOH]$ concentration ratio. Goethite (α-FeOOH) of poor crystallinity precipitated at low pH values. The formation of hematite was explained by the mechanism of internal crystallization in geothite particles. The transformations of $[Fe(OH)_2]/[Fe(OH)_3]$ mixture to substoichiometric magnetite ($Fe_{3-x}O_4$), goethite, and further to hematite at 90 °C were also followed. Substoichiometric magnetite was the final precipitation product in suspensions with $[FeSO_4]/[NaOH]$ stoichiometric concentration ratio for $Fe(OH)_2$ precipitation.

In continuation of our previous study[1], the precipitation of Fe-oxides, during the controlled oxygenation of $FeSO_4$ solutions by air, has been inve-

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stigated. The influence of the reaction conditions on the chemical composition and structural properties of Fe-oxides was systematically studied.

EXPERIMENTAL

Precipitation of Fe-oxides

Analar grade $FeSO_4 \cdot 7H_2O$, NaOH, 27% NH_3 (aq.), H_2SO_4, ethanol, and bidistilled water were used. The fine grained $FeSO_4 \cdot 7H_2O$ salt was kept in O_2-free atmosphere to prevent the Fe^{2+} oxidation into Fe^{3+}. Experimental conditions for the preparation of Fe-oxides are given in Table I.

TABLE I

Experimental Conditions for the Preparation of Samples

Sample	Chemical composition of solution*,**	Time of preparation (hours)	Time of aeration (hours)	Flow rate (l/min)	Speed of mixing (rpm)	Temperature of oil-bath (°C)	Final pH
FEO-1	200 ml H_2O	6	6	0.4	250	90	2.08
FEO-2	200 ml H_2O	6	6	0.4	200	70	2.37
FEO-3	200 ml H_2O	6	6	0.4	500	50	2.90
FEO-4	200 ml H_2O	6	6	0.4	500	30	3.27
FEO-5	see text						
FEO-6	see text						
FEO-7	160 ml H_2O+40 ml (27% NH_3)	2	2	0.4	500	90	8.9
FEO-8	160 ml H_2O+40 ml (27% NH_3)	6	6	0.4	550	90	6.90
FEO-9	160 ml H_2O+40 ml (27% NH_3)	18	18	0.4	500	90	3.78
FEO-10	160 ml H_2O+40 ml (27% NH_3)	36	36	0.4	300	90	2.45
FEO-11	see text						
FEO-12	187 ml H_2O+13 ml (27% NH_3)	6	6	4	500	90	4.00
FEO-13	194 ml H_2O+6 ml (27% NH_3)	6	6	4	500	90	3.40
FEO-14	197 ml H_2O+3 ml (27% NH_3)	6	6	4	550	90	2.85
FEO-15	200 ml H_2O	6	6	4	500	90	2.25
FEO-16	198 ml H_2O+2 ml 0.2 M NaOH	6	6	4	500	90	2.20
FEO-17	196 ml H_2O+4 ml 0.2 M NaOH	6	6	4	700	90	2.14
FEO-18	192 ml H_2O+8 ml 0.2 M NaOH	6	6	4	650	90	2.13

Table I cont'd.

FEO-19	185 ml H_2O+15 ml 0.2 M NaOH	6	6	4	600	90	2.20
FEO-20	175 ml H_2O+25 ml 0.2 M NaOH	6	6	4	600	90	2.21
FEO-21	200 ml 0.2 M NaOH	6	6	4	600	90	3.65
FEO-22	150 ml H_2O+50 ml (27% NH_3)	2	—	—	600	90	10.50
FEO-23	150 ml H_2O+50 ml (27% NH_3)	4	—	—	500	90	10.50
FEO-24	160 ml H_2O+40 ml (27% NH_3)	2	—	—	500	90	10.43
FEO-25	160 ml H_2O+40 ml (27% NH_3)	6	6	0.4	300	90	4.69
FEO-26	160 ml H_2O+40 ml (27% NH_3)	6	—	—	300	90	10.11
FEO-27	197 ml H_2O+3 ml (27% NH_3)	6	—	—	400	90	3.63
FEO-28	197 ml H_2O+3 ml (27% NH_3)	6	6	4	300	90	2.65
FEO-29	160 ml H_2O+40 ml 0.1 M H_2SO_4	6	6	4	500	90	1.30

* For the preparation of samples FEO-1 to FEO-24 and FEO-29, to each solution 5.588 g of $FeSO_4 \cdot 7H_2O$ was added.

** For the preparation of samples FEO-25 to FEO-28, to each solution 16.765 g of $FeSO_4 \cdot 7H_2O$ was added.

Samples FEO-1 to FEO-6 were prepared at different temperatures (90 °C→*RT*) and without addition of alkali. The second group of samples (FEO-7 to FEO-14) was prepared in the presence of NH_3 alkali. The third group of samples (FEO-15 and FEO-16 to FEO-21) was precipitated to investigate the effects of NaOH alkali on the precipitation process from $FeSO_4$ solution. The fourth group of samples (FEO-22 to FEO-28) was precipitated to investigate the effects of aeration on the chemical and structural properties of precipitates. Sample FEO-5 was produced by the precipitation, at room temperature, from $FESO_4$ solution containing 1540 ml bidistilled H_2O and 43.04 g of $FeSO_4 \cdot 7H_2O$ salt. The time of precipitation was 10 days. A reflux condenser, cooled by air, was mounted onto the reaction duced by the precipitation, at room temperature, from $FeSO_4$ solution containing for the preparation of sample FEO-6 were the same as in the previous case, except that the time of precipitation was 28 days. Sample FEO-29 was a yellow-greenish solution after 6 hours of oxygenation. The reaction vessel used at higher temperatures was made of glass and fitted with five inlet necks. The reflux condenser, cooled by water, was mounted onto the reaction vessel. The glass mixer was movable with an electromotor and the angular speed of the mixer was measured. The isolation between the reaction vessel 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 vessel. Flow rates of the air were adjusted to commercial devices. A very careful purification of precipitates was performed. Samples were dried under vaccum.

Instrumentation

Mössbauer spectra were recorded using a commercial Mössbauer spectrometer produced by Wissenschaftliche Elektronik GmbH (D-8130 Starnberg, West Germany). A ^{57}Fe/Rh, α-Fe and α-Fe_2O_3 absorbers, were used. Isomer shifts are given relative to α-Fe.

X-ray powder diffraction measurements were performed at room temperature using a counter diffractometer with monochromatized Cu$K\alpha$ radiation. Iron oxides and oxyhydroxides were easily identified according to the data published by the Joint Committee on Powder Diffraction Standard, International Center for Diffraction Data, Powder Diffraction File (Swarthmore, Pa., USA). The following identification cards were used: No. 13—534 for α-Fe_2O_3 (space group $R3c$, $a = 0.5034$ nm, $c = 1.3752$ nm, $Z = 6$), No. 19-629 for Fe_3O_4 (space group $Fd3m$, $a = 0.83967$ nm, $Z = 8$), and No. 29—713 for α-FeOOH (space group $P\,b\,n\,m$, $a = 0.4608$ nm, $b = 0.9956$ nm, $c = 0.30215$ nm, $Z = 4$). Particular attention was paid to accurate measurement of diffraction angles in order to distinguish nonstoichiometric magnetite from stoichiometric Fe_3O_4, and these two from maghemite, γ-Fe_2O_3 (JCPDS-PDF Card No. 24-81).

RESULTS

Mössbauer Spectroscopy

The results of the phase analysis of Fe-oxides precipitated from $FeSO_4$ solutions are shown in Table II. In the interpretation of the Mössbauer spectra, the results and observations of other researchers were also used.[2-6] The Mössbauer spectroscopic results obtained in this study can be summarized as follows.

TABLE II

Phase Analysis of Fe-oxides Precipitated from $FeSO_4$ Solutions

Sample	Composition	
	Mössbauer spectroscopy	X-ray diffraction
FEO-1	α-FeOOH	α-FeOOH
FEO-2	α-FeOOH	α-FeOOH
FEO-3	spectra not recorded	α-FeOOH
FEO-4	spectra not recorded	amorphous
FEO-5	ferrihydrite + FeOOH	amorphous
FEO-6	ferrihydrite + FeOOH	amorphous
FEO-7	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-8	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-9	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-10	$Fe_{3-x}O_4$ + α-Fe_2O_3 + α-FeOOH	$Fe_{3-x}O_4$ + α-Fe_2O_3 + α-FeOOH
FEO-11	$Fe_{3-x}O_4$ + α-Fe_2O_3 + α-FeOOH (small amounts)	$Fe_{3-x}O_4$ + α-Fe_2O_3 + α-FeOOH
FEO-12	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-13	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$ + α-FeOOH (traces)

Table II cont'd.

FEO-14	$Fe_{3-x}O_4$ + α-FeOOH (?) (small amount)	$Fe_{3-x}O_4$ + α-FeOOH
FEO-15	α-FeOOH	α-FeOOH
FEO-16	α-FeOOH	α-FeOOH
FEO-17	α-FeOOH	α-FeOOH
FEO-18	α-FeOOH	α-FeOOH
FEO-19	α-FeOOH	α-FeOOH
FEO-20	α-FeOOH	α-FeOOH
FEO-21	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-22	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-23	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-24	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-25	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-26	$Fe_{3-x}O_4$	$Fe_{3-x}O_4$
FEO-27	$Fe_{3-x}O_4$ + α-FeOOH (small amount)	$Fe_{3-x}O_4$ + α-FeOOH (small amount)
FEO-28	α-FeOOH + $Fe_{3-x}O_4$ or γ-Fe_2O_3	α-FeOOH + $Fe_{3-x}O_4$
FEO-29	No precipitate (yellow-greenish solution)	

Samples FEO-1 to FEO-6 show distinct differences in the Mössbauer spectra, as a function of the precipitation temperature of Fe-oxides. Mössbauer spectra of samples FEO-1 and FEO-2, recorded at room temperature, are shown in Figure 1. The hyperfine magnetic lines are very broad, and their shapes deviate considerably from Lorentzian. Also, the values of the hyperfine magnetic fields are decreased in relation to the well-crystallized goethite. The spectrum of sample FEO-1 contains a central quadrupole doublet of small intensity. The intensity of this doublet is increased in the spectrum of sample FEO-2. The central quadrupole doublet disappeared at liq. N_2 temperature, thus indicating a partial presence of the superparamagnetic α-FeOOH particles. Figure 1 indicates that geothite formed at 70 °C (sample FEO-2) is less crystallized than goethite formed at 90 °C (sample FEO-1).

Figure 2 shows the Mössbauer spectra of samples FEO-5 and γ-FeOOH. The standard sample of γ-FeOOH was precipitated from $FeCl_2$ solution.[1] The Mössbauer spectrum of sample FEO-5 is characterized by a asymmetric doublet. The shape of this doublet and line-width indicate the superposition of two doublets. These doublets can be ascribed to the amorphous $Fe(OH)_3$ (ferrihydrite) and the superparamagnetic FeOOH.

Samples FEO-7, FEO-8, FEO-9 and FEO-10 were precipitated from $FeSO_4$ solution by adding an appropriate amount of 27% NH_3 (aq.). The preparation

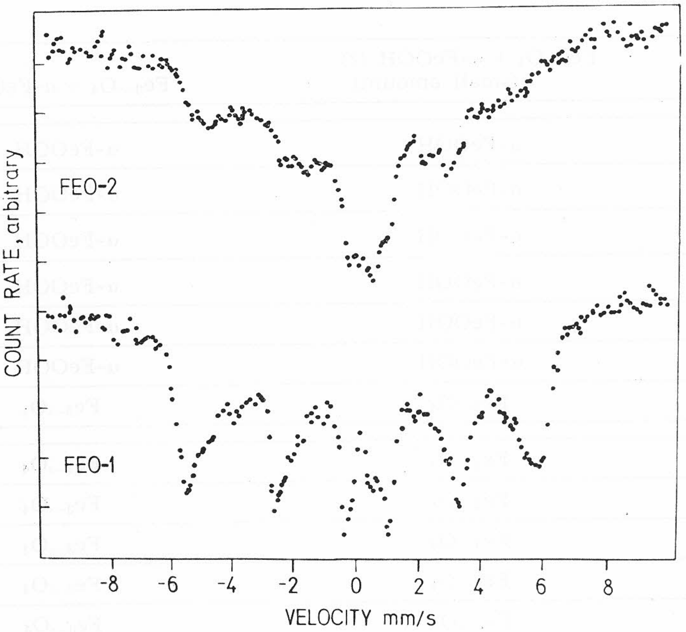

Figure 1. Mössbauer spectra of samples FEO-1 and FEO-2 recorded at room temperature

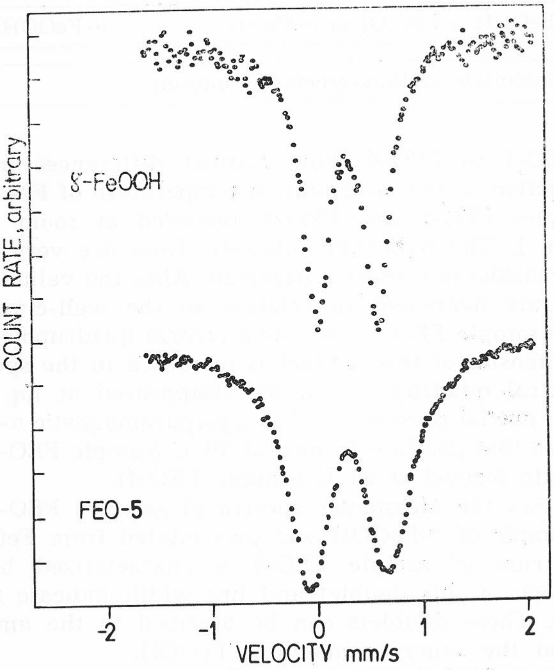

Figure 2. Mössbauer spectra of samples FEO-5 and γ-FeOOH recorded at room temperature

time of these samples varied between 2 and 36 hours. Sample FEO-11 was produced by additional heating of the suspension containig precipitate FEO-10 (7 days at 90 °C, and without aeration). Spectra of samples FEO-7, FEO-8 and FEO-9 are typical of the substoichiometric magnetite. The Mössbauer spectrum of sample FEO-9 corresponds to a very substoichiometric magnetite. In sample FEO-10, the formation of α-FeOOH and α-Fe_2O_3 in small amounts was observed. With a prolonged time of heating the amount of α-Fe_2O_3 increased (sample FEO-11).

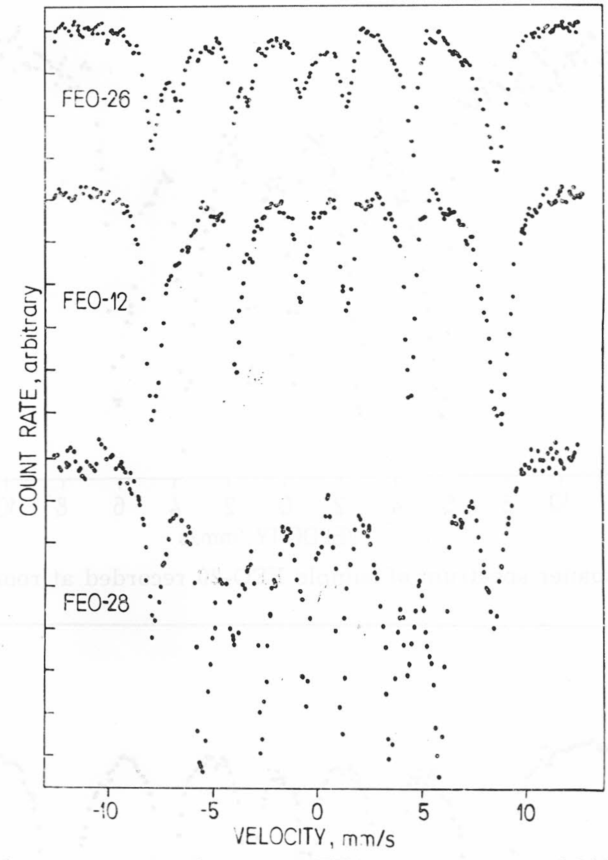

Figure 3. Mössbauer spectra of samples FEO-28, FEO-12 and FEO-26 recorded at room temperature

Figure 3 shows the Mössbauer spectra of samples FEO-26, FEO-12 and FEO-28. The stoichiometry of sample FEO-26 corresponds to $Fe_{2.91}O_4$. Mössbauer spectrum of sample FEO-12 indicates an additional oxidation of Fe^{2+} ions in substoichiometric magnetite. The influence of the lines of inner sextet on the shape of Mössbauer spectrum of sample FEO-12 is visible. The spectra of samples FEO-12, FEO-13 and FEO-14 are very similar. The Mössbauer spectrum of sample FEO-28 can be ascribed to a very substoichiometric magnetite or γ-Fe_2O_3.

On the basis of Mössbauer spectroscopic measurements, it can be concluded that samples FEO-15 to FEO-20 contain geothite of varying crystallinity.

The crystallinity of goethite increases in the order from FEO-15 to FEO-20. The Mössbauer spectrum of sample FEO-20 is shown in Figure 4.

Mössbauer spectra of samples FEO-22 to FEO-26 are similar and correspond to substoichiometric magnetite ($Fe_{3-x}O_4$). Figure 5 shows the Mössbauer spectrum of sample FEO-24 recorded at room temperature. Mössbauer spectrum of sample FEO-28, containing a mixture of α-FeOOH and $Fe_{3-x}O_4$ (or γ-Fe_2O_3), is shown in Figure 3.

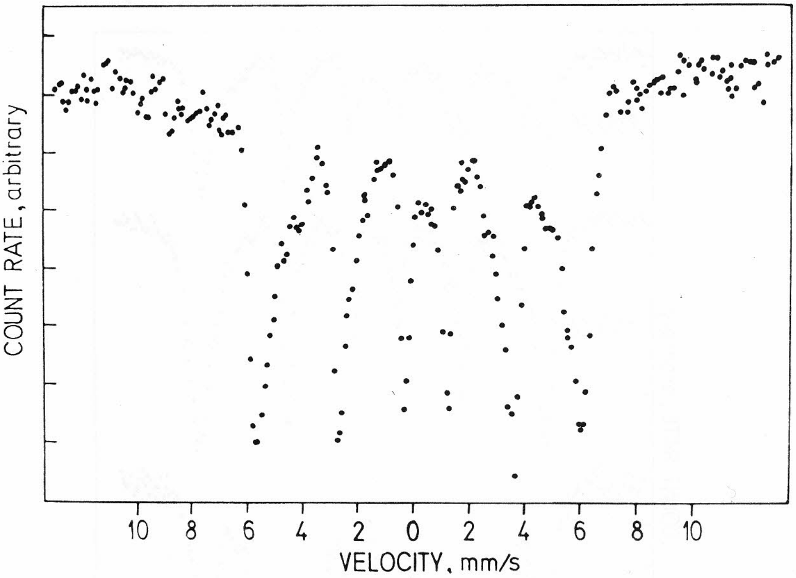

Figure 4. Mössbauer spectrum of sample FEO-20 recorded at room temperature

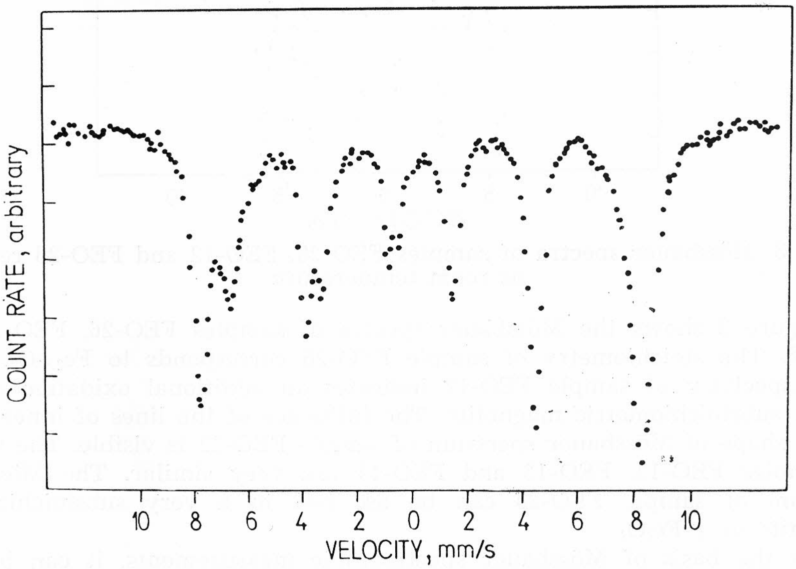

Figure 5. Mössbauer spectrum of sample FEO-24 recorded at room temperature

X-ray Diffraction

The results of the phase analysis are given in Table II, parallel to the Mössbauer spectroscopic data. One can see that the two sets of data are in very good agreement, and that the two methods are complementary (*e. g.* the analysis of samples FEO-5 and FEO-6).

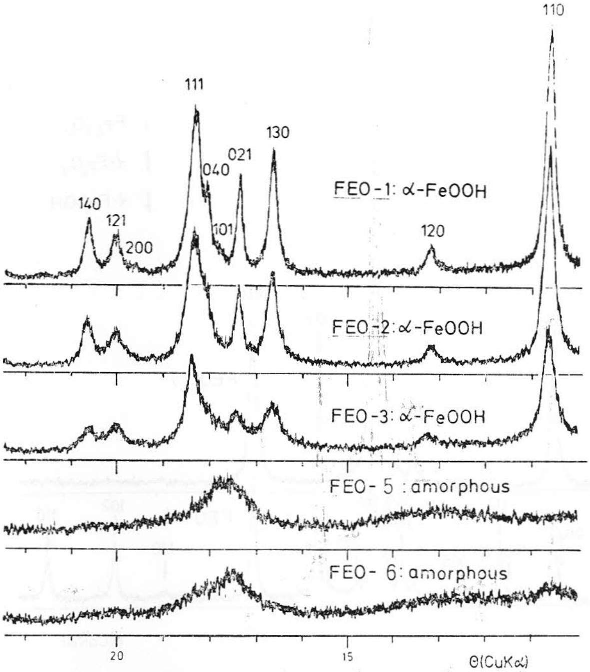

Figure 6. Characteristic X-ray diffraction patterns of samples FEO-1, FEO-2, FEO-3, FEO-5 and FEO-6 (radiation: monochromatized Cu*K*α).

Samples FEO-1 to FEO-3 show the X-ray diffraction pattern of α-FeOOH. Diffraction line intensities decrease and diffraction line widths increase as the temperature of the sample preparation decreases. Sample FEO-4 is amorphous, as well as samples FEO-5 and FEO-6. Characteristic parts of X-ray diffraction patterns are shown in Figure 6. One can notice a gradual change in the diffraction pattern from sample FEO-1 to sample FEO-6.

Samples FEO-7, FEO-8 and FEO-9 show the diffraction pattern of substoichiometric magnetite, $Fe_{3-x}O_4$. Its unit-cell parameter is very similar for all samples and is within the average value (0.8365 ± 0.0010 nm). The same value of the unit-cell parameter of substoichiometric magnetite, within the limits of experimental error, has been found for samples in other groups in this work. This value is in agreement with the one for substoichiometric Fe_3O_4 (0.8363 ± 0.0008 nm) found in our previoius work,[1] and in contrast to the value found for stoichiometric Fe_3O_4 (0.8388 ± 0.0005 nm). The diffraction line widths of substoichiometric magnetite are bigger than for the stoichiometric Fe_3O_4. Samples FEO-10 and FEO-11 contain α-Fe_2O_3 and α-FeOOH in addition to $Fe_{3-x}O_4$, which is dominant. The fraction of α-Fe_2O_3 in sample FEO-11 is bigger than in sample FEO-10. Characteristic parts of X-ray diffraction patterns of samples FEO-7 and FEO-11 are shown in Figure 7.

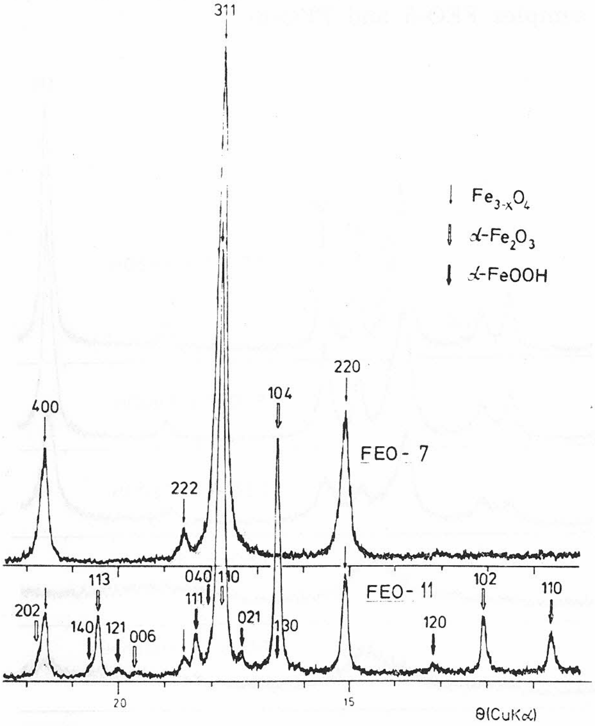

Figure 7. Characteristic X-ray diffraction patterns of samples FEO-7 and FEO-11 (radiation: monochromatized Cu*K*α).

The diffraction pattern of sample FEO-12 corresponds to $F_{3-x}O_4$. The patterns of sample FEO-13 and FEO-14 indicate the presence of a small fraction of α-FeOOH, besides the dominant component, $Fe_{3-x}O_4$. The diffraction lines of $Fe_{3-x}O_4$ are narrower for sample FEO-14 than for the two other samples.

Samples FEO-15 to FEO-20 show similar diffraction patterns corresponding to α-FeOOH. The diffraction line width exhibits a tendency to decrease with the increase in NaOH concentration. Samples FEO-10 and FEO-20, show a smaller diffraction line width than sample FEO-1. Sample FEO-21, prepared at the maximum concentration of NaOH, is substoichiometric magnetite.

The diffraction patterns of samples FEO-22 to FEO-26 correspond to $Fe_{3-x}O_4$. Samples FEO-27 and FEO-28 contain $Fe_{3-x}O_4$ and α-FeOOH, the latter being dominant in sample FEO-28. The diffraction lines of $Fe_{3-x}O_4$ for samples FEO-27 and FEO-28 are narrower than for other samples in this group.

DISCUSSION

The precipitation of Fe-oxides from $FeSO_4$ solution, under very different experimental conditions, has been the subject of a number of studies.

Šolcova *et al.* described[7] a procedure for the preparation of pure lepidocrocite (γ-FeOOH) from 0.36 M $FeSO_4$ solution at pH 7. Oxygenation of $FeSO_4$ by air was performed at room temperature. Transformation of synthetic γ-FeOOH in aqueous solutions of $FeSO_4$ was also studied.[8] Experimental results were discussed in terms of the dissolution of the less stable γ-FeOOH and the crystallization of α-FeOOH, which further transformed to α-Fe_2O_3. Šolcova *et al.* studied[9] precipitation from $FeSO_4$ solutions, and they detected α-FeOOH and amorphous $Fe_2O_3 \cdot nH_2O$ in neutral and weakly alkaline solutions. At a higher pH value goethite (α-FeOOH) was formed. The same group of authors described[10] crystallization of α-FeOOH and α-Fe_2O_3 from $FeSO_4$ solutions which were oxygenated by air.

Lepidocrocite samples of varying crystallinity were also prepared[11] starting from a solution of $FeSO_4$ and they were investigated by Mösbauer spectroscopy. The influence of the crystallinity on the Mössbauer spectrum of lepidocrocite (γ-FeOOH) was also investigated[12] by Murad and Schwertmann.

Experimental conditions for the formation of Fe_3O_4 by the air oxydation of $Fe(OH)_2$ suspension were investigated.[13,14] Tamaura *et al.*[15] studied the transformation of α-FeOOH to Fe_3O_4 by adsorption of Fe^{2+} on γ-FeOOH. Sugimoto and Matijević investigated[16] the formation of uniform spherical magnetite particles by crystallization from $Fe(OH)_2$ gels.

Preparations of Fe_3O_4 and α-FeOOH from $FeSO_4$ solutions have been described.[17–19] Synthetic acicular α-FeOOH particles were widely used as a starting material for the production of magnetic particles (*e. g.* γ-Fe_2O_3), whose coercive force derived mainly from a shape anisotropy.[20,21] The preparation of yellow pigment (α-FeOOH) from $FeSO_4$ solution has also been reported.[22]

δ-FeOOH can be prepared by several methods,[23,24] including (a) very rapid bubbling of oxygen through a suspension of $Fe(OH)_2$, (b) rapid oxidation of $Fe(OH)_2$ with H_2O_2 or other peroxides or persulphates in aqueous suspensions, and (c) exposure of dried $Fe(OH)_2$ to oxygen. Method (b) is by far the most commonly used.

Although the preparations of Fe-oxides from $FeSO_4$ solutions have been the subject of many studies, a considerable uncertainty still exists about the mechanism of precipitation, as well as about the real structural properties of Fe-oxides formed.

In this work, the oxygenation of Fe^{2+} ions was performed by air at two different flow rates (0.4 or 4 l/min). A few experiments were performed without the air oxygenation.

The oxygenation of Fe^{2+} ions can be affected by several factors,[25] such as ferrous ion and oxygen concentrations, the solution pH, the kinds of coexisting anions etc. Tamura and coworkers found[26] that the oxygenation of Fe^{2+} was accelerated by the presence of Fe(III)-oxyhydroxides. Goto and coworkers investigated[7] the mechanism of oxygenation of Fe^{2+} ions in neutral solutions. According to them, the oxidation of Fe^{2+} into Fe^{3+} ions can be described by a sequence of several reactions. The rate-determining step is the reaction between $[Fe(H_2O)_6]^{2+}$ and hydrated oxygen in the form of $[O_2 \cdot HO]^-$

complex. The existence of the $O_2 \cdot HO^-$ complex is assumed to be a consequence of the dissociation equilibrium of dissolved O_2 in water:

$$O_2 \cdot H_2O \rightleftarrows O_2 \cdot HO^- + H^+$$

The hydroxyl group of the $O_2 \cdot HO^-$ complex substitutes one H_2O molecule in the $[Fe(H_2O)_6]^{2+}$ complex and one electron is transferred to the oxygen molecule by the bridge mechanisms. The result of these reactions is the formation of the $[Fe(H_2O)_5OH]^{2+}$ complex ion and the O^-_2 radical.

Iron(III)-oxyhydroxydes accelerate the oxygenation of Fe^{2+} ions at neutral pH values (pH ~ 6—7). However, when Fe^{2+} ions are oxygenated in the presence of an equivalent amount of NaOH at pH ~ 9, the reaction proceeds very fast at the beginning of the precipitation process, but almost stops with the formation of magnetite (Fe_3O_4). In these conditions, the rate of Fe^{2+} oxidation decreases. Evidently, the mechanism of oxygenation of Fe^{2+} ions in alkaline medium is different from the one observed in solutions at near neutral pH or at slightly acidic pH. The Fe^{3+} ions can be also produced by the thermal decomposition of $Fe(OH)_2$ precipitate at a low oxygen (O_2) content.

The results of this study indicate a strong dependence of the chemical composition and structural properties of Fe-oxides formed on the $[Fe^{2+}]/[OH^-]$ concentration ratio at the beginning of the precipitation process, on the rate of oxygenation, time of precipitation, temperature, and the kind of alkali (NH_4OH or NaOH).

Samples FEO-1 to FEO-6 and FEO-15 were precipitated from $FeSO_4$ solutions without alkali addition. Phase analysis of samples FEO-1 to FEO-3 and FEO-15 showed only the presence of goethite. However, there were pronounced differences in the crystallinity of goethite precipitated at different temperatures. The crystallinity of goethite decreased with decrease in the temperature of precipitation.

These differences in crystallinity of goethite were revealed by both Mössbauer spectroscopy and X-ray diffraction. The two methods are in very good aggrement (see Figures 1 and 6). Mössbauer spectra of the isolated goethite particles show a pronounced asymmetric broadening of lines. Also, Mössbauer spectra contain the central quadrupole doublet of varying intensity, due to the presence of superparamagnetic particles. The Mössbauer spectrum of sample FEO-20 (see Figure 4) indicates that the crystallinity of this sample is better than that of sample FEO-1.

The Mossbauer spectra shown in Figure 1 indicate the presence of goethite with intermediate particle sizes. Also, these particiles are not well crystallized. A similar shape of the Mössbauer spectrum was recorded for the rust formed during the atmospheric corrosion of steel.[28,29]

Generally, goethite exhibits[30-32] a complex variety of Mössbauer spectra depending upon the sample crystallinity or/and particle size, lattice-substituted impurities (notably Al^{3+}), and the spectrum measurement temperature. Well-crystallized goethite is characterized by a typical six-line Mössbauer spectrum with peak intensity ratios approximating to 3 : 2 : 1 : 1 : 2 : 3.

The X-ray diffraction patterns of samples FEO-1 to FEO-4 also indicate distinct regularities (see Figure 6). A tendency of decrease in diffraction line intensity and increase in the diffraction line width of α-FeOOH with decrease in temperature (90 °C to 30 °C) was observed. The X-ray diffraction pattern of sample FEO-4 is characteristic of an amorphous material. Also, the diffraction line width shows a tendency to decrease from sample FEO-15 toward sample FEO-20. Samples FEO-19 and FEO-20 show a diffraction line width smaller than sample FEO-1. These results indicate the sensitivity of X-ray diffraction to the varying crystallinity of α-FeOOH.

Magnetite precipitated from $FeSO_4$ solutions, when the concentration of NH_4OH or NaOH was relatively high at the beginning of the precipitation process (see (Tables I and II). Table II indicates that in the course of this work only substoichiometric magnetite ($Fe_{3-x}O_4$) was precipitated. The capabilities of Mössbauer spectroscopy and X-ray diffraction made it possible to follow changes in the stoichiometry of magnetite.

Magnetite has the inverse spinel structure in which the cations occupy tetrahedral and ostahedral sites in the face-centered cubic close-packed oxygen lattice. The Fe^{3+} ions are distributed evenly between the tetrahedral and octahedral sites, whereas Fe^{2+} ions occupy only the octahedral sites. The Mössbauer spectrum of large particles of magnetite shows two sextets of lines at room temperature. The spectral component M_1 (outer sextet) is a contribution from the tetrahedral Fe^{3+} ions, and M_2 component (inner sextet) from the octahedral Fe^{2+} and Fe^{3+} ions. The increase in the intensity of M_1 component and the corresponding decrease in the intensity of M_2 component are indicative of magnetite nonstoichiometry. The stoichiometry, particle size and magnetic properties of magnetite are very sensitive to the mode of its preparation. In the same sense, magnetite formed during the corrosion of steel in aqueous medium is very sensitive to environmental conditions. The stoichiometry of magnetite is always better on an adherent layer owing to the more reductive conditions. The concentration of Fe^{2+} and $Fe(OH)^+$ ions is higher in an adherent layer than in a nonadherent, because the oxygen diffusion into the adherent layer is suppressed.

On the basis of the literature data[33] and the measured Mössbauer spectrum of sample FEO-26 (see Figure 2), it can be concluded that the stoichiometry of this sample corresponds to $Fe_{2.91}O_4$. Sample FEO-12 is more substoichiometric than sample FEO-26. Mössbauer spectrum of sample FEO-28 indicates a mixture of α-FeOOH + $Fe_{3-x}O_4$ or γ-Fe_2O_3. The X-ray diffraction of sample FEO-28 does not indicate γ-Fe_2O_3, but $Fe_{3-x}O_4$.

The mechanism of the formation of Fe-oxides from $FeSO_4$ solution, for the experimental conditions applied in this work, can be interpreted as follows.

In the experimental systems, with no alkalic addition or with addition of small amounts of alkali, Fe^{2+} ions are oxidized into Fe^{3+} ions with O_2 from the air. The possible mechanism of Fe^{2+} oxidation with O_2 in aqueous solutions has already been discussed. The Fe^{3+} ions undergo an intensive hydrolysis at 90 °C. The reactions of Fe^{3+} hydrolysis are accelerated at elevated temperature. When a small amount of NH_4OH or NaOH is added, the corresponding amount of $Fe(OH)_2$ is formed, but with a decrease in pH this compound dissolves rapidly. Iron(III) hydroxy complexes can be considered precursors of FeOOH in the precipitation process from $FeSO_4$ solution. The hydrolysis of Fe^{3+} is followed by the nucleation of structures, which are responsible for the formation of geothite (α-FeOOH), lepidocrocite (γ-FeOOH), and

»amorphous« iron(III) hydroxide. In our experiments, goethite (α-FeOOH) is formed at elevated temperatures. On the other hand, at room temperature an amorphous iron(III) hydroxide phase (ferrihydrite) is formed.

On the basis of the measured Mössbauer spectra, the presence of very fine FeOOH particles in »amorphous« precipitate is also possible. In this work, there was no attempt to record the Mössbauer spectra of samples FEO-4, FEO-5 and FEO-6 at very low temperatures (liq. He), in order to make a distinction between ferrihydrite and the superparamagnetic α-FeOOH and/or γ-FeOOH. Samples FEO-4, FEO-5 and FEO-6 are »amorphous« for X-rays. The presence of superparamagnetic α-Fe_2O_3 is unlikely under the given experimental conditions.

In »amorphous« iron(III) hydroxyde, Fe^{3+} ions are octahedrally coordinated by a mixture of O^{2-}, OH^- and OH_2. On the basis of the X-ray diffraction and the Mössbauer spectroscopy of »amorphous« iron(III) hydroxyde, it has been suggested that oxygen ions form a hexagonal close-packed lattice.[34–38] Kobayashi and Uda suggested[39] that the structure of »ferric hydroxide gel« is close to that of γ-FeOOH.

At high pH values, iron(II) hydroxide is precipitated. Oxidation of $Fe(OH)_2$ by oxygen from the air at 90 °C leads to the formation of magnetite. This process is accompanied by a decrease of pH in the suspension. The formation of magnetite by the thermal decomposition of $Fe(OH)_2$ is characteristic of the precipitation from $FeSO_4$ solution at a low O_2 content. The oxygenation of magnetite suspension leads to the formation of substoichiometric magnetite. With further oxidation, $Fe_{3-x}O_4$ transforms into structures close to γ-Fe_2O_3. These structures dissolve, due to their instability at low pH values. After the formation of magnetite, the pH-decrease and the formation of Fe^{3+} proceed slowly. Goethite can also form parallel with magnetite. These transformations are illustrated by samples FEO-7, FEO-9, FEO-10 and FEO-11 (see Table II and Figure 7). At a prolonged time of heating (>18 hours), hematite is also formed (samples FEO-10 and FEO-11).

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SAŽETAK

Mössbauerova spektroskopija i difrakcija X-zrake željeznih oksida pripravljenih iz otopine $FeSO_4$

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Kemijska i strukturna svojstva željeznih oksida, pripravljenih iz otopine $FeSO_4$, izrazito su ovisna o koncentracijskom odnosu $[Fe^{2+}]/[OH^-]$, o brzini oksidacije Fe^{2+}, vremenu taloženja, temperaturi i vrsti lužine (NH_4OH ili NaOH). Getit (α-FeOOH) različitog stupnja kristalizacije i podstehiometrijski magnetit se talože pri 90 °C. Stupanj kristalizacije α-FeOOH praćen je s pomoću Mössbauerove spektroskopije i difrakcije X-zraka. Mössbauerova spektroskopija pokazala je da stehiometrija $Fe_{3-x}O_4$ varira između $Fe_{2.91}O_4$ i približno $Fe_{2.67}O_4$. Međutim, difrakcija X-zrake dokazala je prisutnost $Fe_{3-x}O_4$, ali ne i maghemita (γ-Fe_2O_3). Hematit (α-Fe_2O_3) nastaje pri specifičnim eksperimentalnim uvjetima. Amorfni željezo(II)-hidroksid taloži se na sobnoj temperaturi. U radu se razmatra mehanizam taloženja željeznih oksida iz otopine $FeSO_4$.