Original scientific paper

THE EFFECT OF SODIUM DODECYL SULPHATE ON THE FORCED HYDROLYSIS of FeCl₃ SOLUTIONS[●]

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Precipitations by the forced hydrolysis of 0.2 M FeCl₃ aqueous solutions between 2 and 72 hours in the presence of 1% sodium dodecyl sulphate (SDS) were investigated. In the absence of SDS a direct phase transformation β-FeOOH → α-Fe₂O₃ *via* dissolution/recrystallization occured in the precipitation system. In the presence of SDS, α-FeOOH as an intermediate phase precipitated and, with a prolonged time of forced hydrolysis, also transformed to α-Fe₂O₃ *via* the dissolution/recrystallization mechanism. On the basis of Mössbauer spectra it was concluded that in the presence of SDS, α-Fe₂O₃ phase possessed a lower degree of crystallinity. In this precipitation process the competition between the stability of Fe(III)-dodecyl sulphate, on one side, and the formation of iron oxide phases, on the other, also played an important role. FE SEM revealed that the big α-Fe₂O₃ particles possessed the substructure. The elongation of primary α-Fe₂O₃ particles produced in the presence of SDS was noticed. This effect can be assigned to the preferential adsorption of dodecyl sulphate groups on nuclei and crystallites of FeOOH and α-Fe₂O₃ phase during the forced hydrolysis of FeCl₃ solutions.

Key words: FeCl₃ hydrolysis; sodium dodecyl sulphate; α-Fe₂O₃; Mössbauer; FT-IR; XRD; FE SEM

INTRODUCTION

Hematite (α-Fe₂O₃) particles have found different applications as pigments, photocatalysts, electrode materials, fine abrasives or cosmetic additives. α-Fe₂O₃ can also be used as an adsorbent for toxic elements or radioisotopes in wastewater treatment. In surface and colloid chemistry these particles are often used as model systems due to their excellent acido-basic surface properties. The investigation of colloid stability of α-Fe₂O₃ particles is important for understanding the nature of this phenomenon.

The simplest way to produce α-Fe₂O₃ particles is by forced hydrolysis in a boiling 0.01 M FeCl₃ solution [1], whereas at temperatures below 70 °C akaganéite (β-FeOOH) particles (spindle- or cigar-shaped) will precipitate. The synthesis and characterization of β-FeOOH and its decomposition products in vacuum were investigated [2]. Musić et

al. [3] used Mössbauer spectroscopy to investigate the hydrolysis of 0.1 M solutions of Fe(NO₃)₃, FeCl₃, Fe₂(SO₄)₃ or NH₄Fe(SO₄)₂ at 90 °C. A proposal was made concerning the mechanism of formation of the oxides and hydroxides of Fe³⁺ ions in these precipitation systems. It is generally accepted that the phase transformation β-FeOOH → α-Fe₂O₃ in hydrolysing FeCl₃ solutions at elevated temperature is operated by a dissolution/recrystallization mechanism [4–6]. The application of Mössbauer spectroscopy in investigating the precipitation of iron oxides has recently been reviewed by Musić et al. [7].

The nano/microstructure of α-Fe₂O₃ plays a very important role in many applications of this iron oxide. For this reason many researchers investigated the conditions for the preparation of α-Fe₂O₃ with different properties. Katsuki and Komarneni [8] used the forced hydrolysis of the FeCl₃ solution under hydrothermal conditions to investigate the influence of morphology on the colour of

the red pigment (α-Fe$_2$O$_3$) for porcelain. Sugimoto et al. [9] noticed remarkably different effects of Cl$^-$, OH$^-$, SO$_4^{2-}$ or PO$_4^{3-}$ anions on the shape and internal structure of α-Fe$_2$O$_3$ particles. Hollow α-Fe$_2$O$_3$ spheres were produced by the forced hydrolysis of the FeCl$_3$ solution containing H$_3$PW$_{12}$O$_{40}$ [10]. Mesoporous α-Fe$_2$O$_3$ particles were produced by the forced hydrolysis of the FeCl$_3$ solution containing L-phenylalanine and N-(3-di methylaminoethylaminopropyl)-N-ethylcarbodiimide hydrochloride [11]. Kandori et al. [12] also investigated the effect of surfactants on the precipitation of colloidal particles by the forced hydrolysis of the FeCl$_3$-HCl solution. The hydrothermal transformation β-FeOOH → α-Fe$_2$O$_3$ in dense aqueous suspensions, prepared by a partial neutralization of the concentrated FeCl$_3$ solution with the concentrated NaOH solution, was investigated by Žic et al. [13]. Žic et al. [14] also investigated the precipitation of α-Fe$_2$O$_3$ from dense β-FeOOH suspensions with ammonium amidosulphonate added. The peanut-type α-Fe$_2$O$_3$ particles, as well as particles in the form of double cupolas interconnected with the neck were obtained. These particles showed the substructure. Double cupolas were porous and consisted of linear chains of small α-Fe$_2$O$_3$ particles (also interconnected) which were directed from the centre toward the surface of cupolas.

The aim of the present work was to obtain more data about the influence of sodium dodecyl sulphate on the crystallization kinetics, phase transformations and particle morphology in the precipitates formed by the forced hydrolysis of aqueous FeCl$_3$ solutions. This work is a continuation of our longtime investigations in the precipitation chemistry of iron oxides (group name for hydroxides, oxyhydroxides and oxides). In many cases the phase analyses of solid hydrolytical products of iron ions are a demanding task, specifically if iron oxide phases vary from amorphous to a well-crystalline nature. For this reason three complementary techniques, ^{57}Fe Mössbauer, FT-IR and XRD were used in the phase analysis. Generally, it is known that surface active agents act very differently on the precipitation processes in dependence on their characteristics (polar, nonpolar, chemical nature of the organic chain, pH).

EXPERIMENTAL

Sample preparation

AnalaR grade FeCl$_3$·6H$_2$O was supplied by Kemika. Sodium dodecyl sulphate (SDS) was supplied by Sigma Aldrich (Cat. No.: 151-21-3; ACS grade reagent). Twice distilled water was prepared in own laboratory and used in all experiments. The stock solution 2M FeCl$_3$ was prepared. The concentration of 0.2M FeCl$_3$ was adjusted in all precipitation systems. The experimental conditions for the preparation of samples are given in Table 1. The yellowish precipitate was formed by adding FeCl$_3$ solution into clear aqueous solution of SDS thus indicating the formation of Fe(III)-dodecyl sulphate. Thus obtained suspension was homogenized in ultrasound bath. The precipitation systems were autoclaved at 160 ^{o}C using a Teflon^R-lined, non-stirred pressure vessel manufactured by Parr Instruments (model 4744). The autoclaves were heated between 2 and 72 h in a DX 300 gravity oven (Yamato; temperature uniformity ±1.9 ^{o}C at 100 ^{o}C and ±3 ^{o}C at 200 ^{o}C). The autoclaving times were corrected for the time needed that the autoclave reaches the predetermined temperature. After a proper autoclaving time the autoclaves were abruptly cooled with cold water. The mother liquor was separated from the precipitate with the ultra-speed centrifuge (Sorvall model Super T21). The separated precipitates were subsequently washed with twice-distilled water and one time with C$_2$H$_5$OH, then dried.

Table 1. Experimental conditions for forced hydrolysis of 0.2 M FeCl$_3$ solution containing SDS

Sample	2M FeCl$_3$ / ml	SDS/ g	H$_2$O / ml	T / ^{o}C	Time of ageing
R1	4		36	160	2 h
R2	4		36	160	6 h
R3	4		36	160	24 h
R4	4		36	160	72 h
S1	4	0.4	36	160	2 h
S2	4	0.4	36	160	6 h
S3	4	0.4	36	160	24 h
S4	4	0.4	36	160	72 h

SDS = sodium dodecyl sulphate; h = hour

Instrumentation

^{57}Fe Mössbauer spectra were recorded at 20 $^{\circ}$C in the transmission mode using a standard configuration by WissEl GmbH (Starnberg, Germany). The ^{57}Co/Rh Mössbauer source was used. The velocity scale and Mössbauer parameters refer to the metallic α-Fe source at 20 $^{\circ}$C. Deconvolution of Mössbauer spectra was made using the MossWin program.

FT-IR spectra were recorded at RT with a Perkin-Elmer spectrometer (model 2000). The powders were mixed with KBr, then pressed into tablets using the Carver press.

XRD patterns were recorded with an APD 2000 powder diffractometer manufactured by Ital-Structures (GNR Analytical Instruments Group, Italy).

The samples were also inspected with a thermal field emission scanning electron microscope (FE SEM, model JSM-7000F) manufactured by Joel Ltd.

RESULTS AND DISCUSSION

The Mössbauer spectra of reference samples R1 to R4 as well as S1 to S4 produced in the presence of SDS surfactant are shown in Figures 1 and 2. The Mössbauer spectrum of sample R1 shows the superposition of two doublets with quadrupole splittings $\Delta_1 = 0.55$ and $\Delta_2 = 0.99$ mm s^{-1}. The parameters of this spectrum can be assigned to β-FeOOH (Table 2). The spectra of samples R2, R3 and R4 are characterized by one sextet with parameters corresponding to α-Fe$_2$O$_3$. The increase in hyperfine magnetic field (HMF) from 51.2 to 51.5 T with the autoclaving time prolonged from 6 and 72 h can be related to crystalline ordering in α-Fe$_2$O$_3$. Upon 2 h forced hydrolysis of the 0.2 M FeCl$_3$ solution containing SDS surfactant (sample S1) a central quadrupole doublet was recorded. This spectrum was fitted for one average doublet with $\Delta = 0.79$ mm s^{-1} and can be assigned to β-FeOOH. The effect of SDS added to the phase composition of a solid hydrolytical product is well visible in the spectrum of sample S2. This spectrum was fitted as a superposition of the central quadrupole doublet and two sextets. The central quadrupole doublet ($\Delta = 0.75$ mm s^{-1}) can be assigned to β-FeOOH (39 %), whereas two sextets with HMF$_{average}$ = 48.5T (~ 56 %) and HMF = 37.4 T (5 %) can be assigned to α-Fe$_2$O$_3$ and α-FeOOH (goethite), respectively. The spectrum of sample S3 showed two sextets, one corresponding to α-Fe$_2$O$_3$ (HMF$_{average}$ = 49.8 T) and the other of small relative intensity due to the presence of a small amount of α-FeOOH (outer peaks in the spectrum denoted with arrows). Sample S4 showed only the presence of the α-Fe$_2$O$_3$ phase characterized by HMF$_{average}$ = 50.7 T.

Table 2. ^{57}Fe Mössbauer parameters for samples R1 to R4 and S1 to S4

| Sample	Line	δ / mm s^{-1}	Δ or E_q / mm s^{-1}	HMF / T	Γ / mm s^{-1}	A / %	Identification
R1	Q1	0.38	0.55		0.30	57	β-FeOOH
	Q2	0.37	0.99		0.33	43	
R2	M	0.37	− 0.21	51.2	0.34	100	α-Fe$_2$O$_3$
R3	M	0.36	− 0.21	51.5	0.29	100	α-Fe$_2$O$_3$
R4	M	0.37	− 0.21	51.5	0.34	100	α-Fe$_2$O$_3$
S1	Q*	0.38	0.79		0.23	100	β-FeOOH
S2	Q*	0.38	0.75		0.54	39	β-FeOOH
	M1	0.37	− 0.26	37.4	0.97	5	α-FeOOH
	M2	0.37	− 0.20	48.5	0.31	56	α-Fe$_2$O$_3$
S3	M	0.37	− 0.21	49.8	0.27	100	α-Fe$_2$O$_3$[**]
S4	M	0.37	− 0.21	50.7	0.25	100	α-Fe$_2$O$_3$

All data are given relative to α-Fe standard.
Key: δ = isomer shift; Δ or Eq = quadrupole splitting; HMF = hyperfine magnetic field;
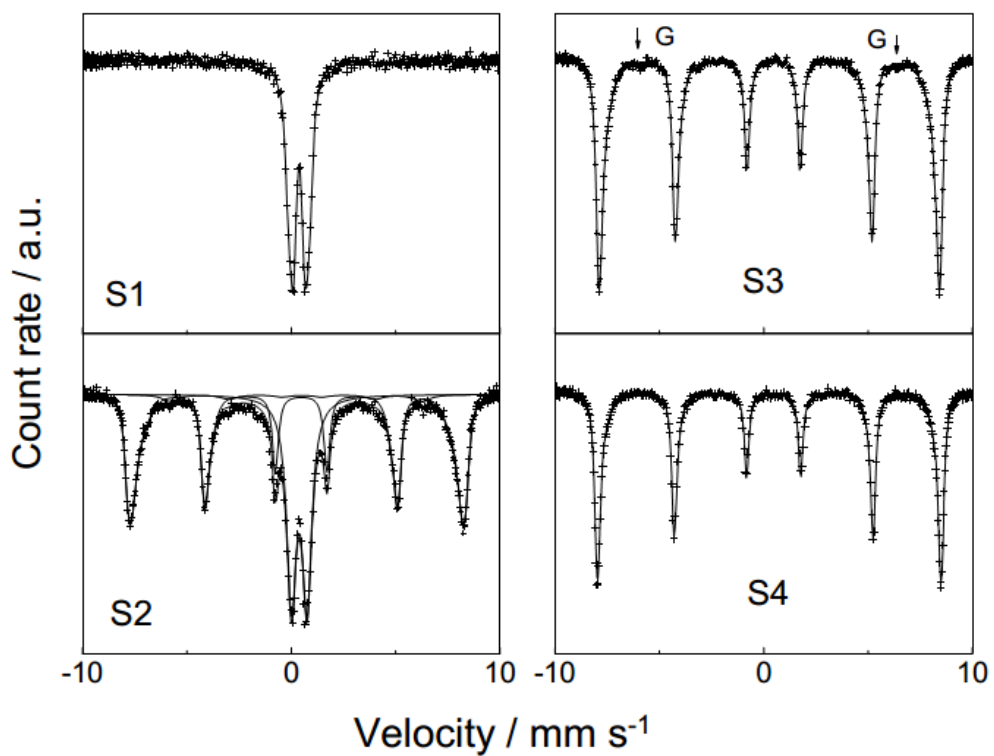Γ = line width; A = area under the peaks
Errors: δ = ± 0,01 mm s^{-1}; Δ or Eq = ± 0,01 mm s^{-1}, HMF = ± 0,2 T
[*] Average quadrupole doublet
[**] Sample S3 also contains small amount of α-FeOOH, as denoted with arrows in Figure 2
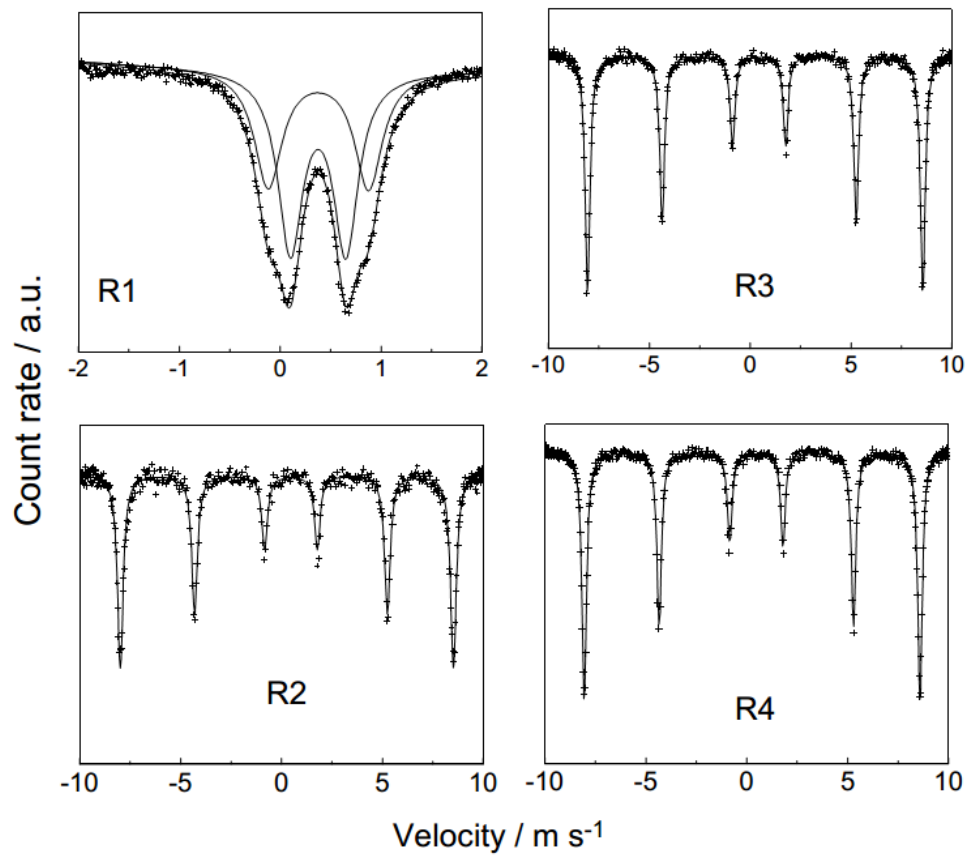
Figure 1. ^{57}Fe Mössbauer spectra of reference samples R1 to R4 produced by forced hydrolysis of 0.2 M FeCl$_3$ solution in the presence of 1% SDS.

Figure 2. ^{57}Fe Mössbauer spectra of samples S1 to S4 produced by forced hydrolysis of 0.2 M FeCl$_3$ solution in the presence of 1 % SDS.

The Mössbauer spectra of samples S1 and S2 were recorded at extended velocity scale and for this reason the central quadrupole splitting subspectrum was fitted for one average spectrum which is assigned to β-FeOOH. The presence of β-FeOOH phase in samples S1 and S2 is confirmed with XRD as shown in Figure 3. The HMF values of α-Fe$_2$O$_3$

calculated for samples S2 to S4 increased from 48.5 to 50.7 T, which are lower values than those corresponding to α-Fe$_2$O$_3$ for reference samples R2 to R4. Evidently, this effect can be assigned to the presence of SDS. The XRD patterns of R and S samples are given in Figure 3.
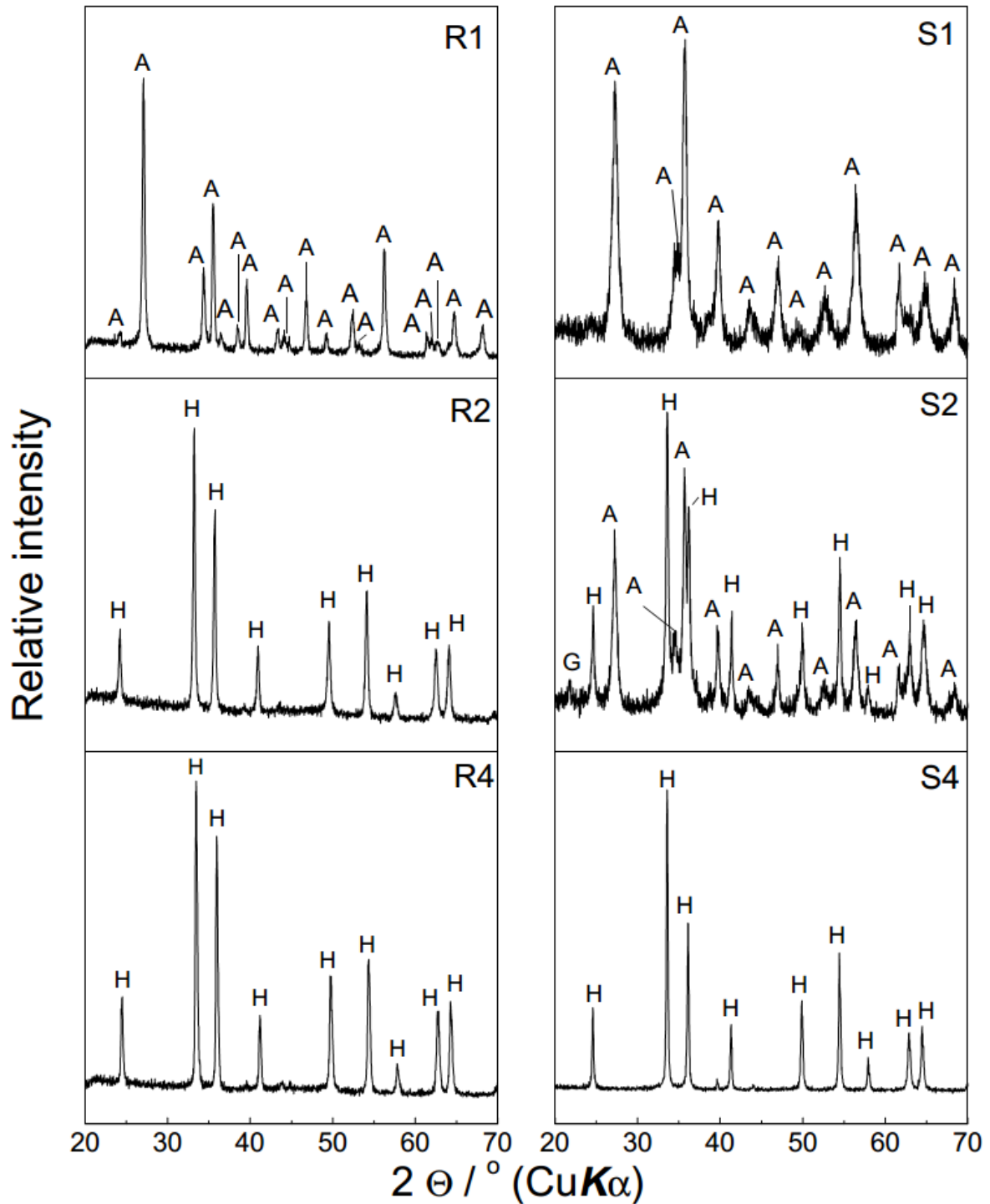
Figure 3. XRD patterns of reference samples R1, R2, R4 and samples S1, S2 and S4 produced
in the presence of 1% SDS (A=Akagenéite; G=Goethite; H=Hematite).

The sharpness of XRD lines of sample R1 (Figure 3) is increased in relation to sample S1 and this can be related to better crystallinity or an increased crystallite size of β-FeOOH precipitated in the absence of SDS. However, sample S1 as well as S2 showed a higher relative intensity of the diffraction line 211 in relation to line 310, which could be related to the preferential adsorption of dodecyl sulphate groups on the selected crystallographic plane of β-FeOOH. The XRD pattern of sample S2 showed a small relative intensity XRD line 110 (denoted as G) due to the presence of a small amount of goethite, and this is in line with corresponding Mössbauer spectrum.

Figure 4 shows the FT-IR spectra of reference samples R1 to R4 and samples S1 to S4 prepared in the presence of SDS. The FT-IR spectra of samples R1 and S1 can be assigned to β-FeOOH. Sample R1 shows an IR band centred at 848 cm^{-1}, two shoulders at 700 and 640 cm^{-1} and two shoulders at 498 and 425 cm^{-1}. Sample S1 shows an IR band at 425 cm^{-1} with a shoulder at 491 cm^{-1}. According to earlier work [15] the band at 848 cm^{-1} and the shoulder at 700 cm^{-1} can be assigned to the deformation vibration of OH groups, whereas the intense shoulder at 640 cm^{-1} can be related to the interaction of Fe-OH groups with Cl$^-$ ions. Generally, β-FeOOH possesses a hollandite-type crystal structure and the structural channels in β-FeOOH produced from the FeCl$_3$ solution contain water and a small amount of Cl$^-$ ions [16]. These Cl$^-$ ions (less than ~ 2 %) in structural channels stabilize the crystal lattice of β-FeOOH and cannot be removed by simple washing. Weckler and Lutz [17] discussed two sets of vibrations at 847 and 820 cm^{-1}, and also those at 697 and 644 cm^{-1} in terms of two O-H...Cl hydrogen bonds present in β-FeOOH. The IR spectrum of β-FeOOH was also the subject of discussion by Murad and Bishop [18]. The FT-IR spectra of samples R2 to R4 can be assigned to α-Fe$_2$O$_3$. Wang et al. [19] tabulated optical parameters for bulk α-Fe$_2$O$_3$ and investigated the influence of the geometrical shape of α-Fe$_2$O$_3$ particles on the corresponding FT-IR spectrum. Generally, the IR spectrum of α-Fe$_2$O$_3$ shows six active vibrations, two A_{2u} (E∥C) and four E_u (E⊥C). The effect of SDS is clearly visible in the spectra of samples S2 to S3. In the FT-IR spectrum of sample S2 the IR bands at 850, 697 and 640 cm^{-1} are due to β-FeOOH and the IR bands at 574, 537 and 482 cm^{-1} are due to α-Fe$_2$O$_3$. Two IR bands at 895 and 796 cm^{-1} are typical of α-FeOOH and are assigned to the Fe-O-H bending vibration (δ$_{OH}$ and γ$_{OH}$, re-

spectively) [20]. The FT-IR spectrum of sample S3 shows only the presence of α-Fe$_2$O$_3$ and a small fraction of α-FeOOH, whereas the FT-IR spectrum of sample S4 can be assigned to α-Fe$_2$O$_3$ as a single phase. In the FT-IR spectra of samples produced in the presence of SDS additional bands are also noticed. For example, in the spectrum of sample S3 four IR bands at 1206, 1126, 1036 and 977 cm^{-1} are well visible. These IR bands can be related to the sulphate group. The $v_3(SO_4)$ fundamental vibration is split into 3 active IR bands due to the formation of a surface bidentate bridging complex between the sulphate group and surface iron atoms [21]. The presence of an IR band at 977 cm^{-1} is due to the $v_1(SO_4)$ vibration. It is generally known that the specific adsorption of oxyanions reaches its maximum at acidic pH values and decreases with an increase in pH values.
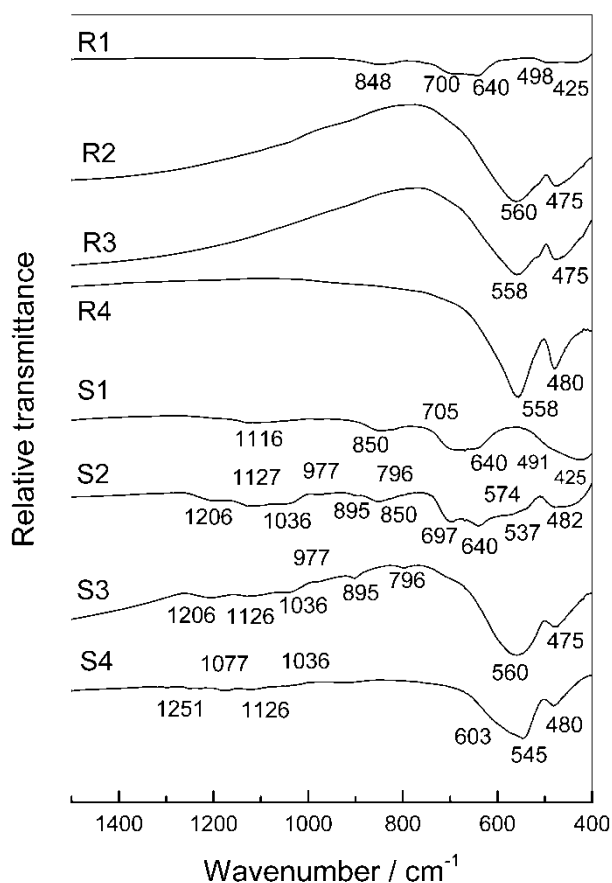

Figure 4. FT-IR spectra of reference samples R1 to R4 and samples S1 to S4.

Ocaňa et al. [22] precipitated spindle-shaped α-Fe$_2$O$_3$ particles by the forced hydrolysis of the Fe(ClO$_4$)$_3$ solution at 100 °C. The phosphate anions that could not be washed out were responsible for

the formation of these particles morphology. The adsorbed phosphates were visible in the IR spectrum as evidence, with several peaks between 1036 and 934 cm^{-1}.

Mössbauer, XRD and FT-IR measurements showed a direct phase transformation β-FeOOH → α-Fe$_2$O$_3$ in reference samples (R) produced by the forced hydrolysis of the 0.2 M FeCl$_3$ solution. In the presence of SDS (samples S1 to S4) the kinetics of this phase transformation is retarded and in samples S2 and S3 produced between 6 and 24 hours of forced hydrolysis a small fraction of an intermediate phase α-FeOOH is detected. Kandori et al. [12] assigned the formation of α-FeOOH phase due to SDS addition in FeCl$_3$-HCl hydrolysing solutions (HCl concentration was fixed; log (HCl) = − 2.50). Musić et al. [23] investigated the effect of HCl additions on forced hydrolysis of FeCl$_3$ solutions. These authors found that under the certain conditions the forced hydrolysis of FeCl$_3$ solution containing only HCl additions may also produce α-FeOOH phase. Wang et al. [24] investigated the precipitation of α-Fe$_2$O$_3$ nanoparticles by the forced hydrolysis of FeCl$_3$ solutions with no additive presence. In dependence on the experimental conditions primary nanoparticles showed different morphologies. It was also reported that beside the β-FeOOH → α-Fe$_2$O$_3$ phase transformation there was also a direct phase transformation of the amorphous fraction into α-Fe$_2$O$_3$.

In the present work, the addition of SDS to the precipitation system caused the formation of a small fraction of α-FeOOH as an intermediate phase, and between 6 and 72 h of autoclaving the HMF value of α-Fe$_2$O$_3$ varied from 48.5 to 50.7 T. These values of HMF are significantly decreased in relation to 51.75 T measured for well-crystalline α-Fe$_2$O$_3$, as reported by Murad and Johnston [25]. It can be concluded that the presence of SDS lowers the crystallinity of precipitated α-Fe$_2$O$_3$.

The FE SEM image of sample R1 (Figure 5a) showed mainly the presence of β-FeOOH rods, but star- and X-shaped particles were also noticed. Sample R2 showed micron size α-Fe$_2$O$_3$ particles (Figure 5b) which consisted of primary α-Fe$_2$O$_3$ nanoparticles, as evidenced by Figure 5c. α-Fe$_2$O$_3$ particles produced upon 72 h of the forced hydrolysis of FeCl$_3$ solutions at 160 $^{\circ}$C (sample R4) are shown in Figure 6a. These particles also showed the substructure (Figure 6b); however, the primary α-Fe$_2$O$_3$ particles increased in size. The agglomera-

tion of β-FeOOH nanorods (sample S1) is visible in Figure 7a. Figures 7 b,c show big (micron size) particles of sample S4 of near spherical and peanut-type shapes, which possess the substructure and consist of fine, elongated (1D) primary α-Fe$_2$O$_3$ particles (Figure 7c).
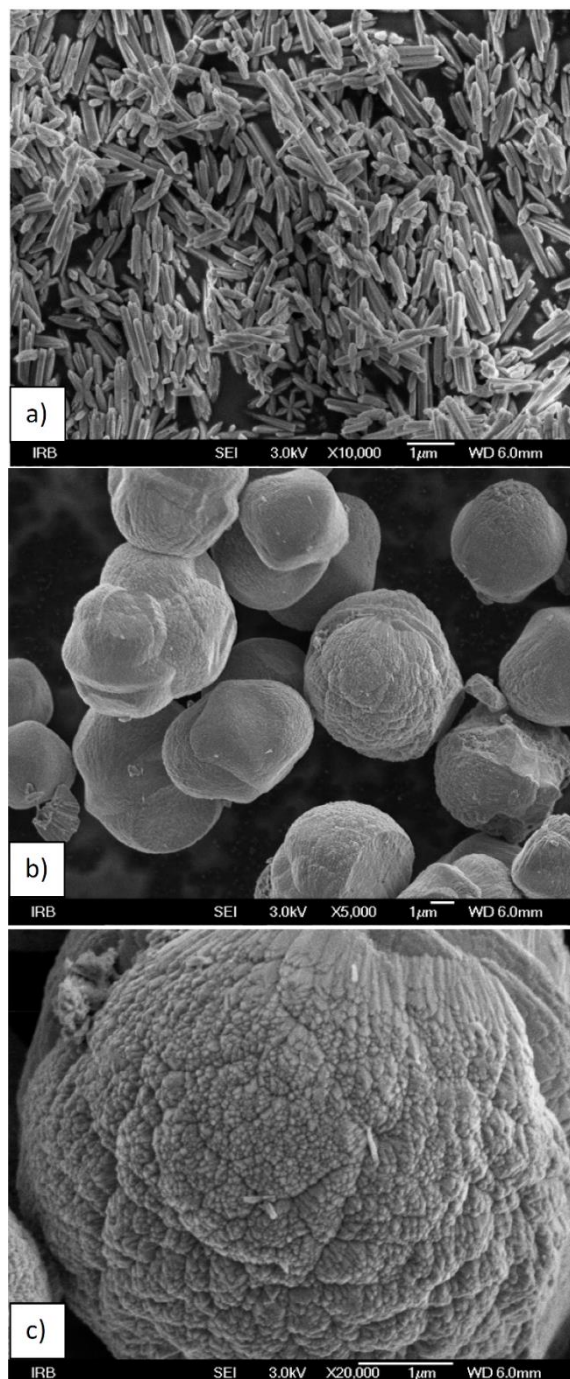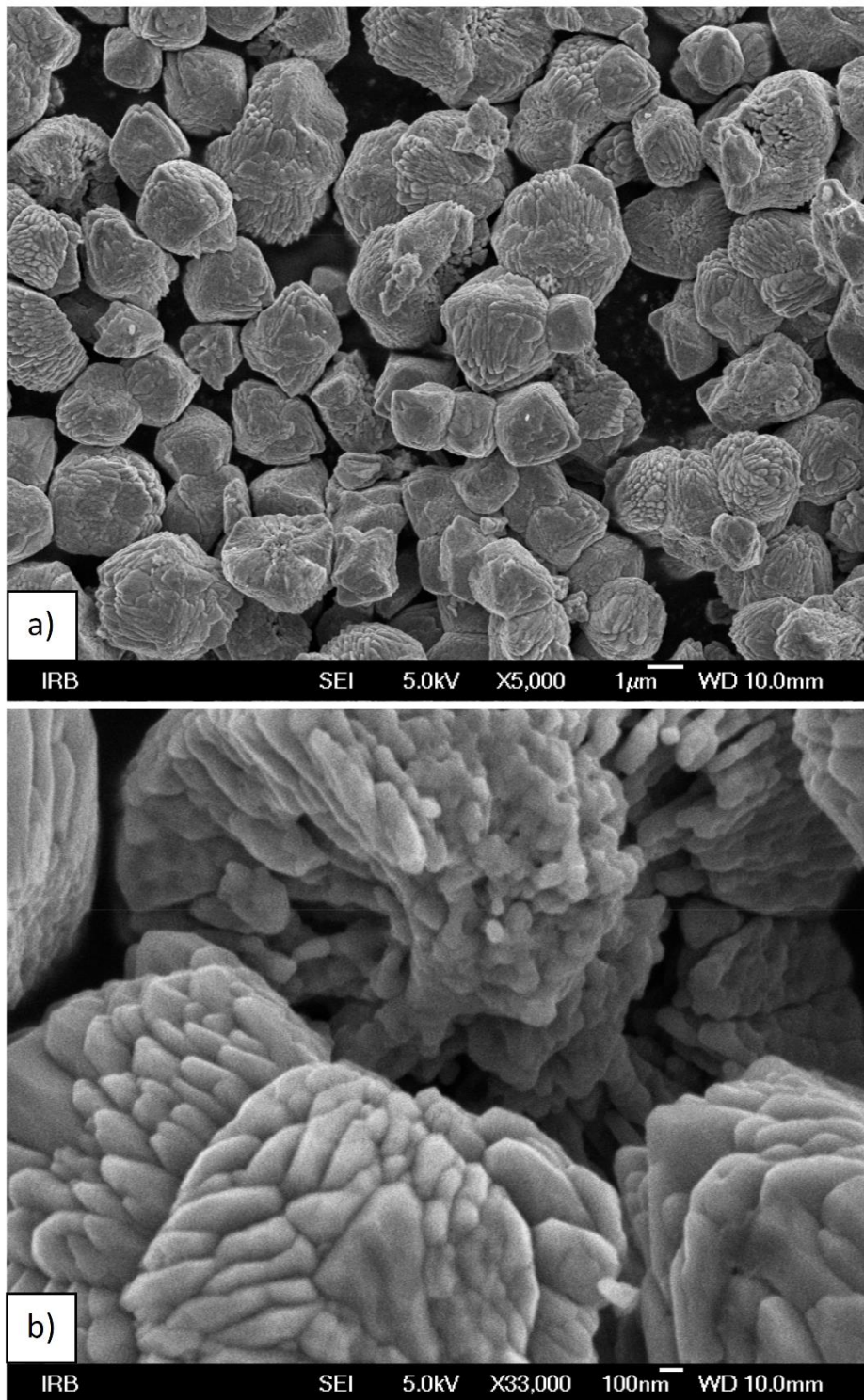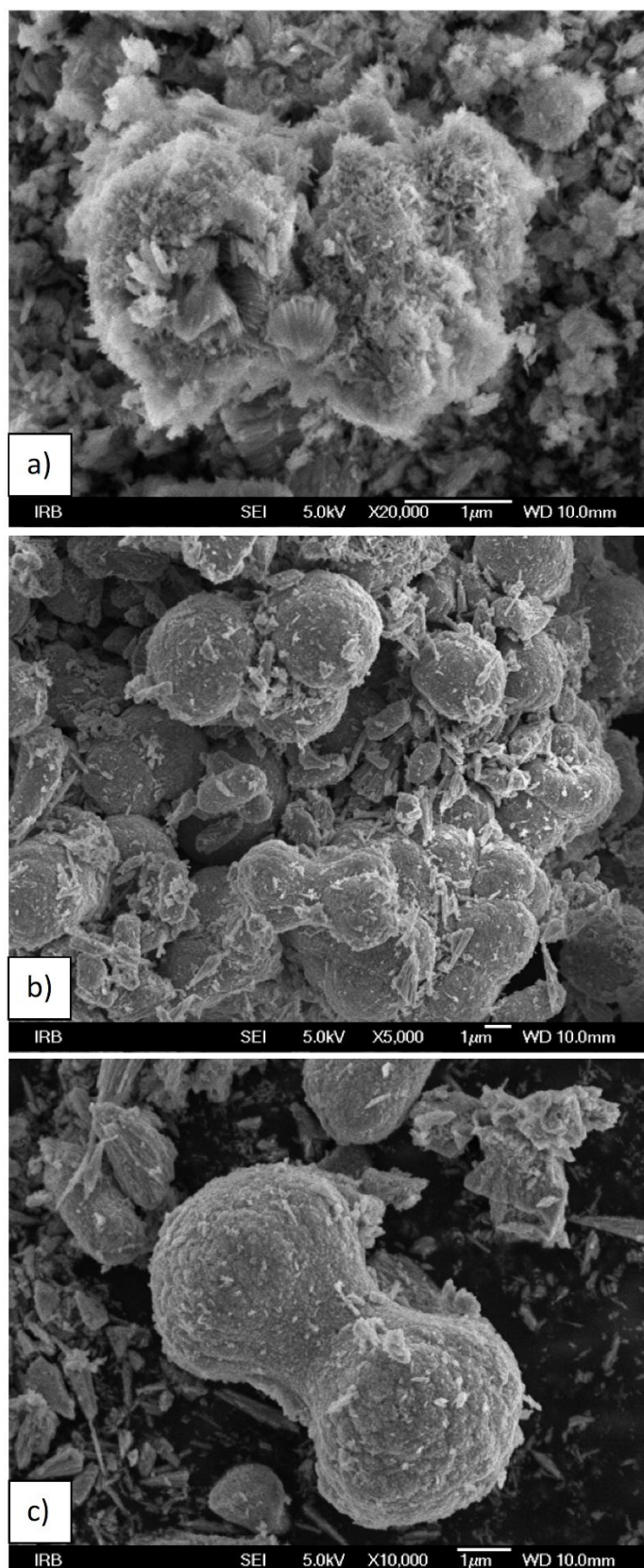

Figure 5. FE SEM images of samples: (a) R1 and (b, c) R2.

Figure 6. FE SEM images of reference samples R4 at different magnifications.

Figure 7. FE SEM images of samples: (a) S1 and (b, c) S4.
The samples were precipitated in the presence of SDS.

CONCLUSION

The effect of SDS (1 %) on the kinetics, phase composition and shape of the particles precipitated by the forced hydrolysis of the 0.2 M FeCl$_3$ solution was investigated. A direct phase transformation β-FeOOH → α-Fe$_2$O$_3$ *via* dissolution/recrystallization was present in the absence of SDS. In the presence of SDS a small fraction of α-FeOOH precipitated, which transformed to the end product α-Fe$_2$O$_3$ also *via* the dissolution/recrystallization mechanism. α-Fe$_2$O$_3$ particles precipitated in the presence of SDS showed lower crystallinity in relation to reference samples, as concluded on the basis of Mössbauer spectra. This effect was explained by the competition between the stability of Fe(III)-dodecyl sulphate on one side and the formation of iron oxide phases on the other side. Precipitated α-Fe$_2$O$_3$ particles showed the substructure, *i.e.*, consisted of much smaller primary particles. The effect of SDS on the microstructure of α-Fe$_2$O$_3$ particles is noticed. The influence of SDS on the forced hydrolysis of FeCl$_3$ solutions can be related to the specific adsorption of sulphate groups on the nuclei and crystallites of FeOOH and α-Fe$_2$O$_3$ phases. The specific adsorption of dodecyl sulphate groups was evidenced by FT-IR.

REFERENCES

[1] J. R. Freyer, A. Gildawie, R. Paterson, High resolution studies of the initial stages of precipitation of hydrous iron oxides, *Eight Int. Congress on Electron Microscopy*, Canberra, 1974, **Vol. 1**, pp. 708–709.

[2] J. M. Gonzáles-Calbet, M. A. Alario-Franco, M. Gayoso-Andrade, The porous structure of synthetic akaganeite, *J. Inorg. Nucl. Chem.*, **43** (1981), pp. 257–264.

[3] S. Musić, A. Vértes, G. W. Simmons, I. Czakó-Nagy, H. Leidheiser Jr., Mössbauer spectroscopic study of the formation of Fe(III)-oxyhydroxides and oxides by hydrolysis of aqueous Fe(III) salt solutions, *J. Coll. Interface Sci.,* **85** (1982), pp. 256–266.

[4] E. Matijević, P. Scheiner, Ferric hydrous oxide sols. III. Preparation of uniform particles by hydrolysis of Fe(III)-chloride, -nitrate, and -perchlorate solutions, *J. Coll. Interface Sci.*, **63** (1978), pp. 509–524.

[5] S. Hamada, E. Matijević, Ferric hydrous oxide sols. IV. Preparation of uniform cubic hematite particles by hydrolysis of ferric chloride in alcohol-water solutions, *J. Chem. Soc. Faraday Trans.*, **I 78** (1982), pp. 2147–2156.

[6] E. K. De Blanco, M. A. Blesa, S. J. Liberman, Comments on the mechanism of the akageneite-hematite phase transformation in hydrothermal solutions, *Reactivity of Solids*, **1** (1986), pp. 189–194.

[7] S. Musić, M. Ristić, S. Krehula, ^{57}Fe Mössbauer spectroscopy in the investigation of the precipitation of iron oxides, Chapter in the book *Mössbauer Spectroscopy: Applications in Chemistry, Biology and Nanotechnology*, Edited by V. K. Sharma, G. Klingelhofer and T. Nishida, Publ. by John Wiley & Sons, 2013, pp. 470–504.

[8] H. Katsuki, S. Komarneni, Role of α-Fe$_2$O$_3$ morphology on the color of red pigment for porcelain, *J. Am. Ceram. Soc.*, **86** (2003), pp. 183–185.

[9] T. Sugimoto, Y. Wang, H. Itoh, A. Muramatsu, Systematic control of size, shape and internal structure of monodisperse α-Fe$_2$O$_3$ particles, Colloids Surfaces A: Physicochem. and Eng. Aspects, **134** (1998), pp. 205–279.

[10] B. Mao, Z. Kang, E. Wang, C. Tian, Z. Zhang, C. Wang, Y. Song, M. Li, *J. Solid State Chem.*, **180** (2007), pp. 489–495.

[11] K. Kandori, N. Hori, T. Ishikawa, Preparation of mesoporous hematite particles by a forced hydrolysis reaction accompanying a peptide production reaction, *Colloids Surfaces: Physicochem. Eng. Aspects*, **290** (2006), pp. 280–287.

[12] K. Kandori, I. Hori, A. Yasukawa, T. Ishikawa, Effect of surfactants on the precipitation and properties of colloidal particles from forced hydrolysis of FeCl$_3$-HCl solutions, *J. Mater. Sci.*, **30** (1995), pp. 2145–2152.

[13] M. Žic, M. Ristić, S. Musić, Microstructural changes in particles detected during the transformation from β-FeOOH to α-Fe$_2$O$_3$ in dense aqueous suspensions, *J. Alloys Comp.*, **464** (2008), pp. 81–88.

[14] M. Žic, M. Ristić, S. Musić, Precipitation of α-Fe$_2$O$_3$ from dense β-FeOOH suspensions with added ammonium amidosulfonate, *J. Mol. Struct.* **924–926** (2008), pp. 235–242.

[15] S. Musić, A. Šarić, S. Popović, Effects of urotropin on the formation of β-FeOOH, *J. Mol. Struct.* **410–411** (1997), pp. 153–156.

[16] A. Šarić, S. Musić, K. Nomura, S. Popović, Microstructural properties of Fe-oxide powders obtained by precipitation from FeCl$_3$ solutions, *Mater. Sci. Eng.*, **B56** (1998), pp. 43–52.

[17] B. Weckler, H. D. Lutz, Lattice vibration spectra. Part XCV. Infrared spectroscopic studies on the iron oxide hydroxides goethite (a), akageneite (b), lepidocrocite (d) and feroxyhite (d), *Eur. J. Solid State Inorg. Chem.*, **35** (1998), pp. 531–544.

[18] E. Murad, J. L. Bishop, The infrared spectrum of synthetic akageneite, β-FeOOH, *Am. Mineral.*, **85** (2000), pp. 716–721.

[19] Y. Wang, A. Muramatsu, T. Sugimoto, FTIR analysis of well-defined α-Fe₂O₃ particles, *Colloid Surf. Sci. A: Physicochem. Aspects*, **134** (1998), pp. 281–297.

[20] S. Krehula, S. Musić, Influence of ageing in an alkaline medium on the microstructural properties of α-FeOOH, *J. Cryst. Growth*, **310** (2008), pp. 513–520.

[21] D. Peak, R. G. Ford, D. L. Sparks, An in situ ATR-FTIR investigation of sulfate bonding mechanisms on goethite, *J. Coll. Interface Sci.*, **218** (1999), pp. 289–299.

[22] M. Ocaňa, M. P. Morales, C. J. Serna, Homogeneous precipitation of uniform α-Fe₂O₃ particles from iron salts solutions in the presence of urea, *J. Coll. Interface Sci.* **212** (1999), pp. 317–323.

[23] S. Musić, S. Krehula, S. Popović, Effect of HCl additions on forced hydrolysis of FeCl₃ solutions, *Mater. Lett.,* **58** (2004), pp. 2640–2645.

[24] W. Wang, J. Y. Howe, B. Gu, Structure and morphology evolution of hematite (α-Fe₂O₃) nanoparticles in forced hydrolysis of ferric chloride, *J. Phys. Chem.*, **C 112** (2008), pp. 9203–9208.

[25] E. Murad, J. H. Johnston, Iron oxides and oxyhydroxides, *in*: G. J. Long (Ed.), *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, **2**, Plenum Pub. Corp. 1987, pp. 507–582.

ЕФЕКТОТ НА НАТРИУМ ДОДЕЦИЛ СУЛФАТ ВРЗ ПРИСИЛНАТА ХИДРОЛИЗА НА РАСТВОРИ НА FeCl₃

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Изучувани се преципитациите при присилна хидролиза на воден раствор од 0.2 M FeCl₃ за времетраење од 2 до 72 часа во присуство на 1% натриум додецил сулфат (SDS). Во отсуство на SDS во преципитациониот систем доаѓа до директна фазна трансформација β-FeOOH → α-Fe₂O₃ преку механизмот растворање/прекристализација. Во присуство на SDS, α-FeOOH како интермедијарна фаза преципитира, а со продолжено време на присилна хидролиза исто така се трансформира во α-Fe₂O₃ преку механизам на растворање/прекристализација. Врз основа на Месбауеровите (Mössbauer) спектри е заклучено дека во присуство на SDS фазата на α-Fe₂O₃ поседува понизок степен на кристалност. Во овој преципитационен процес, важна улога игра и компетицијата помеѓу стабилноста на Fe(III)-додецил сулфатот, од една страна, и формирањето на фазите од оксидите на железото, од друга страна. FE SEM покажа дека крупните честички на α-Fe₂O₃ поседуваат супструктура. Забележано е издолжување на примарните честички на α-Fe₂O₃ добиени во присуство на SDS. Овој ефект може да му се припише на преферираната атсорпција на додецил сулфатните групи врз нуклеусите и кристалитите од FeOOH и фазата на α-Fe₂O₃ во текот на присилната хидролиза на растворите на FeCl₃.

Клучни зборови: FeCl₃ хидролиза; натриум додецил сулфат; α-Fe₂O₃; Месбауер (Mössbauer); FT-IR; XRD; FE SEM