Structural properties of precipitates formed by hydrolysis of Fe$^{3+}$ ions in Fe$_2$(SO$_4$)$_3$ solutions

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The structural properties of the solid phase, formed by the hydrolysis of Fe$^{3+}$ ions in Fe$_2$(SO$_4$)$_3$ solutions at 90 or 120°C, were investigated using X-ray diffraction, $^{57}$Fe Mössbauer spectroscopy, Fourier transform–infrared spectroscopy (FT–IR) and transmission electron microscopy. The concentration regions of Fe$_2$(SO$_4$)$_3$ were determined for the precipitation of goethite, α-FeOOH, or hydronium jarosite, H$_3$OFe$_3$(OH)$_4$(SO$_4$)$_2$, as a single phase. Superparamagnetic behaviour of α-FeOOH particles was observed. Hydrolysis of Fe$^{3+}$ ions in 0.1 M Fe$_2$(SO$_4$)$_3$ solutions at 120°C produced H$_2$OFe$_3$(OH)$_4$(SO$_4$)$_2$ and basic sulphate, Fe$_4$(OH)$_{10}$SO$_4$. The interpretation of $^{57}$Fe Mössbauer and FT–IR spectra is given.

1. Introduction
Precipitation of iron(III) oxyhydroxides and oxides from Fe(III)-salt solutions has been studied by many authors. It was observed that the phase composition of precipitate, morphology and particle size depended on different factors, such as the concentration of Fe(III)-salt, pH, temperature, precipitation time, etc. For the same concentration of Fe$^{3+}$ ions and the same conditions of slow hydrolysis, the nature of the corresponding anion (Cl$^-$, F$^-$, ClO$_4^-$, NO$_3^-$, SO$_4^{2-}$) may change the phase composition of hydrolytical products, as well as the shape of the particles.

Investigation of the influence of sulphate anions on the precipitation of iron(III) oxyhydroxides and oxides is important from the practical point of view (pigments, catalysts, atmospheric corrosion, etc.). For instance, the phase composition of the rust, generated during the atmospheric corrosion of steel, and the corresponding phase transformations, were dependent on the presence of SO$_4^{2-}$/OH$^-$ in the atmosphere [1].

Musić et al. [2–4] investigated the phase composition, crystallinity, stoichiometry and $^{57}$Fe nuclear magnetic properties of oxide precipitates formed from FeSO$_4$ solutions. The chemical and structural properties of the oxide precipitates were strongly dependent on the [Fe$^{3+}$]/[OH$^-$] concentration ratio at the beginning of the precipitation process, on the rate of oxygenation, the precipitation temperature, the atmosphere and the kind of alkali (NH$_4$OH or NaOH) added.

The influence of sulphate anions on the formation of iron(III) oxide was investigated by the titration of acidified 6.25 × 10$^{-2}$ M Fe$_2$(SO$_4$)$_3$ solution with NaOH [5]. Phase analysis of the precipitates showed the presence of the α-FeOOH, α-Fe$_2$O$_3$ and amorphous phase. It was concluded that sulphate anions could promote or suppress the formation of iron oxides, depending on the experimental conditions. The precipitation of jarosite-type compounds was not observed.

Matijević et al. [6] found conditions for the precipitation of monodispersed basic iron(III) sulphate particles from acidic solutions, and also emphasized the role of FeSO$_4^2-$ complex in the formation of basic iron(III) sulphates [7]. Musić et al. [8] investigated the mechanism of the formation of iron(III) oxyhydroxides and oxides using hydrolysis of iron(III)-salt solutions at elevated temperature. The hydrolysis of Fe$^{3+}$ ions in the nitrate and chloride solutions started with the formation of simple hydroxy complexes, and this process was followed by the formation of polymeric species. The hydroxy polymers in the nitrate solution were not presumed to include the nitrate ions in the polymer chain, whereas the polymers formed in chloride solution contained some chloride ions in place of the OH$^-$ ions. The next step in the precipitation process was the formation of o xo-bridges and the development of α-FeOOH or β-FeOOH structure. In the sulphate solution, the formation of FeSO$_4^2-$ complex suppressed the polymerization process and the formation of the oxyhydroxides and oxides. Basic iron(III) sulphates were formed instead.

The crystalline jarosite and a compound described as amorphous Fe(III) hydroxysulphate were found in the precipitates formed by the oxidation of 0.1–0.2 M FeSO$_4$ solutions with Thiobacillus ferrooxidans cells [9]. Bigham et al. [10] investigated a poorly crystallized Fe(III) oxyhydroxy sulphate produced by the bacterial oxidation of Fe$^{2+}$ in acid mine waters. The
content of the crystal unit-cell of this compound was determined as Fe2O16(OH)12(SO4)2. The stoichiometry of this compound varied up to Fe1eO16(OH)16(SO4)3.

The precipitation of jarosite-type compounds was extensively investigated by Dutrizac et al. [11–18], because this precipitation process is important in metallurgy. For instance, in the zinc industry, the precipitation of jarosites can be used to remove excess of iron, sulphate and alkali ions from zinc sulphate–sulphuric acid solutions. The advantages of this process include the excellent settling and filtration properties of the precipitates, and low losses of divalent metals, such as Zn²⁺, Cu²⁺ and Ni²⁺.

Iron jarosites are described by the general formula MFe₅(OH)₉(SO₄)₃, M = H₃O⁺, Na⁺, K⁺, Rb⁺, Ag⁺, Tl⁺, NH₄⁺, ½ Pb²⁺ or ½ Hg²⁺. They can be used as raw material for the production of iron oxide pigments. The experimental conditions for the conversion of jarosite-type compounds into iron oxides were investigated [19, 20]. Musić et al. [21] also investigated the thermal decomposition of basic iron(III) sulphates.

The aim of the present investigation was to obtain more information about chemical and structural properties of the precipitates generated by the hydrolysis of Fe³⁺ ions in Fe₂(SO₄)₃ solutions. It is known that small changes of the experimental conditions can affect significantly the phase composition and morphology of particles formed by hydrolysis of Fe³⁺ ions. For this reason, in the present work the number of experimental parameters, which affected the process of hydrolysis of Fe³⁺ ions, was restricted. Fe₂(SO₄)₃ solutions were heated at elevated temperature in order to accelerate the hydrolysis of Fe³⁺ ions. Three parameters were controlled during the precipitation process: (a) initial concentration of Fe₂(SO₄)₃ solution, (b) temperature, and (c) precipitation time.

2. Experimental procedure

The precipitations were performed in glass autoclaves (Schott, Germany) at 90 or 120 °C. Precipitates were washed with bidistilled water. The separation of the precipitate from the mother liquor was performed using a Sorvall RC2-B ultra-speed centrifuge (maximum 20000 r.p.m.). Experimental conditions for the precipitation of hydrolytical products from Fe₂(SO₄)₃ solutions are given in Tables I and II.

Structural properties of precipitates were investigated by X-ray diffraction (XRD), ⁵⁷Fe Mössbauer spectroscopy and Fourier transform–infrared spectroscopy (FT–IR), while the shape of particles was investigated by transmission electron microscopy (TEM). X-ray diffraction (XRD) powder patterns were taken at room temperature using a counter diffractometer with monochromatized CuKα radiation (Philips diffractometer, proportional counter and graphite monochromator). XRD patterns were interpreted using data available in the literature [22]. ⁵⁷Fe Mössbauer spectra were recorded using equipment made by Wissel. Mössbauer spectra were fitted using the SIRIUS program. All FT–IR spectra were recorded with spectrometer made by Perkin–Elmer. The specimens were pressed into disc form using spectroscopically pure KBr. In the present paper the FT–IR spectra are presented as relative transmittance versus the wave number. Transmission electron microscopy was performed with an electron microscope made by Opton.

3. Results and discussion

The results of XRD phase analysis of all samples are given in Tables III and IV. XRD powder patterns of samples S1, S2 and S3, shown in Fig. 1, can be ascribed to α-FeOOH, goethite. XRD lines are broadened and this effect can be interpreted in terms of poor crystallinity of precipitated goethite and small size of crystallites. Fig. 2 shows XRD powder pattern of sample S9 with well-defined diffraction lines, which correspond to H₂O₆Fe₃(OH)₉(SO₄)₂, hydronium jarosite. The phase analysis of precipitates indicated that at lower Fe₂(SO₄)₃ concentrations goethite was formed as a single phase, while at higher Fe₂(SO₄)₃ concentrations hydronium jarosite was formed alone. These results can be explained by a high tendency of Fe³⁺ ions at lower concentrations to make hydroxy complexes which undergo polymerization. On the other hand, at higher concentrations of Fe³⁺ the formation of the...