Synthesis of $\alpha$-Fe$_2$O$_3$ via oxidative hydrolysis of iron(II) sulphate

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The influence of the main reaction parameters (temperature, pH and concentration) in the oxidative hydrolysis of iron(II) sulphate in an acid medium on the properties of the obtained $\alpha$-Fe$_2$O$_3$ and its applicability in ferrite production has been studied. The addition of manganese(II) ions catalyses the process in the homogeneous phase, probably by activation of oxygen. The obtained results are discussed within the framework of the assumed reaction mechanism, which includes an homogeneous reaction and a heterogeneous one with the participation of the oxidative hydrolysis product $\alpha$-FeOOH.

1. Introduction
Iron oxides with defined properties find wide application in industry. The efficiency of their production depends mostly on the quality of the raw materials and on the technological process. The creation of scientific basis for the production of $\alpha$-Fe$_2$O$_3$ with controlled properties is a rather difficult task, mainly due to the scarce information on the mechanism of the chemical processes taking place during synthesis. Therefore, detailed studies of the different steps of the synthesis are necessary. One of the most convenient raw material for production of iron oxides is iron(II) sulphate (it is a by-product in some metal-processing technologies or is obtained by dissolving of iron scrap), due to its low price and the ecological effect of its utilization.

In the present paper we have studied at different conditions the reaction of oxidative hydrolysis of water solution of technical iron(II) sulphate, obtained by dissolving of low quality steel scrap, and the properties of the obtained $\alpha$-Fe$_2$O$_3$. The obtained results give information, necessary for optimization of the production technology and throw additional light on some aspects of the process mechanism.

2. Experimental details
The oxidative hydrolysis of water solution of iron(II) sulphate

$$4\text{FeSO}_4 + 8\text{NH}_3 + 6\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{FeOOH} + 4(\text{NH}_4)_2\text{SO}_4$$

was carried out in a laboratory reactor “Contalab” (“Contaves”, Switzerland). The reactor allows complete automatic control of all reaction parameters – temperature, pH, intensity of stirring. The amount of NH$_4$OH introduced in the reactor was computer controlled, using an electronic balance, thus providing for a constant pH of the suspension. The apparatus ensures high reproducibility of the obtained results. For each test we use 330 ml of iron(II) sulphate solution with defined concentration. During the experiments air is blown through the solution at a rate of 51 min$^{-1}$. The rate of the stirrer is 400 r min$^{-1}$. At higher rates no change in the reaction rate is observed. The desired temperature of the reaction is reached in an argon flow. Technical FeSO$_4$$\cdot$7H$_2$O was used in most tests (Mn, 0.1–0.3 wt %; Ca, 0.05–0.15 wt %; Mg, 0.05–0.15 wt %). In some experiments FeSO$_4$$\cdot$7H$_2$O was used with or without the addition of MnSO$_4$$\cdot$5H$_2$O (both of analytical grade). The obtained precipitate of iron(III) oxyhydroxide was filtered, washed until the absence of sulphate ions, dried at 100–110 °C and calcined at 750 °C for 3 h.

The phase composition of the samples, the form and the size of the crystallites were determined by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Mössbauer spectroscopy. The XRD analysis was performed on a TYP M-62 apparatus using CuK$_\alpha$ emission. The TEM pictures were taken on a JEM-100 M microscope. The Mössbauer spectra were recorded on an electrodynamic “Wissenschaftliche Electronic” spectrometer at a constant acceleration mode, using $^{57}$Co as a source in copper matrix (activity of 40 mCi). Thin folio of $\alpha$-Fe with density of 20 mg cm$^{-2}$ was used as a standard reference.

3. Results and discussion
Fig. 1 shows the dependence of the degree of oxidation of iron(II) sulphate on the time at temperature 30 °C, pH = 4.5 and different concentrations of the initial solutions of technical FeSO$_4$: 80 g l$^{-1}$, 150 g l$^{-1}$ and 300 g l$^{-1}$. The oxidation curves have a peculiar form, with a change of the slope after 90–120 min from the beginning of the process, i.e. in the initial period the rate of oxidation is considerably higher. The observed form of the kinetic curves could be explained as follows. It could be suggested from the literature [1, 2] and our results [3], that the oxidation Fe$^{2+} \rightarrow$ Fe$^{3+}$
The dependence of the degree of oxidation of iron(II) sulphate ($X$) on the time at $T = 30\,^\circ\mathrm{C}$, $\mathrm{pH} = 4.5$, and initial concentration of iron(II) sulphate: 1, 80 g l$^{-1}$; 2, 150 g l$^{-1}$; 3, 300 g l$^{-1}$. Curves 1', 2' and 3' are obtained at the same conditions, but in the presence of an inhibitor.

processes via two routes: homogeneous and heterogeneous. At that, the heterogeneous reaction takes place on the surface of the already formed iron(III) hydroxide or oxyhydroxide.

Taking into account that the heterogeneous reaction proceeds at a much lower rate, one could explain the observed form of the kinetic curves. This suggestion is supported by the fact, that the higher the initial concentration of iron(II) sulphate (Fig. 1, curve 3) the more pronounced is the change in the slope of the curves, because the homogeneous reaction is quickly impeded by the rapid increase of the amount of iron(III) oxyhydroxide. In connection with the suggestion that the oxidative hydrolysis proceeds via two routes, we carried out experiments with addition in advance of freshly precipitated iron(III) oxyhydroxide to the reaction mixture. From Fig. 2 it can be seen that the addition of 30 wt % of $\alpha$-FeOOH to the solution of iron(II) sulphate decreases the reaction rate at the very beginning of the process. The reaction rate in this case is comparable to the rate observed in the second stage of iron(II) sulphate oxidation without addition of a solid phase, when this phase is accumulated as a product of the oxidation process. The results permit certain conclusions concerning the improvement of the oxidative hydrolysis technology [4]. If in the apparatus design a step is included, where the solid phase is continuously removed from the reaction solution (e.g. by circulation through a filter), then continuous high rate of oxidation can be ensured, since the homogeneous reaction would be the prevailing one.

The effect of temperature on the oxidative hydrolysis of iron(II) sulphate can be also explained with the suggestion of the two routes of reaction mechanism. Fig. 3 shows the curves of the degree of oxidation versus temperature in the interval 30–60 °C, at constant pH value of 4.5 and 150 g l$^{-1}$ concentration of

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**Figure 1** Dependence of the degree of oxidation of iron(II) sulphate ($X$) on the time at $T = 30\,^\circ\mathrm{C}$, $\mathrm{pH} = 4.5$, and initial concentration of iron(II) sulphate: 1, 80 g l$^{-1}$; 2, 150 g l$^{-1}$; 3, 300 g l$^{-1}$. Curves 1', 2' and 3' are obtained at the same conditions, but in the presence of an inhibitor.

**Figure 2** Dependence of the degree of oxidation of iron(II) sulphate ($X$) on the time at $T = 30\,^\circ\mathrm{C}$, $\mathrm{pH} = 4.5$: 1, $C_{\text{s,so}} = 150\,\text{g}\,\text{l}^{-1}$; 2, same as 1, but with addition of 30 wt % of $\alpha$-FeOOH.

**Figure 3** Dependence of the degree of oxidation of iron(II) sulphate ($X$) on the time at pH = 4.5, $C_{\text{s,so}} = 150\,\text{g}\,\text{l}^{-1}$ and temperature of: 1, 30 °C; 2, 40 °C; 3, 50 °C; 4, 60 °C.