Synthesis of α-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 α-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 α-FeOOH.
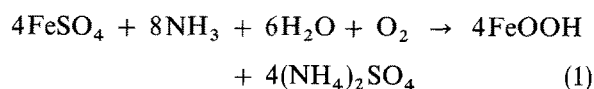
1. Introduction

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 α-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 α-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

$$4FeSO_4 + 8NH_3 + 6H_2O + O_2 \rightarrow 4FeOOH$$
$$+ 4(NH_4)_2SO_4 \tag{1}$$

was carried out in a laboratory reactor "Contalab" ("Contraves", 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 5 l 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$_4$–xH$_2$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$_4$–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 "Wiessenschaftliche Electronic" spectrometer at a constant acceleration mode, using ^{57}Co as a source in copper matrix (activity of 40 mCi). Thin folio of α-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+} → Fe^{3+}
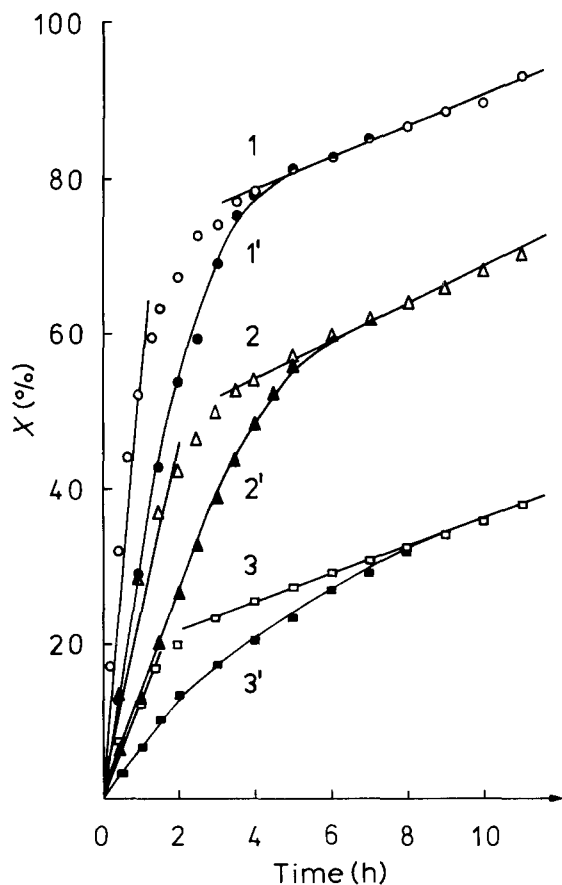
Figure 1 Dependence of the degree of oxidation of iron(II) sulphate (X) on the time at $T = 30\,°C$, pH $= 4.5$ and initial concentration of iron(II) sulphate: 1, $80\,\mathrm{g\,l^{-1}}$; 2, $150\,\mathrm{g\,l^{-1}}$; 3, $300\,\mathrm{g\,l^{-1}}$. Curves $1'$, $2'$ and $3'$ are obtained at the same conditions, but in the presence of an inhibitor.

proceeds 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 α-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
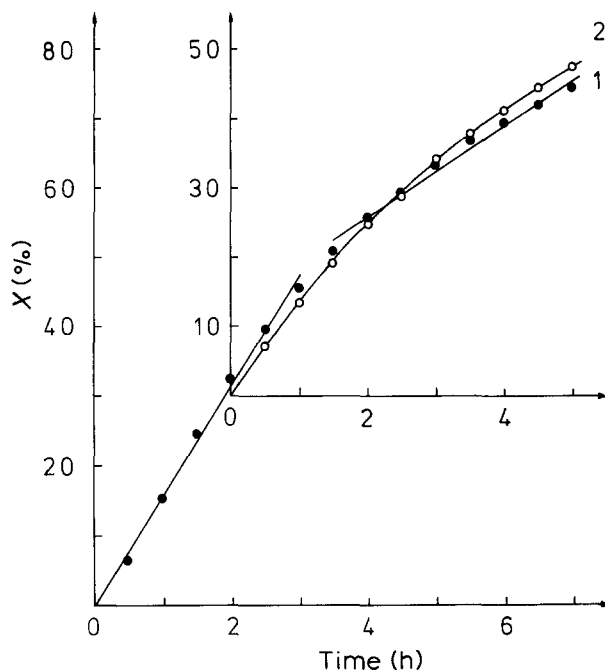

Figure 2 Dependence of the degree of oxidation of iron(II) sulphate (X) on the time at $T = 30\,°C$, pH $= 4.5$: 1, $C_{FeSO_4} = 150\,\mathrm{g\,l^{-1}}$; 2, same as 1, but with addition of 30 wt % of α-FeOOH.

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 $150\,\mathrm{g\,l^{-1}}$ concentration of
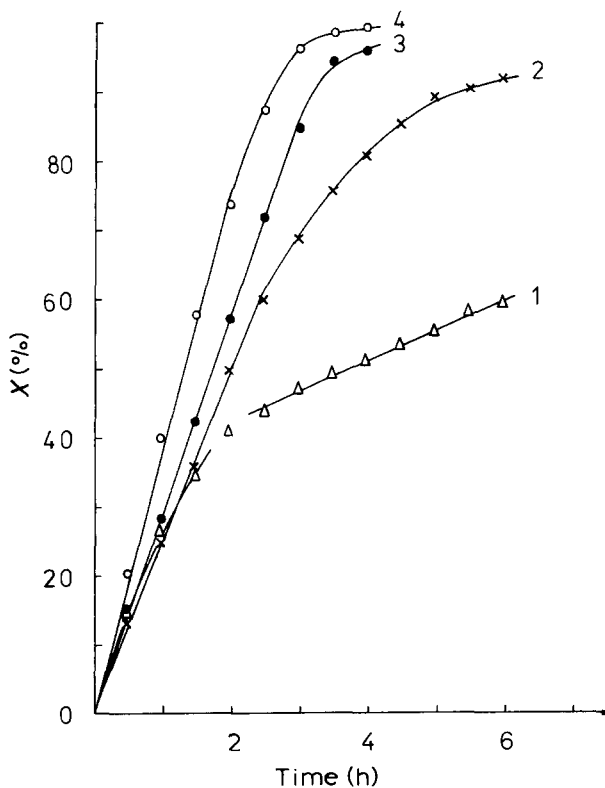

Figure 3 Dependence of the degree of oxidation of iron(II) sulphate (X) on the time at pH $= 4.5$, $C_{FeSO_4} = 150\,\mathrm{g\,l^{-1}}$ and temperature of: 1, $30\,°C$; 2, $40\,°C$; 3, $50\,°C$; 4, $60\,°C$.

Sample	Preparation conditions				Phase composition		
	T (°C)	pH	C_{FeSO_4} (g l^{-1})	Average size of particles, d (μm)	density (g cm^{-3})	XRD analysis	
						dried	calcined
CF 38	30	4.5	80	0.13	3.72	–	α-Fe$_2$O$_3$
CF 315	30	4.5	150	0.14	3.92	α-FeOOH + 15% γ-FeOOH	α-Fe$_2$O$_3$
CF 330	30	4.5	300	0.16	4.35	–	α-Fe$_2$O$_3$
CF 340	30	4.5	400	0.18	4.80	–	α-Fe$_2$O$_3$
CF 415	40	4.5	150	0.16	4.28	α-FeOOH + 5% γ-FeOOH	α-Fe$_2$O$_3$
CF 515	50	4.5	150	0.19	4.56	α-FeOOH	α-Fe$_2$O$_3$
CF 615	60	4.5	150	0.22	4.68	α-FeOOH	α-Fe$_2$O$_3$

initial solution of iron(II) sulphate. It is obvious, that with the increase of temperature the characteristic change of the slope of the kinetic curves disappears. This could be explained by the higher energy of activation of the heterogeneous process and the connected stronger effect of temperature on it. As would be shown below, the discussed change in the relative participation of the homogeneous and heterogeneous processes with temperature strongly influences the properties of the obtained iron oxide.

It is well known [5], that transition metal ions are good catalysts for the oxidation of Fe^{2+} to Fe^{3+} in acid medium. The chemical analysis of the used technical iron(II) sulphate indicates, that the main transition metal impurity is manganese. It is natural to suggest, that the high initial rate of oxidation of technical iron(II) sulphate is caused by the catalytic effect of Mn^{2+} ions. That is why we carried out comparative studies of the oxidation process with pure and technical iron(II) sulphate. Fig. 4 indicates, that the
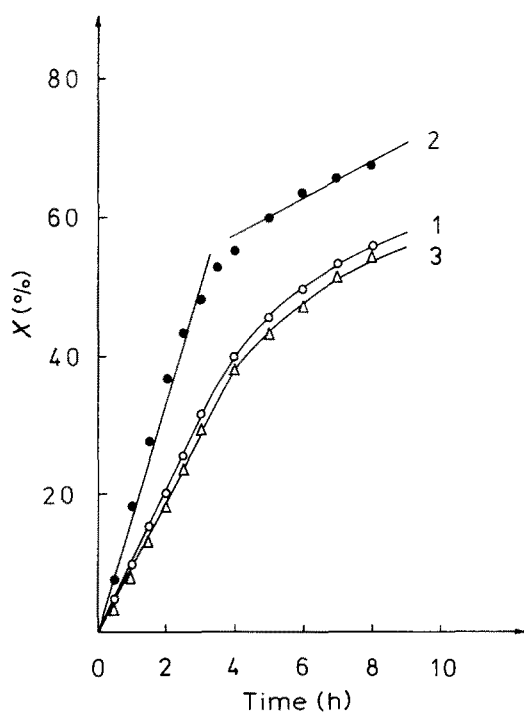

Figure 4 Dependence of the degree of oxidation of iron(II) sulphate (X) on the time at $T = 30$ °C, pH $= 4.5$ and $C_{FeSO_4} = 150$ g l^{-1}: 1, pure FeSO$_4$; 2, FeSO$_4$ + 0.3 wt % MnSO$_4$; 3, FeSO$_4$ + 0.3 wt % MnSO$_4$ + inhibitor.

addition of MnSO$_4$ to the pure FeSO$_4$ leads to a considerable increase of the reaction rate, i.e. strong catalytic effect is observed. This effect reproduces quite well the high oxidation rate in the initial period of oxidation of technical iron(II) sulphate (Fig. 1).

The existence of this catalytic effect in homogeneous phase was confirmed by the addition of an inhibitor to the solution of iron(II) sulphate. We used N-phenyl-β-naphthylamine of concentration 10^{-3} mol l^{-1}. We observed complete suppression of the catalytic effect of Mn^{2+} ions, both when we used pure (Fig. 4, curve 3) and technical (Fig. 1, curves 1', 2', 3') iron(II) sulphate.

The catalytic effect of Mn^{2+} ions is of considerable practical importance. When the oxidative hydrolysis is carried out at pH $= 4.5$, as it is in our case, manganese ions are not precipitated as hydroxide. This permits the use of this catalytic effect in the technological process without polluting the obtained iron oxide. An advantageous fact is that manganese is often contained in steel alloy or it can be easily added when the initial reaction solutions are being prepared.

Of particular importance is the question about the influence of the reaction conditions of oxidative hydrolysis on the properties of the obtained iron oxide. The experimental results are given in Table I. Chemical analysis of the obtained samples of α-Fe$_2$O$_3$, carried out by atomic absorption analysis (AAA), indicates the high purity of the product. At the specific conditions of preparation (low pH) the content of manganese impurities in the iron oxide is by an order of magnitude lower than in the initial iron(II) sulphate (less than 0.02 wt %), while the content of calcium and magnesium decreases 2 to 3 times (Ca, 0.02–0.03 wt %; Mg, 0.02–0.03 wt %). The content of Fe$_2$O$_3$ is higher than 99.4 wt % and Fe^{2+} ions were not discovered (determined colourimetrically).

A clearly-expressed influence of the initial concentration of iron(II) sulphate and of the reaction temperature on the phase composition and the form of the crystallites is observed. The XRD data indicate, that at lower synthesis temperature the dried samples contain besides α-FeOOH also small amounts of γ-FeOOH. The latter disappears at higher preparation temperature (Table I). The average size of the iron oxyhydroxide particles also increases with the increase of temperature and concentration. Two doublets with parameters $\delta = 0.34$–0.36 mm s^{-1} and $\Delta = 0.54$–0.56 mm s^{-1} are observed in the Mossbauer spectra of

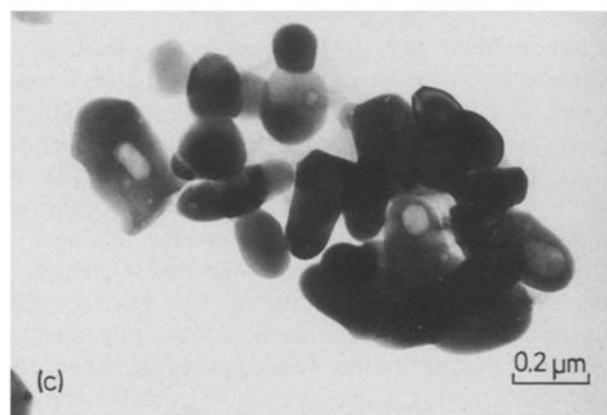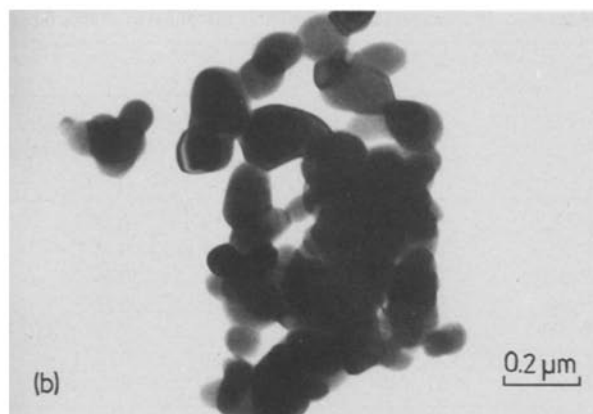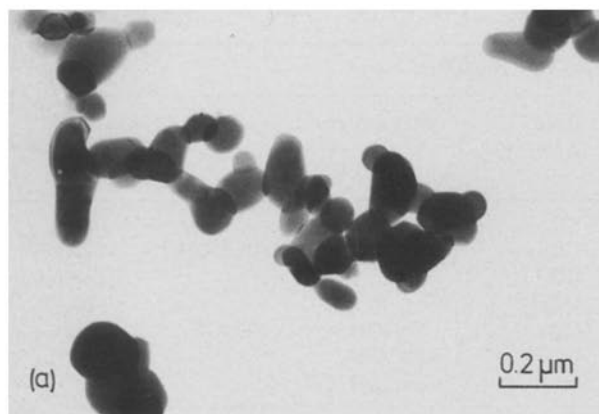*Figure 5* TEM pictures of α-Fe_2O_3 at different conditions of preparation: (a) $T = 30\,°C$, pH = 4.5, $C_{FeSO_4} = 150\,g\,l^{-1}$; (b) $T = 30\,°C$, pH = 4.5, $C_{FeSO_4} = 300\,g\,l^{-1}$; (c) $T = 60\,°C$, pH = 4.5, $C_{FeSO_4} = 150\,g\,l^{-1}$.

the dried samples. These spectral components belong to particles of γ-FeOOH and α-FeOOH. The particles of the latter phase manifest superparamagnetic behaviour. At higher temperature the superparamagnetic α-FeOOH phase disappears. After calcining at 750 °C for 3 h, all samples consist of well crystallized α-Fe_2O_3 with hexagonal structure (Table I). Fig. 5 shows TEM pictures of samples obtained at different conditions. The average size of the particles obtained in the 30–60 °C temperature interval increases with temperature from 0.14 μm for the sample CF 315 to 0.22 μm for the sample CF 615 (Table 1), preserving the form and the shape of the crystallites. With the increase of the initial concentration of iron(II) sulphate, the density and average size of the particles increase considerably. However, the change of temperature strongly influences the particle size and density on the preparation conditions, this could be explained by the previously-discussed mechanisms of oxidative hydrolysis – the homogeneous and the heterogeneous. It is also important to mention the existence of two steps in the formation of the particles – the formation of initial nuclei and their enlargement. The initial concentration of iron(II) sulphate in solution influences even more strongly the process of nuclei formation, while the synthesis temperature has a stronger influence on the enlargement of the crystallites. At low initial concentrations of iron(II) sulphate and low temperatures, due to the higher energy of activation of the heterogeneous process, in the presence of Mn^{2+} ions, the homogeneous reaction prevails. This leads to the formation of a larger number of nuclei – monomer amorphous particles. The increase in temperature and

initial concentration of iron(II) sulphate would favour the heterogeneous process on the surface of the already-formed large amount of iron(III) oxyhydroxide particles. Subsequently, this would stimulate the enlargement and aggregation of the initial particles – a process which is strongly influenced by temperature.

One of the most important applications of α-Fe_2O_3 is the production of ferrites. In agreement with the present ideas on the mechanism of ferrite formation during thermal treatment of oxide powder mixtures, the new phase is formed and grows at the phase boundary between the powder oxides via diffusion. At that, a certain isotactic effect is observed – dense crystallites of well-crystallized initial particles form dense and defectless ferrites. Therefore, the question arises of how to control the density and form of α-Fe_2O_3 particles by changing the technological parameters with the aim of obtaining dense and defectless crystallites.

As we have already noted, high temperature and especially high concentrations favour the formation of
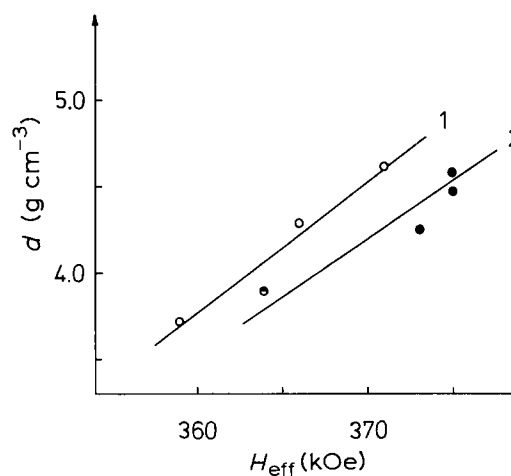

Figure 6 Dependence of H_{eff} on the density of α-Fe_2O_3 depending on: 1, the initial concentration of iron(II) sulphate: 2, the temperature of oxidative hydrolysis.

high density α-Fe_2O_3 particles. Information on the detailed structure of the crystal lattice can be obtained by Mössbauer spectroscopy. Highly appropriate for this purpose is the value of the effective magnetic field (H_{eff}). Fig. 6 shows the dependence of H_{eff} of the most intensive component of the Mössbauer sextet of dried samples, on the density of the subsequently-formed α-Fe_2O_3. It can be noted, that the density correlates with H_{eff}, indicating the presence of a higher structural order, which in turn leads to a more homogeneous 'magnetic structure'. This result gives ground to the use of the density of α-Fe_2O_3 powders as a criterion for their applicability in ferrite production. The value of H_{eff} can also be used for the same purpose, since it gives direct information on the degree of orderness and on the homogeneity of the crystal lattice of α-Fe_2O_3.

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