OXIDATION OF FERROUS SULPHATE IN NEUTRAL AND WEAKLY ALKALINE SOLUTIONS

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Oxidation of $FeSO_4$ by air oxygen has been studied in aqueous solutions of constant acidity. The effect of various reaction conditions (of acidity, temperature, concentration of $FeSO_4$, and of the air flow through the suspension) on the yield of various modifications of ferric oxide-hydroxides in the product mixture is described and the mechanism of the process is discussed. Reaction products prepared in the neutral and weakly alkaline solutions contain predominantly lepidocrocite (γ-FeOOH), amorphous $Fe_2O_3.n\,H_2O$ (ferrihydrite), at higher pH values also goethite (α-FeOOH) is formed. Their mutual ratios depend strongly on the solution acidity.

In the oxidation of ferrous sulphate solutions a series of products is formed, the composition and properties of which depend on the oxidation conditions. Among the products of the complete oxidation one may find not only various ferric oxide-hydroxides, *i.e.*, α-FeOOH (goethite)[1-3], γ-FeOOH (lepidocrocite)[3,4], δ-FeOOH[1,5], amorphous ferric gel (ferrihydrite)[6] but also Fe_3O_4 (magnetite)[1,6] and various basic sulphates (jarosites, *etc.*)[2]. Oxidation of $FeSO_4$ in an acidic solution is described in many publications[7-10]. It is assumed that the oxidation rate depends on the concentration of $Fe(OH)^+$ ion[7]. However, if also the $Fe(OH)_2$ phase appears in the system, the reaction proceeds much faster by a different mechanism. Under these conditions blue-green solid intermediates are formed in this system during the oxidation reaction. In the published literature these intermediates are commonly called "green rust" and the reaction mechanism has evidently a topochemical character[11].

When the above-quoted experiments and procedures for the preparation of individual modifications of these ferric oxides and oxide-hydroxides were repeated it has been found that the phase composition of products and the morphology of their particles depend strongly on the reaction conditions of the oxidation precipitation, particularly on the acidity. The influence of reaction conditions on the phase composition of products in the oxidation precipitation of $FeSO_4$ solutions has not been so far described in the published literature in such detail that the published data would make a reproducible preparation of well-defined ferric oxide-hydroxides possible.

In order to obtain a more detailed description of the oxidation reaction mechanism of ferrous salts the oxidation of $FeSO_4$ by air oxygen in neutral and alkaline aqueous solutions has been studied with the pH value of the system maintained constant during the oxidation.

EXPERIMENTAL

Reagents

Ferrous sulphate and the 25% aqueous solution of ammonia (both of the analytical grade) were of the Lachema (Brno) production.

Procedures

The oxidation reaction was carried out in a 3 dm^3 glass vessel kept in a thermostat. A glass electrode combined with a standard calomel electrode (S.C.E.) for recording and regulation of acidity, a gauge for temperature regulation and an equipment for the electrochemical measurement of the concentration of dissolved oxygen were immersed into the reaction mixture. The reaction mixture was stirred with the Reaktron-type stirrer with a variable revolving rate which also served for the dispersion of air fed into the solution by a tube the outlet of which was under the stirrer. The input of the neutralizing agent was controlled by an automatic burrette ABU-13 and by the pH-meter (Radiometer, Copenhagen). In course of the experiment the air flow was kept constant, temperature was maintained within ±1°C, and the acidity within ±0·02 of the pH value.

1·5 dm^3 of the $FeSO_4$ solution, free of any oxidized solute, was transferred into the reaction vessel and heated to the reaction temperature. The acidity was adjusted to the desired pH value under the flow of argon. Then the inert gas flow was exchanged for the air flow of a prescribed flow rate and the oxidation reaction began. Due to the oxidation and hydrolysis of the formed Fe^{3+} the reaction solution became more acidic so that ammonia had to be added continuously to the reaction mixture to maintain the given pH value. After the reaction had been completed the product was filtered, washed with distilled water, disposed of water by washing with acetone and ether and finally dried freely on air at the room temperature.

Methods

The surface area was determined by a thermal desorption method according to Nelsen and Eggertsen using an apparatus modified by Mangel[12].

The infrared spectra were measured with the Beckman IR-20 spectrometer in the wavenumber range 250—4 000 cm^{-1} in the TlBr tablets.

The micropraphs of the preparations and of the electron diffraction pattern were obtained with the transmission electron microscope TESLA BS 242 E. The samples were dispersed in water. The preparations were observed in the nascent form without metallization, the accelerating voltage was 60 kV.

The powder X-ray structural analysis was done with the apparatus DRON 2·0 using the Co_{K_α} line emission.

The Mössbauer spectra were measured at 293 and 5 K with the 512-channel constant-acceleration Mössbauer spectrometer using the ^{57}Co source in Pd matrix.

RESULTS AND DISCUSSION

γ-FeOOH (lepidocrocite) is the main product of the oxidation precipitation of ferrous sulphate in the neutral and weakly alkaline solutions. In several cases also a small amount of other crystalline ferric oxide-hydroxides, particularly of α-FeOOH, was found among the products. In such a case along with lepidocrocite also another phase with poorly developed crystalline structure, most probably ferric oxide-hydroxide of the ferrihydrite or δ-FeOOH type, is formed. However, this product cannot be unambiguously identified with the powder X-ray structural analysis as both ferrihydrite and δ-FeOOH render very broad and relatively low-intense diffraction lines. Moreover, their positions are very close to the diffraction lines of lepidocrocite which, when formed under these conditions, has very small particles (of the specific surface of about 150 m^2/g) and therefore broadened diffraction lines as well.

The infrared spectra of several ferric oxides and oxide-hydroxides and of several reaction products are given in Fig. 1. From this figure it is evident that the products of the oxidation precipitation of ferrous sulphate contain along with γ-FeOOH also a large amount of another modification, probably ferrihydrite, and that they do not contain other crystalline modifications of ferric oxides or oxide-hydroxides.

This conclusion has been confirmed also by the analysis of the Mössbauer spectra. The spectrum of δ-FeOOH should present a magnetic splitting at temperatures higher than 77 K even with very small particles while both γ-FeOOH and ferrihydrite exhibit under these conditions only the quadrupole splitting[13,14]. At 5 K the spectra of samples prepared at pH 9 and 10 are composed of two six-line figures corresponding to two different values of the hyperfine field $HF_1 = 37{\cdot}242$ MA/m and $HF_2 = 41{\cdot}062$ MA/m. The lower value of the hyperfine field is in very good agreement

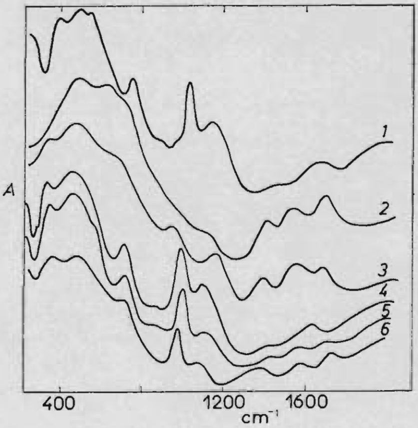

FIG. 1

Infrared spectra of products of the oxidation precipitation of ferrous sulphate. *1* γ-FeOOH, *2* ferrihydrite (amorphous $Fe_2O_3.nH_2O$), *3* δ-FeOOH. Products of precipitation at 20°C at various pH values: *4* pH 7, *5* pH 8·5, *6* pH 10 with the published value for lepidocrocite[13] (37·401 MA/m) while the value HF_2 agrees satisfactorily with the data for ferrihydrite[14] (40·346 MA/m).

With respect to the fact that of all crystalline modifications of ferric oxide-hydroxides only the presence of γ-FeOOH has been proved by the powder X-ray structural analysis and with regard to the results of the measurements of the infrared and Mössbauer spectra it can be concluded that the products of the oxidation precipitation of ferrous sulphate at pH 7 – 10 contain only γ-FeOOH with an admixture of poorly crystalline or amorphous ferric oxide-hydroxide which is – according to the Mössbauer spectra – identical with ferrihydrite (which can be prepared, *e.g.*, by the neutralization of $Fe(NO_3)_3$ by ammonia at the room temperature[14]).

The kinetics of the oxidation precipitation of the $FeSO_4$ solution was studied in the pH range 6 – 10. The concentration of dissolved oxygen as a function of the reaction time and the amount of ammonia consumed for the neutralization of the acid released during the hydrolysis are given in Figs 2 and 3.

At pH > 7 the concentration of dissolved oxygen is very low in the whole course of the reaction. It is evident that the reaction does not proceed in the kinetic region

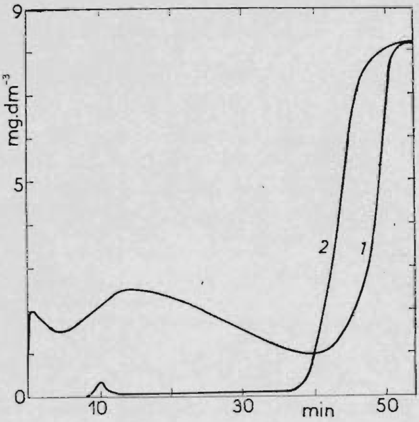

FIG. 2

Concentration changes of dissolved oxygen during the oxidation precipitation. *1* pH 7, *2* pH 8·5

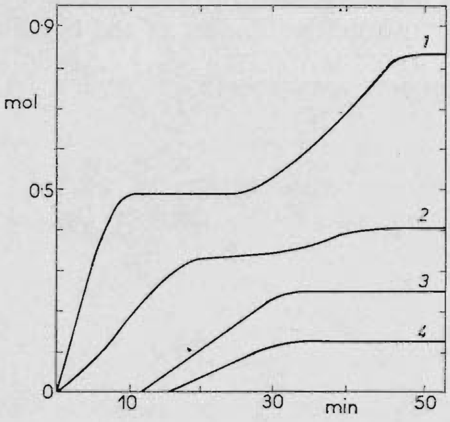

FIG. 3

Consumption of the neutralizing agent during the oxidation precipitation of ferrous sulphate at 20°C. $FeSO_4$ concentration 0·36 mol dm^{-3}, reaction volume 1·5 dm^3. *1* pH 7, *2* pH 8·5, *3* pH 9, *4* pH 9·5 and that the rate-determining step is the dissolving of oxygen in the liquid. Therefore also the resulting oxidation rate depends first of all on the efficiency of the dispersion of air oxygen in the liquid and it is nearly independent of all other reaction conditions (acidity, temperature, concentration of $FeSO_4$).

At $pH < 7$ the concentration of dissolved oxygen was found to be higher. Already from the beginning of the reaction a solid yellow-orange product (a mixture of goethite and lepidocrocite) was precipitated and remained unchanged during the reaction. The higher concentration of oxygen is caused by the slowing down of the chemical reaction at lower values of pH. The overall reaction rate is given not only by the absorption of oxygen but also by the chemical reaction itself. Ammonia is consumed continuously and there is no reason to assume that the reaction proceeds in more steps.

The oxidation in the pH range $7-8{\cdot}5$ is more complex. The curve of the ammonia consumption has a typical plateau that indicates (at least) a two-step reaction mechanism. The reaction proceeds differently even visually. At these values of pH no precipitate of $Fe(OH)_2$ is present at the beginning of the reaction. During the first period of oxidation the solution colour changes to a deep-blue shade but any formation of the precipitate cannot be observed. Complex ferric-ferrous ions described by Misawa[15,16] are probably formed. During the next stage a deep-green precipitate ("green rust") is precipitated from the solution. At the end of this reaction stage no more ammonia is consumed and the curve of the consumption of the neutralizing agent exhibits a plateau. In the following reaction step the precipitate of "green rust" is oxidized without any consumption of the neutralizing agent. Only in the final oxidation step, during which solid ferric oxide-hydroxides are formed in the reaction mixture, the sulphate anions are released from the "green rust" precipitate and the neutralizing agent is consumed again.

At higher pH values, when already at the beginning of the reaction a sufficient amount of $Fe(OH)_2$ is precipitated, the formation of the "green rust" precipitate proceeds without any consumption of the neutralizing agent in the initial stages of oxidation. The adsorbed SO_4^{2-} ions are then released in the final reaction stage.

To understand better the reaction mechanism in the neutral solution samples were taken during the oxidation and their electron micrographs and electron diffraction patterns were made.

The electron micrographs proved the formation of hexagonal leaflets of the "green rust" precipitate and their growth during the initial stage of oxidation. In the following course of the reaction the leaflets gradually change into morphologically different particles typical for γ-FeOOH. From the electron diffraction patterns it follows that a crystalline precipitate is present during the whole process. It is also evident that lepidocrocite is formed in the reaction products only when the neutralizing agent is again consumed during the reaction and the "green rust" precipitate is transformed into the ferric oxide-hydroxides.

Tables I–III present the results of the phase composition of the final oxidation products on the acidity, reaction temperature, initial concentration of $FeSO_4$, and on the oxidation rate given by the amount of air dispersed in the suspension. It is evident that the value of pH is the factor that affects the phase composition of products most substantially. The importance of other parameters is – in the range in which their effect on the oxidation process has been studied – much lower. At pH > 10 the reaction products contain even a certain amount of α-FeOOH (goethite). The morphology of product particles is rather little dependent on the reaction conditions. As far as γ-FeOOH is formed in the reaction it is produced in the form of typical leafy crystals. The products with higher content of ferrihydride contain even very

TABLE I

The effect of acidity of the solution and of temperature on the phase composition (%) of the products of oxidation precipitation of $FeSO_4$[a]

pH Value of the reaction	γ-FeOOH	α-FeOOH	Ferrihydrite	SO_4^{2-}
		Product composition at 5°C		
6·5	100	0	0	1·32
7·0	100	0	0	0·53
7·5	80	0	20	0·28
8·0	70	0	30	0·36
8·5	50	0	50	0·10
9·0	40	0	60	0·30
9·5	40	0	60	0·0
10·0	38	2	60	0·07
10·5	35	5	60	0·01
		Product composition at 20°C		
7·0	100	traces	0	1·26
7·5	100	traces	0	1·08
8·0	90	0	10	0·32
8·5	80	0	20	0·35
9·0	90	0	10	0·32
9·5	70	2	28	0·01
10·0	60	2	38	0·04
10·5	25	25	50	0·03

[a] Air flow rate through the suspension: 1·67 dm^3/min dm^3 of suspension; the initial $FeSO_4$ concentration: 0·36 mol dm^{-3}

small (~ 10 nm) spheroidal particles. The specific surface of products depends very little on the reaction conditions and it ranges from 150 to 170 m^2/g. Hence, these are substances with very small particles, indeed.

These results of the $FeSO_4$ oxidation precipitation studies in aqueous solutions are of a great value particularly because they were done at constant values of pH which is a parameter that has the highest effect on the phase composition of products and also on the morphology of their particles. In most of the previously published works

TABLE II

The effect of the oxidation rate on the phase composition of products (%) of the oxidation precipitation of $FeSO_4$ in the aqueous solution[a]

Air flow rate $dm^3/min\ dm^3$ susp.	Oxidation time min	Phase composition of products	
		γ-FeOOH	ferrihydrite
0·33	41·0	100	0
0·70	35·0	100	0
1·00	30·1	85	15
1·67	22·9	80	20
2·68	18·5	90	10
4·35	13·7	80	20

[a] Temperature 20°C, pH 8·5.

TABLE III

The effect of $FeSO_4$ concentration on the composition (%) of the products of oxidation precipitation[a]

$FeSO_4$ concentration	Phase composition	
	γ-FeOOH	ferrihydrite
0·12	70	30
0·18	85	15
0·36	80	20

[a] Temperature 20°C, pH 8·5, air flow rate 1·67 $dm^3/min\ dm^3$ of the suspension.

on the oxidation precipitation of $FeSO_4$ the neutralizing agent was added at the beginning of the oxidation process and in the course of the reaction there were uncontrolled changes of pH due to the hydrolysis of the oxidation products and also due to the formation and decomposition of the "green rust" precipitate. Also the duration of oxidation was usually several hours due to low-intense stirring and air dispersion so that at higher values of pH (>9) the "green rust" precipitate was very often transformed into magnetite (Fe_3O_4). Due to these facts there are discrepancies in the published works on the oxidation precipitation of ferrous sulphate in the neutral and weakly alkaline solutions concerning the data on the reaction conditions under which the individual ferric oxide-hydroxides are formed and also the published properties of products are considerably different. From our results it follows that for the properly controlled preparation of ferric oxides and oxide-hydroxides by the oxidation precipitation of aqueous solutions of ferrous salts it is necessary to control not only the reaction temperature, the dispersion of air oxygen and the initial concentration of $FeSO_4$, but above all the value of pH that has the greatest effect on the properties of the oxidation products.

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