Studies on the Oxidation of Iron(II) Ion during the Formation of Fe_3O_4 and α-FeO(OH) by Air Oxidation of $Fe[OH]_2$ Suspensions

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The formation of Fe_3O_4 and α-FeO(OH) during the course of the air oxidation of $Fe[OH]_2$ suspensions has been studied at pH 11.0 and 65 °C. When the sulphate concentration is low (0.03 mol dm^{-3}), the oxidation proceeds in three stages: (1) formation of iron(III) oxides and slower formation of Fe_3O_4; (2) rapid formation of Fe_3O_4; and (3) linear formation of Fe_3O_4. When the sulphate concentration is high (0.60 mol dm^{-3}), α-FeO(OH) is formed accompanied by a slow formation of amorphous γ-FeO(OH). The oxidation rates observed in the stationary state are due to the oxidation of Fe^{II} adsorbed on the surface of the solid phase.

RECENTLY, metal ion-bearing ferrites have been synthesized by air oxidation of $Fe[OH]_2$ suspensions containing metal ions at pH 7—12 and at temperatures of 65 and 80 °C.[1-8] The background to this study is the previous fundamental studies on the formation of Fe_3O_4 in solution. Feitknecht[9] first reported that Fe_3O_4 is formed by air oxidation of $Fe[OH]_2$ suspensions. Kiyama[10] subsequently studied the reaction conditions and indicated that Fe_3O_4 is readily obtained at temperatures above 60 °C and in the range pH 7—10. He also suggested that Fe_3O_4 is formed by the condensation of $[Fe(OH)]^+$ and an iron(III) hydroxo-complex which is formed by oxidation of $[Fe(OH)]^+$. Misawa *et al.*[11] reported that there are two processes in the Fe_3O_4 formation: the slow air oxidation of green rusts and green complexes, and neutralization of a solution containing iron(II) and iron(III) ions ($Fe^{II}/Fe^{III} = 1/2$). However, the processes in solution are as yet poorly understood.

The purpose of the present study is to clarify (1) how Fe_3O_4 and α-FeO(OH) are formed during the course of the air oxidation of $Fe[OH]_2$ suspensions, and (2) how sulphate ions affect the formation of Fe_3O_4 and α-FeO(OH).

EXPERIMENTAL

Analytical grade chemicals were used. The air for oxidation was bubbled through a washing vessel containing K[OH] solution to remove carbon dioxide. For the preparation of $Fe[OH]_2$ suspensions, the reaction vessel used in previous studies[3-7] was adopted. A solution of $Fe[SO_4]$ was adjusted to pH 10.0 at 65 °C, centrifuged, and washed three times with deaerated distilled water. The final precipitate was resuspended in distilled water and kept under a nitrogen atmosphere. For the oxidation experiments, 0.1- and 0.5-dm^3 reaction vessels, to which glass, calomel, and platinum electrodes and a condenser were fitted, were used. The iron(II) and total iron contents of samples were determined by means of 2,2′-bipyridyl.[12]

Oxidation of $Fe[OH]_2$ *Suspensions.*—Sodium sulphate solution (0.01 dm^3) of desired concentration (0.03 or 0.60 mol dm^{-3}) and a $Fe[OH]_2$ suspension (2.76 mmol, 0.04 dm^3) were placed under a nitrogen atmosphere in a reaction vessel (0.1 dm^3). Nitrogen gas was bubbled into the suspension through a glass tube with a small hole at the end. When a constant pH (pH 11.0, 65 °C) had been attained, oxidation was initiated by passing a mixture of nitrogen and air (0.477 dm^3 min^{-1}) in place of pure nitrogen. The oxygen concentration in the solution, $[O_2]$, was calculated by assuming $p(N_2) + p(O_2) + p(H_2O) = 1$ atm in the gas phase, using Henry's constant (8.845×10^{-4} mol dm^{-3} at atm^{-1} at 65 °C).†

During the course of the air oxidation, samples were removed at appropriate intervals. For a study of the effect of time on the oxidation, the sample was quenched in H_2SO_4 (1 : 1) and the iron(II) and total iron contents were determined. For the study of the effect of time on the consumption of $Fe[OH]_2$ and the formation of products [Fe_3O_4 and iron(III) oxides] during the air oxidation, the sample was transferred to an acetate buffer solution (pH 4.1, 0.05 mol dm^{-3}) freed from oxygen, and centrifuged. With this buffer solution, only the $Fe[OH]_2$ phase dissolved, and Fe_3O_4 and iron(III) oxides were precipitated. The precipitate was washed with the acetate buffer solution and distilled water. The iron(II) and total iron contents in the supernatant and precipitate were determined. Within the analytical errors, the iron(II) content in the supernatant was equivalent to the total iron content. Therefore, the amount of $Fe[OH]_2$ present during the course of the air oxidation was evaluated from the iron(II) content. The amount of Fe_3O_4 in the precipitate was calculated from the iron(II) content in the precipitate (assuming that the stoicheiometric amount of Fe_3O_4 is formed), and the amount of iron(III) oxides was calculated from the excess of Fe^{III} over the iron content of the stoicheiometric Fe_3O_4 in the precipitate.

To identify the phases of the products in the precipitates, the latter were washed three times with acetone, dried under a nitrogen atmosphere at room temperature, and their i.r. spectra were recorded by the KBr-disc technique.

Kinetic Experiment on the Oxidation of Iron(II) *dissolved in Solution.*—After passing nitrogen gas into distilled water (0.36 dm^3) for 1 h at 65 °C in a reaction vessel (0.5 dm^3), appropriate amounts of $Na_2[SO_4]$ and a $Fe[OH]_2$ suspension (0.05 mmol, 0.01 dm^3) were added and the pH was adjusted to 11.0. When the $Fe[OH]_2$ precipitate had completely dissolved (after *ca.* 30 min), oxidation was initiated by passing a mixture of nitrogen and air ($[O_2] = 7.49 \times 10^{-6}$ mol dm^{-3}). Samples were removed at appropriate intervals, quenched in H_2SO_4, and the iron(II) content was determined.

The Fe^{II} was almost completely oxidized in 30 min, and an iron(III) oxide was precipitated. This precipitate will subsequently be referred to as ' the iron(III) oxide precipitate.' Its i.r. spectrum showed bands for amorphous γ-FeO(OH) (950—1 100 and around 500 cm^{-1})[13] and for α-FeO(OH)

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† Throughout this paper: 1 atm = 101 325 Pa.

(890 and 795 cm^{-1}).[14] This precipitate was used for the experiment described below.

Kinetic Experiment on the Oxidation of Iron(II) *adsorbed on ' the Iron*(III) *Oxide Precipitate.'*—Iron(II) hydroxide (1.20 µmol) was added to a suspension of ' the iron(III) oxide precipitate ' (1.20 µmol) and almost completely (more than 95 mol %) adsorbed at pH 11.0, 65 °C, and low and high sulphate concentrations (0.03 and 0.60 mol dm^{-3}). Oxidation was then initiated ($[O_2] = 7.49 \times 10^{-6}$ mol dm^{-3}) and the iron(II) content of the suspension was determined at appropriate times.

RESULTS AND DISCUSSION

Formation of Fe_3O_4 *and* α-FeO(OH) *during Air Oxidation.*—To investigate how $Fe[OH]_2$ is consumed and how the products [Fe_3O_4 and iron(III) oxides] are formed during the air oxidation, the amounts of $Fe[OH]_2$, Fe_3O_4, and iron(III) oxides in the reaction suspension were determined during the course of air oxidation. The results are given in Figure 1.

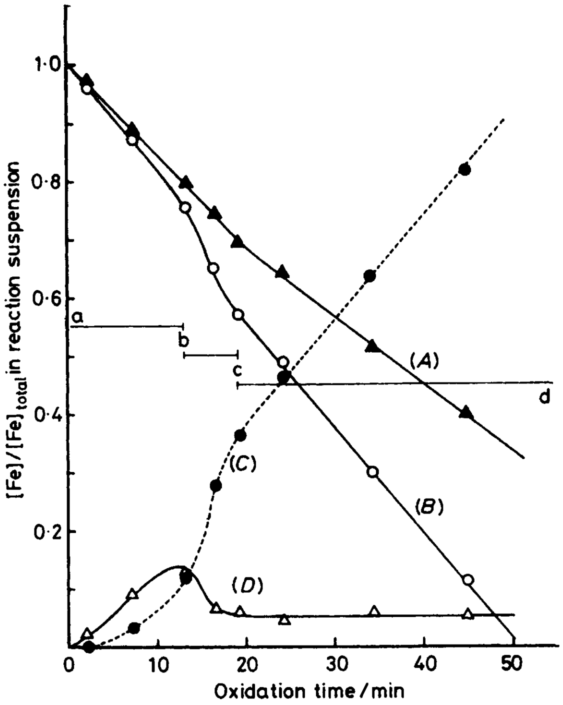

FIGURE 1 Time variation of the amounts of products Fe_3O_4 (*C*) and iron(III) oxides (*D*) and of $Fe[OH]_2$ (*B*) and Fe^{II} (*A*) in the reaction suspension during the course of the air oxidation (pH 11.0, 65 °C, 0.03 mol dm^{-3} $Na_2[SO_4]$, $[O_2] = 3.95 \times 10^{-5}$ mol dm^{-3})

Curve (*B*) shows the relationship between the disappearance of the $Fe[OH]_2$ phase and the oxidation time at pH 11.0, 65 °C, and a low sulphate concentration (0.03 mol dm^{-3}) ($[O_2] = 3.95 \times 10^{-5}$ mol dm^{-3}). The formation of Fe_3O_4 and iron(III) oxides during the air oxidation are represented by curves (*C*) and (*D*), respectively. Curve (*A*) shows the relationship between the iron(II) content of the reaction suspension and the oxidation time. From curves (*C*) and (*D*) in the region a—b (early stage of the oxidation), it can be seen that iron(III) oxides are formed when the rate of formation of Fe_3O_4 is low. However, in the region b—c, the amount of Fe_3O_4 [curve (*C*)] rapidly increases, with a corresponding rapid decrease in the amount of the $Fe[OH]_2$ phase [curve (*B*)] and of the amount of iron(III) oxides [curve (*D*)]. This shows that Fe_3O_4 is formed in the region b—c by a rapid reaction between the iron(III) oxides and $Fe[OH]_2$ (or Fe^{II}).

After the rapid formation of Fe_3O_4, the amount of Fe_3O_4 increased linearly with oxidation time in the region c—d [curve (*C*)], and its rate of formation became constant. This region is referred to as the ' stationary state.' From curves (*A*) and (*B*), it can be seen that, in the stationary state, Fe^{II} in the reaction suspension is oxidized linearly with time [curve (*A*)] and the $Fe[OH]_2$ is also consumed linearly with time [curve (*B*)]. The ratio of the rate of oxidation of Fe^{II} in the stationary state [slope of curve (*A*)] to that of the $Fe[OH]_2$ consumption [slope of curve (*B*)] is just 2/3. This indicates that a stoicheiometric form of Fe_3O_4 is formed in the stationary state. As seen from curve (*D*) in the region c—d, no formation of the iron(III) oxides takes place in the stationary state. Thus, in the stationary state, formation of the stoicheiometric Fe_3O_4 takes place preferentially.

These results show that the oxidation of the $Fe[OH]_2$ suspension at a low sulphate concentration (0.03 mol dm^{-3}) proceeds in three stages: (1) (region a—b), formation of iron(III) oxides and slower formation of Fe_3O_4; (2) (region b—c), rapid formation of Fe_3O_4; and (3) (region c—d), stationary-state formation of Fe_3O_4.

Figure 2 shows the i.r. spectra of the products (precipitates separated from the $Fe[OH]_2$ phase) formed during the air oxidation. Curves (*a*) and (*b*) correspond to the region a—b in Figure 1. The band at 570 cm^{-1} is characteristic for Fe_3O_4 and those at 890 and 795 cm^{-1} for α-FeO(OH).[14] The bands at 950—1 100 cm^{-1} and a broad absorption around 500 cm^{-1} are due to amorphous γ-FeO(OH).[13] From spectra (*a*) and (*b*) it can be seen that the band intensities for γ-FeO(OH) decrease, whereas those for α-FeO(OH) and Fe_3O_4 increase. This suggests that amorphous γ-FeO(OH) is transformed to α-FeO(OH) and Fe_3O_4 during the oxidation in the region a—b.

Curves (*b*)—(*d*) correspond to the region b—c in Figure 1. It can be seen that the band intensities for α-FeO(OH) remain almost constant while that for Fe_3O_4 becomes very high with decreasing band intensities for amorphous γ-FeO(OH). In spectrum (*d*), the bands for amorphous γ-FeO(OH) have disappeared completely. This shows that, in region b—c, the amorphous γ-FeO(OH) is readily transformed to Fe_3O_4. In this region, as seen in Figure 1, Fe_3O_4 is rapidly formed with rapid consumption of $Fe[OH]_2$ and a corresponding decrease in the amount of the iron(III) oxides. These results suggest that amorphous γ-FeO(OH) is rapidly and preferentially transformed to Fe_3O_4 in the reaction with Fe^{II} derived from $Fe[OH]_2$.

Spectra (*d*) and (*e*) correspond to the region c—d (stationary state). The band intensities of α-FeO(OH) remain low and perhaps even become lower. As mentioned above (Figure 1), in the stationary state, a constant and a small amount of iron(III) oxide was found. This amount seems to correspond to that of the α-FeO(OH) phase observed in the i.r. spectra (*d*) and (*e*). From these results, it can be concluded that the formation of α-FeO(OH) is complete within 20 min of the commencement of oxidation (in the region a—c) and that Fe_3O_4 is preferentially formed in the stationary state (region c—d).

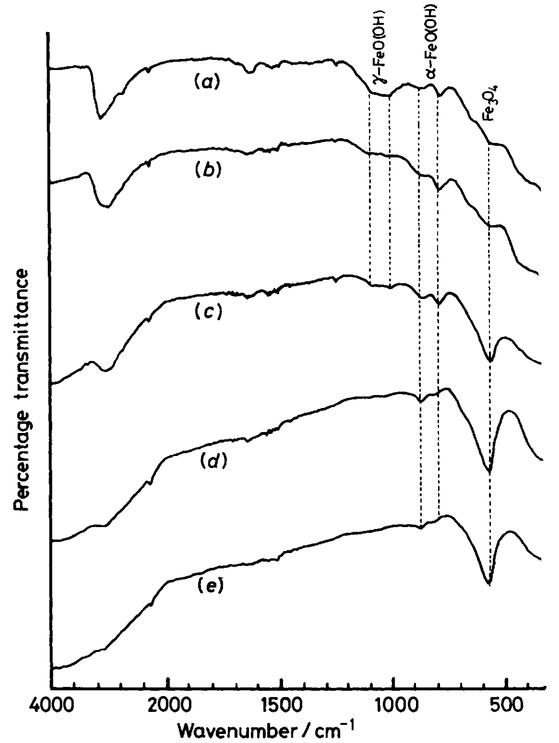

FIGURE 2 Infrared spectra of the products formed in the course of the air oxidation of the $Fe[OH]_2$ suspension (conditions as in Figure 1). Oxidation time: 3 (*a*), 10 (*b*), 16 (*c*), 20 (*d*), or 80 min (*e*)

Figure 3 shows the i.r. spectra of the products formed and taken at appropriate intervals during the air oxidation of the $Fe[OH]_2$ suspension at a high sulphate concentration (0.60 mol dm^{-3}). In spectrum (*a*) (12 min oxidation time), bands for the amorphous γ-FeO(OH) and α-FeO(OH) are seen. From spectra (*a*) and (*b*) (12—31 min oxidation time), it can be seen that the band intensities for α-FeO(OH) strongly increase. Thus, under these conditions, α-FeO(OH) was rapidly formed at an early stage of the reaction. However, the amount of α-FeO(OH) formed then became steady, accompanying the formation of a small amount of γ-FeO(OH) [spectra (*b*)—(*d*) (31—80 min oxidation time)]. In this region, Fe^{II} in the reaction suspension is oxidized linearly with time (stationary state). Thus, in the stationary state at the high sulphate concentration, Fe^{II} is oxidized at a constant rate, but no Fe_3O_4 is formed. Instead, α-FeO(OH) is formed accompanied by slow formation of amorphous γ-FeO(OH).

Oxidation on the Surface of the Solid Phase during the Stationary State.—It has been reported that, when the Fe^{II} dissolved in solution is oxidized by oxygen at a constant pH, the oxidation rate is given by equations (1) and (2).[15,16] To clarify whether or not the oxidation

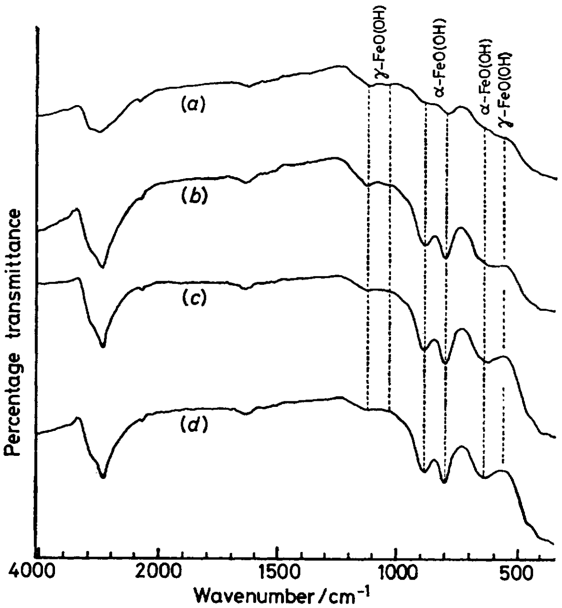

FIGURE 3 Infrared spectra of the products formed in the course of the air oxidation of the $Fe[OH]_2$ suspension (pH 11.0, 65 °C, 0.60 mol dm^{-3} $Na_2[SO_4]$, $[O_2] = 3.95 \times 10^{-5}$ mol dm^{-3}). Oxidation time: 12 (*a*), 31 (*b*), 45 (*c*), or 80 min (*d*)

$$-\,d[Fe^{II}]/dt = k_1[Fe^{II}] \qquad (1)$$

$$= k_2[O_2][Fe^{II}] \qquad (2)$$

rate in the stationary state is determined by the oxidation reaction between the Fe^{II} dissolved in solution and oxygen, the oxidation rate actually observed in the stationary state was compared with that evaluated from the equations (1) and (2). The k_1 and k_2 values were obtained from a study of the variation of $\log([Fe^{II}]/[Fe^{II}]_0)$ with time for the air oxidation of the Fe^{II} dissolved in solution (0.12 mmol dm^{-3}) at pH 11.0, 65 °C, and $[O_2] = 7.49 \times 10^{-6}$ mol dm^{-3}. Here, $[Fe^{II}]_0$ is the initial iron(II) concentration before the air oxidation. The $\log([Fe^{II}]/[Fe^{II}]_0)$ values decreased linearly with the oxidation time in the initial state. The k_1 values thus obtained are given in Table 1, and the k_2 values evaluated

TABLE 1

Comparison of the oxidation rate, v_1, of Fe^{II} dissolved in solution with that of the $Fe[OH]_2$ suspension at high and low sulphate concentrations (pH 11.0, 65 °C, $[O_2] = 3.95 \times 10^{-5}$ mol dm^{-3})

$[SO_4^{2-}]$ / mol dm^{-3}	$10^{-3}k_1$ / s^{-1}	$10^{-4}\,v_1$	$10^{-4}\,v$
		mmol s^{-1}	
0.03	6.14	0.255	5.32
0.60	5.37	0.200	5.50

at high and low sulphate concentrations (0.60 and 0.03 mol dm^{-3}) are 7.17×10^2 and 8.20×10^2 dm^3 mol^{-1} s^{-1}, respectively. The iron(II) concentration in solution in the stationary state, which was analysed after a rapid filtration under a nitrogen atmosphere, was *ca.* 0.014 mmol dm^{-3} at high and low sulphate concentrations (pH 11.0, 65 °C, $[O_2] = 3.95 \times 10^{-5}$ mol dm^{-3}). The oxidation rates, v_1, of the Fe^{II} dissolved in solution in the stationary state, estimated from equations (1) and (2), are also given in Table 1.

The oxidation rates, v, actually observed during the stationary state in the course of the air oxidation of the Fe[OH]$_2$ suspension are given in Table 1. It can be seen that the oxidation rates estimated for Fe^{II} dissolved in the reaction solution are about 1/20—1/15 of those actually observed in the stationary state. Thus, the observed oxidation rate cannot be explained by the oxidation of Fe^{II} dissolved in the reaction solution.

When the relationship between the oxidation rate v and the oxygen concentration in the reaction solution was studied a linear relationship was obtained between $1/v$ and $1/[O_2]$, showing that the oxidation rate can be related to the Langmuir adsorption isotherm. This suggests that the actual oxidation rate in the stationary state is determined by the oxidation of Fe^{II} adsorbed on the solid phase, and is proportional to the fraction of the surface that is covered with oxygen. The oxidation rates v evaluated from the linear relationship between $1/v$ and $1/[O_2]$ at $[O_2] = 7.49 \times 10^{-6}$ mol dm^{-3} are given in Table 2.

TABLE 2

Comparison of the oxidation rate, v_s, of Fe^{II} adsorbed on the iron(III) oxide precipitate with that of the Fe[OH]$_2$ suspension, v, evaluated from the linear relationship between $1/v$ and $1/[O_2]$ at $[O_2] = 7.49 \times 10^{-6}$ mol dm^{-3}

$[SO_4^{2-}]$ / mol dm^{-3}	$10^{-4}\,v_s$ / mmol s^{-1}	$10^{-4}\,v$ / mmol s^{-1}
0.03	1.96	1.75 ± 0.06
0.60	1.20	1.16 ± 0.14

Curves (*a*) and (*b*) in Figure 4 show the relationship between the oxidation of Fe^{II} adsorbed on 'the iron(III) oxide precipitate' and the oxidation time at high [curve (*a*)] and low [(*b*)] sulphate concentrations (pH 11.0, 65 °C, $[O_2] = 7.49 \times 10^{-6}$ mol dm^{-3}). The Fe^{II} adsorbed was oxidized linearly with time, and the oxidation rates, v_s, obtained are given in Table 2. It can be seen that the v_s values are fairly consistent with the v values. 'The iron(III) oxide precipitate' has a high adsorption capacity for Fe^{II} and almost all of the Fe^{II} derived from the Fe[OH]$_2$ was adsorbed on the oxide precipitate whose amount was equal to that of the Fe^{II}.

As mentioned above, the oxidation of the Fe^{II} in solution in the stationary state seems unlikely. The good agreement between the oxidation rate observed in the stationary state and that obtained for Fe^{II} adsorbed on 'the iron(III) oxide precipitate' suggests strongly that the oxidation reaction takes place on a solid phase such as iron(III) oxide. However, as mentioned previously, no iron(III) oxides were formed in the stationary state, only Fe$_3$O$_4$. This suggests that an iron(III) oxide, formed by oxidation of the Fe^{II}, reacts with Fe^{II} to form Fe$_3$O$_4$. This means that the Fe^{II} is adsorbed on the iron(III) oxide to give Fe$_3$O$_4$. When the Fe$_3$O$_4$-formation process is allowed to continue on the surface of the Fe$_3$O$_4$ particles [formation of a iron(III) oxide layer on the surface of the Fe$_3$O$_4$ particles by oxidation of the Fe^{II} adsorbed on the surface, and adsorption of Fe^{II} on this layer to give Fe$_3$O$_4$], the Fe$_3$O$_4$ particles will grow in size.

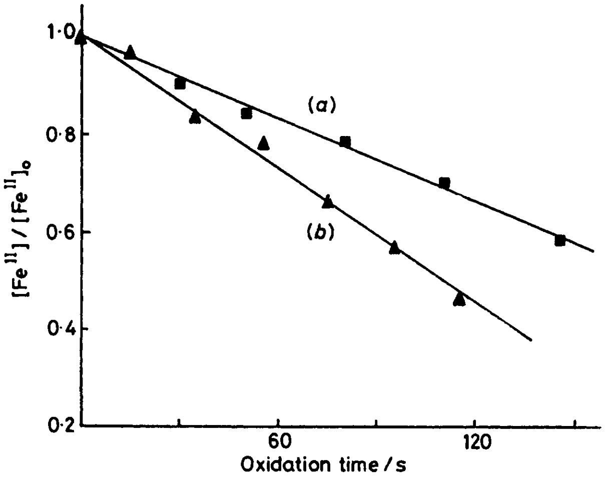

FIGURE 4 Time variation of $[Fe^{II}]/[Fe^{II}]_0$ during the oxidation of the Fe^{II} adsorbed on the iron(III) oxide precipitate at 0.60 (*a*) and at 0.03 mol dm^{-3} Na$_2$[SO$_4$] (*b*)

Thus, the oxidation rate observed during the stationary state in the course of the air oxidation of the Fe[OH]$_2$ suspension is considered to be due the oxidation of Fe^{II} adsorbed on the iron(III) oxide layer of the Fe$_3$O$_4$ particles. When the adsorbed Fe^{II} is oxidized, a new iron(III) oxide layer will be formed. On the other hand, some parts of the layer will be transformed to Fe$_3$O$_4$ by reaction with the Fe^{II} adsorbed. However, when the sulphate concentration is high, the transformation of the iron(III) oxide layer to Fe$_3$O$_4$ is suppressed and the transformation to α-FeO(OH) takes place preferentially.

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