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Iron Compounds Formed by the Aerial Oxidation of Ferrous Salt Solutions

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Many reports have been published on the formation of iron compounds, α-FeOOH, γ-FeOOH, and Fe_3O_4, by the oxidation of aqueous suspensions of ferrous precipitates, such as hydroxide, carbonate, and basic sulfate.1-5) Accroding to these reports, their formation depends on the oxidation rate, the temperature, the pH, *etc.* However, no detailed report has yet been presented on the formation of iron compounds by the oxidation of ferrous salt solutions in which no ferrous precipitate is present. In this note experimental results will be reported on the formation of iron compounds by the aerial oxidation of such ferrous salt solutions.

Experimental

Procedure. Aqueous solutions of ferrous salts were prepared by dissolving ferrous salt of an analytical grade in water. Three liters of each solution were poured into a round flask with a capacity of about 4 *l*. This flask had four inlet necks, into which a thermometer, a reflux condenser, a temperature regulator, and an air-introducing tube (0.7 cm in internal diameter) were inserted. The flask was quickly heated up to a given temperature. Compressed air was then blown into it at the rate of 200 *l*/hr so as to oxidize and stir the solution. During oxidation the temperature was kept constant. Each iron compound precipitated was filtered, washed with water, and then dried at about 105°C.

Identification. Each iron compound obtained was examined by a usual chemical analysis and by the X-ray diffraction method using Mn filtered Fe-K_α radiation.

Results and Discussion

Table 1 shows the kind of iron compounds formed by the oxidation of ferrous salt solutions at 70°C for 30 hr. In connection with the starting solution, in a $FeSO_4$ solution only α-FeOOH is obtained; in the other solutions, mixtures of α-FeOOH and the other compounds are obtained, depending on the kinds and concentrations of the anions present. It is expected that the content of each compound in the mixture depends on the oxidation time by which the composition of the solution is determined. In order to verify this, the following experiments were conducted by use of a fractional precipitation method.

TABLE 1. IRON COMPOUNDS FORMED BY THE AERIAL OXIDATION OF FERROUS SALT SOLUTIONS WITH 0.72 M IN THE FERROUS ION AT 70°C FOR 30 hr

Starting solution	pH value	Iron compounds formed
$FeSO_4$	1.9	α-FeOOH
$FeSO_4(NH_4)_2SO_4$	1.8	α-FeOOH≈(NH_4)-$Fe_3(OH)_6(SO_4)_2$
$FeCl_2$	1.7	β-FeOOH≈α-FeOOH
$FeCl_2(NH_4Cl)_2$	1.2	β-FeOOH>α-FeOOH
$FeBr_2$	1.6	α-FeOOH> γ-FeOOH>α-Fe_2O_3

0.72 M-$FeCl_2$ and 0.72 M-$FeSO_4$ solutions were oxidized at 70°C. After 20 hr, the precipitates formed were sufficiently separated from the solutions by filtration, after which the whole filtrates were further oxidized at 70°C for 20 hr. This treatment was repeated several times every 20 hr. With repeated oxidation, the concentration of the free acid in each filtrate, HCl or H_2SO_4, and its Fe^{3+}/Fe^{2+} ratio increased. Table 2 shows the iron compounds fractionally precipitated for different oxidation times. After the first 60 hr of the total oxidation time has passed, only a basic sulfate is formed in the $FeSO_4$ solution, whereas in the $FeCl_2$ solution β-FeOOH is formed with a slight amount of α-FeOOH even after 100 hr. The X-ray diffraction pattern of the basic sulfate obtained (Fig. 1) shows that it differs sharply from a jarosite-type basic sulfate, as will be described later. Its composition was $(Fe_2O_3)_2SO_3(H_2O)_5$ (Found: Fe_2O_3, 65.3; SO_3, 16.8; H_2O, 17.9 wt%).

TABLE 2. IRON COMPOUNDS FRACTIONALLY PRECIPITATED BY THE OXIDATION OF 0.72 M-$FeCl_2$ AND 0.72 M-$FeSO_4$ SOLUTIONS FOR DIFFERENT TIMES AT 70°C

Time (hr)	$FeCl_2$ solution	$FeSO_4$ solution
to 20	α-FeOOH≈β-FeOOH	α-FeOOH
20 to 40	β-FeOOH>α-FeOOH	α-FeOOH>basic sulphate[a]
40 to 60	β-FeOOH>α-FeOOH	basic sulphate[a]> α-FeOOH
60 to 80	β-FeOOH>α-FeOOH	only basic sulphate[a]
80 to 100	β-FeOOH$\gg$α-FeOOH	
100 to 120	β-FeOOH$\ggg$α-FeOOH	

a) Its chemical composition was $(Fe_2O_3)_2SO_3(H_2O)_5$.

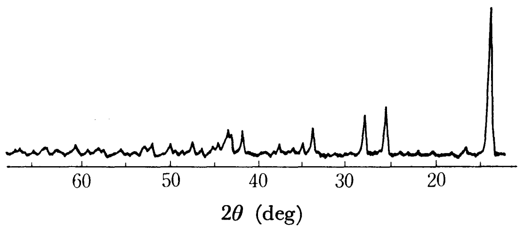

Fig. 1. X-Ray diffraction pattern of the $(Fe_2O_3)_2SO_3(H_2O)_5$ by using Fe-$K\alpha$ radiation.

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1) W. H. Albrecht, *Ber.*, **62** 1475 (1729).
2) G. Schikorr, *Z. Anorg. Allg. Chem.*, **191** 322 (1930).
3) U. Schwertmann, *ibid.*, **298**, 337 (1959).
4) W. Feitknecht, *Z. Electrochem.*, **63** (1) 34 (1959).
5) J. D. Bernal, E. R. Dusgputa, and A. L. Mackay, *Clay. Min. Bull.*, **4** (21) 15 (1959).

The addition of NH_4Cl to the $FeCl_2$ solution and that of a sulfate to the $FeSO_4$ solution favorably affected the formation of β-FeOOH and a basic sulfate respectively. Only β-FeOOH began to be formed at 70°C in the filtrate obtained by oxidizing a mixture of 0.72 M-$FeCl_2$ and 1.44 M-NH_4Cl solutions at 70°C for 20 hr. Also, only a basic sulfate began to be formed at 70°C in the filtrate obtained from a mixture of a 0.72 M-$FeSO_4$ solution and one of 0.72 M-K_2SO_4, Na_2SO_4 or $(NH_4)_2SO_4$ solution at 70°C for 20 hr. Its composition was $RFe_3(SO_4)_2(OH)_5$(R= K, Na, or NH_4), and its crystal structure was of the jarosite type.[6]

By blowing the air into the chloride or the sulfate solution, some of the ferrous ions in it are oxidized to ferric ions, which are then hydrolyzed to form both the acid, HCl or H_2SO_4, and α-FeOOH as the first precipitate. As oxidation progresses, the concentration of the ferric chloride or ferric sulfate increases with an increase in that of HCl or H_2SO_4, and β-FeOOH or the basic sulfate begins to be formed as the second precipitate. This may indicate that their formation is closely connected with the kinds and concentrations of the ferric complex ions in such solutions.

The kinds of the iron compounds formed in the chloride or the sulfate solutions did not depend strongly on the temperature, but that of the iron compounds formed in a ferrous bromide solution did. When the temperature was decreased, an amorphous compound was formed instead of α-FeOOH in the former solutions. Table 3 shows the iron compounds which were formed by the oxidation of a 0.33 M-$FeBr_2$ solution at various temperatures for 20 hr. It was also found that γ-FeOOH, α-FeOOH, β-FeOOH, and α-Fe_2O_3 were all formed by oxidizing a mixture of $FeCl_2$ and excess NaI solutions under conditions similar to the above.

TABLE 3. IRON COMPOUNDS FORMED BY THE AERIAL OXIDATION OF A 0.33 M-$FeBr_2$ SOLUTION AT VARIOUS TEMPERATURES FOR 20 hr

Temp. (°C)	Iron compounds obtained
10	β-FeOOH
20	β-FeOOH > α-FeOOH
40	γ-FeOOH ≈ α-FeOOH
65	α-FeOOH > γ-FeOOH > α-Fe_2O_3
80	α-Fe_2O_3 ≈ α-FeOOH > γ-FeOOH

It is known that, on the slow oxidation of $Fe(OH)_2$ in a ferrous salt solution with a pH of about 7, γ-FeOOH can be obtained by selecting the proper oxidizing conditions. In this case a dark green compound, called a green rust, I or II, is always formed before the formation of γ-FeOOH. Accordingly, the presence of the green rust has so far been considered to be indispensable for the formation of γ-FeOOH. Since the solutions of $FeBr_2$ and the mixture of $FeCl_2$ and NaI were acidic ($pH<3$), no iron compound containing ferrous ions was formed as the intermediate one. In conclusion, γ-FeOOH can be formed not only by the slow oxidation of the green rust in the solution, but also by that of the ferrous salt solution by selecting the proper conditions.

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[6] "Dana's System of Mineralogy, Vol. 2," J. Wiley and Sons, New York (1951) p. 560.