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Coprecipitation Behavior of Zinc in the Oxygenation Process of Ferrous Iron

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To understand the fixation of metal ions in soils and water, the coprecipitation of zinc and cobalt with hydrous ferric oxide generated in the oxygenation process of ferrous ion was investigated. As a preliminary experiment, several oxygenation reactions of ferrous ion ran at various pH values by bubbling oxygen gas or air. The rate of oxygenation was the first order with respect to Fe(II). The over-all rate constant, k, at 25°C was found to be 2.7×10^{13} liter^2 mole^{-2} atm^{-1} min^{-1} in case of the oxygen bubbling.

The coprecipitation of zinc was scarcely affected by the zinc concentration in the parent solution. This shows that zinc ion is not adsorbed on the surface of hydrous ferric oxide but is distributed between the hydrous ferric oxide and the parent solution. Zinc ion was found to be coprecipitated in the hydrous ferric oxide obeying the Doerner and Hoskins logarithmic distribution law, judging from the four possible distribution coefficients calculated. Distribution and adsorption phenomena seem to exist together in the coprecipitation of cobaltous ion, considering some dependency of pH and cobalt concentration on the coprecipitated amount.

INTRODUCTION

The hydrous oxides of iron and manganese, in general, furnish the principal control on the fixation of heavy metals in soils and fresh water sediments, where hydrous oxides of iron and manganese are nearly ubiquitous in clays, soils, and sediments. According to Jenne,[1] adsorption or desorption of the heavy metals occurs in response to such factors as the metal concentration in question, the other metal concentrations, pH and the amounts of inorganic and organic complex ion formers.

Authors believe that, in addition to the factors described above, the coprecipitation behavior of these metals when hydrous ferric oxide is precipitated in response to the oxygenation reaction of ferrous ion should be also one of the important factors in controlling the concentration of the metals in soils and fresh waters. In the present paper, the main object is to examine whether the metal ions such as zinc and cobalt are coprecipitated as the precipitates generated from the oxygenation of ferrous iron are formed.

EXPERIMENTAL

Apparatus and Reagents

Spectrophotometric measurements for the determination of ferric iron were made with a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer using 1.00 cm transmission cells.

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Radioactivity countings were performed with a TEN NaI(Tl) (44.5 mm in dia.×50.8 mm) well type scintillation counter, EA-14, connected with a Metro dekatron scaler, Model MCL-6B. All pH measurements were made using a Hitachi-Horiba pH meter, model F-5.

Standard stock solutions of $ZnCl_2$ and $CoCl_2$ were prepared by dissolving the reagent grade metals or oxides in hydrochloric acid, followed by diluting them to make each 10^{-4} M solution. Radioactive isotopes, cobalt-60, and zinc-65 were supplied from New England Nuclear, Boston, Mass., U.S.A.. Both isotopes were used as chlorides in hydrochloric acid solution. Ferrous iron solutions were freshly prepared by dissolving Mohr's salt, $[(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O]$, in dilute $HClO_4$. Various pH values were controlled by using acetate buffer solutions. The water used for all the results reported here was purified by redistilling the distilled water in a borosilicate glass still.

All other reagents were also the reagent grade materials.

Experimental Conditions

To a 2.0 l borosilicate Erlenmeyer flask were added about 1.9 l of redistilled water and 20 ml of 4.0 M sodium acetate-acetic acid buffer. The flask connected with an Allihn condenser was placed in a thermostatic bath and the solution was vigorously stirred with a magnetic stirrer during the run. After the temperature equilibrium was attained, air or oxygen gas was bubbled through this stirred solution. After being saturated with the air or the oxygen gas, a suitable volume of a trace metal solution with an appropriate amount of radioactive isotopes was added in the flask, and the resulting solution was diluted to 2.0 l. Two milliliters of 0.2 M ferrous solution were added and a stopwatch was started. The pH value of the test solution at this point was measured. At appropriate intervals of time, aliquots of the test solution were withdrawn, separated centrifugally and placed in sulfuric acid solution to quench the reaction. Trace metal activities in the solution phase were counted with a NaI scintillation counter. The ferrous iron content of each aliquot was determined spectrophotometrically after the neutralization with sodium acetate, using 1,10-phenanthroline as a color reagent.

RESULTS AND DISCUSSION

Oxygenation of Ferrous Iron

Several extensive studies on oxygenation of ferrous iron have been made in homogeneous acid solutions.[2~5] Stumm and Lee[6] showed that the rate of oxygenation of ferrous iron in bicarbonate solutions followed the law:

$$\frac{-d[Fe(II)]}{dt} = k[Fe(II)]P_{O_2}(HO^-)^2 \qquad (1)$$

As a preliminary experiment to examine the coprecipitation behavior of trace metal ions, the oxygenation rate of ferrous iron under the condition of the present work was studied. Several oxygenation reaction runs at various pH values bubbling air or oxygen gas are plotted in Figs. 1 and 2. The rate of oxygenation in the present work was also the first order with respect to Fe(II). This is evident from the linear relationship in the semilogarithmic plots of Figs. 1 and 2. As shown in these figures, the change in the

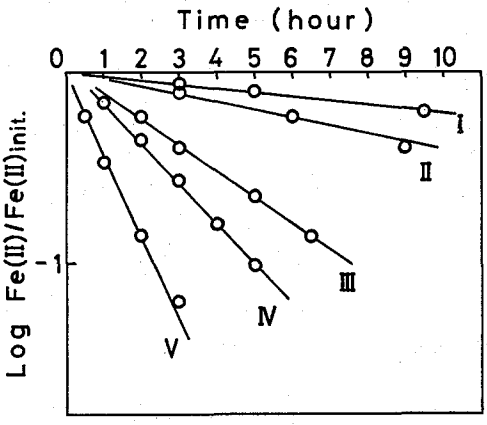

Fig. 1. Oxygenation rate of Fe(II) at various pH by bubbling the air.
Fe: 2.0×10^{-4} M, CH_3COONa: 4.0×10^{-2} M, temp.: 25°C,
pH: I 5.82, II 5.99, III 6.18, IV 6.34, V 6.50

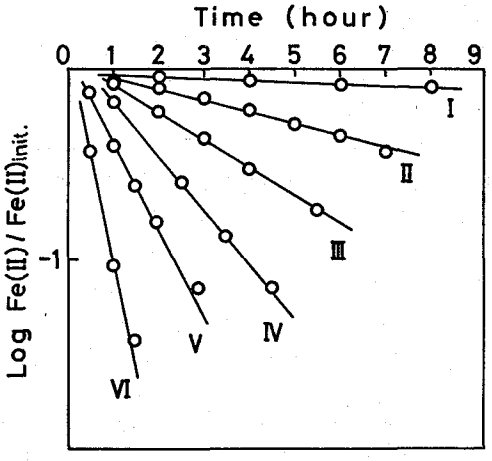

Fig. 2. Oxygenation rate of Fe(II) at various pH by bubbling the oxygen.
Fe: 2.0×10^{-4} M, CH_3COONa: 4.0×10^{-2} M, temp.: 25°C
pH: I 5.43, II 5.89, III 6.18, IV 6.30, V 6.38, VI 6.50

Table I. Rate Constants of Fe(II) Oxygenation by Bubbling the Air

pH	k (liter^2 mole^{-2} atm^{-1} min^{-1})
6.00	1.47×10^{14}
6.18	1.35×10^{14}
6.20	1.36×10^{14}
6.26	1.08×10^{14}
6.32	1.00×10^{14}
6.50	1.08×10^{14}
	Av. 1.22×10^{14}

Table II. Rate Constants of Fe(II) Oxygenation by Bubbling the Oxygen Gas

pH	k (liter^2 mole^{-2} atm^{-1} min^{-1})
5.89	3.50×10^{13}
6.18	2.10×10^{13}
6.30	2.20×10^{13}
6.38	2.04×10^{13}
6.50	3.08×10^{13}
	Av. 2.70×10^{13}

rate of reaction with pH can be explained by the influence of hydroxy ions on the reaction rate. Tables I and II list the over-all rate constant, k, in Eq. (1) for a set of experimental runs. The values for k at 25°C have been found to be 2.7×10^{13} liter^2 mole^{-2} atm^{-1} min^{-1} in case of the oxygen bubbling, 1.22×10^{14} in case of the air bubbling. The over-all rate constant, k, in the oxygen system is somewhat lower than that in the air system. This may be caused by the pronounced effect of oxygenation reaction by impurity in the air.

Coprecipitation of Zinc

In order to examine the effect of zinc concentration, the oxidation reaction of ferrous iron was performed in the solutions containing zinc ranging from 10^{-8} to 10^{-6} M, by bubbling the oxygen gas; the initial concentrations of ferrous iron and acetate ion were 2.0×10^{-4} and 4.0×10^{-2} M; initial pH was 6.15; the thermostat was regulated at 25°C. The results are shown in Fig. 3, in which the percentages of the coprecipitated zinc are plotted against the fractions of precipitated hydrous ferric oxide. As shown in Fig. 3, no significant change in the coprecipitation behavior of zinc was observed in the concentration range investigated. This fact means that zinc ion is not adsorbed on the surface of hydrous ferric oxide, but distributed between the solution phase and the hydrous ferric oxide as the oxidation reaction proceeds. Actually, zinc ion was scarcely adsorbed by

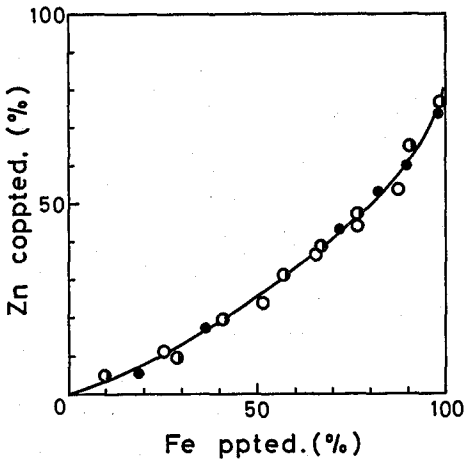

Fig. 3. Effect of zinc concentration.

Fe: 2.0×10^{-4} M, CH_3COONa: 4.0×10^{-2} M, pH: 6.15, temp.: 25°C
Zn: ○ 1.0×10^{-6} M, ● 1.0×10^{-7} M, ◑ 1.0×10^{-8} M

the hydrous ferric oxide which was precipitated by the oxygenation reaction.

In order to compare with the present coprecipitation system, authors investigated the adsorption of zinc with the usual hydrous ferric oxide which was prepared by adding sodium hydroxide into the ferric chloride solution. As seen in Fig. 4, the adsorbed zinc was only about 10 percent at pH 6.15, while the zinc coprecipitated in the oxygenation process attained to around 80 percent at the same pH value as seen in Fig. 3. This supports that the zinc coprecipitation in the present system is not an adsorption type, but mainly a distribution one.

The coprecipitation behavior of zinc at pH 6.15, 6.50, and 6.90 was examined as shown in Fig. 5. The oxygenation rate of ferrous iron is the second order with respect to hydroxy ion as seen in Eq. 1, and this indicates that the rate is much influenced by the pH value. The oxygenation reaction of ferrous iron at pH 6.90 was too fast to observe

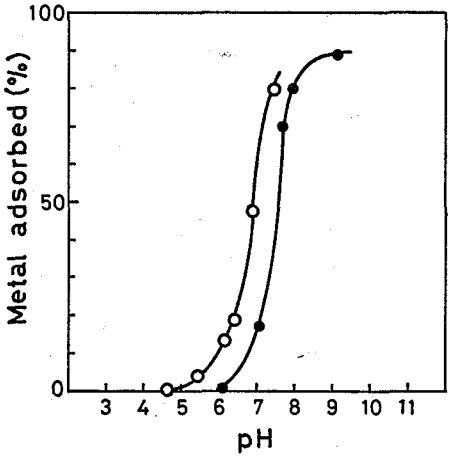

Fig. 4. Adsorption of zinc and cobalt with ferric hydroxide.
○: 1.0×10^{-8} M Zn, ●: 1.0×10^{-8} M Co

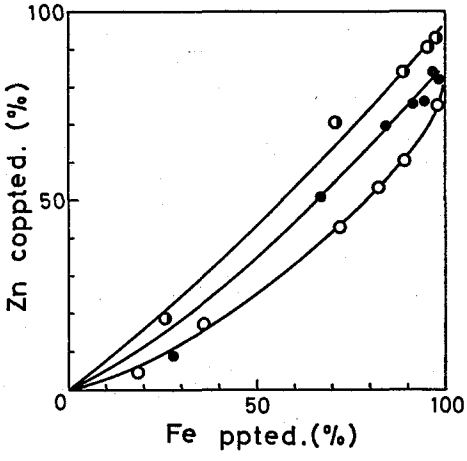

Fig. 5. Effect of pH on zinc coprecipitation.
Fe: 2.0×10^{-4} M, CH_3COONa: 4.0×10^{-2} M, Zn: 1.0×10^{-7} M, temp.: 25°C, pH: ○ 6.15, ● 6.50, ◑ 6.90

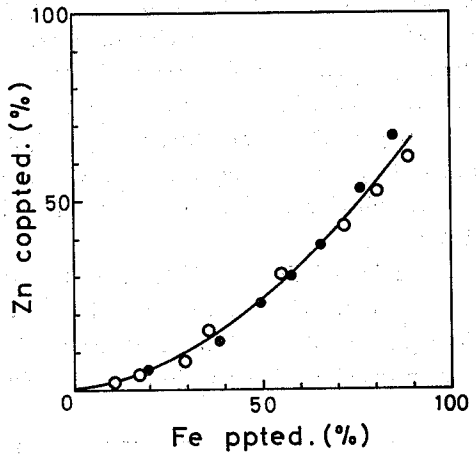

Fig. 6. Effect of temperature.
Fe: 2.0×10^{-4} M, CH_3COONa: 4.0×10^{-2} M, Zn: 1.0×10^{-7} M,
temp.: ○ 25°C, ● 45°C,

the distribution behavior of zinc. Therefore, hydroxylammonium chloride was added to suppress the oxygenation rate at pH 6.90. In the figure 5, the coprecipitation of zinc seems to increase as the pH value rises. But this may be caused by the overlap of the adsorption and distribution parts of zinc, judging from the fact that the hydrous ferric oxide prepared from the solution at pH 6.90 shows some adsorption ability.

The oxygenation reaction was also performed at 45°C. As shown in Fig. 6, the coprecipitation of zinc was almost identical at both 25°C and 45°C.

Distribution Mechanism of Zinc

In order to examine the distribution behavior of zinc in the oxygenation process of ferrous iron, four conceivable distribution coefficients were calculated. The first, called the homogeneous distribution coefficient, D, was employed by Chlopin[7] and Henderson *et al.*[8]; it is expressed as follows:

$$\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{crystal}} = D\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{solution}} \tag{2}$$

The second, offered by Doerner and Hoskins,[9] is called the logarithmic distribution coefficient, λ; it is expressed as follows;

$$\log\left(\frac{\text{initial quantity}}{\text{quantity left in soln.}}\right)_{\text{tracer}} = \lambda \log\left(\frac{\text{initial quantity}}{\text{quantity left in soln.}}\right)_{\text{carrier}} \tag{3}$$

The present equilibrium is represented by the following equation, taking account of the charges of ions:

$$2Fe^{3+}{}_{\text{cryst.}} + 3Zn^{2+}{}_{\text{soln.}} \rightleftarrows 2Fe^{3+}{}_{\text{soln.}} + 3Zn^{2+}{}_{\text{cryst.}} \tag{4}$$

Thirdly, the equilibrium constant, D', in the present system is defined as follows:

$$D' = \frac{[Fe^{3+}]^2_{soln.}[Zn^{2+}]^3_{cryst.}}{[Fe^{3+}]^2_{cryst.}[Zn^{2+}]^3_{soln.}} = \left(\frac{[Fe^{3+}]^2}{[Zn^{2+}]^3}\right)_{soln.} \cdot \left(\frac{[Zn^{2+}]^3}{[Fe^{3+}]^2}\right)_{cryst.} \quad (5)$$

$[Fe^{3+}]_{cryst.}$ is nearly equal to unity and $[Zn^{2+}]_{cryst.}$ is equal to $(m_{Zn}/m_{Fe})_{cryst.}$, where m_{Fe} and m_{Zn} denote the mole fractions in the crystal phase. Then equation (5) can be written:

$$\frac{m_{Zn}}{m_{Fe}} = D'^{1/3} \frac{[Zn^{2+}]_{soln.}}{[Fe^{3+}]^{2/3}_{soln.}} \quad (6)$$

Lastly, the equation in consideration of the charges of ions is derived in a similar way to the equation proposed by Gordon.[10] This distribution coefficient, λ_g is written as follows:

$$\log X_i/X_f = 1.303\lambda_g(Y_i^{1/3} - Y_f^{1/3}) \quad (7)$$

where X_i and Y_i represent the initial concentrations of zinc and iron in the solution phase; X_f and Y_f denote the final concentrations of zinc and iron in the solution phase.

The distribution coefficients, D, D', λ, and λ_g, calculated from the Eqs. (2), (3), (6), and (7) are represented in Table III. The results show that the logarithmic distribution coefficient, λ, has a better invariability throughout the reaction process, that is, the present system obeys the Doerner and Hoskins logarithmic distribution law.

Coprecipitation of Cobaltous Cobalt

The coprecipitation behavior of cobaltous cobalt was examined in the same way as the zinc coprecipitation. The percentages of the coprecipitated cobalt in the fraction of hydrous ferric oxide at pH 6.30, 6.83, and 7.20 are plotted in Fig. 7. In the experiment

Table III. Four Possible Distribution Coefficients of Zinc at pH 6.15

Fe ppted. (%)	Zn coppted. (%)	D	D'	λ	λ_g
Zn: 1.0×10^{-7} M					
35.8	17.2	0.372	2.01	0.426	1.34
56.7	30.9	0.341	2.30	0.442	1.48
71.6	43.1	0.300	2.39	0.448	1.60
81.2	53.3	0.264	2.45	0.456	1.74
86.3	57.4	0.214	1.79	0.429	1.72
89.7	59.8	0.171	1.21	0.401	1.67
Zn: 1.0×10^{-8} M					
9.5	4.5	0.449	2.50	0.461	1.37
40.9	20.0	0.361	1.99	0.424	1.35
56.1	29.5	0.327	2.00	0.425	1.42
65.8	38.7	0.328	2.58	0.456	1.59
75.7	47.7	0.293	2.58	0.458	1.68
90.1	65.5	0.209	2.29	0.460	1.93

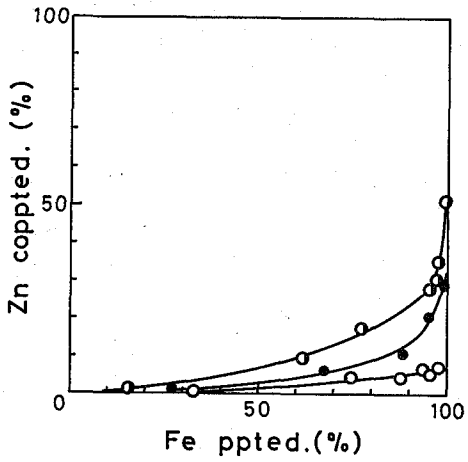

Fig. 7. Effect of pH on cobalt coprecipitation.
Fe: 2.0×10^{-4} M, CH_3COONa: 4.0×10^{-2} M, Co: 1.0×10^{-7} M, temp.: 25°C, $NH_2OH\cdot HCl$: 2.0×10^{-2} M in case of pH 6.83 and 7.20
pH: ○ 6.30, ● 6.83, ◑ 7.20

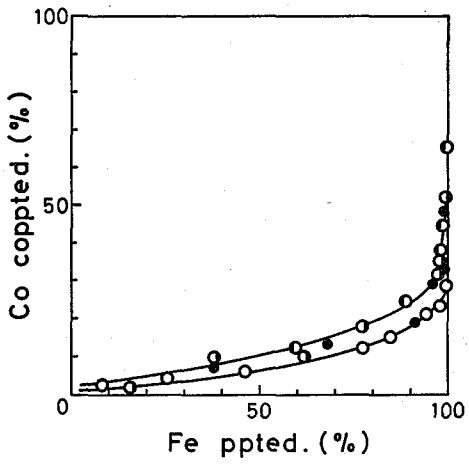

Fig. 8. Effect of cobalt concentration.
Fe: 2.0×10^{-4} M, CH_3COONa: 4.0×10^{-2} M,
$NH_2OH\cdot HCl$: 2.0×10^{-2} M, pH: 7.20, temp.: 25°C
Co: ○ 1.0×10^{-5} M, ● 1.0×10^{-6} M
◑ 1.0×10^{-7} M, ◐ 1.0×10^{-8} M

at pH 6.83 and 7.20, hydroxylammonium chloride was added to make the oxygenation rate slower. The coprecipitation of cobaltous cobalt increases with the rise of pH as shown in Fig. 7. To check whether the coprecipitation of cobalt is a distribution type or an adsorption one, hydrous ferric oxide was precipitated from the solutions containing 10^{-5} to 10^{-8} M of cobalt at pH 7.20. As seen in Fig. 8, there is a tendency for cobalt coprecipitation to increase as the concentration of cobalt decreases. It seems that the distribution and adsorption types exist together in the present coprecipitation system, judging from the dependency of pH and cobalt concentration on the coprecipitated amount.

This is not inconsistent with the fact that the newly prepared hydrous ferric oxide adsorbs cobaltous cobalt to some extent as shown in Fig. 4.

REFERENCES

(1) E. A. Jenne, "Trace Inorganics in Water," R. F. Gould, Ed., Chap. 21, Amer. Chem. Soc., Washington, D.C., 1968.
(2) M. Cher and N. Davidson, *J. Amer. Chem. Soc.*, **77**, 793 (1955).
(3) R. E. Huffman and N. Davidson, *ibid.*, **78**, 4836 (1956).
(4) A. P. Lamb and L. W. Elder, *ibid.*, **53**, 137 (1931).
(5) A. M. Posner, *Trans. Faraday Soc.*, **49**, 382 (1953).
(6) W. Stumm and G. F. Lee, *Ind. Eng. Chem.*, **53**, 143 (1961).
(7) W. Chlopin, *Z. anorg. u. allgem. Chem.*, **143**, 97 (1925).
(8) L. M. Henderson and F. C. Kracek, *J. Amer. Chem. Soc.*, **49**, 738 (1927).
(9) H. A. Doerner and W. M. Hoskins, *ibid.*, **47**, 662 (1925).
(10) L. Gordon, M. L. Sulutsky, and H. H. Willard, "Precipitation from Homogeneous Solution," John Wiley & Sons, New York, 1959, p. 132.