

# Coprecipitation Effects in Solutions Containing Ferrous, Ferric, and Cupric Ions

By J. D. HEM *and* M. W. SKOUGSTAD

CHEMISTRY OF IRON IN NATURAL WATER

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## CHEMISTRY OF IRON IN NATURAL WATER

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### COPRECIPITATION EFFECTS IN SOLUTIONS CONTAINING FERROUS, FERRIC, AND CUPRIC IONS

By J. D. HEM and M. W. SKOUGSTAD

#### ABSTRACT

Precipitates of ferric hydroxide that form when solutions containing ferrous iron are raised in pH or Eh may remove other ions from solution by coprecipitation. Solutions containing from 1 to 10 ppm (parts per million) of iron and about 0.5 ppm of copper were adjusted to pH values ranging from 3.8 to 8.5 by adding sodium carbonate or sodium bicarbonate. More copper was lost from solutions whose pH was 5.5 or more than would have been expected had iron been absent. Stable or metastable colloidal suspensions of ferric hydroxide have a positive zeta potential and do not adsorb copper; but when the zeta potential decreases or becomes negative as a result of a change (increase) in the pH of the solution, copper is adsorbed by the ferric hydroxide precipitate.

Iron precipitating from water samples after they have been collected may remove dissolved copper. Samples from which iron has precipitated can be acidified at the time of analysis to return all the copper to solution. Precipitation of iron can be prevented by lowering the pH of the sample to 4.5 or less at the time of collection if the amount of copper originally dissolved is to be determined.

#### OCCURRENCE OF FERRIC HYDROXIDE IN NATURAL WATER

The Eh (redox potential) and pH of many ground waters are favorable for the presence of ferrous iron in solution. However, precipitates of ferric hydroxide may form as a result of oxidation and hydrolysis when iron-bearing ground water comes in contact with air. The precipitates may form at spring orifices, at well discharge openings, or even in aquifers. Conversely, the oxidation rate may be slow enough so precipitates will not form until some time after the water has been withdrawn from the well or spring. The slow precipitation of ferric hydroxide, sometimes related to bacterial action, may result in accumulation of iron in water mains and plumbing systems. Deposits of ferric hydroxide are commonly observed in water sample bottles as a result of the slow oxidation of dissolved ferrous iron. The physical nature of the ferric hydroxide precipitate depends on pH, concentrations of iron and other ions in solu-

tion, temperature, and other factors. Under certain conditions, the precipitate may be a rapidly settling floc that effectively removes small suspended particles and even some dissolved ions from solution.

Stable sols of colloidal ferric hydroxide can be prepared in the laboratory. Surface water commonly contains a few hundredths of a part per million of iron that seems to be present as a stable suspension of particles in the colloidal size range; minor amounts of dissolved undissociated ferric hydroxide may be present (Hem and Cropper, 1959).

In general, the pH controls the solubility of ferric iron, in water in contact with air, and less than 0.01 ppm (parts per million) will be present in dissociated form unless the pH is less than about 4.8. The value of the ratio  $\text{Fe}^{+3} : \text{Fe}^{+2}$  is a function of the Eh of the environment. Water in contact with air is subjected to oxidation because of the presence of oxygen in the air. The precipitation of hydrated ferric oxide (ferric hydroxide) occurs naturally in lakes and sometimes produces ores of economic importance.

The Eh and pH of sea water are high enough to make the oceans decidedly unfavorable for the retention of iron in solution. Hence, iron that is brought in by drainage from land areas is mostly precipitated in the ocean (Goldschmidt, 1954, p. 665-666). Mechanisms involved in the precipitation process have been studied by oceanographers (Goldberg, 1954). The scavenging effect of ferric hydroxide precipitates possibly explains the presence of certain rare metals in sea water in amounts much less than saturation (Krauskopf, 1956; Goldberg and Arrhenius, 1956).

The scavenging effects of ferric hydroxide that have been described in the literature were studied in the laboratory using solutions at the dissolved-solids concentration of sea water. The chemical behavior of iron in water having dissolved-solids concentration of potable water is of more direct interest for this discussion. No doubt trace metals are also removed from iron-bearing fresh water when ferric hydroxide precipitates out of solution. The work described here was done to determine how much dissolved copper might be lost from a dilute solution from which ferric hydroxide was precipitating and to determine what conditions control the rate and efficiency of removal of copper. The behavior of ferric hydroxide sols and precipitates, which is a function of pH, aeration, and other conditions, needs to be considered to evaluate the loss of copper ions from solution. The effects of ferric hydroxide precipitation on the content of other heavy metal ions in natural water are approximately indicated by the behavior of copper.

The laboratory studies were made in Denver, Colo., by the Geological Survey as a part of research in the chemistry of iron by the Water Resources Division. Helpful suggestions were furnished by colleagues of the authors in the Geological Survey and by E. D. Goldberg, Scripps Institute of Oceanography, La Jolla, Calif., who reviewed the manuscript.

#### CHARACTERISTICS OF SUSPENDED FERRIC HYDROXIDE

Ferric sulfate or chloride and ferrous sulfate are sometimes used as coagulants in the treatment of public or industrial water supplies. However, alum is more commonly used. The coagulant forms a precipitate in the water that is capable of attracting and coprecipitating suspended clay particles. The precipitate also helps remove organic colloids and microorganisms and settles out at the surface of the filter sand as a permeable deposit which is readily removed by back washing.

When a ferric salt is added to water, hydrolysis produces ferric hydroxide and lowers the pH of the water. For a ferric hydroxide precipitate to form on the addition of ferrous sulfate to a water requires oxidation of the iron to the ferric state. Oxidation can be speeded by aeration or by raising the pH. The coagulant to be used in a water treatment plant is selected by experiments with the water to be treated, but, in general, if the water has a low initial pH, ferric salts give better results than alum. A satisfactory ferric hydroxide floc can usually be formed by adding ferric salts to water at any pH of more than about 4.5, but the behavior of the precipitate is influenced by dissolved ions, amount and kind of suspended matter present, temperature, mechanical agitation of the solution, and other factors (Fair and Geyer, 1954, p. 623-624).

Under some conditions, instead of a floc, a very finely divided precipitate of ferric hydroxide, which has the properties of a colloid, may form. The small amounts of iron in much natural water that has been aerated can be removed with a filter whose pores are 0.45 microns in diameter (Hem and Cropper, 1959). Probably this material is also colloidal ferric hydroxide.

Precipitates of ferric hydroxide produced in the laboratory by raising the pH of iron-bearing water commonly are flocculent. The formation of ferric hydroxide precipitates in much natural water, however, is caused by an increase in Eh, which sometimes is accompanied by an actual decrease in pH. The precipitates that form as a result of slowly increasing Eh are not commonly flocculent. Ferric hydroxide may adhere to the walls of the container in which the

reaction occurs or may form small suspended particles that settle very slowly.

### PROPERTIES OF COLLOIDS

Colloidal particles range in diameter from about 0.001 to about 1 micron, and they carry an electrostatic charge. The mutually repulsive forces acting among particles having a like charge help to prevent the particles from settling by gravity. The charge is negative on some types of colloids and positive on others. In a water suspension, each particle is surrounded by a shell of oriented water molecules, which are attracted to the particle and retained by the electric charge. Between the water shell and the solution is a shear zone where the hydrated particle is no longer rigidly connected to the molecules of the solvent. The electric potential between the hydrated particle and the molecules of the solvent at the shear zone is called the zeta potential; it is a measure of stability of the colloid as well as of the behavior of the colloidal particle toward dissolved ions or toward other suspended particles. The zeta potential is affected by pH and can be neutralized by changes in pH or by the effects of anions and cations in solution. The charge on some kinds of colloidal particles can be changed from positive to negative by raising the pH. The point at which the zeta potential changes from positive to negative (zeta potential=0) is called the isoelectric point.

Colloidal particles of ferric hydroxide are commonly positively charged, although Fair and Geyer (1954, p. 618) point out that a negatively charged sol can be produced at a high pH. Ions in solution tend to neutralize the charge on colloidal particles so that a few hundred parts per million or more of dissolved solids help form comparatively large ferric hydroxide particles. Clay particles, organic colloids, and most of the other suspended solids that occur naturally in water are negatively charged. Ferric or aluminum hydroxide removes the turbidity and color of natural water because negatively charged particles are attracted to the positively charged hydroxide particles. The charges on the colloidal particles are thus neutralized, and the uncharged aggregates join to form a rapidly settling precipitate.

### EFFECTS OF COLLOIDS ON HEAVY METAL IONS

Heavy metal ions in solution have a positive charge; hence, they would not be attracted to positively charged ferric hydroxide particles. Colloidal dispersions of heavy metal oxides or hydroxides commonly also have a positive charge. The positive zeta potential of ferric hydroxide suspensions decreases, however, as pH increases;



therefore an alkaline suspension of ferric hydroxide might be capable of attracting and precipitating heavy metal ions.

In his discussion of the behavior of hydrous iron oxide colloids, Krause (1928) stated that ferric hydroxide has an isoelectric point at pH 5.2. Near this pH, the zeta potential on ferric hydroxide particles suspended in dilute solutions should, therefore, be small; and at a pH of more than 5.2, the potential should actually be negative. The conditions in the solutions used in the present study, however, are different from those used by Krause.

Heavy metal ions may be lost from solutions stored in glass bottles by adsorption of some of the ions on the glass. A glass surface has some areas of unsatisfied negative valence and can, therefore, attract cations. Positively charged particles, such as those of ferric hydroxide, may also be attracted to the glass surface; hence, ferric hydroxide films may tend to adhere to the sides of sample containers. At a low enough pH, however, the glass surface will be covered with adsorbed hydrogen ions, and metallic ions or hydroxide particles will not be attracted to the glass.

Hydroxides of heavy metals will precipitate independently when the pH of the solution becomes high enough. The factors that might affect the loss of copper from solutions in which ferric hydroxide is precipitating include the pH, the magnitude and sign of the zeta potential, the size of the individual particles of ferric hydroxide, and the concentrations of ions in the solution. Copper can be present in solution as cupric ions and as complexes such as  $\text{CuOH}^+$  or  $\text{CuCl}^+$ . There also are carbonate complexes of copper; the normal or basic carbonates of copper have low solubilities. The behavior of ferric hydroxide suspensions and cupric ions was considered in the preparation of the laboratory study.

#### COMPOSITION OF LABORATORY TEST SOLUTIONS

A series of 24 test solutions containing ferrous and ferric iron and traces of copper was prepared. For solutions 1 to 11 in table 1, an iron stock solution was made by dissolving pure iron wire in a measured amount of concentrated hydrochloric acid. After the wire was completely dissolved the solution was diluted with distilled water to a concentration of about 300 ppm of iron in about 2.0 normal hydrochloric acid. The diluted solution was then heated to near-boiling temperature, and clean copper shot was added to reduce all  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$ . Complete reduction was accomplished within 5 minutes. The solution was then poured away from the copper shot, cooled to room temperature, and stored in a clean glass-stoppered

bottle. Boiling the solution with copper shot served a threefold purpose—most of the dissolved air was removed,  $\text{Fe}^{+3}$  was reduced to  $\text{Fe}^{+2}$ , and simultaneously  $\text{Cu}^{+2}$  was introduced into solution.

A series of 10-milliliter portions of the stock solution was transferred to 1-liter beakers and diluted to about 1 liter with freshly boiled distilled water. The resulting solutions had a pH of about 2.0 and contained about 3 ppm of iron and about 0.6 ppm of copper. Each solution was brought to a selected pH by adding solid sodium bicarbonate; the final pH was determined with a pH meter. The solutions had about the same iron and copper content, but they ranged in pH from 3.8 to 5.8 in increments of 0.2 pH unit. Each solution was analyzed for iron and copper immediately after the pH was adjusted to its initial value. The portion of the solution used for the first analysis was not filtered or centrifuged. The solutions were then permitted to stand exposed to air for a period of from 2 to 7 days. Before each subsequent analysis in this series was made, a portion of the solution was transferred to a 50-milliliter centrifuge tube and centrifuged for 0.5 to 1.0 hour at 1,500 rpm (about 500 times the force of gravity). The portion for analysis was then taken from the centrifugate. Analyses on each solution were made at intervals, usually daily. The results of the pH, ferrous and ferric iron, and copper determinations are given in table 1.

TABLE 1.—*Ferrous and ferric iron and copper content, in parts per million, and pH of test solutions at several time intervals after preparation*

Solution	Ion	Time after preparation, in days								
		0	$\frac{1}{4}$	1	2	3	4	5	6	10
1	pH	3.8		3.9	3.9					
	$\text{Fe}^{+2}$	3.1		2.4	2.5					
	$\text{Fe}^{+3}$	.07		.06	.00					
	Cu	.61		.62	.62					
2	pH	4.0		4.2	4.3					
	$\text{Fe}^{+2}$	3.0		2.4	2.4					
	$\text{Fe}^{+3}$	.23		.10	.10					
	Cu	.62		.62	.63					
3	pH	4.2		4.8	5.1					
	$\text{Fe}^{+2}$	2.6		2.4	1.6					
	$\text{Fe}^{+3}$	.47		.17	.17					
	Cu	.64		.64	.61					
4	pH	4.4		5.3	6.1					
	$\text{Fe}^{+2}$	2.5		1.7	.05					
	$\text{Fe}^{+3}$	.53		.38	.25					
	Cu	.62		.57	.52					
5	pH	4.6		5.4			7.3			
	$\text{Fe}^{+2}$	2.3		.92			.00			
	$\text{Fe}^{+3}$	.80		.17			.00			
	Cu	.62		.57			.09			
6	pH	4.8	5.0	5.4	6.2	7.1			7.6	
	$\text{Fe}^{+2}$	1.7	1.5	.38	.00					
	$\text{Fe}^{+3}$	1.1	.27	.06	.00					
	Cu	.58	.58	.54	.33	.15			.03	
7	pH	5.0	5.1	5.5	6.4	7.3			7.8	
	$\text{Fe}^{+2}$	1.8	1.3	.13						
	$\text{Fe}^{+3}$	1.2	.15	.05	.00					
	Cu	.59	.54	.50	.30	.08				
8	pH	5.2		5.6	6.2	7.0			8.0	
	$\text{Fe}^{+2}$	1.7		.00	.00					
	$\text{Fe}^{+3}$	1.5		.02	.00					
	Cu	.64		.51	.39	.20			.02	

TABLE 1.—Ferrous and ferric iron and copper content, in parts per million, and pH of test solutions at several time intervals after preparation—Continued

Solution	Ion	Time after preparation, in days								
		0	¼	1	2	3	4	5	6	10
9	pH	5.4	-----	5.9	6.7	7.3	-----	-----	8.3	-----
	Fe <sup>++</sup>	1.6	-----	.00	.00	-----	-----	-----	-----	-----
	Fe <sup>+++</sup>	1.5	-----	.00	.00	-----	-----	-----	-----	-----
	Cu	.63	-----	.47	.30	.17	-----	-----	.02	-----
10	pH	5.6	5.7	6.2	-----	-----	8.3	8.5	-----	-----
	Fe <sup>++</sup>	.9	.00	.00	-----	-----	-----	-----	-----	-----
	Fe <sup>+++</sup>	2.2	.24	.00	-----	-----	-----	-----	-----	-----
	Cu	.63	.44	.38	-----	-----	.04	-----	-----	-----
11	pH	5.8	5.9	6.5	-----	-----	8.5	8.6	-----	-----
	Fe <sup>++</sup>	.8	.00	.00	-----	-----	-----	-----	-----	-----
	Fe <sup>+++</sup>	2.4	.30	.00	-----	-----	-----	-----	-----	-----
	Cu	.63	.43	.29	-----	-----	.03	-----	-----	-----
12	pH	4.1	-----	-----	-----	4.1	4.1	-----	4.0	4.4
	Fe <sup>++</sup>	-----	-----	-----	-----	2.2	2.2	-----	1.2	-----
	Fe <sup>+++</sup>	-----	-----	-----	-----	.80	.90	-----	1.8	-----
	Cu	-----	-----	-----	-----	.52	.52	-----	.50	.50
13	pH	4.5	-----	-----	-----	4.6	4.5	-----	4.5	4.6
	Fe <sup>++</sup>	-----	-----	-----	-----	1.4	2.1	-----	.57	-----
	Fe <sup>+++</sup>	-----	-----	-----	-----	1.6	.5	-----	1.6	-----
	Cu	-----	-----	-----	-----	.55	.55	-----	.55	-----
14	pH	5.0	-----	-----	-----	5.1	5.1	-----	5.2	5.5
	Fe <sup>++</sup>	-----	-----	-----	-----	.34	.24	-----	.01	.00
	Fe <sup>+++</sup>	-----	-----	-----	-----	.20	.04	-----	.05	.03
	Cu	-----	-----	-----	-----	.46	.40	-----	.41	.35
15	pH	5.5	-----	-----	-----	6.1	6.1	-----	6.2	6.6
	Fe <sup>++</sup>	-----	-----	-----	-----	.00	.00	-----	.00	-----
	Fe <sup>+++</sup>	-----	-----	-----	-----	.03	.00	-----	.00	-----
	Cu	-----	-----	-----	-----	.31	.16	-----	.17	.10
16	pH	6.2	-----	-----	-----	6.7	6.9	-----	6.9	7.1
	Fe <sup>++</sup>	-----	-----	-----	-----	.00	-----	-----	-----	-----
	Fe <sup>+++</sup>	-----	-----	-----	-----	.01	-----	-----	-----	-----
	Cu	-----	-----	-----	-----	.16	.07	-----	.09	.10
17	pH	6.5	-----	-----	-----	6.9	7.1	-----	7.1	-----
	Fe <sup>++</sup>	-----	-----	-----	-----	.00	-----	-----	-----	-----
	Fe <sup>+++</sup>	-----	-----	-----	-----	.02	-----	-----	-----	-----
	Cu	-----	-----	-----	-----	.11	.04	-----	.04	-----
18	pH	7.0	-----	-----	-----	7.4	7.5	-----	7.6	-----
	Fe <sup>++</sup>	-----	-----	-----	-----	.00	-----	-----	-----	-----
	Fe <sup>+++</sup>	-----	-----	-----	-----	.03	-----	-----	-----	-----
	Cu	-----	-----	-----	-----	.11	.04	-----	.04	-----
19	pH	7.5	-----	-----	-----	7.9	8.0	-----	8.0	-----
	Fe <sup>++</sup>	-----	-----	-----	-----	.00	-----	-----	-----	-----
	Fe <sup>+++</sup>	-----	-----	-----	-----	.02	-----	-----	-----	-----
	Cu	-----	-----	-----	-----	.07	.03	-----	.04	-----
20	pH	8.0	-----	-----	-----	8.2	8.2	-----	8.2	-----
	Fe <sup>++</sup>	-----	-----	-----	-----	.00	-----	-----	-----	-----
	Fe <sup>+++</sup>	-----	-----	-----	-----	.06	-----	-----	-----	-----
	Cu	-----	-----	-----	-----	.08	.01	-----	.03	-----
21	pH	8.5	-----	-----	-----	8.6	8.6	-----	8.6	-----
	Fe <sup>++</sup>	-----	-----	-----	-----	.00	-----	-----	-----	-----
	Fe <sup>+++</sup>	-----	-----	-----	-----	.03	-----	-----	-----	-----
	Cu	-----	-----	-----	-----	.07	.04	-----	.03	-----
22	pH	5.5	5.5	5.8	-----	-----	6.1	-----	6.5	-----
	Fe <sup>++</sup>	-----	.00	.00	-----	-----	.00	-----	.00	-----
	Fe <sup>+++</sup>	0	.00	.00	-----	-----	.00	-----	.00	-----
	Cu	.5	.48	.42	-----	-----	.33	-----	.37	-----
23	pH	5.5	5.5	5.8	-----	-----	6.1	-----	6.5	-----
	Fe <sup>++</sup>	-----	.11	0	-----	-----	.00	-----	-----	-----
	Fe <sup>+++</sup>	1.0	.21	.07	-----	-----	.03	-----	-----	-----
	Cu	.5	.54	.38	-----	-----	.38	-----	.32	-----
24	pH	5.5	5.5	5.8	-----	-----	6.2	-----	6.6	-----
	Fe <sup>++</sup>	-----	1.3	.00	-----	-----	.00	-----	-----	-----
	Fe <sup>+++</sup>	10	.6	.08	-----	-----	.04	-----	-----	-----
	Cu	.5	.21	.26	-----	-----	.19	-----	.15	-----

A second series of solutions (12 to 21 in table 1) was prepared to extend the pH range given by the first 11 solutions. A new iron stock solution that had a pH of about 2.0 was used. Parts of this solution and a copper stock solution made up from reagent grade copper sulfate and demineralized distilled water were mixed and diluted to give a

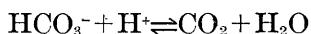
series of solutions containing about 3 ppm of iron and about 0.5 ppm of copper. Each of these solutions was then adjusted in pH by adding solid sodium carbonate. One solution was prepared for each 0.5 pH unit from 4.1 to 8.5. The pH, ferrous and ferric iron, and copper in these solutions were determined at intervals over a period of 10 days.

The iron and copper contents were determined in parts of the sample that had been filtered through a plastic membrane filter having pores 0.45 micron in diameter. The filtering removed suspended and at least the larger colloidal-size particles. The initial set of determinations was made after the solutions had stood for 3 days.

The last 3 solutions, 22 to 24, in table 1, initially contained 0.5 ppm copper and were all adjusted to the same pH, but they contained different amounts of iron initially in order to check the effect of the quantity of ferric hydroxide precipitated. The pH selected for these solutions was 5.5 because it seemed to be the lowest value that was accompanied by extensive losses of copper from solution. Iron concentrations initially present were 0.0, 1.0, and 10 ppm respectively. By the time the iron determinations were made a few hours later, most of the iron had already precipitated. Stock solutions used were the same as those used for solutions 12 to 21.

### DISCUSSION OF RESULTS

The pH of all the solutions increased with time; although in solutions of low pH, the increase was relatively minor. The buffer system in all the solutions was the same as that of most natural water and involved dissolved carbon dioxide and bicarbonate ions. However, the amount of carbon dioxide present in most of these solutions was much larger than the amount that can be retained in equilibrium with the partial pressure of carbon dioxide in the air. Carbon dioxide, therefore, is lost from solution, and the pH increases as indicated by the equilibrium:



The amount of bicarbonate that can be present at a pH of less than 5.0 is minor; hence, loss of carbon dioxide from the more acid solutions had only a minor effect on the pH.

The choice of sodium carbonate or bicarbonate for neutralizing these solutions was perhaps unfortunate because it did not permit the establishment of a stable pH. Almost any other buffer system that could have been selected, however, would also cause complex  $\text{Fe}^{+3}$  ions to form. Acetate, citrate, tartrate, or phosphate buffers, for example, would be unsuitable. Probably neutralization with a strong base,

such as sodium hydroxide, would not have been satisfactory because the resulting solution would not have been buffered.

The gradual rise in pH of the test solutions assured complete precipitation of ferric hydroxide and enabled convenient evaluation of loss of  $\text{Cu}^{+2}$  from the solution. Bicarbonate systems are present in natural water, so they are appropriate for this work, although most natural water does not contain such an excess of carbon dioxide.

All pH measurements were made with a pH meter having a glass electrode and a saturated calomel reference electrode. Results of these measurements are given in table 1.

### BEHAVIOR OF IRON

The first analysis of solutions 1 to 11 was made without centrifuging because all the solutions were clear and no precipitate was visible at the time. The results for iron, however, probably include some suspended iron as well as that actually in solution. (See table 1.) The fact that the centrifugate or filtrate for each subsequent analysis was clear does not alone give positive assurance that finely divided suspended ferric hydroxide was absent. The samples having a pH of less than 5.0 had a noticeable color, which was due possibly to ferric hydroxide colloids. Solution 14 had no evidence of precipitated iron after 10 days, although it was yellow and most of the iron was removed by filtration.

Data in table 1 indicate that the amount of ferrous iron at 0 time in solutions 1 to 11 tends to decrease as the amount of ferric iron tends to increase, and most of the iron in solution 11 was present in the ferric form. These solutions were prepared 1 or 2 at a time over a period of several days, and evidently the decrease in ferrous iron at 0 time resulted from oxidation of the stock solution during this period. Cher and Davidson (1955) state that cupric ions have a catalytic effect in the oxidation of ferrous ions. The oxidation reaction would normally be very slow at the low pH (about  $-0.3$ ) of the stock solution.

Ferrous iron was determined by the colorimetric bipyridine method. Distilled water was used in place of hydroxylamine hydrochloride to avoid reducing any ferric iron. The sum of ferrous and ferric iron was determined in a second sample to which hydroxylamine hydrochloride reagent was added, and the amount of ferric iron was determined by subtracting the amount of ferrous iron from the total.

The amount of ferric iron present in solutions 1 to 11 at 0 time, computed from the solubility product of ferric hydroxide, was in excess of the equilibrium quantity for the pH at that time. However, the explanation for this excess seems fairly evident. The stock

solution had a very low pH (somewhat less than 0); therefore, it could contain large amounts of ferric ions. The diluted aliquots still had a low enough pH to retain the ferric ions without any precipitation of ferric hydroxide. As soon as the sodium bicarbonate was added, the pH increased; but the precipitation of ferric hydroxide was not immediate. The results in table 1 indicate, however, that ferric iron precipitated from solution in a day or two at a pH of 5.0 or more and that the rate of precipitation was more rapid for the solutions whose initial pH was greater than 5.0 than for solutions whose initial pH was less than 5.0.

The results in table 1 also indicate the rate of oxidation of ferrous iron. In solutions 1 and 2, the rate of this reaction is slow; however, in solutions 3 to 11, the rate seems to be pH dependent, and it increases rapidly as pH increases (Hem and Cropper, 1959).

#### BEHAVIOR OF COPPER

Each filtered or centrifuged solution was analyzed for copper at the same time it was analyzed for iron. (See table 1.) Copper was determined by the colorimetric (dihydroxyethylthiocarbamic acid) method, in which a blank was used to correct for the absorption of iron citrate complex at 425 millimicrons, the wavelength at which the copper complex is measured. The blank was prepared from a separate, identical volume of sample, in which all reagents except the color-forming reagent were added. The spectrophotometer was set to read 0 absorbance with the blank.

The chemistry of copper in dilute solutions is complex, and only major features were taken into account in these experiments. Data given by Latimer (1952, p. 184-187) indicate that the Eh at which copper is oxidized from  $\text{Cu}^+$  to  $\text{Cu}^{+2}$  in acid solution is about 0.15 v. This Eh is less than the Eh attained in the test solutions and is much less than the expected Eh in solutions in contact with air. Consequently, cupric ( $\text{Cu}^{+2}$ ) ions were to be expected in the test solutions.

The compounds of lowest solubility that cupric ions might form in these solutions are the hydroxide ( $K_{sp}=1.6\times 10^{-19}$ ) and the carbonate ( $K_{sp}=2.5\times 10^{-10}$ ). In the presence of a copper activity of  $10^{-5}$  molal, about the amount present initially in the solutions, the carbonate would not precipitate until the activity of the carbonate ion exceeded  $2.5\times 10^{-5}$  molal. The amounts of carbonate, bicarbonate, and carbon dioxide in the solutions were not determined but can be estimated from the pH at 0 time. The total content of bicarbonate and related species decreased with time owing to loss of carbon dioxide to the air. If all the bicarbonate had been retained, a carbonate activity sufficient to precipitate copper carbonate might have been

reached at pH 8 in solutions 1 to 11 and at a higher pH in the other solutions.

The solubility product for copper hydroxide indicates that the hydroxide would have begun to precipitate from these solutions when the pH reached about 7.3. In the computation, the effect of other ions in the solutions on the activity coefficient for copper was considered. The effect of copper complexes, however, was not considered, and it might increase the solubility of both hydroxide and carbonate; the hydroxide seems to be definitely less soluble than the carbonate.

The dashed line on figure 11, which is based on the solubility product of cupric hydroxide, indicates the solubility of copper in solutions of 0.01 ionic strength (about the concentration of solutions 12 to 21). Solutions of 0.01 ionic strength whose pH is more than 8.0 should contain less than 0.02 ppm of copper. At pH 9.0 in the presence of carbonate ion, an anionic complex of the form  $\text{Cu}(\text{CO}_3)_3^{-4}$  could occur. Latimer (1952) gives a stability constant for this complex which indicates it could be important at pH greater than 9.0 but this is outside the range of present interest.

The copper content of most of the solutions decreased with time. A large part of the copper was lost after all the iron had precipitated as ferric hydroxide when the pH was more than 6.0. In solutions whose pH remained less than 5.5, however, nearly all the copper remained in solution even when some iron was lost by ferric hydroxide precipitation. The critical level of pH above which copper is lost from solution evidently lies between pH 5.5 and 6.0; although in solution 14 and to a lesser extent in some others, some precipitation did take place between pH 5.0 and 5.5. These facts are in accord with the statement by Krause (1928) that the isoelectric point for ferric hydroxide is at pH 5.2.

Copper could be lost from solution at a pH of less than that at which cupric hydroxide would precipitate by several mechanisms. Copper could have been adsorbed by the glass surface of the sample bottles. The amount of adsorption would be pH dependent but would be affected by the iron content of the solutions. Ferric ions, being trivalent, would be more strongly adsorbed by the glass than the divalent cupric ions. Solution 22, which contained copper but no iron, lost about 0.11 ppm of copper by the time it had reached the pH of 6.5. The amount of copper lost was much greater in solutions 23 and 24 which contained iron. Adsorption on the glass probably was a minor factor in most of the solutions in this study. Except for solution 22, the ionic strength of the solutions was high enough to minimize the adsorption of copper on the glass surfaces.

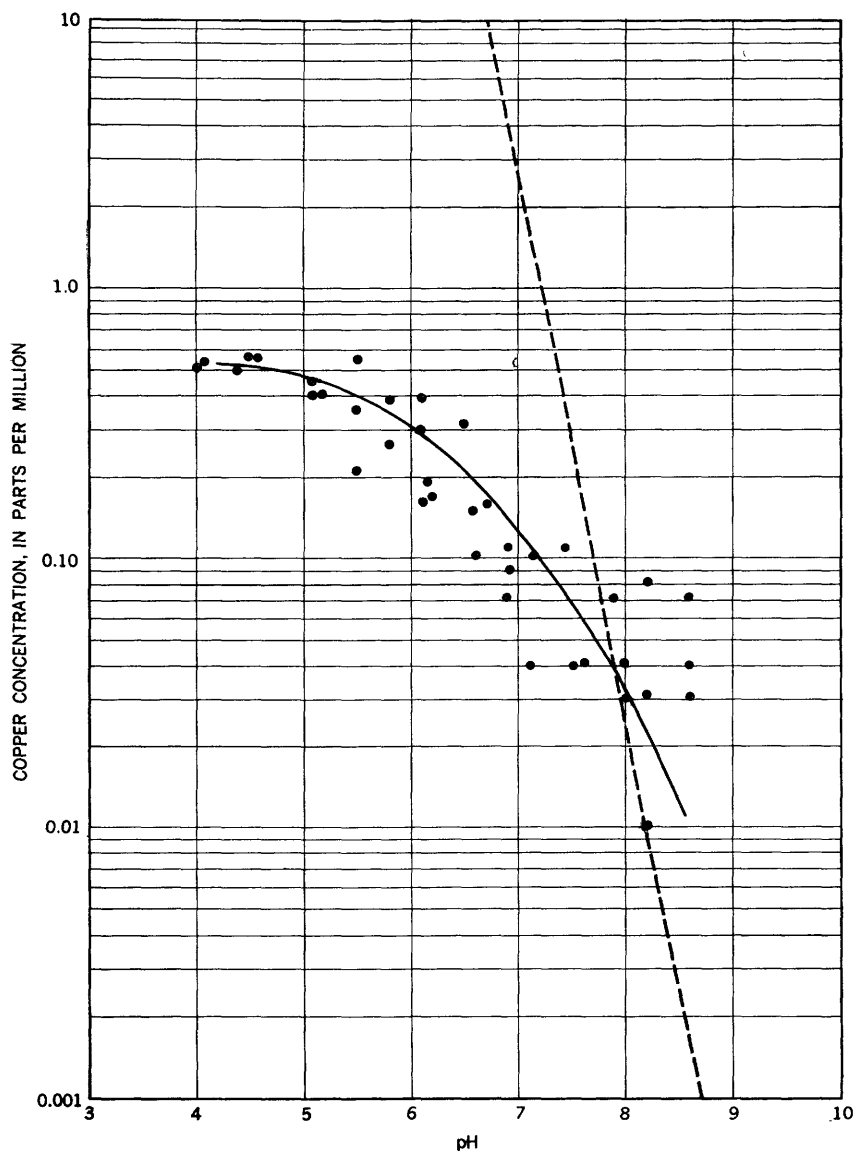


FIGURE 11.—The relation of concentration of copper to pH in test solutions containing ferric hydroxide (solid line) and the theoretical relation of concentration of copper to pH in solutions of 0.01 ionic strength (dashed line).



Copper could be carried on the ferric hydroxide precipitate by adsorption, incorporated into the crystal lattice of the precipitate, or more loosely attached and carried down by occlusion. Colloidal particles of ferric hydroxide are positively charged at low pH and would not be favorable for adsorption of cations. Increasing pH decreases the intensity of positive charge and permits the ferric hydroxide particles to increase in size until they are large enough to settle out. The loss of iron from solution as the pH increases is accompanied by a loss of copper. The amount of dissolved copper decreased slowly after the iron had all precipitated, suggesting that the copper ions are attracted to the surface of the precipitated ferric hydroxide.

In solutions 14 and 23, a fairly stable ferric hydroxide colloid formed, and no precipitate was visible, although the solutions were yellow. The size of the suspended particles apparently tended to increase with time, however. In solution 14, for example, after 3 days, 0.20 ppm of ferric iron passed through the filter; but after 10 days, only 0.03 ppm of ferric iron passed through the filter. The copper remaining in solution after 3 days was about 80 percent and after 10 days about 60 percent of the original amount. The colloidal-size particles of ferric hydroxide must have a positive charge, but the strength of the charge decreases and pH increases as time passes. The pH of solution 14 did not become high enough to permit all the copper to be adsorbed.

The pH of the solutions increased with time so that the effects of time and of pH on copper content cannot be easily separated. However, some of the data in table 1 indicate the effect of pH. For example, in solutions 15 to 17, most of the iron had precipitated after 3 days, and the copper remaining in solution at that time was a function of the pH. At pH 6.1 in solution 15, about 60 percent of the copper originally present was still in solution; at pH 6.7 in solution 16, about 30 percent of the copper remained; and at pH 6.9 in solution 17, about 20 percent of the copper remained. At pH's of more than 6.9, the amount of copper remaining after 3 days was from 10 to 20 percent of the amount originally present. At a pH of more than about 5.2, the ferric hydroxide tends to become negatively charged. The rate of adsorption of copper will increase as the negative potential at the surface of the precipitate increases. However, the direct precipitation of copper hydroxide becomes significant at a pH of more than 7.3.

The general relation between pH and copper content of these solutions is shown by the curve on figure 11, which is based on determined pH and copper content of solutions 12 to 21, and 23 and 24. The com-

puted activity coefficient of cupric ions is 0.7 at 0.01 ionic strength. The solubility-product relation shown by the dashed line contains the activity-coefficient correction of 0.7. If a solution containing 0.55 ppm of copper and 0 ppm of iron is raised in pH, no copper should be lost until the pH reaches about 7.3. Solutions 1 to 11 had a higher ionic strength than solutions 12 to 24; therefore, solutions 1 to 11 retained a somewhat larger amount of copper in solution at a given pH than solutions 12 to 24. Solution 22 was not used in preparing figure 11 as that solution contained no iron.

The loss of copper from solution at a pH of less than that at which copper hydroxide should be precipitated seems logically to be the result of ferric hydroxide precipitates. The amount of copper that will be lost is probably also a function of the amount of ferric hydroxide present. Data from solutions 23 and 24 suggest that increasing iron content by a factor of 10 increases the copper coprecipitated by only a factor of 2. Other effects related to the behavior of ferric hydroxide suspensions are involved in the coprecipitation, but they cannot be evaluated because of insufficient experimental data.

### CONCLUSIONS

Ferric hydroxide precipitates commonly form positively charged colloids at low pH. The positive charges on the colloidal particles would attract negatively charged particles or ions, but cations probably would not be adsorbed appreciably by ferric hydroxide unless the positive charges on the ferric hydroxide particles were neutralized. Neutralization was evidently accomplished between pH 5.0 and 6.0 in the solutions used in this study. Precipitates of ferric hydroxide formed at a pH of more than about 5.5 adsorbed copper ions. Copper may in part be included in the crystal lattice of the ferric hydroxide as the particles grow and precipitate, but the experimental data suggest that adsorption is more important than incorporation in the crystal lattice. Adsorption is probably the best explanation of the decrease in copper that took place in most of the solutions after the ferric hydroxide precipitate had formed and settled out. To be stable in acid solution, a colloidal suspension of ferric hydroxide must consist of positively charged particles. The adsorption of a small amount of copper by the stable suspensions of ferric hydroxide indicates the probable importance of aggregates of neutral or perhaps negatively charged precipitated ferric hydroxide particles as a means of copper removal.

In natural water, copper and probably other trace heavy metals would coprecipitate with ferric hydroxide only if the iron precipitated under certain conditions. The results of the experiments sug-

gest that the conditions most favorable for coprecipitation would include a neutral or alkaline pH, so that the normal positive charge on ferric hydroxide particles would be neutralized. If precipitation occurred at low pH, some anions might be adsorbed. Iron ores commonly contain such impurities as arsenic and phosphorus, the presence of which is probably related to adsorption of anions as the iron precipitated.

Colloidal suspensions of ferric hydroxide in natural water probably do not carry any large amounts of other cations by adsorption on the hydroxide particles because of the small concentration of ferric hydroxide that can occur in stable suspension. However, the behavior of some of the trace constituents in natural water may be affected by adsorption on colloidal ferric hydroxide. The effects of adsorption by ferric hydroxide or other colloidal matter should be considered in future studies of trace constituents in natural water.

Particles of iron oxides or hydroxides that settle out in stream sediments may carry adsorbed copper or other metals under certain conditions. However, the effect of iron compounds is minor compared with the effect of clays and other mineral species that have a natural excess of negative electrostatic charge and are more capable of adsorbing cations.

When samples of iron-bearing water whose pH is more than 5.5 are analyzed for trace metals, any iron that has precipitated in the sample container should be brought back into solution by lowering the pH so that adsorbed metals will be determined in the correct concentrations. The amount of copper adsorbed is probably relatively minor in iron precipitates that form in water whose pH is less than about 5.0.

The results of these studies suggest that copper can be retained in solution in iron-bearing water by acidification to pH 4.5. This pH can be readily attained by adding a small amount of acetic or other weak acid to samples at the time of collection.

Future studies of the adsorption of trace constituents of solutions by ferric hydroxide precipitates might well utilize radiochemical methods. Some of the trace constituents of interest are themselves radioactive, and suitable isotopes can be obtained to extend the radiochemical procedure to copper and other ions.

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