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PRECIPITATION OF IRON IN AERATED GROUND WATERS

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INTRODUCTION

A survey of 31 iron removal plants conducted in Illinois in 1960[4] revealed that, at the time of sampling, the finished water in eighteen of these plants contained iron in excess of 0.3 mg per l that is the United States Public Health Service (USPHS) recommended limit for the element in public water supplies.[5] All of the plants surveyed used aeration, usually by coke-tray aerators, brief detention for 1 hr or less following aeration, and filtration by pressure type rapid sand filters.

The aeration device at every plant could effectively introduce dissolved oxygen into the raw water in excess of the stoichiometric requirement for oxidizing the soluble ferrous iron present. However, the question was raised whether the detention time provided in these plants was sufficient to allow for oxidation and complete precipitation of iron. The purpose of the present study was to determine, insofar as is possible in natural ground waters, the factors that govern the kinetics of iron precipitation so that a more rational

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[4] Komolkrit, K., "Measurement of Redox Potential and Determination of Ferrous Iron in Ground Waters," thesis presented to the Univ. of Illinois, at Urbana, Ill., in January, 1962, in partial fulfilment of the requirements for the degree of Master of Science.
[5] "Public Health Service Drinking Water Standards," Publication No. 96, U. S. Pub. Health Service, U. S. Govt. Printing Office, Washington, D. C., April, 1962.
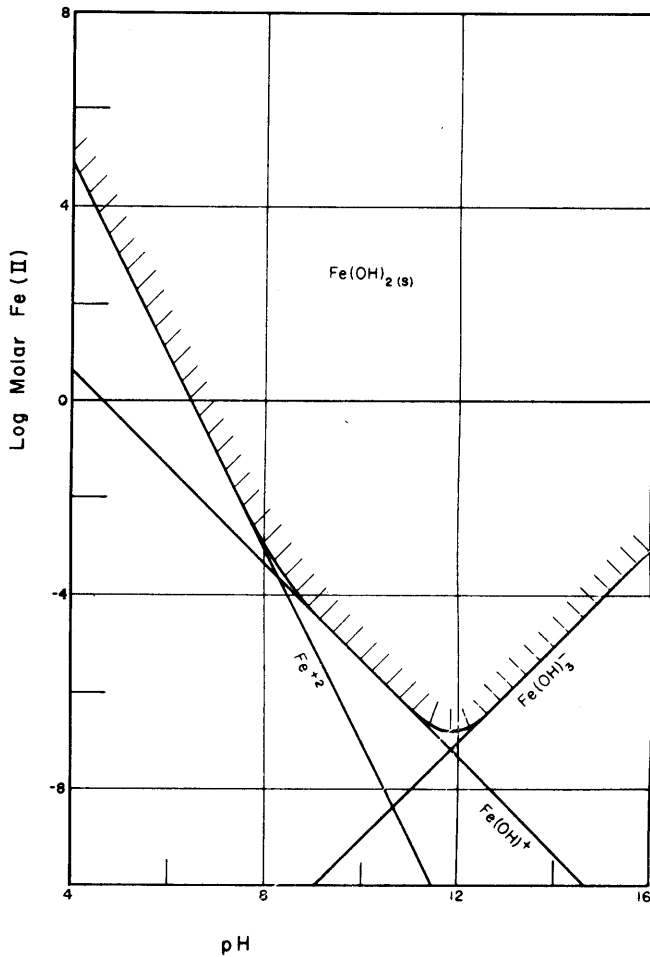
FIG. 1.—SOLUBILITY OF $Fe(OH)_{2(s)}$ IN A NON-CARBONATE NON-SULFIDE SOLUTION

approach could be applied to the engineering design of reaction basins in iron removal plants.

THEORETICAL CONSIDERATIONS

Solubility of Iron.— In natural ground waters, soluble iron exists mainly in the bivalent state. Some trivalent ferric iron may also exist in solution especially in aquifers where low pH values are encountered. In alkaline waters devoid of sulfides, phosphates and organic compounds, iron will precipitate from aqueous solution as ferrous hydroxide, ferrous carbonate, ferric hydrox-

ide, or mixtures thereof depending on the concentration of oxidizing agents and pH.

Fig. 1 shows the solubility characteristics of ferrous iron in waters devoid of any carbonate or sulfide species. The equilibria represented by reactions 1, 2, and 9 in Table 1 were considered in computing the solubility of ferrous iron. The boundary of the shaded area in Fig. 1 defines the maximum solubility. Iron will precipitate as ferrous hydroxide from natural ground waters containing approximately 10^{-4} M per 1 Fe, only at pH values higher than 9 and under anaerobic conditions.

In any alkaline natural water, the solubility of ferrous iron is limited by the solubility of ferrous carbonate to a pH of 9 above which the solubility equilibria of ferrous hydroxide become limiting again (reactions 2 and 9, Table 1). The solubility of ferrous iron in distilled water to which 10^{-2} eq per 1 of alkalinity has been added is shown in Fig. 2. The equilibria represented by reactions 7, 8, and 10 in Table 1 were used in computing the solubility in this case. Theoretically, iron that precipitates from a supersaturated solution of this type would be either ferrous carbonate or ferrous hydroxide depending on the pH. Under practical conditions, however, the precipitation of basic carbonates, e.g., $\left[Fe(OH)_2 \cdot FeCO_3\right]$, with somewhat different solubility characteristics is probable, especially in the pH range of 8 to 11.[9] Because it is believed that the solubility of ferrous carbonate should regulate the quantity of ferrous iron found in natural ground waters having alkalinities of 10^{-2} eq per 1 and within a pH range of 6 to 9, it is difficult to explain why the quantity of ferrous iron found in ground waters exceeds the predicted solubility by an order of magnitude.

Fig. 3 shows the solubility characteristics of ferric iron that are governed by the solubility equilibria of ferric hydroxide represented by reactions 3, 4, 5, and 10 in Table 1. On aeration or by the addition of oxidizing agents, iron is oxidized from the ferrous to the ferric form. Once oxidized, the solubility of iron is severely limited over a wide pH range (4 to 13) by the solubility of ferric hydroxide. To take advantage of this solubility restriction, the basic step in the removal of iron is the oxidation of ferrous iron to the ferric form.

Redox Equilibria for Iron.—Electrons and protons are present in all waters. Their activities can be measured electrometrically as oxidation-reduction potential (ORP or E_h) and pH, respectively. A theoretical model useful in illustrating the various redox equilibria for iron is the E_h-pH diagram, also known as the stability-field diagram, which is computed from chemical equilibria data. The E_h-pH diagram shown in Fig. 4 was constructed for a typical central Illinois ground water (Clinton), where the alkalinity is 10^{-2} eq per 1 and the total activity of iron is approximately 4×10^{-5} M per 1. The

[6] Leussing, O. L., and Kolthoff, J. M., "The Solubility Product of Ferrous Hydroxide and the Ionization of Aquo-Ferrous Ion," Journal of American Chemical Society, Washington, D. C., Vol. 75, 1953, p. 2476.

[7] Gayer, K. H., and Woontner, L., "The Solubility of Ferrous Hydroxide and Ferric Hydroxide in Acidic and Basic Media at 25. C," Journal of Physical Chemistry, Washington, D. C., Vol. 60, 1956, p. 1569.

[8] Latimer, W. M., "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952, pp. 220-233.

[9] Stumm, W., and Lee, G. F., "The Chemistry of Aqueous Iron," Schweizerische Zeitschrift für Hydrologie, Birkhauser Verlag, Basel, Vol. XXII, 1960, pp. 295-319.

[10] Fair, G. M., and Geyer, J. C., "Water and Waste-Water Disposal," John Wiley & Sons, Inc., New York, N. Y., 1963, p. 473.

TABLE 1.—IRON EQUILIBRIA

No.	Reaction[a]	Equilibrium Constant, 25°C	Reference
	Solubility and Acidity		
1	$Fe(OH)_{2(s)} = Fe^{+2} + 2OH^-$	8×10^{-16}	6
2	$Fe(OH)_{2(s)} + OH^- = Fe(OH)_3^-$	8.3×10^{-6}	7
3	$Fe(OH)_{3(s)} = Fe^{+3} + 3OH^-$	6.6×10^{-38}	8
4	$Fe(OH)_{3(s)} = Fe(OH)_2^+ + OH^-$	5.13×10^{-17}	Computed
5	$Fe(OH)_{3(s)} = FeOH^{++} + 2OH^-$	2.57×10^{-26}	Computed
6	$Fe(OH)_{3(s)} + OH^- = Fe(OH)_4^-$	$\sim 10^{-5}$	9
7	$FeCO_{3(s)} = Fe^{++} + CO_3^=$	2.11×10^{-11}	8
8	$HCO_3^- = H^+ + CO_3^=$	4.69×10^{-11}	10
9	$Fe(OH)_{2(s)} = FeOH^+ + OH^-$	4×10^{-10}	6
10	$FeCO_{3(s)} + OH^- = FeOH^+ + CO_3^=$	3.15×10^{-5}	Computed
11	$FeOH^{++} + H^+ = Fe^{+++} + H_2O$; $\log \dfrac{a_{Fe^{++}}}{a_{FeOH^{++}}} = 2.43 - pH$		Computed
12	$Fe(OH)_{3(s)} + 2H^+ = FeOH^{++} + H_2O$; $\log a_{FeOH^{++}} = 2.41 - 2\,pH$		Computed
		pH Zone of Influence	
	Redox Reactions		
13	$Fe^{++} + 2e^- = Fe$; Eh = $-0.440 + 0.0295 \log Fe$		Computed
14	$Fe^{+++} + e^- = Fe^{++}$; Eh = $0.771 + 0.0591 \log \dfrac{a_{Fe^{+++}}}{a_{Fe^{++}}}$		Computed

TABLE 1.—CONTINUED

No.	Reaction[a]	Equilibrium Constant, 25°C	Reference
	Redox Reactions		
15	$Fe(OH)_{2(s)} + H^+ + e^- = Fe^{++} + H_2O$; $Eh = 0.915 + 0.0591\,pH + 0.0591\,\log \dfrac{a_{FeOH^{++}}}{a_{Fe^{++}}}$	2.43 – 3.90	Computed
16	$Fe(OH)_{3(s)} + 3H^+ + e^- = Fe^{++} + 3H_2O$; $Eh = 1.06 - 0.1773\,pH - 0.0591\,\log a_{Fe^{++}}$	3.90 – 6.05	Computed
17	$Fe(OH)_{3(s)} + CO_3^= + 3H^+ + e^-$ $= FeCO_{3(s)} + 3H_2O$; $E_o = -0.672$	6.05 – 9.10	Computed
18	$Fe(OH)_{3(s)} + H^+ + e^- = Fe(OH)_{2(s)} + H_2O$; $Eh = 0.271 - 0.0691\,pH$	9.10 – ?	Computed
19	$Fe(OH)_{2(s)} + 2H^+ + 2e^- = Fe + 2H_2O$; $Eh = -0.0475 \cdot 0.0591\,pH$	9.10 – ?	Computed
20	$FeCO_{3(s)} + 2e^- = Fe + CO_3^=$ $E_o = -0.756$	6.05 – 9.10	Computed
	O_2 – H_2O System		
21	$O_2 + 4H^+ + 4e^- = 2H_2O$; $Eh = 1.229 - 0.0591\,pH + 0.0148\,\log \left(P_{O_2}\right)$		Computed
	H^+ – H_2 System		
22	$2H^+ + 2e^- = H_2$; $Eh = 0.0591\,pH - 0.0295\,\log \left(P_{H_2}\right)$		Computed

[a] $Fe(OH)_{2(s)}$ = ferrous hydroxide in solid phase.

equilibria considered in constructing the diagram are listed in Table 1. The numbers on the lines correspond to the respective reactions in Table 1. Each boundary line on the shaded area represents an equilibrium between a solid and an ionic species, and the total activity of soluble iron at any point on these lines is 4×10^{-5} M per l. Lines 11, 14, and 15 represent equilibria between two ionic species.
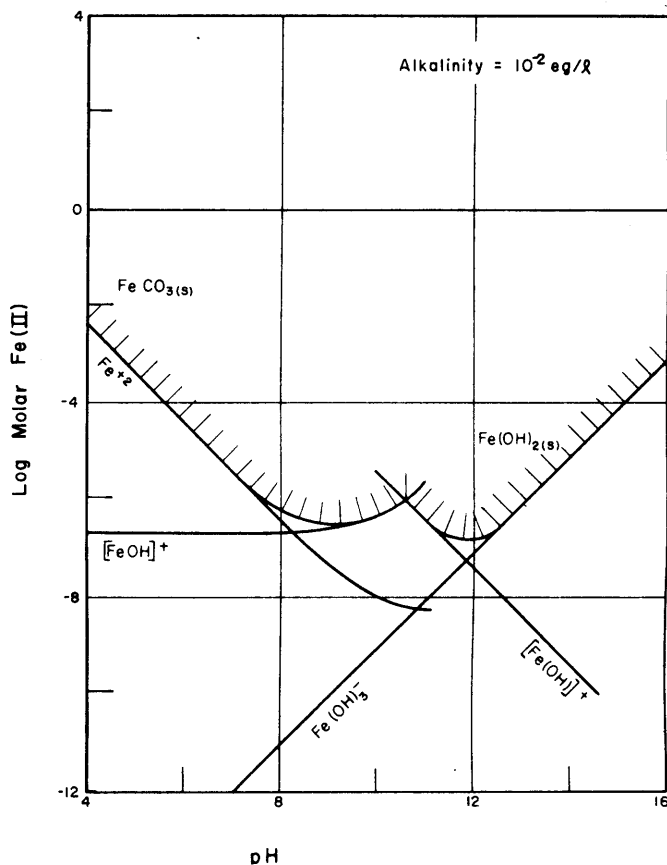

FIG. 2.—SOLUBILITY OF FERROUS IRON IN A CARBONATE-BEARING WATER (Above pH 11.5, the alkalinity exceeds 10^{-2} eg/ℓ)

The activity ratio of two ions on any of these lines is unity. The diagram depicts E_h-pH regions in which ferrous carbonate and ferric hydroxide predominate at equilibrium. However, ferrous carbonate may be expected to precipitate in the region of ferric hydroxide stability yielding a mixed precipitate because the relative proportions of ferrous carbonate and ferric
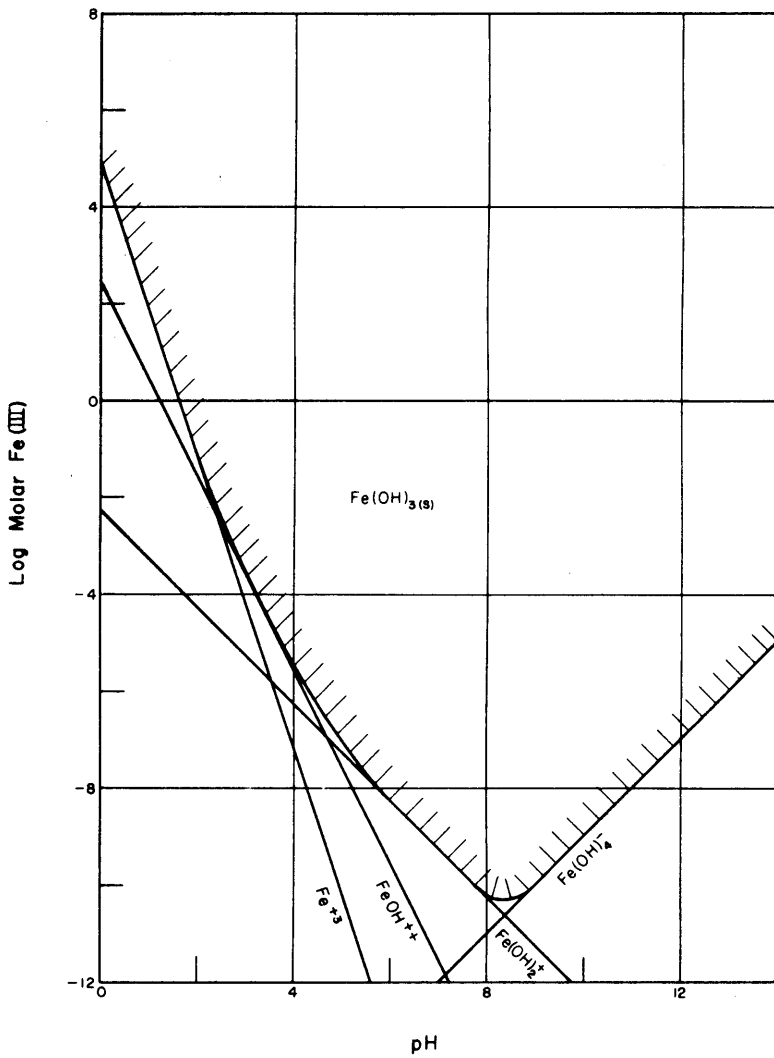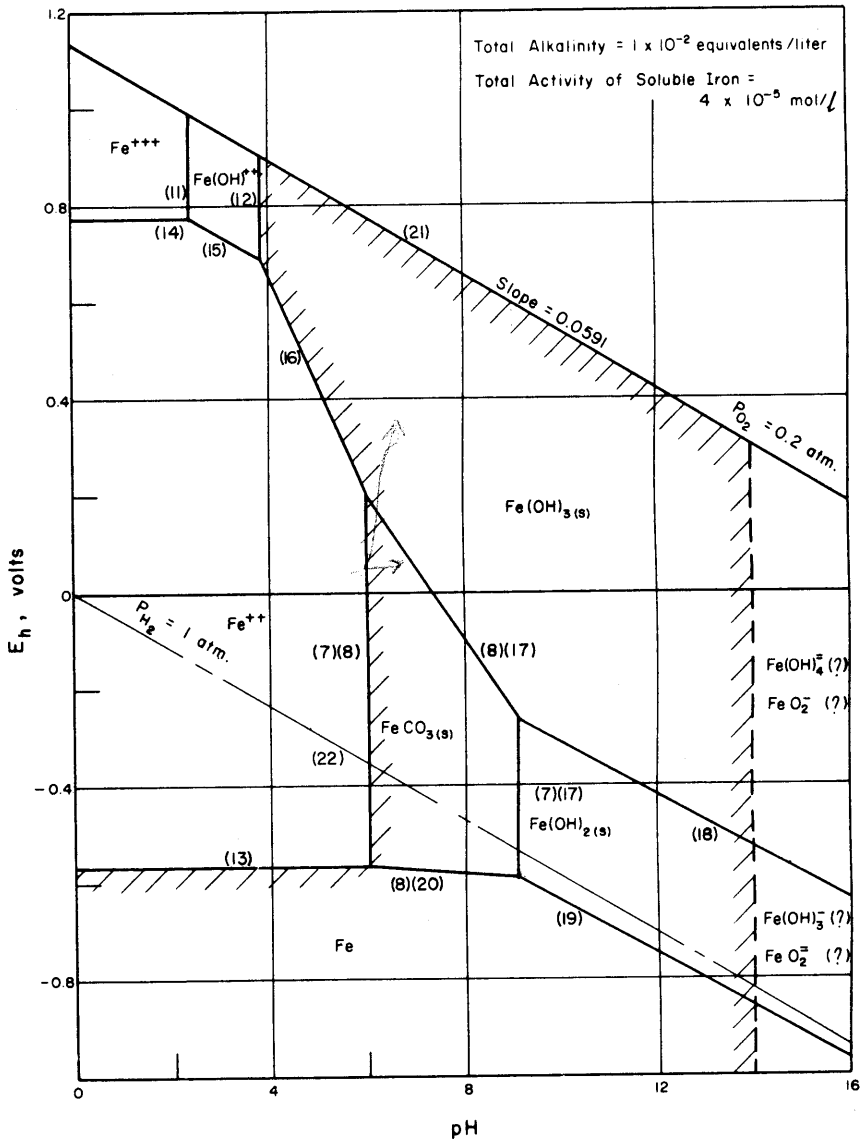
FIG. 3.—SOLUBILITY OF Fe(OH)3(s)

FIG. 4.—E_h-pH DIAGRAM FOR THE NATURAL WATER AT CLINTON, ILLINOIS

hydroxide in the precipitate will be determined by the kinetics of oxidation and precipitation.

The Kinetics of Iron Oxidation.—Various investigators have studied the rate of iron oxidation. All have concluded that the rate of ferrous iron oxidation is of the first order with respect to the ferrous iron concentration and the partial pressure of oxygen as shown in Table 2. In addition, the oxidation rate has been found to be strongly dependent on pH. The kinetics suggested by H. H. Boorsma[13] consider the concentration of carbon dioxide in the case of waters containing bicarbonates.

Studies by W. Stumm and G. F. Lee have shown that oxidation of ferrous iron should be expected to occur rapidly in well-oxygenated waters at pH values exceeding 7.2.[14] The synthetic waters used in obtaining the oxygenation curves shown in Fig. 5 had alkalinities ranging from 450 mg per 1 to 1950 mg per 1 as $CaCO_3$.

TABLE 2.—KINETICS OF FERROUS IRON OXIDATION

Source	Equation
G. Just (1908)[11]	$-\dfrac{d\left[Fe^{+2}\right]}{dt} = k \cdot \dfrac{\left[Fe^{+2}\right]\left[O_2\right]}{\left[H^+\right]^2}$
J. Holluta (1957)[12]	$\dfrac{d\left[Fe^{+3}\right]}{dt} = k \cdot \left[Fe^{+2}\right]\left[O_2\right]$ (k dependent on pH)
H. Boorsma (1954)[13]	$\dfrac{d\left[Fe\left(HCO_3\right)_2\right]}{dt} = \dfrac{\left[Fe\left(HCO_3\right)_2\right]\left[O_2\right]}{\left[CO_2\right]^2}$
W. Stumm and G. Lee (1961)[14]	$-\dfrac{d\left[Fe^{+2}\right]}{dt} = k \cdot \left[Fe^{+2}\right]\left[O_2\right]\left[OH^-\right]^2$

Rate of Iron Precipitation.—As indicated in Table 3, Illinois ground waters are supersaturated with respect to ferrous carbonate. The molar concentration product, $\left[Fe(II)\right]\left[CO_3^=\right]$, indicates that the iron concentration is 20 to 30 times that which would be predicted from the theoretical solubility product for ferrous carbonate, 2.11×10^{-11} moles per 1 at 25° C. When ground waters supersaturated with respect to ferrous carbonate are aerated, the pH in-

[11] Just, G., "Kinetische Untersuchung der Autoxydation des in Wasser gelosten Ferrobicarbonats," Zeitschrift für Physikalische Chemie, Leipzig, Germany, Vol. 63, 1908, pp. 385-420.

[12] Holluta, J., and Eberhardt, M., "Uber geschlossene Enteisenung durch Schnellfiltration," Vom Wasser, Vol. XXIV, Weinzeim, Germany, 1957, pp. 79-98.

[13] Boorsma, H. H., "Les Principes de la Deferrisation, de la Demanganisation, et de la Nitrification dans la Pratique de L'epuration des Eaux Souterraines," XXVIIe Congres de Chimie Industrielle, a Bruxelles, Vol I, 1954, p. 340.

[14] Stumm, W., and Lee, G. F., "Oxygenation of Ferrous Iron," Industrial and Engineering Chemistry, Easton, Pa., Vol. 53, 1961, p. 143.

TABLE 3.—CHARACTERISTICS OF ILLINOIS GROUND WATERS

Plant	Raw Water					Aerated Water			
	pH	Fe(II), mole per 1	$CO_3^=$ mole per 1	Molar conc.[a] product $[Fe(II)][CO_3^=]$	Half-life,[b] $T_{\frac{1}{2}}$, min.	Equil. pH[c]	Alk. mg per 1 as $CaCO_3$	Dissolved Oxygen,mg per 1[d]	Temp.° C
Clinton	7.58	0.33×10^{-4}	15.3×10^{-6}	5.06×10^{-10}	4.3	7.78	610	7.35	13.0
Danvers	7.47	0.36×10^{-4}	16.3×10^{-6}	5.88×10^{-10}	6.5	7.68	512	6.40	13.5
Windsor	7.10	0.90×10^{-4}	6.91×10^{-6}	6.22×10^{-10}	13.2	7.48	520	7.20	14.5
Forrest	7.40	0.46×10^{-4}	11.2×10^{-6}	5.15×10^{-10}	16.0	7.72	475	7.72	10.5
Deland	7.10	0.72×10^{-4}	5.3×10^{-6}	3.82×10^{-10}	22.5	7.67	456	7.67	13.0
Cisco	7.45	0.63×10^{-4}	12.5×10^{-6}	7.90×10^{-10}	25.6	7.71	458	6.70	13.5
Wapella	7.32	0.85×10^{-4}	9.0×10^{-6}	7.65×10^{-10}	36.0	7.67	410	6.40	12.0
Arcola	7.30	0.75×10^{-4}	6.7×10^{-6}	5.01×10^{-10}	54.0	7.49	355	6.90	12.5

a Theoretical K_{sp} for $FeCO_3$ = 2.11×10^{-11} mole per 1 at 25° C.
b The half-life, $T_{\frac{1}{2}}$, is the time required to reduce the Fe(II) to one half its original value.
c Equilibrium pH refers to the pH obtained following aeration of the raw water.
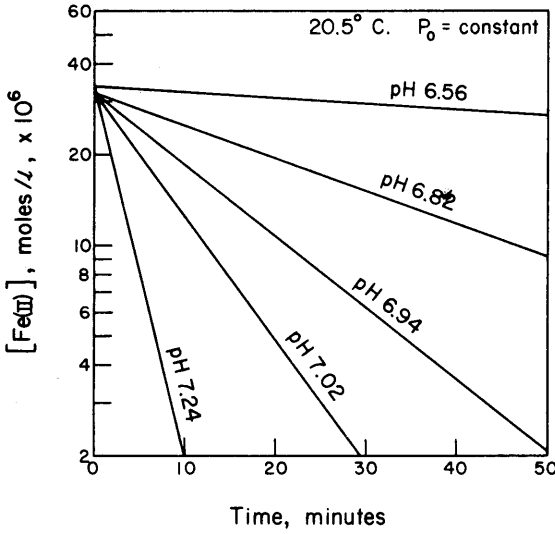d Dissolved oxygen following aeration of the raw water.

FIG. 5.—OXYGENATION RATE OF FERROUS IRON IS
PROPORTIONAL TO Fe(II) AND IS STRONGLY INFLU-
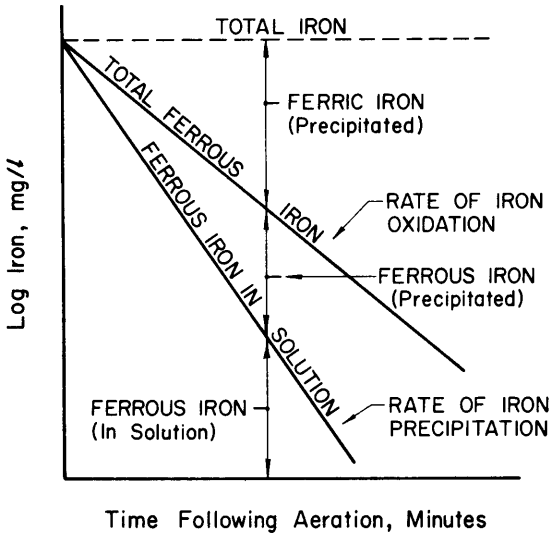ENCED BY pH (After Stumm and Lee, I & E C, 53, 143,
1961)

FIG. 6.—RATE OF IRON OXIDATION AND RATE OF
IRON PRECIPITATION

creases because of the loss of carbon dioxide, thereby further increasing the degree of supersaturation. As a result, the precipitate formed may be expected to contain both ferrous carbonate and ferric hydroxide. The rate of precipitation of iron would therefore be determined by the rate of oxidation of ferrous iron plus the rate of ferrous carbonate precipitation. Fig. 6 illustrates the essential difference between the rate of iron oxidation and the rate of precipitation.

Frequently, when natural waters are analyzed for ferrous iron, samples are acidified to preserve or stabilize them. Because of the decrease in pH, any ferrous precipitate present is returned to the solution and measured along with the ferrous iron in the solution. This may be referred to as the total ferrous iron. In the field studies described herein, the rate of iron precipitation was measured by a method that, it is postulated, determines only the iron remaining in solution. Ferrous iron in solution was determined by buffering samples to near-neutral pH, followed by the addition of the colorimetric reagent, bathophenanthroline, and the extraction of the ferrous-bathophenanthroline complex with iso-amyl alcohol. The intensity of the color complex formed was then determined spectrophotometrically.

FIELD STUDIES

The procedure used to determine the rate at which soluble ferrous iron is converted to an insoluble form was chosen in an effort to simulate the conditions of actual plant operation. Investigations were conducted at eight water treatment plants in central Illinois. At each of these plants, an 8-liter sample of ground water was taken directly from a well used as a raw water supply for the municipality. The ground water sample was aerated for 2 min to raise
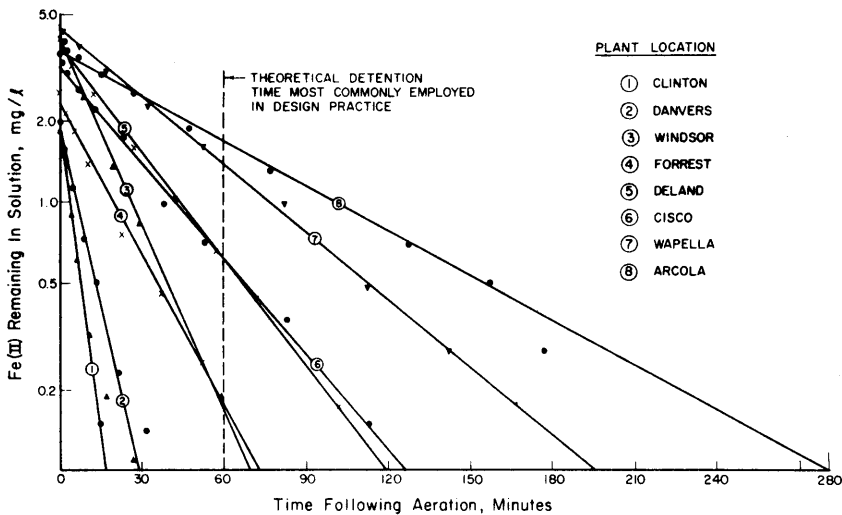

FIG. 7.—PRECIPITATION OF IRON IN ILLINOIS GROUND WATERS

the dissolved oxygen concentration to 6 mg per l or more. Laboratory studies of natural ground waters had indicated that the rate of iron precipitation is unaffected by dissolved oxygen if the concentration exceeds 5 mg per l. The sample was then allowed to stand undisturbed. At various recorded times, aliquots of the aerated ground water sample were taken for analysis of the ferrous iron in solution. In addition, other samples of the ground water were taken for analysis of total dissolved solids, alkalinity, sulfates, chlorides, and chemical oxygen demand.

For each of the waters tested, a plot of the log of the ferrous iron in solution versus reaction time was found to be linear, indicating that the precipitation of ferrous iron from solution was governed by a first order reaction with respect to ferrous iron concentration. Thus, iron precipitation may be expressed in terms of half-life analogous to radioactive decay. The log "ferrous iron remaining in solution" versus "time following aeration" relationships are shown in Fig. 7 for the eight Illinois ground waters. The half-life values derived from these curves range from 4.3 min to 54 min as shown in Table 3. Obviously, because of the initial iron concentration in the raw water, a 1-hr design reaction period was inadequate for complete iron precipitation with four of these waters, and a bare minimum for two others.

Equilibrium pH.—Ground waters, although entirely devoid of dissolved oxygen as pumped from the ground, are supersaturated with CO_2. As a result, aeration increases the pH. In waters having low alkalinities and, hence, low buffer capacities, the pH will decrease gradually as the iron hydrolyzes resulting in an increase in the acidity of the waters. As is seen from Fig. 8, the pH does not decrease after the initial increase in the Illinois ground waters studied. This is true because of the high alkalinities of these waters (355 mg per l to 610 mg per l as $CaCO_3$). The pH achieved after aeration may be taken, therefore, as the "equilibrium pH" and considered to be the pH at which the iron was precipitated.

Effect of pH and Alkalinity.—It has frequently been observed that the hydroxyl ion concentration is the most important factor influencing the rate of iron oxidation. However, a plot of equilibrium pH versus the rate of precipitation, expressed as half-life, $T_{1/2}$, for the Illinois ground waters studied, (Fig. 9), indicates only a remote relationship.

Conversely, a comparison of alkalinity and precipitation rate, (Fig. 9 and Table 2), indicates a more definite relationship. Higher alkalinities are seen to be associated with shorter half-lives, or more rapid precipitation rates.

The dependency of iron precipitation on alkalinity can be seen from the equation derived from a regression analysis of the data. It has the form

$$T_{1/2} \text{ (mins.)} = 522 - .33 \times 10^{14} \text{ (OH)}^{-2} - 183 \log \text{ (Alkalinity)} \quad . . .(1)$$

The correlation coefficient is computed as 0.969 and the standard error as $\pm$ 4.05 min. The 95% confidence limits are $\pm$ 8.10 min, therefore. It should be noted that this empirical expression was derived from data on waters having equilibrium pH values from 7.5 to 7.8 and alkalinities in the range of 355 mg per l to 610 mg per l as $CaCO_3$. No extrapolations beyond these boundaries should be made.

The rate of iron precipitation, as shown in Fig. 6, should equal or exceed the rate of iron oxidation. However, the observed rates of precipitation in aerated Illinois ground waters are far less than might have been expected
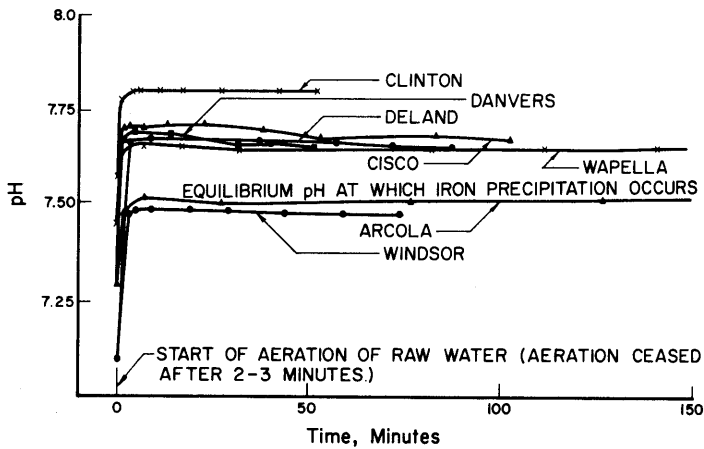
FIG. 8.—EFFECT OF AERATION ON THE pH OF GROUND WATERS
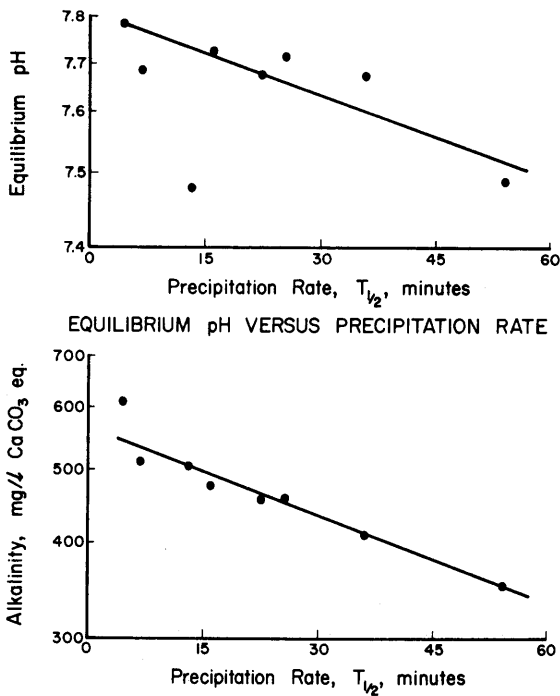

EQUILIBRIUM pH VERSUS PRECIPITATION RATE

FIG. 9.—ALKALINITY VERSUS PRECIPITATION RATE

from a comparison with the rates of oxidation as presented by Stumm and Lee (Fig. 5). A possible explanation for the observed difference may be that some ligand is present in Illinois ground waters that retards the oxidation of iron. Larson has speculated on the formation of $FeHCO_3^+$, a ferrous bicarbonate complex.[15] In addition, the ground waters studied had temperatures lower than 20° C. As Stumm and Lee have shown, the rate of iron oxidation is retarded significantly at low temperatures.[14]

CONCLUSIONS

The conclusion that may be drawn from the large alkalinity dependency of the precipitation rate is that the precipitates formed are primarily carbonates rather than hydroxides. More recent work has also indicated that a large part of the iron precipitated from Illinois ground waters is in the ferrous, rather than the ferric, form.[16]

Finally, from the results obtained, it is clear that the use of a single specified reaction time for iron precipitation is not applicable for all ground waters. A more suitable approach to the selection of a reaction time would be the direct measurement of the rate of iron precipitation.

ACKNOWLEDGMENTS

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[16] Goswami, S. R., "The Relation of the Oxidation-Reduction Potential to the Ferrous-Ferric Equilibrium in Ground Waters," Special Problem, Univ. of Illinois, Urbana, Ill., January, 1965.