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Oxygenation of Ferrous Iron

This study of the reaction between ferrous iron and oxygen emphasizes the role oxygenation catalysts play in the deferrization process. Application of these catalysts may markedly increase the rate of over-all iron removal from natural waters

IRON BEARING WATERS are often deferrized by oxidizing the ferrous iron with dissolved oxygen and then removing the resulting ferric oxide floc by sedimentation or filtration. Ferrous iron in river water—e.g., pollution by mine drainage or iron pickling wastes—not only disturbs the oxygen balance but reduces the pH and forms suspended matter as ferric oxide—$Fe_2O_3 \cdot XH_2O$, where X may vary. The capability of iron to undergo reversible oxidation or reduction reactions is related to the metabolic cycles of nearly all other elements of importance and especially to the distribution of oxygen in impounded surface waters. The corrosion of, and the subsequent occurrence of "red water" in a water distribution system with iron piping is influenced by the oxygenation rate of ferrous iron (22). A quantitative investigation of the reaction between ferrous iron and oxygen is needed in order to understand the many roles iron may play in natural waters. Special attention should be given to the kinetics of this reaction; the rate at which it proceeds depends on several parameters including pH, temperature, concentration of dissolved oxygen, and catalysts.

The investigations reported here have shown that the rate of oxygenation of ferrous iron in bicarbonate solutions follows the law:

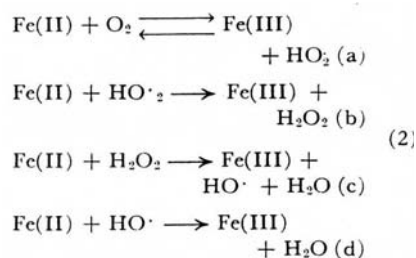$$\frac{-d[Fe(II)]}{dt} = k[Fe(II)]P_{O_2}(HO^-)^2 \quad (1)$$

Catalysts (especially Cu^{+2}) in trace quantities, as well as anions which form complexes with ferric iron ($H_2PO_4^-$), increase the reaction rate significantly, while small amounts of Fe(III), Cl^-, SO_4^{-2} have no effect on the reaction rate.

Previous Studies

Many reliable and extensive studies have been made in homogenous acid solutions (6, 12, 14, 20). The conclusions

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reached in these investigations have yielded valuable clues on the mechanism of the reaction between ferrous iron and oxygen, but they do not necessarily apply to bicarbonate-containing waters.

Weiss (25) suggested that the oxygenation of ferrous iron proceeds in the following sequence:

$$Fe(II) + O_2 \rightleftharpoons Fe(III) + HO_2^{\cdot} \quad (a)$$
$$Fe(II) + HO^{\cdot}_2 \longrightarrow Fe(III) + H_2O_2 \quad (b)$$
$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + HO^{\cdot} + H_2O \quad (c) \qquad (2)$$
$$Fe(II) + HO^{\cdot} \longrightarrow Fe(III) + H_2O \quad (d)$$

These reactions as written are not balanced with respect to hydrogen ions and are not intended to specify the dependence of the reaction rate on this variable. The rate determining step is believed to be Reaction 2,a thus indicating that the oxygenation rate is of the first order with respect to both the concentration of Fe(II) and dissolved oxygen.

$$\frac{-dFe(II)}{dt} = k[Fe(II)] (O_2) \quad (3)$$

The rate of oxidation is dependent upon the nature of the anion present, and increases as the complexing affinity of the anion to ferric iron increases (12). Thus under acid conditions, the rate is found to decrease in the following series: hydroxide, pyrophosphate (12), phosphate (16), chloride (20), sulfate (12, 14), and perchlorate (10). The rate law is in accordance with Equation 3 for the first four media in this list, but a second order dependence of the rate on the ferrous iron concentration has been found in sufficiently acid solutions of H_2SO_4 and $HClO_4$. In addition to complexing agents, many substances, especially those which hasten the decomposition of peroxides in the presence of ferrous iron— platinum, charcoal, and cupric salts— accelerate the oxidation of ferrous salt by oxygen (13).

While in acid media only a small dependence of the oxygenation rate upon the hydrogen ion concentration is observed (10, 12), a very pronounced pH dependence is observed in less acidic solutions (1, 11, 13, 24). However, except for the very early study of Just (13), no quantitative investigations have been undertaken on the rate of ferrous iron oxygenation in the buffer system of natural waters.

Solubility of Iron. Studies on iron oxidation in bicarbonate solutions are complicated by the slight solubility of ferrous and ferric iron in such solutions. Ferrous constituents generally are more soluble than ferric constituents. Table I gives a survey of the equilibria that must be considered for the evaluation of their respective solubilities. In bicarbonate waters, the solubility of ferrous iron is controlled by the solubility of $FeCO_3$, and can be estimated by

$$[Fe^{+2} + Fe(OH)^+] = \frac{(H^+) + 2K_5}{(alk) K_6} \left[K_3 + \frac{K_4 K_w}{(H^+)} \right] \quad (4)$$

where K_w, is the ion product of water and alk is the alkalinity $[(HCO_3^-) + 2(CO_3^{-2}) + (OH^-)]$ in equivalents per liter and the numbered K values refers to the respective equation in Table I. Equation 4 is valid up to a pH of about 9 (23).

In order to estimate the solubility of ferric iron, equilibria 6 to 9 in Table I must be considered. Experimental investigations (7, 9) in basic and neutral solutions (pH values 6 to 11) have shown that solubility of ferric hydroxide is markedly independent of the hydroxyl ion concentration. This observation has led to the proposal that $Fe(OH)_3$ (s) is in equilibrium with undissociated molecular $Fe(OH)_3$ (equilibrium 9, Table I).

Experimental Method

It is not feasible to study, within the pH range of natural waters, the kinetics of oxygenation of ferrous iron in homogenous solutions (Table I). Kinetic investigations in heterogenous solution are less amenable to rigid interpretation owing to the super-imposition of interfacial factors which operate at the phase boundaries on to the homogenous reac-

Table I. Solubility Equilibria

No.	Reaction	Equilibrium Constant at 25° C.	Reference
	Fe(II) Solubility		
1	$Fe(OH)_2(s) = Fe^{+2} + 2OH^-$	8×10^{-16}	(17)
2	$Fe(OH)_2(s) = Fe(OH)^+ + OH^-$	4×10^{-10}	(17)
3	$FeCO_3(s) = Fe^{+2} + CO_3^{-2}$	2.1×10^{-11}	(15)
4	$FeCO_3(s) + OH^- = Fe(OH)^+ + CO_3^{-2}$	1×10^{-5}	(15)
5	$HCO_3^- = H^+ + CO_3^{-2}$	4.8×10^{-11}	(15)
	Fe(III) Solubility		
6	$Fe(OH)_3(s) = Fe^{+3} + 3OH^-$	$\sim 10^{-36}$	(7)
7	$Fe(OH)_3(s) = Fe(OH)_2^+ + OH^-$	1.7×10^{-15}	(18)
8	$Fe(OH)_3(s) = Fe(OH)^{+2} + 2OH^-$	6.8×10^{-25}	(18)
9	$Fe(OH)_3(s) = Fe(OH)_3{}^a$	2.9×10^{-7}	(7, 9)
10	$2Fe(OH)^{+2} = Fe_2(OH)_2^{+4}$	30	(18)

^{a} Undissociated molecular ferric hydroxide.

tion. As the initial purpose of this investigation is to study the chemical reaction between dissolved ferrous iron and oxygen, the concentrations of reactants must be chosen in such a way as to minimize specific surface effects on this reaction. All experiments were conducted with *dissolved* ferrous iron concentrations of less than $5 \times 10^{-5}M$, such that no precipitation of ferrous carbonate was encountered even though the conditions of the experimental runs that were made above pH 7 were such that the solubility product for $FeCO_3$ was occasionally exceeded. The existence of these supersaturated solutions of ferrous carbonate can be explained by the tendency of carbonate to remain in solution in the absence of crystallization nuclei. During the course of reaction, no precipitation or floc was observed; colloidal ferric hydroxide was formed, but this appeared to have no effect on the kinetics, since incipient addition of ferric iron up to $10^{-4}M$ did not alter the reaction rate.

The partial pressure of oxygen and the pH was maintained constant during each run by bubbling a mixture of CO_2 and air from a compressed gas cylinder through the test solution. The amount of ferrous iron remaining at a given time was determined photometrically in aliquots of the test solution, in which the reaction was quenched by the immediate addition of H_2SO_4, reducing the pH to about 1.

Because of the low concentrations of ferrous iron used, a very sensitive analytical method was needed. Since the recommended methods (2, 3) lacked both sensitivity in the concentration range used and specificity for ferrous iron in the presence of ferric iron, a modified technique using 4,7-dipheny1-1,10-phenanthroline (bathophenanthroline) was developed (16). With this reagent the colored Fe(II)-bathophenanthroline complex can be extracted into *n*-hexyl alcohol, thereby enhancing sensitivity as well as specificity.

Preparation of Reagents and Experimental Conditions. The water used for all the results reported here was purified by redistilling glass distilled water in an all borosilicate glass still. Reagent grade chemicals were used in all test solutions.

The ferrous iron solutions were freshly prepared by dissolving $Fe(ClO_4)_2$ (G. F. Smith Chemical Co.) in $0.1M$ $HClO_4$. Bicarbonate-CO_2 buffers were prepared from Na_2CO_3 solution by bubbling an air-CO_2 mixture through the solution. Various pH values were obtained by using different air-CO_2 mixtures. These air-CO_2 compressed gas mixtures were prepared and analyzed by General Dynamics Corp., Boston, Mass. The test solutions were well thermostated ($\pm 0.2°$ C.) and were vigorously stirred during the run. All pH measurements were made with a Beckman Model G pH meter. During any one run the pH was kept constant within 0.04 pH units.

To a 1.5-liter borosilicate glass beaker was added a Na_2CO_3 solution. After temperature equilibrium was attained, an air-CO_2 mixture was bubbled through this stirred solution. When the pH of the solution had reached the equilibrium value for the particular partial pressure of CO_2 in the gas mixture being used, the ferrous iron solution was added and a stopwatch was started. The volume of test solution at this point was 1.0 liter. At appropriate time intervals, aliquots of the test solution were withdrawn and placed in sulfuric acid solution to quench the reaction. Colloidal ferric hydroxide was dissolved by boiling this acid solution.

The ferrous iron content of each aliquot was determined colorimetrically after neutralization with sodium acetate, using a Beckmann DU spectrophotometer.

Results

Stoichiometry. The reaction of Fe(II) with oxygen generally leads directly to ferric oxides or hydroxides. The stoichiometric relationship being

$$Fe(II) + 1/4O_2 + 2OH^- + 1/2H_2O \rightarrow Fe(OH)_3\ (s) \quad (5)$$
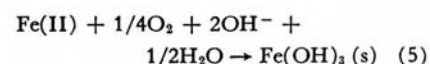
The oxidation may occur under certain conditions—especially in buffer solutions with pH values greater than 6—in a stepwise fashion over the mixed iron(II)-(III) hydroxides and magnetite (7, 8). The ferrous iron in these intermediates is only very slowly oxidized, if at all (8). It was experimentally ascertained that under the condition of the kinetic investigation reported here, the oxygenation of ferrous iron was in agreement with Equation 5. These measurements were made by quantitatively determining the oxygen uptake with a Warburg manometer apparatus.

Oxygenation Rates. Several representative reaction runs at a constant partial pressure of oxygen and at various pH values are plotted in Figure 1. The rate of oxidation was first order with respect to Fe(II) and independent of the Fe(III) concentration. This is evident from the time dependence of any one reaction (linear relationship in semilogarith-

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Effect of Oxygenation of Ferrous Iron on Surface Waters

Prime examples are the rivers draining the coal mining areas of Pennsylvania, Ohio, and West Virginia. As a result of acid mine drainage, these waters contain large quantities of iron and have low pH values. Fifty per cent of the acidity in acid mine drainage arises from the oxygenation of ferrous iron; the remainder arises from the oxygenation of sulfide or polysulfide. In many cases, the drainage from these mines contains appreciable quantities of ferrous iron which, upon entering a stream, reacts with the dissolved oxygen present to form unsightly ferric oxide deposits. The accompanying reduction in pH may inhibit the self-purification of the river by providing an unfavorable environment for microorganisms.

Water treatment operators who derive their raw water from reservoirs are also well aware of the common occurrence of high iron concentration in the hypolimnetic zones during periods of stagnation and stratification of the reservoir. Water supplies derived from ground waters that have passed through iron bearing strata frequently contain appreciable quantities of ferrous iron which, upon exposure to the atmosphere, are oxidized to insoluble ferric oxide.

mic plot of Figure 1). This first order dependence with respect to Fe(II) of the reaction rate was also confirmed by experimental runs in which the initial Fe(II) concentration was widely varied. Incipient addition of ferric iron up to concentrations of $10^{-4}M$ did not alter the reaction rate.

The oxygen concentration in the reaction solution was kept in excess and constant during each run. Since different investigators agree with respect to the dependence of the rate of reaction on the oxygen concentration, this dependence was not investigated in a rigorous manner. The partial pressure of oxygen was varied only between 76 and 155 mm. However, the results support the finding of others, that the rate of oxygenation of ferrous iron is dependent on the partial pressure of oxygen to the first power. Thus the rate law accounts for the

Table II. Dependence of Rate on Partial Pressure of Oxygen and (OH⁻)

Alkalinity 2.9 to 3.9×10^{-2} equiv. per liter. Temp. 20.5° C.

P_{O_2} Atm.	$(OH^-)^a$ $\times 10^8$	$k_o{}^b$ Min.$^{-1}$ $\times 10^2$	k'^c $\times 10^2$	k^d Min.$^{-1}$ Atm.$^{-1}$ Liter^2 Mole^{-2} $\times 10^{-13}$
0.107	1.86	0.063	0.589	1.70
0.107	2.51	0.090	0.841	1.33
0.153	3.16	0.233	1.53	1.53
0.153	4.56	0.478	3.13	1.50
0.153	5.02	0.492	3.21	1.28
0.174	7.25	1.71	9.82	1.87
0.184	9.12	2.44	13.2	1.59
0.184	12.0	4.65	25.3	1.76
0.195	18.2	9.13	46.8	1.41
0.195	22.4	17.8	91.4	1.83

^{a} Computed from measured pH ($K_w = 0.7 \times 10^{-14}$). ^{b} $2.3\, k_o =$ slope of first order plots (Figure 1); $k_o = \dfrac{-d \ln [\text{Fe(II)}]}{dt}$. ^{c} $k' = k_o/P_{O_2}$. ^{d} $k = k'/(OH^-)^2$.

change in Fe(II) concentration during the course of the reaction at a constant pH value as a function of Fe(II) concentration and partial pressure of oxygen, P_{O_2}.

The change in the rate of reaction with pH as shown in Figure 1 can be explained by the influence of hydroxyl ions on the reaction rate. The logarithm of the rate constants $k_o, (k_o = -d \ln [\text{Fe(II)}]/dt$ divided by the partial pressure of oxygen, is plotted as a function of pH of the test solution in Figure 2. The line through the points as plotted has a slope of 2, thus indicating a 100-fold increase in the rate of reaction for an increase of one pH unit; there is a second order relationship between the rate of reaction and the hydroxyl ion concentration:

$$\frac{-d\,[\text{Fe(II)}]}{dt} = k[\text{Fe(II)}]P_{O_2}(OH^-)^2 \quad (7)$$

Table II lists k_o and the over-all rate constant k for a typical set of experimental runs. The value for k at 20.5° C. has been found to be 1.5 (± 0.5) X 10^{13} liter^2 mole^{-2} atm.$^{-1}$ min.$^{-1}$ (or $k_m = 1.1\pm0.5$ X 10^{10} liter^3 mole^{-3} if oxygen is expressed in mole per liter rather than in atm.) The data presented in Figure 2 were obtained with solutions with an alkalinity [$(HCO_3) + 2(CO_3{}^{-2})$ + (OH^-)] between 9 X 10^{-3} and 3.9 X 10^{-2} equivalent per liter.

Figure 2 shows that the temperature dependence of this reaction is large. For a given pH, the rate increases about 10-fold for a 15° C. temperature increase. Since the pH has been measured at solution temperature, this apparent temperature dependence can, however, be accounted for by the variation in OH-ion activity with temperature for a given pH, owing to temperature variation in k_m. Essentially the same rate constants k_m have been obtained for the three temperatures investigated, thus indicating an

activation energy of approximately zero. [For constant (H^+) rather than (OH^-) an activation energy of 23 kcal. can be calculated.]

The Weiss radical mechanism *(25)* can be invoked to describe the oxidation kinetics with respect to the rate dependence on (Fe^{+2}) and N. As Abel *(1)* has shown, the Weiss mechanism cannot be enlarged, to account for the second order dependence on (OH^-). The second order dependence on (OH^-) is in accord with the earlier publication of Just *(13)* and the theoretical discussion of Abel *(1)*. In systems of phosphoric acid, Cher and Davidson *(6)* obtained a second order dependence on ($H_2PO_4^-$). Hydroxyl ions can be considered as complex formers having a stronger affinity for Fe(III) than ($H_2PO_4^-$).

Close examination of the data presented in Figure 2 shows that reaction rates obtained in solution of lower alkalinity tend to be of smaller magnitude and more scattered than those obtained in solutions of higher alkalinity. This effect is especially pronounced at the higher pH values where the reactions are rapid. This discrepancy could be caused by the slow response of the HCO_3^--CO_2 buffer system to localized acidity changes induced by the oxygenation reaction. However, the possibility of a slight base catalysis by CO_3^{-2} cannot be excluded.

Catalytic Effects. Cupric ion is an efficient catalyst in many oxidation reactions and its catalytic effect has been studied in the oxygenation of ferrous iron in acid solutions *(6, 12, 14)*. Figure 3 shows that even trace quantities of Cu^{+2} have a pronounced effect on the reaction rate.

The catalytic effect is considerable for $Cu^{+2} = 3$ X $10^{-7}M$, but increases only slowly with increasing Cu^{+2}. These results are qualitatively in agreement with
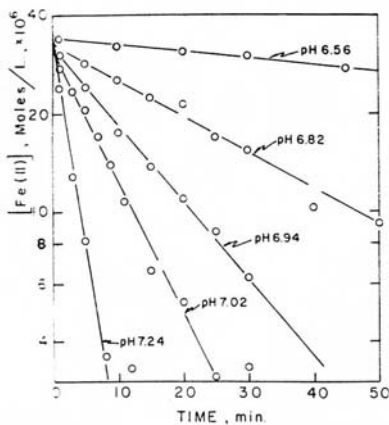

Figure 1. Oxygenation rate of ferrous iron is proportional to Fe(II) and is strongly influenced by pH

20.5° C. P_O = const.

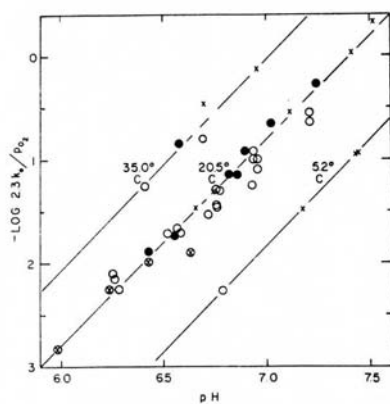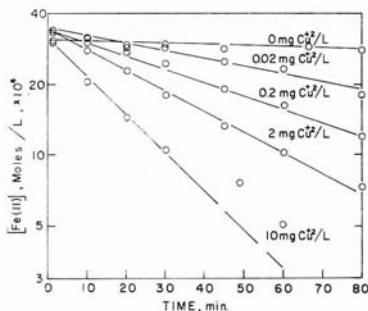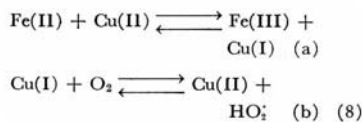**Figure 2. An increase by one pH must increase oxygenation rate 100-fold**

Figure 3. Cu^{+2} catalyzes the oxygenation reaction

$20.5°$ C. P_{O_2} = const. pH = 6.0

results obtained in acid systems by Cher and Davidson *(6)*. The results of these authors have been accounted for by the following mechanism:

$$Fe(II) + Cu(II) \rightleftharpoons Fe(III) + Cu(I) \quad (a)$$

$$Cu(I) + O_2 \rightleftharpoons Cu(II) + HO_2^{\cdot} \quad (b) \quad (8)$$

The $HO_{\cdot 2}$ is assumed to react further with Fe(II) as in the Weiss mechanism (Equation 2).

The data obtained do not permit the formulation of a meaningful rate expression which would account satisfactorily for the catalytic effect of copper. However, several qualitative statements can be made. The same proportionate acceleration of the oxygenation rate was observed at any pH value within the pH range investigated. The runs made in the presence of Cu^{+2} show the same temperature dependence as those made in the absence of Cu^{+2}. The catalytic effect of Cu^{+2} is dependent upon both the initial ferrous and ferric iron concentrations. Higher initial ferrous iron concentrations and/or an incipient addition of ferric iron causes an increased rate of reaction. There is a saturation concentration of Cu^{+2} for any given initial ferrous iron above which further addition of Cu^{+2} has little or no effect on the reaction rate. The addition of various amounts of complex formers such as glycine, tetramine, and ethylene diamine tetraacetate did not affect the reaction rates. The latter two complexing agents markedly retard the oxygenation reaction in the absence of Cu^{+2}. Copper complexes appear to be as effective catalysts as the aqueous copper ions.

Some results of a preliminary survey on the effects of other catalysts are represented in Figure 4 illustrating that other metal ions (Mn^{+2}, Co^{+2}) as well as anions (besides OH^-) which form complexes with Fe(III) ($H_2PO_4^-$, metaphosphate) are capable of hastening the oxygenation reaction. This figure shows that the reaction in Cambridge tap water which contains no analytically detectable Cu^{+2} is considerably faster than the reaction in synthetic water of similar mineral composition. Addition of chloride and sulfate (10 mg. per liter) had no effect on the oxidation rate.

Practical Aspects

Oxidation of ferrous iron is only one step in the deferrization process. Flocculation and sedimentation (or filtration) certainly may codetermine the over-all iron removal rate in surface waters and in iron removal plants. Many constituents present in natural waters may accelerate or decelerate the oxidation as well as the flocculation reaction. It can be inferred from our experiments, however, that the oxidation reaction may be the controlling factor up to pH values around 7. In the more alkaline pH range, flocculation may be the slowest step. At pH values above 8, diffusion or the oxygen rather than the chemical reaction determines the oxidation rate.

In many natural waters organic matter may stabilize ferric oxide colloids or may increase the Fe(III) solubility by complex formation. Generally, iron removal is very slow under such conditions *(5, 19)*. Most organic impurities are known to hasten oxygenation reactions; under these conditions, difficulties in iron removal are apparently due to slow flocculation and cannot necessarily be overcome by an increase in pH. Coagulation of iron(III) is fast in many natural waters within the pH range 5 to 7 *(4, 5, 21)* and ferric oxide removal by sand filtration is best within the same pH range *(21)*. Under such conditions, however, oxidation rates are slow. Here the application of oxidation catalysts—e.g. Cu^{+2} may prove very efficient. For a given pH and oxygen concentration, the addition of as little as 0.02 mg. per liter reduces the oxygenation time by a factor of 5.

Acknowledgment

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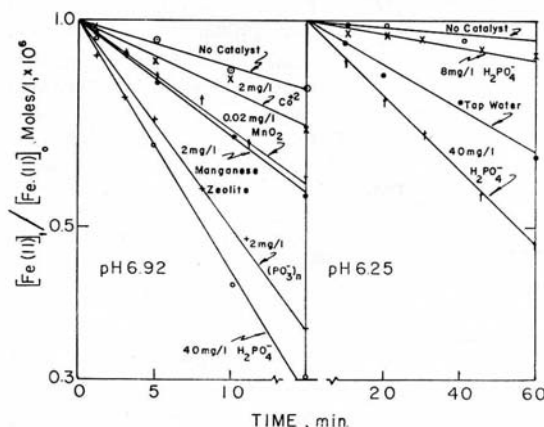(25) Weiss, J., *Naturwissenschaften* **23**, 64 (1935).

Figure 4. Insidious trace quantities of impurities may strongly accelerate the oxidation reaction