

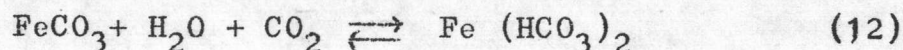
### III THEORETICAL CONSIDERATIONS

#### Mechanism of Solution of Iron

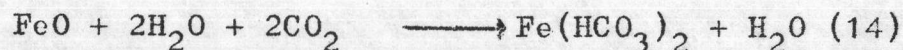
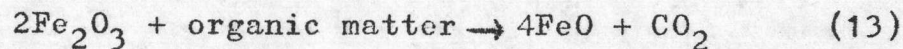
Iron occurs in almost all soils and rocks in the forms of oxides, sulfides and carbonates. As an oxide it may appear as ferrous oxide or red hematite ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), or brown hematite or limonite ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). As carbonate it occurs as siderite ( $\text{FeCO}_3$ ), and iron in the sulfide form is known as iron pyrites ( $\text{FeS}$ ).

In ground water, iron commonly exists in the soluble ferrous state. The mechanisms by which iron may enter ground water, according to GHOSH (1965) are as follows:

a) solution due to the presence of excess  $\text{CO}_2$ , which possibly results from bacterial reactions converting insoluble ferrous carbonate, ( $\text{FeCO}_3$ ), into highly soluble ferrous bicarbonate,  $\text{Fe}(\text{HCO}_3)_2$ , as typified by Eq. 12:



b) solution under anaerobic conditions, possibly due to the presence of soil bacteria, which reduce ferric iron to the ferrous form in the first step, often when it is dissolved by  $\text{CO}_2$  as shown in Eq. 13 and 14:



c) solution of organic color bodies from vegetative growths in which iron, both ferrous and ferric, is complexed with stable organic compounds. This type of water is commonly found when the source is a swampy area.

#### Factors Influencing Iron Removal

Important factors to be taken into account in iron removal processes have been discussed extensively by many investigators. GHOSH and others (1966) have concluded from

their studies that the factors are primarily as follows:

Solubility of iron Table 2 shows solubility equilibria of iron after GHOSH (1965). Graphs developed from these equilibrium values showing solubility of ferrous hydroxide in solid phase ( $\text{Fe(OH)}_2(\text{s})$ ) in non-carbonate and non-sulfide solution are shown in Fig.II . The solubility of ferrous iron in carbonate bearing waters and the solubility of ferric hydroxide in solid phase ( $\text{Fe(OH)}_3(\text{s})$ ) are shown in Fig.III and Fig.IV respectively.

A comparison of Fig.II with Fig.III indicates that any form of alkalinity reduces the solubility of the bivalent iron considerably. For example, at pH 9.0 , the total soluble ferrous iron in a non-carbonate water as seen from Fig.II , is  $5 \times 10^{-5}$  mol./1 (2.8 mg/l) whereas in a carbonate bearing water (total alkalinity  $10^{-2}$  eq./1 or 500 mg/l as  $\text{CaCO}_3$ ), it is seen in Fig.III that the solubility is  $3.16 \times 10^{-7}$  mol./1 . This shows that ferrous iron existing in a carbonate-bearing water will have more tendency to form crystal nuclei and precipitate than if the iron is in a non-carbonate water at the same pH of 9 .

Fig.IV , shows the solubility characteristics of trivalent iron. This solubility is limited by the equilibria of ferric hydroxide,  $\text{Fe(OH)}_3(\text{s})$ . At pH 9.0 the concentration of total trivalent iron that can exist in saturation equilibrium with  $\text{Fe(OH)}_3(\text{s})$  is  $10^{-10}$  mol./1 ( $5.6 \times 10^{-6}$  mg/l). This also indicates that at pH 9.0 , ferric hydroxide has more tendency to precipitate than the ferrous form in carbonate-bearing water. The solubility of ferric iron may be much higher if it is complexed with organic or inorganic ligands other than the hydroxyl group ( $\text{OH}^-$ ) .

Oxidation kinetics of ferrous iron The basic equation describing the oxidation of ferrous iron by oxygen is given as:





Various investigators have studied the rate of iron oxidation and have generally concluded that the rate of ferrous iron oxidation and the rate of ferrous iron oxidation is of the first order with respect to the ferrous iron concentration and the partial pressure of oxygen. JUST (1908) postulated that the rate was first order with respect to ferrous iron and oxygen and second order with respect to  $\text{CO}_2$  as shown in the following relationship:

$$-\frac{d \left[ \text{Fe}(\text{HCO}_3)_2 \right]}{dt} = K \cdot \frac{\left[ \text{Fe}(\text{HCO}_3)_2 \right] \left[ \text{O}_2 \right]}{\left[ \text{CO}_2 \right]^2}$$

He further stated the relationship between the rate and pH as shown below:

$$-\frac{d \left[ \text{Fe}^{++} \right]}{dt} = K \cdot \frac{\left[ \text{Fe}^{++} \right] \left[ \text{O}_2 \right]}{\left[ \text{H}^+ \right]^2}$$

Where K is the overall rate constant for a typical set of experimental runs. He concluded that the rate of oxidation of ferrous iron increased with  $\text{HCO}_3^-$  ion concentration, but decreased with concentration of free  $\text{CO}_2$ .

STUMM and LEE (1961) established an equation for the kinetics of oxidation of ferrous iron in their work with highly alkaline solutions:

$$-\frac{d \left[ \text{Fe}^{++} \right]}{dt} = K \left[ \text{Fe}^{++} \right] \left[ \text{O}_2 \right] \left[ \text{OH}^- \right]^2$$

They have shown that oxidation of ferrous iron should be

expected to occur rapidly in well-oxygenated water at pH values exceeding 7.2. Another study of catalytic effects on the rate of oxidation by certain anions and cations indicated that addition of trace amounts of  $\text{Cu}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Co}^{++}$  and  $\text{H}_2\text{PO}_4^-$  would hasten the rate of oxidation of ferrous iron.





Table II Equilibria for Iron, after GHOSH (1965)

No.	Equation	Equilibrium constant at 25°C
1	$\text{Fe}(\text{OH})_2(\text{s})^* = \text{Fe}^{+2} + 2\text{OH}^-$	$8 \times 10^{-16}$
2	$\text{Fe}(\text{OH})_2(\text{s}) = \text{FeOH}^+ + \text{OH}^-$	$4 \times 10^{-10}$
3	$\text{FeCO}_3(\text{s}) = \text{Fe}^{+2} + \text{CO}_3^{=}$	$2.11 \times 10^{-11}$
4	$\text{FeCO}_3(\text{s}) + \text{OH}^- = \text{FeOH}^+ + \text{CO}_3^{=}$	$5.05 \times 10^{-16}$
5	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{=}$	$4.7 \times 10^{-11}$
6	$\text{Fe}(\text{OH})_2(\text{s}) + \text{OH}^- = \text{Fe}(\text{OH})_3^-$	$8.3 \times 10^{-6}$
7	$\text{Fe}(\text{OH})_3(\text{s}) = \text{Fe}^{+3} + 3\text{OH}^-$	$6.6 \times 10^{-38}$
8	$\text{Fe}(\text{OH})_3(\text{s}) = \text{Fe}(\text{OH})_2^+ + (\text{OH})^-$	$5.13 \times 10^{-17}$
9	$\text{Fe}(\text{OH})_3(\text{s}) = \text{FeOH}^{++} + 2\text{OH}^-$	$2.57 \times 10^{-26}$
10	$\text{Fe}(\text{OH})_3(\text{s}) + \text{OH}^- = \text{Fe}(\text{OH})_4^-$	$10^{-5}$
11	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	$10^{-14}$
12	$\text{Fe}(\text{OH})_3(\text{s}) = \text{Fe}(\text{OH})_3(\text{d})^{**}$	$2.9 \times 10^{-7}$

\* $\text{Fe}(\text{OH})_2(\text{s})$  means ferrous hydroxide in solid phase.

\*\* $\text{Fe}(\text{OH})_3(\text{d})$  means undissociate  $\text{Fe}(\text{OH})_3$  in solution.



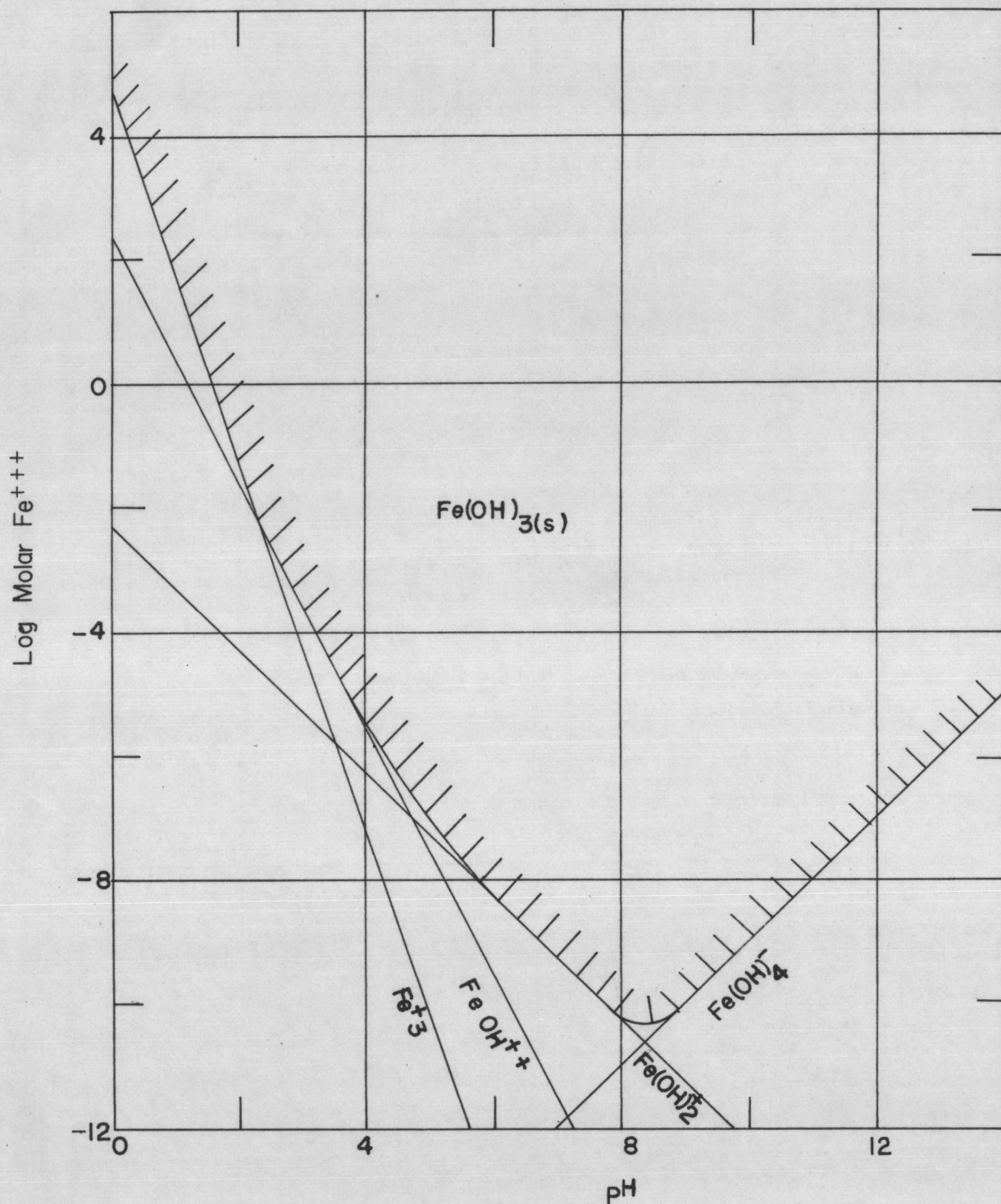


Fig. II Solubility of  $\text{Fe(OH)}_3(\text{s})$

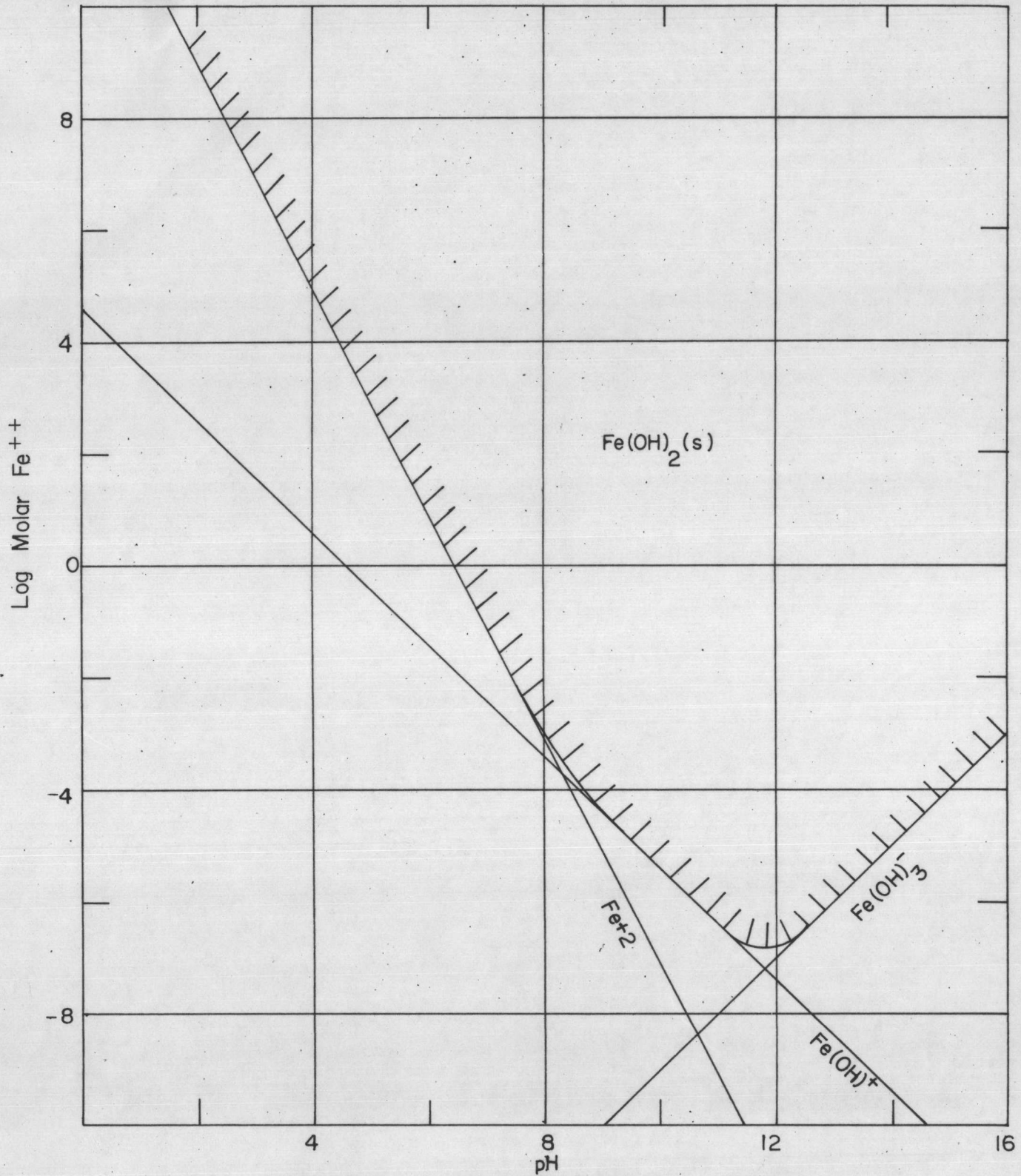


Fig. III Solubility of  $\text{Fe(OH)}_2(\text{s})$  in a Non-Carbonate  
Non-Sulfide Solution



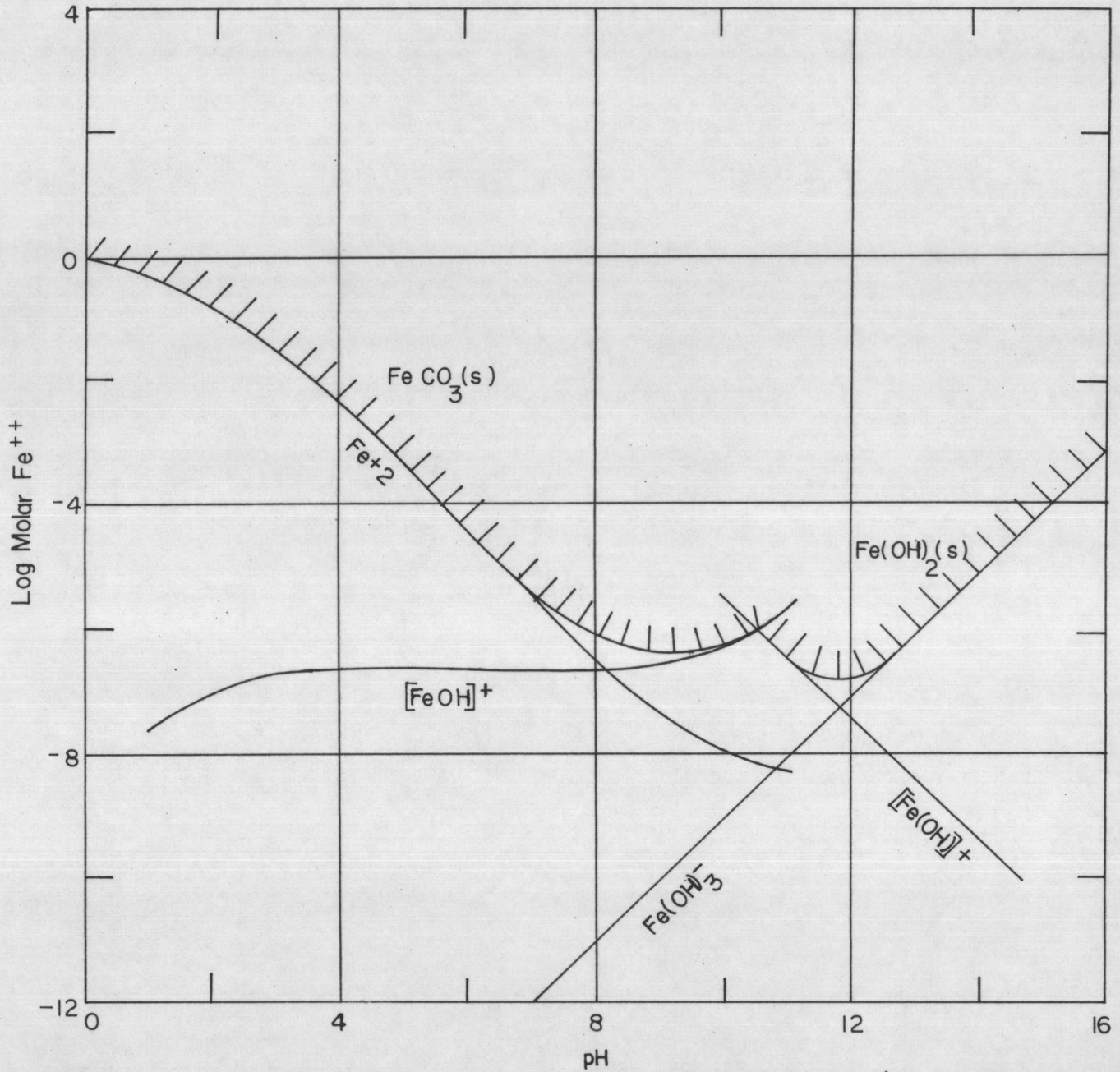


Fig. IV Solubility of Ferrous Iron in a Carbonate Bearing Water ( $\text{Alk} = 10^{-2} \text{ eq/l}$ )



Redox potential ( $E_h$ ) measurements of a water express the net of all oxidizing and reducing constituents. The presence or absence of substances affecting  $E_h$  in ground water might also influence ferrous equilibria conditions and the kinetics of iron oxidation.

Table III Physical and Chemical Characteristics of Raw, Aerated, Finished Waters after Treatment with 128 mg/l of alum and 128 mg/l of lime with no Sludge Blanket

Characteristics	Water	Sample No.	
		3	12
Temperature °C	R	29.0	28.5
	A	28.5	28.0
	W	27.0	26.5
pH	R	6.00	6.00
	A	6.90	6.95
	W	8.30	8.40
Alkalinity ( $HCO_3$ ), mg/l as $CaCO_3$	R	160	160
	A	158	154
	W	196	210
Total Hardness mg/l as $CaCO_3$	R	144	144
	A	142	138
	W	220	218
$CO_2$ mg/l	R	230	225
	A	21	20
	W	8	8
Total Fe <sup>++</sup> mg/l	R	6.90	6.70
	A	6.15	6.00
% oxidizing		10.90	10.50
Total Fe, mg/l	R	8.20	8.00
	A	6.85	6.80
	W	2.10	0.92
% Rem. by Aerater		16.50	15.00
Total % Removal		74.40	88.50

Note: R = Raw water  
A = Aerated water  
W = Finished water