CIVIL ENGINEERING STUDIES

SANITARY ENGINEERING SERIES NO. 12

A STUDY OF THE RATE OF OXIDATION OF IRON IN AERATED GROUND WATERS

By
M. M. GHOSH

Supported By
NATIONAL INSTITUTES OF HEALTH
U. S. PUBLIC HEALTH SERVICE
RESEARCH PROJECT WP-17

DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
AUGUST, 1962

A STUDY OF THE RATE OF OXIDATION OF IRON IN AERATED GROUND WATERS

by

MRIGANKA M. GHOSH

Supported by
National Institutes of Health
U. S. Public Health Service
Research Project WP-17

Department of Civil Engineering
The University of Illinois
Urbana, Illinois

August, 1962

ABSTRACT

Studies were made of a variety of Illinois ground waters to determine the factors affecting the oxidation rate of ferrous iron. The raw waters were drawn from wells at different water treatment plants throughout central Illinois.

In the first phase of this investigation a set of bench scale experiments were performed to determine if dissolved oxygen concentration of the water following aeration, the temperature of the water, and slow mixing of the aerated ground water samples had any significant influence on the rate of oxidation of ferrous iron. It was found that a small rise in temperature during the iron oxidation process did not have a significant influence on the rate. The dissolved oxygen introduced during aeration did have a pronounced effect on the oxidation reaction kinetics when present in small amounts. When the dissolved oxygen was in excess of the stoichiometric requirement or approached the saturation value, it did not influence the rate of oxidation to any great extent. At all the iron removal plants that were investigated, the dissolved oxygen level was in excess of stoichiometric value. Hence, for practical purposes, the effect of dissolved oxygen on the rate of oxidation of ferrous iron was considered insignificant. Slow mixing following aeration was not found to enhance the rate of oxidation of ferrous iron.

In the second phase of the investigation, field studies were made at eight different plants to study the effects of some of the constituents of the natural waters on the oxidation rate of the ferrous iron. In these studies the amounts of dissolved oxygen introduced in the natural water samples were in excess of the stoichiometric requirements and hence the effect of dissolved oxygen on the oxidation rate of ferrous iron was neglected in this phase of the study. Some care was taken, however, to try to aerate each water sample in a similar manner so as to obtain consistent D. O. concentrations.

The field studies showed that sulfates and chlorides did not have any significant influence on the oxidation rate when present in the small amounts found in all the waters studied. On the other hand, the equilibrium pH (the pH of the water after aeration) and the alkalinity of the water following aeration showed a significant influence on the rate of oxidation of ferrous iron. As the rate was found to be independent of the initial ferrous iron present in the natural water, the "radioactive decay equations" were successfully used in evaluating the rate kinetics. The equations used were,

$$\lambda = \frac{0.693}{T_{\frac{1}{2}}} \quad \dots\dots\dots\dots\dots\dots \quad \text{I}$$

$$A = A_o \, e^{-\lambda t} \quad \dots\dots\dots\dots\dots\dots \quad \text{II}$$

where,

t = time elapsed to reduce Fe^{++} iron concentration from A_o to A

λ = rate of oxidation

$T_{\frac{1}{2}}$ = half life

A = concentration of Fe^{++} at time "t"

A_o = initial Fe^{++} iron concentration.

$T_{\frac{1}{2}}$ was used as a parameter to measure the rate of oxidation of ferrous iron. This was graphically computed from the slope of the line representing the log of ferrous iron remaining plotted against time.

Finally a trivariate regression analysis was made with data from the field experiments and the following equation was formulated to relate half life, equilibrium pH, and the total alkalinity of the water following aeration:

$$T_{\frac{1}{2}} = 521.854 - 0.3278 \times 10^{14} \, (OH^-)^2 - 182.931 \log_{10} (\text{Alk.}) \pm 8.10$$

where,

$T_{\frac{1}{2}}$ = half life in minutes

(OH^-) = hydroxyl ion concentration in mol/l (from equilibrium pH)

Alk = Total alkalinity as mg/l of $CaCO_3$

The equation is considered valid for equilibrium pH values between 7.48 to 7.78 and alkalinity values between 354 to 610 mg/l expressed as $CaCO_3$.

It is hoped that the equation may be useful in predicting the half life of ferrous iron oxidation in any water of known equilibrium pH and total alkalinity. Based on the rate of oxidation, the design of iron removal facilities may be put on a more rational basis. It should be realized, however, that the equation may not hold true for waters with characteristics widely different from those investigated in this study.

ACKNOWLEDGEMENTS

The entire experimental work presented in this thesis was done under Research Grant WP-17 (formerly RG 6436) from the United States Public Health Service, National Institutes of Health, entitled "Fundamental Factors in the Treatment of Iron Bearing Waters." The author gratefully acknowledges the permission to use the data.

The author also wishes to thank Dr. R. S. Engelbrecht, advisor, Dr. J. T. O'Connor, Assistant Professor, and Mr. G. E. Margrave of the Bureau of Public Water Supplies, Illinois Department of Public Health for their encouragement, guidance and assistance.

Thanks are also due to Mr. Lloyd Robinson, Mr. Kusug Komolrit and other laboratory staff who were connected with this work. The cooperation of all the municipal treatment plant operators is gratefully acknowledged.

Lastly, the author wishes to thank Mr. N. Chaudhuri and Mr. A. Rehman for drawing the figures.

This report was submitted as a thesis in partial fulfillment of the requirements for the degree of Master of Science in Sanitary Engineering under the direction of R. S. Engelbrecht, Professor of Sanitary Engineering.

TABLE OF CONTENTS

Chapter		Page
	ACKNOWLEDGEMENTS	iii
	LIST OF TABLES	v
	LIST OF FIGURES	vi
I	INTRODUCTION	1
	A. Nature of the Problem	1
	B. Purpose and Scope of the Study	3
II	PRESENT KNOWLEDGE AND THEORETICAL CONSIDERATIONS	8
	A. Present Knowledge	8
	B. Rate of Oxidation and Iron Removal	10
	C. The Basic Concept of the Study	15
III	EXPERIMENTAL EQUIPMENTS AND PROCEDURES	20
	A. Bench Scale Studies	20
	B. Field Studies	25
IV	EXPERIMENTAL RESULTS AND DISCUSSION	31
	A. Bench Scale Studies	31
	B. Field Studies	47
V	CONCLUSIONS	75
VI	AREAS OF FUTURE STUDY	79
VII	BIBLIOGRAPHY	80
	APPENDIX A	83
	Equilibria of Naturally Occurring Iron	83
	APPENDIX B	95
	Equipment and Analytical Techniques	95
	APPENDIX C	102
	Statistical Analysis	102

LIST OF TABLES

Table No.		Page
1	SUMMARY OF ANALYTICAL METHODS	30
2	OXIDATION FOR DIFFERENT AERATION PERIODS	33
3	OXIDATION WITH DIFFERENT AERATION RATES - EXPERIMENT 1	37
4	OXIDATION WITH DIFFERENT AERATION RATES - EXPERIMENT 2	38
5	RAW WATER CHARACTERISTICS	49
6	EXPERIMENTAL DATA FROM THE FIELD EXPERIMENTS	50
7	COMPARISON BETWEEN PLANT AND EXPERIMENTAL DATA	51
8	EXPERIMENTAL DATA - CISCO, ILLINOIS	60
9	COMPARISON BETWEEN EXPERIMENTAL AND COMPUTED HALF LIFE	71

LIST OF FIGURES

Figure No.		Page
1	BENCH SCALE APPARATUS	21
2	FLOWMETER CALIBRATION	23
3	DISSOLVED OXYGEN CONCENTRATIONS WITH DIFFERENT AIR FLOW RATES	24
4	COMPARISON OF OXIDATION OF IRON AT DIFFERENT D. O. LEVELS	34
5	COMPARISON OF OXIDATION AT DIFF. D. O. LEVELS	35
6	OXIDATION OF IRON AT DIFFERENT D. O. LEVELS	40
7(a)	COMPARISON OF DIFF. WATERS UNDERGOING OXIDATION AT APPROX. SAME D. O. LEVELS	42
7(b)	COMPARISON OF DIFF. WATERS UNDERGOING OXIDATION AT APPROX. SAME D. O. LEVELS	43
7(c)	COMPARISON OF DIFF. WATERS UNDERGOING OXIDATION AT APPROX. SAME D. O. LEVELS	44
8	INFLUENCE OF FLOCCULATION ON OXIDATION OF IRON	46
9(a)	Fe^{++} IRON OXIDATION	57
9(b)	pH VARIATION DURING OXIDATION	58
9(c)	TITRATION CURVE	59
10	COMPARISON OF Fe^{++} OXIDATION RATES OF DIFFERENT NATURAL WATERS	63
11	COMPARISON OF pH VARIATIONS DURING OXIDATIONS	64
12	EQUILIBRIUM pH vs. $T_{1/2}$	66
13	ALKALINITY vs. $T_{1/2}$	66

I. INTRODUCTION

A. Nature of the Problem

1. Natural Source

Iron is relatively abundant in the earth's crust. The element is a principal constituent of many igneous rocks, especially those containing basic silicate materials. Divalent iron links the chain of silicon oxygen tetrahedra in minerals like pyroxines and amphiboles. Trivalent iron replaces aluminum in a few silicate minerals. Iron is common, also, in the form of oxide and sulfide. Sedimentary rocks contain various forms of which ferric oxides are most common. Geochemical data indicate that iron weathered out of solid minerals is not long retained in solution in water but is redeposited in solid oxides or hydroxides.

Iron occurs in two oxidation states, the divalent ferrous form and the trivalent ferric form. Iron in aqueous solution is subject to hydrolysis. The iron oxides produced by these reactions, especially the ferric forms, have low solubility. The retention of iron in aqueous solution is influenced by the pH of the solution. In most natural waters, the pH is not low enough to prevent hydroxides from forming, and under oxidizing conditions practically all the iron is precipitated as ferric hydroxide. Another important feature of the chemical behavior of iron in solution is the formation of complex ions with inorganic as well as organic materials. However, the following chief causes can be attributed to the presence of iron in ground water (4).

a) Iron bearing minerals dissolve in waters having low pH.

b) The reduction of ferric compounds in soil or in organic matter also causes iron to dissolve.

c) Anaerobic decomposition of organics at reservoir bottoms promotes conditions under which iron will return to solution.

2. The Cause of Concern

The presence of iron in drinking waters is often undesirable if it exceeds the specified limits set forth by the United States Public Health Service (USPHS) which says that the amount of iron and manganese present together in drinking water should not exceed 0.3 mg/l.

A survey by Longley (25) in the field of iron removal revealed that in the state of Illinois, the total number of iron removal installations serve about one percent of the state's total population. Of these, about one-third are not reducing the iron concentration to satisfactory levels. Their performance indicate that iron removal is really unpredictable, especially in smaller installations where simple and automatic operation is essential.

High concentrations of iron may lead to the following complaints:

a) Metallic tastes,

b) Discoloration of industrial products involving wet processes ,

c) Stains on household utensils, porcelain glassware and clothes ,

d) In cooling waters precipitates of ferric hydroxides clog piping and stimulate growth of iron bacteria in distribution lines causing "red water" problems. Deposits cause differential heating in boilers with the accompanying danger of bursting ,

e) In the rapidly growing use of demineralizers for high pressure boiler waters, iron and manganese hydroxides may clog the ion exchangers and reduce their efficiency.

Iron removal is accomplished by one of two different methods in practice:

1. Oxidation

a) Aeration for oxidation or use of other chemical oxidants

followed by filtration with or without sedimentation prior to filtration.

b) Filtration through manganese zeolite.

$$4Fe(HCO_3)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3 + 8CO_2 \qquad \text{............I}$$

2. Ion exchange not preceded by oxidation. This combines softening with iron removal.

$$Na_2Z + Fe(HCO_3)_2 \longrightarrow FeZ + 2Na(HCO_3) \qquad \text{..............II}$$

These two processes are used today with considerable success. The most widely used method of iron removal consists of aeration, settling and filtration. The principles involved are:

a) Conversion of soluble ferrous iron in ground water to insoluble ferric forms in a single oxidative step.

b) Settling of the ferric floc

c) Filtration. The exact mechanism by which iron is removed by a sand filter is not known fully but three possible mechanisms are suggested in all the literatures pertaining to this field.

i) Adsorption and reaction phenomena based on the adsorption of flocs on the sand grains and subsequent oxidation.

ii) Catalytic effect of previously deposited material on the filter medium.

iii) Possible promotion of an oxidation reaction owing to long contact between thin films of water and sand grains.

B. Purpose and Scope of the Study

The speed of reaction determines the adequate design criteria of any iron removal unit and therefore its first cost. The present study is devoted completely to determining which major factors, inherent in natural ground water, affect the rate of oxidation of ferrous iron. The number of variables

affecting the reaction rate is too great for a definitive evaluation. The major influences, however, have been quantitatively defined. In general the factors considered may be classified as:

1. The independent variables which bear a direct relationship with the rate of oxidation. These may be physical or chemical.

Physical:

a) Temperature of water during the oxidation process

b) Effect of slow mixing following aeration

Chemical:

a) Presence of high or low amount of sulfate

b) Presence of high or low alkalinity

c) Presence of other anionic constituents, such as, chlorides, nitrates and phosphates.

d) Catalytic effects of other cations in the water, such as copper (Cu), aluminum (Al), and zinc (Zn), which tend to accelerate or retard the speed of reaction.

e) Amount of dissolved oxygen and the method of application:

i) Short aeration period at high rate of air flow

ii) Long aeration period at low rate of air flow

f) The pH of the water after aeration.

g) Presence of complex forming organic material.

2. Dependent variables -- This takes into account the effects of two or more variables occurring simultaneously which are related to the oxidation rate and at the same time independent among themselves. Some of the variables were found to have a very insignificant effect on the rate of iron oxidation and, as such, they were not considered. This could be done with reasonable approximation from experience with most well waters in the state of Illinois and from the pertinent literature in the field.

The study was divided into two phases:

a) Bench Scale Study with Champaign City Water:

These studies were done to determine what effects physical factors such as, the temperature, the dissolved oxygen (D. O.) levels in the waters, the method of application of air, and the effects of slow flocculation following aeration, had on the reaction rate.

b) Field Studies:

These studies were initiated when it was found that the original character of the ground water changed considerably by the time it was transported to the laboratory. In this phase raw water was drawn from wells and immediately aerated at the plant site in a small scale aeration unit. Following this the water was allowed to settle. The parameters measured were:

1. The dissolved oxygen of the ground water before and after aeration.

2. The concentration of ferrous iron in the raw water and in the aerated sample as it gradually oxidized. This was done at regular intervals until there was no visible color when the sample was fixed with colorimetric reagents such as 1,10-Bathophenanthroline. This indicated that ferrous iron was no longer present.

3. The pH of the water was measured as it was taken out of the well and also after aeration. During the experiment pH was monitored and recorded each time a sample was collected for ferrous (Fe^{++}) iron determination. The parameter used from this measurement was the pH immediately after aeration. This shall be referred to as the equilibrium pH hereafter. The equilibrium pH was considerably higher than the pH of the well water as it came directly from the aquifer since aeration brought about the release of CO_2 from solution.

4. A titration curve was plotted in the field so that the alkalinity (chiefly HCO_3^-) of the water and its buffer capacity at the equilibrium

pH could be determined.

5. Additional analyses were made for:
   i) Chemical Oxygen Demand (C. O. D.),
   ii) Sulfate ($SO_4^=$),
   iii) Chloride, (Cl^-), and
   iv) Total solids present in the water.

Operational data from the plant were also collected for comparison with results obtained in this study. Complete data were collected from eight different plants in the state of Illinois, all of which used well waters having different chemical characteristics.

Attempts were made to determine the relationships between the rate of oxidation and the measured parameters. Since it was found that for each test the oxidation of ferrous iron followed a monomolecular first-order reaction pattern with respect to the ferrous iron concentration remaining, the parameter used to express oxidation rate was the "Half Life" or time needed to reduce the Fe^{++} iron concentration by 50 percent ($T_{1/2}$). This value was observed to be a constant for a particular ground water. This follows from the linear relationship of the logarithm of the ferrous iron remaining with time.

Different plots were made for $T_{1/2}$ vs each parameter. The parameters which showed a possible correlation with the "Half Life" when plotted separately were chosen for a multiple regression analysis.

From the findings a trivariate regression analysis was set up as follows: Half Life ($T_{1/2}$) = k (Equilibrium pH, Alkalinity).

In this case $T_{1/2}$ is the response and pH and alkalinity are assumed to be independent of each other so that interaction terms are neglected in the general analysis. The multiple regression coefficients were also computed. From the statistical treatment an equation was set up relating the half life,

the alkalinity and the equilibrium pH. This equation may prove to be useful in the design of iron removal units provided the water in question falls within the limitations of the statistical analysis.

The dissolved oxygen content of the water was not considered as a variable affecting iron oxidation. Most of the plants operate at a D. O. level close to saturation. The D. O. level is consequently much higher than is theoretically needed to oxidize the ferrous iron present. Oxygen was not a limiting factor in any of the field experiments.

It has been reported in the literature that certain cations, such as copper (Cu^{++}), enhance the oxidation rate of ferrous iron to a great extent. It is felt that a study of the catalytic effects of these cations should be extended to natural waters. This might offer a valuable contribution to the process design for iron removal operations.

II. PRESENT KNOWLEDGE AND THEORETICAL CONSIDERATIONS

A. Present Knowledge

In order to study the oxidation phenomenon of ferrous iron, a knowledge of various equilibria involving Fe^{++} and Fe^{+++} species in natural waters is essential.

Iron as well as the other cations and anions in natural ground water are derived from solid phase rock minerals in contact with water. The chemical reactions involved in the solution and deposition of iron are more readily reversible than other cations and the amount of iron present is sensitive to certain characteristics of the water.

The most common species of ferric iron in natural waters is ferric hydroxide, $Fe(OH)_3$ or more correctly $Fe_2O_3 \cdot 3H_2O$. At equilibrium in the pH range of 5 to 8, this compound is largely in the solid state, the solubility being very low (15). Relatively stable colloidal suspensions of ferric hydroxide can exist over much of this pH range. Ferric hydroxide is a weak base and ionizes as $Fe(OH)^+$, FeO^+, $FeOH^{++}$ and Fe^{+++}. At high pH, anions like FeO_2^- (ferrite) form. Ferric ions have high affinity towards formation of complexes with inorganic anions such as chlorides, phosphates, sulfates and even carbonates (35). All of these are found in natural waters. Organic complexes may also be formed.

Hem and Cropper (15) have reported that the ferrous oxidation state is weaker than the ferric state in its complexing properties and forms few complexes with inorganic ions. But $Fe(OH)_2$, on the other hand, is a stronger base than ferric hydroxide and gives $FeOH^+$ and Fe^{++} on ionization. Generally, most often ferrous iron is present as Fe^{++} iron in natural waters.

According to Hem (14) the principal equilibria associated with the solution or deposition of iron in ground water include:

a) The hydrolysis and precipitation of hydroxides

b) The solution and precipitation of carbonates

c) Oxidation-reduction reactions

d) The solution and precipitation of sulfides, and

e) The formation of complex ions and chelation.

These equilibria are almost always interrelated and may exist simultaneously in ground water. It has been reported (14) that equilibrium can be reached in systems involving only iron and hydrogen ions but it was not reached if a carbon dioxide or a sulfate reduction phase is present in the system. These findings indicate that a chemical equilibrium exists between the dissolved iron and other solutes in ground waters as well as the solid phase minerals in the aquifer.

The complexity of the aqueous iron system frequently is not fully appreciated. Many of the anomalous properties of iron compounds which are described in the literature can be explained by considering, besides the solubility equilibria of ferrous and ferric hydroxides, the many other possible equilibria (solubility, complex formation, oxidation-reduction and hydrolysis) that may exist in iron bearing waters. In addition, the kinetics of each of these equilibrium reactions must also be considered.

In oxygenated waters, ferrous iron is converted to the ferric state. The rate of oxidation in pure solution has been found by Hem (14) to be dependent on the hydrogen ion concentration and temperature of the solution. Moreover, ferrous constituents tend to show a greater solubility than ferric constituents.

In appendix A a discussion is presented relative to the various species of iron present in ground water.

B. Rate of Oxidation and Iron Removal:

From the stoichiometric relationship:

$$2Fe^{++} + \tfrac{1}{2}O_2 + 2H^+ = 2Fe^{+3} + H_2O,$$

it would appear that acid solutions should favor the oxidation of ferrous iron. Experimentally, it has been found that the rate of the oxidation reaction is retarded by the acidity of the water and that the hydrogen ions tend to stabilize ferrous solutions. It is assumed that the slow rates under acid conditions are due to slow stepwise reduction of oxygen molecule as suggested by Weiss (40):

$$Fe^{+2} + O_2 \rightleftharpoons Fe^{+3} + HO_2 \text{ (perhydroxyl) } \ldots\ldots\ldots\ldots\ldots \text{(a)}$$

$$Fe^{+2} + HO_2 \rightleftharpoons Fe^{+3} + H_2O_2 \text{ (hydrogen peroxide) } \ldots\ldots \text{(b)}$$

$$Fe^{+2} + H_2O_2 \rightleftharpoons Fe^{+3} + OH^- + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(c)}$$

$$Fe^{+2} + OH \rightleftharpoons Fe^{+3} + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(d)}$$

The reactions, of course, are not balanced with respect to hydrogen and as Weiss suggests, the rate determining step in oxidation of ferrous iron is equation (a). From this the rate of oxidation can be said to bear a first order dependence with respect to dissolved oxygen and ferrous iron. The equations do not indicate a dependence of rate on the hydrogen ion concentration.

Hence, the reaction kinetics is represented by the following equation:

$$-\frac{d(Fe^{+2})}{dt} = k\ (Fe^{+2})\ (O_2) \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{III}$$

Just (16) has reported on oxidation of ferrous iron with homogeneous solutions of bicarbonate and his results are in agreement with the above

equation (III).

The oxidation of ferrous iron is effected by hydrolysis, (OH^-) combining with ferrous hydrate to form ferric hydrate and the (H^+) ions combining with oxygen to form H_2O. Hydrolysis is retarded by acids and accelerated by alkalies and by contact with the rough surfaces in filters or aerators or previously formed precipitates of $Fe(OH)_3$ (38). Pinz (28) expressed oxidation as a time reaction and gave the mathematical formulation:

$$K = \frac{1}{t} \cdot \frac{A}{A-x}$$

or,

$$k = k_1 \cdot \frac{1}{t}$$

where,

t = time elapsed after oxygen is introduced

A = initial ferrous iron concentration

x = ferrous iron oxidized in time "t"

So, if the proportionality constant "K" for a given water is high, it can be readily oxidized. Weston (38) reported that the presence of carbon dioxide (CO_2) produced an eightfold increase in the reaction rate. Just (18), as mentioned previously, reported that in solutions of ferrous carbonate ($FeCO_3$), the velocity of the reaction is inversely proportional to the square of carbonic acid (H_2CO_3) concentration. This approaches the findings of Weston (38). Neither of these studies involved a consideration of pH or its change during the process of oxidation when CO_2 in ground water is released through aeration and (H^+) ions are liberated through the dissociation of H_2CO_3 and HCO_3^- ions.

The effect of CO_2 on the oxidation reaction rate was also observed by other investigators. Applebaum (1) states that the oxidation of ferrous iron is a rapid reaction, but that some waters do not respond rapidly to oxidation because of a high concentration of CO_2. This is also supported by

Johnston (17). Thorough and long aeration or alkalization is necessary to remove CO_2 and enhance oxidation of ferrous iron. The theoretical amount of oxygen required for total oxidation is 0.14 mg/l per mg/l of ferrous iron. But this is not the only criterion governing the rate of oxidation. Other factors reported to retard the oxidation rate are:

1. Low total solids and high alkalinities (2). In general, well waters in the midwestern states have high bicarbonate alkalinities. Contradicting the above statement, these waters respond readily to oxidation by aeration. This has also been verified by Longley (25). With waters low in total solids and low in total alkalinities as found along the eastern seaboard, even thorough removal of CO_2 by efficient aeration does not suffice to insure rapid and complete oxidation. Additional treatment is therefore necessary.

2. Low pH reaction (1). Iron in acid waters is usually present as sulfates and requires the addition of alkalies to raise the pH to 8 or 9 prior to filtration.

3. Organic matter. Chelated iron requires special oxidizing agents, coagulation and sedimentation.

4. Excessive aeration (39). This has been reported to interfere with satisfactory iron removal. Overaeration is of no value. On the other hand, it increases the corrosiveness of the water. Limiting aeration, i.e., absorption of oxygen to a fraction of saturation (about 50 percent (4)), is adequate for most natural waters. Bouthillier (4) has tried to correlate pH directly with the solubility of iron and has also correlated CO_2 with pH. His work involved the use of synthetic waters only. According to Bouthillier pH is largely controlled by the dissolved CO_2 content. For waters with pH values between 4.5 and 10.3 and not too low alkalinity (up to 250 mg/l as $CaCO_3$), the approximate relationship was:

$$CO_2\ (mg/l) = (H^+) \times T \times 1.94 \times 10^6$$

where,

T = Total alkalinity as mg/l of $CaCO_3$

H^+= (H^+) ion concentration in mol/l

Also,

$$(Fe^{+2})(OH^-)^2 = 1.64 \times 10^{-14} = \text{Solubility product of } Fe(OH)_2$$

and,

$$(Fe^{+3})(OH^-)^3 = 1.1 \times 10^{-36} = \text{Solubility product of } Fe(OH)_3$$

So,

$$Fe^{++} \text{ in mg/l} = \frac{1.64 \times 10^{-14} \times 56 \times 1000}{(OH^-)^2}$$

and,

$$Fe^{+++} \text{ in mg/l} = \frac{1.1 \times 10^{-36} \times 56 \times 1000}{(OH^-)^3}$$

The pH, therefore, affects the solubility of Fe^{++} and Fe^{+++} iron. It can be inferred that the CO_2 content controls the pH and, hence, the oxidation reaction. This is purely a theoretical concept. Objections arise owing to a lack of experimental verification.

Stumm and Lee (35) have reported some valuable results from their work on oxygenation of ferrous iron. According to their work, oxygenation of ferrous iron was found to follow the equation:

$$Fe^{+2} + 1/4\ O_2 + 2OH^- + 1/2\ H_2O \longrightarrow Fe(OH)_3$$

when carried out in buffered solutions having pH values greater than 6 and at a constant partial pressure of oxygen during oxidation. The oxygen concentration was always present in excess in the sample. The partial pressure of oxygen was varied from 76 to 155 mm so as to determine its effect on the oxidation rate. The rate law postulated by Stumm and Lee is:

$$-\frac{d(Fe^{+2})}{dt} = k'(Fe^{+2})\ Po_2$$

where,

Po_2 = Partial pressure of oxygen.

This accounts for the changes in ferrous iron during the course of reaction at a constant pH value. In another phase of the study the effect of pH on the oxidation rate was investigated and it was reported that for an increase of one pH unit, the rate of oxidation increased a hundredfold. There was a second order relationship between the rate of reaction and the hydroxyl ion concentration, therefore. Finally, the overall reaction rate can be expressed as follows:

$$-\frac{d(Fe^{+2})}{dt} = k\ (Fe^{+2})\ Po_2\ (OH^-)^2$$

where,

k = Reaction rate constant,

Po_2 = Partial pressure of oxygen, and

(OH^-) = Hydroxyl ion concentration.

All the experimental data of their study were obtained from solutions having alkalinities [$(HCO_3^-) + 2(CO_3^=) + (OH^-)$] between 9.0×10^{-3} and 3.9×10^{-2} equivalents per liter. In their studies, the effect of anions, such as $(H_2PO_4^-)$, $(SO_4^=)$, (Cl^-), on the oxidation rate was not considered since the concentrations of these constituents were presumably negligible in their controlled system.

In the work presented herein an attempt has been made to extend the investigation of oxygenation kinetics to the more heterogeneous systems of natural waters. It is, of course, realized that such investigations are generally less amenable to rigorous interpretation owing to superimposition of interrelated factors which operate in natural water systems.

C. The Basic Concept of the Study:

Studies in the laboratory were made with natural waters to find out if the observed reaction kinetics were in agreement with the findings of other investigators regarding the initial ferrous iron and dissolved oxygen concentrations. It was found that, within reasonable limits, even in natural waters, the reaction kinetics can be expressed as follows:

$$-\frac{d(Fe^{+2})}{dt} = k\ (Fe^{+2})(O_2)$$

Oxygen was introduced by a variety of methods to determine whether physical factors, such as violent agitation during aeration or slow mixing subsequent to the introduction of oxygen, would influence the reaction kinetics. No significant influence on the rate of oxidation was found to be due to the method of applying oxygen. The main purpose of the study was to relate the oxygenation kinetics to practical operational problems at iron removal plants. The temperature of ground waters is relatively constant in any plant throughout the process of iron removal. Therefore, temperature was not considered in this study.

In a previous study a survey of plants in the state of Illinois was made (19) for the purpose of collecting operational data on various unit operations. This study revealed that in almost all plants surveyed, the well waters, following aeration, had a dissolved oxygen concentration of 8 to 9 mg/l. Therefore, this variable was neglected in the current study since it is clear that the availability of oxygen is neither a limiting factor nor a large variable.

In the statistical analysis of the results obtained during the study, the initial iron and dissolved oxygen concentrations were not included as variables. On the other hand, the influence of pH and other common anions on the oxidation rate was evaluated. Anions such as Cl^-, $SO_4^=$ as well as

total solids and C. O. D. did not show any significant influence on the reaction rate. The following hypotheses guided the selection of variables:

Hypothesis: 1 Variable: Detention time

Most of the plants having iron removal problems are not providing sufficient detention time for complete oxidation.

Hypothesis: 2 Variable: (OH^-)

The rate of reaction can be increased by pH adjustment. Reaction rates and thus the total reaction time should be predictable from the (OH^-) concentration of the water. It was confirmed that the pH of natural water changes during aeration. As a mater of fact, it was found to increase after aeration due to the release of CO_2 from the water. After this change, the pH remained more or less constant. The equilibrium pH (pH after aeration) was chosen as the test variable instead of the pH of the raw water because the equilibrium pH represents the conditions under which the oxidation of ferrous iron will occur. The pH during oxidation is expected to decrease somewhat, due to hydrolysis of iron.

Hypothesis: 3 Variable: Alkalinity or the "Buffer Capacity"

The buffer capacity or indirectly the alkalinity of a water at the pH of oxidation (equilibrium pH) will influence the "overall rate of oxidation" by exerting control over the variation in pH due to iron hydrolysis.

For an "overall rate of oxidation" the parameter measured is the time needed to reduce ferrous iron concentration by 50 percent. Since it was found that the rate of oxidation for any water was constant with respect to time, the concept of "half life," as a measure of oxidation time, could be applied. The well known "radioactive decay equation" can conveniently be used for expressing the reaction rate,

$$\lambda = \frac{0.693}{T_{1/2}}$$

where,

λ = rate of decrease of Fe^{++} iron in an oxygenated solution of Fe^{++} iron

$T_{1/2}$ = the time needed for 50 percent oxidation of Fe^{++} iron (data obtained experimentally)

A regression analysis was set up to find out the best correlation between the most significant variables such as half life, alkalinity and pH which could be generalized as $T_{1/2} = f$ (Alkalinity, pH) $= f$ (Alkalinity, OH^-). This correlation equation could be used to predict the total reaction time needed between introduction of oxygen and filtration, to reduce the iron concentration to an acceptable limit. This information may also be applicable in establishing design criteria for reaction basins.

Studies have been done by other workers mainly on synthetic waters to investigate the effects of the complexing affinity of the ferric iron with various anions. It has been found that the oxidation rate was very dependent on the anions present in that the rate of oxidation increases as the complexing affinity of an anion for ferric iron increases (13). Under acid conditions the rate of oxidation has been found to decrease in the presence of the following anions in decreasing order (35): hydroxide, pyrophosphate (13), phosphate, chloride (30), sulfate (20) and perchlorate (12). Of course, only synthetic waters were used by the investigators to determine these results on complexing affinity. The rate law for oxidation is in accordance with the equation: $-\frac{d(Fe^{+2})}{dt} = k\,(Fe^{+2})\,(O_2)$ for the first four anions. A second order relationship between the ferrous iron concentration and the rate is found in sufficiently acid solutions of H_2SO_4 and $HClO_4$. In addition, those substances which hasten decomposition of peroxides in the presence of ferrous iron (i.e., platinum, charcoal, and cupric salts) accelerate the oxidation of ferrous salts (18).

The rate of oxidation of ferrous iron in H_3PO_4 or NaH_2PO_4 solutions has been studied by some researchers (6). It has been stated as a homogeneous reaction; the rate law being expressed as:

$$-\frac{d(Fe^{+2})}{dt} = k\ (Fe^{+2})\ Po_2\ (H_2PO_4^-)^2$$

The rate determining step is:

$$Fe^{+2} + O_2 \longrightarrow Fe^{+3} + HO_2$$

which is in agreement with Weiss (40), who postulated the one electron reaction mechanism. Cu^{++} ions have been found to have a pronounced effect on the oxidation reaction of Fe^{++} iron (35) (6). The reaction proceeds in the following manner (again unbalanced with respect to hydrogen ions):

$$Fe^{+2} + Cu^{+2} \rightleftarrows Fe^{+3} + Cu^{+}$$

$$Cu^{+} + O_2 \rightleftarrows Cu^{++} + HO_2$$

$$Fe^{+2} + HO_2 \longrightarrow Fe^{+3} + H_2O_2$$

Lamb and Elder (20) have shown that in an acid medium (>0.1 M H_2SO_4 solution) the rate law is:

$$-\frac{d(Fe^{+2})}{dt} = k\ (Fe^{+2})^2\ (O_2)\ (H^+)^o$$

i.e., the rate determining step involves a two electron oxidation mechanism:

$$2Fe^{+2} + O_2 \longrightarrow 2Fe^{+3} + H_2O_2$$

This is, of course, not in agreement with the one electron oxidation mechanism.

In none of the above studies is any inhibition by Fe^{+3} demonstrated to be due to the reaction:

$$Fe^{+3} + HO_2 \longrightarrow Fe^{+2} + O_2 .$$

From the above discussion, it becomes clear that a quantitative knowledge of the rate of ferrous iron oxidation by oxygen as a function of pH and other constituents of natural water may lead to a better understanding of the deferrization processes in natural waters.

III. EXPERIMENTAL EQUIPMENTS AND PROCEDURES

A. Bench Scale Studies

These studies were initiated to determine the effect of the dissolved oxygen content on the rate of oxidation of ferrous iron. For each experiment, three eight liter samples were placed in three nine liter jars so that the behavior of iron oxidation at at least three different levels of dissolved oxygen could be determined simultaneously. A sketch of the bench scale apparatus is shown in Figure 1.

1. Equipment:

The equipment consisted of,

a) Temperature Control: A constant temperature water bath was used to equilibriate the temperature of the experimental water with that of the bath before introducing air to the experimental water.

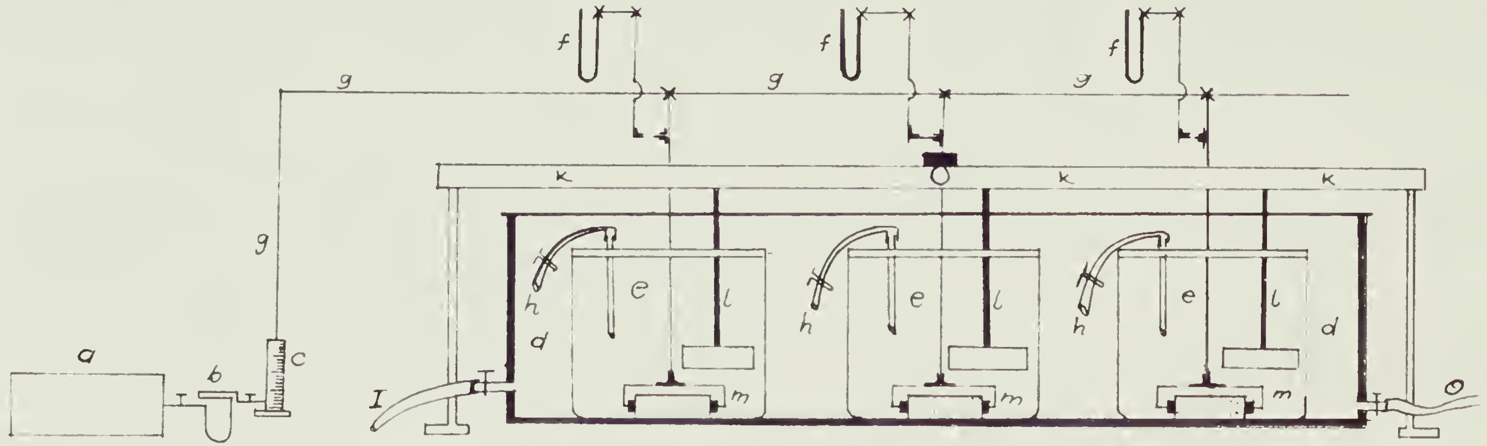
b) Stirring Mechanism: A standard jar test stirrer was used to stir the samples thoroughly during aeration. In some experiments, slow stirring following aeration was done to see if it would affect the rate of oxidation of the ferrous iron.

c) Aeration Mechanism: An air compressor was used for the air supply which was metered by a flowmeter manufactured by Fisher Scientific (Catalog No. 11-164). The air was introduced into the experimental water through carborundum cylinders.

d) Sampling Mechanism: Initially a special device was designed to collect the samples at regular intervals from all the jars, at the same time. By means of a vacuum pump, a vacuum was pulled through a suction line branching off into the three jars. Samples were collected simultaneously from all three jars and immediately fixed with appropriate reagents for determining iron and D. O.

This method did not work very well due to the fact that the collection

FIG. 1



BENCH SCALE APPARATUS

LEGEND:

a - COMPRESSOR

b - AIR FILTER

c - FLOW METER

I - INLET FOR COOLING WATER

d - WATER BATH

e - NINE LITER JAR

f - MANOMETER

g - AIR LINE

h - SAMPLING SIPHON

k - STIRRING MACHINE

l - PADDLE

m - AIR DIFFUSER

o - OUTLET FOR COOLING WATER

—X— VALVE

of the samples could not be synchronized in all three sampling bottles due to a variation in vacuum through the different branches of the suction line. Ultimately, it was decided to collect samples from each jar by separate siphons. The depth of sampling point below the surface of water was kept constant for all samples collected.

2. Description of the Experimental Procedure:

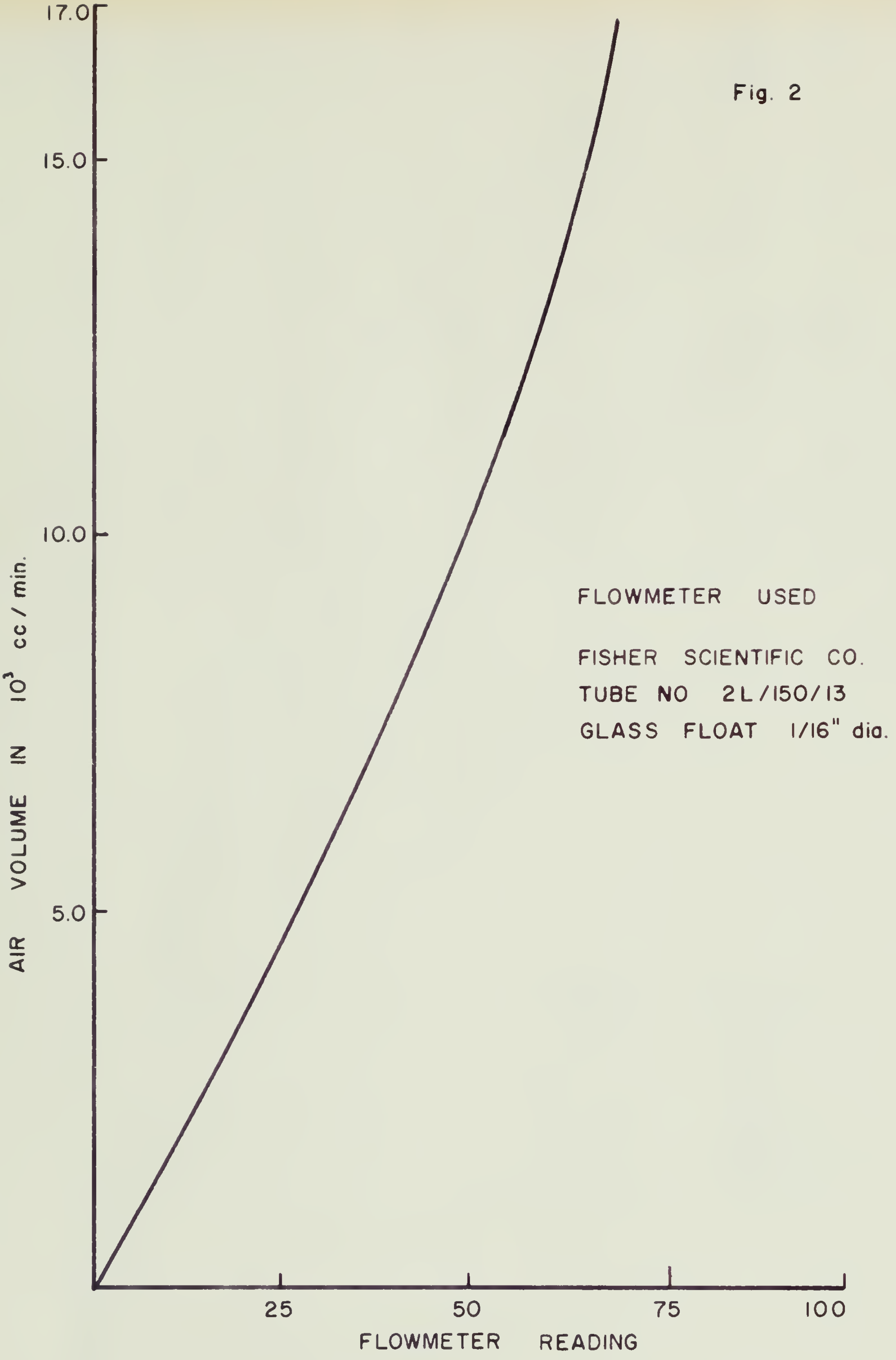
Most of the bench scale studies were done with raw water obtained from the well at the Champaign-Urbana treatment plant. The water was brought to the laboratory just before the experiment was initiated. Long storage was avoided to guard against oxidation and precipitation of ferrous iron by exposure to atmospheric oxygen.

Different levels of D. O. were obtained by controlling the air flow and the time of aeration. Air from a compressor passed through the flow meter into a common header which branched off in three lines, each leading to a separate jar. Manometers were connected to each of the three air lines, so as to maintain a constant head loss in each system.

Initially a set of curves were plotted (Figures 2 and 3) showing the dissolved oxygen concentrations obtained at various air flow rates (expressed as the reading on the air flow meter). These data were obtained experimentally. It should be realized that the absorption of oxygen by natural waters may vary depending upon the constituents of the water. Therefore, the absorption efficiency should be determined separately for each water examined. However, since the waters studied were almost similar in composition a single "absorption plot" was used for all experiments.

After the experimental water had reached temperature equilibrium, simultaneous aeration was done in the three jars but for different lengths of time so as to add different amounts of dissolved oxygen to each. In most of the experiments aeration was of short duration and accompanied by thorough stirring.

Fig. 2

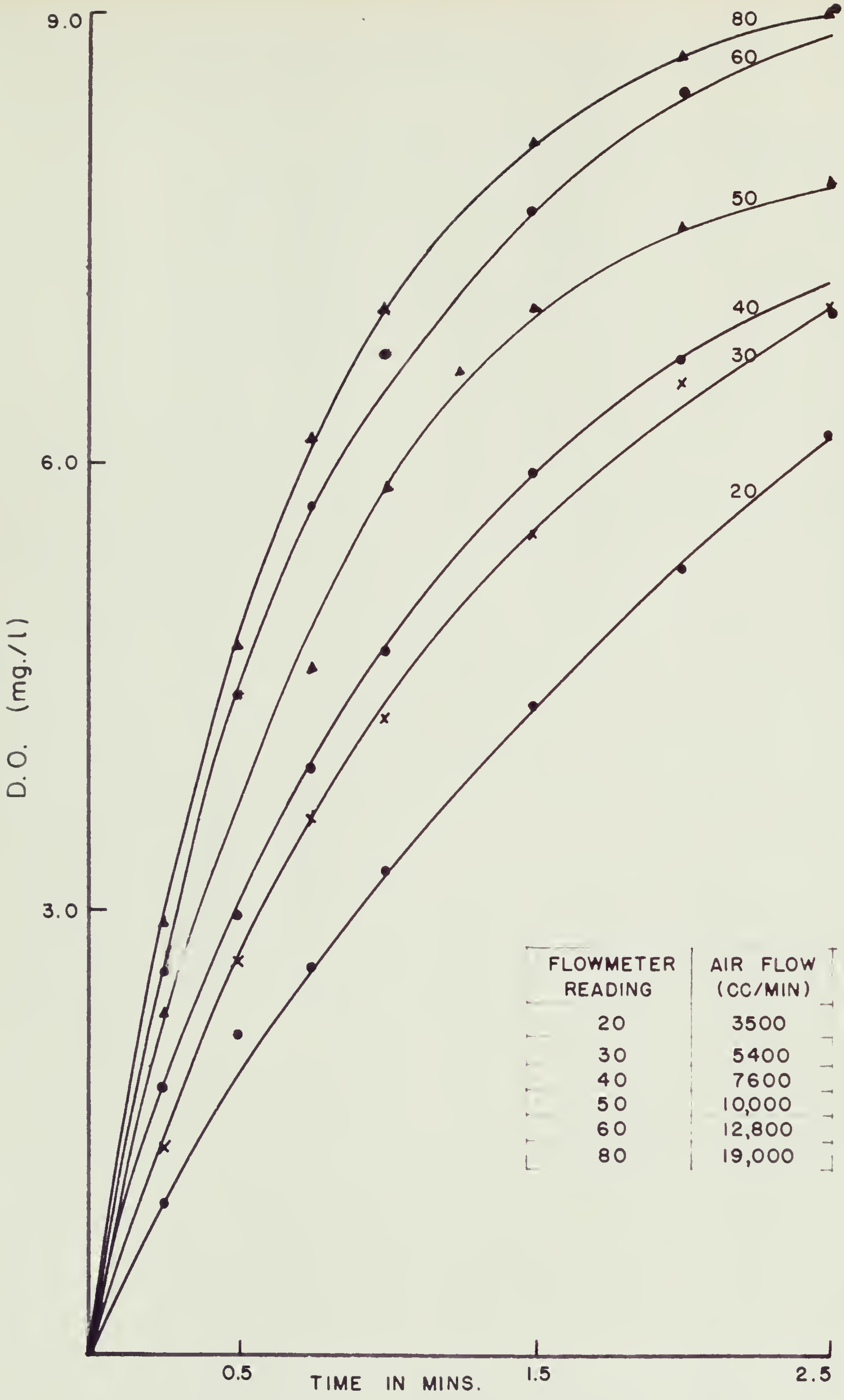


FLOWMETER CALIBRATION

AIR FLOW RATES WITH DIFFERENT FLOWMETER SETTINGS

(Sintered glass diffuser used)

FIG. 3



DISSOLVED OXYGEN CONCENTRATIONS WITH DIFFERENT AIRFLOW RATES

3. Analyses made on the Raw Water and the Aerated Water:

a) Raw Water:

The raw water for each experiment was analyzed for:

i) Alkalinity

ii) Hardness

iii) Chemical Oxygen Demand

iv) Sulfates

v) Chlorides

b) Aerated Water:

Following aeration, an aliquot of each experimental water was collected at regular intervals and analyzed for,

i) Ferrous and total iron

ii) Dissolved oxygen

iii) Temperature

iv) pH and Redox Potential (Eh)

As expected, the ferrous iron indicated a regular decrease as the oxidation reaction proceeded.

The chemistry and methods of the various determinations are described in Appendix B. In general, procedures as outlined in Standard Methods, 11th Edition, were followed.

B. Field Studies

Experience gained from bench scale experiments showed that in transporting water samples from the plants to the laboratory, a significant amount of ferrous iron was oxidized and precipitated. Because of this, it was decided to conduct experiments in the field at actual plant sites. This had a two-fold advantage over the laboratory experiments with natural waters.

1. The possibility of oxidation of ferrous iron, prior to the start of the experiment, was eliminated.

2. All the field experiments were completed during the winter months and as the experiments were carried out at the plant with freshly drawn water, chances of a change in temperature before or during the experiment were minimized. A rise of 1° to 2° C was noted in the experimental water during the experiment in almost all the natural waters. So, any adverse influence of temperature change on the oxidation rate was not considered to be significant.

a) Equipment used in the Field Studies:

A nine liter jar with a plexiglass cover was used to hold each eight liter experimental sample. In the cover, holes were drilled for the air line, siphon line for sampling, and for two electrodes used to measure the pH. A thermometer was also inserted for recording the temperature. Again, an air compressor and a carborundum diffuser were used for aeration. As in the bench scale studies, the air flow was metered and controlled.

b) Procedure of Field Experiments:

1) Collection of raw water sample: Approximately eight liters of raw well water was collected taking proper precautions not to aerate the samples during collection. Immediately after collection, samples were taken for the determination of ferrous iron and D. O. The pH was also measured. Samples for Fe^{++} iron were immediately fixed with proper reagents and the total iron sample was acidified.

2) Based on the results of the bench scale studies, the experimental water samples were aerated for 1-2 minutes at high rates. In this study it was not intended to determine the influence of dissolved oxygen on the oxidation rate. It was found that most of the plants treating iron bearing waters operate at D. O. level close to saturation and it was intended to simulate actual operating conditions as close as possible, in the experiment. Therefore, the water was aerated at high rate for a short duration, to ensure that there was sufficient dissolved oxygen in the experimental water.

c) Measurements and Determinations:

1) pH Measurement:

This was one of the most important measurements involved in the field study. The measurement was done with all possible precautions. The pH measurements were made by using a Beckman Instruments, Inc., Model "N" pH meter. The pH was measured directly in the experimental water whenever a sample was collected for ferrous iron determination. In all raw waters investigated, there was an appreciable increase in pH following aeration. Subsequently, the pH remained constant until the end of the experiment. In some waters, the pH dropped slightly towards the end of the experiment, possibly due to hydrolysis of iron.

2) Temperature:

Temperature was recorded each time a sample was collected for iron analysis. There was a slight fluctuation in temperature in most of the waters during the experiment. As most of the experiments were completed during the winter months, the temperature of the raw water in the aquifer and the temperature of air above ground were approximately the same. Therefore, no special precaution was adopted for temperature control. The maximum temperature recorded during an experiment, was approximately 3° C. There was no measurable influence on the solubility of the iron compounds in the experimental water, due to this change in temperature.

3) Dissolved Oxygen:

Samples for D. O. analysis were taken three times during each experiment.

i) Raw water, as it was obtained from the well

ii) Aerated water (immediately after aeration)

iii) Treated water (at the end of the experiment)

The D. O. samples were fixed with the necessary reagents in the field

while the final titration with sodium thiosulfate was done in the laboratory. Because it was observed that the D. O. content of the experimental waters did not change during the course of bench scale experiments, samples were not collected as frequently for D. O. analysis as for ferrous iron determination.

4) Alkalinity and Buffer Capacity:

A titration curve was obtained for each experimental water electrometrically, using 0.2 N HCl as the titrant. Data were obtained to make a plot of pH versus volume of titrant needed for each experimental water. The titration of each sample was continued to a pH of 4.5 for the determination of total alkalinity. Buffer capacity is expressed as equivalents per pH unit. Experimentally, it was determined by drawing a tangent to the titration curve at the equilibrium pH, the slope of the tangent being the buffer capacity.

5) Iron Determination:

i) Ferrous iron:

Immediately after collecting a sample, it was fixed with necessary reagents for color development. The reagent used for forming Fe^{++} iron complex was 4,7- diphenyl- 1,10 phenanthroline ($C_{24}H_{16}N_2$). The procedure followed was exactly the same as described by Stumm and Lee (23) using bathophenanthroline. In the field, the samples were extracted with iso amyl alcohol and diluted to 50 ml with reagent grade ethyl alcohol. The colorimetric analysis was made using a Model DU spectrophotometer, manufactured by Beckman Instruments, Inc., Fullerton, California

It has been shown by previous workers (19) (23) that the color produced by the Fe^{++} iron-bathophenanthroline complex is stable and does not change with time. So, the time elapsed between fixing the samples with the reagents in the field and analyzing them spectrophotometrically in the laboratory was not critical.

After beginning the experiment, ferrous samples, as described above, were collected at regular intervals by siphoning into a beaker without trapping any air in the siphon hose. Aliquots were then pipetted into separatory funnels for color development and solvent extraction.

ii) Total iron:

Samples were collected in the same way as that for ferrous iron. Subsequently, however, an aliquot was pipetted into an Erlenmeyer flask containing 2 ml of concentrated HCl for stabilizing iron and preventing any precipitation. The rest of the analysis was carried out in the laboratory. In this case, the reagent used for color development was orthophenanthroline or 1,10-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) (36).

A summary of all analytical determinations used in both phases of the work, are presented in Table 1.

TABLE 1

SUMMARY OF ANALYTICAL METHODS

Determination	Std. Method 11th Ed.	Method Used	Results Expressed as	Comment
Alkalinity	Yes	Electric Titrimeter	mg/ℓ of $CaCO_3$	-
Chloride	Yes	$HgNO_3$ Method	mg/ℓ of $C\ell^-$	-
COD	Yes	Dichromate reflux	mg/ℓ O_2 consumed	Dilution technique used. No chloride correction. $AgSO_4$ catalyst
Total Iron	Yes	Orthophenanthroline	mg/ℓ - Fe	Spectrophotometer. Distilled water blank used.
Ferrous Iron	No	Bathophenanthroline (Reference (37))	mg/ℓ - Fe^{++}	Spectrophotometer and standard curve used.
Dissolved Oxygen	Yes	Winkler - modified	mg/ℓ - O_2	Azide modification
pH	Yes	Glass and calomel electrodes	pH unit	Beckman, Model N pH meter
Total Solids	Yes	-	mg/ℓ - Tol. solids	-
Sulfates	Yes	Gravimetric	mg/ℓ - SO_4	-
Carbon Dioxide	Yes	Nomograph	mg/ℓ - CO_2	This was computed from available data.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Bench Scale Studies

Raw water from Champaign-Urbana plant was used to determine the amount of D. O. obtained with different air flow rates and with different periods of aeration. These results are represented in Figures 2 and 3. Theoretically, each natural water will have its own oxygen absorption characteristics, depending on the constituents of the water. However, experience had shown that variation in water constituents did not have a pronounced effect on the absorption characteristics. Moreover, these curves were prepared so as to determine the approximate air flow rate required to obtain a specific predetermined value of dissolved oxygen concentration in a water sample to be investigated.

A number of experiments were made using Champaign-Urbana water to show the effects of oxygen concentration on the oxidation rate. These runs were made during summer and early fall and as such there was a difference between the air temperature and the temperature of the well water. Correspondingly, increases in the water temperature were observed during the various experiments.

The pH of the water could not be held constant and in each experiment, a rise of 0.3 to 0.4 pH unit following aeration was observed. This was due to the release of CO_2 and other acidic dissolved gases such as H_2S. However, the specific effect of pH or its change was not evaluated in these experiments.

The first set of graphs and tables show the results of the experiments made using the Champaign-Urbana raw water. These include the studies which were made to determine the effects of flocculation and the effects of D. O. on the oxidation rate. The initial ferrous iron content of the waters

was not the same in all the experiments. This was due to the normal variation in the ground water composition from day to day as well as the different lengths of time the water was stored in the refrigerator before an experiment could be made.

Due to variations in the initial ferrous iron concentrations of the raw waters, the parameter used to plot the oxidation curves was percent of the initial ferrous iron oxidized versus time. Quantitatively, the oxidation rate or the time needed for 50 percent conversion of ferrous to ferric iron could not be computed from the results. Each plot of "log of Fe^{++} remaining vs time" yielded a slightly curved graph. Thus, reliable estimate of the rate was not possible. However, a visual comparison of different oxidation curves reveals qualitatively the variation in the oxidation rates of the same water with different dissolved oxygen levels and of different waters with the same dissolved oxygen concentrations.

Using Champaign-Urbana raw water, Figures 4 and 5 show a slight flattening towards the end of each experiment when the ferrous iron concentration in the experimental sample approaches the limit of analytical sensitivity. A cuvette of one centimeter light path was used in the spectrophotometer throughout the study, and it appears that the short light path influenced and limited the detection of the ferrous iron, particularly when the concentration was very low (less than 0.1 ppm).

A number of experiments were performed with Champaign-Urbana raw water using low air flow rates of long durations for aeration. Table 2 gives the results of a typical experiment using 5, 10 and 15 minute aeration periods on three samples of the same water. Same results for Fe^{++} remaining with time is shown in Figure 4. From the results it is evident that the difference in D. O. contents (2.26 mg/l, 4.98 mg/l, and 6.56 mg/l) has a definite influence on the oxidation rate. There was an increase in the rate of oxidation with higher D. O. concentrations.

TABLE 2

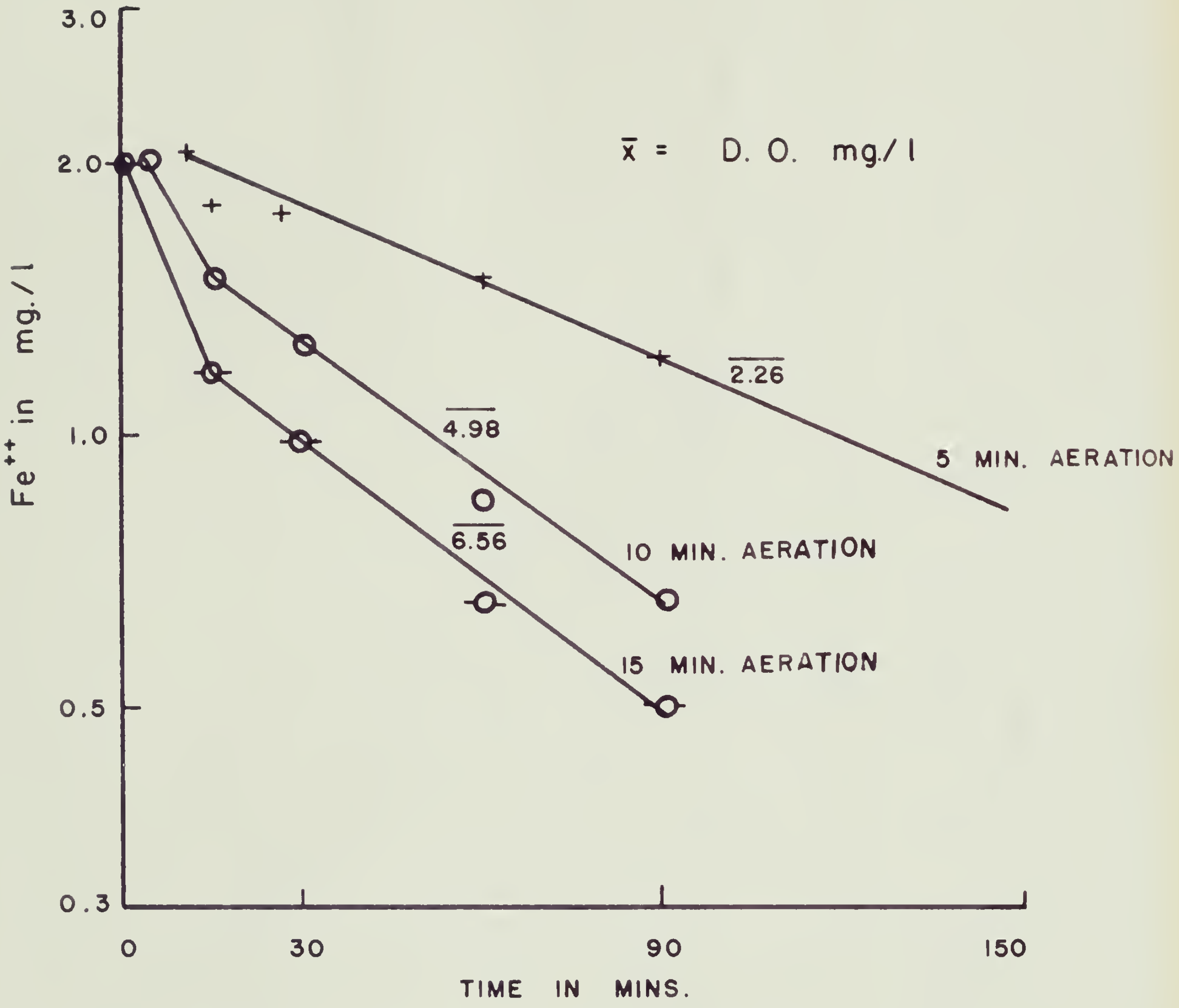
OXIDATION FOR DIFFERENT AERATION PERIODS

No.	Time (mins)	Fe^{++} (mg/l)			D. O. (mg/l)			pH			Temp. (°C)			Comments
		1	2	3	1	2	3	1	2	3	1	2	3	
1	0	-	-	2.00	-	-	0.67	-	-	7.20	-	-	14.0	Aeration for #3 started
2	5	-	2.00	-	-	0.67	-	-	7.20	-	-	13.9	-	Aeration for #2 started
3	10	2.00	-	-	0.67	-	-	7.20	-	-	13.2	-	-	Aeration for #1 started
4	15	1.80	1.48	1.36	2.26	4.98	6.56	7.20	7.35	7.45	-	-	-	Aeration ended
5	30	1.76	1.30	1.00	2.21	4.96	6.54	7.30	7.40	7.50	13.2	13.4	13.6	-
6	60	1.48	0.86	0.66	-	-	-	-	-	-	-	-	-	-
7	90	1.20	0.66	0.50	-	-	-	-	-	-	-	-	-	-
8	170	0.96	0.52	0.48	2.21	4.95	6.52	7.40	7.50	7.61	13.2	13.2	13.2	End of run

Note: Other raw water constituents for the Champaign-Urbana water are as follows:

Total iron:	2.50 mg/l
Alkalinity:	334.0 mg/l as $CaCO_3$
Hardness (total):	280.0 mg/l as $CaCO_3$
Hardness (Calcium):	143.0 mg/l as $CaCO_3$
NH_3-Nitrogen:	1.30 mg/l

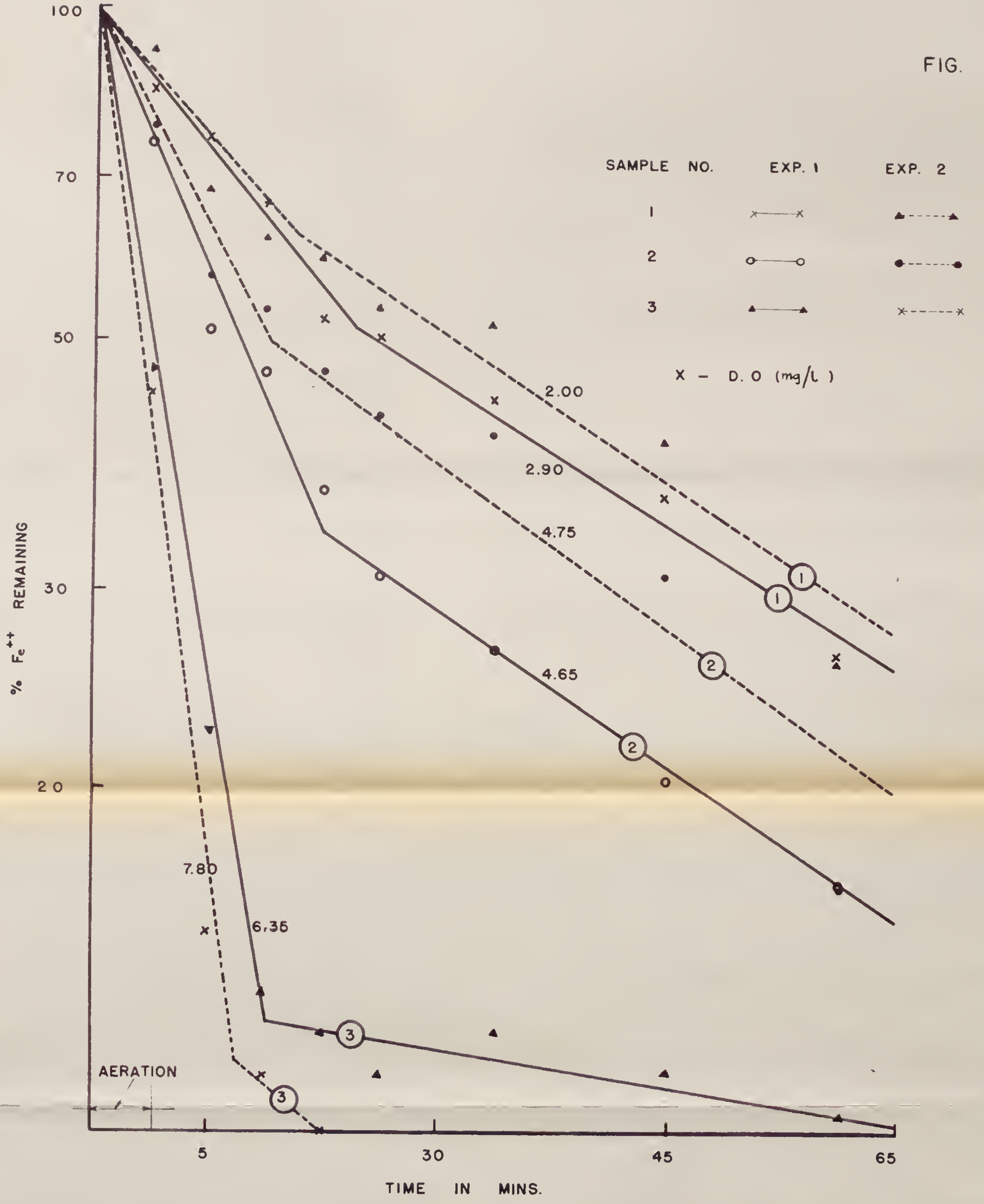
FIG. 4



COMPARISON OF OXIDATION OF IRON AT DIFFERENT D. O. LEVELS

(CHAMPAIGN - URBANA PLANT WATER)

FIG. 5



COMPARISON OF OXIDATION AT DIFF. D. O. LEVELS

(CHAMPAIGN-URBANA PLANT WATER)

The results of the two experiments described as Experiment 1 and Experiment 2 are presented in Table 3 and Table 4, respectively. The results of both these experiments are shown graphically in Figure 5. Champaign-Urbana raw well water was used for both of these experiments and the characteristics of the raw water are presented in Table 3.

The details of aeration in the two experiments were as follows:

Experiment 1

Flow meter reading: 40

Air flow rate (vide Figure 2): 7600 ml/min.

Sample No.	Length of Aeration	D. O., mg/l, (Determined)	D. O., mg/l, (from Figure 3)
1	30	2.90	2.95
2	60	4.65	4.70
3	100	6.35	6.30

Experiment 2

Flow meter reading: 50

Air flow rate (vide Figure 2): 10,000 ml/min.

Sample No.	Length of Aeration	D. O., mg/l, (Determined)	D. O., mg/l, (from Figure 3)
1	15	2.00	2.30
2	45	4.75	4.80
3	150	7.80	7.82

The results are shown in Figure 5 as percent of initial ferrous iron remaining at different time intervals. This was done since there was a slight difference in initial iron concentrations in the three water samples. By expressing the results in percent, the discrepancy between starting conditions of different samples was overcome.

TABLE 3

OXIDATION WITH DIFFERENT AERATION RATES - EXPERIMENT I

(Ferrous iron concentrations are expressed in mg/l)

No.	Time (mins)	Iron Analysis						D. O. (mg/l)			pH			Remarks
		1		2		3		1	2	3	1	2	3	
		Fe^{++}	%*	Fe^{++}	%	Fe^{++}	%							
1		2.00	100.0	1.96	100.0	1.96	100.0	0.35	0.35	0.35	7.1	7.1	7.1	Initial condition
2	0	1.68	84.0	1.48	75.5	0.92	46.9	2.90	4.65	6.35	7.3	7.3	7.3	After aeration
3	5	1.52	76.0	1.00	51.0	0.44	22.4	-	-	-	-	-	-	-
4	10	1.32	66.0	0.92	46.9	0.26	13.3	-	-	-	-	-	-	-
5	15	1.04	52.0	0.72	36.7	0.24	12.2	-	-	-	-	-	-	-
6	20	1.00	50.0	0.60	30.6	0.22	11.2	-	-	-	-	-	-	-
7	30	0.88	44.0	0.52	26.5	0.22	11.2	-	-	-	-	-	-	-
8	45	0.72	36.0	0.40	20.4	0.20	10.2	-	-	-	-	-	-	-
9	60	0.52	26.0	0.32	16.3	0.20	10.2	2.71	4.57	6.19	7.3	7.3	7.3	End of run

---

* Percent Fe^{++} remaining

TABLE 4

OXIDATION WITH DIFFERENT AERATION RATES - EXPERIMENT 2

(Ferrous iron concentrations are expressed in mg/l)

No.	Time (mins)	Iron Analysis						D. O. (mg/l)			pH			Remarks
		1		2		3		1	2	3	1	2	3	
		Fe^{++}	%*	Fe^{++}	%	Fe^{++}	%							
1		1.88	100.0	1.96	100.0	1.60	100.0	0.40	0.35	0.35	7.1	7.1	7.1	Initial condition
2	0	1.72	91.5	1.52	77.6	0.72	45.0	2.00	4.75	7.80	7.3	7.3	7.3	After aeration
3	5	1.28	68.1	1.12	57.1	0.24	15.0	-	-	-	-	-	-	-
4	10	1.16	61.7	1.04	53.1	0.18	11.3	-	-	-	-	-	-	-
5	15	1.12	59.6	0.92	46.9	0.16	10.0	1.90	4.65	7.75	-	-	-	-
6	20	1.00	53.2	0.84	42.8	0.10	6.3	-	-	-	-	-	-	-
7	30	0.96	51.1	0.80	40.8	0.06	3.8	-	-	-	-	-	-	-
8	45	0.76	40.4	0.60	30.6	0.04	2.5	-	-	-	-	-	-	-
9	60	0.48	25.5	0.32	16.3	0.02	1.3	1.90	4.65	7.72	7.3	7.4	7.45	End of run

---

* Percent of Fe^{++} remaining

The initial total iron concentrations of the samples were as follows:

Experiment 1	Total iron:	2.40 mg/l
Experiment 2	Total iron:	2.42 mg/l

The D. O. values indicated in Figure 5 represent the D. O. in the sample immediately after aeration.

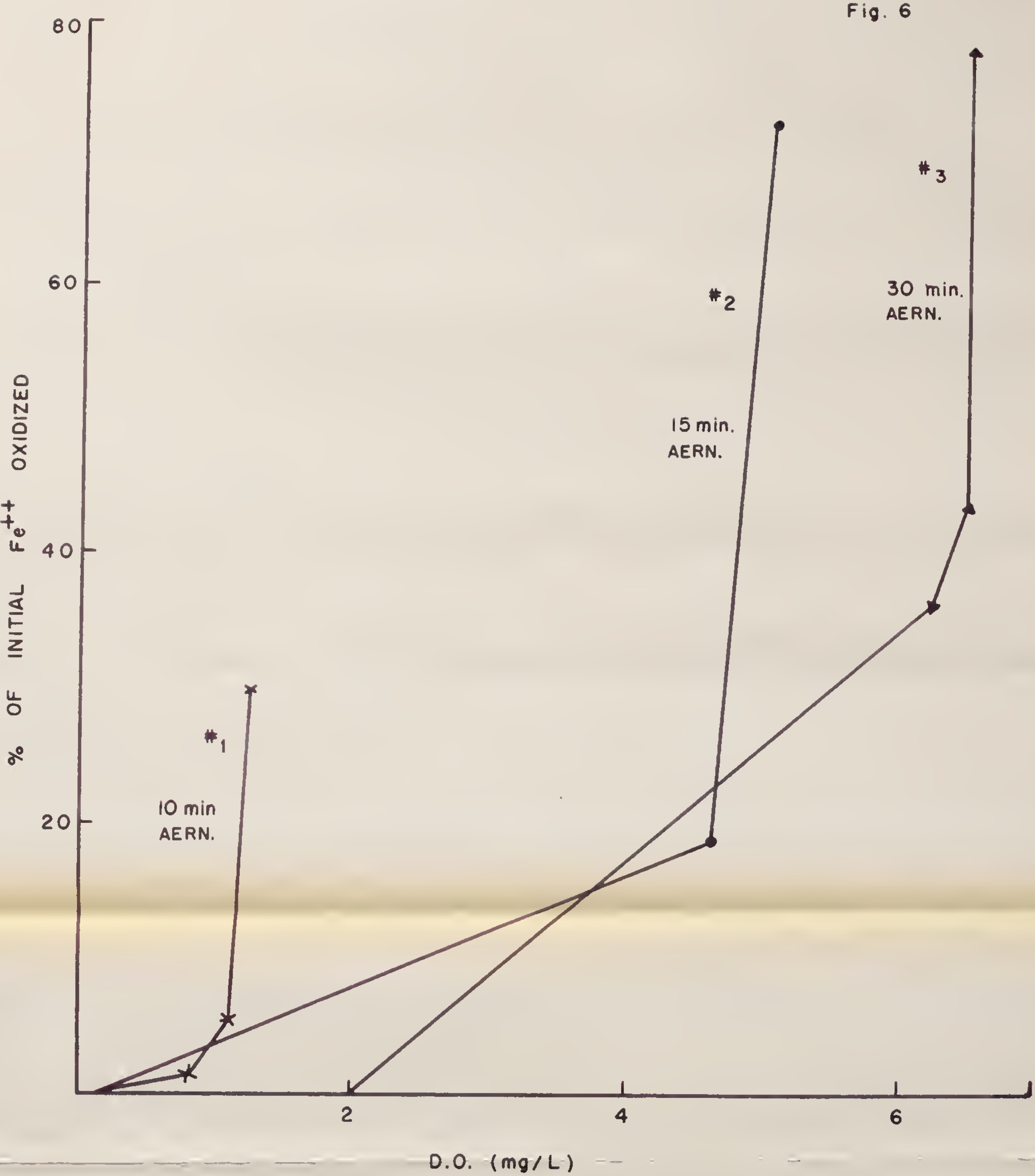
Figure 6 shows the effect of dissolved oxygen concentration on the percent oxidation of ferrous iron. This experiment was performed with raw water from Cisco, Illinois plant, having an initial ferrous iron concentration of 13.8 mg/l. To obtain different D. O. concentrations in the experimental samples, aeration with low rates was continued for different periods. In each experimental sample the gradual increase of D. O. was recorded along with the ferrous iron remaining at each time a sample was collected. The dissolved oxygen concentrations in the three samples at the end of the aeration period (10, 15, 30 minutes) were 1.25 mg/l, 5.15 mg/l, and 6.65 mg/l, respectively, in 1, 2, and 3. For oxidizing 13.8 mg/l of ferrous iron, the theoretical amount of oxygen needed is:

$$13.8 \times 0.14 = 1.932 \text{ mg/l}$$

By inspection it is evident that, in sample 1, the low D. O. limited the oxidation of ferrous iron whereas in samples 2 and 3 the dissolved oxygen was always in excess. All the three experiments were carried out for 4 hours and 10 minutes and the amounts of the ferrous iron in the three samples at the end of the experiment were 4.8 mg/l, 2.3 mg/l and 1.6 mg/l, respectively.

The results show that a D. O. value 5.15 mg/l or 6.65 mg/l did not make a significant change in percent ferrous iron oxidized which was 75 percent in both the cases. It appears that when dissolved oxygen approaches saturation, it does not have a significant effect on the oxidation rate. However, at low dissolved oxygen concentrations, the oxygen deficit will limit and retard the oxidation process.

Fig. 6



OXIDATION OF IRON AT DIFFERENT D. O. LEVELS

In the next phase of the bench scale study, raw waters from different plants were transported to the laboratory, where experiments were made to determine the pattern of oxidation in different waters which contained approximately the same amount of dissolved oxygen. The oxidation of ferrous iron has been expressed as percent of initial ferrous iron content and plotted against time on semilog paper. These results have been grouped separately and presented in Figures 7(a), 7(b), 7(c) as:

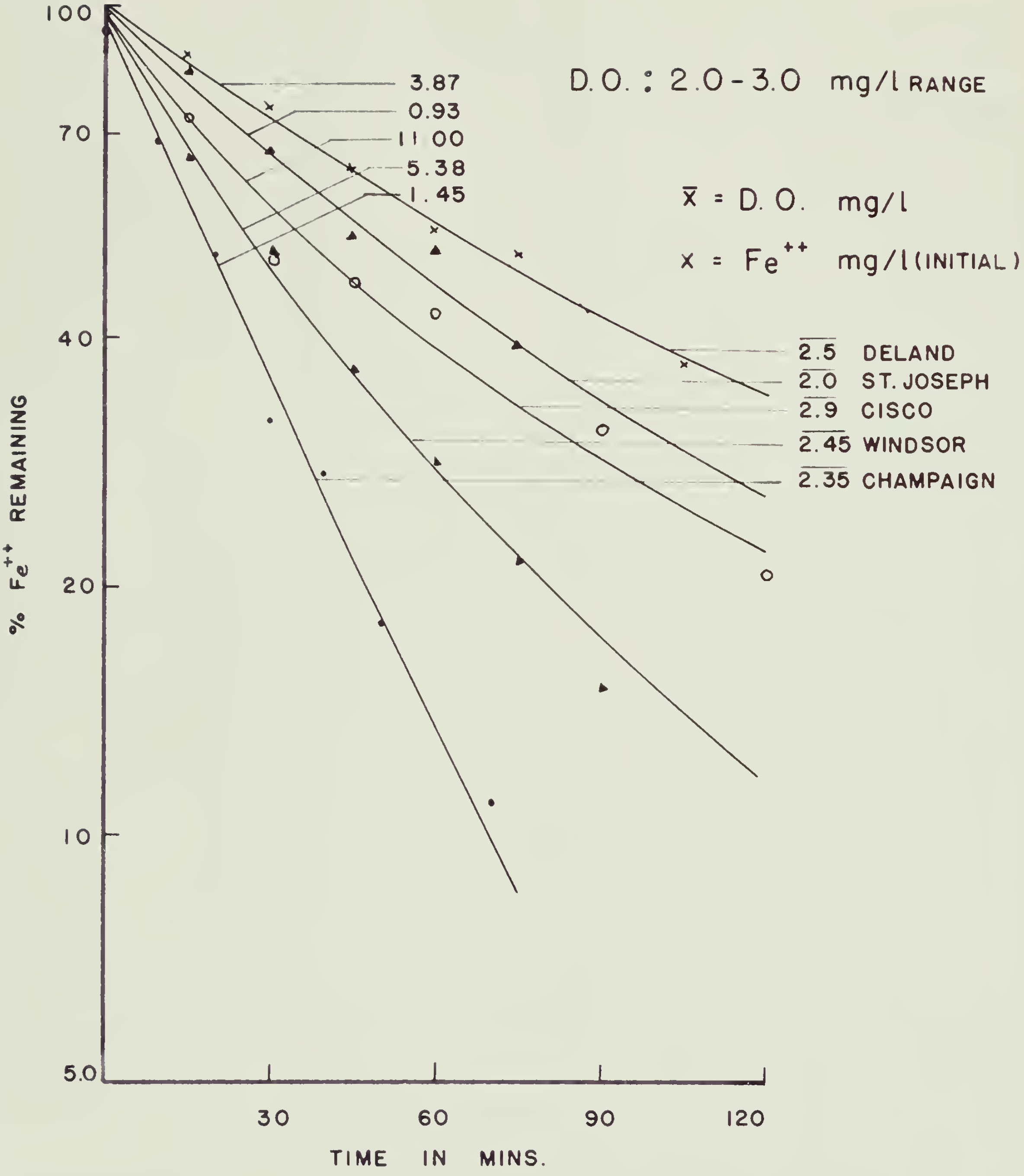
Figure 7(a) Oxidation at a D. O. level of approximately 2.0-3.0 mg/l
Figure 7(b) Oxidation at a D. O. level of approximately 3.5-5.5 mg/l
Figure 7(c) Oxidation at a D. O. level of approximately 6.0-8.0 mg/l

The D. O. obtained after aeration and the initial ferrous iron concentration for each experiment, has been shown on the graph.

A study of these graphs reveals that each water has its own specific iron oxidation pattern. Dissolved oxygen concentration is not the only criterion by which the oxidation time can be predicted. Depending on the other characteristics of the water, besides its D. O. content, the oxidation time will vary.

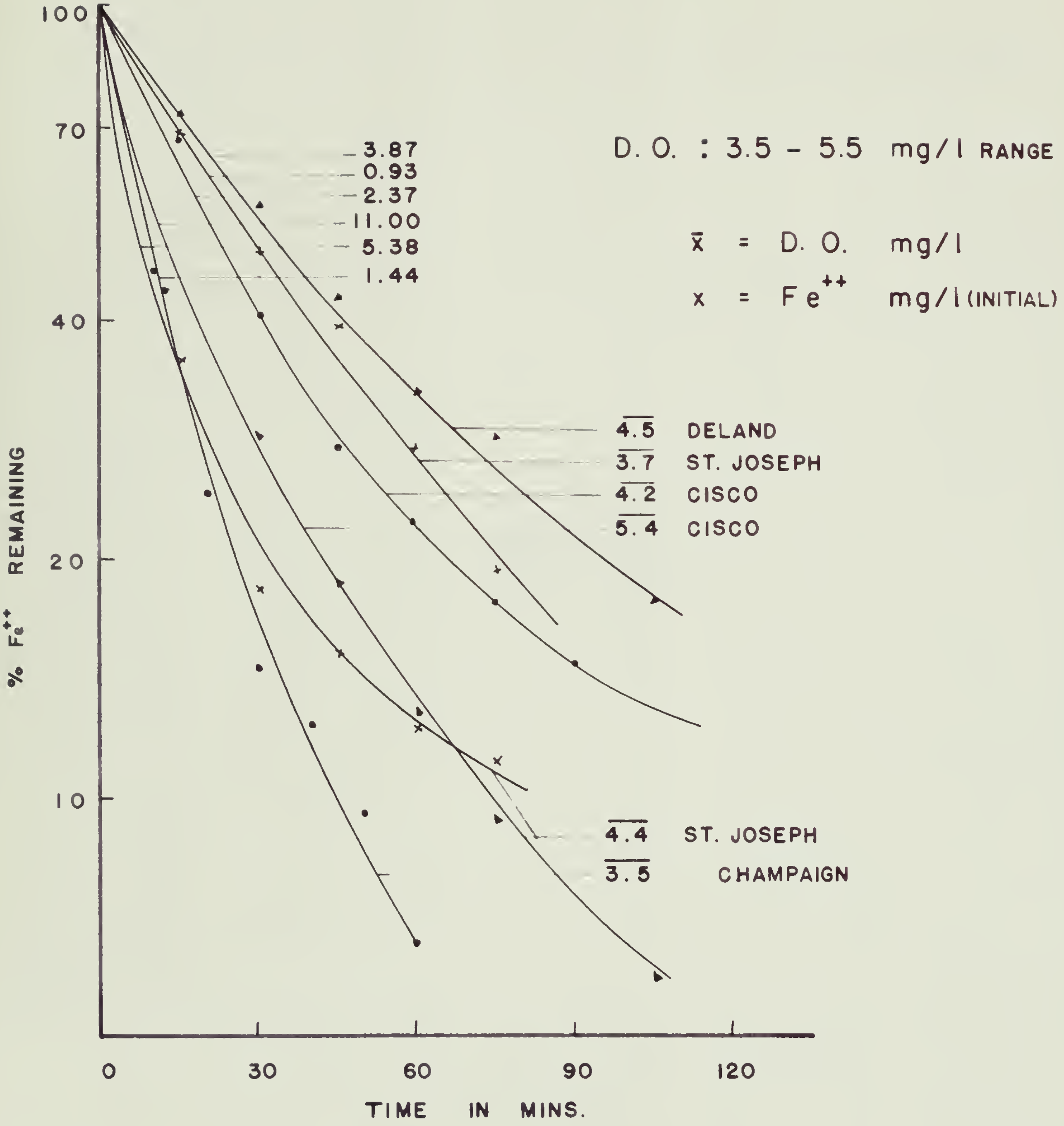
It is important to recognize that at high D. O. levels, near saturation, the rate of oxidation is not strongly affected by changes in the D. O. content. At low D. O. levels, the oxidation rate is very sensitive to slight D. O. changes. It would not appear, therefore, that the rate of oxidation is a linear function of D. O. as stated by Stumm and Lee (35). Instead, it appears to be more of a stoichiometric limitation. Operational data indicate that, most of the plants observed in this study, operate at a D. O. level close to saturation. Sometimes, the water after aeration is even supersaturated with oxygen. From the above findings it can be concluded that if the dissolved oxygen in the water following aeration is sufficiently in excess of the stoichiometric requirement, the variation in D. O. content does not significantly

FIG. 7 (a)



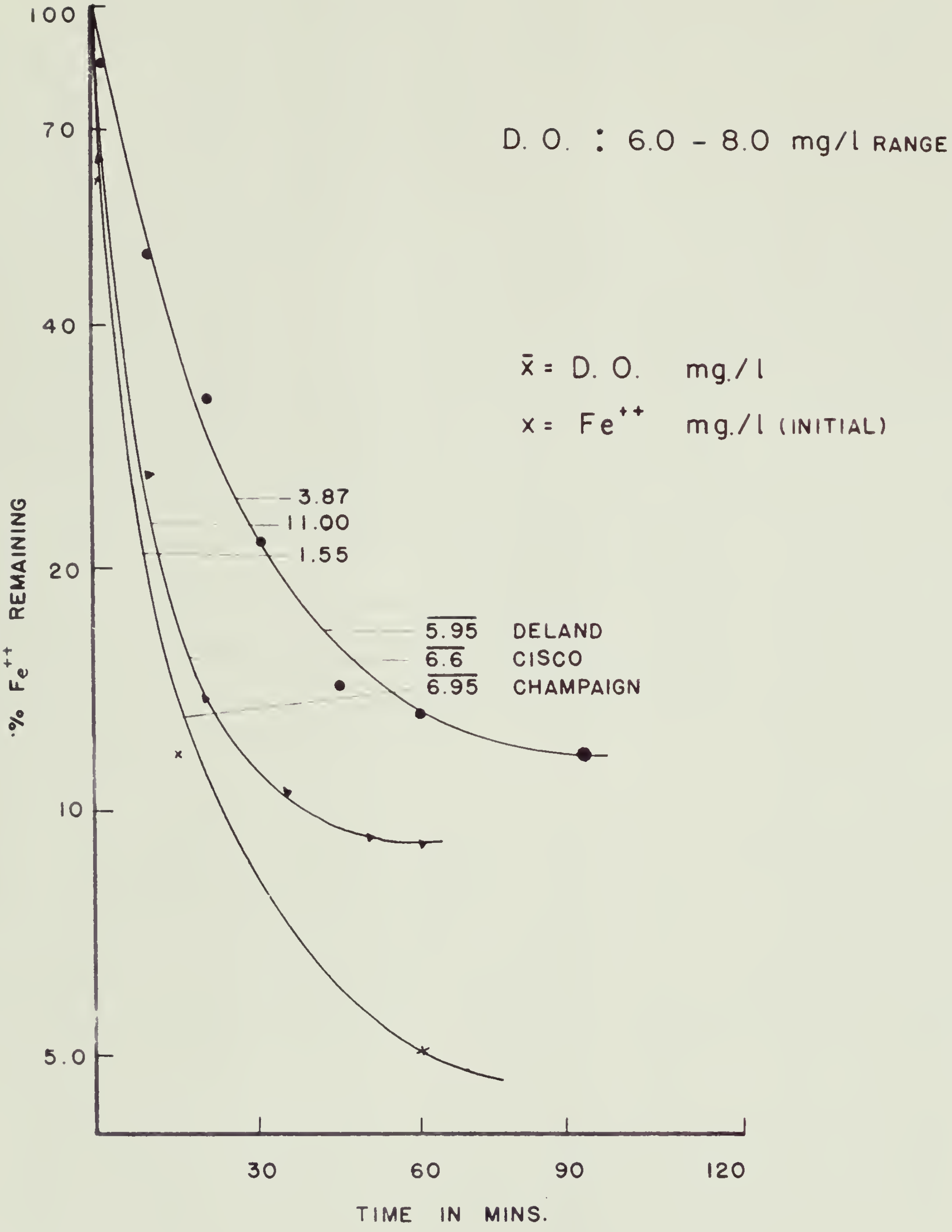
COMPARISON OF DIFF. WATERS UNDERGOING OXIDATION AT APPROX. SAME D. O. LEVELS

FIG. 7(b)



COMPARISON OF DIFF. WATERS UNDERGOING OXIDATION AT APPROX. SAME D. O. LEVELS.

FIG. 7 (c)



COMPARISON OF DIFF. WATERS UNDERGOING OXIDATION AT APPROX. SAME D. O. LEVELS

influence the rate of ferrous iron oxidation.

A number of experiments were made to study the influence of slow mixing or flocculation following the aeration of natural waters. Figure 8 represents a typical experiment of this type. Using Champaign-Urbana raw water, three different samples were prepared. By the time the experiment was started there were slight variations in the ferrous iron concentrations of the samples. However, each of the samples were aerated for ten minutes at a very low rate to achieve a dissolved oxygen content of approximately 4.4 mg/l. Then, the samples were stirred slowly for different lengths of time, namely, 10, 20 and 30 minutes for samples 1, 2 and 3, respectively.

The results, as shown in Figure 8, clearly indicate that flocculation has no effect on the oxidation rate. This is quite logical since flocculation is expected to enhance the formation of ferric hydroxide flocs and better precipitation. As such, this operation may help overall iron removal by way of better precipitation but does not influence the rate of oxidation of ferrous iron.

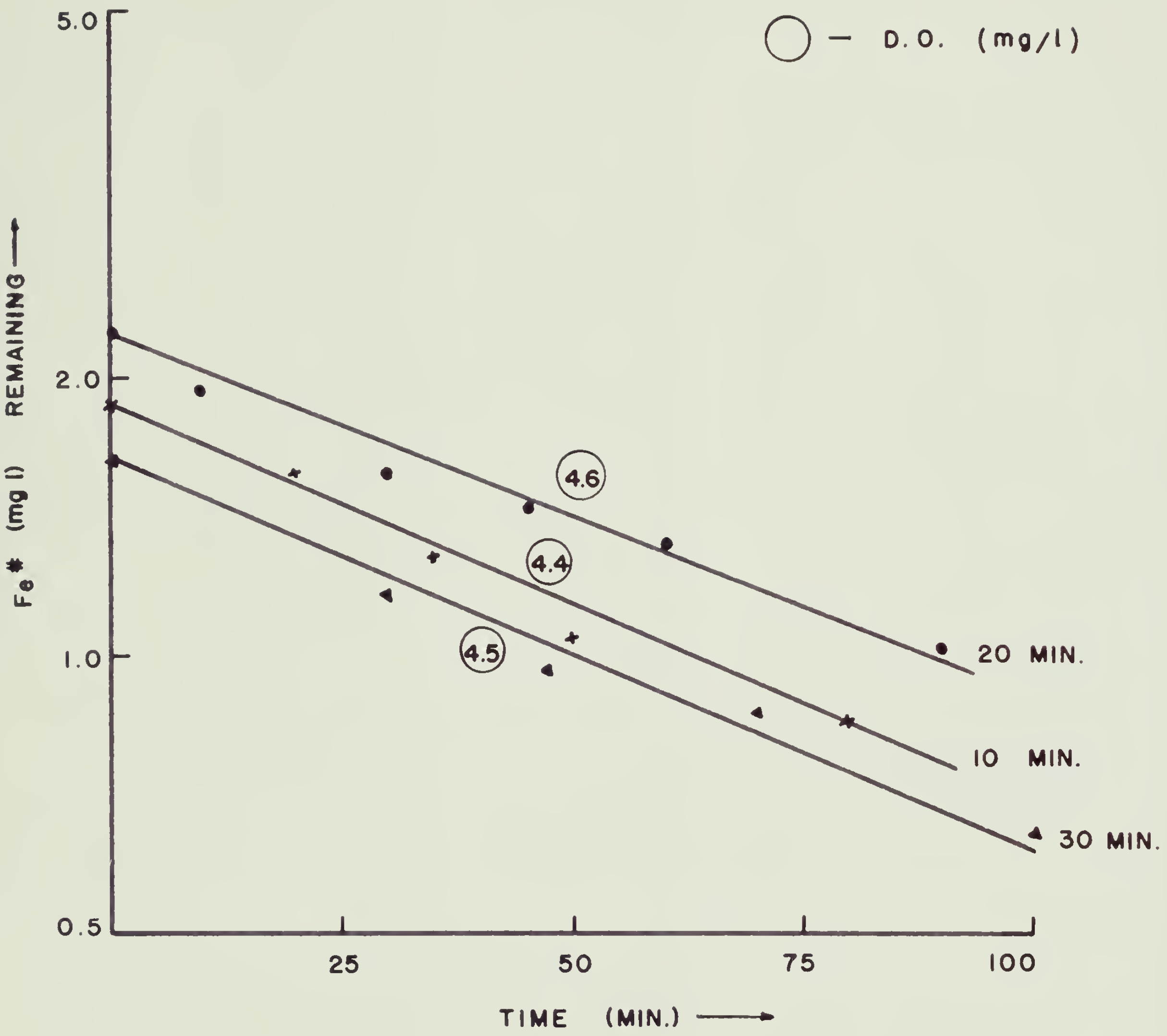
Summary and Discussion of Results Obtained from the Bench Scale Studies:

The bench scale studies were initiated chiefly to investigate the effect of varying dissolved oxygen concentrations on the oxidation of ferrous iron. Another aim was to determine if slow mixing would affect the oxidation rate.

As the study was conducted during the summer months, the tendency of the water sample temperature to rise during an experiment was eliminated by using a constant temperature bath. In practice, a rise of 2° - 3° C only in the water temperature can be expected in all iron removal plants. Hence, it was not decided to study the effects of temperature separately.

In some cases the oxidation rate apparently does not seem to be

FIG. 8



INFLUENCE OF FLOCCULATION ON OXIDATION OF IRON

(CHAMPAIGN-URBANA PLANT WATER)

constant. In almost all cases, the graph for ferrous remaining vs time on semilog paper, flattens towards the end of the experiment. This is due to the limitation in the analytical detection for ferrous iron. If a longer light path, 5 or 10 cm., were used, a better detection could have been made.

In general, the results of the bench scale studies show that the rate of ferrous iron oxidation is affected by low concentrations of D. O. especially when it approaches the stoichiometric requirement for the oxidation of ferrous iron initially present. But this influence becomes insignificant as the dissolved oxygen concentration approaches saturation. Most of the iron removal plants achieve D. O. levels which approach or even exceed saturation. So the possibility of dissolved oxygen being a significant factor in limiting oxidation rates in actual plant operations does not appear to be an important consideration.

From the results presented in Figure 8, it can be observed that flocculation does not influence the oxidation rate of ferrous iron. It is expected that by slow mixing, previously formed precipitates of ferric hydroxide can be made to agglomerate and settle out. Thus, flocculation helps in overall iron removal by promoting settling and filtration.

The findings of the bench scale studies assisted in eliminating those variables which do not significantly affect the oxidation of ferrous iron. In the next phase of the study, the D. O. was not considered as a variable. This, of course, does not quite agree with the results presented by Stumm and Lee (35).

B. Field Studies

1. Results:

Following the bench scale studies, a set of field studies was planned so as to eliminate a number of drawbacks inherent in the bench scale studies,

such as the change of temperature of the raw water samples and the oxidation of ferrous iron during transportation from the field to the laboratory. In short, field studies resulted in more carefully controlled experiments under conditions close to those found in practice.

In planning the parameters to be measured in this study, due considerations were given to the major results of the bench scale studies. The dissolved oxygen content of the water was not considered to be a significant variable in this study because most of the plants operated at D. O. levels close to saturation. Also, the temperature of the water was observed not to change significantly during actual treatment as carried out at a plant. Therefore it was eliminated as a variable. Nevertheless, it should be realized that a wide variation of temperature does effect the solubility of ferrous and ferric hydroxides and their hydroxo complexes. At the same time it may affect the oxidation rate. A small increase in temperature of 1° to 2° C will affect the solubility of iron compounds but slightly.

Oxidation studies were carried out at eight different plants using raw well waters. Pertinent operational data were also obtained from each plant. Table 5 shows the characteristics of the raw waters from the different plants investigated.

Table 6 shows the data obtained experimentally from the oxidation studies. This table contains values for half life ($T_{1/2}$), equilibrium pH, buffer capacity, β, total alkalinity, carbon dioxide, D. O. after aeration and initial ferrous iron. As the pH values of the waters were below 8.0, the alkalinity was mainly in the form of bicarbonates and is expressed as mg/l of $CaCO_3$. The buffer capacity is expressed as equivalents per pH unit.

Table 7 gives a comparison between plant operational data and the data from the field experiments. This information indicates how well the experimental system simulates the actual plant operation. The table contains

TABLE 5

RAW WATER CHARACTERISTICS

No.	Plant	Iron (mg/l)		D. O. (mg/l)	Temp. (°C)	pH	Alkalinity (mg/l) as $CaCO_3$	Chloride (mg/l)	C.O.D. (mg/l)	Sulfate (mg/l)	Total Solids (mg/l)
		Fe^{++}	Total								
1	Cisco	3.52	3.92	nil	13.3	7.45	458.0	7.5	4.6	23.6	484.0
2	Clinton	1.83	2.08	0.15	13.0	7.58	610.0	3.2	2.5	-	521.0
3	Wapella	4.72	5.09	nil	12.0	7.32	410.0	3.7	nil	12.0	446.0
4	Windsor	4.98	5.72	0.20	14.5	7.10	585.0	5.8	9.2	75.1	817.0
5	Danvers	2.00	2.48	0.05	13.5	7.47	592.0	39.2	1.6	46.0	512.0
6	Arcola	4.14	4.44	nil	12.2	7.30	354.5	16.5	26.5	25.2	861.0
7	Deland	4.03	4.73	0.05	12.3	7.10	456.0	3.7	2.3	42.8	352.0
8	Forrest	2.56	2.90	0.10	10.0	7.40	475.0	5.0	1.8	74.2	487.0

TABLE 6

EXPERIMENTAL DATA FROM THE FIELD EXPERIMENTS

No.	Plant	Initial Fe^{++} (mg/l)	D. O. after Aeration (mg/l)	$T_{1/2}$ (mins)	Equilibrium pH	Total Alkalinity (mg/l as $CaCO_3$)	Buffer Capacity (β) (Equiv./pH)
1	Cisco	3.52	6.70	25.6	7.71	458.0	1.52×10^{-3}
2	Clinton	1.83	7.35	4.3	7.78	610.0	2.28×10^{-3}
3	Wapella	4.72	6.40	36.0	7.67	410.0	1.68×10^{-3}
4	Windsor	4.98	7.2	13.2	7.48	585.0	4.47×10^{-3}
5	Danvers	2.00	6.35	6.5	7.68	592.0	1.65×10^{-3}
6	Arcola	4.14	6.70	54.0	7.49	354.5	1.29×10^{-3}
7	Deland	4.03	7.50	22.5	7.67	456.0	2.51×10^{-3}
8	Forrest	2.56	7.60	16.0	7.72	475.0	1.68×10^{-3}

TABLE 7

COMPARISON BETWEEN PLANT AND EXPERIMENTAL DATA

No.	Source	Fe^{++} (mg/l)	Total Iron (mg/l)	D.O. (mg/l)	pH	Temp. (°C)
1	Cisco - Experimental:					
	Initial	3.52	3.92	nil	7.45	13.3
	After aeration	3.28	3.84	6.70	7.71	-
	End of run	0.15	3.83	6.80	7.67	14.0
	Cisco - Plant data:					
	Initial	3.52	3.92	nil	7.45	13.3
	After aeration	0.20	-	7.05	7.69	13.9
	End of run	0.05	0.28	0.55	6.90	13.9
2	Clinton - Experimental					
	Initial	1.83	2.08	0.15	7.58	13.0
	After aeration	1.49	2.15	7.35	7.78	13.0
	End of run	0.05	2.13	7.30	7.80	14.1
	Clinton - Plant data:					
	Initial	1.83	2.20	0.15	7.58	13.0
	After aeration	0.02	-	8.2	7.75	13.6
	End of run	0.02	0.80	1.82	7.60	14.2

TABLE 7 (Cont'd.)

No.	Source	Fe^{++} (mg/l)	Total Iron (mg/l)	D.O. (mg/l)	pH	Temp. (°C)
3	Wapella - Experimental:					
	Initial	4.72	5.09	nil	7.32	12.0
	After aeration	4.28	5.09	6.40	7.67	12.0
	End of run	0.04	5.09	6.40	7.65	12.0
	Wapella - Plant data:					
	Initial	4.72	5.09	nil	7.32	12.0
	After aeration	0.05	4.84	9.00	7.73	13.0
	End of run	0.05	0.33	0.25	7.73	13.0
4	Windsor - Experimental:					
	Initial	4.98	5.82	0.20	7.10	14.5
	After aeration	4.06	5.72	7.20	7.48	-
	End of run	0.12	5.68	7.20	7.48	15.8
	Windsor - Plant data:					
	Initial	4.98	5.72	0.20	7.10	14.5
	After aeration	0.17	5.67	8.75	7.62	12.0
	End of run	0.05	0.92	-	7.72	15.0

TABLE 7 (Cont'd.)

No.	Source	Fe^{++} (mg/l)	Total Iron (mg/l)	D.O. (mg/l)	pH	Temp. (°C)
5	Danvers - Experimental:					
	Initial	2.00	2.48	0.05	7.47	13.5
	After aeration	1.58	2.56	6.35	7.68	-
	End of run	0.09	2.52	6.25	7.65	13.8
	Danvers - Plant data:					
	Initial	2.00	2.48	0.05	7.48	13.5
	After aeration	0.03	2.52	7.45	7.71	13.5
	End of run	nil	0.66	0.73	7.71	13.7
6	Arcola - Experimental:					
	Initial	4.14	4.44	nil	7.30	12.0
	After aeration	3.98	4.48	6.70	7.49	-
	End of run	0.28	4.48	6.90	7.52	13.3
	Arcola - Plant data:					
	Initial	4.14	4.44	nil	7.30	11.0
	After aeration	0.03	4.40	8.90	7.53	11.0
	End of run	0.02	0.33	0.15	7.58	11.0

TABLE 7 (Cont'd.)

No.	Source	Fe^{++} (mg/l)	Total Iron (mg/l)	D.O. (mg/l)	pH	Temp. (°C)
7	Deland - Experimental:					
	Initial	4.03	4.73	0.05	7.10	12.3
	After aeration	3.57	4.52	7.50	7.67	-
	End of run	0.17	4.31	7.50	7.65	14.0
	Deland - Plant data:					
	Initial	4.03	4.73	0.05	7.10	12.3
	After aeration	0.09	3.96	9.10	7.69	12.0
	End of run	0.04	0.38	8.95	7.65	14.0
8	Forrest - Experimental:					
	Initial	2.56	2.92	0.10	7.40	10.0
	After aeration	2.13	2.91	7.60	7.72	-
	End of run	0.15	2.92	7.65	7.70	11.0
	Forrest - Plant data:					
	Initial	2.56	2.90	0.10	7.40	10.0
	After aeration	0.06	2.90	9.10	7.88	10.5
	End of run	0.06	1.20	5.80	7.69	9.0

data on:

a) ferrous and total iron in the water at the three different stages of the treatment process namely, initially, after aeration and at the end of the run. At some plants, due to practical difficulties, water samples could not be collected at the point where it leaves the aerator. Instead, samples were collected prior to entering the filtration unit. So, in reality the data from plant operation marked as "after aeration", gives a measure of the change that occurred in the plant water after aeration and settling. This naturally cannot be directly compared with the experimental data taken "after aeration" which refer to those taken immediately after aeration before settling could take place.

Experimental data taken at the "end of run" are those which were collected at the end of the experiment which did not involve any filtration. Plant data taken at the "end of run" are those data which were collected from the treated water samples which underwent filtration. Therefore, the difference between the plant and experimental data at the "end of run" may be attributed to the filtration process.

b) the dissolved oxygen contents of the samples from the three stages of the treatment process are as described in (a). This value also did not change greatly during the treatment process. But in some plants, a marked decrease in D. O. content was noted following filtration. This was probably due to the metabolic activities of the biological growth in the filters. This assumption is purely speculative owing to the lack of any experimental data to support it.

c) The pH values for experimental and plant samples from the three stages of the treatment process are as described in (a). With most of the waters it can be seen that this variable did not change appreciably after an initial increase following aeration.

c) from Table 7 it can be seen that the increase in the temperature of the experimental as well as the plant water during the treatment process is only 1° to 2° C. This increase in temperature presumably did not have any significant influence on the rate of oxidation of ferrous iron.

The data from a typical experiment are presented in Figures 9(a), 9(b) and 9(c) and in Table 8. Figures 9(a), 9(b) and 9(c) show, respectively, the "iron oxidation", the "pH variation", and the "titration curve used to determine the total alkalinity and the buffer capacity." This experiment was done with the raw water at Cisco, Illinois.

Figure 9(a) represents the oxidation curve. The half life and the total time required for effective oxidation may be computed from the curve as follows:

a) Time required for reducing ferrous iron from 2.0 mg/l to 1.0 mg/l (50 percent reduction) is found to be 25.6 minutes from the graph.

b) Assuming the acceptable concentration of ferrous iron in the water prior to filtration to be 0.2 mg/l when the initial ferrous iron is 3.52 mg/l, the necessary reaction time can be found as follows. The well known decay equations can be used to express the oxidation of ferrous iron:

$$\lambda = \frac{0.693}{T_{1/2}} \quad \text{.........................(1)}$$

and,

$$A = A_o e^{-\lambda t} \quad \text{.......................(2)}$$

where,

λ = rate of oxidation of Fe^{++} iron

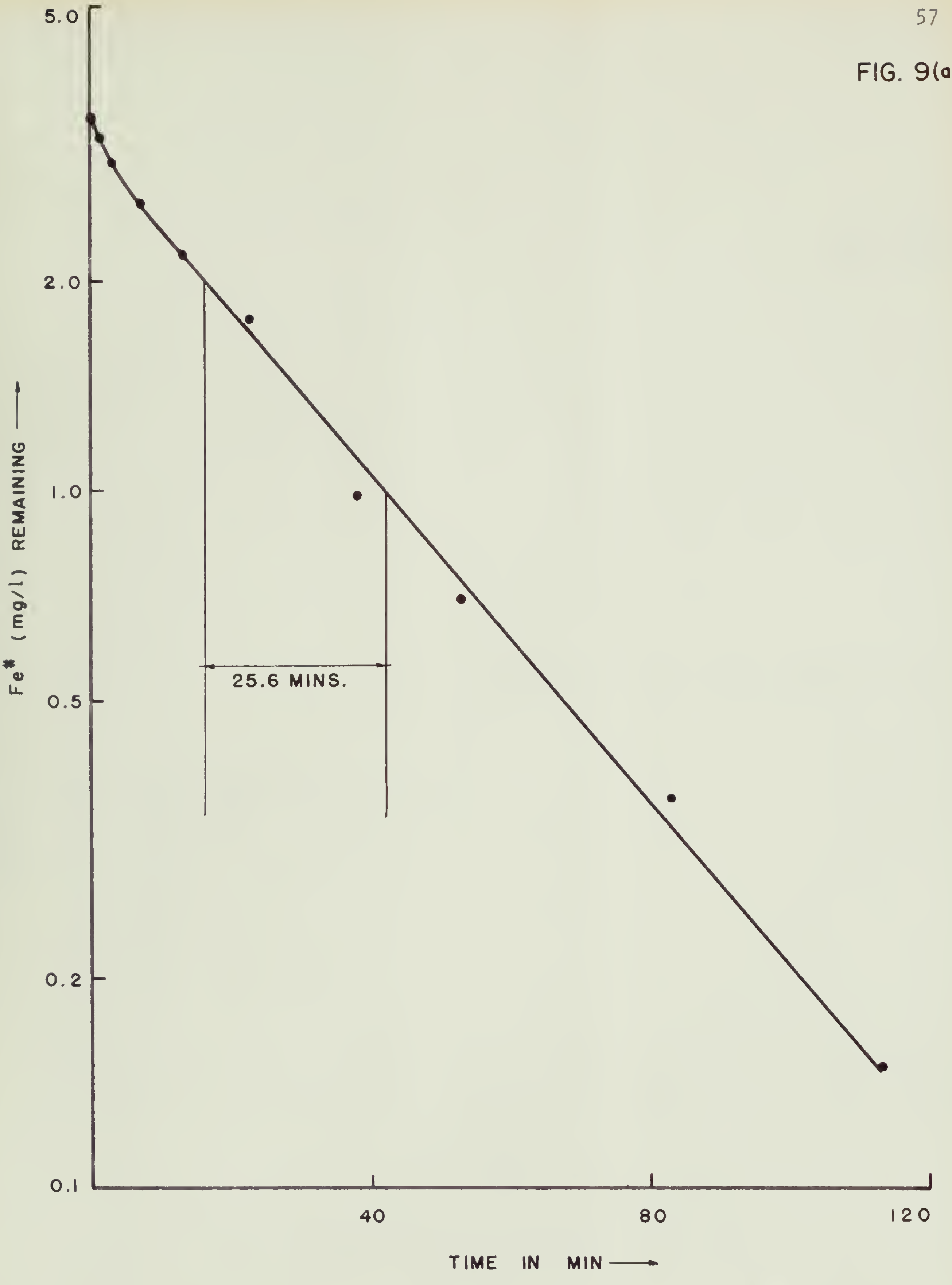
$T_{1/2}$ = half life in minutes

A = concentration of Fe^{++} iron at any time "t"

A_o = initial concentration of Fe^{++} iron

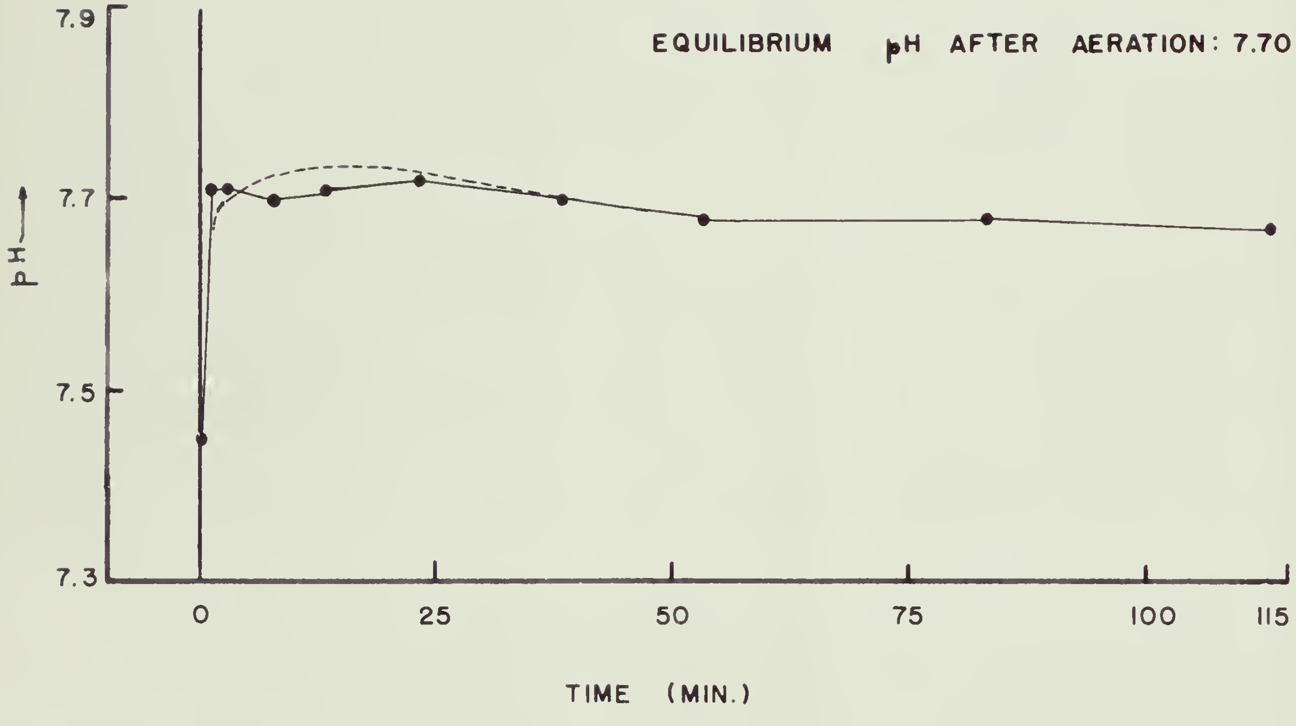
t = time elapsed in minutes

FIG. 9(a)



Fe^{++} IRON OXIDATION (CISCO, ILL.)

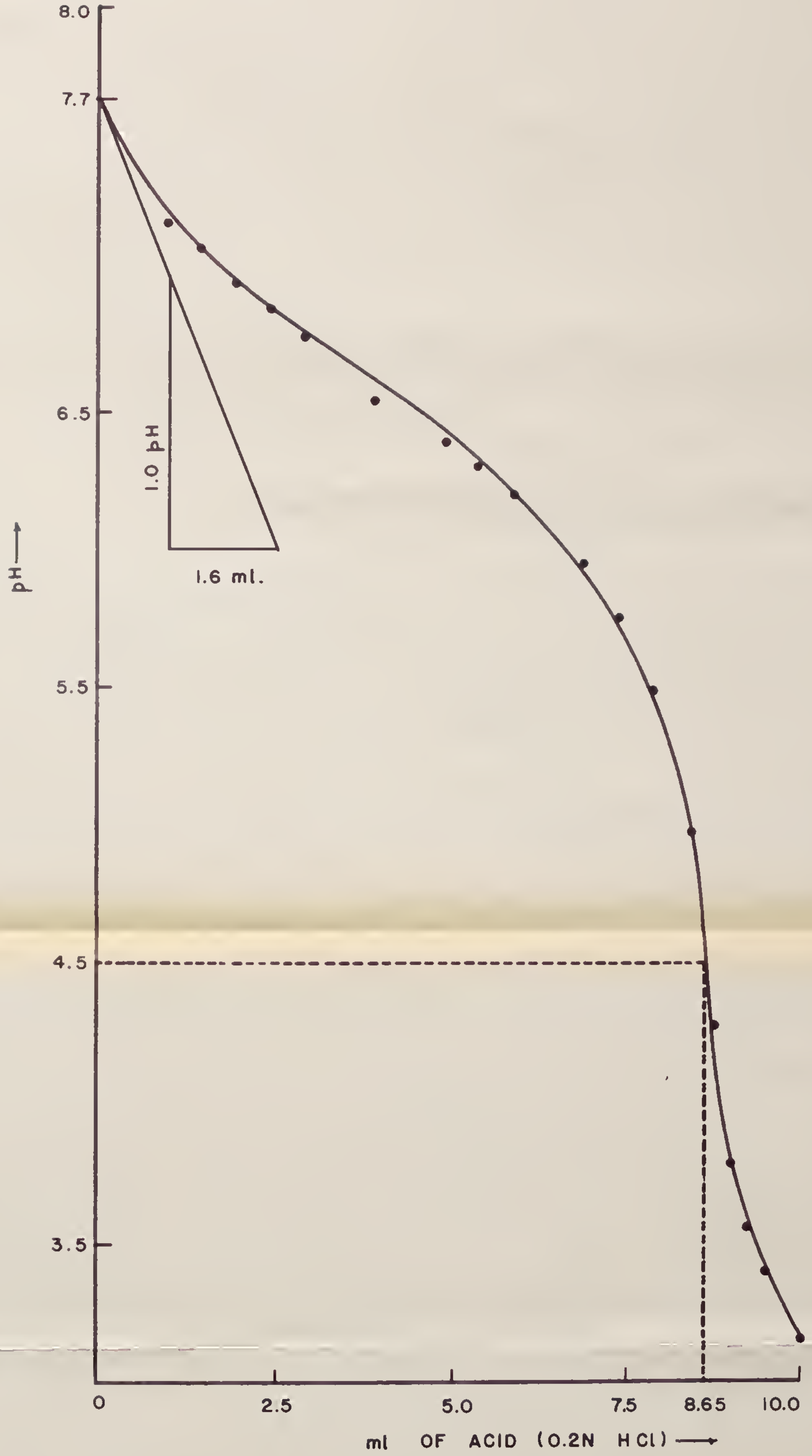
FIG. 9 (b)



pH VARIATION DURING OXIDATION

(CISCO, ILL.)

FIG. 9(c)



TITRATION CURVE

(CISCO, ILL.)

TABLE 8

EXPERIMENTAL DATA - CISCO, ILLINOIS

No.	Time (mins)	Fe^{++} (mg/l)	Total Iron (mg/l)	D. O. (mg/l)	Temp. (°C)	Remarks
1	0	3.52	3.92	nil	13.3	Initial (fresh water from well)
2	1	3.28	3.84	6.70	-	Immediately after aeration
3	3	3.00	-	-	-	-
4	7	2.60	-	-	-	-
5	13	2.20	-	-	-	-
6	23	1.76	-	-	-	-
7	38	0.98	-	-	-	-
8	53	0.70	-	-	-	-
9	83	0.36	-	-	-	-
10	113	0.15	3.83	6.80	14.0	End of run

In this case from Figure 9(a),

$$T_{1/2} = 25.6 \text{ minutes}$$

So,

$$\lambda = \frac{0.693}{25.6}$$

$$= 0.0271/\text{min.}$$

Substituting for λ in Equation 2,

$$0.2 = 3.52e^{-0.0271t}$$

or,

$$t = 103.8 \text{ minutes}$$

Thus, 103.8 minutes is the time required to reduce the initial ferrous iron concentration of 3.52 mg/l to 0.2 mg/l.

Figure 9(b) shows the variation in pH during the oxidation process. It can be seen that following aeration, there is a sharp increase in pH after which it remains fairly constant. Towards the end of the experiment, a slight decrease is noticed. This may be due to iron hydrolysis. Because of a slight variation in pH following aeration, the mean equilibrium pH was used for calculations. In this case the mean equilibrium pH was 7.70.

Figure 9(c) represents the standard titration curve for the Cisco raw water. The titrant used was 0.2 N HCl and for a 190 ml sample, the volume of titrant needed was 8.65 ml, when titrated to a pH of 4.5. Hence, the alkalinity can be computed as follows:

$$\text{Alkalinity} = 8.65 \times 0.2 \times \frac{10^3}{190}$$

$$= 9.17 \text{ meq/l}$$

Buffer capacity, β, can be computed as follows:

A tangent is drawn to the titration curve at the equilibrium pH of 7.70. The slope is 1.6 ml of titrant per pH unit.

So,

$$\beta = (1.6 \times 0.2) \times \frac{10^3}{190}$$

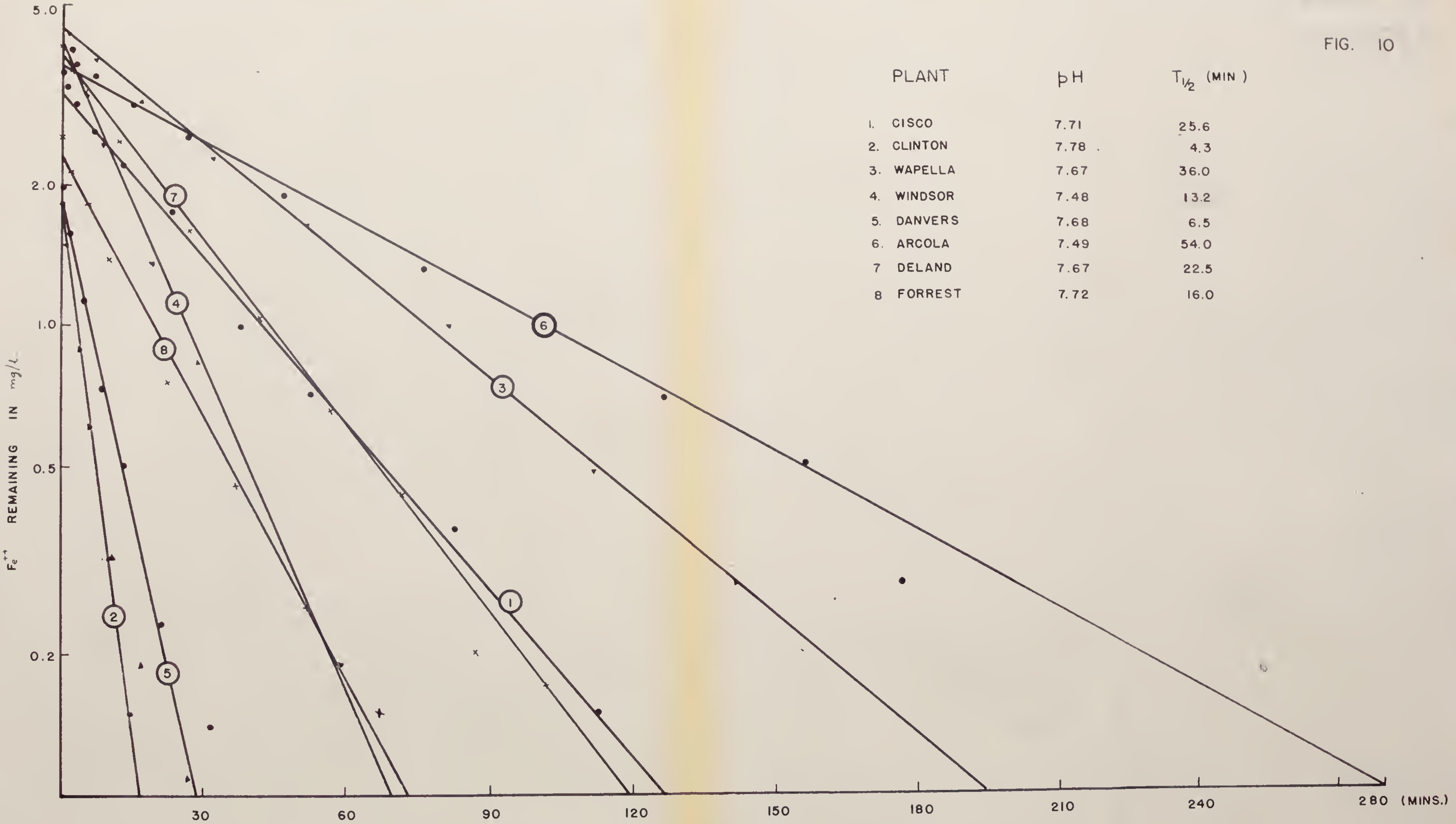
$$= 1.52 \times 10^{-3} \text{ eq/pH}$$

Figure 10 shows the oxidation curves for the eight different waters. The name of the plant, the equilibrium pH of the water, and the half life in minutes for each plant are given in the figure. There appears to be an increase in the oxidation rate of ferrous iron with higher equilibrium pH values. From the curves, it can be seen that a pH difference of 0.22 units (between Arcola and Cisco) makes a difference of 28.4 minutes in the half lives of these two waters.

The variation in pH during the oxidation process is shown in Figure 11. It is seen that irrespective of the initial pH of the water, there is a definite increase in the pH after aeration, after which it remains fairly constant. Towards the end of the experiment there is a slight increase in pH with some waters, which could be due to iron hydrolysis. The dissolved oxygen contents of the waters ranged from 6.0 to 7.5 mg/l in all the waters, but depending on the CO_2 content and probably other constituents of the water, there was a difference in the magnitude of increase in pH.

Analyses were made for sulfate, chloride, C. O. D. and total solids in all the raw waters. These data are presented in Table 5. The influence of these various constituents of the raw water on the oxidation rate was also investigated in this study. To start with, a graphical correlation was attempted separately between half life and each of these measured variables. The chloride, sulfate and C. O. D. content of the water did not seem to have

FIG. 10



PLANT	pH	$T_{1/2}$ (MIN)
1. CISCO	7.71	25.6
2. CLINTON	7.78	4.3
3. WAPELLA	7.67	36.0
4. WINDSOR	7.48	13.2
5. DANVERS	7.68	6.5
6. ARCOLA	7.49	54.0
7 DELAND	7.67	22.5
8 FORREST	7.72	16.0

COMPARISON OF Fe^{++} OXIDATION RATES OF DIFFERENT NATURAL WATERS

(SHOWING INFLUENCE OF pH ON RATE)

FIG. 11

COMPARISON OF pH VARIATIONS DURING OXIDATION

any interpretable correlation with the half life. Moreover, the concentration of all of these constituents was low as compared to another chemical constituent, the alkalinity. It was concluded that at such low concentrations, sulfates, chlorides and C. O. D. did not have any significant influence on the oxidation rate. Equilibrium pH showed some correlation with $T_{1/2}$ as shown in Figure 12. In Figure 13, the log of the total alkalinity is plotted against $T_{1/2}$. This, too, shows a probable correlation. The number next to each point on these two curves refers to the corresponding serial number for the plant as entered in Table 5.

2. Statistical Analysis of the Data:

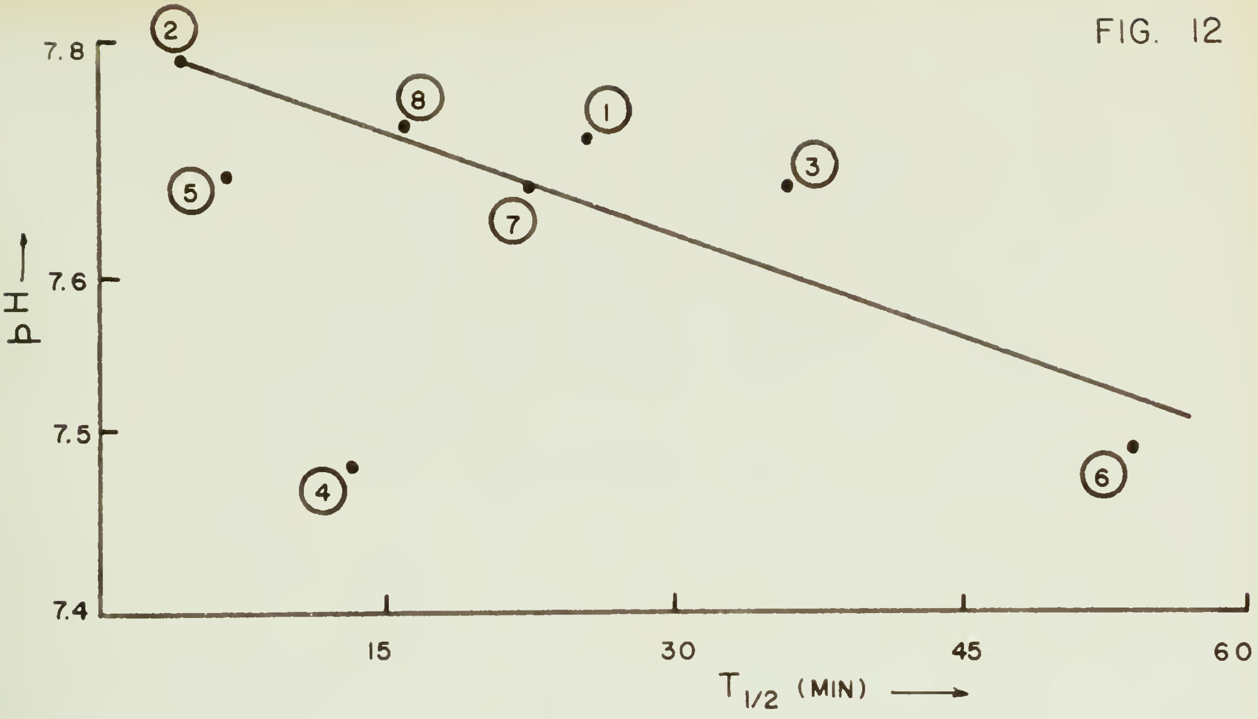
A trivariate linear regression analysis was performed on the data obtained from the field studies. For the reasons mentioned earlier, sulfate, chloride, and C. O. D. were not used as variables in this analysis. From preliminary statistical analyses, these variables seemed to have little effect on the oxidation rate. Dissolved oxygen concentrations were always near saturation and as such it was considered to be a constant in this analysis. This was also confirmed by the bench scale studies. As the pH of the waters remained constant after aeration till to the end of the experiments, it was assumed that the waters had sufficient buffering capacity to maintain a constant pH. Therefore, buffer capacity had no effect on the oxidation reaction. The consideration of equilibrium pH as stated above, takes into account the effect of buffer capacity. The remaining variables, namely the equilibrium pH and the alkalinity, seemed to have a significant influence on the oxidation rate.

The regression analysis was performed with the data from the eight field runs using the method outlined by Duncan (9).

The general equation for the universe plane of regression involving the variables, X_1, X_2, and X_3, can be represented as:

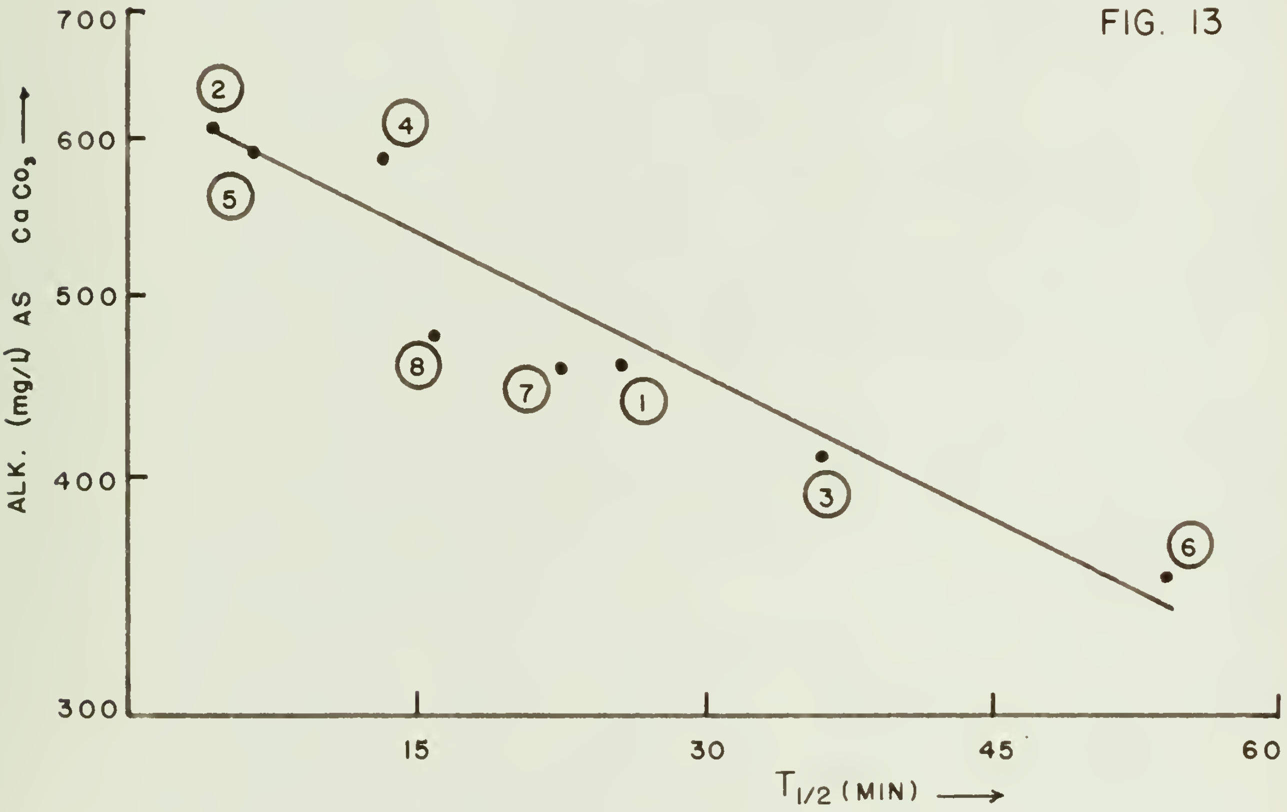
$$X_{1r'} = a_{1.23'} + b_{12.3'}X_2 + b_{13.2'}X_3$$

FIG. 12



EQUILIBRIUM pH vs. $T_{1/2}$

FIG. 13



ALKALINITY vs. $T_{1/2}$

with origin at $X_1 = X_2 = X_3 = 0$

In this equation the subscripts indicate what the variables are. Thus, $a_{1.23}$, is the constant term in the regression equation in which X_1 is the dependent variable and X_2 is an independent variable, and $b_{13.2}$, is the coefficient of X_3 in the regression equation in which X_1 is the dependent variable and X_2 and X_3 are the independent variables.

The equation derived to represent an estimate of the universe equation is,

$$X_{1r} = a_{1.23} + b_{12.3}X_2 + b_{13.2}X_3$$

$$(\text{origin at } X_1 = X_2 = X_3 = 0)$$

The derivation is made employing the method of least squares. The necessary condition for this is,

$$\Sigma\ (X_1 - X_{1r})^2 \qquad \text{a minimum}$$

In this study a general equation was set up as follows:

$$T_{1/2} = a_{1.23} + b_{12.3}\ (\text{pH}) + b_{13.2}\ (\text{Alakalinity}) \pm E,$$

where $T_{1/2}$ is the response and hence the dependent variable, pH and alkalinity are the two independent variables and "E" is an estimate for error in this analysis.

Three trials were made using different combinations of the variables and the one yielding minimum error was accepted to formulate the equation. In the first trial the variables chosen were,

$T_{1/2}$ = dependent variable
pH = independent variable No. 1
$\log_{10}$ Alkalinity = independent variable No. 2
(Alkalinity being expressed as ppm of $CaCO_3$)

The equation obtained was,

$$T_{1/2} = 187.899 + 0.062\ \text{pH} - 61.835\ \log_{10}\ (\text{Alk}) \pm 32.6$$

and the confidence limit of the analysis was 95 percent. This was discarded as the error was too high. In the second trial, the equation obtained was,

$$T_{1/2} = 111.544 - 0.381 \times 10^{14} (OH^-)^2 - 8.1015 \times 10^3 (Alk) \pm 10.06$$

where,

$T_{1/2}$ = half life in minutes
(OH^-) = hydroxyl ion concentration (from pH)
Alk = alkalinity in eq/l

In the final trial, the error was minimized by using,

$(OH^-)^2$ = variable No. 1 (influence of pH)
$\log_{10}(Alk)$ = variable No. 2 (influence of alkalinity)
(Alkalinity being expressed as ppm of $CaCO_3$)
$T_{1/2}$ = dependent variable (expressed in minutes)

The equation obtained with these parameters was,

$$T_{1/2} = 521.854 - 0.3278 \times 10^{14} (OH^-)^2 - 182.931 \log_{10}(Alk) \pm 8.10$$

The unbiased estimate of the variance around the universe plane of regression as represented by the above equation is,

$$s_{1.23} = 4.05 \text{ minutes}$$

Within 95 percent confidence limit (C. L.), the estimate of the standard error was,

$$E = 2(s_{1.23}) = 2 \times 4.05 = 8.10 \text{ minutes}$$

A universe multiple regression correlation coefficient can be estimated, the procedure and detailed calculations for which are presented in Appendix C. In this analysis the estimate of this coefficient was,

$$\hat{R}_{1.23} = 0.969$$

Hence, it may be estimated that the square of the hydroxyl ion concentration at

equilibrium pH, $(OH^-)^2$ and log of alkalinity together account for 96.9 percent of the variance in the half life of ferrous iron oxidation in all the waters investigated.

A detailed calculation procedure for the complete analysis is presented in Appendix C.

It should be realized that the relationship is simplified greatly by avoiding the interaction terms in this analysis. In the trial analyses, these interaction terms (between alkalinity and equilibrium pH) were considered and were seen to have almost no influence on the "response", that is, the half life $(T_{1/2})$.

It is felt that some other correlation is possible between these parameters which may reduce the error of analysis even more. Nevertheless, the above equation for the trivariate regression plane may be used to predict the time needed to oxidize 50 percent of the ferrous iron present in any particular water where equilibrium pH and total alkalinity are known.

3. Limitations of application of the equation:

The equation was developed using eight different waters which had low sulfate, low chloride, and low C. O. D. concentrations. A high alkalinity content is a general characteristic of most well waters in the state of Illinois. However, those waters which have low alkalinity seem to have a low rate of ferrous iron oxidation. It should be realized that such an equation, as developed in this study, is not applicable in general for all ground waters. More precisely, such an equation is valid for waters having the following characteristics which can be defined as the boundary conditions for this equation.

a) Waters should have low sulfate, chloride and other anionic species which are described in Appendix A and which may influence the oxidation rate.

b) The C. O. D. concentration, or in other words, the organic content of the water, should be low. Though not verified experimentally as yet, it is felt that organic matters may chelate ferrous and ferric iron and hence such waters may be difficult to oxidize. In the presence of a high organic concentration, this equation may not be usable in predicting the necessary reaction time for ferrous iron oxidation.

c) The D. O. content of the waters should always be in excess of the theoretical requirement for the oxidation of ferrous iron, preferably near saturation. Limited concentration of D. O., as found in bench scale studies, may greatly influence the oxidation rate and hence defeat the purpose of this equation in predicting the half life.

d) This equation may not be valid for waters undergoing large temperature changes during oxidation, i.e., greater than 2°C to 3°C.

e) The equation is valid for an equilibrium pH range of 7.48 to 7.78 and an alkalinity concentration of 354.0 to 610.0 expressed as mg/l of $CaCO_3$.

f) This equation may be useful for designing iron removal facilities. But for waters with high alkalinity and high equilibrium pH, it is applicable only for predicting that the reaction time will be less than those with low alkalinity and low equilibrium pH. The exact time may not be accurately predicted. This is evident from Table 9 where a prediction for Clinton water does not compare too well, so far as the half life is concerned. Nevertheless the equation is valid for all waters which fall within the boundary conditions mentioned above. This is because the error of such an analysis is homoscedastic. The discrepancy between the theoretical and the actual value for half life is smaller when the half life is appreciably long than it is when the half life is short.

TABLE 9

COMPARISON BETWEEN EXPERIMENTAL AND COMPUTED HALF LIFE

No.	Plant	$T_{1/2}$ (experimental) in mins.	$T_{1/2}$ (computed) in mins.	Total Reaction Time "t" in mins.*
1	Cisco	25.6	26.30 ± 8.10	106.0
2	Clinton	4.3	0.45 ± 8.10	Not determined
3	Wapella	36.0	32.58 ± 8.10	130.0
4	Windsor	13.2	12.51 ± 8.10	52.0
5	Danvers	6.5	7.11 ± 8.10	22.2
6	Arcola	54.0	52.12 ± 8.10	196.0
7	Deland	22.5	24.10 ± 8.10	90.0
8	Forrest	16.0	17.21 ± 8.10	53.0

---

* Reaction time needed to reduce Fe^{++} iron concentration to USPHS limit of 0.3 mg/l (Based on computed value of half life)

4. Testing of the Equation

In Table 9, the experimental values as well as the computed values for the half lives of different waters are presented for comparison. Also, the theoretical detention time needed for completion of the oxidation reaction has been computed. This refers to the time required between the introduction of oxygen and filtration in order to reduce the ferrous iron concentration to 0.3 mg/l. It is assumed that whatever is oxidized can be removed by settling and filtration. Hence iron in solution, which is unoxidized ferrous iron, would be present in the finished water. For satisfactory treatment, the ferrous iron content of the treated water, which would be equal to the total iron assuming one hundred percent removal of all oxidized iron, should not exceed the USPHS limit of 0.3 mg/l.

The computations for the total reaction times are made as follows from the following formulae:

$$\lambda = \frac{0.693}{T_{1/2}} = \text{rate of reduction of concentration of } Fe^{++} \text{ iron}$$

and,

$$A = A_o e^{-\lambda t}$$

where,

$T_{1/2}$ = half life (computed from the equation)

A_o = initial concentration of ferrous iron

A = final concentration of ferrous iron (0.3 mg/l)

t = total reaction time (theoretical)

5. Discussion of the Results Obtained from Field Studies

The main purpose of the field studies was to determine the relationship between the rate of iron oxidation and some of the possible constituents of ground waters which influence this rate. If quantitatively evaluated,

these relationships may be used to predict the oxidation rate if the significant independent variables in the water are known. This, in turn, would help to determine the total reaction time needed and, hence provide a design criteria for iron removal facilities.

In these studies it was found that sulfates and chlorides, if present in low concentrations, less than 20.0 mg/l, in well waters, did not influence the oxidation of ferrous iron. This is not in agreement with the findings of some investigators (30) (20). Of course, these investigators worked with controlled synthetic water systems and with much higher concentrations of sulfates and chlorides than were encountered in the natural waters in this study.

The chemical oxygen demand (C. O. D.) of the natural waters did not appear to influence the oxidation rate. It is believed that organic matter chelated with iron may affect the iron oxidation reaction even though it has not been experimentally verified. This could be more of a significant problem in the removal of iron from surface waters.

The pH dependence of the oxidation rate was very pronounced as anticipated. The results of Stumm and Lee (35) are in agreement with this finding. In their synthetic water systems, they found that an increase of one pH unit increased the rate a hundredfold. After working with natural water systems, it was evident that nothing so definite can be said based solely on pH. It must be recognized that in a heterogeneous system, as in a natural water, many other factors can influence the oxidation rate. For the waters investigated, only bicarbonate alkalinity seemed to have a significant influence on the oxidation rate in addition to the equilibrium pH. Applebaum (2) and Longley (25) observed that waters containing high alkalinities are easier to treat. However, they did not observe any definite relationship between alkalinities and oxidation rate.

In using the equation for practical design purposes, the limitations

should be realized. For a water having a composition very different from those mentioned in this study, a separate equation may have to be formulated taking into account other variables shown to influence the oxidation rate besides the pH and the alkalinity.

Much has been said about the dependence of the oxidation rate on the D. O. content or the partial pressure of oxygen (35) (18). In this study it was found that so long as the dissolved oxygen was near saturation, it did not influence the oxidation rate. From Table 6, it can be seen that the D. O. contents of all the waters studied were approximately the same, but the half lives varied immensely.

Another interesting aspect was observed (Table 7) in the plant data for D. O. at different stages. It was found that in all the plants there was a significant decrease in D. O. concentration after filtration. This decrease may be related to the biological growth in the filter. It is possible that from a study of the organic matter balance from the influent and the effluent of the filter, useful information may be obtained which may explain the loss of D. O. in the filters.

From Table 6 it can be seen that pH alone does not control the oxidation rate of iron. In the case of the raw waters at Danvers and Windsor, Illinois, the pH values are lower than at the other plants. However, due to high alkalinities the reaction times for these waters are much shorter than for the other waters. For water with a high alkalinity as well as a high equilibrium pH, the oxidation reaction is very rapid, as in Clinton, Illinois (Table 6).

V. CONCLUSIONS

The following major conclusions have been drawn from the experimental results of the bench scale and the field studies. Wherever possible, a comparison has been made between the findings of other investigators and the findings from these studies.

1. In natural water, where the D. O. concentration approaches the stoichiometric requirement for the oxidation of the ferrous iron present in the raw water, it directly controls the rate of oxidation of ferrous iron. This is in agreement with the findings of Just (19) and Stumm et al. (35). However, if the D. O. concentration is in excess of this requirement, it does not have a significant influence on the oxidation rate.

2. Temperature changes during an oxidation process may influence the solubility equilibria of ferrous and ferric iron in natural waters which in turn may control the oxidation reaction. With all natural waters studied, the maximum rise of temperature noted varied between 1° to 2°C during the process of oxidation. Such an increase in temperature presumably does not significantly affect the oxidation rate and is of little significance.

3. In the bench scale oxidation studies, it was found that slow mixing following aeration did not influence the rate of oxidation reaction. Nevertheless, it is believed that such an operation might improve overall iron removal in settling and filtration units by promoting the agglomeration of precipitated ferric hydroxide.

4. In all natural waters studied, the rate of oxidation was found to be constant and not a function of the initial ferrous iron concentration. Hence the well known "radioactivity decay equations":

$$T_{1/2} = \frac{0.693}{\lambda}$$

and,

$$A = A_o e^{-\lambda t}$$

can be conveniently employed to compute the time needed to reduce the ferrous iron concentration of a natural water by fifty percent. It is also applicable in determining the total reaction time required to reduce the ferrous iron content of natural water to an acceptable limit, 0.3 mg/l according to the USPHS standard. The values of total reaction time computed on the basis of the calculated half life are shown in Table 9.

5. The concentrations of sulfates, chlorides were found to be very low in all the waters studied. No interpretable relationship was found between the concentrations of these anions and the half life of iron oxidation. It is concluded, therefore, that low concentrations (less than 20 mg/l) of these anions do not have a significant influence on the rate of oxidation. However, this is not in agreement with the results of other investigators (30) (20) who worked with only synthetic waters in controlled homogeneous systems. Nothing definite has been found regarding the influence of such anions on the oxidation rate of ferrous iron present in natural waters.

6. The pH of all the natural waters studied were found to remain constant following aeration throughout the subsequent treatment processes employed in the plants. This phenomenon was also confirmed by the studies reported on earlier in this thesis. In both cases, however, there was a definite increase in the pH of all ground waters following aeration. This was due to the release of carbon dioxide from the ground water and subsequent equilibriation of the water with the carbon dioxide of the atmosphere. In the aquifer the waters are generally supersaturated with carbon dioxide and aeration physically strips it out. A rise in pH after aeration was also reported by Longley (25) and Applebaum (2) in their studies. No definite correlation was noted in the present study between the percent decrease of CO_2

and the increase in pH. This was not in agreement with Longley (25) who found a linear relationship between CO_2 and pH. In this study, the pH of the waters after aeration, defined as the equilibrium pH, was used as a parameter instead of the pH of the water as it comes from the aquifer. As it was not possible to hold the initial pH of the water constant without altering the original system by introducing a buffer, equilibrium pH was assumed to be a better parameter for such a study. Depending on the CO_2 content, each water exhibited a different equilibrium pH.

7. The half life of all the waters appeared to be a function of the square of the hydroxyl ion concentration of the water after aeration and the total alkalinity. As the pH of all the waters was between 7.48 to 7.78, the alkalinity was predominantly bicarbonate.

8. An equation was developed with half life as the dependent variable and $(OH^-)^2$ and log(Alk) as the two independent variables. This equation can effectively be used to predict the total reaction time needed in any iron removal plant employing aeration, from the measured values of the equilibrium pH and the total alkalinity. However, it should be realized that in a hetereogeneous system such as that of a natural water, other factors may play an important role in controlling the rate of the oxidation reaction. Hence, for waters with compositions widely different from those investigated in this study, the developed equation may not hold true. In other works, it is applicable within the boundary conditions discussed earlier. As the error of the statistical analysis is homoscedastic, the equation may be applied over the whole range of each variable considered in this analysis.

From the equation, it can be said that, in general, ferrous iron in waters with high alkalinity and high equilibrium pH can be oxidized by aeration within a reasonable length of time. Longley (25) concluded from his study that a high concentration of alkalinity favored oxidation which is in agreement with

the above finding. Applebaum (2) and Stumm et al. (35) have stressed the importance of pH in controlling the oxidation of ferrous iron. Contrary to Stumm et al. (35), who said that an increase in one pH unit would increase the rate hundredfold, it was found that nothing so definite can be concluded in the case of natural waters if only the pH is known. From the proposed equation, it is evident that $T_{1/2}$ is more of a function of alkalinity than it is of equilibrium pH.

9. Many investigators (2) (5) (14) (25) (34) believe that organic matter in natural waters may stabilize ferric hydroxide colloids or may increase the solubility of ferric iron by chelation. However, Stumm and Lee (35) are of the opinion that most organic impurities should hasten the oxidation reaction. Hence, the difficulties in iron removal under such conditions are due to slow flocculation and not to slow oxidation. Therefore, with a high concentration of organic matter, high concentration of alkalinity and high equilibrium pH may not necessarily accelerate the iron oxidation reaction in the discussed manner. The C. O. D. data from the field studies did not show any relation to the half life values of the waters investigated. Probably the oxidation reaction, as stated by Stumm and Lee (35), is not influenced by the organic matter, at least when they are present in low concentration (less than 50 mg/l of C. O. D., found in this study). However, there is not sufficient data available to support any statement regarding the significance of organic matter as it affects the removal of iron from ground waters and a generalized statement will be premature.

VI. AREAS OF FUTURE STUDY

There are many treatment plants today which have iron removal facilities that are not removing iron satisfactorily from the water. Many aspects of the problem remain to be studied if engineers are to design iron removal plants with assurance of satisfactory performance. This objective is complicated by the fact that each water has its individual characteristics.

In some of the treatment plants investigated, a tremendous loss of dissolved oxygen was noticed as a result of filtration. In Morton, Illinois, Crowser (8) observed that the loss of D. O. was always accompanied by reduction of ferric iron in the filter. Therefore, the occurrence of biological growths in filters with respect to D. O. uptake and reduction of ferric iron should be studied. Possible "nitrification" in the so called "ripened" filters should also be investigated.

Many constituents present in the hetereogeneous system of a natural water may accelerate or retard the oxidation reaction as well as affect the overall iron removal by influencing flocculation or sedimentation. The presence of Cu^{++} or other cations reportedly promotes the oxidation reaction (35) (7).

Intensive studies in these areas may offer solutions to many of the practical problems of iron removal that are yet unsolved.

VII. BIBLIOGRAPHY

1. Applebaum, S. B., "Removal of Iron and Manganese from Water", Industrial and Engineering Chemistry, 26, 10, 925 (Sept., 1934)

2. Applebaum, S. B., "Iron and Manganese Removal", Water and Sewage Works, 103, 6, 258 (June, 1956)

3. Bjerrum, J., et al., Stability Constants of Metal Ion Complexes, The Chemical Society, London, 1958

4. Bouthillier, P. H., "Removal of Iron from Water", Municipal Utilities, 89, 1, 28, (Jan., 1951)

5. Camp, T. R., Root, D. A., and Bhoota, B. V., "Effects of Temperature on Rate of Floc Formation", Jour. AWWA, 32, 11, 1913, (Nov., 1940)

6. Cher, M., and Davidson, N., "The Kinetics of Oxygenation of Ferrous Iron in Phosphoric Acid Solutions", Jour. Amer. Chem. Soc., 77, 793, (Feb., 1935)

7. Clifford, W. E., et al., "Catalyses of Air and Hypochlorite Oxidation of Uranium Compounds in Carbonate Leach Slurries", U.S.A.E.C. Report - RMO 2621, Arthur D. Little, Inc., (June, 1956)

8. Crowser, K. E., et al., "Iron Removal Practices with Illinois Ground Waters", Water and Sewage Works, 98, 12, 504 (Dec., 1951)

9. Duncan, A. J., Quality Control and Industrial Statistics, Chap. XXXIII, Richard D. Irwin, Inc., 1959

10. Feitknecht, W., "Über die Oxydation von festen Hydroxverbindungen des Eisens in wässerigen Lösungen", Zeitschrift für Elektrochemie, 63, 34 (1959)

11. Gayer, K. H., and Woonter, L., "The Solubility of Ferrous Hydroxide and Ferric Hydroxide in Acidic and Basic Media at 25° C," Jour. Phys. Chem., 60, 1569 (Nov., 1956)

12. George, P., "The Oxidation of Ferrous Perchlorate by Molecular Oxygen", Jour. Chem. Soc., London, 4349 (Nov.-Dec., 1954)

13. Hauffman, R. E., and Davidson, N., "Kinetics of the Ferrous Iron-Oxygen Reaction in Sulfuric Acid Solutions", Jour. Amer. Chem. Soc., 78, 4836 (Oct., 1956)

14. Hem, J. D., "Restraints on Dissolved Iron Imposed by Bicarbonate, Eh and pH", U. S. Geological Survey, Water Supply Paper, 1459-B

15. Hem, J. D., and Cropper, W. H., "Survey of Ferrous-Ferric Equilibria and Redox Potentials", U. S. Geological Survey, Water Supply Paper, 1459-A

16. Hutchinson, G. E., A Treatise on Limnology, Vol. I, John Wiley and Sons, N. Y., 1957

17. Johnston, J., "The Determination of Carbonic Acid, Combined and Free, in Solution, Particularly in Natural Waters", Jour. Amer. Chem. Soc., 38, 947 (May, 1916)

18. Just, J., "Kinetische Untersuchung der Autooxydation des in Wasser gelösten Ferrobicarbonats", Berichte der deutschen chemischen Gesellschaft (Berlin), 40, 3695 (1907)

19. Komolrit, K., "Measurement of Redox Potential and Determination of Ferrous Iron in Ground Waters", M. S. Thesis, Dept. of Civil Engineering, University of Illinois, 1962

20. Kraus, K. A., and Moore, G. E., "Anion Exchange Studies. VI. The Divalent Transition Elements, Manganese and Zinc in Hydrochloric Acid", Jour. Amer. Chem. Soc., 75, 1463 (Mar., 1953)

21. Lanford, O. E., and Kiehl, S. J., "A Study of the Reaction of Ferric Ion with Orthophosphate in Acid Solutions with Thiocyanate as an Indicator for Ferric Ions", Jour. Amer. Chem. Soc., 64, 291 (Feb , 1942)

22. Latimer, W. M., Oxidation Potentials, Prentice Hall, New York, 1953

23. Lee, G. F., and Stumm, W., "Determination of Ferrous Iron in Presence of Ferric Iron with Bathophenanthroline", Jour. AWWA, 52, 1567 (1960)

24. Leussing, O. L., and Kolthoff, J. M., "The Solubility Product of Ferrous Hydroxide and the Ionization of the Aquo-Ferrous Ion", 75, 2476 (1953)

25. Longley, J. M., "The Removal of Iron from Water by Aeration and Filtration", M. S. Thesis, Dept. of Civil Engineering, University of Illinois, 1961

26. Milburn, R. M., "A Spectrophotometric Study of the Hydrolysis of Iron (III) Ion. III. Heats and Entropies of Hydrolysis", Jour. Amer. Chem. Soc., 79, 537 (Feb., 1957)

27. Moore, G. E., and Kraus, K. A., "Adsorption of Iron by Anion Exchange Resins from Hydrochloric Acid Solutions", Jour. Amer. Chem. Soc., 72, 5792 (Dec., 1950)

28. Pinz, W. T., Schillings Journal für Gasebeleuchtung und Wasserversorgung, 35, 164 (Referred to in reference No. 38 in this thesis. Weston, R. S., "Purification of Ground Waters Containing Iron and Manganese", Trans. ASCE, 64, 113, 1909)

29. Pourbaix, M. J. N., Thermodynamics of Dilute Aqueous Solutions, E. Arnold, London, 1949

30. Posner, A. M., "The Kinetics of Autooxidation of Ferrous Ions in Concentrated HCl Solutions", Trans. Faraday Soc., 49, 382 (1953)

31. Rabinowich, E., and Stockmayer, W. H., "Association of Ferric Ions with Chloride, Bromide and Hydroxyl Ions (A Spectroscopic Study), Jour. Amer. Chem. Soc., 64, 335 (Feb., 1942)

32. Ringbom, A., Solubilities of Sulfides, Analytical Section, IUPAC, 1952

33. Stumm, W., "Investigation on the Corrosive Behavior of Water", Proc. ASCE, Sanitary Engineering Division, 86, No. SA 6, Part I (Nov., 1960)

34. Stumm, W., and Lee, G. F., "The Chemistry of Aqueous Iron", Schweizerische Zeitschrift für Hydrologie, Vol. XXII (1960)

35. Stumm, W., and Lee, G. F., "Oxygenation of Ferrous Iron", Industrial and Engineering Chemistry, 53, 2, 143 (Feb., 1961)

36. Standard Methods for Examination of Water and Waste Water, 11th Edition, American Water Works Association, 1961

37. Sykes, K. W., "The Reaction Between Ferric and Iodide Ions. Part II. The Influence of Ionic Associations", Jour. Chem. Soc., London, 124 (Jan.-Mar., 1952)

38. Weston, R. S., "The Purification of Ground Waters Containing Iron and Manganese", Trans. ASCE, 64, 113, (1909)

39. Weston, R. S., "Some Recent Experiences in the Deferrization and Demanganization of Water", Jour. NEWWA, 28, 27 (1914)

40. Weiss, J., "Elektronenübergangsprozesse im Mechanismus von Oxydation - und Reduktionsreaktionen in Lösungen", Die Naturwissenschaften, 23, 64 (1935)

APPENDIX A

Equilibria of Naturally Occurring Iron

The current knowledge of the various species of iron present in the ground waters as well as their chemical behavior are presented in this appendix.

Soluble ferrous iron occurs mainly in the form of the following ions:

$[Fe(H_2O_6)]^{+2}$, $[Fe(H_2O)_5\ (OH)]^{+2}$, and $[Fe(H_2O)_3\ (OH)_3]^-$ (11) (24)

The solubility of these constituents is primarily controlled by the solubility of $Fe(OH)_2$, $FeCO_3$, FeS. Other insoluble ferrous salts are of less practical significance in natural waters.

1. Ferrous hydroxide

In the absence of the CO_2 and H_2S constituents (HCO_3^-, $CO_3^=$, HS^-, $S^=$) the solubility of ferrous iron is limited by the solubility equilibria of $Fe(OH)_2$. Because of different soluble hydroxo complexes $[Fe(OH)]^+$, $[Fe(OH)_3]^-$, the solubility product for ferrous hydroxide (Equation 1 of Table A) does not define total soluble Fe^{++} iron in aqueous solution. The equilibria represented by Equations 2 and 3 in Table A must also be considered. The maximum possible concentration of Fe^{++} iron in solution is:

$$Fe(II)_t \text{ in mol/l} = Fe^{+2} + [Fe(OH)]^+ + [Fe(OH)_3]^-$$

and can be computed as follows:

$$Fe(II)_t = \frac{K_{1/2}}{K_w} (H^+)^2 + \frac{K_2}{K_w} (H^+) + \frac{K_3 K_w}{(H^+)}$$

where,

K_w = ionization constant of water (10^{-14} at 27°C)

K_1, K_2, K_3 are the equilibrium constants of the reactions 1, 2, 3, in Table A.

TABLE A

Eqn. No.	Reaction	Eqlm. Constant at 25°C	Reference
	Fe(II) Solubility		
1.	$Fe(OH)_2(s) = Fe^{+2} + 2OH^-$	8×10^{-16}	(24)
2.	$Fe(OH)_2(s) = Fe(OH)^+ + OH^-$	4×10^{-10}	(24)
3.	$Fe(OH)_2(s) = [Fe(OH)_3]^-$	8.3×10^{-6}	(11)
4.	$FeCO_{3(s)} = Fe^{+2} + CO_3^{-2}$	2.1×10^{-11}	(22)
5.	$FeCO_{3(s)} + OH^- = [Fe(OH)]^+ + CO_3^{-2}$	1.0×10^{-5}	(34)
6.	$HCO_3^- = H^+ + CO_3^{-2}$	4.8×10^{-11}	(22)
7.	$FeS_{(s)} = Fe^{+2} + S^{-2}$	6×10^{-18}	(32)
8.	$FeS_{(s)} + OH^- = [Fe(OH)]^+ + S^{-2}$	3×10^{-12}	(34)
9.	$FeS_{(s)} + 3OH^- = [Fe(OH)_3]^- + S^{-2}$	6.2×10^{-8}	(34)
10a.	$H_2S\ (aq) = H^+ + HS^-$	1×10^{-7}	(32)
10b.	$HS^- = H^+ + S^{-2}$	1.3×10^{-13}	(32)
	Complex Formation		
11.	$Fe^{+2} + Cl^- = [FeCl]^+$	2.3	(34)

TABLE A (Cont'd.)

Eqn. No.	Reaction	Eqlm. Constant at 25°C	Reference
12.	$Fe^{+2} + nCl^{-} = [FeCl_n]^{2-n}$	-	(20)
13.	$Fe^{+3} + Cl^{-} = [FeCl]^{+2}$	30.0	(31)
14.	$[FeCl]^{+2} + Cl^{-} = [FeCl_2]^{+}$	4.5	(31)
15.	$Fe^{+3} + nCl^{-} = [FeCl_n]^{3-n}$	-	(31)
16.	$Fe^{+3} + SO^{-2} = Fe(SO_4)^{+}$	1.5×10^{-4}	(37)
17.	$Fe^{+3} + HPO_4^{-2} = [Fe(HPO_4)]^{+}$	4.5×10^{10}	(21)
18.	$2\ [Fe(OH)]^{+2} = [Fe_2(OH)_2]^{+4}$	30.0	(26)
19.	$2Fe^{+3} + 2H_2O = [Fe_2(OH)_2]^{+4} + 2H^{+}$	1.4×10^{-3}	(26)

Eqn. No.	Redox Reaction*	ΔF°	$\Delta F^{\circ\prime}$ (at pH 7.0)
20.	$2Fe^{+2} + \frac{1}{2}O_2 + 2H^{+} = 2Fe^{+3} + H_2O$	-21.2	-
21.	$2Fe^{+2} + \frac{1}{2}O_2 + 4OH^{-} + H_2O = 2Fe(OH)_3(s)$	-79.4	-41.1
22.	$2Fe(OH)_2(s) + \frac{1}{2}O_2 + H_2O = 2Fe(OH)_3(s)$	-37.9	-37.9
23.	$2FeCO_3(s) + \frac{1}{2}O_2 + 4OH^{-} + H_2O$ $= Fe(OH)_3(s) + CO_3^{-2}$	-50.1	-11.8

TABLE A (Cont'd.)

Eqn. No.	Redox Reaction	ΔF° *	$\Delta F^{\circ\prime}$ (at pH 7.0)
24.	$2FeS + \frac{3}{2}O_2 + 3H_2O = 2Fe(OH)_3(s) + 2S(s)$	-113.2	-113.2
25.	$2FeS + \frac{9}{2}O_2 + 4OH^- + H_2O = 2Fe(OH)_3(s) + 2SO_4^{-2}$	-431.6	-393.3
26.	$2Fe(OH)_3 + 3S^{-2} = 2FeS(s) + S(s) + 6OH^-$	-8.6	-66.0

---

* ΔF° = Free energy when all reacting substances are at unit activity (oxygen = 1 atm.)

$\Delta F^{\circ\prime}$ (at pH 7.0) = F when all reacting substances are at unit activity except H^+ ions which are at 10^{-7} mol/l.

ΔF negative means the reaction is thermodynamically spontaneous.

Equations 20 to 25 have been taken from reference (34).

2. Ferrous Carbonate

In waters of low alkalinity, the carbonate ion concentration, even at low pH, is sufficient to limit the iron solubility. The solubility of $FeCO_3$ is much lower than that of $CaCO_3$. For a water saturated with $CaCO_3$, the concentration of Fe^{++} will be 200 times less than the concentration of Ca^{++}. This applies up to a pH of 8 to 9. Above this pH, Equation 5 of Table A applies. The maximum concentration of ferrous iron can be expressed as follows:

$$Fe(II)_t = \frac{(H^+) + 2K_6}{(Alk)\ K_6} \left[K_4 + \frac{K_5 K_w}{H^+}\right]$$

where,

$$Alk = [HCO_3^- + 2CO_3^= + OH^-]$$

$$Fe(II)_t = \text{Total } Fe^{++} \text{ in solution}$$

This expression is valid up to pH 9.0 for waters having alkalinities less than 10 mg/l. The equilibrium constants in the above equation refer to the corresponding numbered equations in Table A. At pH 8 to 11 basic carbonates, e.g., $[Fe(OH)_2 \cdot FeCO_3]$, with slightly different characteristics may form.

3. Ferrous Sulfide

The presence of small amounts of sulfur through bacterially mediated reduction of sulfate is inconsistent with the presence of appreciable amounts of soluble ferrous iron. Equations 7-10 in Table A are intended to establish such solubility relationships. According to Stumm and Lee (34) ferrous solubility in natural sulfide-containing waters is dependent up to a pH of 10 on the solubility product of FeS (Equation 7, Table A). and can be estimated as follows:

$$Fe_t^{++} = \frac{K_7}{(S_t^=)}\left(1 + \frac{(H^+)}{K_{10b}} + \frac{(H^+)^2}{K_{10b} \cdot K_{10a}}\right)$$

The equilibrium constants correspond to the respective numbered equations in

Table A. If the sulfide concentration is very low, the Fe^{++} solubility may not be limited by the solubility product of FeS. For example, at pH 7.0, when $[(\text{Alkalinity})/S^{=}_{(t)}] > 3 \times 10^{3}$, $FeS_{(s)} + CO_3^{=} = FeCO_{3(s)} + S^{=}$; $K = \frac{K_7}{K_4} = 2.9 \times 10^{-7}$, the reaction goes from left to right, i.e., the solubility product of $FeCO_3$ imposes the limit on the concentration of iron in solution.

4. Ferrous-ferric Hydroxides

A slight oxidation of $Fe(OH)_2$ tends to decrease its solubility only slightly (24). With higher oxidation, the solubility of $Fe(OH)_2$ decreases considerably. Feitknecht (10), while performing some X-ray analyses on the lattice changes in $Fe(OH)_2$ crystals during oxidation, determined that $Fe(OH)_3$ formed on the surface of Fe^{++} - Fe^{+++} hydroxo salts has the same solubility as amorphous $Fe(OH)_3$. He also postulated that the slow oxidation of Fe^{++} - Fe^{+++} hydroxo salts in buffered solutions containing low concentrations of dissolved oxygen may lead to the formation of Fe_3O_4. However, it is not yet established if magnetite is involved in the iron equilibria in natural waters (22) (29).

5. Tendency of Iron to Form Complexes

Complex formation in solution consists of the replacement of molecules in the solvate shell of the free metal cation by other ligands (3). Complex formation of iron with $(OH)^-$ ion leading to hydroxo complexes have already been accepted as postulated by Weiss (40). Some investigators have worked on the formation of complexes with other bases. Equations 11-17 in Table A illustrate the results of this work.

Anionic chloroferrate (Fe^{++}) can occur in solutions at least 4M in HCl (20) whereas chloroferrate (Fe^{+++}) can occur in solutions 1M in HCl (27). The exchange of molecule in the solvate shell of the cation can best be described as:

$$Fe(OH)^{+2} + Cl^- = FeCl^{+2} + OH^-$$

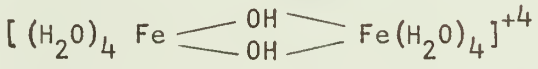
Complex formation of ferric ions with phosphate components giving various phosphate complexes is also pronounced (6). But these studies have been performed with synthetic waters under controlled conditions. In the literature there is no evidence that the results of this study apply to natural waters.

Many organic bases form very strong soluble iron complexes with ferrous and ferric ions and may increase the solubility of iron. In natural surface waters, high concentrations of organic materials such as humic acids and lignin derivatives are frequently associated with high concentrations of soluble iron. Reports on complex formation with organic matters in ground waters are, however, scarce. It is also possible that, in waters rich in organic materials, colloidal ferric hydroxide is stabilized as a sol and protected by organic compounds (16).

Ferric hydroxo complexes and, to some extent, ferrous hydroxo complexes have a pronounced tendency to take part in polymerization reactions. This has been suggested by some (34) as a possible mechanism for the precipitation of insoluble colloidal iron hydroxo polymers. The simplest reaction producing dimeric species is:

$$2[Fe(H_2O)_5(OH)]^{+2} = [Fe_2(H_2O)_8\ (OH)_2]^{+4} + 2H_2O$$

The dimeric ion is of sufficient stability to exist in appreciable concentrations (Equation 18 in Table A). The probable bond between the two metal ions involves two hydroxo bridges.



$$[(H_2O)_4\,Fe \begin{smallmatrix} OH \\ OH \end{smallmatrix} Fe(H_2O)_4]^{+4}$$

The dimers provide extra hydroxides through hydrolysis and form more hydroxo bridges (34).

$$[Fe_2(H_2O)_8\ (OH)_2]^{+4} + H_2O = [Fe_2(H_2O)_7\ (OH)_3]^{+3} + H_3O^+$$

$$[Fe_2(H_2O)_7\ (OH)_3]^{+3} + [Fe(H_2O)_5\ (OH)]^{+2} = [Fe_3(H_2O)_5\ (OH)_4]^{+5} + 2H_2O$$

A series of reactions like these lead to the formation of metastable hydroxo polymers of iron which ultimately precipitate. Since cationic ferric hydroxo compleses prevail in slightly acid or neutral acid solutions, positively charged ferric oxide colloids are formed in this pH range. There is much evidence that colloidal ferric oxides are stabilized by organic matter which may exist in nature (16).

The simultaneous occurrence of so many independent and interdependent equilibria makes it difficult to evaluate the characteristics and chemical behavior of aqueous iron in natural waters during the process of valence change by any chemical method.

6. Oxidation-Reduction

From the previous discussions it is apparent that both ferrous and ferric iron are not very soluble in natural bicarbonate-bearing waters. Despite this fact, the iron content of natural water is of considerable significance. In the chemistry of water treatment, the capacity of iron to undergo reversible oxidation-reduction reactions plays an important role.

The intensity of relative oxidizing power of reductants or oxidants is conveniently expressed by the redox potential which is a characteristic of the redox system in the thermodynamic equilibrium. Thus, in describing any oxidation-reduction reaction, as in ferrous iron oxidation, the redox potential may prove to be an important tool.

A change in the activity affects the electrode potential of the system according to Nernst's Equation. The oxidation potential depends upon

the hydrogen ion concentration of the system. Hence the potential and pH of the system may be represented by a point on the pH-Eh diagram (29). For the iron water system a pH-Eh diagram has been shown by Hem (14).

The Nernst equation for a Fe^{++} - Fe^{+++} system can be expressed as follows (14):

$$E = +0.771 + 0.059 \log \frac{(Fe^{+3})}{(Fe^{+2})} \quad \text{at } 25^{\circ}C$$

where,

E = potential established by dipping a clean platinum wire into a solution containing Fe^{++} and Fe^{+++} ions.

Many investigators have tried to use this method for the investigation of oxidizing and reducing conditions in natural waters. However, extensive measurements of redox potential have failed to yield results amenable to intelligible interpretation. With natural waters it is difficult to keep all the variables under control and establish an equilibrium condition at the electrode surface. Such systems are complex and involve numerous reacting components. For example, various soluble iron ions, dissolved oxygen, pH, alkalinity, organic oxidation and reduction systems all influence the oxidation-reduction potential. Few of these components are controllable in natural water systems. The presence of ferrous and ferric iron in natural waters is definitely reflected in the redox potential of the water. But the use of the redox potential equation or its modification to explain the ratio of soluble ferrous to ferric ratio in natural waters is yet to be shown.

From Equations 20 to 25 in Table A it can be seen that reactions shall proceed theoretically from left to right even for pH conditions existing in natural waters. Ferric iron may be reduced in the presence of suitable reductants (Equation 26, Table A). It is evident that in some natural waters ferric iron may be reduced by the presence of H_2S constituents which are unstable thermodynamically in the presence of dissolved oxygen. This may account

for an increase in the ferrous iron content of some natural waters as they come out of the aquifer. The amounts of iron present and their oxidation states are consequently the results of the chemical equilibria that involve other ions. Because the oxidation and reduction of iron and the precipitation of ferric hydroxide are relatively rapid at pH levels commonly found in the natural water systems, the iron contained in natural waters should generally be in equilibrium with other constituents of the water and with the solid phase materials in contact with water.

The most well defined equilibria in natural ground water is the carbon dioxide-bicarbonate-carbonate equilibria. It determines the limits for solubility of iron under reducing conditions, because of its effect on pH and because of the low solubility of $FeCO_3$. The presence of high bicarbonate may prevent changes in Eh from affecting iron content.

7. Natural Buffer System

The buffer system for most natural ground waters can be evaluated in terms of the bicarbonate-carbonate system. The free carbon dioxide or the undissociated carbonic acid is difficult to determine but it can be computed within limits from initial pH and bicarbonate and carbonate concentrations. The dissociation of carbonic acid (H_2CO_3) involves the following steps:

$$H_2CO_3 \rightleftarrows HCO_3^- + H^-$$

$$\frac{(H^+)\ (HCO_3^-)}{(H_2CO_3)} = 4.16 \times 10^{-7} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$HCO_3^- \rightleftarrows CO_3^= + H^+$$

$$\frac{(H^+)\ (CO_3^=)}{(HCO_3^=)} = 4.84 \times 10^{-11} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

For natural waters subject to a constant partial pressure of CO_2 and in contact with inert solids in the aquifer, the relative amounts of each species can be computed theoretically. This approach naturally assumes that all dissolved CO_2 combines with water and forms carbonic acid although it is not precisely the case. These steps are of considerable importance in controlling the hydrogen ion concentration in natural water. In waters containing large amounts of H_2CO_3 constituents, the following equilibria are also quite common.

$$CaCO_3 + H^{+1} \rightleftarrows HCO_3^{-1} + Ca^{+2}$$

$$FeCO_3 + H^{+1} \rightleftarrows HCO_3^{-1} + Fe^{+2}$$

The reaction which is responsible for the precipitation of ferrous iron in natural water when it is stored involves oxidation and hydrolysis and can be expressed as follows:

$$Fe^{+2} + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^{+1} + e^{-1}$$

$FeCO_3$ is not stable under oxidizing conditions. Due to oxidation and precipitation of each Fe^{++} ion three hydrogen ions are released. As a result pH may change appreciably during oxidation (14).

Knowing the activities of bicarbonate, calcium and ferrous iron, the pH of the system may be computed from the $FeCO_3$ and $CaCO_3$ equilibria as follows:

$$pH = -\log \frac{(Fe^{+2})\ (HCO_3^{-1})}{4.6 \times 10^{-1}}$$

$$pH = -\log \frac{(Ca^{+2})\ (HCO_3^{-1})}{0.97 \times 10^{2}}$$

These two pH values can conveniently indicate the degree to which the solid phase carbonate will be in equilibrium with water (14).

If the ground water involves calcium carbonate and ferrous carbonate equilibria, the measured and computed pH values should tally within ± 0.5 pH unit for both the systems. On the other hand if it is in agreement with only one system, it will indicate the dominance of such a system on the equilibrium conditions. Total disagreement indicates non-equilibrium conditions.

APPENDIX B

Equipment and Analytical Techniques

1. List of Equipment and Manufacturers

a. Air compressor - All State Air Compressor Company

b. Diffuser for aeration - Carborundum cylinder, 3 inches long, 1 inch i.d., 1 3/4 inches o.d.

c. Air flow meter - Fisher Scientific Company
Tube No. 2-L-150/13 with 1/16" diameter glass float.

d. pH meters - Beckman Instruments, Inc.
  i) Model N - Battery operated.
  ii) Model H_2 - Line operated.

e. Spectrophotometer - Beckman Instruments, Inc.
  Model DU.

2. Analytical Techniques

A. Total Hardness Determination

1. Preparation of Titra Versenate Solution

Dissolve 4.0 gms of TitraVer powder (Cat. No. 204) in 750 ml of distilled water. Titrate 25 ml of standard $CaCl_2$ solution with TitraVer solution and adjust the dilution of TitraVer stock so that 1 ml of this solution is equal to 1 mg of $CaCO_3$ in strength.

2. Preparation of Standard Calcium Chloride Solution

Dissolve 1.000 gm of reagent grade dry primary standard $CaCO_3$ (Cat. No. 120) in a little dilute HCl. Dilute exactly to 1 liter. One ml of this solution represents 1 mg of $CaCO_3$.

3. The UniVer Hardness Test

Add 1 gm of UniVer I or II powder to a 50 ml sample. Titrate with

standard TitraVer until the color changes from red to pure blue. Total hardness expressed as mg/l of $CaCO_3$ is determined by multiplying the volume of titrant in milliliters by 20 to express the results in mg/l. For other size samples another multiplier is used.

B. Calcium Hardness Determination

Reagent indicator - CalVer II

End point - wine red to blue

Quantity - 0.1 gm of dry powder per 50 ml of sample

Procedure:

1. Transfer a 50 ml (or other convenient size) sample into a beaker
2. Add 1 ml of 8N NaOH solution
3. Add 0.1 gm of CalVer II indicator
4. Titrate with standard TitraVer solution till color changes
5. Computation of Calcium hardness is the same as that for total hardness.

C. Total Alkalinity and Buffer Capacity

Titrant - 0.2N HCl

Equipment - Beckman Model H_2 pH meter
Magnetic Stirrer

Procedure:

1. Take 100 to 200 ml of water sample and place it on magnetic stirrer.
2. Carry out titration with 0.2N HCl with incremental addition of titrant and record both pH change and amount of titrant added (cumulative).
3. For total alkalinity, continue titration down to pH 4.5.

4. Computation:

i) Alkalinity:

If x = milliliters of 0.2N HCl needed for the titration and,

y = size of sample,

then,

$$\text{Alk.} = \frac{(x)\ (0.2)}{y},\ \text{eq/l} = \frac{(x)\ (0.2)\ (50 \times 1000)}{y},\ \text{mg/l as CaCO}_3$$

ii) Buffer Capacity:

Draw a tangent to the titration curve at the point of equilibrium pH. The slope of the tangent gives the buffer capacity (β).

If x = ml of 0.2N HCl to change the pH by y units in a sample of z ml, then,

$$\beta\ (\text{equivalents/pH unit}) = \frac{(x)\ (0.2)}{(z)\ (y)}$$

Theoretically, it can be determined as follows (33):

$$\beta = 2.3\ \left[\frac{(H^+)(\text{Alk})}{(H^+) + 2K_2}\ \frac{(H^+)}{(H^+) + K_1} + \frac{K_2}{(H^+) + K_2} + (H^+) + (OH^-)\right]$$

where,

β = buffer capacity in equivalents per pH unit

K_1, K_2 are the first and second acidity constants of $CO_2 \cdot H_2O$ (Carbonic acid), respectively ($K_1 = 4 \times 10^{-7}$ and $K_2 = 4.6 \times 10^{-11}$).

H^+ = Hydrogen ion concentration in Moles/liter

Alk. = Alkalinity in equivalents per liter.

Therefore, β depends on the alkalinity and, even more so, on the pH of the water.

D. Chlorides, Sulfates, Total Solids, C. O. D.

These determinations were made exactly in the same manner as outlined

in the Standard Methods - 11th Edition.

For determining C. O. D., the dichromate oxidant as well as the ferrous ammonium sulfate titrant were diluted 10 times as the C. O. D.'s of the waters investigated were very low.

E. Dissolved Oxygen

The Modified Winkler test as described in the Eleventh Edition of Standard Methods was used for D. O. determinations. On field samples, the final titration with $Na_2S_2O_3$ was performed in the laboratory.

F. Ferrous Iron

The analysis was performed as outlined by Stumm and Lee (23) using bathophenanthroline.

1. Reagents:
    - a. Indicator reagent - Bathophenanthroline; 4,7 -diphenyl- 1, 10 phenanthroline ($C_{24}H_{16}N_2$)

Dissolve 0.0332 gm of bathophenanthroline crystals in 50 ml of reagent grade absolute ethyl alcohol and dilute to 100 ml by adding distilled water.

- b. Extracting alcohol - reagent grade isoamyl alcohol
- c. Diluting alcohol - reagent grade ethyl alcohol
- d. Sodium acetate - 10% solution. Dissolve 10 gm of sodium acetate in 100 ml of distilled water.
- e. Standard iron solution:

Ferrous ammonium sulfate ($Fe(NH_4)_2\ SO_4 \cdot 6H_2O$) was used to make standard solutions. Dissolve 0.7022 gm of dried reagent grade ferrous ammonium sulfate in 20 ml of conc. H_2SO_4 and 50 ml of iron free distilled water. Dilute to 1 liter by adding distilled water, shake well. This stock solution therefore contains 0.1 mg of Fe^{++} iron per 1 ml. This is a very stable solution.

Still, it was stored in dark bottles. Any dilution of the stock could be made for experimental purposes. From time to time, for reference, another stock solution was made out by dissolving highly polished "iron wire for standardizing" in 20 ml of 6N · H_2SO_4. This was diluted to 1 liter to give 0.2 mg of ferrous iron per ml of the stock solution.

2. Procedure for determination of ferrous iron:

a. Pipette 5 or 10 ml of sample into a 125 ml separatory funnel. The size of the sample will depend on the concentration of iron.

b. Add 4 ml of standard sodium acetate solution to the sample.

c. Add 15 ml of standard bathophenanthroline to the sample and shake it lightly.

d. Add 10 ml of isoamyl alcohol for extracting, shake vigorously and let the sample stand quiescently for at least 5 minutes.

e. Discard the lower portion of the liquid and transfer the top colored fraction completely in a 50 ml volumetric flask. Dilute the sample up to 50 ml mark with reagent grade ethyl alcohol.

f. Prepare a reagent blank exactly in the same way as described in steps 1 - 5 using 10 ml of distilled water instead of a regular sample.

g. The intensity of color developed is measured in a Beckman model DU spectrophotometer against the reagent blank as follows:

Slit opening	0.02 mm
Light path	1.0 cm
Wave length	533 mμ

The transmittance is measured in percent.

h. The standard calibration curve for bathophenanthroline was obtained by using various concentrations of standard iron solution (iron wire or ferrous ammonium sulfate). A plot of the logarithm of transmittance versus the iron concentration in mg/l gives a straight line in accordance with

Beer's law.

i. Knowing the percent transmittance of any unknown sample, its iron content was computed from the standard calibration curve. As the sample size may or may not be 10 ml, a suitable multiplier has to be used to determine the concentration in mg/l.

G. Total Iron

1. Reagents:

a. Concentrated hydrochloric acid (HCl)

b. Hydroxylamine hydrochloride:

Dissolve 10 gm of $NH_2OH \cdot HCl$ in 100 ml of distilled water.

c. Ammonium acetate buffer solution:

Dissolve 250 gm of ammonium acetate in 150 ml of distilled water and 700 ml glacial acetic acid. Make up to a liter using distilled water.

d. Orthophenanthroline solution:

Dissolve 1 gm of 1, 10-phenanthroline monohydrate in 1 liter of distilled water and heat to boiling at approximately 80° C. The solution is stored in a brown bottle away from any light source.

e. Standard iron solution is prepared in the same way as that outlined for the ferrous iron determination. The total iron determination may be used for checking the concentration of the standard iron solutions.

2. Procedure for determining total iron:

a. Pipette a 25 ml or larger sized sample (depending on the iron content of the water) into a 125 ml Erhlenmeyer flask containing 2 ml of conc. HCl.

b. Add 1 ml of hydroxylamine hydrochloride solution and a few boiling glass beads to the sample. Heat to boiling.

c. Transfer the sample after it has cooled to a 100 ml volumetric flask.

d. Add 10 ml of ammonium acetate buffer.

e. Add 10 ml of orthophenanthroline solution.

f. Shake and make up to the 100 ml mark with distilled water.

g. Measure the light transmittance against a distilled water blank in a spectrophotometer with 0.02 mm slit opening, 1 cm light path and 512 mμ wave length.

h. Compute the total iron content from the standard calibration curve for total iron.

APPENDIX C

Statistical Analysis

The statistical analysis to be presented here was based on the method of "Trivariate Regression Analysis" as outlined by Duncan (9). The theoretical formulation and assumptions for such an analysis are briefly shown below.

Let the equation, that is derived as an estimate of the universe equation, be:

$$X_{1r} = a_{1.23} + b_{12.3} X_2 + b_{13.2} X_3 \quad \text{(origin at } X_1 = X_2 = X_3 = 0\text{)}$$

If this is derived by the method of least squares, we must have,

$$\Sigma (X_1 - X_{1r})^2 \qquad \text{a minimum}$$

or,

$$\Sigma (X_1 - a_{1.23} - b_{12.3} X_2 - b_{13.2} X_3)^2 \qquad \text{a minimum.}$$

The necessary conditions for this are:

$$\Sigma X_1 - Na_{1.23} - b_{12.3} \Sigma X_2 - b_{13.2} \Sigma X_3 = 0$$

$$\Sigma X_1 X_3 - a_{1.23} \Sigma X_2 - b_{12.3} \Sigma X_2^2 - b_{13.2} \Sigma X_2 X_3 = 0$$

$$\Sigma X_1 X_3 - a_{1.23} \Sigma X_3 - b_{12.3} \Sigma X_1 X_3 - b_{13.2} \Sigma X_3^2 = 0$$

These are the least square normal equations for estimating the universe regression equation. Referring the variables to their mean values, $a_{1.23}$ becomes zero and the three normal equations reduce to two, which are:

$$b_{12.3} \Sigma x_2^2 + b_{13.2} \Sigma x_2 x_3 = \Sigma x_1 x_2$$

$$b_{12.3} \Sigma x_2 x_3 + b_{13.2} \Sigma x_3^2 = \Sigma x_1 x_3$$

where,

$$\Sigma x_1^2 = \Sigma X_1^2 - N\bar{X}_1^2$$

$$\Sigma x_2^2 = \Sigma X_2^2 - N\bar{X}_2^2$$

$$\Sigma x_3^2 == \Sigma X_3^2 - N\bar{X}_3^2$$

$$\Sigma x_1x_2 = \Sigma X_1X_2 - N \bar{X}_1\bar{X}_2$$

$$\Sigma x_1x_3 = \Sigma X_1X_3 - N \bar{X}_1\bar{X}_3$$

$$\Sigma x_2x_3 = \Sigma X_2X_3 - N \bar{X}_2\bar{X}_3$$

and,

$$\bar{X}_1 = \frac{X_1}{N}$$

$$\bar{X}_2 = \frac{X_2}{N}$$

$$\bar{X}_3 = \frac{X_3}{N}$$

Again,

$$a_{1.23} = \bar{X}_1 - b_{12.3} \bar{X}_2 - b_{13.2} \bar{X}_3$$

The variance around the universe plane of regression is estimated from the following equation if deviations are taken from the mean value.

$$\Sigma v_{1.23}^2 = \Sigma x_1^2 - b_{12.3} \Sigma x_1x_2 - b_{13.2} \Sigma x_1x_3$$

The unbiased estimate of the variance around the universe plane of regression is:

$$s_{1.23}^{2} = \frac{\Sigma v_{1.23}^{2}}{N-3}$$

The multiple correlation coefficient for the analysis can be estimated from,

$$\hat{R}_{1.23}^{2} = 1 - \frac{s_{1.23}^{2}}{s_{1}^{2}}$$

where,

$$s_{1}^{2} = \frac{\Sigma x_{1}^{2}}{N-1}$$

The standard estimate of error is,

$2(s_{1.23})$ for 95 percent confidence limit (C. L.)

TABLE A

Plant	$T_{1/2}$ (mins)	Equilibrium pH	Alkalinity (mg/l of $CaCO_3$)
Cisco	25.6	7.71	458.0
Clinton	4.3	7.78	610.0
Wapella	36.0	7.67	410.0
Windsor	13.2	7.48	585.0
Danvers	6.5	7.68	592.0
Arcola	54.0	7.49	354.5
Deland	22.5	7.67	456.0
Forrest	16.0	7.72	475.0

The parameters chosen for the analysis were the square of the hydroxyl ion concentration, as calculated from the equilibrium pH, and the log of alkalinity as independent variables with $T_{1/2}$ as the dependent variable. In Table B these parameters are shown along with the nomenclature, that will be used in the analysis.

TABLE B

Plant	$T_{1/2}$ (mins)	$(OH^-)^2$	$\log_{10}$ (Alkalinity)
	(X_1)	(X_2)	(X_3)
Cisco	25.6	26.32×10^{-14}	2.6620
Clinton	4.3	35.88×10^{-14}	2.7860
Wapella	36.0	34.11×10^{-14}	2.6135
Windsor	13.2	9.12×10^{-14}	2.7680
Danvers	6.5	22.80×10^{-14}	2.7730
Arcola	54.0	9.50×10^{-14}	2.5508
Deland	22.5	34.11×10^{-14}	2.6600
Forrest	16.0	27.46×10^{-14}	2.6775
ΣX_i	178.1	199.30×10^{-14}	21.4908
$\bar{X}_i$	22.2625	24.9125×10^{-14}	2.6864
$(X_i)^2$	495.6189	620.6327×10^{-28}	7.2165

TABLE C

Plant	X_1^2	X_2^2 (x 10^{-28})	X_3^2	X_1X_2 (x 10^{-14})	X_1X_3	X_2X_3 (x 10^{-14})
Cisco	655.36	692.7424	7.0860	673.792	68.1472	70.0638
Clinton	18.49	1287.3744	7.7618	154.284	11.9798	99.9617
Wapella	1296.00	1163.4921	6.8304	1227.960	94.0860	89.1465
Windsor	174.24	83.1744	7.6618	120.384	36.5376	25.2442
Danvers	42.25	519.8400	7.6895	148.200	18.0245	63.2244
Arcola	2916.00	90.2500	6.5066	513.000	137.7432	24.2326
Deland	506.25	1163.4921	7.0756	767.475	59.8500	90.7326
Forrest	256.00	754.0516	7.1690	439.360	42.8400	73.5242
Σ	5864.59	5754.4170	57.7810	4044.455	469.2083	536.1300

The following terms are calculated from the tables presented before.

$$\bar{X}_1\bar{X}_2 = 554.6145 \times 10^{-14}$$

$$\bar{X}_1\bar{X}_3 = 59.8049$$

$$\bar{X}_2\bar{X}_3 = 66.9249 \times 10^{-14}$$

$$\Sigma\ x_1^2 = \Sigma\ X_1^2 - N\bar{X}_1^2 = 1899.6387$$

$$\Sigma\ x_2^2 = \Sigma\ X_2^2 - N\bar{X}_2^2 = 789.3554 \times 10^{-28}$$

$$\Sigma\ x_3^2 = \Sigma\ X_3^2 - N\bar{X}_3^2 = 0.04915$$

$$\Sigma\ x_1x_2 = \Sigma\ X_1X_2 - N\bar{X}_1\bar{X}_2 = -\ 392.46 \times 10^{-14}$$

$$\Sigma\ x_1x_3 = \Sigma\ X_1X_3 - N\bar{X}_1\bar{X}_3 = -\ 9.2306$$

$$\Sigma\ x_2x_3 = \Sigma\ X_2X_3 - N\bar{X}_2\bar{X}_3 = 0.7308 \times 10^{-14}$$

Least square equations of the analysis are:

$$(789.3554 \times 10^{-28})b_{1.23} + (0.7308 \times 10^{-14})b_{13.2} = -\ 392.46 \times 10^{-14} \ldots (1)$$

$$(0.7308 \times 10^{-14})b_{12.3} + (0.04915)b_{13.2} = -\ 0.2306 \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Solving the equations simultaneously,

$$b_{12.3} = -\ 0.3278 \times 10^{14}$$

$$b_{13.2} = - 182.9307$$

and,

$$a_{1.23} = \bar{X}_1 - b_{12.3}\,\bar{X}_2 - b_{13.2}\,\bar{X}_3$$

$$= 521.854$$

$$(s_{1.23})^2 = \frac{\Sigma v_{1.23}^{\ 2}}{N-3} = \frac{\Sigma x_1^{\ 2} - b_{12.3}\Sigma\, x_1x_2 - b_{13.2}\,\Sigma\, x_1x_3}{N-3}$$

(N=3 in this case)

$$= 16.4801$$

$$s_{1.23} = 4.05$$

So, for 95 percent C. L., estimate of standard error is,

$$E = \pm 8.10 \text{ mins.}$$

The multiple correlation coefficient of the plane of regression is,

$$\hat{R}_{1.23}^{\ 2} = 1 - \frac{s_{1.23}^{\ 2}}{s_1^{\ 2}}$$

$$= 0.956$$

or,

$$\hat{R}_{1.23} = 0.969$$

So, the final equation for the universe plane of regression is as follows,

$$T_{1/2} = 521.854 - 0.3278 \times 10^{14}\ (OH^-)^2 - 182.931 \log_{10} (\text{Alkalinity}) \pm 8.10$$

where,

$T_{1/2}$ = half life in minutes

OH^- = hydroxyl ion concentration in mol/l (computed from "Equilibrium pH")

Alkalinity = Total alkalinity in mg/l of $CaCO_3$