

## CHAPTER II

### THEORETICAL CONSIDERATION

#### 2.1 Chemistry of Iron

These elements belong to the Subgroup VIIA in the Periodic Table and like other transition elements they exist in a number of oxidation state. The chemistry of aqueous iron is primarily involved the II and III oxidation state.

Ferrous iron has a tendency to be oxidized into ferric state and hydrolyzed to a ferric hydroxide form.

#### 2.2 Kinetics of Redox Reaction of Iron

The equilibrium equation of ferrous which oxidized to ferric as follow:-



WERNER STUMM (1970) studied the rate of iron oxidation and found that in a solution pH 5.5, the rate of iron oxidation was the first order reaction with respect to the concentration of both Fe(II) and  $\text{O}_2$  and second order reaction with respect to the OH concentration the oxidation kinetics follow the rate law:-

$$\frac{-d(\text{FeII})}{dt} = k [\text{FeII}] [\text{OH}^-]^2 p_{\text{O}_2} \quad \dots(1)$$

where k is the rate constant

$$[\text{FeII}] = \text{concentration of Fe}^{++}$$

$$[\text{OH}^-] = \text{concentration of hydroxyl ions}$$

$$p_{\text{O}_2} = \text{partial pressure of } \text{O}_2$$

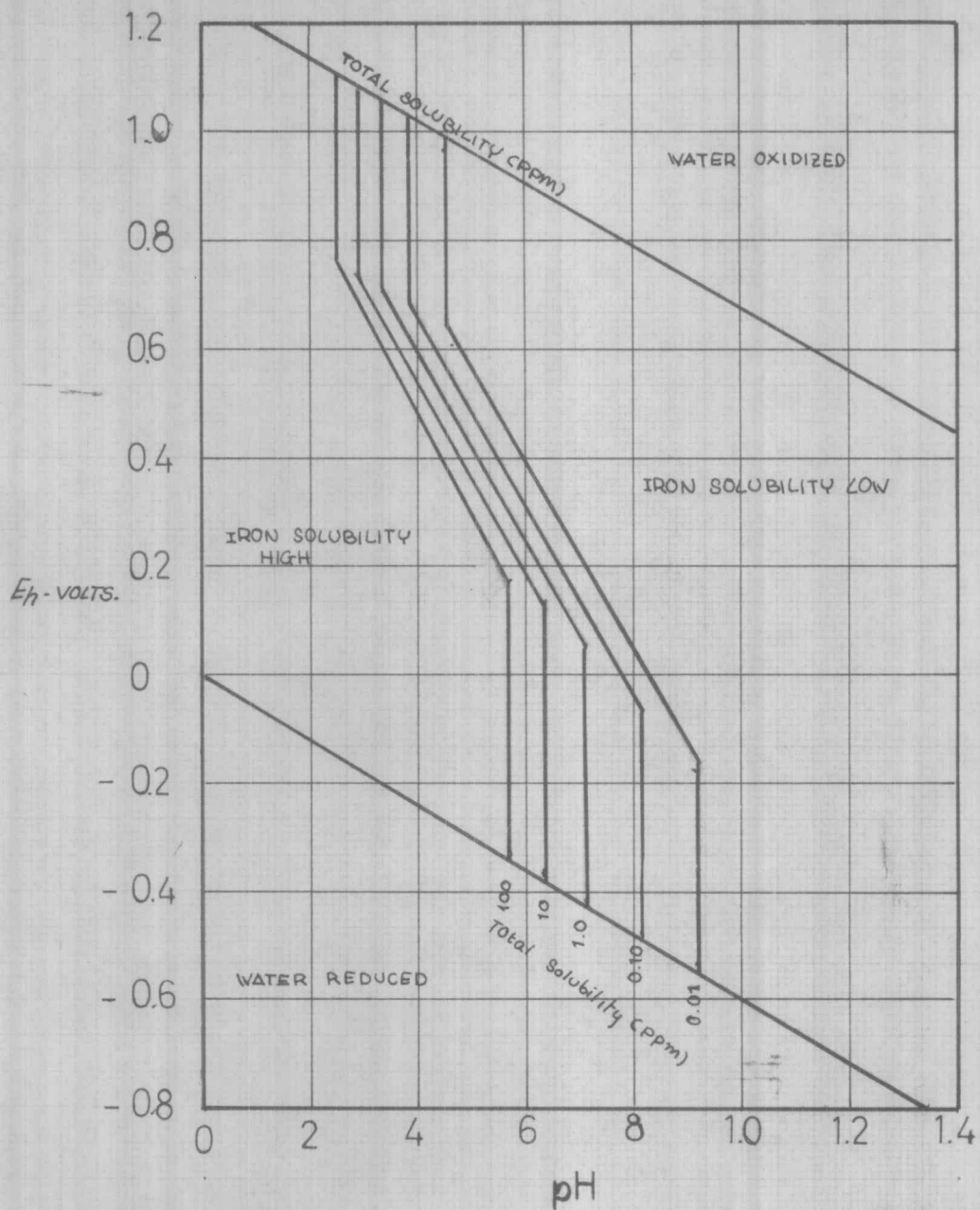


Fig. 1. Solubility of Iron in Relation to pH and  $E_h$

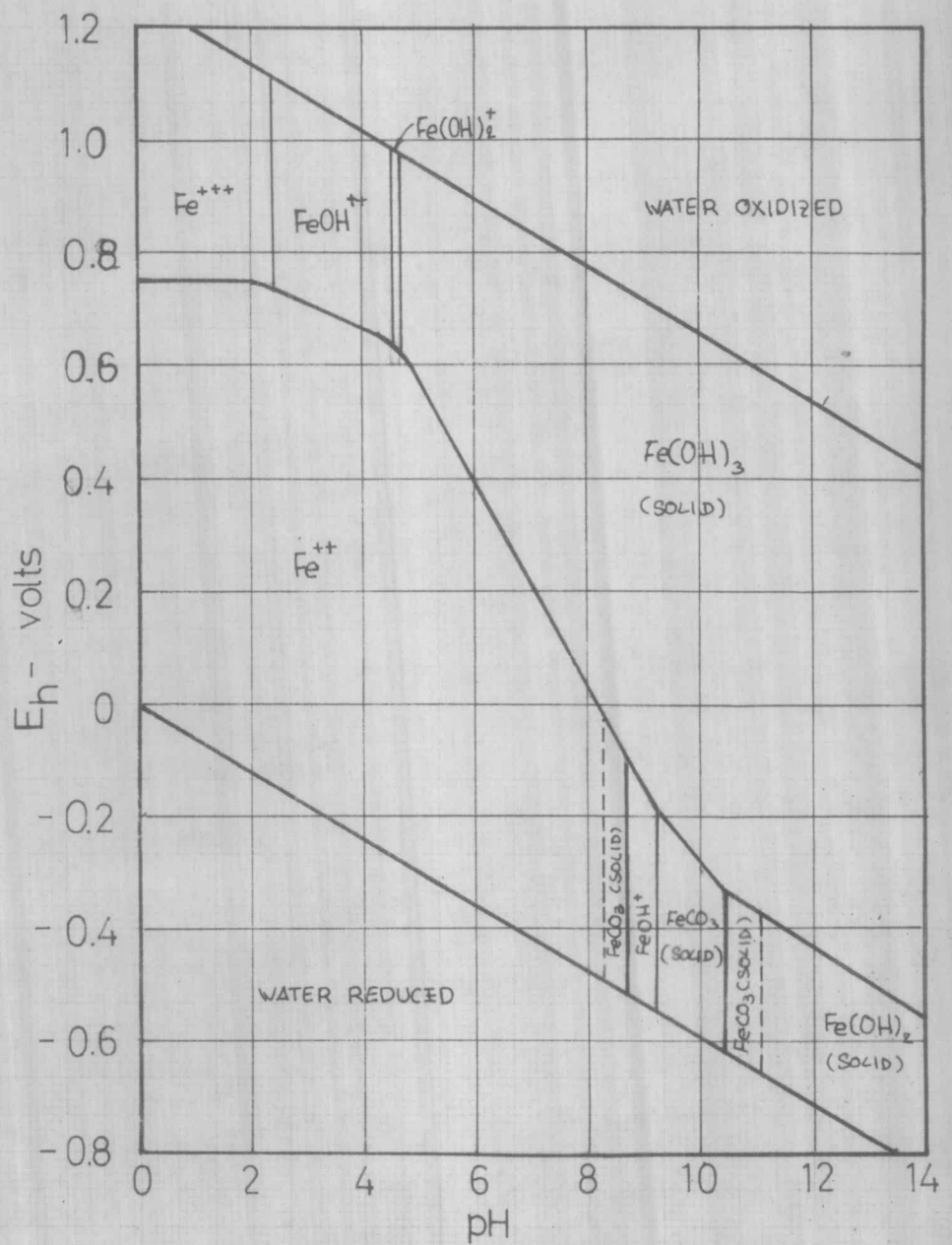


Fig . 2. Stability Field Diagram  
( 0.01 ppm dissolved Fe )

The oxidation in a bicarbonate solution appears

$$\frac{-d(\text{FeII})}{dt} = k \frac{[\text{Fe}(\text{HCO}_3)_2] [\text{O}_2]}{[\text{CO}_2]^3} \dots\dots(2)$$

The rate of oxidation increases by the increasing of  $\text{HCO}_3^-$  concentration and decreases with the concentration of  $\text{CO}_2$ .

JOHN D. HEM (1961) studied the measurement of  $E_h$  of ground water by using the equation

$$E_h = E_o + \frac{RT}{nf} \log_e \frac{a_{\text{ox}}}{a_{\text{red}}}$$

$E_h$  = Redox potential

$E_o$  = Standard potential in typical experiment

$a_{\text{ox}}$  &  $a_{\text{red}}$  = Effective concentration of oxidized and reduced substance in the chemical system

$R$  = Universal gas constant (1.987 cal. /degree per mole or 8.314 joules per degree per mole)

$T$  = Absolute temperature

$n$  = Number of electrons represented by a number multiple of  $e$  in the redox equation

f = Faraday constant (23,060 cal/volt or  
96,484 coulombs per gram. equivalent.)

in the oxidation equation



so

$$\text{Eh} = E_0 + \frac{RT}{nf} \log \frac{[\text{FeOH}^{+2}][\text{Fe}^{+2}][\text{OH}^-]}{[\text{Fe}^{+2}]}$$

from this equation the Redox Potential is decreased by the decreasing of OH concentration. The lower Eh is, the less oxidizing  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$

In his studied, the curve was developed from the value of redox potential (Eh) and pH as show in Fig.1 and Fig.2. From Fig.1 at pH 9 the redox potential of the chemical reaction that was given a  $\text{Fe}(\text{OH})_3$  (s) is - 0.2 which showed that ferrous had more tendency to form crystal nuclei and precipitate. In Fig.2 at pH 9 the solubility of iron is very low at the same Eh that is 0.01 ppm. It means that  $\text{Fe}(\text{OH})_3$  (s) is very difficult to dissolve back to the solution.

### 2.3 Factor Influencing Iron Removal

#### 2.3.1 The Solubility of Hydroxide of Iron

The solubility of iron hydroxide varies with the pH of the solution, Table 1 show the solubility equilibrium of iron. The equilibrium constant is developed in graph and is shown in fig 3 and 4.

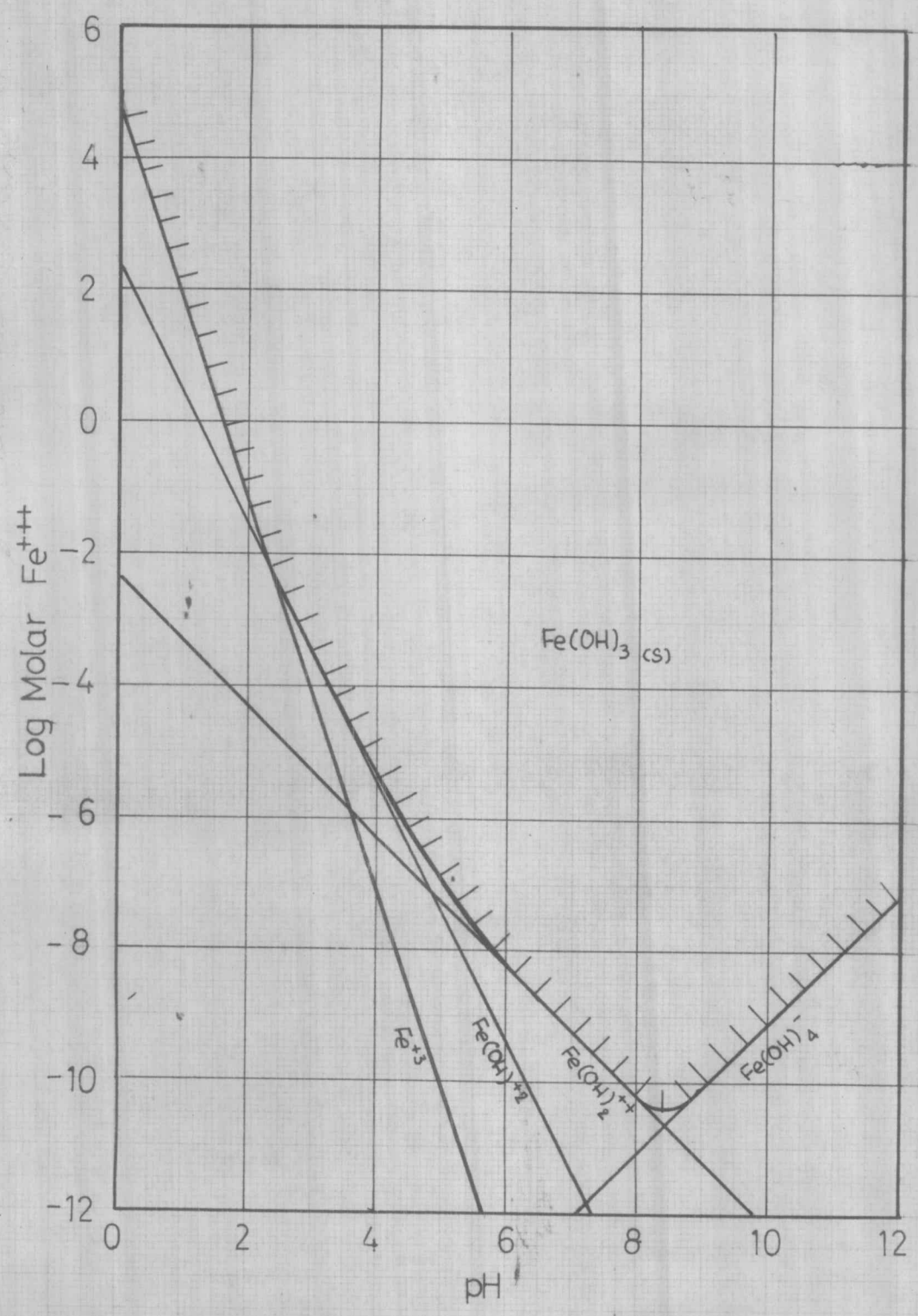


Fig. 3. Solubility of Fe(OH)<sub>3</sub> (s)

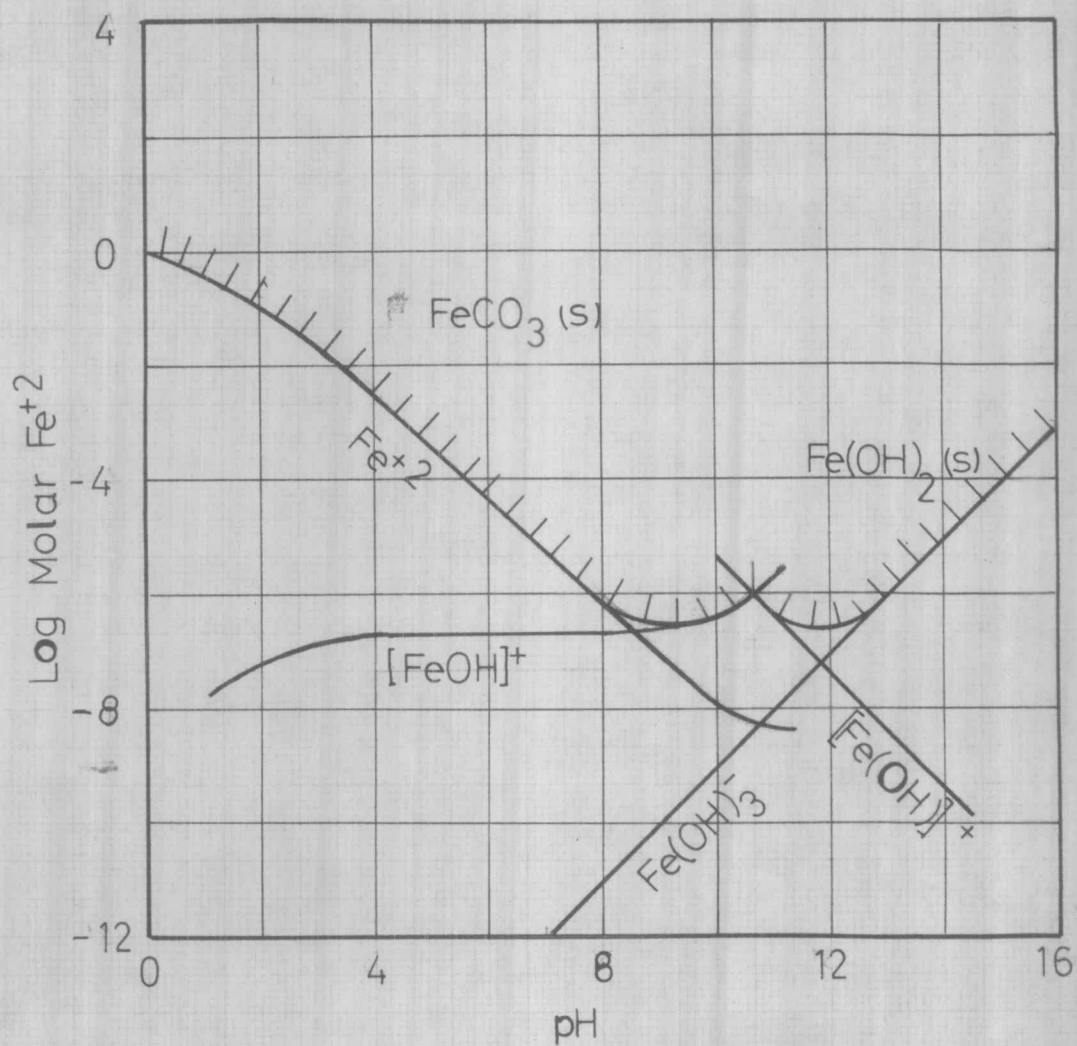


Fig. 4. Solubility of Ferrus Iron in Carbonate Bearing Water

Table I. Equilibrium constants.

Equilibrium		Equilibrium constant
$\text{Fe}(\text{OH})_2(\text{aq})$	$= \text{FeOH}^+ + \text{OH}^-$	$2 \times 10^{-5}$
$\text{FeOH}^+$	$= \text{Fe}^{++} + \text{OH}^-$	$4.5 \times 10^{-6}$
$\text{Fe}(\text{OH})_2(\text{c})$	$= \text{Fe}^{++} + 2\text{OH}^-$	$1.8 \times 10^{-15}$
$\text{Fe}(\text{OH})_2(\text{c})$	$= \text{FeOH}^+ + \text{OH}^-$	$4 \times 10^{-10}$
$\text{Fe}(\text{OH})_2(\text{c})$	$= \text{FeO}_2\text{H}^- + \text{H}^+$	$5 \times 10^{-19}$
$\text{Fe}(\text{OH})_3(\text{aq})$	$= \text{Fe}(\text{OH})_2^+ + \text{OH}^-$	$2.5 \times 10^{-8}$
$\text{Fe}(\text{OH})_2^+$	$= \text{FeOH}^{++} + \text{OH}^-$	$4.5 \times 10^{-10}$
$\text{FeOH}^{++}$	$= \text{Fe}^{+++} + \text{OH}^-$	$2.7 \times 10^{-12}$
$\text{Fe}(\text{OH})_3(\text{c})$	$= \text{Fe}^{+++} + 3\text{OH}^-$	$6 \times 10^{-38}$
$\text{Fe}(\text{OH})_3(\text{c})$	$= \text{Fe}(\text{OH})_2^+ + \text{OH}^-$	$5.3 \times 10^{-17}$
$\text{Fe}(\text{OH})_3(\text{aq})$	$= \text{Fe}^{+++} + 3\text{OH}^-$	$4.0 \times 10^{-29}$
$\text{Fe}^{+++} + \text{Cl}$	$= \text{FeCl}^{++}$	33
$\text{FeCl}_2^+ + \text{Cl}$	$= \text{FeCl}_3(\text{aq})$	.1

Note aq = aqueous state

c = solid state



In comparison of fig.3 and fig.4 the curve indicate that alkalinity reduces the solubility of iron, as an example in pH 9 in fig.3 solubility of iron is  $10^{-10}$  and in carbonate bearing water the solubility is  $10^{-6}$  (fig.4). This shows that Iron tends to precipitate in crystal form in carbonate bearing water than in noncarbonate bearing water.

### 2.3.2 Ionization of Water

WERNER STUMM (1970) has studied the ionization of water and found that temperature affected the ionization of water. The ionization equation is



As show in fig.5 the  $\text{OH}^-$  concentration increase with the temperature. By the equation (1) the  $\text{OH}^-$  concentration increased the rate of oxidation.

### 2.4 Hydrolysis of Ferric Iron

JOHN D. HEM (1961) reported that oxidation of ferrous iron was followed by the hydrolysis of ferrous to hydrous ferric oxide.

As the following equation.

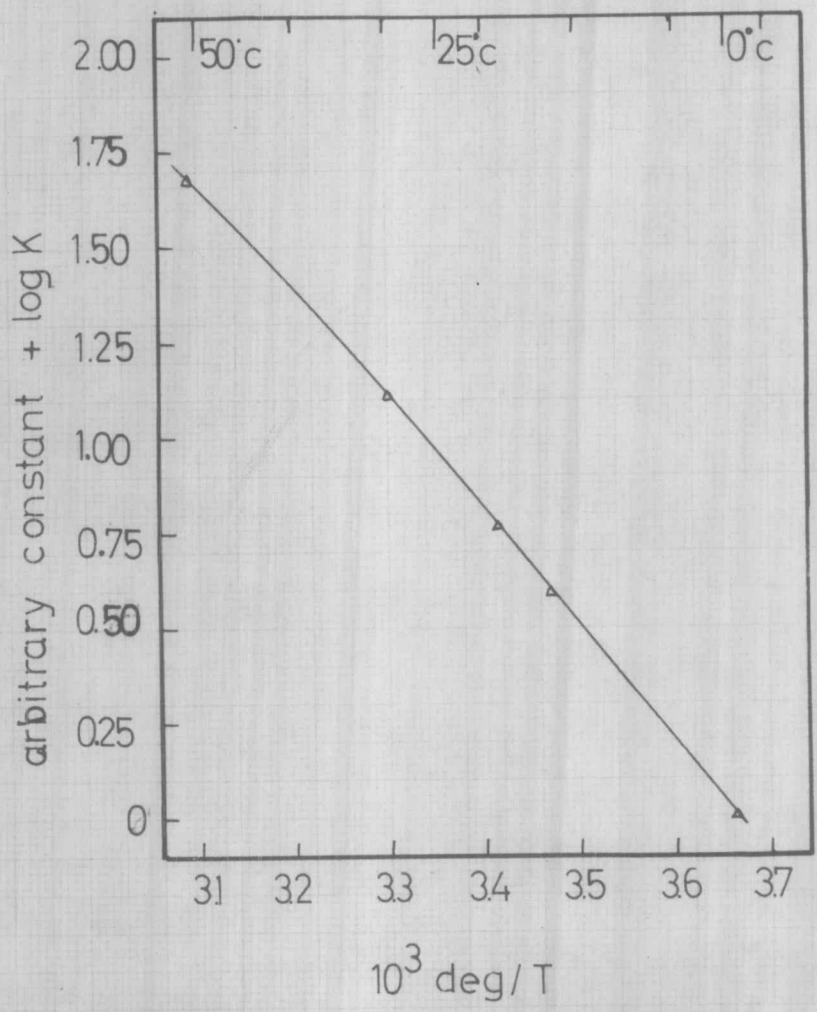
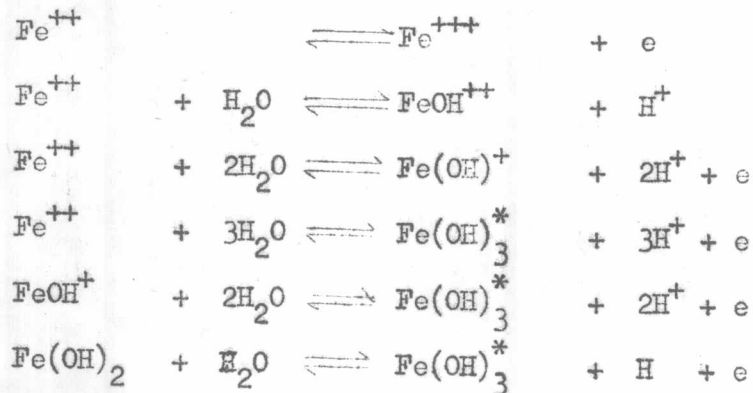


Fig. 5. Equilibrium constant and temp. curve for ionization of water



\* solid state

The size of  $\text{Fe}(\text{OH})_3$  particle varies with pH of the solution. The diameter may be smaller than  $100 \text{ \AA}$ . The precipitation can be interpreted in term of formation of polynuclear complexes. As has been illustrated for  $\text{OH}^-$  as a ligand, the present of metal complexing species will affect the solubility of  $\text{Fe}(\text{OH})_3$ .

### 2.5 Effect of Alkalinity to the Formation of Floc.

In the natural water of pH range of 6 to 9 and having a alkalinity value between 400 ppm to 500 ppm as  $\text{CaCO}_3$ , the dissolve iron possible to be precipitated in tri-valent form as  $\text{Fe}(\text{OH})_3$  and bivalent form as  $\text{FeCO}_3$ . GHOSH (1966) found that, the rate of iron precipitation was governed by the alkalinity and pH of the water as shown by the following relationship

$$T^{\frac{1}{2}} = 522 - 0.33 \times 10^{14} [\text{OH}^-]^2 - 183 \log \Delta^{\pm 8.10} \dots (4)$$

where  $T^{\frac{1}{2}}$  = Half-life in minutes or time required for one-half of the ferrous iron in solution to be precipitated.

$OH^-$  = Molar concentration of hydroxyl ions.

$\Delta$  = Alkalinity in mg/l as  $CaCO_3$

## 2.6 Formation of Floc.

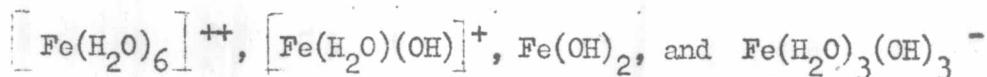
The ferric iron formed as a result of the oxidation of ferrous iron is hydrolyzed according to the equation.



The insoluble hydrated ferric oxide can exist in two forms, namely the solid form, and the floc form. Solid form can grow in larger agglomerates, which become floc. This flocculated particles are more easily filtered.

The basic step in the formation of hydroxopolymers of any metal is a stepwise hydrolysis. For ferrous iron, the most common hydrolysis products that may exist in natural of water are

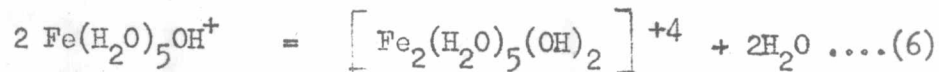
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For ferric ion, the most common hydrolysis products are  $FeOH^{++}$ ,  $Fe(OH)_3$  and  $Fe(OH)_4^-$  and it was found that aquo-ferric ions has far more affinity toward hydrolysis than the aquo-ferrous ion. Ferric hydroxo complexes have been known



to polymerize as shown by the reaction:



### 2.7 Nature of Zeta potential

The basic meaning of Zeta Potential is illustrate in fig.6. The pictured colloidal particle is electronegative charge.

The Zeta Potential is the potential at the surface that separated the immobile part of the double layer from the diffuse part. It is a simultaneous measure of the charge of the diffuse layer (per unit surface of the colloidal) and of its extent to the force and distance overwhich the particles can repel each other and thus prevent flocculation.

The ZP in the range of 15-25 mV prevents agglomeration and when drop ZP to about  $0 \pm 5$  mV the colloid can coagulate and settle down (RIDDICK 1961).

### 2.8 Electrohydraulic Effect

YUKIN (1938) the Russian Scientist, refined and demonstrated the primitive technique of electrohydraulics after that LAWRENCE (1969) explained that electrohydraulic effect is suddently released a stored electrical energy by high speed electronic switches and immersed electrodes. It created an intense mechanical shock wave.

A basic electrohydraulic system is shown in fig.7.

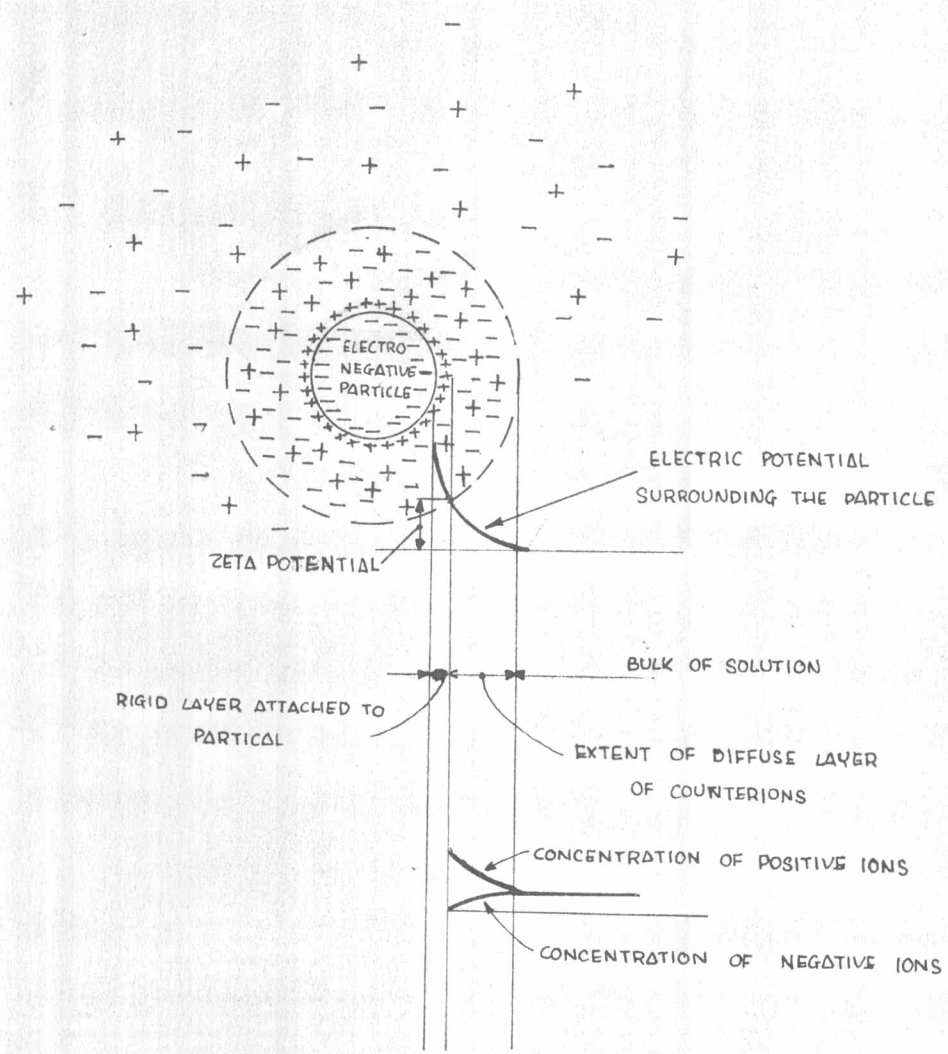


Fig. 6. Colloid Particle With Zeta Potential

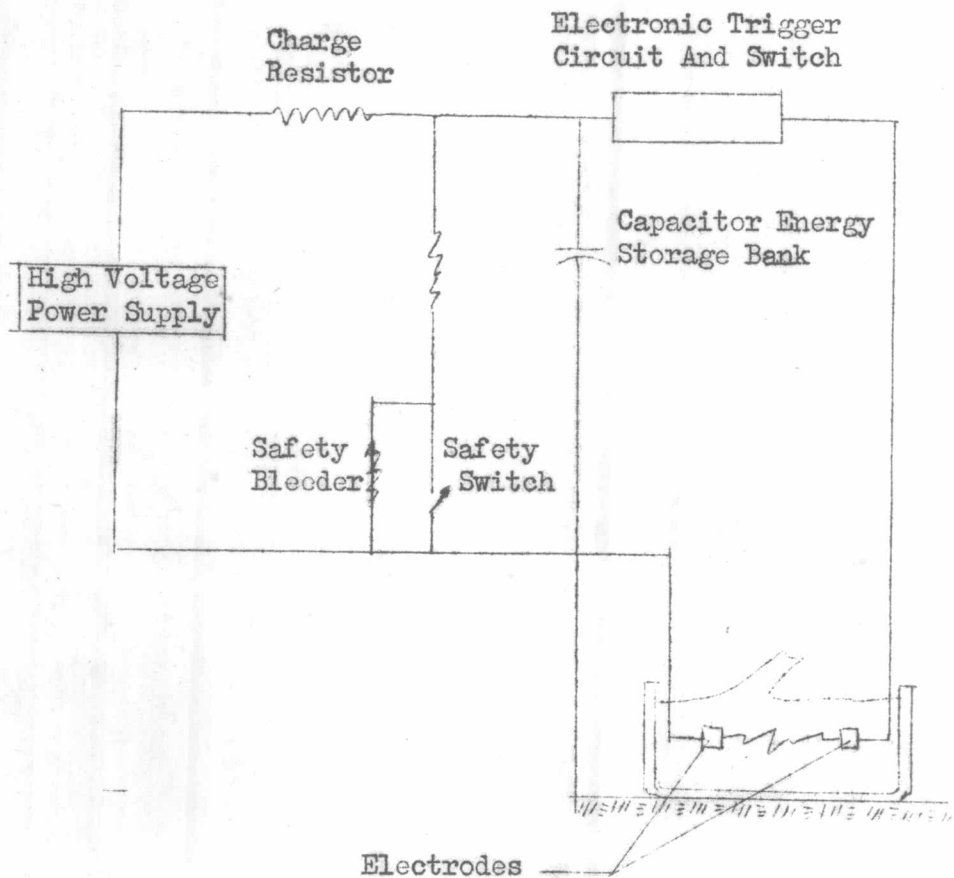


Fig.7 Electrohydraulic System Has Power Supply, Trigger, Storage Capacitor, and Submerged Electrodes in Circuit.

The necessary high voltage, about 20 kV, is obtained from line operator dc. power supply and charges a capacitor storage bank rated from 1 - 15 microfarads. Safety devices "bleed" the circuit via high resistance discharge parts. When electronic trigger circuit is activated, energy is rapidly dumped into concentric or opposing sparkgap electrodes submerged in the water-filled tank. The resulting

shock wave sheared metal sheet as shown in fig.8



Fig. 8 Shock Wave Shearing Metal.

Although the outward appearance of the electrohydraulic effect is that of a simple chemical explosion, for example, flash of light noise, its constituents are much more complex.

Unlike a chemical explosion whose dynamics are measured in terms of millisecond, the sudden release of stored energy results in the generation of a small vapor bubble which, for all practical purposes, acquires the characteristics of a plasma. Its temperature can be as high as  $30,000^{\circ}\text{C}$ , accompanied by pressures estimated to peak out at approximately 20,000 atmospheres. Active chemical species generated by the short-term plasma include hydroxyl radical (OH), ozone, and oxygen. This attendant electrochemistry is recognized as an effective method for destroying harmful micro-organisms in water and it might, in time, lead to the development of economical methods for treating polluted river and streams.



An electrohydraulic discharge unit suitable for laboratory application is shown in fig.9. The safety spark gap,  $C_s$ , protect the main storage capacitor ( $C_c$ ) from rupture caused by over voltage.

Using equation,  $W = \frac{1}{2}CE^2$ , it can be shown that the efficiency for concerning electrical power to the electrohydraulic is a about 50%.

The energy can be fed to variety of high speed release devices, such as the ignitron or triggered spark-gap, to provide a rapid dumping cycle.

However, automatic pulsing which requires an exact determination of power supply capabilities is not too common is simple electrohydraulic application. The flasher can be used to trigger the UJT. This provides additional assurance that the energy storage capacitor  $C_e$  has been charged to its maximum design potential. The method, as drawn, depict, a non-synchronized, free running trigger mode. The UJT trigger circuit and  $C_e$ 's charging rate must be synchronized for marin and related application.

## 2.9 Electrophoretic Clarification of water

HILER, E.A. & LYLE, W.M. (1970) was investigate the direct use of electric currents and electric fields to bring about water clarification and purification. Electrophoretic and electrochemistry systems appear well adapted for removal of this electrical charged pollutant and in

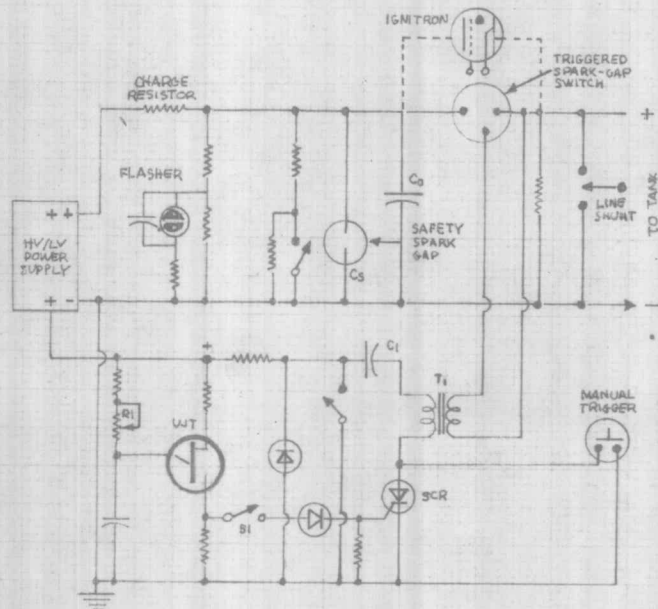


Fig. 9 Power Unit Schematic Diagram. Either a Trigger Spark Gap or Ignitron Can Be Used to Discharge Capacitor  $C_0$  into an External Work Circuit.

addition have the potential of being entirely automated. Numerous design concepts are advanced and test by using laboratory models. This include a phoretic removal, and porous filter and electrode grid models which in incorporated both electrophoretic and electrochemistry capabilities.

Successful water clarification was attained with the parallel plate model only when the influent water was of very low electrical conductivity. Electrolysis products at high conductivity cause sufficient turbulence to disrupt completely electrophoretic transport. In addition primary and secondary chemical reaction took place owing to electrolysis, which altered the characteristic of the suspension.

The case of automation with an electrophoretic system does not justify the high cost of water treatment by this method. Water purification by electrochemical means overcome this problem and was successful both operationally and economically, as a result of the experiment testing a sample design of a small semiautomated electrochemistry water system is offered which incorporates electrochem-flocculation, settling, and electrochem-disinfection operation.

#### 2.10 Spaulding Precipitator.

BABCOCK(1950) studied the efficiency in removing iron from ground water by using spaulding precipitator, as

the schematic diagram shows in the fig.10

In his studied, he found that it is easier to remove the precipitate of iron in floc form than in solid form. He used alum as a coagulant and lime to raise pH, to flocculate  $Fe_2O_3$ . The floc can be removal easily by sand filter.

Moreover, he found that pH is the prime importance in a process of this type. It was found that the optimum pH zone was 8.5 - 9.1. This type of treatment, approximately 95% of iron was removed. The chemical used and percentage of iron removal are shown in the table II

Table II. Chemical use in the spaulding precipitator

Source	Alun (gpg)	line (gpg)	pH	Fe (ppm)	% Feremoval
Raw water	-	-	6.3	4.4	-
Aerated	-	-	6.8	4.2	5%
Precipitated	7.3	7	9.2	0.2	95%
Precipitated	4.0	5	9.0	0.17	96%
Precipitated	2.8	3.5	9.0	0.2	95%
Precipitated	2.5	2.5	8.9	0.33	93%

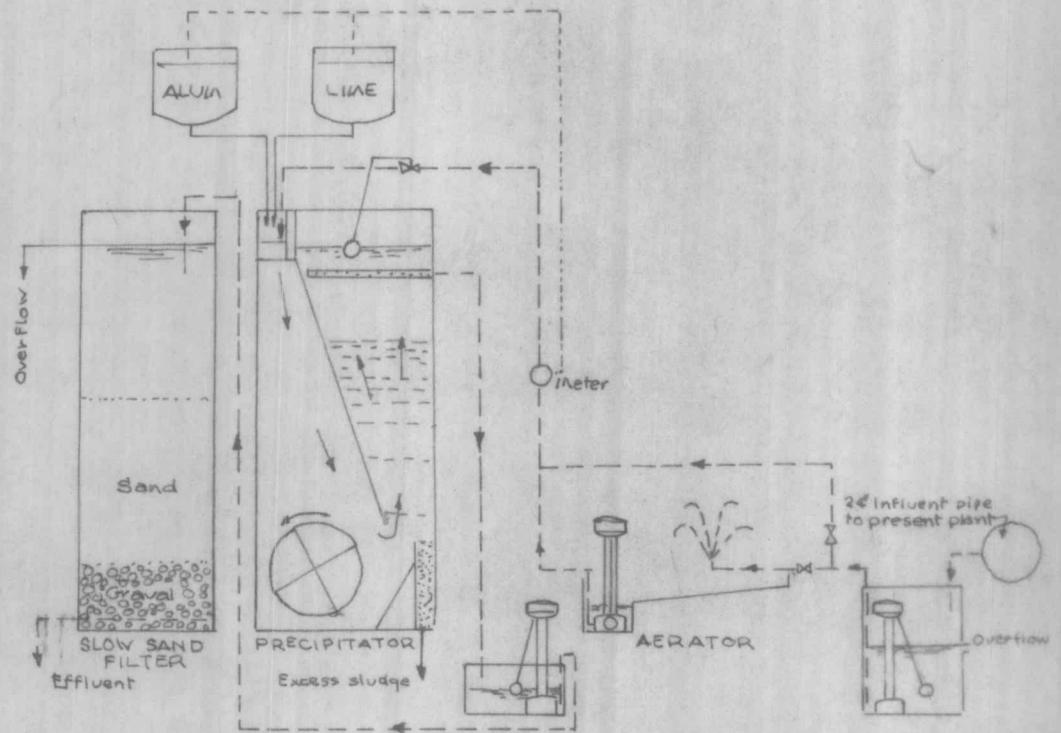


Fig. 10 SCHEMATIC DIAGRAM OF PILOT PLANT  
( BABCOCK 1950 )

### 2.11 Mechanism of Electrical Field Column

THAMNOON (1972) studied the clarification of water by electrical means and concluded that the electric field can split out the protective shell of water molecules surrounding the suspended particle and also neutralized the electrical charge on the surface of the surface of the suspended particle, causing the agglomeration of particle. In deferrilization, the mechanism of the electric field is that the electricity is transformed to electrical wave form which create the electrohydraulic effect. This electrohydraulic effect has an high enough energy to lose one of the outer shell electron of  $Fe^{+2}$  to form  $Fe^{+3}$ . Then  $Fe^{+3}$  will hydrolyze to form a colloidal particle of  $Fe(OH)_3(s)$ . And some  $Fe^{+2}$  will form with  $HCO_3^-$  to form precipitate of  $FeCO_3$ , as the following equations:-



and

