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# OIL PRODUCTION ENHANCEMENT THROUGH A STANDARDIZED BRINE TREATMENT

Final Report

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August 1995

Performed Under Contract No. DE-AC22-92MT92008

The Pennsylvania State University
University Park, Pennsylvania

**Bartlesville Project Office**
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**Bartlesville, Oklahoma**

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# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

## Abstract

In order to permit the environmentally safe discharge of brines produced from oil wells in Pennsylvania to the surface waters of the Commonwealth and to rapidly brings as many wells as possible into compliance with the law, the Pennsylvania Oil and Gas Association (POGAM) approached the Pennsylvania State University to develop a program designed to demonstrate that a treatment process to meet acceptable discharge conditions and effluent limitations can be standardized for all potential stripper wells brine discharge.

This project has been underway since 1987. After the initial studies, the first phase of this project was initiated. A bench-scale prototype model was developed for conducting experiments in laboratory conditions. The experiments pursued in the laboratory conditions were focused on the removal of ferrous iron from synthetically made brine. Iron was selected as the primary heavy metals for studying the efficiency of the treatment process. The results of a number of experiments in the lab were indicative of the capability of the proposed brine treatment process in the removal of iron. Concurrent with the laboratory experiments, a comprehensive and extensive kinetic study was initiated. This study was necessary to provide the required data base for process modeling. This study included the investigation of the critical pH as well as the rate and order of reactions of the studied elements: aluminum, lead, zinc, and copper.

In the second phase of this project, a field-based prototype was developed to evaluate and demonstrate the treatment process effectiveness. These experiments were conducted under various conditions and included the testing on five brines from different locations with various dissolved constituents: Red Valley brine, Warren brine, Cooper brine, Kine brine, and Bradford brine. Although the field model

was constructed for treating brine with the flow rate up to 1 bbl/d, significant results in the reduction of heavy metals were obtained up to 16 bbl/d. The process modeling for the treatment process was also performed in this phase by incorporating the laboratory and field works.

Due to the low concentration of many heavy metals such as aluminum, copper, lead, and zinc in the tested brine (in the field), no conclusive results were obtained for these elements. However, laboratory studies has indicated promising results in removal of these metals from synthetically made brine.

The outcome of this research has been a software package, currently based on iron's reactivity, to be used for design purposes. The developed computer program was refined as far as possible using the results from laboratory and field experiments. The treatment process and software is fine-tuned to ensure their applicability to all brine discharge from stripper wells in the state's oil producing region.

# 1. Preamble

Water production is an unavoidable by-product associated with producing from oil and gas formations. The amount of water produced depends on the producing lifetime of the well, reservoir water saturation, location of perforations, etc. However, regardless of the volume of the water production, treatment measures should be taken prior to the discharge of the water. Disposal of produced water, commonly called brine, has been of great concern to the oil industry as well as governmental agencies and environmental regulators. The presence of dissolved species in the water produced with oil and gas has posed difficulties for the oil and gas industries. The water treatment process chosen for the purification of water must be such that undesirable chemical species are eliminated from the solution. With current technology, there are different methods for the treatment of produced brine. These methods include a number of physical and chemical processes, such as aeration, filtration and oxidation with chlorine or potassium permanganate. However, considering the economic constraints involved with oil and gas production, meeting the discharge criteria has imposed some concerns.

The Appalachian Basin oil and gas industry is composed primarily of small, independent producers operating oil and gas wells in the states of New York, Pennsylvania, West Virginia, Kentucky and Tennessee. The wells operated by these independents produce very small quantities of hydrocarbons. For example, in 1989, Appalachian producers operated 101,274 oil wells while only producing 21,626,000 barrels of oil, less than one percent of the country's total 1989 production. Because of this small daily production, an average of less than one barrel of oil per day, almost all producing wells in the Appalachian Basin are considered

stripper wells. Because of the large number of wells needed to produce such low volumes of hydrocarbons, operators of these wells conduct business on the basis of very thin profit margins. The typical Appalachian oil earned a mere $13.76 per day in 1989. The slim profit margins associated with operating these economically marginal oil wells make them extremely sensitive to increases in operating costs or decreases in the price paid for the commodity produced. The cost associated with treating the brine prior to discharge imposes additional economic costs. As a result of these costs, marginal stripper wells are being abandoned.

Appalachian Basin oil wells typically produce, along with the oil, small volumes of waste-water, brine. For example, 87% of the primary stripper oil wells produce less than one barrel of brine per day. This brine has been identified as a potential source of environmental hazard, and each oil well site where brines are produced is a potential candidate for regulatory control under the U.S. Environmental Protection Agency's National Pollutant Discharge Elimination System (NPDES) permitting program. The Department of Environmental Resources in October 4, 1991, issued this general NPDES permit for application to discharge of production fluid from primary recovery and gas drive stripper oil well facilities located in the Commonwealth of Pennsylvania to certain classes of streams and rivers. A stripper well includes those facilities covered br 40 CFR Part 435 Subpart F-Stripper Subcategory. There is no fee associated with this permit and the intent behind its inception was to simplify the application process. Discharge limitations include definition with respect to flow, total suspended solids, oil and grease, total iron, acidity, total alkalinity and pH. Monitoring requirements are generally specified on a quarterly basis. Presently, brines produced from stripper oil wells are exempt from the Clean Water Act's zero-discharge effluent guideline and conse-

quently, the operator may treat and discharge brine into surface streams. In some states, however, independent producers are also subject to separate state permit programs designed to address identical issues.

In Pennsylvania, for example, oil well operators may use the stream discharge option for brine disposal if they are able to satisfy the NPDES permit requirements of the Clean Water Act as implemented in the Pennsylvania Department of Environmental Resources (DER) Part I permit process and the Part II Water Quality permit requirements of the state's Clean Streams Law. The two programs are administered and enforced by the DER, and the stripper wells must be implementing the two program adopted in 1987. But compliance with them has been virtually impossible for Pennsylvania's independent stripper oil well operators because of the excessive costs incurred in completing the appropriate applications. To apply for the necessary discharge permits, an operator must pay two application fees of 500 dollars each, provide chemical analysis of the produced water quantifying no less than 29 parameters, and design an engineering plan for a treatment facility adequate to bring the produced water into compliance with water quality standards. The cost of the required analytic work for the NPDES permit ranges from 500 to 900 dollars, and the cost of the engineering study required by the Part II permit has, in the past, ranged between 5000 and 50,000 dollars. The total costs incurred by a well operator, exclusive of his own administrative and clerical support, for each site required to comply with the NPDES and Part II permits requirements equals a minimum of 6,500 dollars. This figure does not include the costs incurred by the operator in constructing, operating and monitoring the performance of the facility once approved by the DER. The financial burden imposed by the permit processes essentially prohibits the operator from complying with regulatory requirements.

Therefore, development of a cost-effective brine treatment process for the environmentally safe discharge of water produced from oil and gas wells into the surface water is of great importance.

# 2. Review of Related Work

## 2.1 - Water Treatment Techniques

There is wide range of technologies where, by physical and chemical means, wastewaters are treated for heavy metals such as iron. The methods and techniques that have been used in the oil industry to eliminate heavy metals from oil-field brine are catalogued by Ostroff, 1965. These include:

- Aeration,
- Chemical Oxidation,
- Ion-Exchange,
- Lime Neutralization,
- Sedimentation,
- Filtration,
- Dilution,
- Soda-Ash Process,
- Distillation,
- Reverse Osmosis.

The treatment and disposal of oil-field brine, which may contain dissolved metal ions, in a manner consistent with environmental regulations, is a problem for the petroleum and natural gas industry. To find solutions to this problem, it is important to understand the behavior of any trace or major element in water. It is also important to know the chemical form of these elements in water. Through oxidation and/or corrosion, metals can be totally removed from or reduced in solutions. Many metals are corrosion resistant, depending on the environment. According to Tomashov (1966), pure metals are corrosion resistant due to the following factors:

1) The metal is corrosion resistant because of its thermodynamic stability. Thermodynamic stability can be explained with the normal equilibrium potential of the metal. A shift to more positive (less negative) values of the potential,

corresponds to an increase in the thermodynamic stability of the metal.

2) The metal is relatively resistant because of passivity. Many passivating films, particularly thin oxide films, are non-porous and possess free electronic and limited ionic conductivity and are formed under highly aerated conditions. This passive state can be destroyed in the presence of active ions such as $Cl^-$, $Br^-$, and $F^-$.

3) The metal is resistant as a result of the formation of insoluble, continuous protective layers of corrosion. These layers can be oxide or hydroxide films or a film of various basic salts .

This literature review maily concentrates on Iron's chemistry and possible ways of its elimination from solution. However, a short literature review for other heavy metals such as copper, aluminum, lead and zinc are included in this section.

The presence of dissolved iron in the water produced with oil and gas has posed difficulties for the producing industry. Iron is an element of the first transition series in the periodic table and has the ability to exist in various oxidation states. This is due to the fact that iron is electron deficient in its d-orbit; therefore it can readily adsorb oxygen and change its state. The important oxidation states of iron are +2, +3, +4, +6. The +2 and +3 are the common oxidation states of iron and +4 and +6 occur only in a highly alkaline medium [Latimer, 1959, c1952]. Iron in the ferrous form is soluble in water and readily oxidizes to ferric iron upon exposure to air. The oxidation of iron by air results in ferric oxide and may be written as [Lehr et al., c1980]:

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3. \qquad (1)$$

Iron in solution forms different species and compounds. The formation and

presence of one form of iron as opposed to others is dependent on the presence and concentration of sulfide ions, carbonate ions, dissolved oxygen, pH of the water, and the oxidation-reduction balance of water. Iron in solution normally is in the form of Ferrous [Fe(II) or $Fe^{+2}$] or Ferric [Fe(III) or $Fe^{+3}$] ions. There are iron compounds that could exist in water as well. Some of these compounds are Ferrous Carbonate ($FeCO_3$), Iron Sulfite (FeS), Ferrous Hydroxide [$Fe(OH)_2$], Ferric Hydroxide [$Fe(OH)_3$], and Ferric Oxide [$Fe_2O_3$] [Patton, 1977]. According to Stumm, the oxidation of Fe(II) occurs in a series of steps [Stumm, 1965]:

$$Fe^{+2} + O_2 \xrightarrow{\text{oxidation}} Fe^{+3}, \tag{2a}$$

$$Fe^{+3} + H_2O \xrightarrow[\text{polymerization}]{\text{hydrolysis}} Fe_n(OH)_m^{+3n-m} + xH^+, \tag{2b}$$

$$Fe_n(OH)_m^{+3n-m} + H_2O \xrightarrow[\text{coagulation}]{\text{precipitation}} Fe(OH)_3(s) + xH^+, \tag{2c}$$

$$Fe(OH)_3(s) \xrightarrow{\text{crystallization}} Fe_2O_3 \,.\, xH_2O(s). \tag{2d}$$

The rate determining step for the above reactions is the oxidation reaction (2a) where ferrous iron is oxidized to ferric iron and later it is hydrolyzised to ferric hydroxide. The overall oxidation reaction of ferrous iron may be written as:

$$4Fe^{+2} + O_2 + 10H_2O \longrightarrow 4Fe(OH)_3 + 8H^+. \tag{3}$$

The above reaction involves two steps, first the oxidation of ferrous to ferric iron :

$$4Fe^{+2} + O_2 + 4H^+ \longrightarrow 4Fe^{+3} + 2H_2O. \tag{3a}$$

Second, hydrolysis of ferric iron to ferric hydroxide:

$$Fe^{+3} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+. \tag{3b}$$

Ferric hydroxide [$Fe(OH)_3$], a product of oxidation reaction commonly known as "yellow boy", is not soluble and will precipitate as a solid phase above a pH of 4.0 [Patton, 1977]. The pH of the medium has a significant effect on the oxidation of Fe(II) such that the potential of oxidation reaction becomes more positive at higher pH values. The measure of oxidizing or reducing potential in a solution is commonly presented by the Nernst equation:

$$Eh = E^o + \frac{RT}{nF} \ln \frac{A_{ox}}{A_{red}}, \tag{4}$$

where

Eh = redox potential,

$E^o$ = universal oxidation potential,

R = universal gas constant (1.98 calories/degree mole),

T = temperature in degrees (Kelvin),

n = number of electron involved in the reaction,

F = Faraday constant (96,484 absolute coulombs),

$A_{ox}$ = activity of oxidized ion,

$A_{red}$ = activity of reduced ion.

The Nernst equation for a solution containing Fe(II) and Fe(III) may be written as [Lingane, 1966]:

$$E = E^o - 0.059 \log \frac{Fe^{+2}}{Fe^{+3}} \quad @\ 25^oC. \tag{5}$$

It was mentioned earlier that the oxidation of dissolved iron strongly depends on the pH of the solution. Figures 2.1 and 2.2 illustrate the stability-field diagrams that are calculated based on the Nernst equation and present the distribution of specific ionic species as a function of pH [Garrels, 1960; Hem and Cropper, 1959].

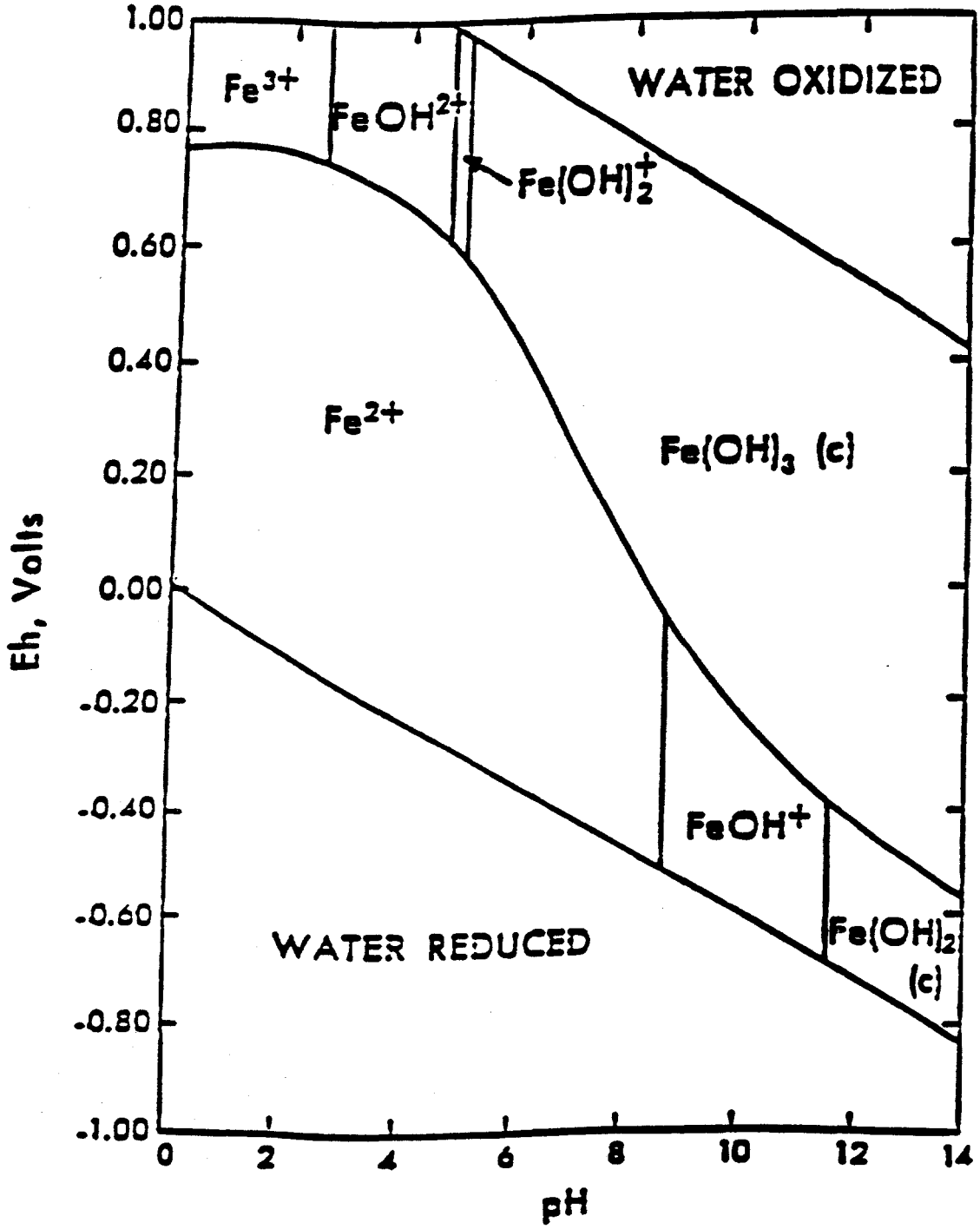


Figure 2.1. Stability - Field Diagram of Aqueous Ferric - Ferrous Iron Oxide System (after Hem and Cropper)

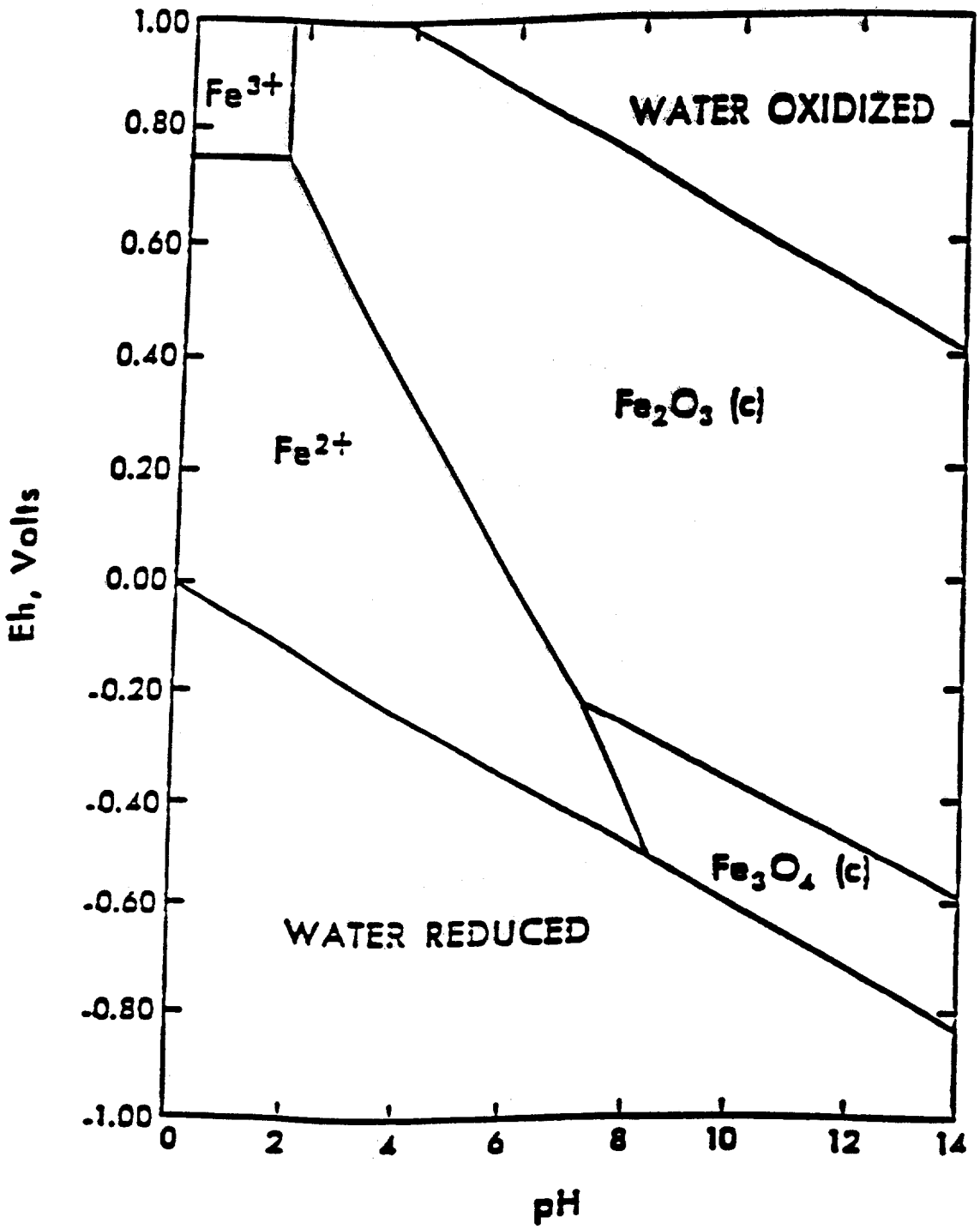


Figure 2.2. Stability - Field Diagram of Aqueous Ferric - Ferrous System (after Garrels)

## 2.2 - Reaction Rate Kinetic of Iron (II)

For a homogeneous reaction, the rate of reaction is function of temperature and concentration of the reactants and products. For the reaction:

$$aA + bB \longrightarrow cC + dD,$$

the rate of reaction of A may be written as:

$$r_A = -\frac{dC_A}{dt} = KC_A^{\alpha}C_B^{\beta}, \tag{6}$$

where

$C_A$ and $C_B$ = reactant concentrations,

t = time,

K = reaction rate constant,

$\alpha$ = order of reaction with respect to A,

$\beta$ = order of reaction with respect to B.

The reaction rate constant, represented by K in the above equation, is independent of concentration and is defined as:

$$K = A \exp(-\frac{E}{RT}), \tag{7}$$

where

A is a constant,

E is the activation energy,

R is the universal gas constant,

T is the absolute temperature.

The rate of ferrous iron oxidation in natural and alkaline solution may be described by the equation [Stumm and Lee, 1961]:

$$-\frac{d[Fe(II)]}{dt} = K[OH^-]^2[O_2][Fe(II)]. \tag{8}$$

The oxidation rate of iron is a first-order reaction with respect to both concentration of dissolved Fe(II) and dissolved oxygen. Since one mg/L of oxygen ($6.25*10^{-8}$ mole) oxidizes seven mg/L ($1.19*10^{-7}$ mole) of dissolved iron, with sufficient oxygen in solution, Iron(II) oxidizes very rapidly to form ferric iron. It should be noted that the solubility of oxygen in water is a function of pressure, temperature and chlorine content, and oxygen is less soluble in salt water than in fresh water. Therefore, the oxidation of Fe(II) is slower in saline solutions such as brine. In an acid medium, there is no dependence of the rate upon hydrogen or hydroxyl ion concentrations and the rate equation (8) becomes [Kim, 1968]:

$$-\frac{d[Fe(II)]}{dt} = K[O_2][Fe(II)]. \tag{9}$$

E. Ackman and P. Kleinmann [1984] express the rate of Fe(II) oxidation as a function of dissolved oxygen [D. O.], and pH :

$$-\frac{d[Fe^{+2}, mol/L]}{dt} = K\frac{[Fe^{+2}, mol/L] * (D.O., mg/L)}{[H^+, mol/L]^2}, \tag{10}$$

where pH > 3.5 and $K = (1.25 * 10^{-14})\ h^{-1}\ mg^{-1}\ mol^{-2}\ L^{+3}$, or

$$-\frac{d[Fe^{+2}, mol/L]}{dt} = K[Fe^{+2}, mol/L] * (D.O., mg/L), \tag{11}$$

where pH < 3.5 and $K = (1.57 * 10^{-35})\ h^{-1}\ mg^{-1}\ L^{+1}$.

Ackman [1984] also reported the necessary amount of time, $t_{1/2}$, for an initial $Fe^{+2}$ concentration to decrease by 50% to $Fe^{+3}$, which can be obtained by integrating equations (10) and (11) when pH and D.O. are assumed constant:

$$t_{1/2} = \frac{(\ln 2) * [H^{+}, mol/L]^2}{K(D.O., mg/L)}, \tag{12}$$

where pH > 3.5 and $K = (1.25 * 10^{-14})\ h^{-1}\ mg^{-1}\ mol^{-2}\ L^{+3}$, or

$$t_{1/2} = \frac{(\ln 2)}{K(D.O., mg/L)}, \tag{13}$$

where pH < 3.5 and $K = (1.57 * 10^{-35})\ h^{-1}\ mg^{-1}\ L^{+1}$.

It has also been reported that in a sufficiently acidic solution of $H_2SO_4$ and $HClO_4$, the oxidation of ferrous iron is a second-order reaction [Stumm, 1965].

## 2.3 - Copper

Copper has a partially filled d-subshell. As a result, copper exhibits a wide variation in properties such as spectral, magnetic, complexing capacity and oxidation state. The oxidation states of +1 and +2 are common (Cotton and Wilkinson, 1976). In moist air, copper is very slowly superficially oxidized. $Cu^{I}$ can be readily oxidized to $Cu^{II}$, but further oxidation to $Cu^{III}$ is difficult. The hydrolysis of the $Cu^{2+}$ ion starts at a pH greater than 4, followed by the precipitation of the copper oxide or hydroxide (Baes, 1976). Dissolution of copper in acids gives the blue-green ion, $(Cu(H_2O)_6)^{2+}$. The blue sulfate, $CuSO_4.5H_2O$ is often used to prepare $Cu^{2+}$ solutions (Cotton and Wilkinson, 1976).

Only small amounts of $Cu^{+}$ can exist in water, unless these ions are stabilized by complexing agents such as sulfide forming $Cu_2S$. The only important hydrolysis product of $Cu^{+}$ is $Cu_2O$. The concentration of $Cu^{2+}$ which can coexist with copper, can be limited due to the insolubility of $Cu_2O$ when the pH is increased. $Cu_2O$ can be further oxidized to form cupric oxide.

$$Cu_2O + \frac{1}{2}O_2 \longrightarrow 2\ CuO$$

The principal hydrolysis product from $Cu^{2+}$ is $Cu_2(OH)_2^{2+}$. According to Baes (1976), cupric hydroxide can be formed as follows:

$$Cu^{2+} + 2H_2O \Longleftrightarrow Cu(OH)_2 + 2H^+$$

Copper has very low tendency to passivate in aqueous environment and reacts easily with oxygen. The oxidation rate increases therefore in aqueous solutions and the following reaction occurs:

$$2\ Cu + 4\ H^+ + O_2 = 2\ Cu^{2+} + 2H_2O$$

Copper has a low corrosion rate in non-oxidizing acids. In HCl solutions on the other hand, the corrosion of copper is higher, because of the formation of complexes such as $CuCl_2^-$ (Leidheiser, 1971). In marine environments, copper chlorides are formed and this accelerates corrosion. In aerated water, corrosion increases with $Cl^-$ concentration and with decreasing pH. The presence of $SO_2$ in the air accelerates the corrosion of copper as well. The formation of oxide films to increase corrosion resistance is very insignificant for copper (Tomashov, 1966). The presence of zinc and aluminum, decreases the corrosion rate of copper (Uhlig 1971).

## 2.4 - Aluminum

Aluminum is a metal with many covalent compounds. Many of the compounds of aluminum are electron deficient. Aluminum has only three electron pairs in the valence shell, hence aluminum atoms can accept another pair of electrons to make up the outer shell (octet forming). According to Heslop (1967), the tendency to complete an octet is shown by the existence of tetrahedral compounds, which could be formulated as complexes. $Al^{3+}$ is unhydrolyzed below a pH of 3. It forms strong complexes with hydroxides and fluorides (Baes, 1976). In the pH range 4-5, $Al^{3+}$ in solution forms aluminum hydroxide. The formation of aluminum hydroxide, results in a smaller percentage change in the $Al^{3+}$ concentration com-

pared to the $H^+$ concentration. The following reaction takes place at room temperature (Baes, 1976):

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$$

At low pH values $Al(OH)_3$ begins to form. At close to neutral pH values, a protective film of $Al_2O_3$ or $Al_2O_3.3H_2O$ is formed, which protects aluminum from further corrosion. At high pH values, $AlO_2^-$ is formed (Shreir et al., 1994). Aluminum reacts in the following way with oxygen when heated to high temperatures:

$$2\ Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3$$

When aluminum is dissolved in concentrated hydrochloric acid, $AlCl_3.\ 6H_2O$ can be crystallized. The solution of aluminum chloride has an acid reaction due to the breakdown of $Al[H_2\ O\ ]_6Cl_3$ (Wood, 1967).

$$2\ Al(H_2O)_6Cl_3 \longrightarrow Al_2O_3 + 6HCl + 9H_2O$$

The $Al^{3+}$ ions which are moderately acidic, give in $H_2O$ the following reactions:

$$[Al(H_2O)_6]^{3+} = [Al(H_2O)_5](OH)^{2+} + H^+$$

The corrosion rate of aluminum increases in chloride medium and the passive film can be destroyed by chlorides. The combination of carbonate, chloride, and copper increases the aluminum corrosion rate significantly (Shreir et al., 1994).

## 2.5 - Lead

Lead atoms exhibit low electronegativity. The bonds in many of their compounds are strongly ionic. Lead occurs usually in its +2 oxidation state (Heslop, 1967). Lead(II) hydroxide can be formed in soft water (Wood, 1967). The lead hydroxide is not a stoichiometric compound and is in actuality a hydrous oxide, $PbO.xH_2O$, where x is variable. PbO occurs in two crystalline forms: litharge (red), the stable form at room temperature, and massicot (yellow). When heated in air,

PbO (litharge) forms first, followed by $Pb_3O_4$, red lead. The following reaction involved red PbO:

$$PbO + H_2O \Longleftrightarrow Pb(OH)_2$$

At room temperature, red PbO might react as follows (Baes, 1976):

$$PbO + 2H^{2+} \Longleftrightarrow Pb^{2+} + H_2O$$

Lead is generally corrosion resistant. Zinc aggravates lead corrosion in most circumstances. Additions of copper may reduce the corrosion resistance. Some corrosion products of lead are: $PbCl_2$, PbO, and $PbO_2$. The corrosion products are insoluble and protect lead from further corrosion. Since lead chloride is less soluble in moderately concentrated hydrochloric acid, the corrosion rate reduces. The corrosion rate increases in NaCl solutions. In marine environments, an initial film of $Pb(OH)_2$ is formed. This $Pb(OH)_2$ film will then react with NaCl to form $PbCl_2$ and NaOH. This may result in corrosion of other materials such as aluminum and iron, once these metals are also present in the solution (Shreir et al., 1994).

The corrosion of the lead metal is very pH dependent. At pH values between 3 and 4, the protective film is formed rapidly. The corrosion is minimum in the neutral zone between 4 and 9, and at high pH values lead corrosion increases rapidly (Tomashov,1966).

## 2.6 - Zinc

Zinc can lose two electrons in the outermost shell and shows no tendency to lose more electrons from the inner shell. Therefore, zinc cannot increase its oxidation state above two. Zinc is fairly electropositive and reacts readily with nonoxidizing acids releasing hydrogen and giving the divalent ions (Cotton, 1973).

The ability of the zinc metal to form a protective layer consisting of zinc

oxide and hydroxide or of various basic salts, enables zinc to be very corrosion resistant. Zinc is therefore used to coat (galvanize) iron. In dry air, a film of zinc oxide is initially formed, because of the influence of atmospheric oxygen. This film soon converts to zinc hydroxide, basic zinc carbonate or other basic salts. The first layer formed, protects zinc from further corrosion. The formation of the protective layer is very pH dependent. The corrosion rate of zinc varies with pH. At pH values of between 4 and 6, the corrosion attack is rapid and the protective layer is formed. Between the pH values of 6 and 12, the corrosion is very slow and at high pH values the corrosion is rapid. In marine environment, the high chloride content would tend to increase the zinc corrosion rate, with the formation of zinc chloride, but the corrosion rate is inhibited by the presence of calcium or magnesium ions (Shreir et al., 1994).

Radeker et al. (1961), investigated the effects of aluminum, copper, and lead on zinc corrosion. They found that small additions of aluminum increases the corrosion rate of zinc, especially if lead is also present. Thus, lead in conjunction with aluminum will increase the corrosion rate of zinc. Copper decreases the corrosion rate of zinc and inclusions of iron and lead accelerate zinc corrosion (Slunder et al., 1983).

## 2.7 - Ion Interaction and Rate of Reaction

In order to understand the rates and chemical processes in natural waters of elements, it is important to have a knowledge of ion interaction. The rates of ionic reaction of metals and non-metals can be affected by the major and minor components of natural waters. According to Millero (1989), the rates of oxidation of metals can be affected by the anions $Cl^-$, $OH^-$, $SO4^{2-}$, $HCO_3^-$ in aqueous solutions.

The formation of

$$Cu^{+} + Cl^{-} \longrightarrow CuCl$$

causes the rates of oxidation of Cu(I) to decrease. The formation of ion pairs

$$Fe^{2+} + Cl^{-} \longrightarrow FeCl^{+}$$

decreases the rates of oxidation of Fe(II) with $O_2$.

The pH of a solution also plays an important role in the reactions of metals and non-metals in aqueous solutions. Increases in the pH can affect metals by providing $OH^{-}$ and $CO_3^{2-}$ that can react with the metals forming hydroxides or carbonates. The oxidation of Fe(II) with $O_2$ has a pseudo first-order rate with respect to oxygen. Stumm and Lee (1961), showed that the oxidation of Fe(II) with $O_2$ has a second-order rate with respect to pH in water. This is also true for seawater and solutions of NaCl.

The oxidation reaction of ferrous iron consumes acid (Raudsepp et al,1986).

$$4Fe^{2+} + O_2 + 4\ HCL = Fe^{3+} + 2H_2O + 4Cl^{-}$$

If there is insufficient acid present, ferric iron is unstable in solution and iron compounds such as $Fe(OH)_3$, FeO(OH) and $Fe_2O_3$ can precipitate. $Fe_2O_3$ is formed by the following reaction

$$2Fe^{3+} + 3H_2O + 6Cl^{-} = Fe_2O_3 + 6HCl$$

The rate of oxidation of ferrous iron can be chemically controlled. The rate of ferrous oxidation can be described as follows:

$$R = K_0\ K_1\ K_2\ a_{H^+}\ a_{Cl^-}\ [Fe^{2+}]\ P_{O_2}$$

The rate of ferrous oxidation is strongly dependent on the activities of $H^{+}$ and $Cl^{-}$ ions in solution. Factors which affect the reaction rate are temperature, oxygen partial pressure, gas rate, gas dispersion, and solution composition.

Awakura (1986), studied the oxidation of Fe(II) in HCl solutions with dissolved oxygen in the presence and in the absence of a cupric catalyst. He found that in HCl solutions, the oxidation rate was proportional to [Fe(II)], $P_{O_2}$ and $a_{HCl}$. In the presence of cupric chloride the overall oxidation reaction in HCl solutions was chemically controlled. Results from the conducted experiments showed that when Fe(II) ions were oxidized to Fe(III) with dissolved molecular oxygen in concentrated HCl solutions containing a small amount of Fe(II), the oxidation rate was first-order with respect to concentration of Fe(II) and proportional to $P_{O_2}$. At higher concentrations of Fe(II) in aqueous HCl solutions, the oxidation rate tends to be related to the ratio [Fe(II)]/[HCl].

The dependency of the oxidation rate on the Fe(II) concentration tends to move from first-order to second-order with increasing value of [Fe(II)]/[HCl]. The oxidation reaction of Fe(II) is an acid consuming reaction, hence the progress of oxidation decreases the concentration of acid in the solution. In cases were the Fe(II) concentration is comparable to or higher than the HCl concentration, the concentration of HCl and thus the $a_{HCl}$ changes as the reaction continues. This influences the oxidation rate significantly. As the Fe(II) oxidation reaction proceeds, $H^+$ ions are consumed, but the concentration of $Cl^-$ ions does not change throughout the reaction. An increase in the Cl concentration will increase the oxidation rate of Fe(II) at first, to decrease the oxidation rate at higher Cl concentrations (Awakura, 1986).

According to Awakura (1986), the oxidation rate of Fe(II) increased greatly in the presence of a Cu(II) catalyst, regardless of the presence or absence of NaCl in solution. The oxidation rate for Fe(II) oxidation in the presence of $CuCl_2$ was not first-order. During the reactions, an obvious decrease in the oxidation rate was

observed. This indicates that Fe(III) produced during the reaction depresses the oxidation rate. The determination of the initial oxidation rate was rather difficult. The assumption was made that the oxidation rate was of second-order with respect to Fe(II) and first-order with respect to Fe(III). The experiments conducted by Awakura (1986), showed that the oxidation rate is proportional to $[(Fe(II)]^2/[Fe(III)]$.

## 2.8 - Produced Water Treatment Management Alternatives:

Due to high salinity and the organic and inorganic constituents of oil-field brine, environmental regulations prohibit the discharge of these waters into surface waters. Where this discharge is permitted, the produced water must be treated to remove the harmful elements. Many studies have been conducted in the mining as well as in the petroleum industry, to eliminate or reduce the toxic elements in produced water.

Oil-field brine may contain some or all of the following elements: carbonate, bicarbonate, sulfate, chloride, calcium, sodium & potassium, iron, barium, total dissolved solids, copper, magnesium, lead, and organic structures. Even though, there are many techniques available for treatment and disposal of waste water, their implementation and operation are very expensive, causing financial strain for petroleum companies, particularly the small independents.

Elements that are found in natural waters may be divided into three groups: major components, minor components, and trace components. Dissolved solids contribute the most to the chemistry of natural waters. Major components comprise ions or salts from these dissolved solids. These components are: Calcium, Magnesium, Sodium, Chloride, Sulfate, Bicarbonate and Carbonate. Minor components

consist of ions that are found occasionally in low concentrations in natural waters or plant waters. These components are often: Barium, Carbon Dioxide, Chromate, Hydrogen Sulfide, Iron, Manganese, Oxygen, Phosphate, Silica, and Sulfite. Most of the elements which are not listed as major or minor elements are found in water in only trace amounts. Some of these elements are: Lead, Nitrite, Nitrate and Copper.

Some relevant methods and technologies that have been used in the oil industry are catalogued by Ostroff, 1965. They include: aeration, chemical oxidation, ion-exchange, lime neutralization, sedimentation, filtration, dilution, soda-ash process, distillation, and reverse osmosis.

The methods listed above have been implemented for reduction of heavy metals, organics, and suspended solid from brine. The aeration and filtration techniques have been found to be very efficient in removal of heavy metals. Generally, treatment technologies can be categorized in four groups: physical, chemical, thermal and biological methods. In most cases however, more than one method is required for a satisfactory result in waste water treatment. A synopsis of these methods will be discussed herein.

### 2.8.1 - Physical Treatment Methods

These, include methods that rely on physical means such as differences in specific gravity, vapor pressure, adsorption, particle size etc. A few of the developed technologies in physical treatment methods are: encapsulation, gravity separation and solidification/stabilization.

A study done by Zaidi et al. (1992), focused on the application of membrane technology to the removal of oil and suspended solids from produced waters using

microfiltration (MF)/ultrafiltration (UF) technology. MF and UF processes offer the potential for generation of high quality effluent water on a more consistent basis than conventional technologies and may offer additional advantages in terms of space and weight savings, and treatment costs. The cost of recycling lines, valves and pumps contribute significantly to the total capital cost of this type of system.

This technology seems capable of reducing the oil content in produced water to low levels. More research needs to be done in the field of comparative studies to evaluate alternative systems designs and flux enhancement techniques on actual produced water samples.

Another physical treatment process which has been used lately is reverse osmosis. Reverse Osmosis process in the San Ardo oil field converted produced brine into freshwater (Oil & Gas Journal, Sep 20, 1993). The conversion process used chemical clarification, softening, filtration, and reverse osmosis (RO). High-salinity water, requires processes such as distillation or reverse osmosis. Distillation is energy intensive and expensive, and is therefore not cost-effective. The mount Poso cogeneration plant, near Bakersfield, CA was the first large-scale RO plant for oil field produced water. The plant treats the produced water by oil separation, clarification, filtration, RO, and dimineralization to produce a boiler feed water for the cogeneration power plant. This process proved ineffective for the San Ardo water. Controlling the stability of produced water, proved to be the key for successful RO operation in San Ardo.

### 2.8.2 - Chemical Treatment Methods

These, include methods that chemically alter contaminants to produce inert constituents, or reduce their toxicity or mobility. These treatments are usually fol-

lowed by other treatments to complete the elimination of hazardous compounds. Some of the new and innovative technologies in this area, mentioned by Dudley et al. (1989), are: chemical transformation, solvent extraction, organic extraction and chemical destruction

### 2.8.3 - Thermal Treatment Methods

These, include processes that employ elevated temperatures to destroy or remove contaminants. A number of thermal treatment methods that have been shown to be applicable to wastewaters and have been mentioned by Dudley et al.(1989) are: advance liquid injection incineration, rotary kiln oxidation, fluid bed incineration, infrared incineration, advance electric reactors, plasma incineration, pyrolysis, molten glass and wet oxidation.

Each of the methods listed above contain different processes, and they are flexible to a variety of different wastes such as solids, liquids, gases, and sludges. Dudley et al. (1989), list and describe advantages and limitations of each of these methods. However, in dealing with large bodies of waste water disposal, the above mentioned methods lose their attactions due to the lack of economic feasibility.

### 2.8.4 - Biological Treatment Methods

Biological treatment includes procedures that use microorganisms to biodegrade contaminants. Naturally occurring or synthetic microorganisms, bacteria, can be used in breaking down and biodegrading chemicals like organic hazardous substances. The most important biological treatment methods include: *In-Situ Biodegradation, Powdered Activated Carbon Treatment* and *Fluid Bed Biological Systems*. Biological treatment methods seem to be very effective in the removal of

organics from wastewater. However, these methods require long residence time, up to several months.

A different technology for water treatment that has recently drawn attention and has been applied in the mining industry is biological water treatment using natural or man-made wetlands. Field studies on wetlands have shown that biological treatments are effective in removing metals such as iron (Fe), nickel (Ni), lead (Pb), copper (Cu), zinc (Zn), arsenic (As), and cadmium (Cd). The concept is based upon the argument that the wetlands vegetation has the ability to uptake inorganic salts and to produce water that contains less total dissolved solids for direct discharge into the surface waters. This results in the accumulation of biomass that contains a high concentration of salts. If the process takes place in a natural wetland, there are two concerns; First, the wetland itself will become contaminated with salts, resulting in a potentially larger environmental problem, and secondly, the surface discharge is regulated. To avoid these issues, the concept of using engineering wetlands has been proposed where the wetlands are contained in a closed system that will not permit the uncontrolled escape of the contaminants into the environment.

According to Klusman 1991, the processes in natural and constructed wetlands include:

1. Exchange of metals by an organic-rich substrate.
2. Sulfate reduction with precipitation of iron and other metal sulfides.
3. Methanation, resulting in production of carbon dioxide and methane.
4. Denitrification with production of ammonium ion.
5. Nitrogen fixation with production of ammonium ion.

6. Iron reduction.

7. Precipitation of metals by ferric oxyhydroxides.

8. Adsorption of metals by ferric oxyhydroxides.

9. Metal uptake by living plants.

Plants in wetlands have two important functions: to simulate microbial processes and to remove metals from aqueous phase (Kleinmann et al., 1991). Metal uptake by plants varies depending on the metal and the kind of plant. For instance, Spagnum has a high tendency to accumulate iron. The metals are recycled when the plants die. The most commonly used plants in wetland construction are: Spagnum, Typha, Algae, and Latifolia.

Another biological water treatment process uses BIO-FIX beads. BIO-FIX beads are porous polymeric beads that contain immobilized biological materials. These beads are fabricated from raw materials such as Algae, Duckweed, Spagnum, and Yeast and are stable in both strong acid and base solutions (Bennet et al,. 1991). The problem with this system include liquid/solid separation and metal removal from load material.

Machemer and Wildeman, (1991), compared adsorption with sulfide precipitation, as metal removal processes from acid mine drainage in a constructed wetland. Metal removal processes from acid mine drainage were studied in an experimentally constructed wetland. The studies suggest that there is competition for organic adsorption sites among Fe, Cu, Zn and Mn. Iron and copper appear to be more strongly adsorbed than Zn and Mn. The adsorption of metals varies with the fluctuation of pH in the outflow water.

The metals Mn, Zn, and Cu are soluble at mine drainage concentrations and a pH of 4.5 (Stumm and Morgan, 1981). This suggests that the most likely metal

removal process occurring is metal adsorption onto organic material. The adsorption of metals varies with the fluctuation of pH in the outflow water.

Recent studies suggest that the waste water treatment methods mentioned above, seem to be effective and environmentally safe. However, there are some difficulties and problems with adopting these systems for treating oil-field brines. The iron removal in these processes like the conventional processes requires considerable amount of residence time. Although the operating costs associated with these processes are lower than the chemical treatment processes, biological waste water treatments are still expensive. Another disadvantage is that the biological treatment systems may not be practical for the oil and gas wells, because of their remote and limited-access locations.

A related concept which is under investigation is the use of plants to treat produced waters to yield a low-volume concentrated brine, which can then be treated using conventional means. This concept is the opposite of the wetland approach in that, the plants enhance the removal of water from the produced waters through evapotranspiration. This evaporative process can substantially reduce the volume of water that requires treatment.

## 2.9 - Reinjection of Produced Water

Injection wells originated in the oil and gas industry in mid-1930's. Since then, this technique has attracted other industries as well. This technique came into favor following the laws and regulations designed for protecting the surface water from pollutants. In the United States, regulatory agencies have classified injection wells into five categories. These classification are made according to the purpose of the wells.

- **Class I:** Wells used to inject hazardous and nonhazardous waste below the lowermost underground source of drinking water.
- **Class II:** Wells associated with the production and storage of oil and gas below the lowermost underground source of drinking water.
- **Class III:** Wells used in special processes such as mining operations to inject fluid above, into, or below an underground source of drinking water.
- **Class IV:** Wells used to inject hazardous waste into or above an underground source of drinking water (currently, this class of wells are banned in the United States).
- **Class V:** Wells used to inject all other wastes into or above an underground source of drinking water.

In general, deepwell injection (Nakles et al., 1992) is the preferred means of disposal for coalbed methane produced waters. The Oil and Gas Board, in accordance with the national Safe Drinking Water Act (SDWA), restricts the injection of produced water into those subsurface regions where the total dissolved solids exceed 10,000 ppm (unless it can be shown that the disposal zone is not a drinking water source) and limits the maximum injection pressure based on a site-by-site maximum which is established to prevent fracturing of the injection zone. These constraints have the effect of increasing the cost of deep well injection. The water quality limit, forces injection into the deeper subsurface zones and the pressure constraints can limit the useful lifetime of the well. These limitations have resulted in only sporadic success in locating subsurface geologic formations that can accept the required quantities of produced water.

Operational as well as environmental limitations often require pretreatment of produced waters prior to deep well injection. Typical treatment processes include

gravity settling, and filtration for the removal of suspended solids. Furthermore, stringent requirements may dictate additional treatment for the removal of trace organics or dissolved salts.

## 2.10 - Ongoing Research on Cost Effective Water Treatment Systems

Most of the new research and studies in this area has been pursued for a similar problem, water production from acid mine drainage. Water flowing from mines contains heavy metals such as iron, which has to be treated before its discharge into the natural waterways. Treating waste water from acid mine drainage involves neutralization, air oxidation, precipitation, and solid/liquid separation. Some of the conventional treatment systems are sodium hydroxide neutralization system and lime and limestone neutralization systems [Staufer and Lovell, 1968].

From the systems mentioned above, the limestone neutralization system, in particular, is of interest. According to Stumm, the dissolution of calcium carbonate in the $CaCO_3$-$H_2O$ system may be written as [Stumm, 1990]:

$$CaCO_3 \longrightarrow Ca^{+2} + CO_3^{-2}. \tag{14a}$$

$$CaCO_3 + H^+ \longrightarrow Ca^{+2} + HCO_3^-. \tag{14b}$$

$$CaCO_3 + 2H^+ \longrightarrow Ca^{+2} + H_2CO_3. \tag{14c}$$

$$CaCO_3 + H_2CO_3 \longrightarrow Ca^{+2} + H_2CO_3^-. \tag{14d}$$

Reaction (14a) occurs under alkaline conditions whereas reaction (14b) occurs under acidic conditions. Limestone (Calcium Carbonate, $CaCO_3$) is often used as a low-cost alkaline agent to raise the pH and to precipitate the iron [Ostroff, 1965]:

$$2Fe^{+2} + 4HCO_3^- + H_2O + 1/2O_2 \longrightarrow 2Fe(OH)_3 + 4CO_2. \tag{15}$$

The reaction rate of calcium carbonate deceases with increasing pH and it is not very effective above a pH of 5.0 [Stumm, 1990, Wentzler et al., 1992]. It was also noted [Patton, 1977] that the solubility of calcium carbonate:

(i) Increases in the presence of Carbon Dioxide.

(ii) Increases as the pH of the solution increases.

(iii) Increases as the salt content of the water increases.

(iv) Decreases as temperature increases.

# 3. A Synopsis of the Proposed Work

## 3.1 - Objective

Given the economic realities existent in the operation of stripper wells, a research program to develop a cost-effective treatment methodology of stripper oil well brine was initiated. The research effort was to produce a computer software package that federal and state agencies and Appalachian stripper well operators could use to provide specific design parameters for a treatment system tailored to their brine discharge. The global objective of this research was to permit the environmentally safe discharge of brines produced from stripper oil wells in Pennsylvania to the surface waters of the Commonwealth in a cost-effective manner and to rapidly bring as many wells as possible into the compliance with the law. The work to achieve the above-elucidated objectives had to take into consideration certain practical aspects of the field and economic nature of production from stripper wells. Theses design considerations included:

- The treatment unit was to be constructed of readily available materials such as plywood and plastic pipe.
- The treatment unit needed to be a gravity flow system since the units could be located at well sites remote from electric power.
- The treatment design needed to be universal in application since stripper well production is from various sand formations which contain brines with a variety of constituent concentrations.

This project has been underway since 1988 to show that a standard treatment process can fully satisfy the requirements of the Part II Water Quality Permit now

utilized in Pennsylvania. Demonstrating that brine treatment and disposal can be standardized should provide the DER with sufficient information to justify the elimination of the engineering cost presently required for each Part II Water Quality Permit. By developing an effective standard brine treatment design that may be scaled according to the characteristics of the receiving stream, this research study could help small independent producers avoid costly professional fees for individualized site and treatment system design. Standardization of the brine treatment process will also justify the use of a "general" permit procedure by the DER, thus eliminating the permit application fee.

The avoidance of such costs will enable a large number of Pennsylvania oil and gas wells to remain in operation while complying with the present requirements of state and federal law. It will permit continuing development of the oil and gas fields in the state by reducing the impact of the cost of compliance on new wells, and the operator would avoid unnecessary fines and penalties which would be imposed as a result of his present economic inability to comply. The project will also avoid loss of much of the labor force and retain future employment opportunities, and preclude millions of dollars of unnecessary expense associated with the premature plugging and abandonment of otherwise productive wells.

## 3.2 - Overall Research Plan

The final goal of this research study was a software package that was to be used as a design tool for a brine facility aimed at the removal of dissolved elements from brine. The system must be capable of treating a wide variety of brines. The strategy developed in order to accomplish the objectives of this research study was:

- To develop a laboratory-based prototype model to proof the concept and con-

duct a number of experiment under control conditions using synthetic brines prepared in the laboratory.

- To develop a field-based prototype model to study the effectiveness of the proposed brine treatment process in treating actual brine from different sand formations with different dissolved chemical constituents.
- To develop the kinetic data base for the reactions and process modeling and to incorporate the experimental data into a PC-model software.

The specific objectives of the developed strategy were:

- Develop a comprehensive data base of stripper wells brines with the view of fingerprinting these brines in terms of their chemical constituents.
- Evaluate and demonstrate the efficacy of the treatment process on a variety of brines common to production from stripper wells at various flow rates.
- Develop a multi-component kinetic data base to quantify the effect of the treatment process on the rate of removal of iron and other dissolved elements.
- Evaluate the effect of temperature on the efficacy of the treatment facility and the reactions inherent to the treatment process.
- Incorporate the effect of temperature in the kinetic model.
- Modify the kinetic model to account for the presence of the elements, their reaction, and the effect of temperature on the rate of removal.
- To develop a data base using the brines being studied to validate the effectiveness of the treatment process.
- Fine-tune the software package needed to design appropriately scaled treatment systems in the field pursuant to requisite federal and state permit standards.

- Develop a program for the transfer of the developed technology to stripper well operators.

## 3.3 - Deliverables

The expected deliverables from this research project included:

- A comprehensive kinetic data base and kinetic model.
- A computer software package to provide design specifications for the brine treatment process.
- A comprehensive report which includes a detailed set of guidelines for the application, design and operation of the brine treatment process.

# 4. Work Performed

## Laboratory Model

### 4.1 - Objective

A bench scale model was constructed to test the effectiveness of the treatment process in removing dissolved elements from brine. The specific objectives of the laboratory evaluation were:

- To determine teatment's efficacy under controlled conditions.
- To refine the treatment process and to provide the data needed to complete the computer program.
- To verify the effectiveness of each component in the developed model.
- To use the collected data for scale-up parameters.

### 4.2 - Principle Behind the Process

Dissolved metals in brine react with oxygen in the air and oxidize and precipitate from the solution. Therefore, in designing the treatment model number of principles had to be accounted for. This principles were:

(I) First, pH of the brine being treated must be raised to a certain level necessary to initiate the oxidation reaction.

(II) Second, air contact with the brine must be adequate to ensure sufficient availability of the oxygen needed for reaction.

(III) Third, sufficient retention time must be imposed to allow for reaction completion.

(IV) Finally, the treated brine must be filtered to eliminate the precipitate and fine particles.

Based on the principles explained above the laboratory and the field-based prototype models were developed. Although the construction of the field model differs for the convenience and durability, the field model is a larger replica of the laboratory model.

## 4.3 - Principal Components of the Developed Model

Realizing the principals behind the oxidation of metal, the developed model was design to composed of four units namely pH adjustment unit, aeration unit, retention tank unit and sand filtration unit. Each of the essential steps in the treatment process is effected in different units. Since this is a continuous process, all the units must be coupled together in such a way that no unit becomes a bottleneck that inhibits treatment rate. Figure 4.1 presents a schematic diagram of the laboratory model. Figures 4.2 through 4.5 also show graphical presentation of each component with its dimensions for the laboratory model.

### 4.3.1 - pH Adjustment Unit

The pH adjustment unit is made up of two packed-bed columns of limestone. The function of these columns is to increase the pH of the brine. Each column is made of transparent 24-in long, 3-in O.D. PVC pipe so that the amount of precipitation on the limestone chips as well as the dissolution of limestone chips in the column(s) can be observed. Limestone columns are vertically oriented and fluid flow is from the bottom to the top to afford maximum contact between the fluid and the limestone chips. The experimental design is such that either one or both lime-

stone columns can be used. In the case of using both, they operate in series. Sampling ports are positioned before and after each limestone column to provide avenues for monitoring pH and iron concentration of the flowing brine.

### 4.3.2 - Aeration Unit

The aeration unit is basically made of a flat surface that is oriented at an angle to the horizontal. This unit is constructed from plexiglass and its function is to expose the brine to air. Within the aeration unit a rectangular box is designed to help the uniform distribution of the fluid on the aeration unit. The aeration unit has an adjustable angle allowing the liquid film thickness on the unit to be changed while it passes through this unit. The basic idea is to maximize air-brine contact and the best non-mechanical way to achieve this is to have a brine flow on the bed of the aeration unit as a thin film. Since the flow rate may vary, an adjustable angle permits the achievement of the thin-film principle. By increasing the angle of aeration unit, the film thickness on the unit decreases allowing larger volume of the effluent to be exposed to air. On the other hand, an increase of the aeration angle will decrease the contact time between the brine and air. The dimensions of this unit are 28 inches long, 12 inches wide and 2.5 inches deep.

### 4.3.3 - Retention Tank Unit

The retention tank's primary function is to provide the necessary avenue to effect separation of the solid precipitate from the treatment fluid. This unit also provides the necessary retention time (residence time) needed for reaction completion. The unit has internal partitions that intersect the direction of flow. They are arranged in such a way that space is left below each partition to allow for flow and

maximize the travel path and therefore increase the retention time. There are two internal partitions in the present system, thus giving us three compartments. Like the aeration unit, the retention tank is also made out of plexiglass and is 24 inches long, 12 inches wide and 12.5 inches deep. The pH and concentration of iron can be measured by taking samples from the sampling ports available before and after the retention tank.

### 4.3.4 - Filtration Unit

The last component in the system is the filtration unit. The function of this unit is to remove the precipitates and fine particles from the solution. The unit is basically a sand box filled with approximately five inches of gravel that is often used for landscaping and approximately two and half inches of white sand placed on the top of the gravel. At the bottom of the vertical pipe that carries the brine from the retention tank to the filtration unit, a 15-inch horizontal pipe is attached. A number of holes are made over the entire length of this horizontal pipe so that brine can be distributed over a larger surface of the sand as opposed to a small area. This unit is 19 inches long, 19 inches wide and 14.5 inches deep and is made out of plexiglass. Samples are taken before and after the filtration unit to investigate the effectiveness of the unit.

## 4.4 - Preparation of Synthetic Brine

Effectiveness of the proposed brine treatment process was studied in the laboratory by using synthetic brine which was contaminated with dissolved iron. Iron was chosen as an indicator of the model's ability in removal of dissolved heavy metals. The procedure by which synthetic brines with various dissolved iron concentration were made in the laboratory is described here. Distilled water was

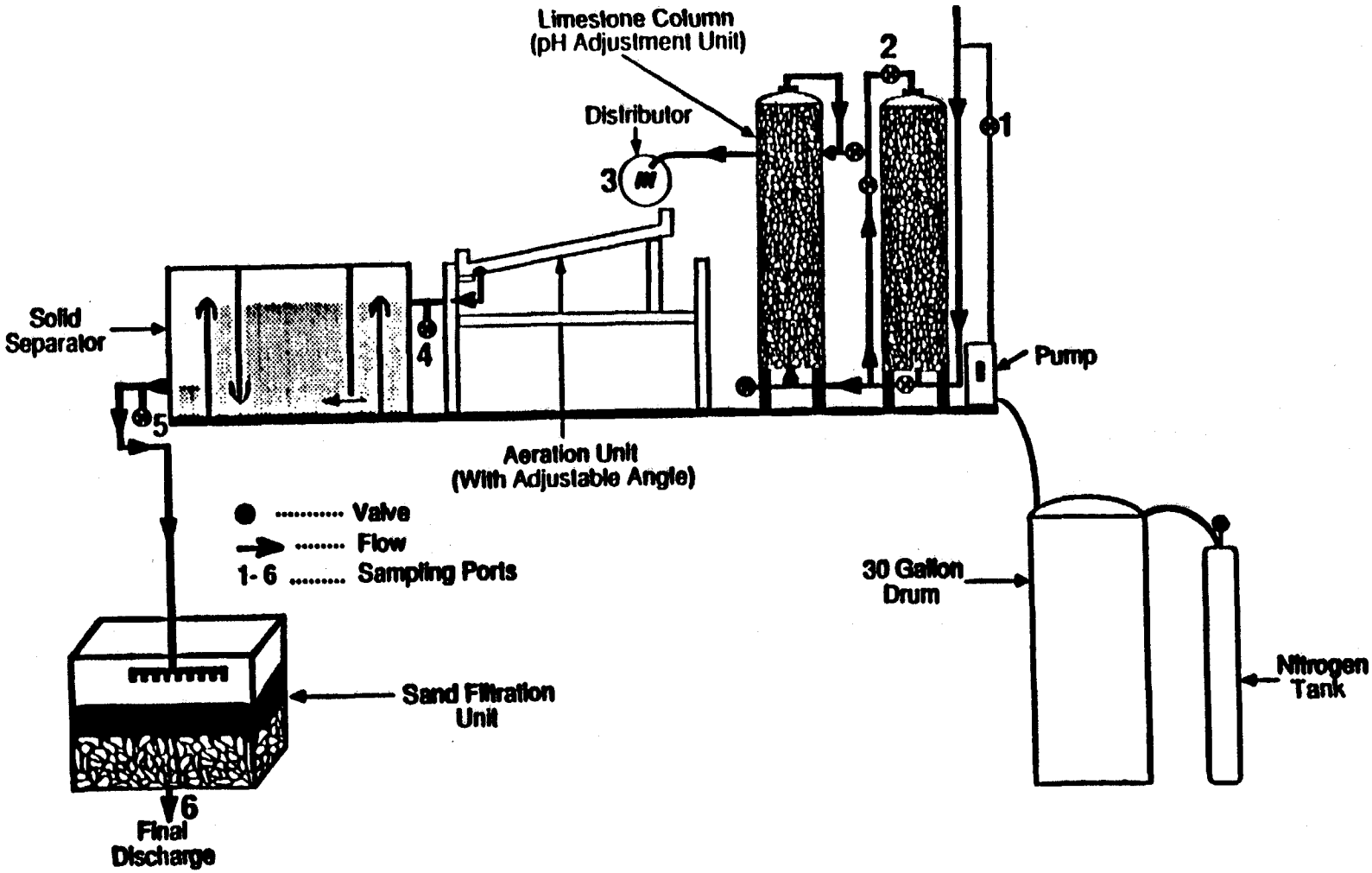


Figure 4.1. Schematic Diagram of the Laboratory-Scale Model

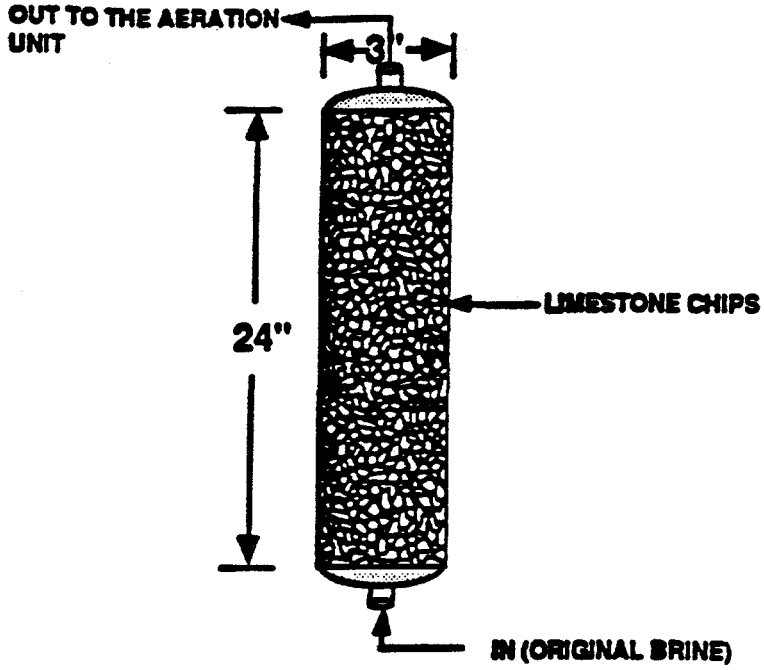


Figure 4.2. Graphical Presentation of the pH adjustment Unit

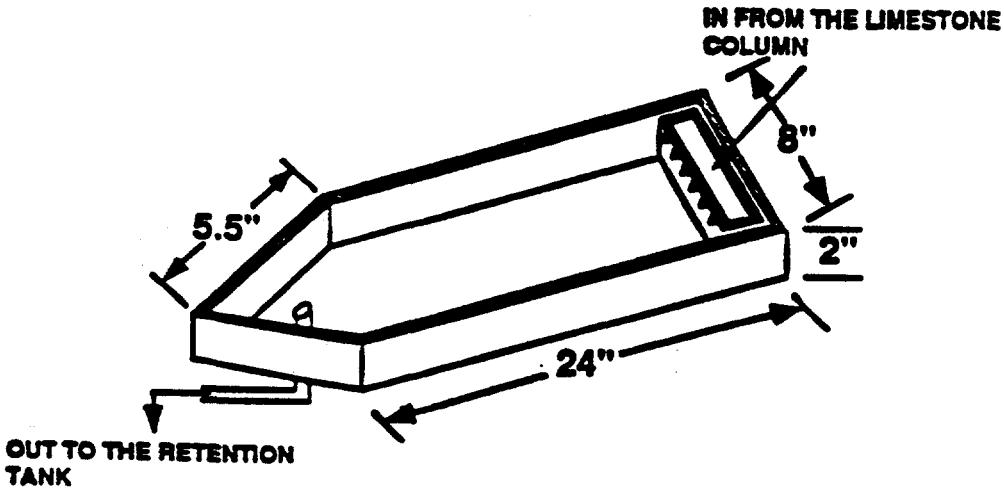


Figure 4.3. Graphical Presentation of the Aeration Unit

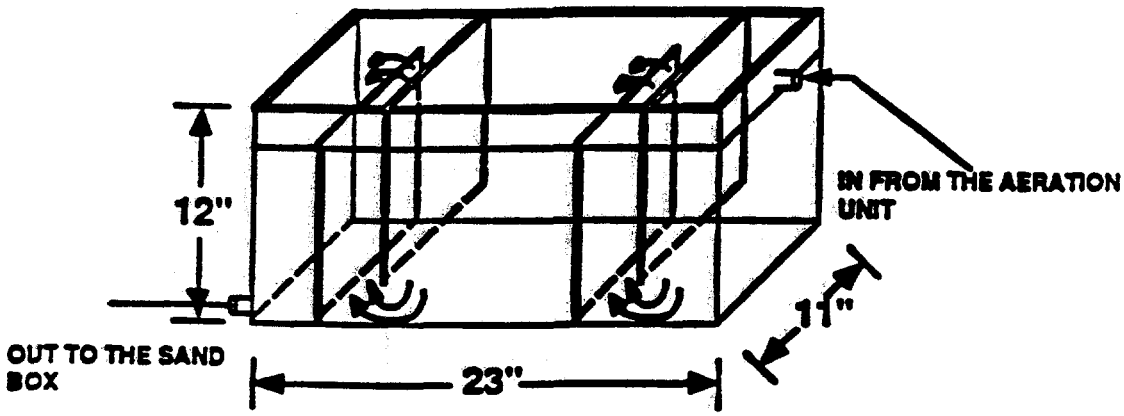


Figure 4.4. Graphical Presentation of the Retention Tank Unit

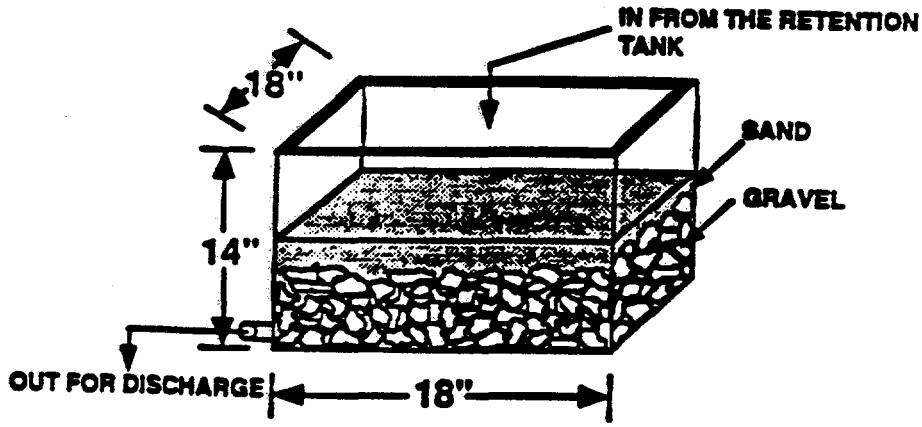


Figure 4.5. Graphical Presentation of the Filtration Unit

stored in a 300-gallon storage tank for a few days to allow the dissolved oxygen in the water to evolve. For each experiment, 30 gallons of the stored water was transferred into an electric water heater unit and was heated to approximately 140° F for further reduction of dissolved oxygen in the water. Distilled water was then drawn from the water heater into a 30-gallon drum and was allowed to cool down to room temperature prior to use. Nitrogen was percolated through the bottom of the drum to induce the elimination of dissolved oxygen in the water. Elimination of the dissolved oxygen from the brine helped to prevent any premature reaction from occurring between iron and oxygen upon the addition of iron.

The estimated concentrations of sodium, chloride, and calcium were approximately 3950, 6765 and 380 ppm, respectively. Therefore, 1140 grams of NaCl and 120 grams of $CaCl_2$ were dissolved in distilled water (in a glass beaker holding approximately 4 liters of distilled water) and then added to the distilled water in the drum to replicate the concentration of salt in brine. The salt solution was added to the distilled water in the drum while the nitrogen was percolating through the bottom of drum to help the mixing process. The appropriate amount of iron salt (Ammonium Iron (II) sulfate) was weighed and poured into a 300 ml glass beaker that contained a mixture of distilled water and hydrochloric acid, HCl (a one-to-one ratio). To duplicate the synthetic brines that contain 50, 100, 150, 200 PPM of dissolved iron, 40, 80, 120, and 160 grams of iron salt were used respectively. The concentrated iron solution was added to the brine in the drum while nitrogen continued to percolate through the bottom. Additional 300 ml of hydrochloric acid was added to the brine in the drum to force the pH of the synthetic brine below 2.0 where no oxidation reaction could occur. Injection of nitrogen gas was continued throughout the experiments to prevent the contact between the brine and air at any

time.

Required ferrous salt for preparing the desired concentration can be determined by:

$$50 \text{ ppm} = 5*10^{-5}$$

Converting the volume from gallon to ml:

$$30 \text{ gallon} * 3785\frac{\text{ml}}{\text{gallon}} = 113550 \text{ ml}$$

Multiplying the volume by the desired concentration:

$$113550 * 5 *10^{-5} = 5.675 \text{ grams} \quad \text{(required iron)}$$

Considering the molecular weight of the iron salt:

$$(NH_4)_2Fe(So_4)_2 \cdot 6H_2O = 392.14 \text{ grams}$$

Considering the molecular weight of iron:

$$Fe = 55.85$$

determining the weight of iron in the Ammonium Iron(II) sulfate Hexahydrate:

(392.14grams) over (55.85grams)) = 7.021

Calculating the amount of Ammonium Iron(II) sulfate Hexahydrate:

5.675 (grams) * 7.021 = 39.85 grams

## 4.5 - Operating Procedure

Using a small water pump, synthetic brine was pumped into a 1- inch diameter PVC pipe from which brine was allowed to flow through the first and then second limestone column. The flow rate at which the experiment was conducted was set manually on the water pump. The pH of the brine was raised by the pH adjustment unit. The effluent from the pH adjustment unit has a pH value of 6.0 or slightly less. It should be noted that the pH increase of the brine by the pH adjustment unit was a function of throughput flow rate and inlet concentration of iron. Table 9 illustrates the effectiveness of the pH adjustment unit in various conditions. Brine from the pH adjustment unit was allowed to flow over the aeration unit where it was exposed to the atmosphere for the first time. Traveling through the aeration

unit, the brine flowed into the retention tank unit and after passing through the partitions within the unit, it finally flowed into the filtration unit where precipitates and fine particles were removed. There were six sampling ports available on the prototype model, allowing one to monitor the pH and the concentration of iron before and after each unit. These sampling ports are located before fluid enters the first limestone column, after exiting the first and second limestone columns, the aeration unit, the retention tank, and the filtration unit.

## 4.6 - Sampling Procedure

During each experiment, at designated time intervals, samples were taken from the sampling ports. Fifty to sixty samples were collected in each experiment to investigate the effectiveness of the treatment process (iron removal) with time. Approximately 150-200 ml of brine sample were taken from the sampling ports and poured directly into paper cups. Promptly, 13 ml of the samples were drawn from the cups and transferred into plastic tubes. Special syringes with filtration capability were used for this transfer (size 0.45 mic, 25 mm). These syringes were required to prevent the entrance of the solid particles into the sampling tubes. The samples in the plastic tubes were immediately acidified using 0.3 ml hydrochloric acid to stop further oxidation reaction. Samples in the plastic tubes later were analyzed for their content of total iron using the Inductively Coupled Plasma method.

Certain volumes of the acidified samples were drawn from their containers into some other plastic test tubes that contained 1.0 ml sodium acetate and 2.0 ml phenanthroline solutions. The volume of the acidified sample added to the chemical mentioned above was a function of ferrous iron concentration. Since all the

experimental work in this study involved approximately 50, 100, 150, and 200 ppm iron (ferrous iron), 1.0, 0.5, 0.25, and 0.25 ml of samples were used. According to the concentration of ferrous iron, solutions in the test tubes turned to light pink to red color. These samples were further analyzed for their content of ferrous iron. The rest of the remaining samples in the cups were used to determine the pH of the solution using a pH meter.

## 4.7 - Analytical Methods

There were three principal analytical instruments used for analyzing the samples which were collected in each experiment (for inorganic compounds). They were the Inductively Coupled Plasma (atomic emission spectrometry), Optical System Spectrometer, and pH meter. The Inductively Coupled Plasma was used to determine the concentration of total iron in solution (ferrous and ferric iron combined). The Optical System Spectrometer was used to determine ferrous iron in the solution. Finally, the pH meter was used to monitor the pH of the samples taken throughout the treatment process. Organic analysis were conducted by extracting the organic compounds using different extraction methods. The extracts were then analyzed with GC/MS.

### 4.7.1 - Inductively Coupled Plasma

The Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) is a powerful analytical instrument capable of detecting many elements such as iron simultaneously. The "ICP-AES" combines high-temperature Argon plasma excitation source with high dispersion. The unique plasma configuration excites the sample in an inert argon atmosphere that effectively reduces the matrix effect normally

associated with methods employing lower temperatures. The sample is aspirated into the argon plasma fireball where sample aerosol droplets are heated between 6000 and 8000 K. The extreme temperature effectively dissociates molecules and imports sufficient energy to the atoms so that the sensitivity of the system is equal to or exceeds that of other methods such as Atomic Absorption. Prior to the analysis of the samples, the instrument had to be calibrated by a set of standard solutions. Atomic Spectroscopy Standard solution for iron that is available commercially was used for calibrating the "ICP-AES". A portion of the standard solution that is highly concentrated (1000 ppm) is diluted to obtain lower concentrated iron standard solutions (ranging from 25 ppm to 200 ppm in increment of 25 ppm). The procedure by which lower atomic spectroscopy iron standards were prepared is shown below:

$$\left(\frac{\text{X ml of high standard solution}}{\text{Total volume}}\right) * \text{Original concentration} = \text{New concentration}$$

For example, 100 ml of 50 ppm standard iron solution can be prepared from the stock solution that contains 1000 ppm iron:

$$\frac{5\text{ ml}}{100\text{ ml}} * 1000\text{ ppm} = 50\text{ ppm}$$

Leeman's "ICP-AES" used for this analysis is totally automated and once the instrument is calibrated is capable of analyzing up to 88 samples at a time. Matrix brine (brine with proper salt concentrations and no iron content) is used for the zero iron standard solution. The "ICP-AES" is a fast and accurate method for determining the total iron concentration, without making a distinction between the ferrous and ferric ion. The detection level of ICP-AES depends on the concentration of the metal being analyzed. At high concentration (e.g. 50 ppm), the detection level of

ICP-AES is about 500 ppb. This limitation is due to some "memory carry over" from the reading of the highly concentrated solution to the low concentrated solution. The accuracy and detection level of the instrument improves when working with low metal concentration solutions; hence it is not limited by a specific metal but rather by concentration. Since iron is the predominate heavy metal in all the brines we have encountered (both in the laboratory and field), the limitation of 500 ppb is the worstcase scenario.

### 4.7.2 - Optical System Spectrometer

The Optical System Spectrometer was used to determine the ferrous concentration of the sample solutions. Some element ions such as iron (in ferrous state) in solution react with certain ion-specific reagents to form intensely colored complexes. In the case of iron, ferrous ions react with 1,10-phenanthroline to form a red-colored complex which absorb light photons. There is a direct relationship between the concentration of ferrous ions and the intensity of absorbed light. Therefore, using a U-V-Visible Spectrophotometer and measuring the absorption of ferrous ion complex, concentration of ferrous iron can be determined. Unlike the Inductively Coupled Plasma, the samples for analysis were treated chemically and the concentration of the iron in the solutions were reduced in order to use the instrument. This instrument had to be calibrated prior to the analysis of the samples as well. Calibrating the instrument required a set of colored standards. The following solutions were prepared for colored standards :

A) Standard iron solution, 1.404 grams of Ammonium Iron(II) Sulfate Hexahydrate is dissolved in 50 ml of distilled water and 20 ml of concentrated sulfuric acid ($H_2$ $So_4$). $KMn_4$ in a drop-wise manner is added to the solution

until a faint pink color persists. Distilled water is added to the solution to increase the volume to 1000 ml. This solution therefore will contain 200 ppm of ferrous iron (200 μg Fe) in one ml.

B) Sodium Acetate solution: 200 grams of Sodium Acetate is dissolved in 800 ml of distilled water and slightly heated up to make up the Sodium Acetate solution.

C) Phenanthroline solution: dissolving 1 gram of 1,10-phenan-throline monohydrate, $C_{12}H_8N_2.H_2O$, in 1000 ml of distilled water by stirring and heating the phenanthroline is prepared.

For making the colored standards, 0.5, 1.5, and 2.5 ml of the standard iron solution is pipetted into three 100 ml volumetric flasks. Then 1 ml of sodium acetate and 2 ml of phenanthroline solution are added to each flask and distilled water is used to dilute the mixture to volume (100 ml). Prepared colored standards will therefore contain 1, 3, and 5 ppm ferrous iron.

### 4.7.3 - pH Meter

A Fisher pH meter is used for determining the pH of the samples taken from the sampling ports. This pH meter was equipped with three different probes for precise readings. While one of these probes adjusted the temperature continuously, one of the other two remaining probes was the reference probe and finally the last probe was the detecting probe. Prior to each experiment, the pH meter was calibrated using buffer solutions ranging from pH 4.0 to pH 10.0.

### 4.7.4 - Determination of Actual Iron Concentration

The measured concentration of total iron (ferrous and ferric) and the ferrous iron by "ICP-AES" and U-V-Visible Spectrophotometer had to be corrected in order to obtain the actual concentration of iron. As mentioned earlier, samples taken throughout the experiments were treated with hydrochloric acid to prevent further oxidation reaction. Also, a small portion of the samples (ranging between 0.25 to 1 ml) had to be added to the required chemicals where U-V-Visible Spectrophotometer was used. Therefore, the sample's original volumes are changed and diluted as a result of which the measured concentrations are lower than the actual concentrations. Extra cautions were taken in working with brines containing high concentration of iron because of the dilution factors involved. A sample of the actual iron concentration determination is presented below. The concentration of iron in these calculations was assumed to be 200 ppm.

Required calculations from the measured iron concentration by "ICP-AES", ferrous and ferric iron combined :

Sample's original volume = 13 ml

Volume of the HCl added to the sample = 0.3 ml

Total volume = 13.3 ml

$$\text{Dilution factor} = \frac{13\ \text{ml}}{13.3\ \text{ml}} = 0.977$$

Measured concentration of iron by "ICP-AES" = 196 ppm

$$\text{Actual concentration of iron} = \frac{\text{Measured concentration of iron}}{\text{dilution factor}}$$

$$= \frac{196\ \text{ppm}}{0.977} = 200.52\ \text{ppm}$$

Required calculations from the measured ferrous iron concentration by U-V-Visible Spectrophotometer:

Sample's original volume = 0.25 ml

Volume of the phenanthroline solution added to the sample = 2 ml

Volume of the sodium acetate solution added to the sample = 1 ml

Volume of the brine matrix = 6.75 ml

Total volume = 10 ml

$$\text{Dilution factor} = \frac{0.25\ \text{ml}}{10\ \text{ml}} = 0.025$$

Measured concentration of ferrous iron = 4.8 ppm

$$\text{Actual concentration of ferrous iron} = \frac{\text{Measured concentration of ferrous iron}}{\text{dilution factors}}$$

$$= \frac{4.8\ \text{ppm}}{0.997 * 0.025} = 196.43\ \text{ppm}$$

It is obvious that small errors in transferring or measuring the samples and other chemical solutions would be magnified into significant errors when the dilution factors are applied in calculations and determinations of actual iron concentrations.

### 4.7.5 - Organic Analysis

Since water samples could have not been injected directly into the instruments, they were first extracted using two extraction methods. The extracts were analyzed by GC and GC/MS. The procedure used for extraction and the GC and GC/MS analyses were:

**1) Hexane Extraction:** 5 ml of n-hexane (HPLC grade) were taken in a separatory funnel and 6 ml of the water sample were added to the hexane. The mixture was shaken for a minute with occasional venting for release of excess pressure. Time was allowed for the hexane layer to separate from the water layer. Then the water layer was separated from the hexane layer.

The extraction procedure was repeated five times, each time with 6 ml of water sample. A total of 30 ml water sample were extracted with 5 ml of hexane. The extracted hexane layer was dried with sodium sulfate in order to remove water if there was any. The 1.0 ml of the dried hexane layer was reduced to 0.2 ml by passing nitrogen through. The reduced hexane layer was then injected into the Gc and GC/MS column for detection of organic compounds.

**2) Methylene Chloride Extraction:** 10 ml of methylene chloride were shaken in a separating funnel with 20 ml of the water samples with occasional venting to release pressure. When the organic layer settled down, it was separated from the water layer. This procedure was repeated five times each time with a new 20 ml portion of the water sample, the total volume of the sample being 100 ml of water sample versus 10 ml of methylene chloride. The extracted sample was dried with sodium sulfate. The 1.0 ml of the dried sample was reduced in volume to 0.2 ml to concentrate the components and 3.0 µl of the sample was injected into the GC and GC/MS.

The samples prepared as above were analyzed on a HEWLETT-PACKARD 5890 II series Gas Chromatograph with FID (Flame Ionization Detector). The column used was RTX-50 which is 50% methyl, 50% phenyl polysiloxane, a slightly polar column. The initial temperature was 40° C with a hold time of 5 minutes and the temperature was raised to 280° C at 4° per minute. The final hold time was 10 minutes. The injector and detector were held at 290° C. The carrier gas was helium with a flow rate of about 1.0 ml/min. The flow rates of air and hydrogen for the FID were held at about 400 ml/min and 35 ml/min respectively to

attain maximum sensitivity. The injections were done using the splitless mode. The volume of injection was 1.0 μl to 3.0 μl according to the concentration of the sample. The samples were injected into the column and the data were collected using a PE Nelson 900 series interface.

A HEWLETT-PACKARD 5890 series II Gas Chromatograph connected to a HP 5971A Mass Selective Detector was used for qualitative analysis. The same temperature program as the one used for the GC was used for GC/MS as well. the TIC (Total Ion Chromatograms) obtained from GC and GC/MS were usually similar, although there were some differences in retention times and peak intensities which were due to the differences in flow rates and the use of different detectors (FID versus mass detector). The compounds were identified and verified using the Wiley/NBS Registry of Mass Spectral Data.

A semi-quantitative analysis of the samples were done using GC/FID and the percentage of the components were calculated using integrated peak intensities after subtracting the integrated area of the solvent and the contaminants. In these quantifications the total integrated intensity of one sample was taken as 100% to compare with the other samples.

## 4.8 - Parametric Studies

In order to understand the effect of different parameters on the brine treatment process a number of experiments were conducted. In these experiments, all the variables except one were kept constant and an extensive study on the effect of each particular parameter on the treatment process in removing *iron* was studied. The variables that were investigated in this parametric study were the following :

(i) Concentration of inlet iron (50, 100, 150, and 200 ppm).

(ii) Flow rate (2, 3, and 4 bbl/d).

(iii) Number of limestone columns (1 and 2).

(iv) Retention time (with and without retention tank).

(v) Angle of aeration unit ($1^o$, $10^o$, and $45^o$ degree).

(vi) Thickness of sand in filtration unit (2.5 and 5.0 inches).

(vii) Temperature (44, 54, and 64 degrees F).

After each experiment, new gravel and sand were placed in the filtration unit. The limestone chips in the pH adjustment columns were changed after each experiment as well. The approach for investigating the effects of the above parameters on the treatment process and the results of these investigations will be discussed here in. It should be noted that the numbers shown in Tables throughout this chapter represent the arithmetic average of the analysis of the last three samples from each sampling ports taken in each experiment.

### 4.8.1 - Effect of Inlet Iron Concentration on the Removal of Iron

The reaction rate between iron in brine and oxygen in the air is affected by the iron concentration in the original brine. Consequently, it affects the effectiveness of the brine treatment. Several sets of experiments were designed to study the effect of inlet concentration of iron on the capability of the model in iron removal. Four different iron concentrations 50, 100, 150, 200 ppm were used in these experiments while the other variables were kept constant in each set of experiments. Table 4.1 presents the results of four runs at these conditions. The results of this study show distinct differences in the concentration of the total iron leaving the system at the discharge point.

Table 4.1. Effect of the Inlet Iron Concentration on the Removal of Iron

| Flow Rate(bbl/d) | Inlet Conc.(ppm) | Discharge Conc.(ppm) |
|---|---|---|
| 2.0 | 50.31 | 0.0 |
| 2.0 | 99.39 | 0.45 |
| 2.0 | 154.80 | 4.51 |
| 2.0 | 190.05 | 15.71 |

These sets of experiments showed that the removal of total iron is greatly affected by the inlet concentration of iron. For instance, at a flow rate equal to 2 bbl/d and the inlet concentration of 50 ppm of iron, all the iron was removed from the brine, whereas under the same conditions, starting with 200 ppm concentration of iron only 92% of iron was removed from the solution. A graphical presentation of inlet iron concentration effect on the removal of iron is illustrated in Figure 4.6 (where 3.0 bbl/d was used) and more detailed results of this study can be viewed in Appendix A, Tables 1 through 4.

### 4.8.2 - Effect of the Brine Throughput Flow Rate on the Removal of Iron

Flow rate is a measure of the capacity of the designed facility for brine treatment. A higher flow rate results in less reaction time between brine and the limestone in the limestone column (pH adjustment unit) as well as less contact time between iron and oxygen because of thicker film in the aeration unit. New sets of experiments were designed where all the variables were kept constant except for the flow rate. The flow rate was varied from 3 bbl/d to 4 bbl/d. For each flow rate, four different inlet concentrations of iron were used. The results of these eight runs and the previous runs where the effect of inlet concentration on the treatment was

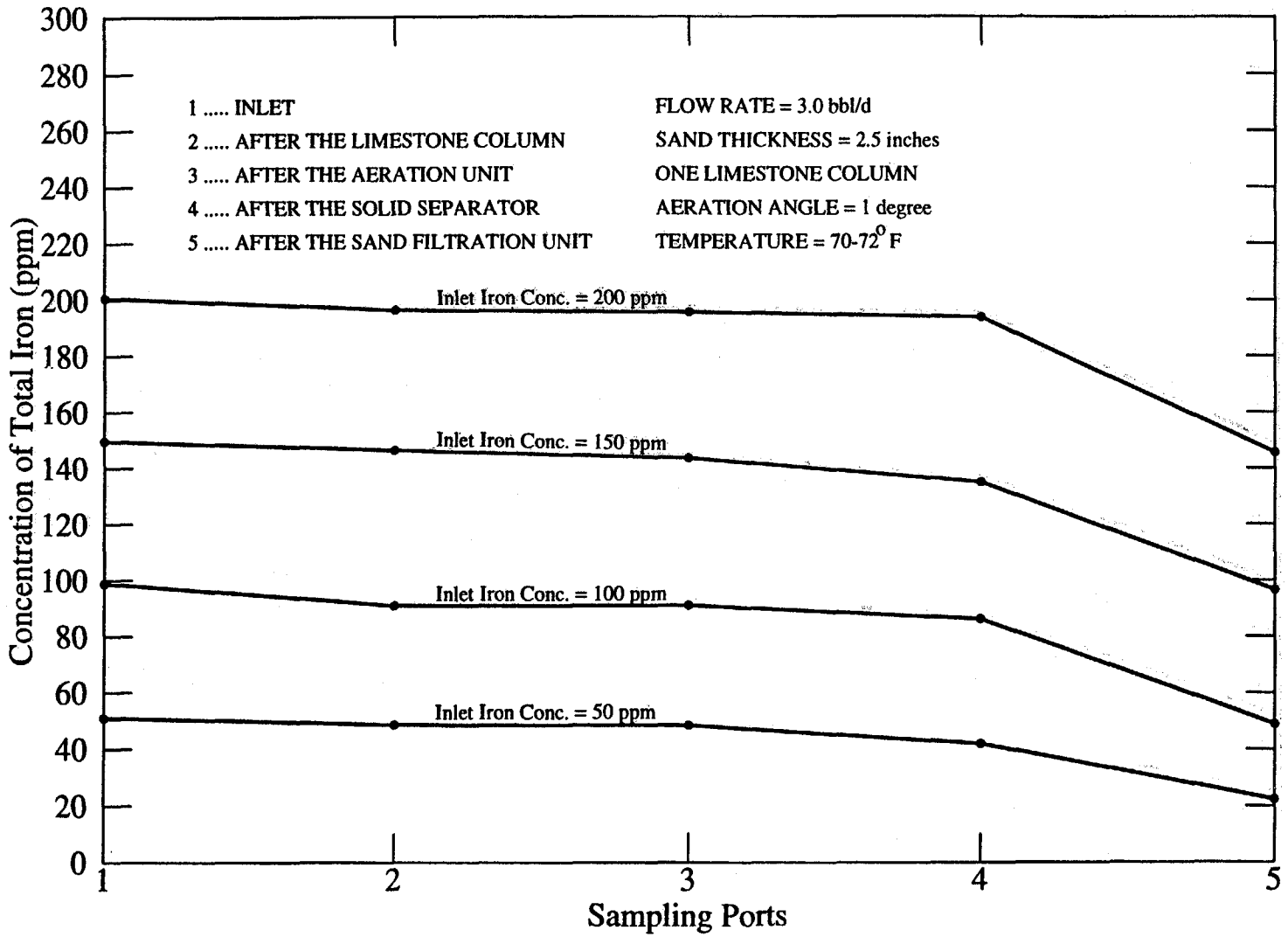


Figure 4.6. Effect of Inlet Iron Concentration on the Removal of Iron

investigated were compared in order to study the effect of flow rate on treatment and to determine the limitations of the system for the scale-up purpose. Table 4.2 shows a summary of the results of this study.

The results clearly show that the flow rate will affect the efficiency of model in removing the total iron significantly. As the flow rate increases, the percentage of total iron removal decreases. At a low flow rate equal to 2.0 bbl/d, the iron removal of the brine treatment was very effective. For example, at inlet iron concentration of 50 or 100 ppm, all the iron was removed after the treatment. Even at an inlet iron concentration of 150 or 200 ppm, more than 90% of the iron was removed after the treatment. At higher flow rates (3.0 or 4.0 bbl/d), the efficiency of iron removal was significantly decreased. For instance, at a flow rate equal to 4.0 bbl/d, the efficiency of the treatment process was reduced to 37%. Therefore, it was concluded that an increase in throughput flow rate, when the aeration angle is fixed, increases the film thickness on the aeration unit and decreases the contact time between the fluid and air, resulting in a decrease in ferrous iron oxidation.

Table 4.2. Effect of the Inlet Iron Concentration and the Throughput Flow Rate on the Removal of Iron

| Flow Rate(bbl/d) | Inlet Conc.(ppm) | Discharge Conc.(ppm) |
|---|---|---|
| 2.0 | 50.31 | 0.0 |
| 2.0 | 99.39 | 0.45 |
| 2.0 | 154.80 | 4.51 |
| 2.0 | 190.05 | 15.71 |
| 3.0 | 50.92 | 22.36 |
| 3.0 | 98.66 | 48.95 |
| 3.0 | 149.49 | 96.59 |
| 3.0 | 200.53 | 145.50 |
| 4.0 | 50.66 | 31.42 |
| 4.0 | 97.82 | 59.48 |
| 4.0 | 149.99 | 118.93 |
| 4.0 | 201.06 | 168.65 |

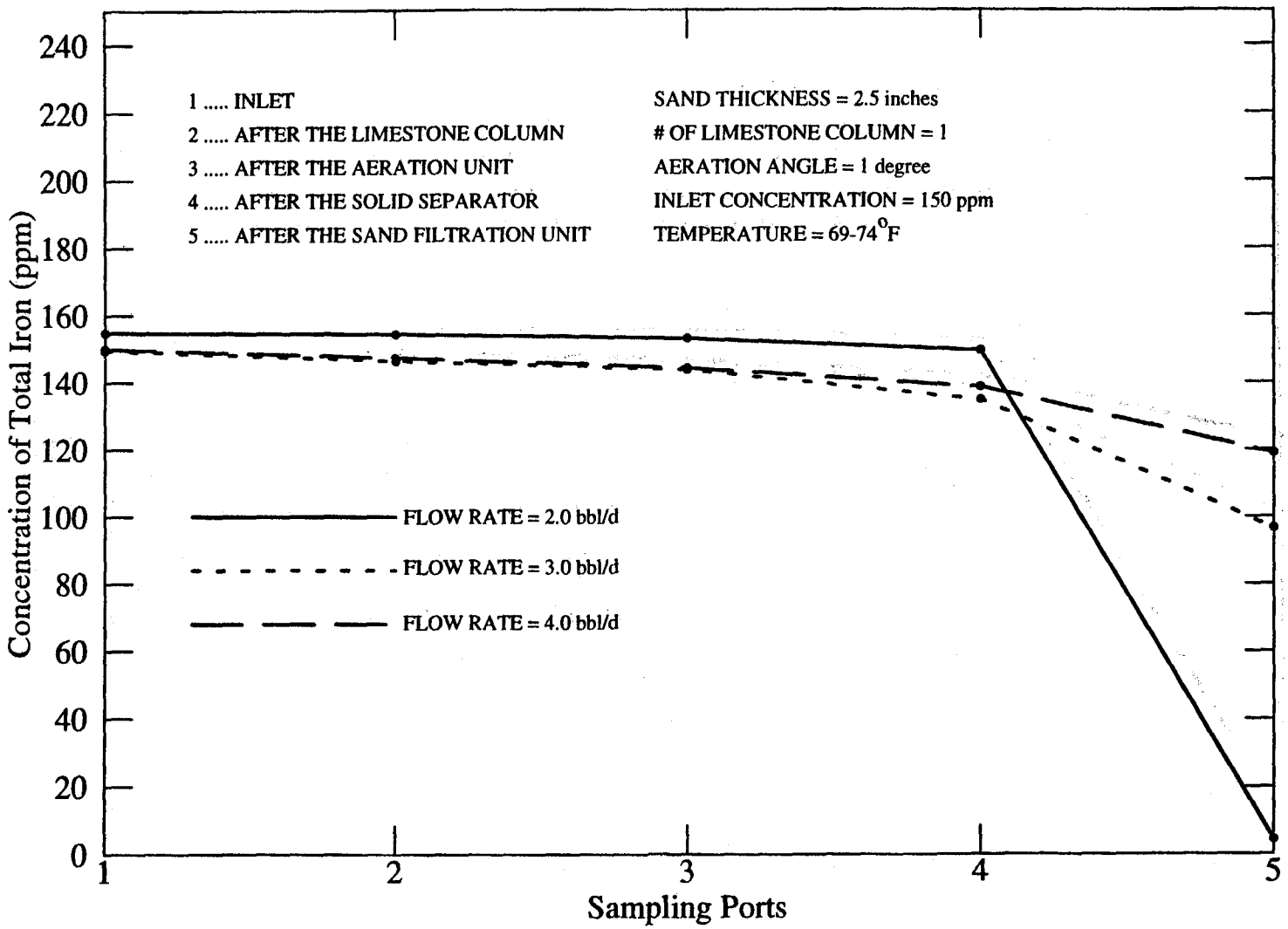


Figure 4.7. Effect of the Brine Throughput Flow Rate on the Removal of Iron

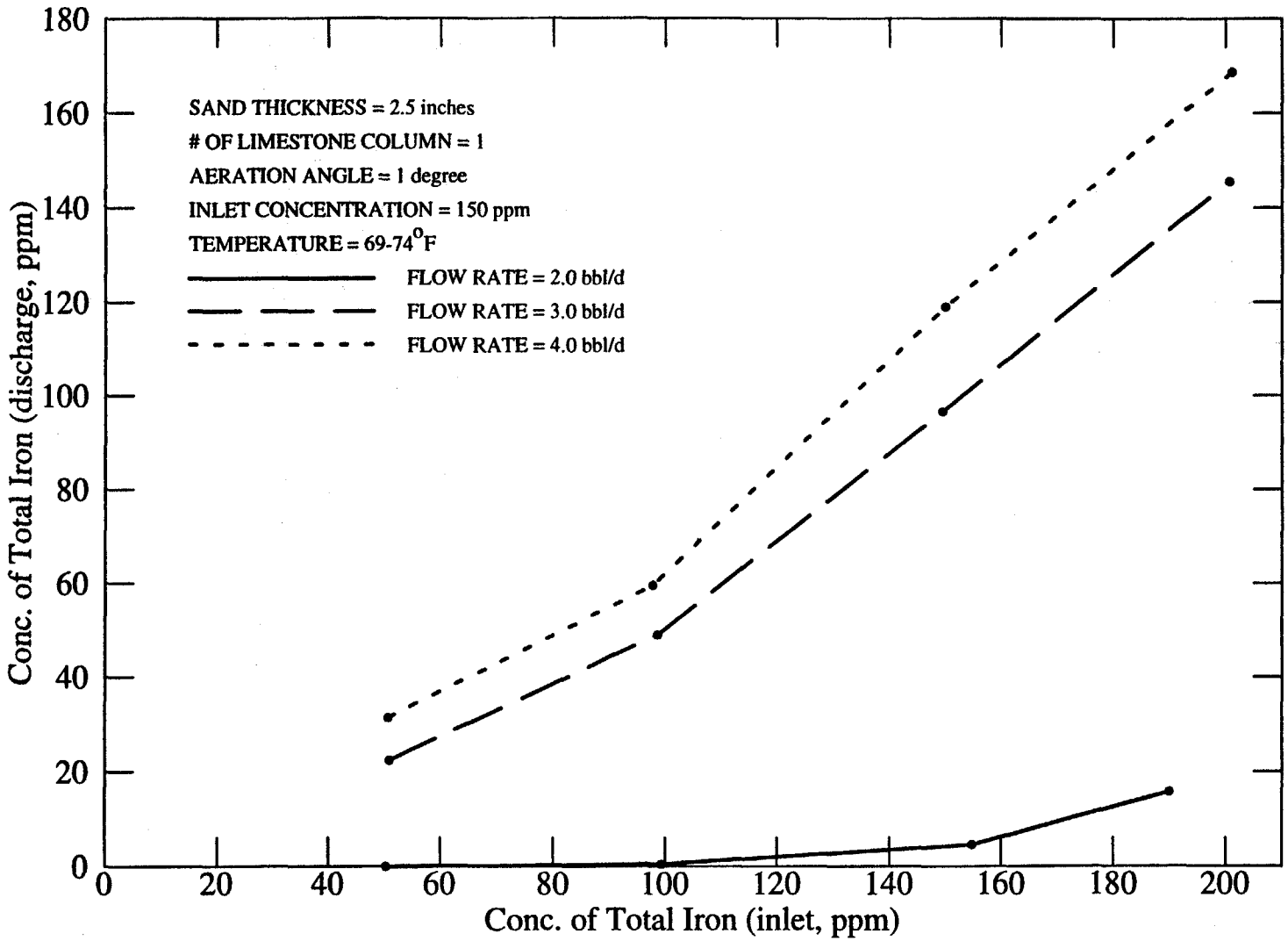


Figure 4.8. Effect of the Flow Rate and Iron Conc.on the Removal of Iron

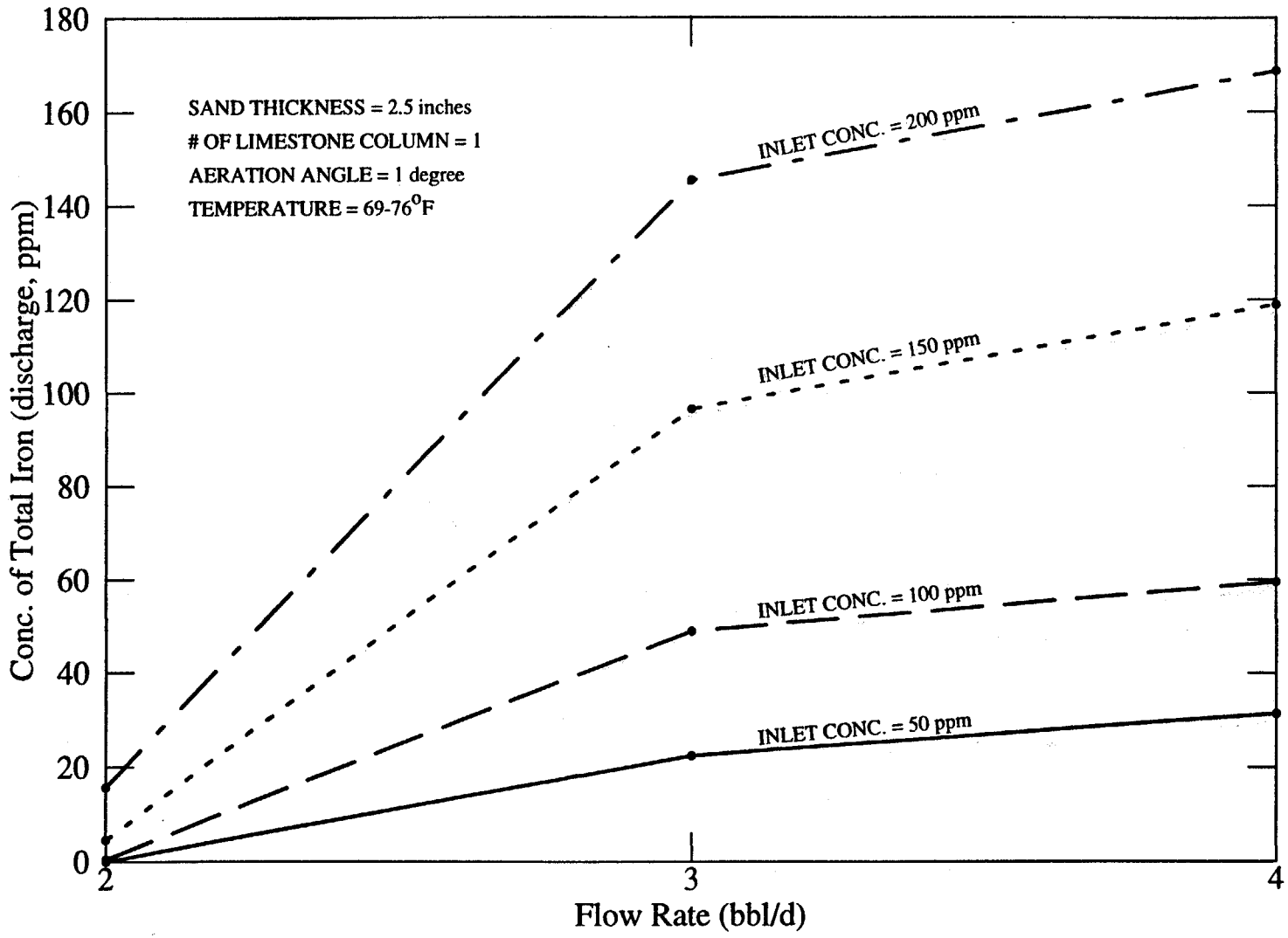


Figure 4.9. Effect of the Flow Rate and Iron Conc.on the Removal of Iron

Figures 4.7, 4.8, and 4.9 and Tables 4 through 12 in Appendix A show the results of the study of throughput flow rate on the treatment process.

### 4.8.3 - Effect of the Limestone Column on the Removal of Iron

The function of limestone was to increase the pH of the brine to a favorable value for the oxidation reaction. The ability of the limestone column to increase the pH of the effluent is a function of throughput flow rate and concentration of iron. Table 4.3 illustrates how the efficiency of a limestone column in raising the pH of the brine was affected by variable throughput flow rates and iron concentrations.

Table 4.3. pH as a Function of Iron Concentration And Throughput Flow Rate

| Flow Rate(bbl/d) | Iron Conc.(ppm) | pH Before | pH After |
|---|---|---|---|
| 2.0 | 50.31 | 1.89 | 6.19 |
| 2.0 | 99.39 | 1.77 | 6.02 |
| 2.0 | 154.80 | 1.89 | 5.89 |
| 2.0 | 190.05 | 2.15 | 5.90 |
| 3.0 | 50.92 | 1.93 | 5.79 |
| 3.0 | 98.66 | 1.96 | 5.74 |
| 3.0 | 149.49 | 1.98 | 5.65 |
| 3.0 | 200.53 | 1.96 | 5.63 |
| 4.0 | 50.66 | 2.16 | 5.75 |
| 4.0 | 97.82 | 2.03 | 5.74 |
| 4.0 | 149.99 | 2.00 | 5.49 |
| 4.0 | 201.06 | 2.07 | 5.51 |

The laboratory facility had two limestone columns, which could have been used individually or in a series. To study the effect of the limestone column on the treatment and the conditions of limestone chips after a number of runs, eight runs

were considered. Keeping all the other variables constant, four runs with one limestone column and four others with two limestone columns were conducted.

The results of this study are shown in Table 4.4 and Figure 4.10. These results of the experimental runs indicated that the addition of the second limestone column led to an increase of the pH of the brine and subsequently had a positive effect on the treatment process. For example, under the same conditions, using one limestone column increased the pH of the brine from 1.90 to 5.75, whereas using two limestone columns led to a pH of 6.00. This small increase in pH affected the removal of iron after the treatment.

Overall, increasing the number of limestone columns aided the removal of iron from brine, indicating that an increase in pH of the brine increases the rate of ferrous iron oxidation when brine is exposed to the air. However, at the low iron concentration of 50 ppm, the increase in iron removal with an additional limestone column was minimal. The small change in the pH of brine caused by the additional limestone column did improve the iron removal at higher inlet concentration; it had an insignificant effect when inlet concentration was low.

Table 4.4. Effect of the Limestone Column on the Removal of Iron

| Limestone Column | Inlet Conc.(ppm) | Discharge Conc.(ppm) |
|---|---|---|
| 1 | 50.92 | 22.36 |
| 2 | 50.31 | 19.41 |
| 1 | 98.66 | 48.95 |
| 2 | 95.14 | 24.86 |
| 1 | 149.49 | 96.59 |
| 2 | 147.14 | 68.63 |
| 1 | 200.53 | 145.50 |
| 2 | 191.44 | 114.09 |

It was also found that the ferric ion deposition on the limestone chips builds

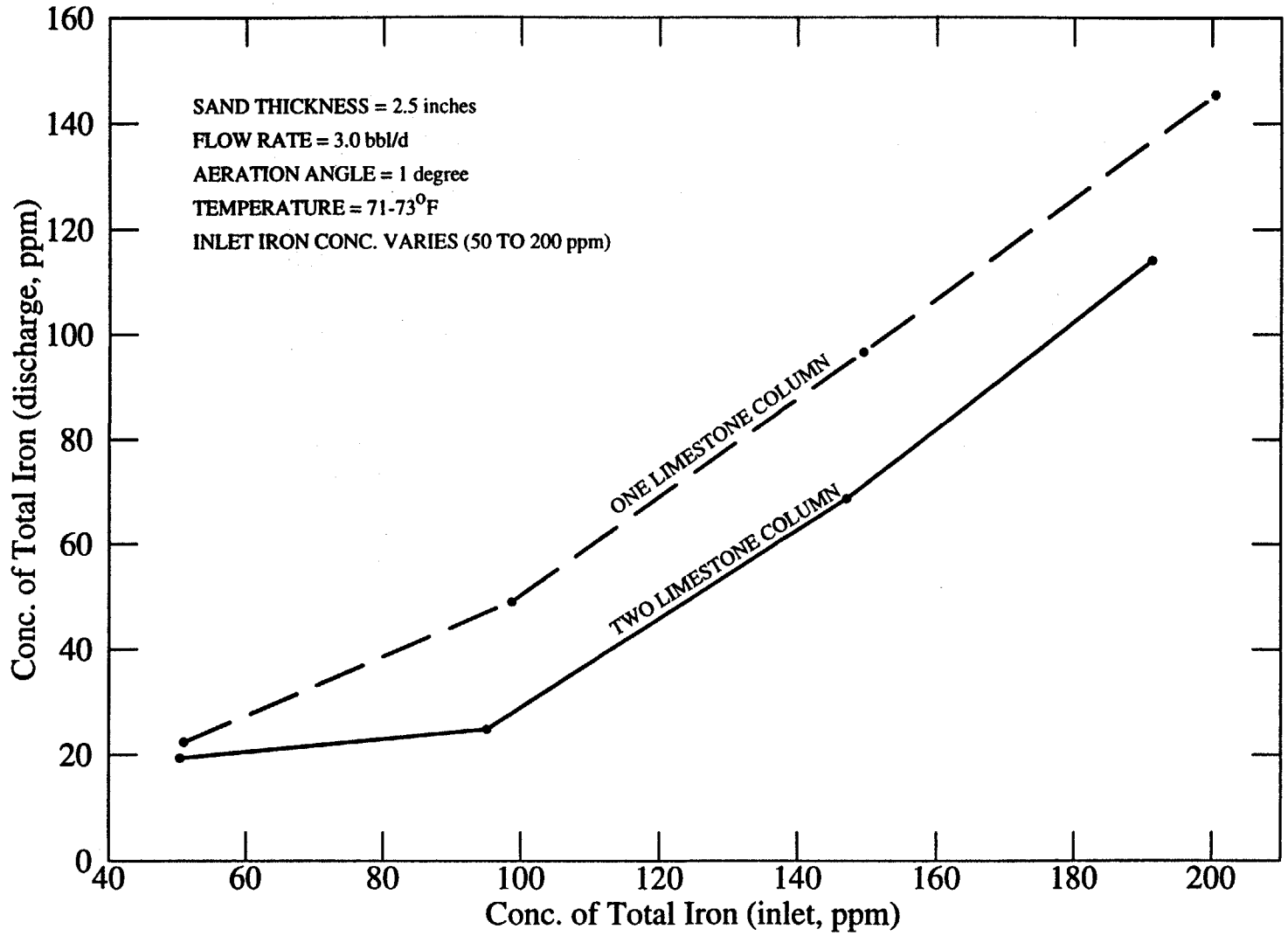


Figure 4.10. Effect of the Limestone column on the Removal of Iron

up gradually. However, most of the deposition occurs when for the very first time the limestone came in contact with the brine solution. Further runs caused a small change in the limestone, suggesting that the limestone in each column can be used for a long period of time without a great effect on their ability to increase the pH, and without being changed. Detailed results of this study are presented in Appendix A in Tables 13 through 16.

### 4.8.4 - Effect of the Angle of Aeration Unit on the Removal of Iron

The angle of aeration unit, together with the brine flow rate, determine the thickness of the brine film passing through the unit, which in turn affects the extent of the reaction between the iron in brine and the oxygen in air. When brine flow rate is fixed, the thickness of the brine film is only dependent on the angle of aeration unit. Increasing the angle will reduce the thickness of the film; however, at the same time, it will also reduce the residence time of the brine in the aeration unit. In order to study the effect of the angle of aeration unit on the treatment, new sets of experiments were designed where the angle of aeration unit was varied from 1 to 45 degree (1, 10, and 45 degrees). The results of this study (presented in Table 4.5 and Figure 4.11) indicated that the effect of changing the aeration angle from 1 to 10 degree on the efficiency of the treatment was inconclusive. However, the data from the runs where the aeration unit was set at 45 degree indicated that a higher angle will have a positive effect on the brine treatment.

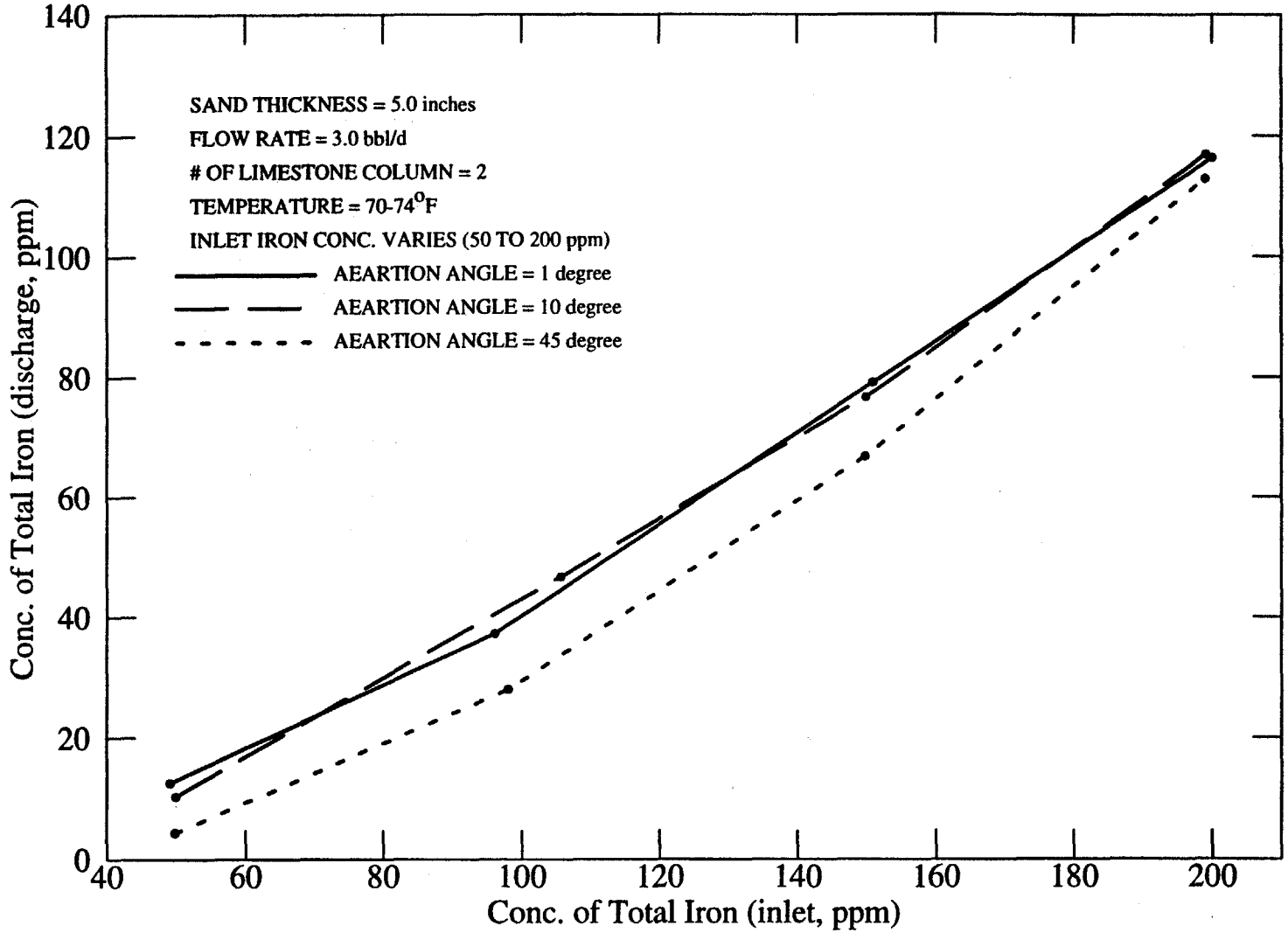


Figure 4.11. Effect of the Aeration Angle on the Removal of Iron

Table 4.5. Effect of the Angle of Aeration Unit on the Removal of Iron

| Angle of Aeration Unit | Inlet Conc.(ppm) | Discharge Conc.(ppm) |
|---|---|---|
| 1° | 49.86 | 12.59 |
| 10° | 49.86 | 10.36 |
| 45° | 49.80 | 4.32 |
| 1° | 96.12 | 37.35 |
| 10° | 105.6 | 46.75 |
| 45° | 97.99 | 28.06 |
| 1° | 150.94 | 79.14 |
| 10° | 149.97 | 76.74 |
| 45° | 149.85 | 66.76 |
| 1° | 200.03 | 116.38 |
| 10° | 199.16 | 116.96 |
| 45° | 198.93 | 112.92 |

Tables 17 through 30 in Appendix A illustrate individual experiments and the results in details. There was an extended study on the effect of the aeration angle on the treatment process after modifying the prototype model in the laboratory explained in the following section.

### 4.8.5 - Modification of the Lab-Based Prototype Model

As mentioned earlier, 30 gallons of synthetic brine was used in each experiment. The running time for each experiment therefore was solely a function of flow rate. The chosen volume of synthetic brine was sufficient for the effects of studied parameters on the treatment process. In order to impose more than one change on the process in each experiment, the prototype model had to be modified. the modification was made by removing the retention tank from the model. The retention tank held approximately five gallons of brine at any time during the experiment. Therefore, by eliminating this component from the model, synthetic brine

was allowed to flow into the filtration unit after the aeration as opposed to the retention tank. By eliminating the retention tank and recovering about five gallons of the synthetic brine which otherwise would have been held in the unit, it was possible to impose few changes during the running time in each experiment.

Being able to study the effect of the retention time on the treatment process was another advantage of eliminating the retention tank. Some runs were conducted without the retention tank and the results were compared to the runs conducted under the same conditions where the retention tank were used. This comparison showed the effect of the retention time, provided by the retention tank, on the treatment process. This study will be further discussed in Section 6.1.7.

The analysis of the samples taken during each experiment for their content of ferrous iron was no longer continued. This decision was made because the preparations for analysis were very time consuming and very sensitive to human errors, as discussed in chapter 4. Furthermore, the effectiveness and performance of the treatment process could satisfactorily be studied and judged by analyzing the content of the samples for total iron (ferrous and ferric ions combined using "ICP-AES").

### 4.8.6 - Expanded Study on the Effect of the Aeration Unit

Since previous studies on the effect of the aeration unit on the treatment process seemed to be inconclusive, additional experiments were pursued to confirm the findings on the effect of the aeration angle on the treatment process. The results of these additional experiments are illustrated in Table 4.6 and Figure 4.12. Iron removal became more effective as the angle of aeration unit was increased from 1 to 45 degrees. At $45^{o}$ angle, the effectiveness of the treatment process was

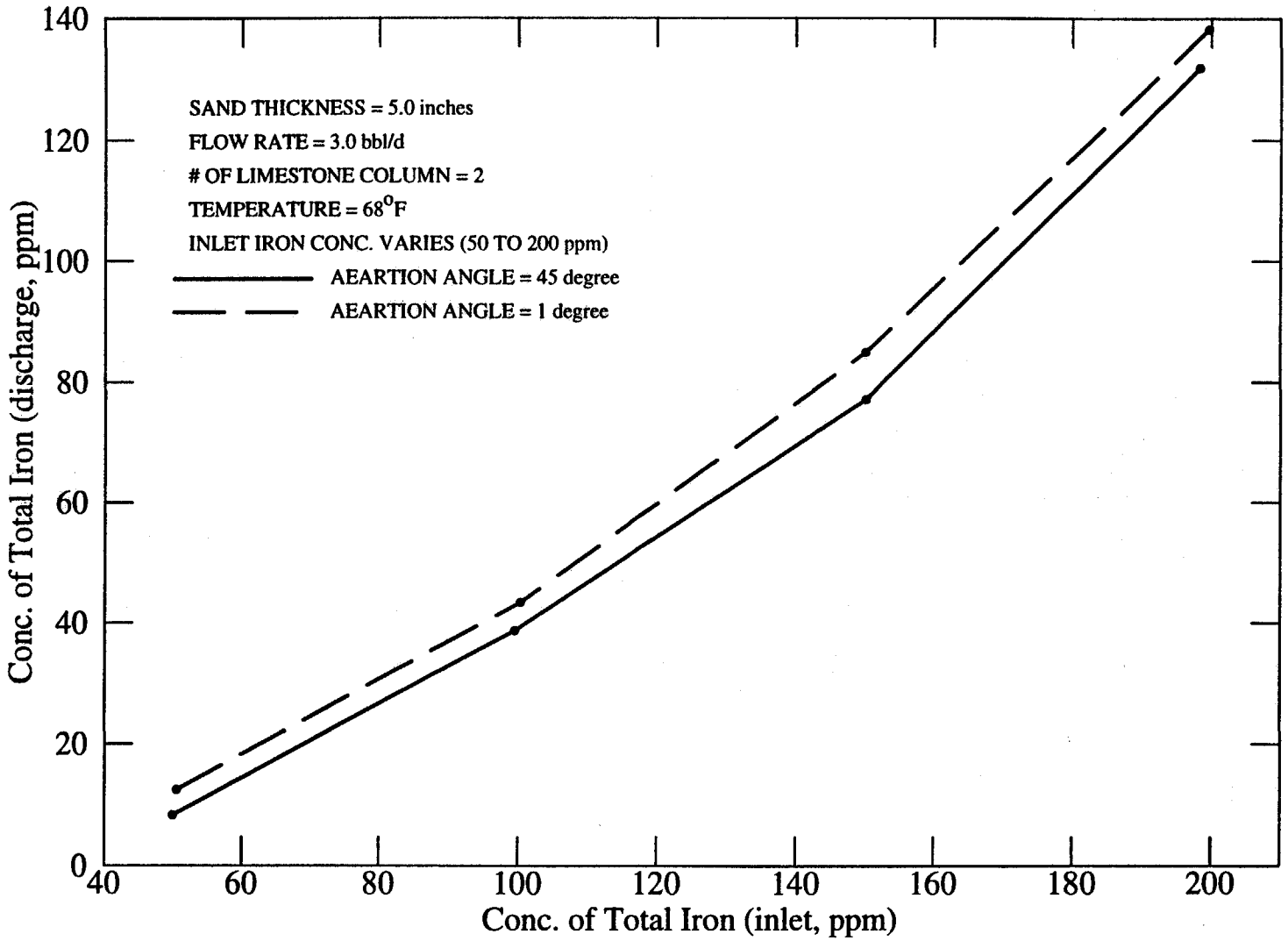


Figure 4.12. Effect of the Aeration Angle on the Removal of Iron After Modifying the Lab Model

increased by 9%, 4%, 5%, and 3% for iron inlet concentration of 50, 100, 150, and 200 ppm, respectively.

Table 4.6. Effect of the Angle of Aeration Unit on the Removal of Iron After Modifying the Lab Model

| Angle of Aeration Unit | Inlet Conc.(ppm) | Discharge Conc.(ppm) |
|---|---|---|
| 1° | 50.51 | 12.49 |
| 45° | 49.93 | 8.23 |
| 1° | 100.29 | 43.35 |
| 45° | 99.49 | 38.73 |
| 1° | 150.18 | 84.90 |
| 45° | 150.13 | 77.08 |
| 1° | 199.69 | 138.24 |
| 45° | 198.32 | 131.88 |

By lowering the aeration angle when the flow rate is fixed, the film thickness forming on the aeration unit becomes thinner allowing more fluid to be exposed to the air which in turn aids the oxidation of iron. It was also noted that the pH of the brine slightly increased as brine passed over the aeration unit. The increase in pH was in relation to the angle of the aeration unit. As the unit's angle increased, the pH of the brine increased as well. The increase of the pH of the effluent passing through the aeration unit might have been due to the entrance of ammonia from the air into the solution. The pH increase of the brine consequently had a positive effect on the treatment process. A more detailed result of this study is included in Tables 31 and 32 of Appendix A.

### 4.8.7 - Effect of the Retention Tank on the Removal of Iron

In order for the oxidation reaction to proceed, brine that is exposed to the air at the favorable pH should be provided with enough time. The function of retention tank is to provide maximum time for iron to complete the oxidation reaction from ferrous to ferric. In order to study the effect of the retention tank on the brine treatment, data from four experimental runs in which the retention tank was removed from the system were compared to four other runs with the retention tank in the system. In this comparison, all the other variables were kept constant.

Table 4.7. Effect of the Retention Time on the Removal of Iron

| Inlet Conc.(ppm) | Retention Tank | Discharge Conc.(ppm) |
|---|---|---|
| 49.85 | No | 25.33 |
| 49.01 | Yes | 12.59 |
| 97.09 | No | 61.18 |
| 96.12 | Yes | 37.35 |
| 147.39 | No | 102.55 |
| 150.94 | Yes | 79.14 |
| 183.39 | No | 125.19 |
| 200.03 | Yes | 116.38 |

As presented in Figure 4.13 and Table 4.7, data from these experiments showed that the use of the retention tank has a significant effect on brine treatment. The effect of the retention tank became more pronounced for brine with higher iron concentrations. For example, at inlet concentration of 50 or 100 ppm, the efficiency of the treatment process was increased by 25% when the retention tank was used in the model. However, only 18% and 10% increases on the treatment's efficiency were observed where 150 or 200 ppm of iron was used in the synthetic brine.

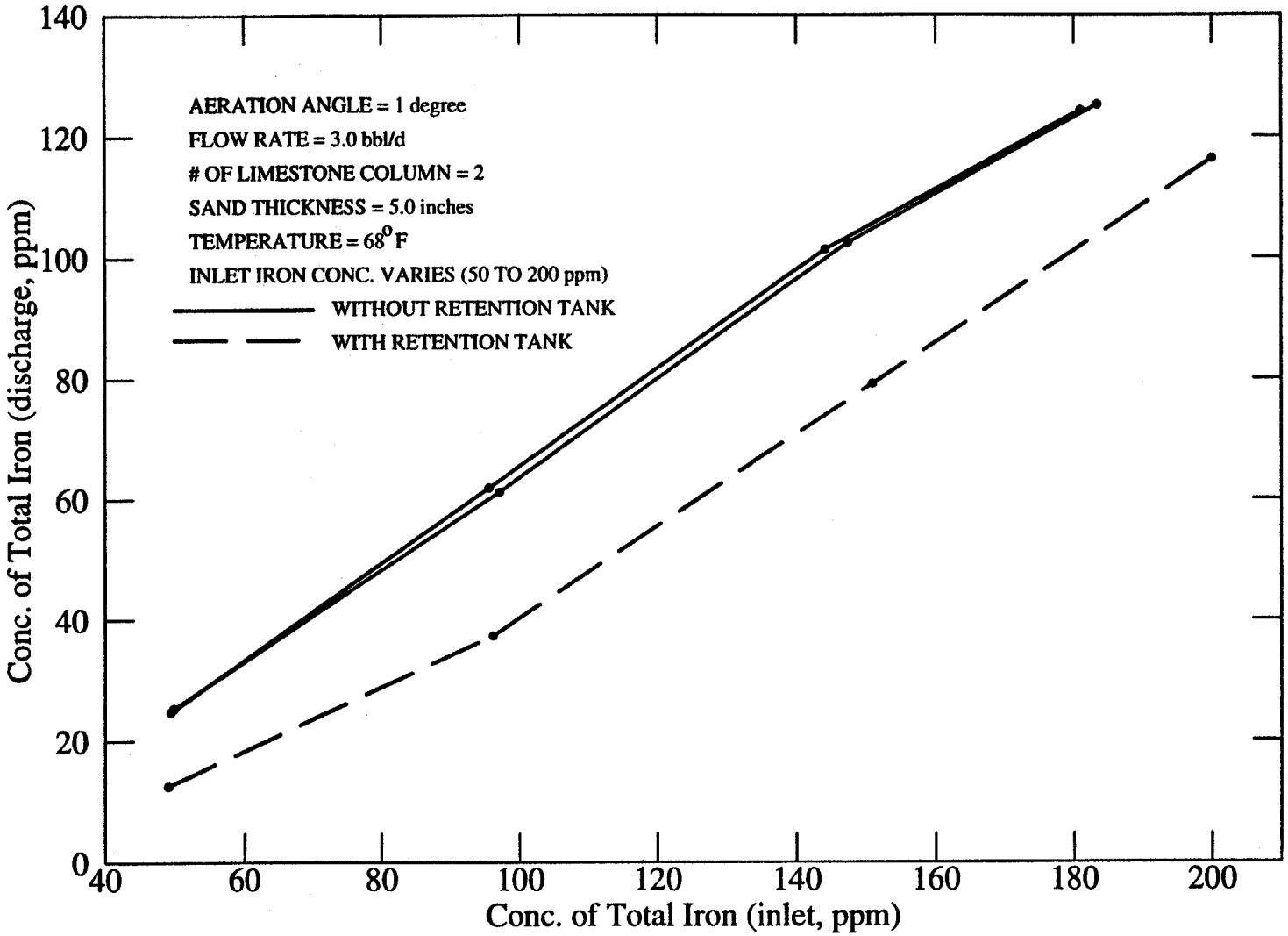


Figure 4.13. Effect of the Retention Tank on the Removal of Iron

These results show the necessity of providing retention time for completion of ferrous iron oxidation reaction. Individual runs, including their results, are included in Appendix A (Tables 17 through 20 and Tables 34 and 35).

### 4.8.8 - Effect of Sand Thickness in the Filtration Unit on the Removal of Iron

The function of sand in the filtration unit was to remove the ferric ion that had been formed through the treatment process as well as complex irons that were suspended in the solution. In order to study the effect of sand thickness on the treatment process, the thickness of sand in the sand box filtration unit was varied from 2.5 inches to 5.0 inches. At a flow rate equal to 3.0 bbl/d and inlet iron concentrations of 50 to 200 ppm in increments of 50 ppm, number of experiments were conducted and the results were analyzed.

The study of the effect of sand thickness in the filtration unit on the removal of iron consisted of two set of runs. The sand thickness in the filtration unit was kept at 2.5 and 5.0 inches for each set of the runs. Each set of runs included four experiments with differing concentration of iron (about 50, 100 ,150,and 200 ppm). the results show that the two different sand thickness do not significantly affect the iron removal efficiency. Therefore, in all the figures, the average values of the two set of runs were used, while in table 4.8, the data are listed with two different sand thickness. The results of this study, presented in Figure 4.14 and Table 4.8 as well as Tables 33 through 36 in Appendix A, indicated that sand thickness had no significant effect on the brine treatment. The slight change in the results may be related to the fact that by increasing the sand thickness, one increases the residence time of brine in the sandbox; however, the time increase is not sufficient and

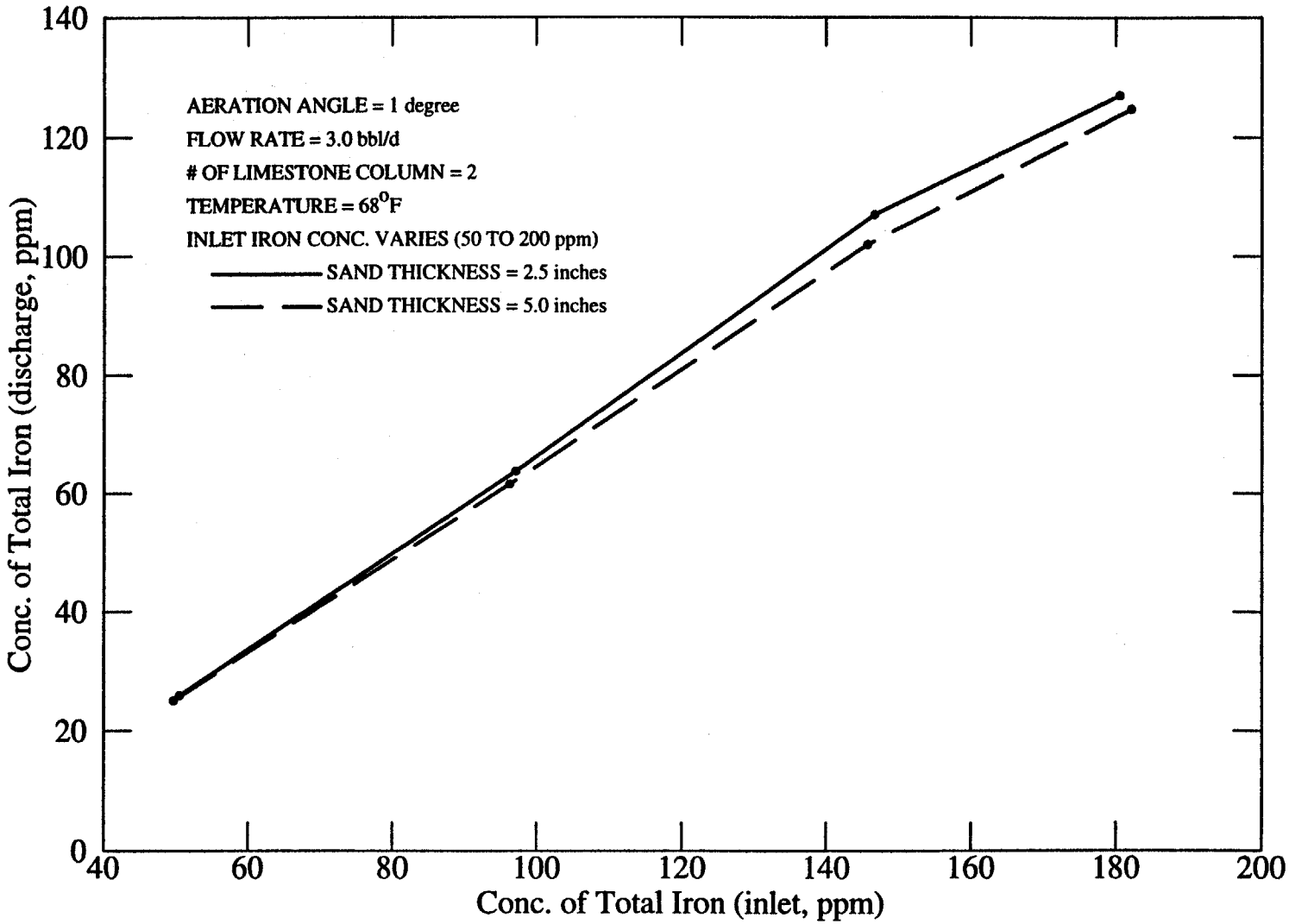


Figure 4.14. Effect of the Sand Thickness in the Filtration Unit on the Removal of Iron

significant to affect the treatment greatly.

Table 4.8. Effect of the Sand Thickness in the Filtration Unit on the Removal of Iron

| Inlet Conc.(ppm) | Sand Thickness | Discharge Conc.(ppm) |
|---|---|---|
| 50.46 | 2.5 | 25.90 |
| 49.64 | 5.0 | 25.07 |
| 97.15 | 2.5 | 63.72 |
| 96.29 | 5.0 | 61.53 |
| 146.72 | 2.5 | 106.99 |
| 145.77 | 5.0 | 102.01 |
| 180.56 | 2.5 | 127.01 |
| 182.18 | 5.0 | 124.76 |

### 4.8.9 - Effect of Temperature on the Removal of Iron

In order to study the sensitivity of the brine treatment process to temperature, a number of experiments had to be conducted at various temperatures. Since the laboratory in which the prototype model was located could not be cooled down below 68° F, the temperature study was postponed to winter season during which time the laboratory was isolated from the rest of the building and all the outside windows were let open to allow the lab temperature to equalize with the outside temperature (with the aid of an electrical fan). Figure 4.15 and Table 4.9 present the results of the effect of the temperature on the treatment process. The effect of the temperature on the treatment process was studied with temperatures ranging from 44° F to 66° F.

Tables 37 through 39 also illustrate detailed results of this study. Results from the temperature study showed that temperature could become a very important fac-

tor in brine treatment. By comparing the experiments that were conducted at 66° and 54° F, little effect of the temperature on the treatment was observed. However, at lower temperatures, a distinct effect on the treatment was experienced (comparison between the results of run at 54° F and 44° F). For instance, at a flow rate equal to 3 bbl/d and inlet iron concentration of 50 ppm, the treatment process was approximately 4% more efficient at 66° F than 54° F. Under the same conditions, the treatment's efficiency was 22% more at 66° F than 44° F.

Table 4.9. Effect of Varying Temperature on the Removal of Iron

| Inlet Conc.(ppm) | Temperature(F) | Discharge Conc.(ppm) |
|---|---|---|
| 50.16 | 44 | 35.37 |
| 48.83 | 54 | 25.87 |
| 50.48 | 66 | 24.87 |
| 97.09 | 44 | 77.19 |
| 101.92 | 54 | 67.79 |
| 98.83 | 66 | 63.56 |
| 143.43 | 44 | 122.50 |
| 146.15 | 54 | 106.75 |
| 145.27 | 66 | 100.50 |
| 177.32 | 44 | 156.84 |
| 185.38 | 54 | 139.15 |
| 180.53 | 66 | 130.87 |

Temperature plays a very important role in chemical reactions. Reaction rates are usually strongly dependent on temperature. For example, temperature greatly affects the solubility of the oxygen in solution. A decrease in temperature reduces the solubility of the oxygen in the brine as a consequence of which, less ferrous iron oxidizes. Therefore, the effectiveness of the treatment at removing iron from brine is lessened.

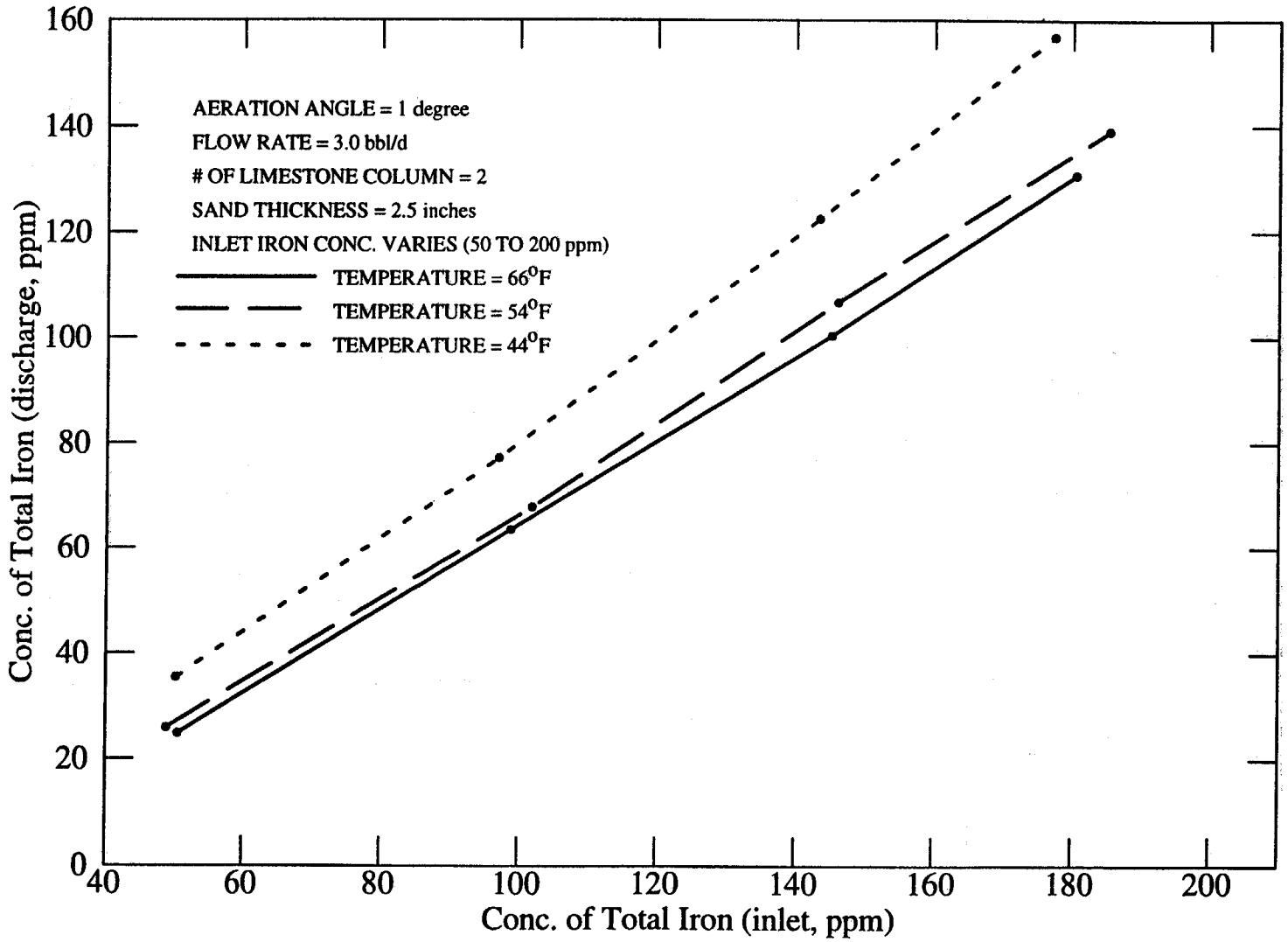


Figure 4.15. Effect of Temperature on the Removal of Iron

## 4.9 - Summary of the Results of the Parametric Studies

This section summarizes the effect of the studied parameters on the treatment process. An increase in the concentration of iron and/or an increase in the throughput flow rate significantly decreased the efficiency of the treatment process in removing iron. The addition of a limestone column increases the pH of the effluent, as a consequence of which, a slight positive effect on the treatment process is observed. An increase of the angle of the aeration unit slightly increased the effectiveness of the treatment process in iron removal. It is also concluded that the retention tank has a significant effect on the treatment process. This conclusion is made based on a number of experiments where the retention tank was removed from the model, thus providing no retention time for the oxidation reaction to take place. Doubling the thickness of the sand in the filtration unit has no significant effect on the treatment process. Finally, the results of the temperature effect on the treatment process indicate that the efficiency of the treatment is significantly reduced at low temperatures.

## 4.10 - Contamination of Sand in the Filtration Unit

An extensive study was conducted to investigate the contamination of sand in the filtration unit. The objective of this study was to understand how the efficiency of the filtration unit would be affected with its extended use (i.e., over a period of days). In addition, the depth of the contamination as a function of time was investigated.

Since this study needed to be performed over a long period of time, synthetic brine was prepared in a 300-gallon storage tank, as opposed to the 30-gallon used in other experiments. The 300-gallon tank was filled with distilled water, and nitrogen gas was bubbled through the tank from the bottom in order to drive out dissolved oxygen in the water so as to prevent any premature reaction from occurring. It was necessary to prepare several 300-gallon tanks of synthetic brine for this study. Fresh gravel and sand were placed in the filtration unit and five specific locations were chosen in the sand filtration unit for observation and sampling. Figure 4.16 shows the sampling locations. The effluent flow rate for this study was 3 bbl/d for a total of 756 gallons and inlet concentration of iron was maintained at approximately 50 ppm. The sand thickness in the filtration unit was kept at 2.5 inches for this study (volume of the sand = 0.47 $ft^3$) . At each time interval, sand core samples of 0.25 inch diameter and one inch length were taken from each sample location and were analyzed to determine the degree of iron contamination. The following describes the procedure for analyzing the sand core samples.

The sand core samples were taken at designated time intervals. Five grams of sand were removed from the bottom of the core and five grams of the sand were removed from the top of the core. Each 5-gram extract was placed in a beaker, and 20 ml of concentrated hydrochloric acid was used to wash the sand to remove any precipitates and to dissolve any remaining iron. These solutions were later appropriately diluted with a dilution factor of 10 and then analyzed for total iron content using "ICP-AES" analysis.

The results of this study are presented in Figures 4.16 through 4.18. It can be seen that the degree of sand contamination increased as more brine flowed through the filtration unit. However, contrary to what might be expected, it was found that

more iron was removed from the brine at later times. This can be seen in Figure 4.18, which shows the concentration of iron at the discharge point as a function of time. After 143 hours, there was virtually no iron left in solution at the discharge point. A possible explanation of this is that the iron precipitates gradually reduced the porosity and permeability of the sand. Less permeable sand would tend to have an increased filtration capacity. The experiment had to be stopped after 144 hours of continuous operation because at approximately this time the permeability of the sand had decreased to a point where approximately 2 inches of liquid accumulated on the surface of the sand.

Information obtained in this study may further be used for predicting the life-time of the sand in the filtration unit and for estimating a time when the sand must be replaced in the filtration unit. A sample calculation based on this study follows:

* Average concentration of iron before the filtration unit: 49 ppm
* Average concentration of iron after the filtration unit: 9 ppm
* Maximum time of continuous treatment operation: 144 hours (6 days)
* Volume of brine passed through filtration unit during this time: 756 gallons
* Total weight of iron contained in this volume of brine: 144 grams
* Total weight of iron removed by filtration unit: 117 grams

From these results, it may be concluded that at various conditions (flow rate, iron concentration, etc.), the sand in the filtration unit will remain functional and will not need to be changed until its permeability is reduced to a point where the brine will not flow through the filtration unit.

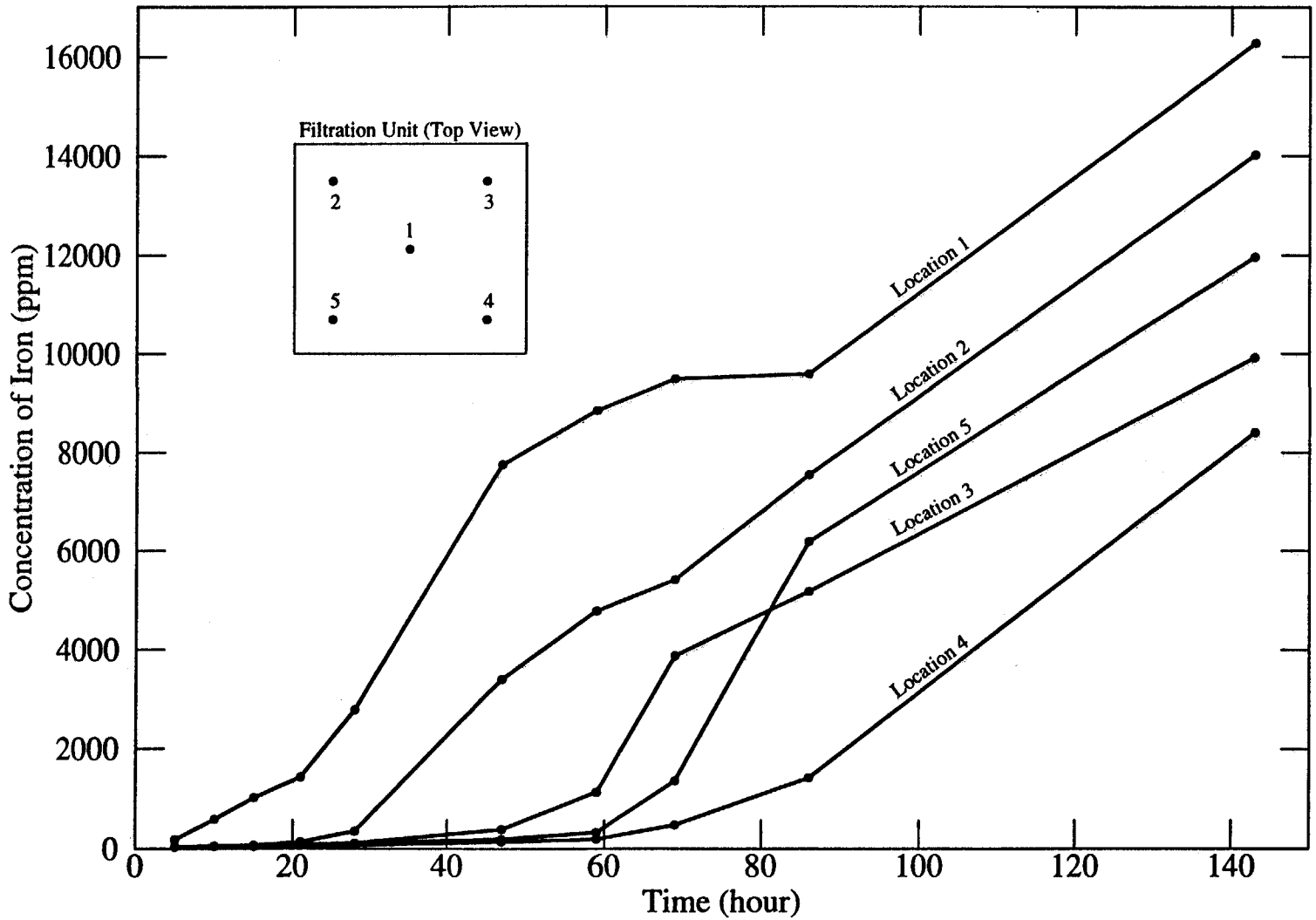


Figure 4.16. Iron Contamination of the Top Portion of the Sand in the Filtration Unit

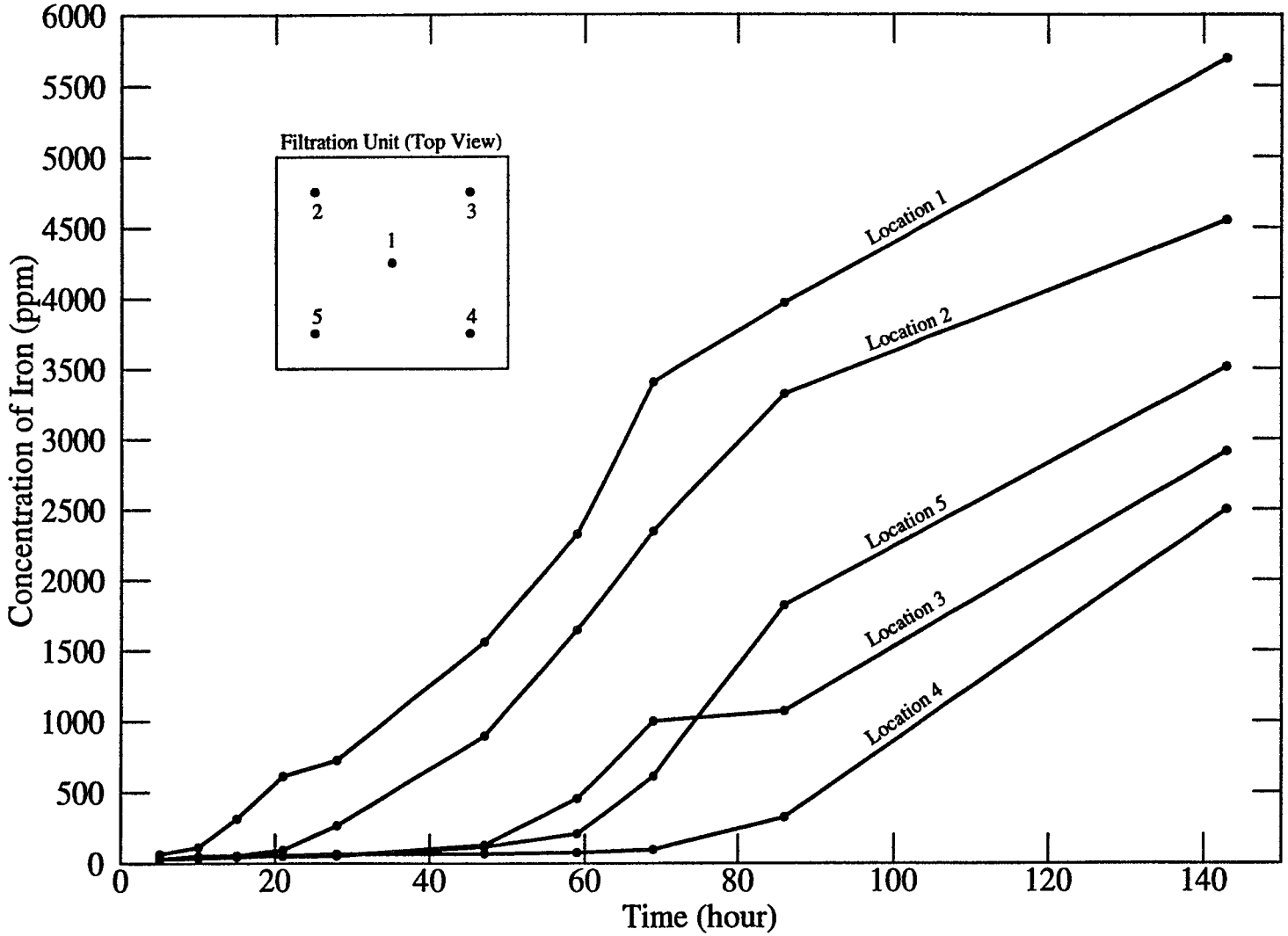


Figure 4.17. Iron Contamination of the Bottom Portion (1" below surface) of the Sand in the Filtration Unit

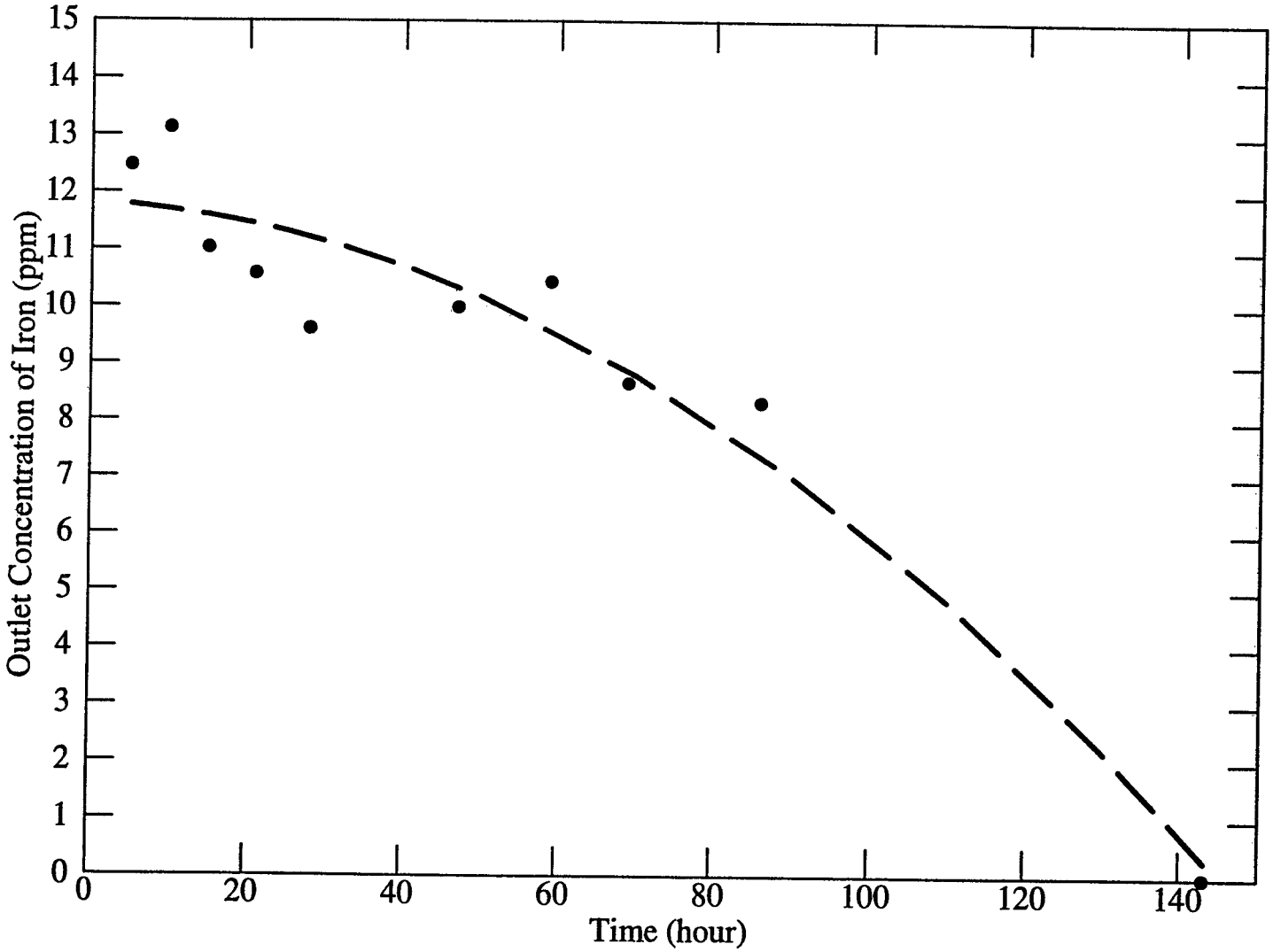


Figure 4.18. Contamination of Iron After Processing Brine VS. Time

## 4.11 - Removal of Other Heavy Metals From Synthetic Brine

Number of experiments were designed to determine the efficacy of the laboratory model in removal of certain metals and to generate the necessary data required for a database to be further used in the design software. Five elements iron, copper, zinc, aluminum and lead were included in these studies, with iron as the principal element of investigation. Single-element studies were conducted for each element to investigate the capability of the system for removal of individual metal. Binary-element studies were conducted to determine the effect of each individual element on the iron removal. Multi-element studies were performed to study the interactions of the elements in brine, syntheticaly made in the laboratory. In order to conduct the experiments close to the situation in the field, the salts concentration of brines in the field must had been determined accurately. To accomplish this text, using wet chemistry, the slainity of brines from certain locations in Pennsylvania were analized. Using the arithmetic mean, the salts concentrations of brine to be prepared synthetically in the laboratory was determined.

### 4.11.1 - Single-Element Studies

Single-Element studies were conducted to investigate the effectiveness of the prototype model in the removal of heavy metals. These studies were conducted for the following elements: iron (Fe), copper (Cu), aluminum (Al), zinc (Zn) and lead (Pb). Furthermore, these studies were compared with the single-element iron (Fe) studies conducted earlier. Test runs were designed to study the effect of the different parameters on the removal of single-elements.

Test runs were conducted for copper, with flow rates of 2 or 4 BBL/D and

inlet concentrations of approximately 50 or 100 ppm. For each experiment either the flow rate or the inlet concentration was changed, while the other parameters were kept constant. In Table 4.10 the effect of flow rate and inlet concentration is shown.

Table 4.10. Effect of Flow Rate & Concentration on Copper Removal

| Flow Rate (BBL/D) | 2 | 4 | 2 | 4 |
|---|---|---|---|---|
| Inlet Concentration (ppm) | 54.5 | 55.2 | 105.2 | 97.3 |
| Outlet Concentration (ppm) | 8.6 | 20.9 | 26.7 | 44.2 |
| % Removal | 84 | 62 | 74 | 44 |
| Number of Limestone Columns: 2, Aeration Angle: $2^{o}$<br>Temperature: $72^{o}$ F, Retention Tank: In Place | | | | |

The test results show that at low flow rates the removal of copper is better than at higher flow rates, given the same inlet concentration. The effect of aeration unit angle and inlet concentration for a given flow rate was also investigated. The test conditions were the same as the previous experiments. Table 4.11 and Table 4.12 show the results of these experiments. In Table 4.13, the effect of higher flow rate and higher aeration angle is shown.

The test results demonstrate that the higher the aeration angle the better the copper removal under given conditions. The best results were obtained at a low flow rate (2 BBL/D) and at a high aeration angle of 45 degrees (which is the maximum aeration angle of the system). At a high flow rate of 4 BBL/D and an aeration angle of 45 degrees, the copper removal is less than in the case of a low flow rate and a high aeration angle under the same conditions.

Table 4.11. Effect of Aeration Angle and Inlet Concentration on Copper Removal

| | | | |
|---|---|---|---|
| Aeration Angle (deg) | 2 | 15 | 45 |
| Flow Rate (BBL/D) | 2 | 2 | 2 |
| Inlet Concentration (ppm) | 54.5 | 53.4 | 50.3 |
| Outlet Concentration (ppm) | 8.6 | 4.7 | 1.8 |
| % Removal | 84 | 91 | 96 |
| Number of Limestone Columns: 2<br>Temperature: 72° F, Retention Tank: In Place | | | |

Table 4.12. Effect of Aeration Angle and Inlet Concentration Continued

| | | | |
|---|---|---|---|
| Aeration Angle (deg) | 2 | 15 | 45 |
| Flow Rate (BBL/D) | 2 | 2 | 2 |
| Inlet Concentration (ppm) | 105.2 | 106.3 | 96.9 |
| Outlet Concentration (ppm) | 26.7 | 16.7 | 11.1 |
| % Removal | 74 | 84 | 87 |
| Number of Limestone Columns: 2<br>Temperature: 72° F, Retention Tank: In Place | | | |

Table 4.13. Effect of Higher Aeration Angle and Flow Rate

| | | |
|---|---|---|
| Aeration Angle (deg) | 45 | 45 |
| Flow Rate (BBL/D) | 4 | 4 |
| Inlet Concentration (ppm) | 48.8 | 94.3 |
| Outlet Concentration (ppm) | 10.1 | 18.7 |
| % Removal | 79 | 80 |
| Number of Limestone Columns: 2<br>Temperature: 72° F, Retention Tank: In Place | | |

The test results of the parametric studies for copper were compared with the iron studies conducted earlier. Even though, it was observed that the iron removal was 100% for the studies done by previously, both the iron and the copper studies follow the same trend. The system was more capable of removing metals at a low flow rate and at a high aeration angle.

The pH of a solution plays an important role in the chemical reactions of metals of non-metals in aquatic solutions. The critical pH of an element, is the pH value whereby the maximum reaction takes place. The critical pH for copper is 5.5 and for iron is 6. Since a pH higher than the critical pH of both elements was reached during the experiments, oxidation reactions occurred readily and this resulted in a significant removal of Fe and Cu. Copper concentration distribution along the flow path in the treatment system was monitored and Appendix A contains the results, including pH. Referring to the single-element studies of iron and copper, it can be stated that the prototype model is able to remove significant amounts of single-elements at low flow rates and high aeration angles, given that the critical pH for oxidation reactions for the elements could be attained in the system. With this in mind, parametric studies were not conducted for the other elements of interest. The studies focused on the efficacy and the capability of the prototype model. Test runs were conducted with high inlet concentrations of the single-elements, low flow rates and varying aeration unit angle. The results of these studies are illustrated in Table 4.14 and Figure 4.19.

The test results show iron removal of 64%, which is much less than the 100% removal achieved in the previous laboratory work. This difference can be explained by comparing the preparation of synthetic brine of the test runs conducted earlier,

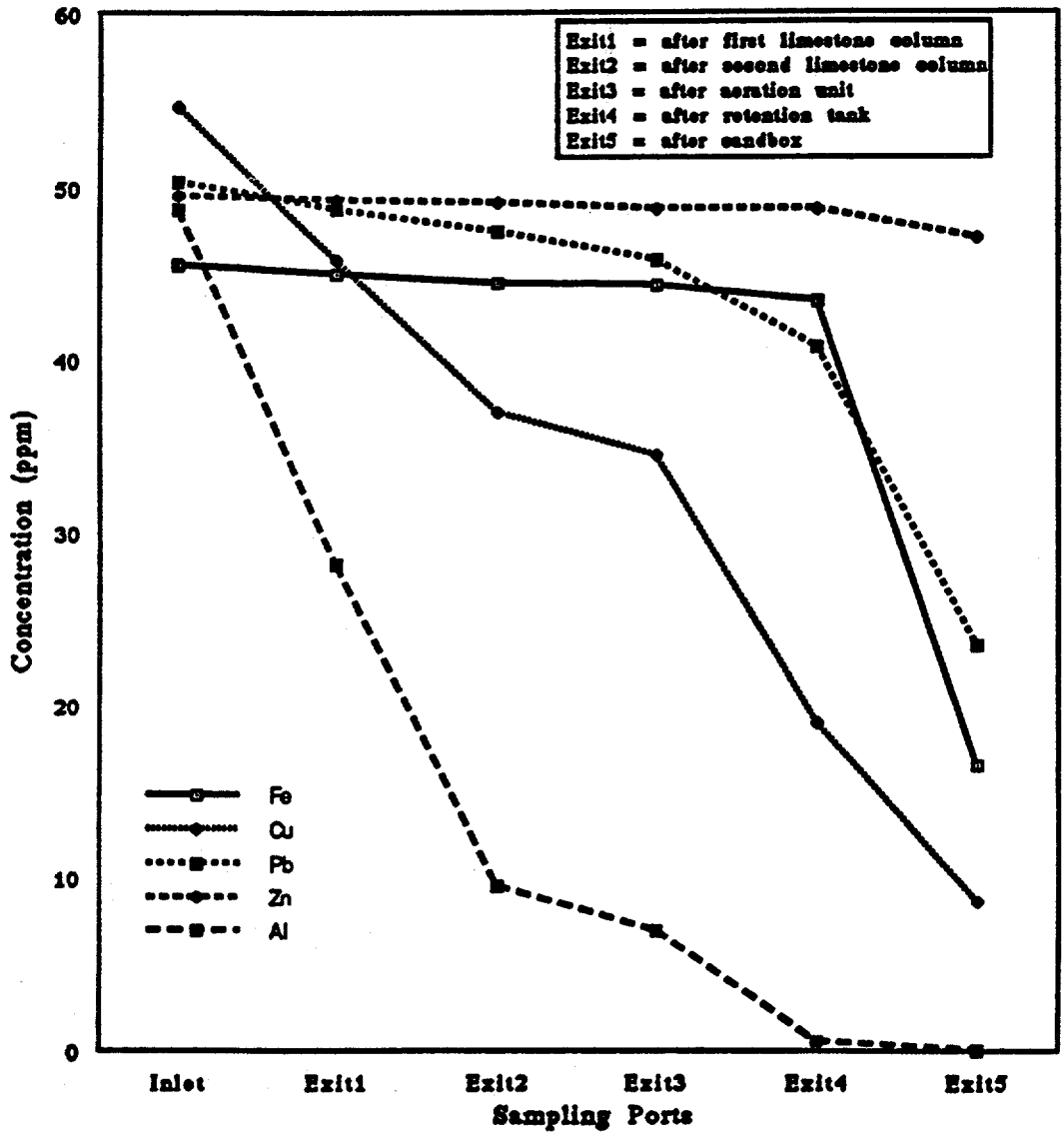


Figure 4.19. Single-Element Removal

with the preparation of the brine for the current test runs. For the studies conducted earlier, brine was prepared using 1,140 grams of sodium chloride and 120 grams of calcium chloride. This resulted in synthetic brine with 3,950 ppm Na, 6,765 ppm Cl and 380 ppm Ca. These values are close to the values found in literature for the contents of oil-field brine.

Table 4.14. Single-Element Removal

| Element | Fe | Cu | Zn | Al | Pb |
|---|---|---|---|---|---|
| Inlet (ppm) | 45.35 | 54.5 | 49.9 | 48.6 | 50.2 |
| Outlet (ppm) | 16.4 | 8.6 | 46.9 | 0.0 | 23.4 |
| % Removal | 64 | 84 | 6 | 100 | 53 |
| Number of Limestone Columns: 2,, Aeration Angle: 2° Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place | | | | | |

The contents of the synthetic brine used for the current studies, are close to Appalachian Basin oil-field data. In order to prepare synthetic brine with contents close to Appalachian oil-field brine, brine from 4 sites was analyzed and the values were averaged. This resulted in dissolving of 1,140 grams sodium chloride and 2,830 grams calcium chloride, to prepare synthetic brine containing 3,950 ppm Na, 22,000 ppm Cl and 9,000 ppm Ca.

The high difference in chloride concentration had an enormous impact on iron removal. Because of the high concentration of chloride ions in the brine, $FeCl_2$ complexes were formed, which in turn decreased the oxidation rate of iron. This is consistent with the findings of Awakura (1986).

In order to investigate a higher aeration angle on metal removal, the aeration unit angle was increased to 45 degrees. Table 4.15 and Figure 4.20 illustrate the

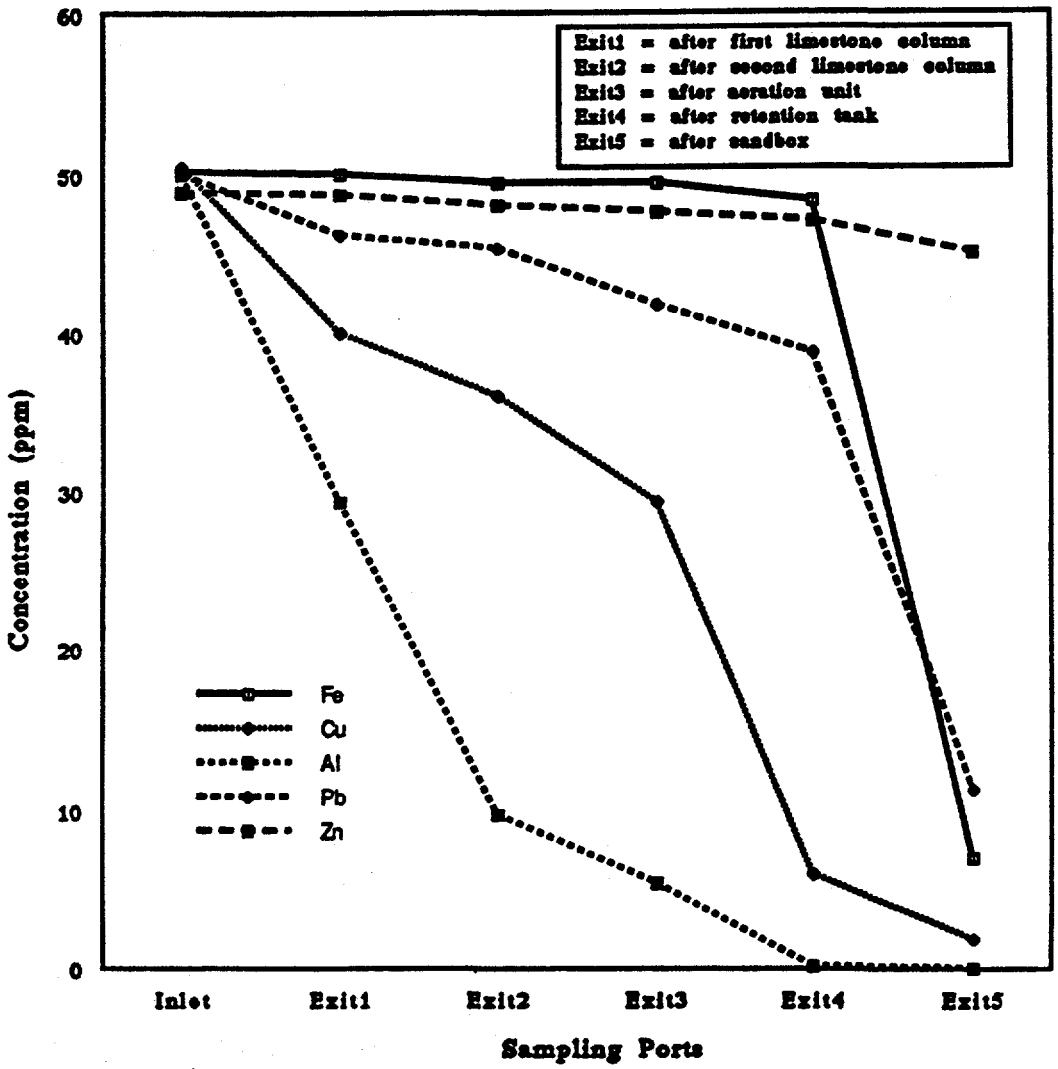


Figure 4.20. Effect of Aeration Angle on Single-Element Removal

effect of higher aeration angle on single-element removal.

Table 4.15. Effect of Higher Aeration Angle on Single-Element Removal

| Element | Fe | Cu | Zn | Al | Pb |
|---|---|---|---|---|---|
| Inlet (ppm) | 50.11 | 50.3 | 48.8 | 50.0 | 50.0 |
| Outlet (ppm) | 7.0 | 1.8 | 45.0 | 0.0 | 11.2 |
| % Removal | 86 | 96 | 8 | 100 | 77 |
| Number of Limestone Columns: 2, Aeration Angle: 45°<br>Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place | | | | | |

The analysis of the single-element studies showed that the system is capable of removing Fe, Cu, and Al to a great extent, and Pb and Zn to a lesser extent. Better results were achieved at a low flow rate (2 BBL/D) and a high aeration unit angle (45 degrees). The removal of iron, copper, and lead increased significantly at a higher aeration angle. The critical pH of Fe and Cu was reached during the experiments, which resulted in the high percentage removal of iron and copper from the system.

Aluminum complexation took place at pH values higher than 3. $Al(OH)_3$ was formed in the limestone columns and aluminum was removed rapidly, since the pH in the limestone columns was higher than 4. In the case of zinc and lead, oxidation processes did not take place, since the critical pH for oxidation reactions for lead and zinc was 8.5 and 10.5 respectively. At lower pH values, between 3 and 4, hydroxide complexes were formed for Zn and Pb. Since Zn could not increase its oxidation state above 2, oxidation reactions did not occur for zinc. The small percentage removal of zinc was due to the zinc hydroxide formation. In high chloride medium, $PbCl_2$ complexes were formed, and with the formation of lead hydroxide complexes at low pH values, a higher percentage of lead was removed compared to

zinc. Since under the test conditions, a pH of 7 or higher was never reached, further metal removal did not take place for zinc and lead. At a higher aeration unit angle of 45 degrees, it was observed that the lead removal increased significantly. This means that a higher aeration angle, has an enormous impact on the lead removal. A higher angle of the aeration unit, resulted in a thinner film of the solution to be exposed to air and thus to allow the $Pb(OH)_2$ formation. In Appendix B, the metal reduction profile along the flow path and the corresponding pH values are shown for each test run.

To study the effect of the retention tank on metal removal, test runs were performed for the elements of interest. Table 4.16 contains the results, including the experimental conditions.

Table 4.16. Single-Element Removal Without Retention Tank

| Element | Fe | Cu | Zn | Al | Pb |
|---|---|---|---|---|---|
| Inlet (ppm) | 49.9 | 50.3 | 50.7 | 48.6 | 46.9 |
| Outlet (ppm) | 31.7 | 28 | 48 | 0.0 | 27 |
| % Removal | 36 | 44 | 5 | 100 | 42 |
| Number of Limestone Columns: 2, Aeration Angle: 2°<br>Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place | | | | | |

The test results demonstrate that the rentention tank is a very important component of the prototype system. The single-element aluminum case was the only one in which the retention tank had no effect on the removal. All the aluminum was removed without the retention tank in place under the given conditions. The other elements show a considerable decrease in the percentage removal without the retention tank in place. Therefore, all further experiments were conducted with the retention tank in place.

### 4.11.2 - Binary-Element Studies

Binary-Element studies of Fe-Cu, Fe-Zn, Fe-Al, and Fe-Pb were conducted to investigate the inhibiting or catalytic effects of the elements on iron oxidation. Table 4.17 contains the results, including the test conditions. Figure 4.21 illustrates the iron removal per sample port from binary-elements.

Table 4.17. Metal Removal from Binary-Element Studies

| Binary-elements | Fe+Cu | | Fe+Zn | | Fe+Al | | Fe+Pb | |
|---|---|---|---|---|---|---|---|---|
| | Fe | Cu | Fe | Zn | Fe | Al | Fe | Pb |
| Inlet (ppm) | 48.8 | 1.16 | 49.4 | 1.15 | 52.5 | 1.00 | 53.3 | 1.11 |
| Outlet (ppm) | 8.1 | 0.4 | 23.8 | 0.97 | 28.6 | 0.0 | 8.7 | 0.12 |
| % Removal | 84 | 68 | 48 | 16 | 46 | 100 | 84 | 89 |
| Number of Limestone Columns: 2, Aeration Angle: $2^{o}$<br>Flow Rate: 2 BBL/D, Temperature: $72^{o}$ F, Retention Tank: In Place | | | | | | | | |

These test results showed that the presence of Cu and Pb has a catalytic effect on the oxidation of iron and that Zn and Al have an inhibiting effect on the iron removal from brine. At the same time, it was observed that the copper removal was lower than the copper removal from single-copper studies, which implied that iron was exercising an inhibiting effect on copper. The presence of iron increased the zinc and lead removal. Iron did not exercise a negative influence on alumnium, since the aluminum removal was 100%. Appendix C, shows the profile of the metal removal along the system for the binary-element systems.

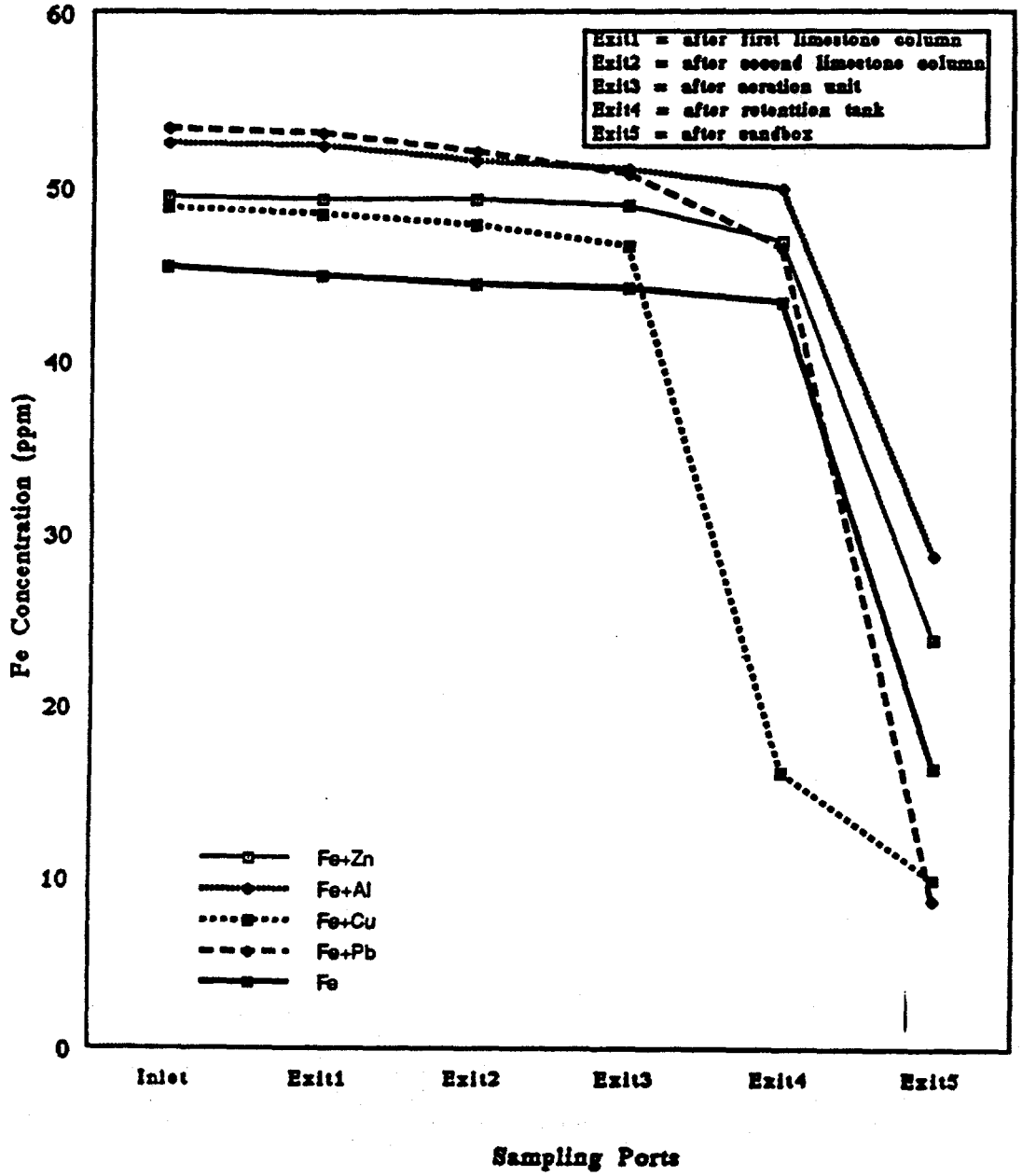


Figure 4.21. Binary-Element Study

### 4.11.3 - Multi-Element Studies

Multi-element studies were conducted to investigate the effect of two or more elements on iron removal. Results of these studies are contained in Tables 4.18 through 4.23. Figure 4.22 illustrates iron removal from multi-element studies. In the case of the combination of Fe, Cu and Al, 90% Fe, 31% Cu, and 97% Al was removed from the solution. Aluminum exercised an inhibiting effect on iron. It was observed that the copper removal from the multi-element study Fe-Cu-Al, was lower than the copper removal from the binary-element study of Fe-Cu. This suggests that Al was exercising an inhibiting effect on copper. Fe exercised an inhibiting effect on copper as well. At the same time, inclusions of iron did not appear to affect the removal of aluminum. The aluminum removal from the Fe-Cu-Al system was 100% as was the case of the single and binary element studies. Aluminum was thus removed from solution with the formation of $Al(OH)_3$ complexes. Despite the inhibiting effect of Al on Fe removal, copper exercised a catalytic effect on iron oxidation, and there was marked increase in Fe removal from the solution.

In the case of Fe, Zn and Cu, 92% Fe, 65% Zn, and 35% Cu was removed from the solution. Iron exercised an inhibiting effect on copper removal, and with Zn in solution, a lower percentage of copper was removed from the system. This implies that Zn exercised an inhibiting effect on iron as well as on copper. Because of the positive influence of iron and copper on zinc, a higher percentage of zinc was removed. With the catalytic effect from copper on iron, a considerably high percentage of iron was removed.

In the case of Fe, Cu and Pb, 93% Fe, 35% Cu and 96% Pb was removed. Both copper and lead, were exercising a catalytic effect on the oxidation of iron. The formation of $PbCl_2$ complexes increased iron removal. The presence of copper

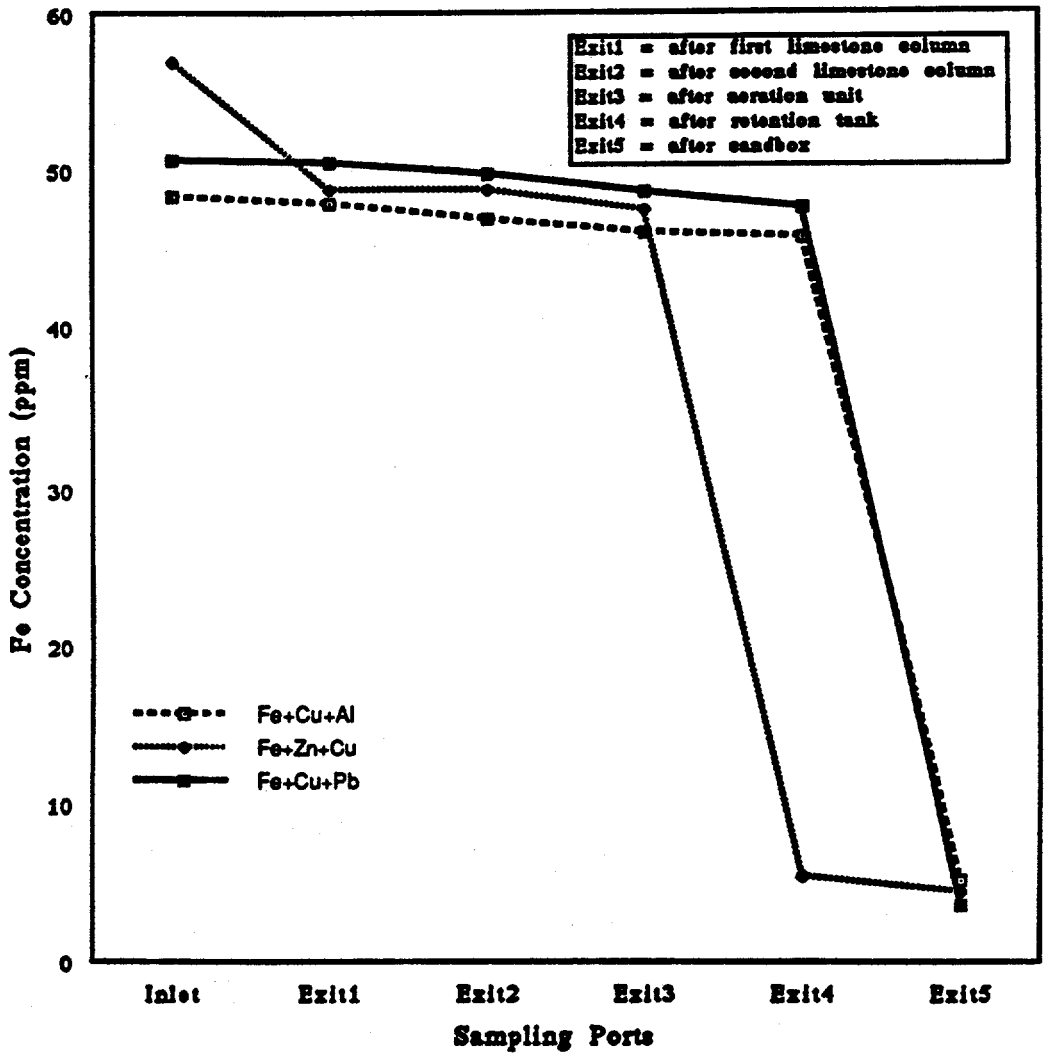


Figure 4.22. Multi-Element Removal

greatly increased lead removal. Iron in turn, exercised an inhibiting effect on copper removal. With lead in the system, the copper removal was much lower than the removal from the binary Fe-Cu system. This implies that lead was exercising an inhibiting effect on copper. Figure 4.23 shows the continuation of iron removal from multi-element studies.

The multi-element test run of Fe, Al, and Pb, resulted in 68% Fe, 99% Al and 87% Pb removal from brine. Inclusions of Fe did not effect the removal of Al negatively. Al in turn, exercised an inhibiting effect on iron removal. The formation of the $PbCl_2$ complexes and NaOH in chloride medium, resulted in increased removal of iron.

The test run of Fe, Al and Zn, resulted in 60% Fe, 90% Al, and 43% Zn removal from the solution. Al and Zn were exercising an inhibiting effect on iron oxidation. The presence of Fe and Al increased the removal of Zn.
Inclusions of zinc in the system, resulted in a decrease of the percentage removal of Al.

The test run of Fe, Zn and Pb, resulted in 82% Fe, 62% Zn and 100% Pb removal from the brine solution. The presence of iron and lead, increased the removal of zinc from the brine solution. Zinc aggravated the removal of lead immense'ly. Despite the inhibiting effect from Zn on iron removal, lead exercised a positive effect on iron and this resulted in a significant percentage removal of iron.

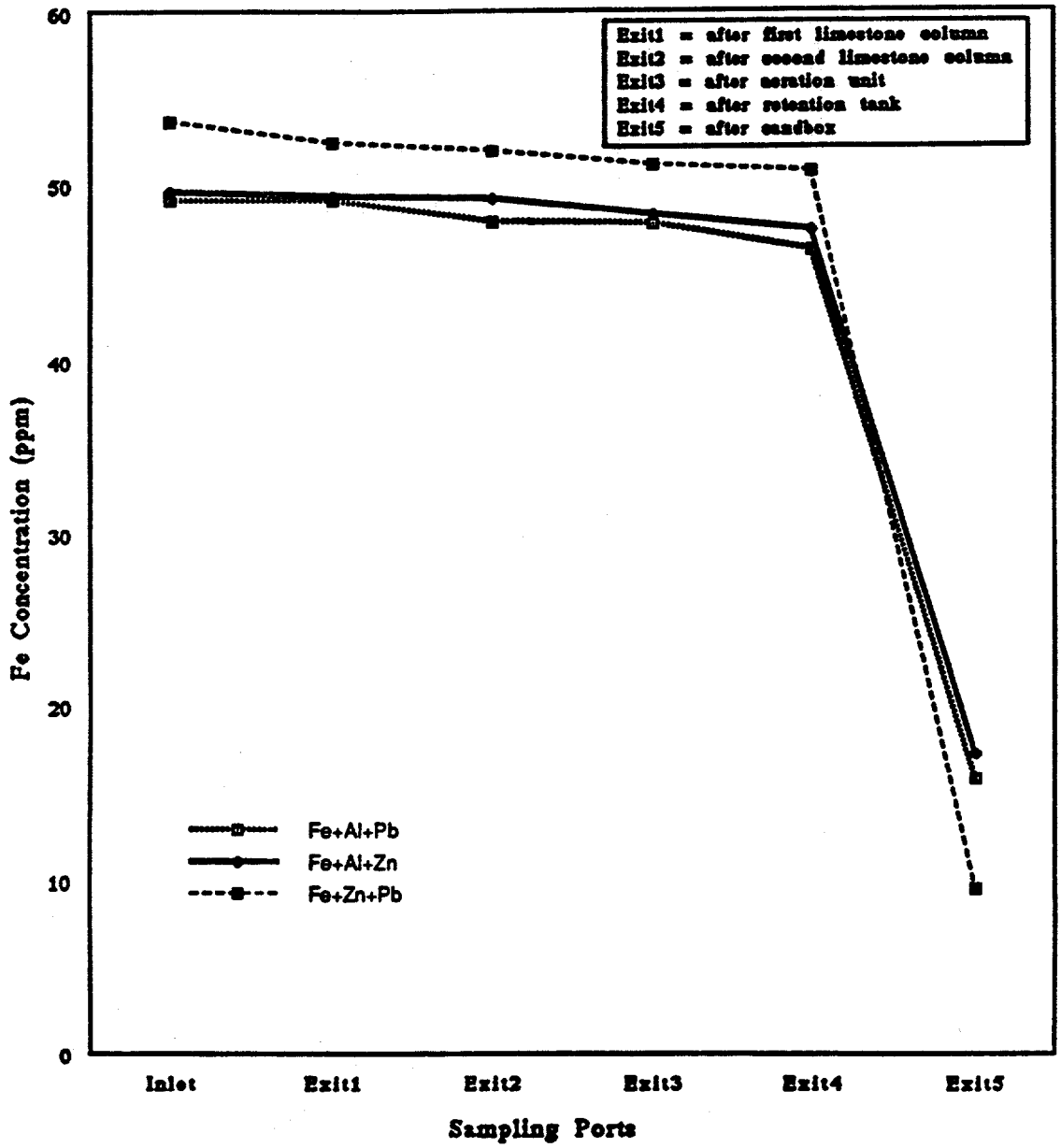


Figure 4.23. Multi-Element Removal Continued

Table 4.18. Metal Removal from the Fe-Cu-Al System

| | Fe | Cu | Al |
|---|---|---|---|
| Inlet (ppm) | 48.8 | 1.19 | 2.5 |
| Outlet (ppm) | 5.08 | 0.82 | 0.07 |
| % Removal | 90 | 31 | 97 |

Number of Limestone Columns: 2, Aeration Angle: 45°
Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place

Table 4.19. Metal Removal from the Fe-Zn-Cu System

| | Fe | Zn | Cu |
|---|---|---|---|
| Inlet (ppm) | 56.8 | 1.26 | 1.24 |
| Outlet (ppm) | 4.4 | 0.44 | 0.80 |
| % Removal | 92 | 65 | 35 |

Number of Limestone Columns: 2, Aeration Angle: 45°
Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place

Table 4.20. Metal Removal from the Fe-Cu-Pb System

| | Fe | Cu | Pb |
|---|---|---|---|
| Inlet (ppm) | 50.6 | 1.02 | 1.03 |
| Outlet (ppm) | 3.5 | 0.66 | 0.04 |
| % Removal | 93 | 35 | 96 |

Number of Limestone Columns: 2, Aeration Angle: 45°
Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place

Table 4.21. Metal Removal from the Fe-Al-Pb System

| | Fe | Al | Pb |
|---|---|---|---|
| Inlet (ppm) | 49.1 | 1.5 | 1.22 |
| Outlet (ppm) | 15.8 | 0.01 | 0.16 |
| % Removal | 68 | 99 | 87 |
| Number of Limestone Columns: 2, Aeration Angle: 45°<br>Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place | | | |

Table 4.22. Metal Removal from the Fe-Al-Zn System

| | Fe | Al | Zn |
|---|---|---|---|
| Inlet (ppm) | 49.6 | 1.3 | 1.14 |
| Outlet (ppm) | 17.2 | 0.13 | 0.65 |
| % Removal | 65 | 90 | 43 |
| Number of Limestone Columns: 2, Aeration Angle: 45°<br>Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place | | | |

Table 4.23. Metal Removal from the Fe-Zn-Pb System

| | Fe | Zn | Pb |
|---|---|---|---|
| Inlet (ppm) | 53.7 | 1.17 | 1.05 |
| Outlet (ppm) | 9.45 | 0.44 | 0.0 |
| % Removal | 82 | 62 | 100 |
| Number of Limestone Columns: 2, Aeration Angle: 45°<br>Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place | | | |

## 4.12 - Simulation of Red Valley Brine

Red Valley Brine, was one of the four brines used to analyze the contents of Appalachian oil-field brine. Red Valley brine contains a relatively high iron concentration and low concentrations of copper, aluminum, zinc and lead. This brine was therefore simulated to evaluate the capability of the laboratory scale prototype model in the removal of heavy metals. Table 4.24 shows the removal of the metals from Red Valley Brine, including the test conditions. Figure 4.24 illustrates the removal of the metals from Red Valley Brine.

Table 4.24. Removal of Metals from Red Valley Brine

| | Fe | Cu | Zn | Al | Pb |
|---|---|---|---|---|---|
| Inlet (ppm) | 39.7 | 1.26 | 0.98 | 2.4 | 1.08 |
| Outlet (ppm) | 3.9 | 0.9 | 0.4 | 0.08 | 0.1 |
| % Removal | 90 | 32 | 60 | 97 | 91 |
| Number of Limestone Columns: 2, Aeration Angle: 45°<br>Flow Rate: 2BBL/D, Temperature: 72° F, Retention Tank: In Place | | | | | |

With all five elements present in the brine, a very high level of iron removal was achieved, because of the catalytic influences of copper and lead. The formiation of $PbCl_2$ complexes increased the iron oxidation considerably. Aluminum and zinc exercised an inhibiting effect on iron, but the presence of iron at the same time, increased the zinc removal. The presence of copper increased zinc as well as lead removal. Zinc aggravated lead removal as well. The percentage copper removal was low, partly because of the inhibiting influence of iron on copper removal. The presence of aluminum, zinc and lead in the system resulted also in a considerably low percentage copper removal.

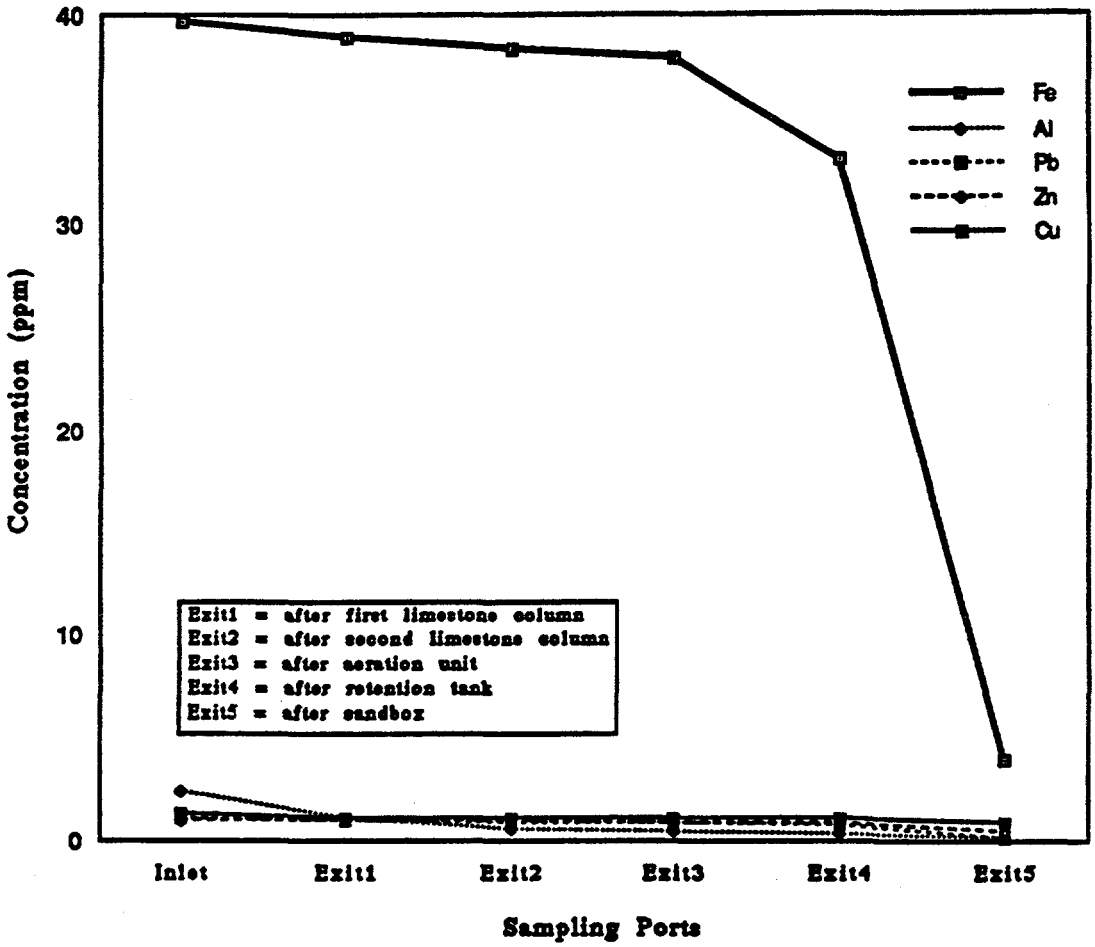


Figure 4.24. Simulation of Red Valley Brine

The concentration of the metals from Red Valley brine was increased and simulated to investigate the performance of the prototype model with high concentrations of metals. Table 4.25 shows the simulation of a higher concentration of metals from the Red Valley brine, incuded the test conditions. Figure 4.25 illustrates the simulation of altered Red Valley Brine.

Table 4.25. Simulation of Altered Red Valley Brine

| | Fe | Cu | Zn | Al | Pb |
|---|---|---|---|---|---|
| Inlet (ppm) | 59.8 | 9.7 | 10.15 | 10.02 | 10.14 |
| Outlet (ppm) | 4.4 | 8.04.6 | 9.5 | 0.30 | 3.24 |
| % Removal | 93 | 17 | 6 | 97 | 68 |
| Number of Limestone Coulmns: 2, Aeration Angle: 45°<br>Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place | | | | | |

The test results show that the iron and aluminum removal are comparable to those of the previous test and thus independent of the inlet concentration under the same conditions. The removal of Fe and Al was greater than or equal to 90% as was the case in the Red Valley brine study. The copper, lead, and zinc removal were reduced substantially at higher inlet concentrations of these elements under the same conditions. Approximately 17% Cu, 68% Pb, and 7.4% Zn were removed from solution. This showed that a higher inlet concentration of these metals in solution, negatively affected the metal removal. A higher inlet concentration of Pb, Zn and Fe in solution resulted in a stronger inhibiting effect from these metals on the Cu removal. In the case of Red Valley brine, the inlet concentrations of zinc and lead were approximately 1 ppm. The presence of the other elements in solution resulted in a 60% and 91% removal for respectively zinc and lead. In the case of

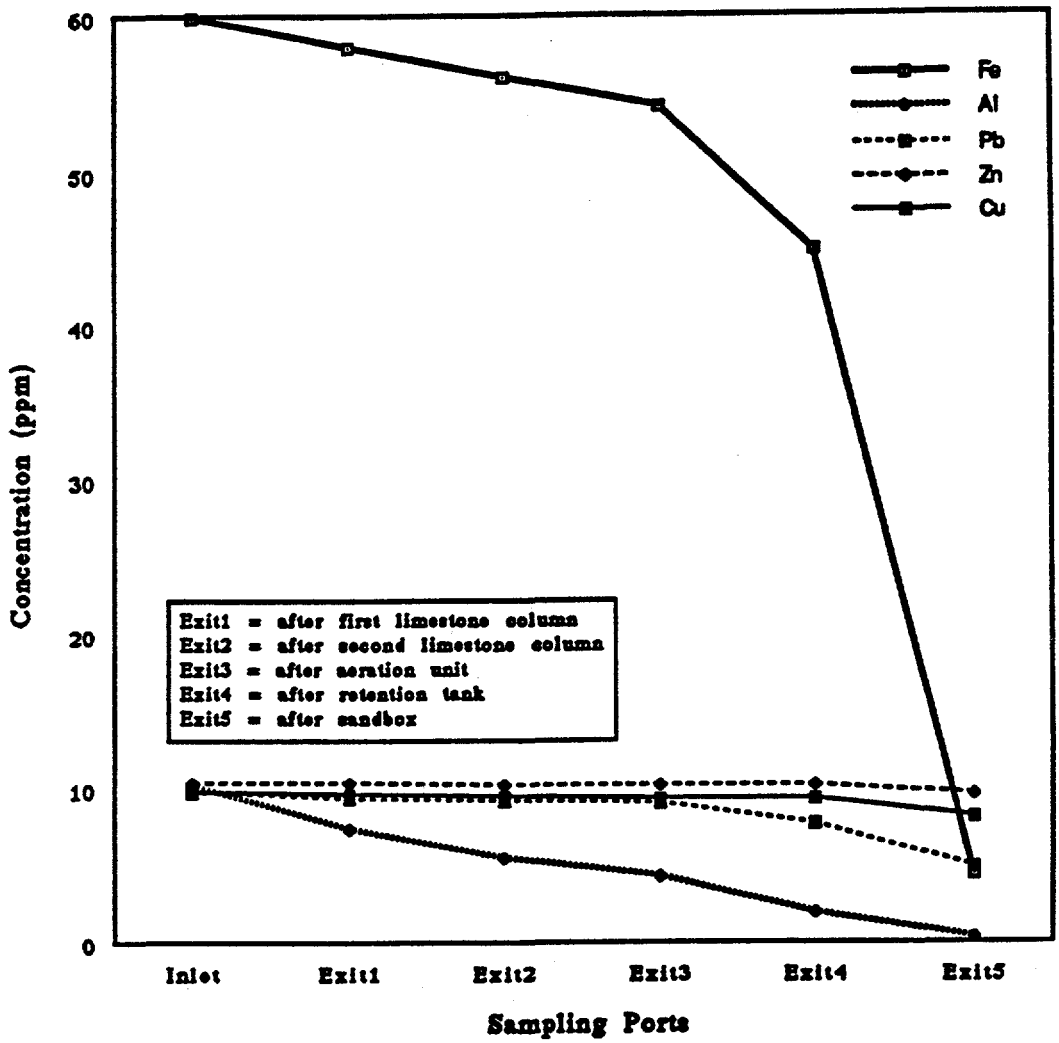


Figure 4.25. Simulation of Altered Red Valley Brine

higher inlet concentrations, Fe and Al were substantially removed from solution while a smaller percentage Zn and Pb hydroxides were formed and thus removed from the system.

## 4.13 - Impact of Constant Material Flow Rate

The effect of constant mass flow of material (metallic) was investigated. In this case, a test run was performed whereby the mass flow of materials was kept constant using the formula:

Mass Flow Rate= Mass (Concentration) * FlowRate

The test run of higher concentration of elements of Red Valley brine (Table 4.25) was compared with a test run with a lower concentration of elements, but with a higher flow rate (Table 4.26). In Table 4.26 the effect of material mass flow rate on metal removal is shown, included the test conditions. In Figure 4.26 this effect is illustrated.

Table 4.26. Simulation of Material Mass Flow on Metal Removal

| | Fe | Cu | Zn | Al | Pb |
|---|---|---|---|---|---|
| Inlet (ppm) | 41.34 | 1.03 | 1.05 | 2.5 | 0.97 |
| Outlet (ppm) | 12.11 | 0.88 | 0.66 | 0.2 | 0.08 |
| % Removal | 71 | 17 | 37 | 92 | 92 |
| Number of Limestone Columns: 2, Aeration Angle: 45°<br>Flow Rate: 2 BBL/D, Temperature: 72° F, Retention Tank: In Place | | | | | |

This test result shows that constant material mass flow had an effect on copper and aluminum removal, since in both tests the removal for these elements was 17% and greater than 90% for copper and aluminum respectively. The constant mass

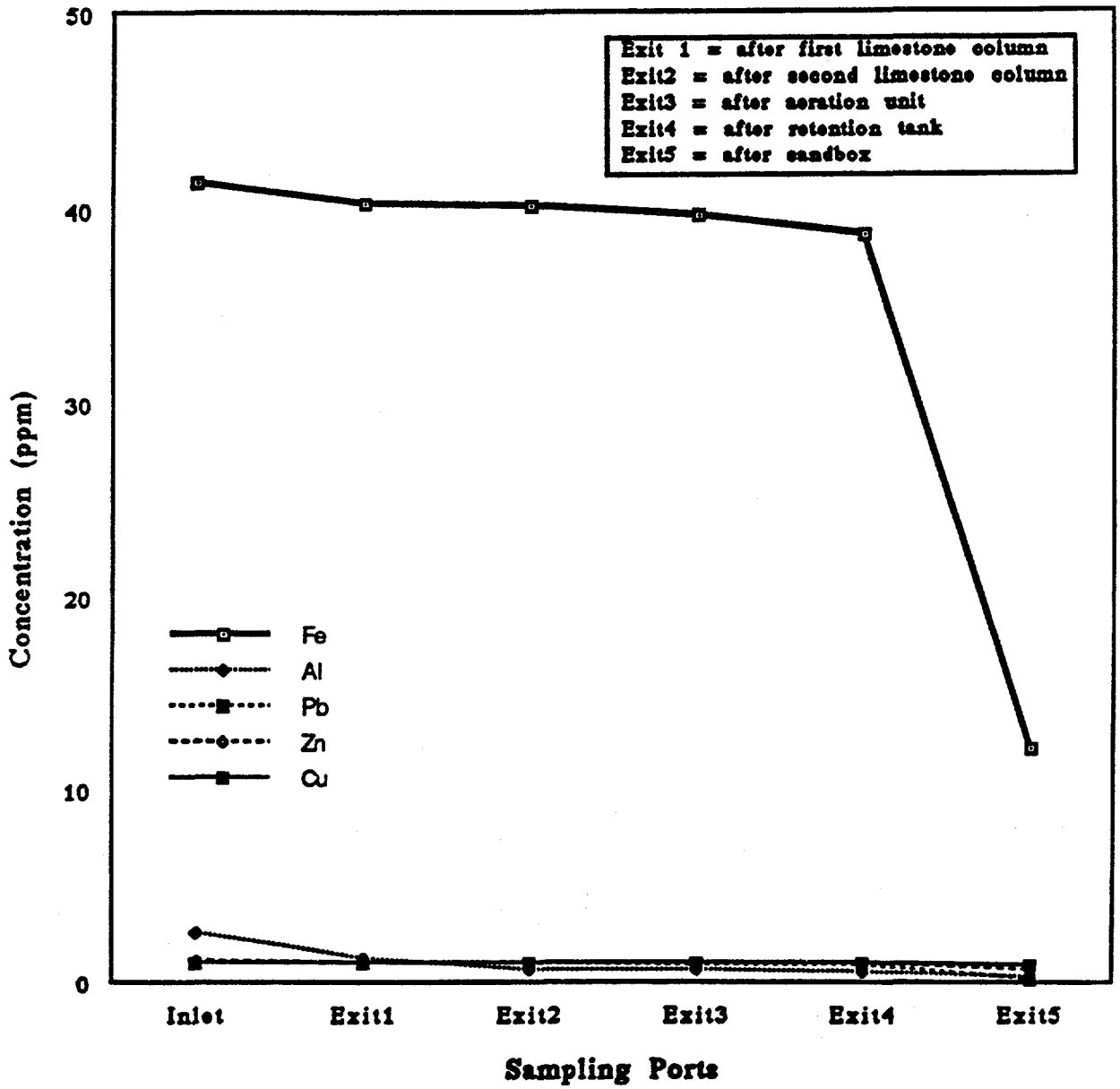


Figure 4.26. Effect of Material Mass FLow Rate on Metal Removal

flow study, had no great impact on lead and zinc, since in the case of low 0.97 ppm inlet concentration for lead and a flow rate of 2.18 BBL/D, more lead was removed than in the case of high inlet concentration of 9.7 ppm lead and 1 BBL/D flow rate. The same could be stated for zinc. Lower inlet concentrations of the elements and a higher flow rate, resulted in a higher percentage removal for zinc and lead. The Zn and Pb removal from the system was thus very dependent on the other elements in the system. In the case of iron, there was no significant effect of constant material mass flow rate on the iron removal. Despite the strong catalytic effects from copper and lead on iron, it was observed that iron removal was strongly dependent on flow rate. At a flow rate of 1 BBL/D, and an inlet concentration of approximately 60 ppm Fe in the system, the Fe removal was much higher compared with the case of inlet concentration of approximately 40 ppm Fe and a higher flow rate of 2.18 BBL/D.

## 4.14 - Error Analysis

Whenever experiments are conducted and measurements are involved, measurement errors will occur. Samples were analyzed with the Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Depending on the expected concentrations, standards were prepared and the concentration of the samples was measured, using linear extrapolation. Three measurements per sample were taken, and the mean of these measurements resulted in the measured concentration per sample. The expected maximum error of the ICP-AES was 5%. In order to calculate the variance and the standard deviation of a set of samples, three samples were taken per sampling port. Measurements were conducted for each sample, and the average measured concentration per sampling port was calculated. Test results

showed that the samples per sampling port, did not vary much in concentration. The sample variance and the standard deviation were calculted therefore, using the following formulas:

$$s^2 = \sum_{i=1}^{n} \frac{(y_i - \bar{y})^2}{n-1} \tag{4.1}$$

$$s = \sqrt{s^2} \tag{4.2}$$

where: $s^2$ = the variance,

$y_i$ = sample measurement,

$\bar{y}$ = sample mean

s = standard deviation

There were no significant differences in the concentration found in samples taken from one sampling port. The following example illustrates the calculation of the variance and standard deviation of the measured inlet concentrations of a test run.

| $y_i$ | $y_i^2$ |
|---|---|
| 50.2 | 2520.04 |
| 50.8 | 2580.6 |
| 50.7 | 2570.49 |
| 151.7 | 7671.13 |

$$\bar{y} = \frac{151.7}{3} = 50.57 \tag{4.3}$$

$$s^2 = \sum_{i=1}^{n} y_i^2 - \frac{(\sum_{1=1}^{n} y_i)^2}{n} \tag{4.4}$$

$$s^2 = 0.16$$

$$s = \sqrt{0.17} = 0.40 \tag{4.5}$$

$$\bar{y} = 50.57 +/- 0.40 \tag{4.6}$$

The error in sample measurement for the inlet concentrations was 0.8 %.

The errors of the measured concentrations of the other sampling ports were estimated likewise. The error in sample measurement for the first limestone column was 0.2%, for the second limestone column 1.3%, for the aeration unit 0.9%, for the solid separator unit 3.36% and for the sand filtration unit 6.7%. The expected maximum error in the system for inlet concentrations of 50 ppm is thus 6.7%, or 50 +/-3.3 ppm.

## 4.15 - Discussion

It was observed that when the critical pH of the single-elements was reached in the system, the metals could be readily removed. The iron and copper studies showed clearly that an oxidation reaction had taken place. The removal of iron and copper was significant when the flow rate was low (2 BBL/D or less) and the aeration unit angle was high (45 degrees).

The removal of single-elements zinc and lead was lower compared to iron and copper. The critical pH of zinc and lead is 10.5 and 8.5 respectively and could not be reached in the prototype system. Oxidation reactions did not take place, but hydroxide complexes were formed for both zinc and lead. Compared to lead, the removal of zinc was low. The removal of lead was higher than that of zinc because lead removal took place in the form of lead chloride and lead hydroxide complexes, while only a small percentage zinc hydroxide was formed.

It was further observed, that aluminum reacted differently from the other single-elements. Aluminum hydroxide complexes were formed at a pH level of 3, and this resulted in an outlet concentration of zero. Most of the aluminum was removed in the limestone columns, since the pH level in the limestone columns was higher than 3. In the case of the other single-elements, the majority of the elements was removed in the sand box.

With relatively high inlet concentrations (approximately 50 ppm), the prototype system was thus capable of substantial removal of the single-elements Fe, Cu, Al, and Pb. Approximate 86% Fe, 96% Cu, 100% Al, 77% Pb, and 8% Zn were removed from the system at inlet concentrations of about 50 ppm, a flow rate of 2 BBL/D and an aeration unit angle of 45 degrees.

The binary-element studies of iron with another element of interest, showed that Cu and Pb were exercising a catalytic effect on the oxidation of iron. The percentage removal of iron from the system increased from 64% for the single-element iron system to 84% for the Fe-Cu and the Fe-Pb systems. From the pseudo-kinetic analysis it was observed also, that copper and lead were exercising a catalytic effect on the oxidation of iron. The reaction rate constant for single-element iron is 0.000068, whereas for the binary system Fe-Cu and Fe-Pb, the values are 0.00016 and 0.000176 respectively. This means, that the K-value for iron was increased by the presence of copper or lead. At the same time, it was observed that iron was also affects the removal of copper and lead. The copper removal of the Fe-Cu system, was 68%, which was lower than the 84% of the single-element copper study. This showed that iron exercises an inhibiting effect on the copper removal and a catalytic effect on lead removal. The lead removal from the Fe-Pb system was 89% and the single-element lead removal was 53% under the same test conditions.

The binary-study for the Fe-Zn system, showed that only 48% of iron was removed from the Fe-Zn system, implying that zinc exercises an inhibiting effect on the oxidation of iron. The K-value for iron from the Fe-Zn system is 0.0000119, which is lower than the K-value for the single-element iron (0.000068). Iron in turn, affected the removal of zinc positively. The zinc removal of the Fe-Zn system increased to 16%, compared with 6% for the single-element zinc removal.

It was further observed that aluminum exercises an inhibiting effect on iron removal, since the iron removal from the Fe-Al system, was only 46%. From the reaction constant values it was also observed that aluminum was affecting the removal of iron negatively. The $K_{Fe}$ value for the Fe-Al system was 0.000059, which was lower than the 0.000068 obtained for single-element iron. Iron in turn, did not affect aluminum. The percentage aluminum removal from the Fe-Al system was the same as the single-element aluminum removal (100%).

The results of the multi-element studies showed that the elements were influencing the removal of one another significantly in the system. With the Fe-Cu-Al system, the iron removal increased to 90%. The copper and the aluminum removal were 31% and 97% respectively. This suggests that even though Al was exercising an inhibiting effect on the Fe removal, the catalytic influence of copper on iron had the upper hand. The removal of copper was very low, because of the presence of both Fe and Al in the system.

The Fe-Zn-Cu system showed that iron was significantly removed from the system. This showed that despite the inhibiting influence of Zn on Fe, copper was exercising a catalytic effect on the iron removal. Iron on the other hand, was exercising an inhibiting effect on copper, and with the inhibiting influence from zinc on copper, the copper removal was only 35%. Both iron and copper were

exercising a catalytic effect on Zn removal, and this resulted in a 65% removal of zinc from the system.

From the Fe-Cu-Pb system, significant percentages of iron and lead were removed. Because of the catalytic influence of both copper and lead on iron, the percentage of iron removal was high. The formation of lead chloride complexes resulted in a marked removal of iron. Copper and iron were exercising a catalytic effect on Pb, which lead to a Pb removal of 96%. The inhibiting effect from iron on copper resulted in a low percentage (35%) of copper removal.

The Fe-Al-Pb system, resulted in a low percentage, 68%, of iron removal. Despite the fact that lead was exercising a catalytic effect on iron removal, with the formation of lead chloride complexes, the iron removal was low. The inhibiting influence of aluminum on iron had the upperhand. It was observed that the aluminum removal was only 87%. This relatively low percentage, suggests that the presence of lead in the system affected the aluminum removal.

The Fe-Al-Zn system resulted in a low percentage of iron removal. This was expected, since both aluminum and zinc were exercising an inhibiting effect on the iron removal from the system. With the presence of zinc in the system, the aluminum removal decreased slightly to 90%. The presence of Al and Fe, increased the removal of zinc to 43%.

From the Fe-Zn-Pb system, 82% iron was removed. The formation of lead chloride complexes increased the removal of iron but at the same time, zinc exercised an inhibiting effect on iron. This resulted in a relatively lower percentage of iron removal. The presence of iron and lead resulted in an increased zinc removal of 62%. Because of the presence of zinc, the lead removal was dramatically increased to 100%.

The simulation of Red Valley brine, where all five elements where present with inlet concentrations of about 40 ppm Fe, 2.5 ppm Al, and 1 ppm of Cu, Zn and Pb, resulted in a relatively high percentage removal (90%) for iron. This is because of the catalytic influence of copper and lead on iron removal, despite the inhibiting effects of aluminum and zinc. Zinc and iron exercised an inhibiting effect on copper, and as a result, only 32% copper was removed. The presence of copper and iron on the other hand, increased the zinc removal to 60%. The lead removal was significantly increased to 91%, because of the presence of zinc and copper. The removal of aluminum from the system was significant.

At increased inlet concentrations of 60 ppm Fe, and 10 ppm of the other elements, iron and aluminum were markedly removed from the system. The percentage removed from the other elements was quite low. A higher inlet concentration of elements in the system resulted in only 17% removal for Cu. Despite the positive influences from iron and zinc on lead, the percentage of lead removed was only 68%. A higher percentage of iron, did not increase the zinc removal. The zinc removal was decreased to 7%. At higher inlet concentrations of the elements of interest, Fe and Al were removed markedly from the system. Copper removal was inhibited much stronger with higher percentages of iron and zinc in the system. Hydroxide formations of Zn and Pb occurred to a lesser extent, because of the large surface area occupied by Fe and Al.

The effect of constant material mass flow rate on metal removal was investigated. Here, the mass flow was kept constant, while the flow rate was varied for the different test runs. The test run with higher concentrations of elements (approximately 60 ppm Fe and 10 ppm of Cu, Al, Zn and Pb and a flow rate of 1BBL/D), which was previously discussed, was compared with a test run, with lower inlet

concentrations of the elements (approximately 40 ppm Fe, 2.5 ppm Al and 1 ppm Cu, Zn and Pb), and a higher flow rate (2.18 BBL/D). This study showed that the concept of constant material mass flow rate could be applied to copper and aluminum, since for both test runs, the percentages of copper and aluminum removed were approximately the same. In both tests, about 17% of the copper and greater than 90% of the aluminum was removed. The constant mass flow concept could not be applied to the other elements, since in the case of lead and zinc, the percentage removal was not the same for both studies. The study with lower inlet concentrations of metals and a higher flow rate, resulted in a higher percentage removal of zinc and lead, compared to the study with high inlet concentrations of metals and a low flow rate. The removal of Zn and Pb was very dependent on the presence of other elements. Zn and Pb removal were thus dependent on the medium. It was obvious that the constant material mass concept could not be applied to iron. A higher inlet concentration of elements and a low flow rate, resulted in a higher percentage iron removal, compared to the case with lower inlet concentration of elements and a high flow rate. The removal of iron is therefore flow rate dependent.

# 5. Kinetics Research

## 5.1 - Preamble

One of the main project deliverables for this research is a computer design package whose purpose is the section by section design of each sub-unit of the brine treatment facility. In order for the code to be able to accurately supply design specifications, it was necessary to create a database. This database contains information describing how the dissolved metals interact in solution. This data must be obtained from numerous laboratory studies.

Critical pH experiments were conducted using a synthetic brine constructed to closely match the brines found in the field. Analysis results of six different field brines were averaged to provide the basis for the synthetic brine. 571 grams of sodium chloride and 171 grams of calcium chloride were added to 15 gallons of distilled water to produce the synthetic brine mixture. Using the prepared synthetic brine with a procedure that would be discussed in detail, the critical pH of element such as aluminum, copper, lead, and zinc were determined. Furthermore, through the experimental studies conducted in the laboratory using the prototype model, the rate and order of reactions for single elements iron, aluminum, copper, lead and zinc were calculated. The reaction rate constant values for iron, $k_{Fe}$, in binary systems were calculated as well.

## 5.2 - Critical pH Studies

Initial runs (Critical pH studies) determined the pH range where each metal under study began to react. These studies helped limit the scope and number of experiments by placing bounds on the pH variable. First, the region of the pH

scale where reactions took place was determined. The critical pH studies decreased the number of experiments that would have to be conducted in future studies by giving guidelines as to what pH values to choose for use in future studies.

### 5.2.1 - Procedure

Each experiment required four liters of the synthetic brine. Temperature of the brine was held constant by a water jacket that was connected to a Neslab temperature control system. This was a necessity as temperature can greatly affect the results of the kinetics studies. Synthetically made brine was continuously aerated to insure maximum air saturation and adequate mixing throughout the four liters of brine. The pH of the brine was continuously monitored with a Fisher Scientific digital pH meter, model 601, equipped with a reverse-sleeve junction reference electrode (cat. # 13-620-61) and a temperature compensation probe (see Figure 5.1). The pH probes required special consideration as the mixtures under study can easily plug standard probe membranes.

Metal stock solutions were prepared by dissolving the metal required in an acid solution and diluting to the required concentration for experimental use. The stock solutions were kept at a very low pH to maintain stable ion concentration. 2000 ppm stock solutions were added to the brine to produce a solution of brine containing 50 ppm of the metal under study.

Since the prepared stock solutions contained rather high acid concentrations, the pH of the brine solution was now very low, preventing any reaction. The pH of the solution was raised by the addition of small amounts of concentrated sodium hydroxide to the solution to adjust the pH value. As the pH gradually increased, 13 ml samples were collected, filtered through 0.45 micron nylon syringe filters,

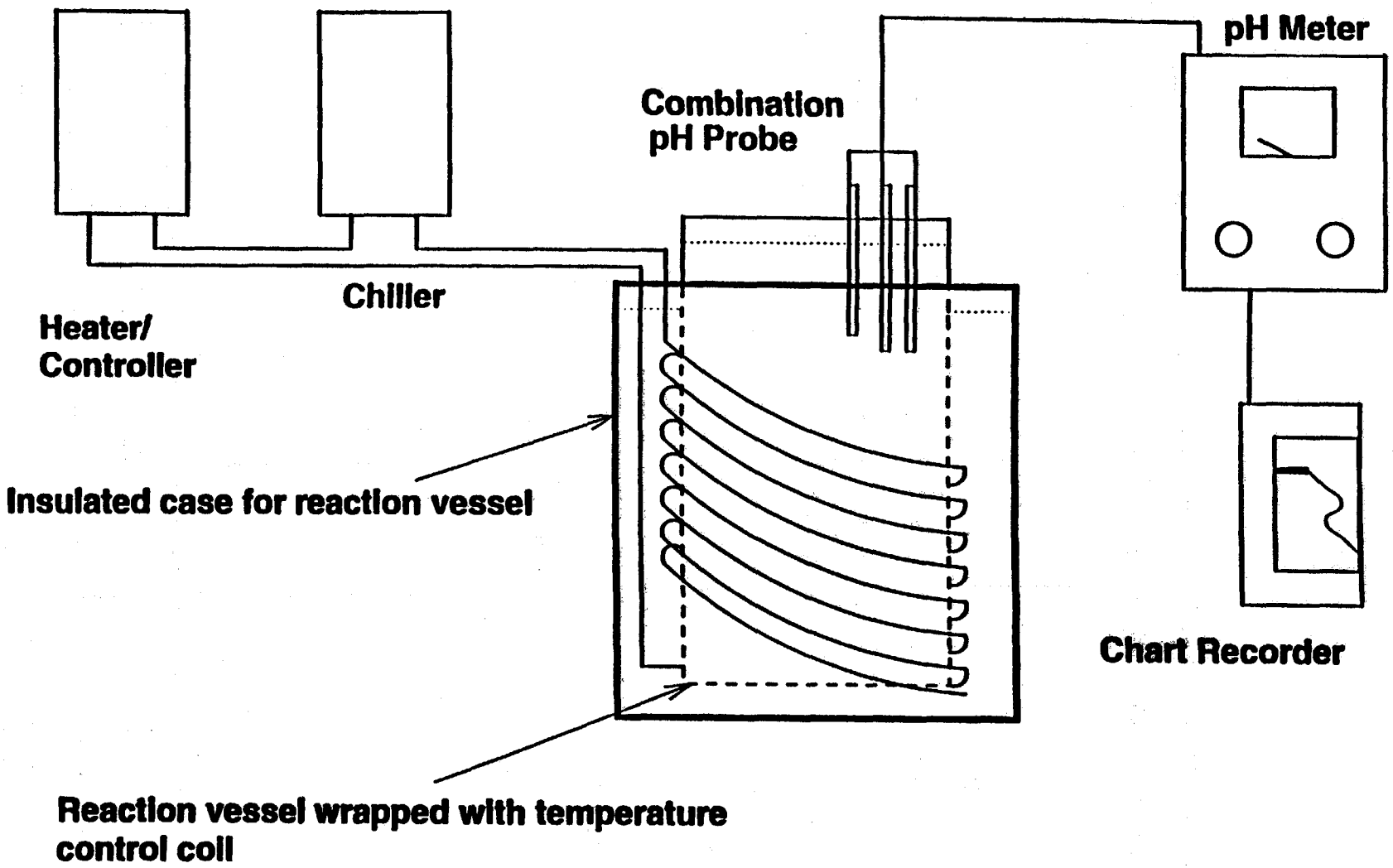


Figure 5.1 - Schematic Diagram of the Laboratory Set Up for Kinetic Study

and acidified by adding 1% by volume of concentrated hydrochloric acid to preserve them for later analysis. Each experiment is stopped when the pH reached a value of 10.0.

### 5.2.2 - Analysis

The collected samples were then analyzed on a Leeman Inductively Coupled Plasma Spectrometer. Plots of the decrease in ion concentration were generated. The point at which steep concentration decreases were observed was marked as the critical pH. Once validated by replicate runs, all future work centered around this pH value as a benchmark for main pH reaction point.

### 5.2.3 - Results

Figures 5.2 through 5.5 show the critical pH data for each of the elements of interest. Figures 5.2 and 5.3 show that the critical pH values for aluminum and copper are 4.8 and 5.5 respectively. Figures 5.4 and 5.5 show that lead and zinc exhibit somewhat different behavior. The critical pH for these two elements is somewhat higher, 7.1 and 7.3. These data have been summarized in Table 5.1.

Table 5.1. Critical pH of the Studied Elements

| Element | pH |
|---|---|
| Aluminum | 4.8 |
| Copper | 5.5 |
| Lead | 7.1 |
| Zinc | 7.3 |

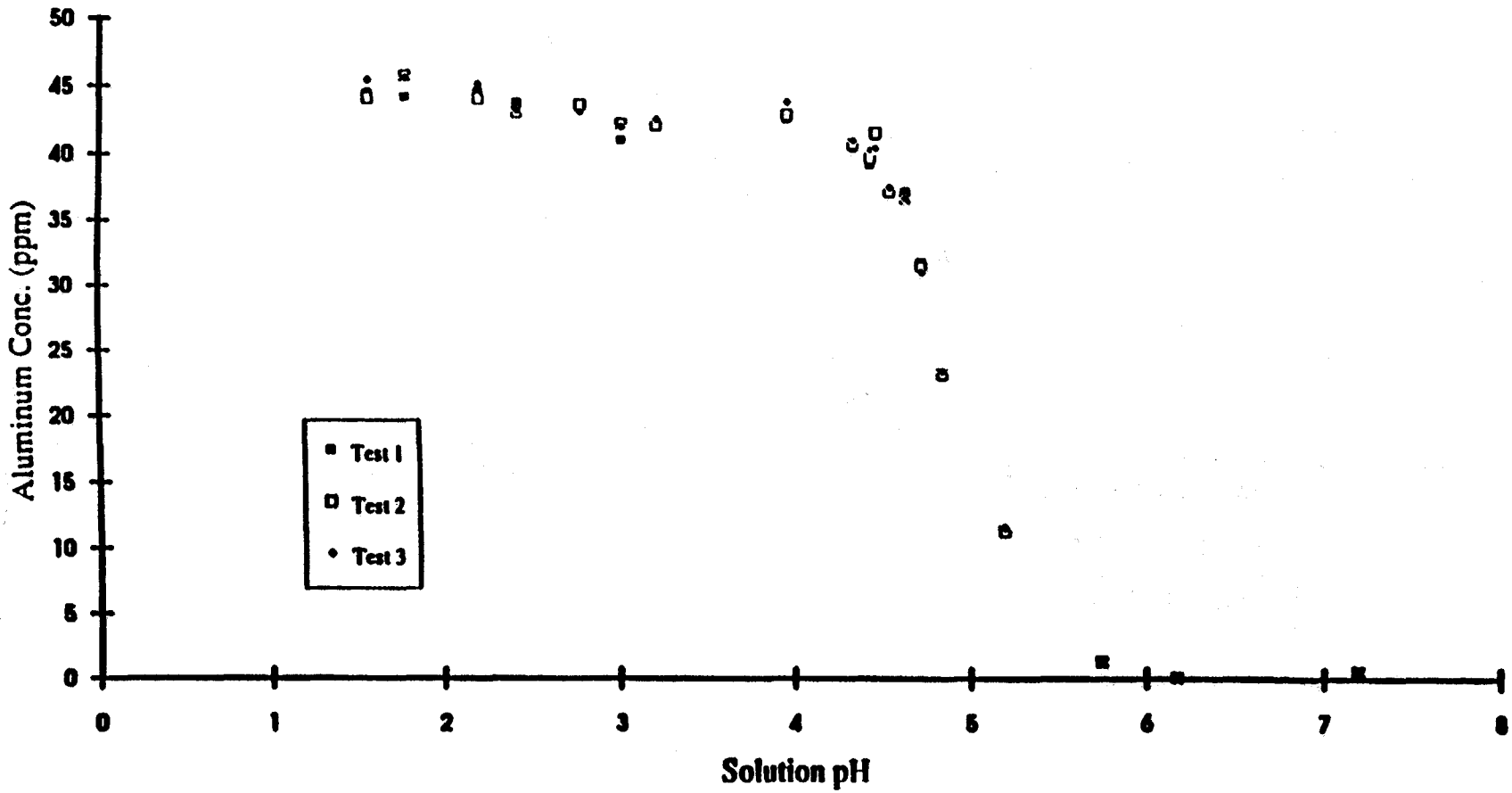


**Figure 5.2 - Critical pH of Aluminum in Brine**

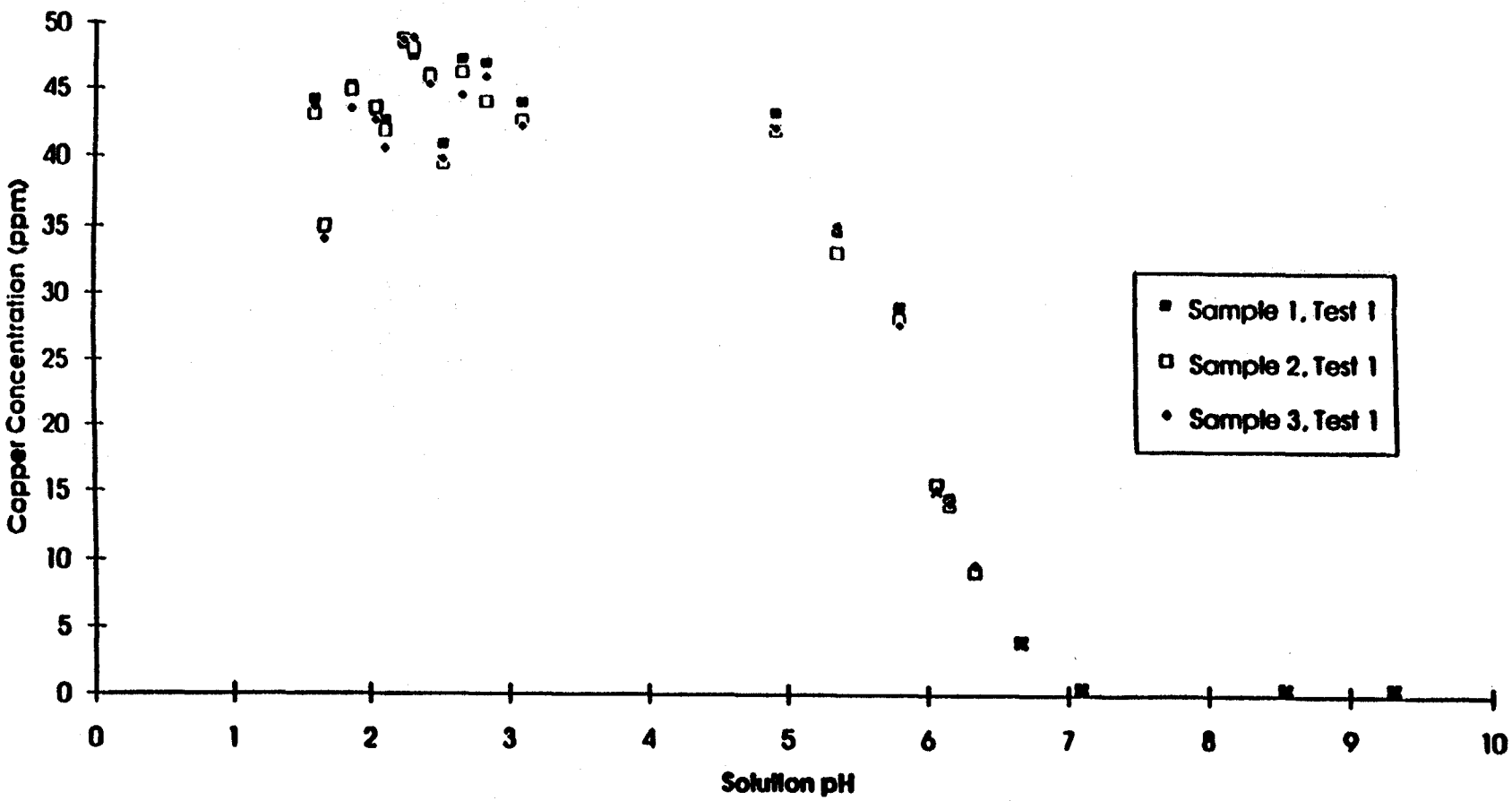


**Figure 5.3 - Critical pH of Copper in Brine**

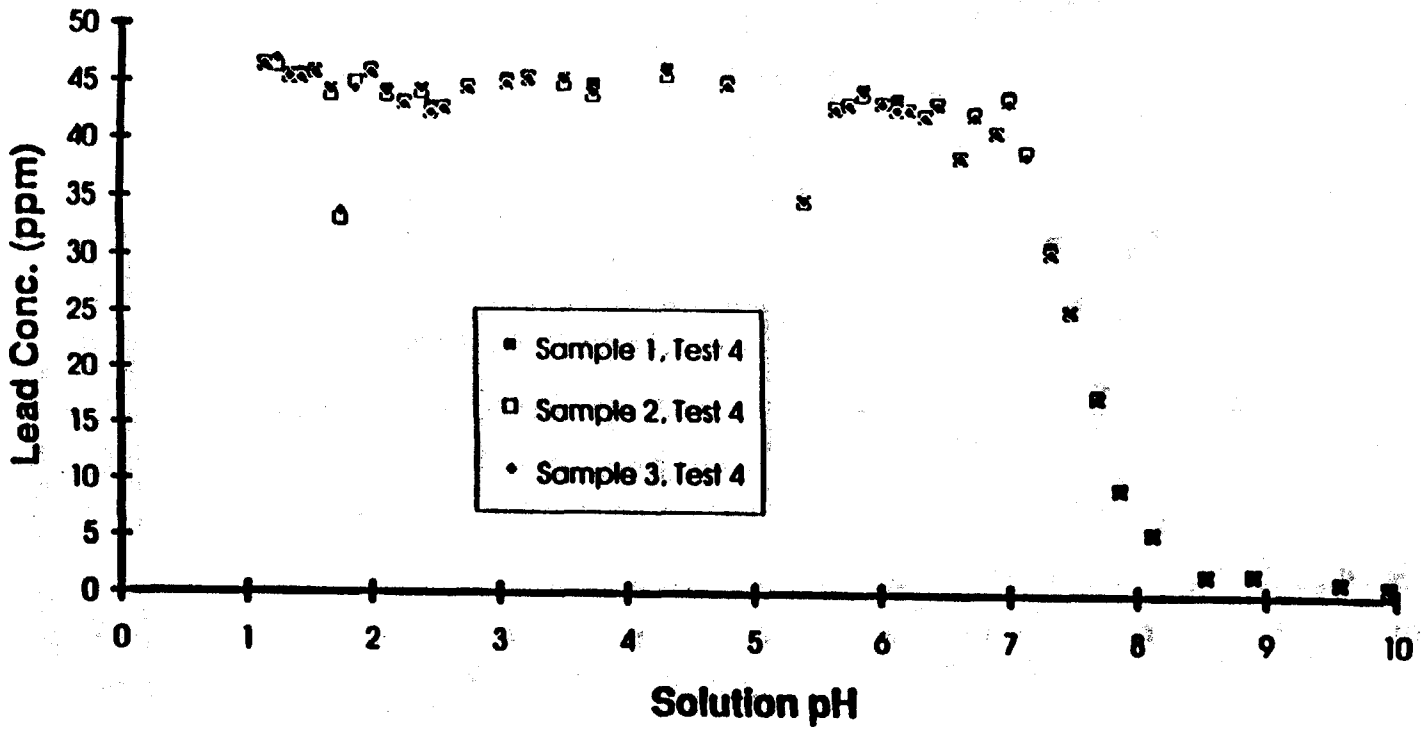


**Figure 5.4 - Critical pH of Lead in Brine**

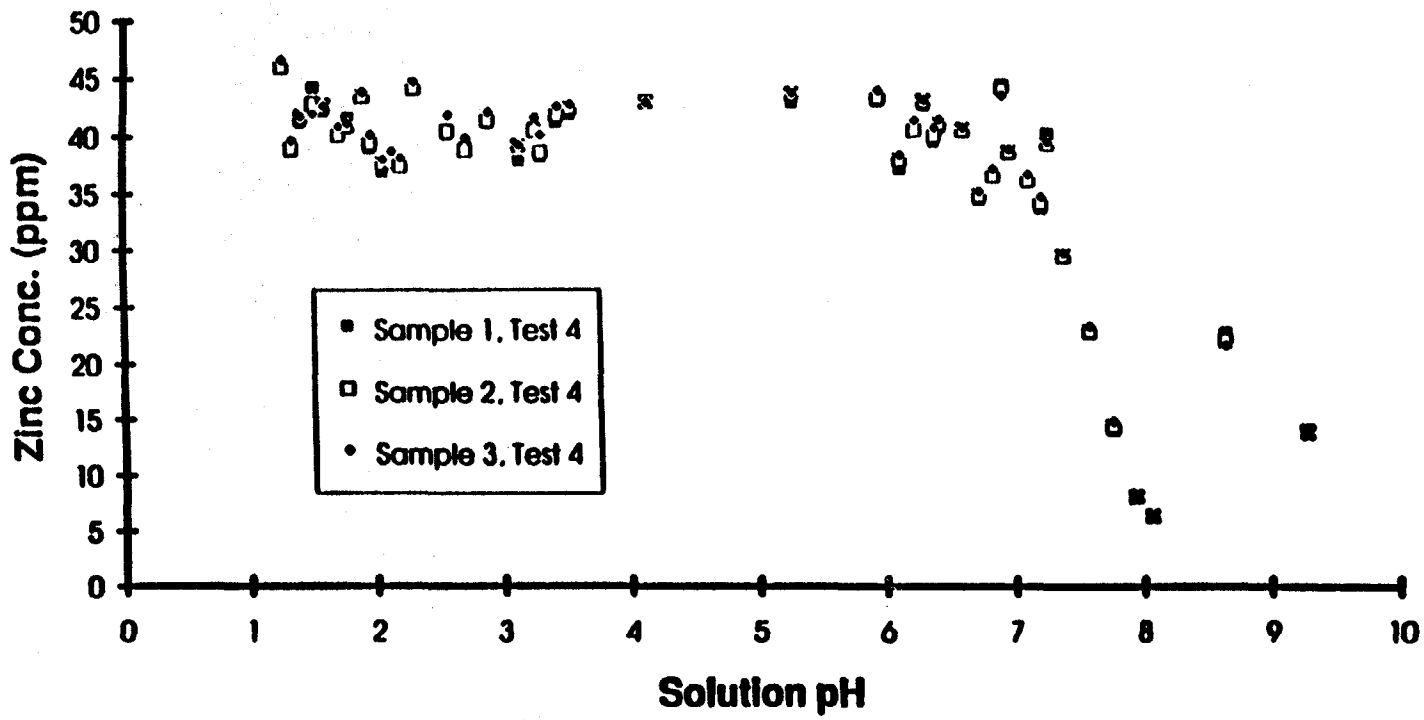


**Figure 5.5 - Critical pH of Zinc in Brine**

## 5.3 - Pseudo-Kinetic Analysis

Experimental studies of chemical reactions generally involve the determination of reaction rates as a function of several variables such as composition, temperature, pressure and/or volume. The rate of reaction can be expressed with the following formula:

$$R = -KC_A^{\alpha} \tag{5.1}$$

where:

R = Reaction rate (Concentration/time),

K = Reaction rate constant (1/time),

$C_A$ = Concentration of reacting element and,

$\alpha$ = Order of reaction.

Here the assumption is made, that equation (5.1) describes the law that governs the reaction given in equation (5.2):

$$R_A = \frac{dC_A}{dt} \tag{5.2}$$

Substituting equation (5.2) in (5.1) yields:

$$\frac{-dC_A}{dt} = KC_A^{\alpha} \tag{5.3}$$

The natural logarithm of both sides of this equation yields:

$$\ln\left[\frac{-dC_A}{dt}\right] = \ln K + \alpha \ln C_A \tag{5.4}$$

The plot of

$$\ln\left[\frac{-dC_A}{dt}\right] \text{ versus } \ln C_A$$

gives a straight line, whose slope is $\alpha$ and the intercept on the ordinate is ln K. In order to utilize this method, the value for $dC_A/dt$ was calculated from the data. The concentration in each sampling port and the residence time for each principal

component of the laboratory unit was measured. Since the laboratory prototype system was a flowing reacting system, the volume of the reacting system could be expressed as:

$$V = \frac{q}{K} \ln \frac{C_{in}}{C_{out}} \tag{5.5}$$

where:

$V$ = Volume,

$q$ = Volumetric flow rate,

$K$ = Reaction rate constant,

$C_{in}$ = Inlet concentration and,

$C_{out}$ = Outlet concentration.

K can be written as follows:

$$K = \frac{q}{V} \ln \frac{C_{in}}{C_{out}} \tag{5.6}$$

where the term $\frac{q}{V} = \tau$ = residence time.

With the measured inlet and outlet concentrations from the conducted experiments, the order of reaction and the reaction rate constants can be calculated. The inlet and outlet concentrations of the elements under investigation with a flow rate of 2 BBL/D, and initial guess values for K and $\alpha$ were inputted in a computer code. The actual $\alpha$-order value for each element under investigation was obtained after a few iterations. With the obtained values of reaction orders for the elements of interest, the reaction rate constant could be calculated with the following equation:

$$K = \frac{1}{\tau\,(1-\alpha)}\, C_{out}^{1-\alpha} - C_{in}^{1-\alpha} \quad \text{(for } \alpha\text{–order reactions not equal 1).} \tag{5.7}$$

For $\alpha = 1$, the reaction rate constant becomes:

$$K = \frac{1}{\tau} \ln C \tag{5.8}$$

The average residence time for the prototype system was 8516 seconds. In Table 5.1 the $\alpha$ and K values for the elements of interest in single-element studies are shown.

Table 5.1: Alpha and K Values for Single-Element Studies

| Element | Alpha | K |
|---|---|---|
| Fe | 1.17 | 0.000068 |
| Cu | 1.56 | 0.000040 |
| Al | 0.57 | 0.00137 |
| Zn | 0.8 | 0.000158 |
| Pb | 0.67 | 0.000287 |

For binary-element studies, the reaction rate can be written as a function of the inlet and outlet concentrations of iron and the other element of interest. With the binary elements iron and copper for example, the reaction rate of iron can be expressed as follows:

$$R_{Fe} = -\frac{d\,C_{Fe}}{dt} = K_{Fe}\,C_{Fe}^{\alpha}\,C_{Cu}^{\beta} \tag{5.9}$$

Hence, we can write:

$$-\frac{d\,C_{Fe}}{C_{Fe}^{\alpha}} = K_{Fe}\,C_{Cu}^{\beta}\,dt \tag{5.10}$$

where:

$C_{Fe}$ = concentration of iron,

$C_{Cu}$ = concentration of copper,

$\alpha$ = order of reaction with respect to iron,

$\beta$ = order of reaction with respect to copper.

We assume that the concentration of copper varies linearly with time in the system, hence the concentration of copper can be expressed as:

$$C_{Cu} = a - bt \tag{5.11}$$

We impose the constraints that at $t = 0$; $C_{Cu} = C_{Cu_{in}}$, and at $t = \tau$; $C_{Cu} = C_{Cu_{out}}$. Therefore:

$$a = C_{Cu_{in}};\ b = \frac{C_{Cu_{in}} - C_{Cu_{out}}}{\tau}$$

Substituting the expressions for a and b in Equation (5.11) yields

$$C_{Cu} = C_{Cu_{in}} - \frac{C_{Cu_{in}} - C_{Cu_{out}}}{\tau}\, t \tag{5.12}$$

It is assumed that the reaction orders from the single-element studies, hold for the binary-element studies. Equation (5.10) becomes then:

$$\text{Fe} \tag{5.13}$$

$K_{Fe}$ can be written as:

$$K_{Fe} = \frac{\int \frac{-d\, C_{Fe}}{C_{Fe}^{\alpha}}}{\int \left(C_{Cu_{in}} - \frac{C_{Cu_{in}} - C_{Cu_{out}}}{\tau}\, t\right)^{\beta} dt} \tag{5.14}$$

Applying the limits of the integration to Equation (5.14) of inlet and outlet concentrations at t=0 and t= $\tau$ respectively, $K_{Fe}$ becomes:

$$\frac{\dfrac{\dfrac{-1}{1-\alpha}\left[C_{Fe_{out}}{}^{1-\alpha} - C_{Fe_{in}}{}^{1-\alpha}\right]}{\left(C_{Cu_{in}} - \dfrac{C_{Cu_{in}} - C_{Cu_{out}}}{\tau}\right)^{\beta+1}}}{(\beta+1)\,\dfrac{C_{Cu_{in}} - C_{Cu_{out}}}{\tau}} \tag{5.15}$$

In Table 5.2 the reaction rate constant values for iron in the binary studies of iron with the other elements of interest is shown.

Table 5.2: Reaction Rate Constant Values for Iron from Binary Studies

| Binary-Elements | $K_{Fe}$ |
|---|---|
| Fe + Cu | 0.00016 |
| Fe + Al | 0.000059 |
| Fe + Zn | 0.0000119 |
| Fe + Pb | 0.000176 |

The calculated reaction rate constants for the Fe-Cu and Fe-Pb systems were higher than that of the single-element iron system. This showed that copper and lead were exercising a catalytic influence on iron removal. On the other hand, the K values for the Fe-Zn and the Fe-Al systems were lower than that of the single-element iron system. This showed that zinc and aluminum were exercising an inhibiting effect on iron removal.

# 6. Field Studies

## 6.1 - Objective

The purposes of the field experiments were:

- To test the efficacy of the treatment system with the real brines from stripper wells of different areas.
- To investigate the effects of various factors, such as weather, temperature, oil content, on brine treatment.
- To develop a comprehensive data base for validating and fine-tuning the process model.

## 6.2 - Development of the Field Model

The field prototype of brine treatment facility was located in Franklin, PA. Figure 6.1 shows the schematic representation of this field facility. The field system is basically a scale-up of the laboratory model. It includes the pH adjustment unit, aeration unit, settling unit, and filtration unit. However, besides these units in the laboratory model, an oil/brine separator is installed before the pH adjustment unit. As its name indicates, the oil/brine separator separates the oil from the brine before the treatment. It is a box with several plates inside, which are arranged in a similar way as that of the settling unit. A by-pass pipe is attached to the oil/brine separator so that the brine flow can by-pass the separator if the oil content of the brine is very low. Two sampling valves are located in each side of the separator so that the brine samples can be obtained before entering and after leaving the separator. The size of the oil/brine separator is about 3.5*2.0*2.5 cubit feet.

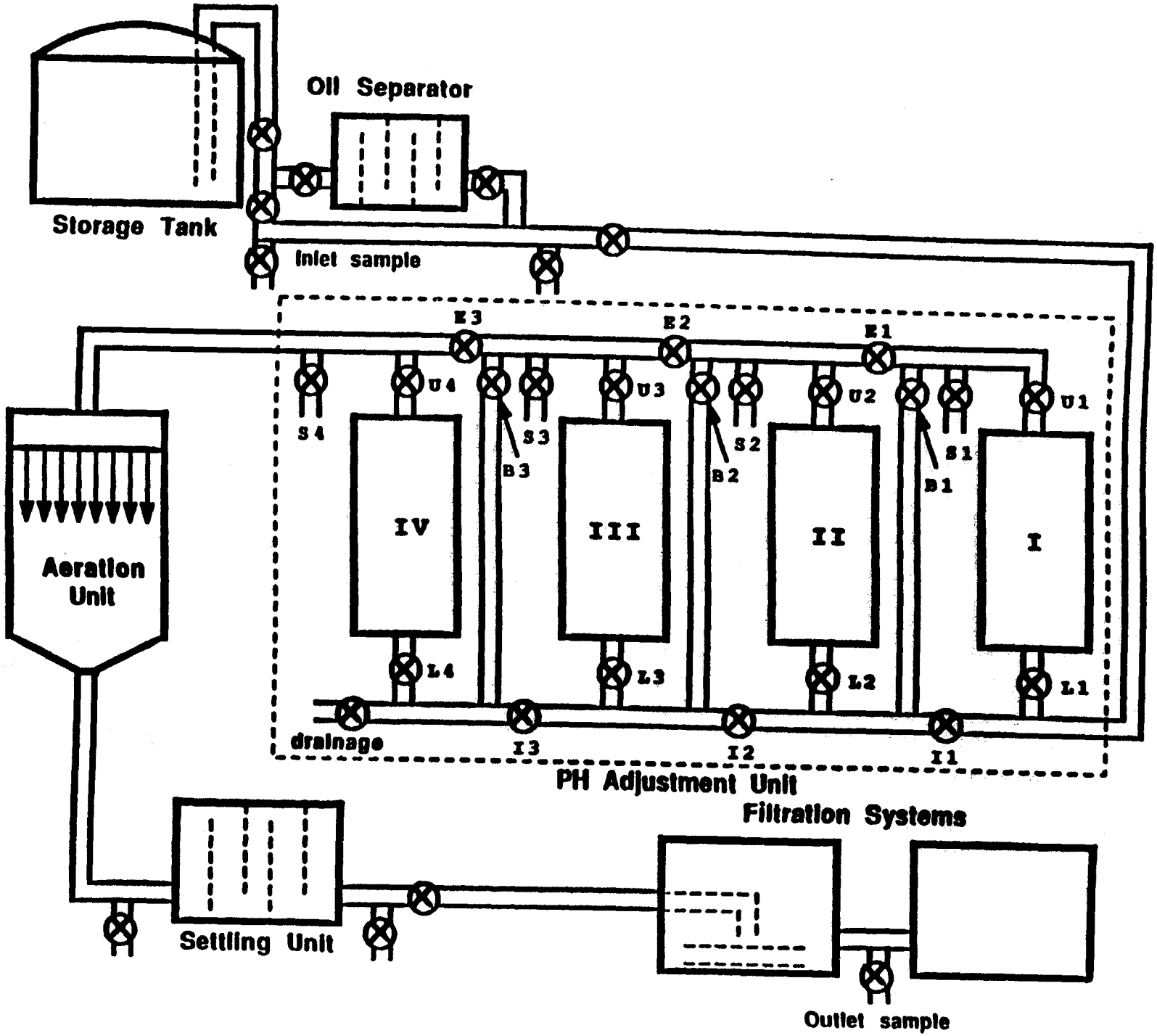


Figure 6.1. Schematic Representation of the Brine Treatment Pilot Unit

The oil/brine separator is considered to be necessary when treating brine at well site. However, during our field experiments, it was found out that this unit is not necessary for the experimental facility. This is principally because in our field experiments, the separation of oil and brine was satisfactorily accomplished in the storage tanks, thus rendering the oil-separation unit redundant. The brine coming out from the bottom of the storage tank contained such an insignificant amount of oil that we did not use the oil separation unit in most of the experiments.

The pH adjustment unit consists of four limestone columns with 26 inches in height and 7.5 inches in diameter each. All the limestone columns as well as all the units are connected by 0.5 inch plastic pipe. Several valves are installed between the columns (see Figure 6.1). These limestone columns can be operated in series or in parallel or in any combination thereof. For example, when valves L1, U1, B1, L2, U2, E2, E3 are open and all the other valves in the unit are closed, brine will flow through columns I and II in series. On the other hand, if valves L1, I1, L2, U1, U2, E1, E2, E3 are open and all the other valves are close, columns I and II will work in parallel. This provides the flexibility of determining the optimal size of the pH adjustment unit. The valve numbers begin with a "S" are sampling valves. Brine samples can be obtained at the inlet and outlet of each limestone column during experiments.

The aeration unit is another important component in this brine treatment facility. The size of the aeration unit is about 45 inches long and 22.5 inches wide. The aeration unit is designed such that its angle is adjustable (Figure 6.2). The angle of the aeration unit, together with brine flow rate, determines the thickness of brine film passing this unit, which, in turn, affects the effectiveness of the reaction between the ions in brine and the oxygen in the air. The adjustable-slope aeration

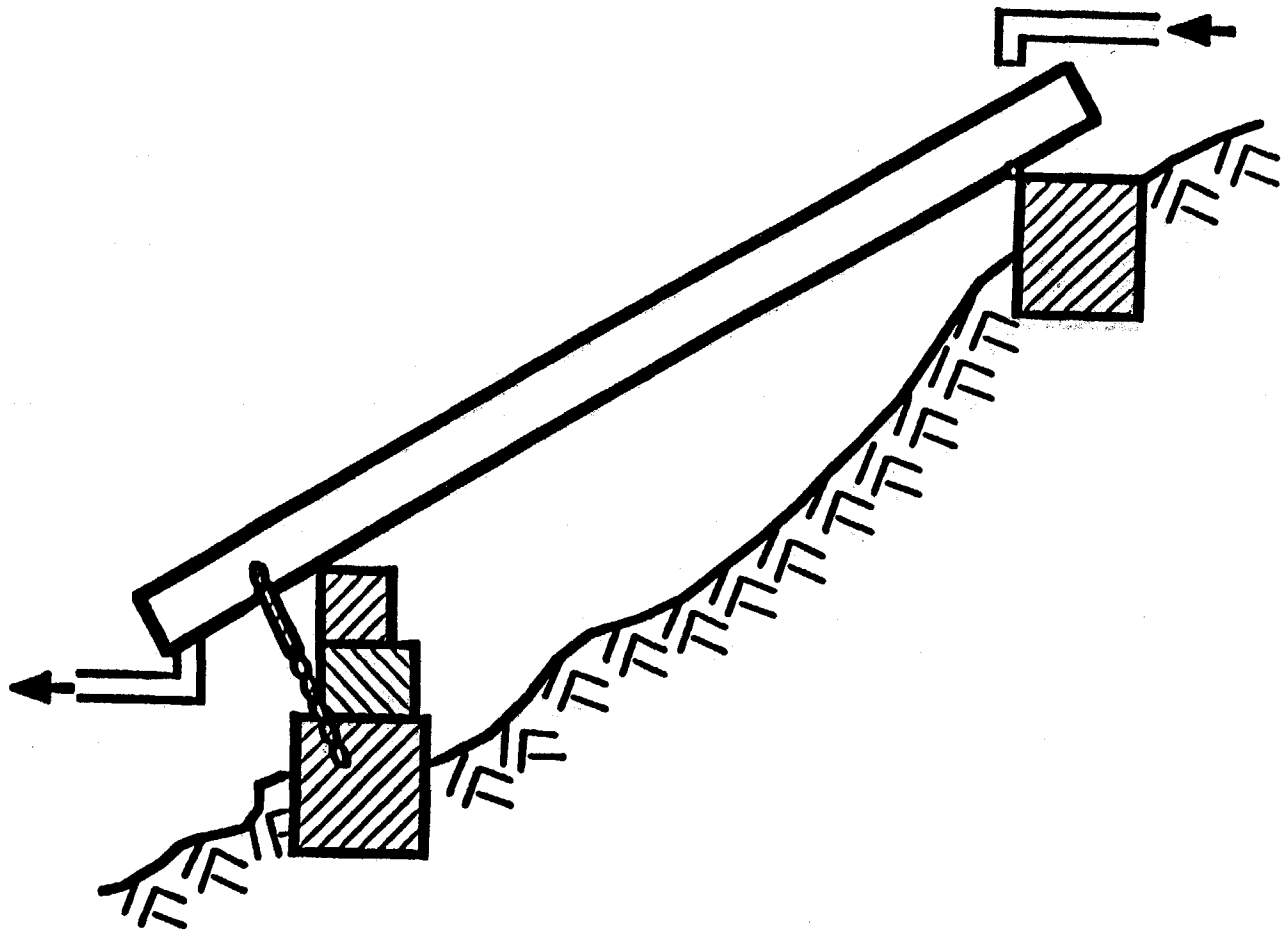

**Figure 6.2. The Adjustable-Slope Aeration Unit**

unit will help in finding the optimal design of the aeration unit.

The size of the settling unit is about the same as that of oil/brine separator unit. A sampling valve is located in the inlet as well as the outlet of the settling unit to obtain brine samples during treatment. A by-pass pipe is also built parallel to the settling unit so that the brine can either flow through the unit or by-pass it.

Two sand boxes are put side by side as the filtration unit. The reason for using two sand boxes is only for having a spare one. The dimensions of each sand box are about 3*3*3 cubit feet. The two sand boxes are connected by pipes in such a way that either of the boxes can be used individually or together. However, it was found out such arrangement is not necessary. Only one sand box was used for the entire experimental period.

## 6.3 - Experimental Procedure in the Field

Brines from stripper wells at different areas of Pennsylvania were delivered to the field test facility location, Franklin, PA by tanker. There were two 70 barrel storage tanks on the site. The storage tanks were lined with fiber-glass to mitigate any reactions between the stored brine and the steel walled tank. The storage tanks are sat several feet above the testing facility. Brine can flow from the storage tank to the testing units by gravity. However, because the flow rate by gravity could be affected by several factors such as the level of brine in the tank, and changes in the permeability of limestone in pH adjustment unit, a U21B type, magnetically coupled centrifugal pump was connected between the oil/brine separator and the pH adjustment unit. The pump can keep the brine flow as steady state as possible during a test. The desired brine flow rate was controlled by partially open the valve located after the pump.

During a test, the brine to be treated flows from storage tank to pH adjustment unit through or by pass the oil/brine separator depending on the oil/grease content of the brine. The valves in the pH adjustment unit are adjusted so that the brine passes the desired number of limestone columns. After passing through the pH adjustment unit, the affluent flows to the aeration unit. Aeration of the brine is achieved by distributing the flowing brine uniformly over this unit. The velocity and the thickness of brine film over the aeration unit are controlled by changing the slope of the unit. After aeration, the brine passes to the filtration unit either through the settling unit or by pass it. The brine treatment is accomplished when the brine is discharged from the filtration unit. Brine samples are taken every hour during each test at all the sample valves located before and after each unit. The weather condition, the temperature, the brine flow rate, the number of limestone columns used, the angle of the aeration unit are recorded. The pH value of the brine are measured at the site using a HACH pH meter, while the brine samples taken from the sampling valves are shipped back to Penn State's university park campus for analysis.

## 6.4 - Discussion of the Results from Field Experiments

Extensive experiments have been conducted on the field pilot model. Five brines collected from the Western and Central part of Pennsylvania have been tested at various conditions. The five brines have different metal concentrations. Tables 6.1 through 6.5 show the average concentration of the metals in each brine. It can be observed from the tables that iron, magnesium and Strontium are the major elements and have relatively high concentrations in these brines. The average iron concentrations in all the five brines range from 8 ppm to 50 ppm.

Table 6.1. Red Valley Brine

| | |
|---|---|
| Fe 40 ppm | Ni 3.0 ppm |
| V < 1 ppm | Cr 1.0 ppm |
| Cu < 1 ppm | Mn 4.0 ppm |
| Zn < 1 ppm | |

Table 6.2. Warren Brine

| | | |
|---|---|---|
| Fe 50 ppm | Ni < 0.5 ppm | Cu < 0.5 ppm |
| Se < 1.0 ppm | Cr < 0.5 ppm | Zn < 0.5 ppm |
| Al 2.5 ppm | Pb < 0.5 ppm | As 1.0 ppm |
| Mn 6.0 ppm | V 2.5 ppm | Be < 0.5 ppm |
| Cd < 0.5 ppm | Co < 0.5 ppm | Hg < 0.5 ppm |

Table 6.3. Cooper Brine

| | | |
|---|---|---|
| Fe 13 ppm | Al 1.7 ppm | Ba < 0.5 ppm |
| Sr 12 ppm | As < 0.5 ppm | Be < 0.5 ppm |
| Cu < 0.5 ppm | Pb < 0.5 ppm | Ni < 0.5 ppm |
| Mg 190 ppm | Mn 1.5 ppm | Se < 0.5 ppm |
| Cd < 0.5 ppm | Cr < 0.5 ppm | V < 0.5 ppm |
| Zn < 0.5 ppm | Co < 0.5 ppm | Hg < 0.5 ppm |

Table 6.4. Kine Brine

| | | |
|---|---|---|
| Fe 8.0 ppm | Al 1.3 ppm | Ba 3.5 ppm |
| Sr 19 ppm | As < 0.5 ppm | Be < 0.5 ppm |
| Cu < 0.5 ppm | Pb < 0.5 ppm | Ni < 0.5 ppm |
| Mg 160 ppm | Mn 1.0 ppm | Cd < 0.5 ppm |
| Cr < 0.5 ppm | Zn < 0.5 ppm | |

Table 6.5. Bradford Brine

| | | |
|---|---|---|
| Fe 11 ppm | Al 2.1 ppm | Ba 1.2 ppm |
| Sr 15 ppm | As < 0.5 ppm | Be < 0.5 ppm |
| Cu < 0.5 ppm | Pb < 0.5 ppm | Ni < 0.5 ppm |
| Mg 250 ppm | Mn 1.5 ppm | Cd < 0.5 ppm |
| Cr < 0.5 ppm | Zn < 0.5 ppm | |

The concentrations of Magnesium and Strontium in the Red Valley brine and Warren brine were not measured, while the concentrations in the other three brines are between 150 ppm and 250 ppm for Magnesium and about 15 ppm for Strontium. While the experimental results show that the removal of iron from the brine by the field facility is very efficient, the removal of Magnesium and Strontium is not very significant. This is probably due to the high critical pH values of Magnesium and Strontium. More work is underway to find an effective way to remove Magnesium and Strontium from brine.

The concentrations of all the other metals are very low. Because of the accuracy of metal analysis, any metal with a concentration below 0.5 ppm could be considered as non-exist. Due to the already low concentrations of these metals in the original brines, no conclusion can be made on the efficiency of removal of these metals by the treatment at this time. However, this work will be continuing through the sponsor of DOE. More field brines will be tested with the field process model. Additional data are needed in order to find the efficiency on removal of these metals from brine.

The field experiments were conducted around the year and under various weather conditions. The temperature under which the brines were treated is between 25° and 86° F. Efforts of treating the brine at a temperature below 25° were failed because of the freeze of brine when passing through the aeration unit. Initially, the capacity of this field pilot model was designed for treating brine at a rate of 1 bbl/D. However, in order to determine its effects on the efficiency of the treatment, the flow rate being tested was up to 16.5 bbl/D.

Figure 6.3 presents the typical results of the field experiments. The curves in the figure show how the concentration of total iron changes from one unit of the

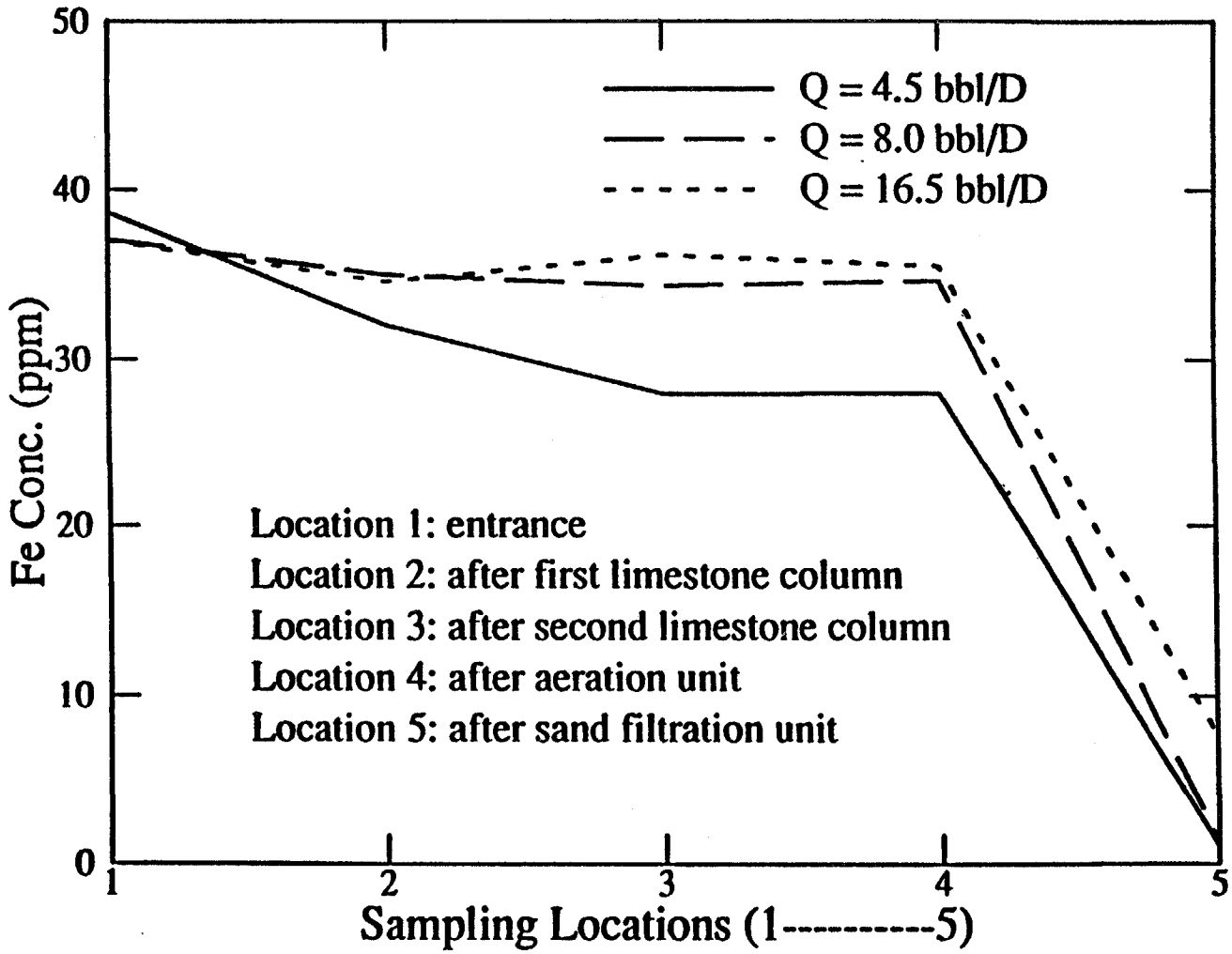


Figure 6.3. Iron Concentration at Different Sampling Locations (field unit)

model to the next one at three different flow rates. It can be observed that after the oxidation reaction at the aeration unit, most of the precipitated iron in the brine is then removed in the sand filtration unit (the last sampling point). With an average inlet iron concentration of 37.5 ppm, the outlet concentration is reduced to about 2 ppm under the flow rates of 4.5 and 8.0 bbl/D. However, at the flow rate of 16.5 bbl/D, the outlet concentration is about 8 ppm. This is expected since an increase in flow rate means an increase of the thickness of brine film through the aeration unit, which implies that the effective contact between brine and oxygen is reduced.

Table 6.6 shows the iron removal of brine treatment as a function of time. The results of three runs are shown in the table. These tests run continuously up to six hours. The iron concentration in the original brine is 20-30 ppm. After the treatment by the field unit, the concentrations of iron are reduced below 2.5 ppm.

Table 6.6. Fe Ion Concentration in Brine Before and After Treatment

| | **Fe Ion Concentration (ppm)** | | | | | | |
|---|---|---|---|---|---|---|---|
| Run No. | Source Brine Sample | Brine After Treatment at Various Time Intervals | | | | | |
| | | 1 hr | 2 hrs | 3 hrs | 4 hrs | 5 hrs | 6 hrs |
| I | 22.92 | 2.52 | 2.30 | 2.16 | 1.99 | 1.92 | 1.82 |
| II | 20.28 | 0.65 | 0.65 | 0.70 | 0.81 | 0.92 | N/A |
| III | 29.04 | 0.70 | 0.82 | 0.95 | 1.15 | 1.56 | 1.75 |

If all the parameters are kept constant, the iron removal from the brine usually are quite stable and the iron concentration of the brine after the treatment would only fluctuate slightly. However, some times, the temperature in the field could change significantly during a day. In such case, even all the other parameters, such as brine flow rate, number of limestone column, and angle of aeration unit kept constant, the brine concentration after the treatment would be affected by the temperature.

## 6.5 - Effect of Limestone Columns

Table 6.7 summarize the effects of brine flow rate and the number of limestone columns on the treatment efficiency for Red Valley brine. During these runs, one, two, three, or four limestone columns were used to test the effect of limestone columns on brine treatment efficiency at different flow rate. The data in the table show that the number of limestone columns has insignificant effect on the brine treatment. With the same flow rate, using more limestone columns does not help to increase the efficiency of the treatment. It indicates that one column of limestone is sufficient for the process.

Table 6.7. Experimental Results of Brine Treatment Pilot Unit

| Flow Rate (bbl/d) | Number of Limestone Column | Fe Ion Concentration (ppm) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Source Brine | Brine After Treatment | Source Brine | Brine After Treatment | Source Brine | Brine After Treatment |
| 4.5 | 2 | 49.23 | 1.60 | 40.33 | 1.37 | 38.67 | 1.01 |
| | 4 | 32.30 | 2.06 | 32.19 | 2.17 | 36.16 | 2.00 |
| 8.0 | 2 | 35.54 | 1.31 | 37.07 | 1.27 | 35.39 | 1.43 |
| | 4 | 34.29 | 1.20 | 35.50 | 1.89 | 31.11 | 2.55 |
| 11.8 | 1 | 31.85 | 2.31 | 28.47 | 2.47 | 28.76 | 2.53 |
| | 3 | 29.76 | 0.95 | 34.02 | 2.04 | 34.95 | 1.95 |
| 16.5 | 1 | 35.11 | 8.29 | | | | |
| | 2 | 35.20 | 7.00 | 36.98 | 7.71 | 34.37 | 8.02 |
| | 4 | 39.42 | 7.38 | 41.14 | 7.65 | | |

The effect of the number of limestone columns was also studied in continuously running tests. Figure 6.4 shows the experimental results designed for this purpose. There are three curves in the figure, each representing one continues test. The brine tested in these runs is from Warren County. Each test started at noon and

ended at early evening, so that the changes of ambient temperature was in a very small range. During each test, all the other parameters were kept constant except the number of limestone columns. From these results, one can observe that one column of limestone is sufficient for the process. Using more columns does not significantly improve the efficiency of the brine treatment. The reason that using more columns does not significantly improve the efficiency of the brine treatment is probably due to the fact that the pH values of the tested brines are relatively high. Table 6.8 shows the pH values of the five brines tested with the field treatment facility.

Table 6.8. Typical pH Values in the Field Unit

| | **pH Value at Various Sampling Locations** | | | | | | |
|---|---|---|---|---|---|---|---|
| Brine | Inlet | After Each Limestone Column | | | | After Aeration | After Filtration |
| | | 1st | 2nd | 3rd | 4th | | |
| Red Valley | 5.96 | 6.10 | 6.12 | 6.17 | 6.20 | 6.22 | 5.99 |
| Warren County | 5.86 | 6.00 | 6.04 | - | - | 6.08 | 5.66 |
| Cooper | 7.12 | 7.09 | 7.07 | 7.08 | 7.07 | 7.19 | 6.89 |
| Kine | 7.06 | 7.16 | - | - | - | 7.28 | 7.18 |
| Bradford Sand | 6.76 | 6.83 | 6.82 | 6.85 | 6.89 | 6.95 | 6.82 |

From the table it can be observed that the pH values of these brines are between 5.86 and 7.12. The limestone columns did not rise the pH value significantly. Therefore, it is understandable that these columns have little effect on the brine treatment. However, based on the laboratory experiments, limestone columns are able to rise the pH value of brine up to 6.0 from a low value ($1 < pH < 2$).

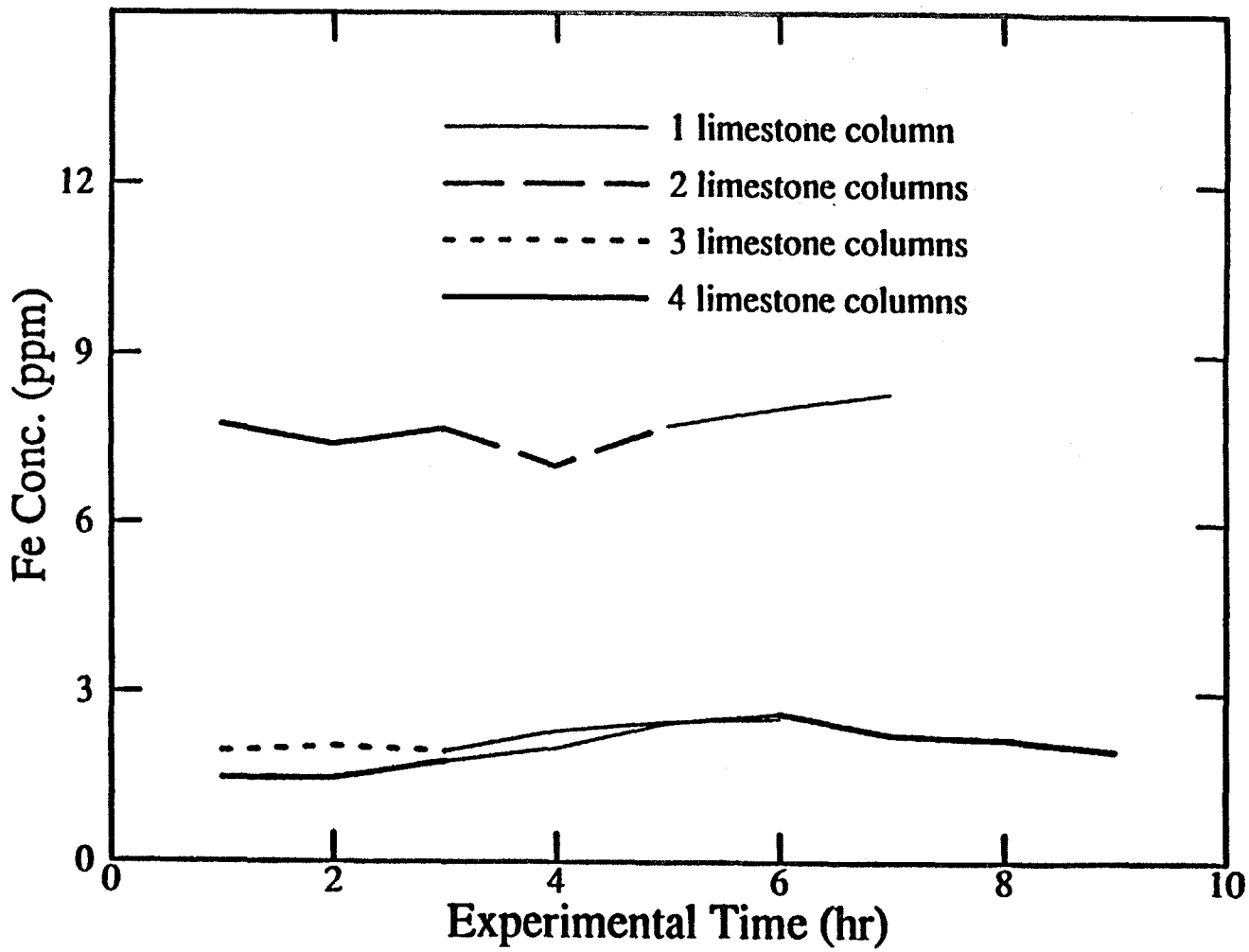


**Figure 6.4. Effect of Limestone Column on Brine Treatment (field unit)**

## 6.6 - Effect of Brine Flow Rate

The effect of brine flow rate is expectable even without conducting any experiment. The key in this process is the thin film created over the aeration unit. With a fixed size of aeration unit, the thickness of brine film over the aeration unit will increase as the flow rate increases. The contact between oxygen in the air and the Fe ion in the brine will be deteriorated with a thicker film; hence the efficiency of the treatment will be reduced. As mentioned earlier, initially, the capacity of this field pilot model was considered for treating brine at a rate of 1 bbl/D. However, in order to determine the optimal design parameters for the treatment, several flow rates were tested with the field treatment facility.

Table 6.7 summarize the effects of brine flow rate on the treatment efficiency for Red Valley brine. The data in the table show that when brine flow rate is below 11.8 bbl/D, it does not have much effect on the iron removal. However, at a flow rate of 16.5 bbl/D, the efficiency of the treatment is reduced. This probably indicates that the thickness of the brine film under a brine flow rate of 11.8 bbl/day can still provide enough contact between the air and brine for Warren County brine. In other words, the field facility can treat Warren County brine for up to 11.8 bbl/day. However, the capacity of a brine treatment facility varies for different brines.

Figure 6.5 shows the effects of flow rate and temperature on brine treatment for brine from Warren County. As expected, the efficiency of brine treatment decreases as the flow rate increases at the same range of temperature. However, it can be observed from the figure that at a higher temperature range, the effect of flow rate on the iron removal is less than that at lower temperature range. This could be due to the fact that at high temperature, the reaction between iron and

oxygen is carried out much faster. Therefore, the effect of thickness of brine film on oxidation reaction is relatively small. On the other hand, at low temperature, the oxidation reaction is slowed down even at low flow rate. Any reduction of the contact between air and brine would reduce the efficiency of the reaction significantly.

The average concentrations of iron in Cooper brine and Bradford Sand brine are about 13 ppm and 11 ppm respectively. Compared with the Red Valley brine and Warren County brine, these concentrations are relatively low. Although the experimental results from these two brines further confirm the conclusions as discussed above, the effect of flow rate on the brine treatment is not so significant in these two brines. Tables 6.8 and 6.9 summarize the test results for Cooper brine and Bradford Sand brine. As the data in the tables show, at the same range of temperature, the efficiency of iron removal slightly decreases as flow rate increases. However, because of the low iron concentration in the original brines, the iron concentration after the treatment is reduced below 3 ppm under all the conditions tested.

Table 6.9. Effect of Temperature and Flow Rate on Brine Treatment
(Iron Concentration After Treatment, ppm, Cooper Brine)

| **Temperature F** | **Flow Rate (bbl/d)** | | | |
|---|---|---|---|---|
| | 4.5 | 8.0 | 12.0 | 16.5 |
| 32 - 50 | 0.3 - 0.9 | 0.8 - 2.0 | 1.4 - 2.5 | 2.0 - 3.0 |
| 50 - 55 | 0.3 - 0.4 | 0.4 - 0.7 | 0.7 - 0.9 | 1.0 - 1.7 |

The effect of flow rate on brine treatment were also investigated for Kane brine. However, because of the low iron concentration in the original brine, no effect of flow rate can be observed within the flow rates tested (4.5 bbl/day - 16.5 bbl/day).

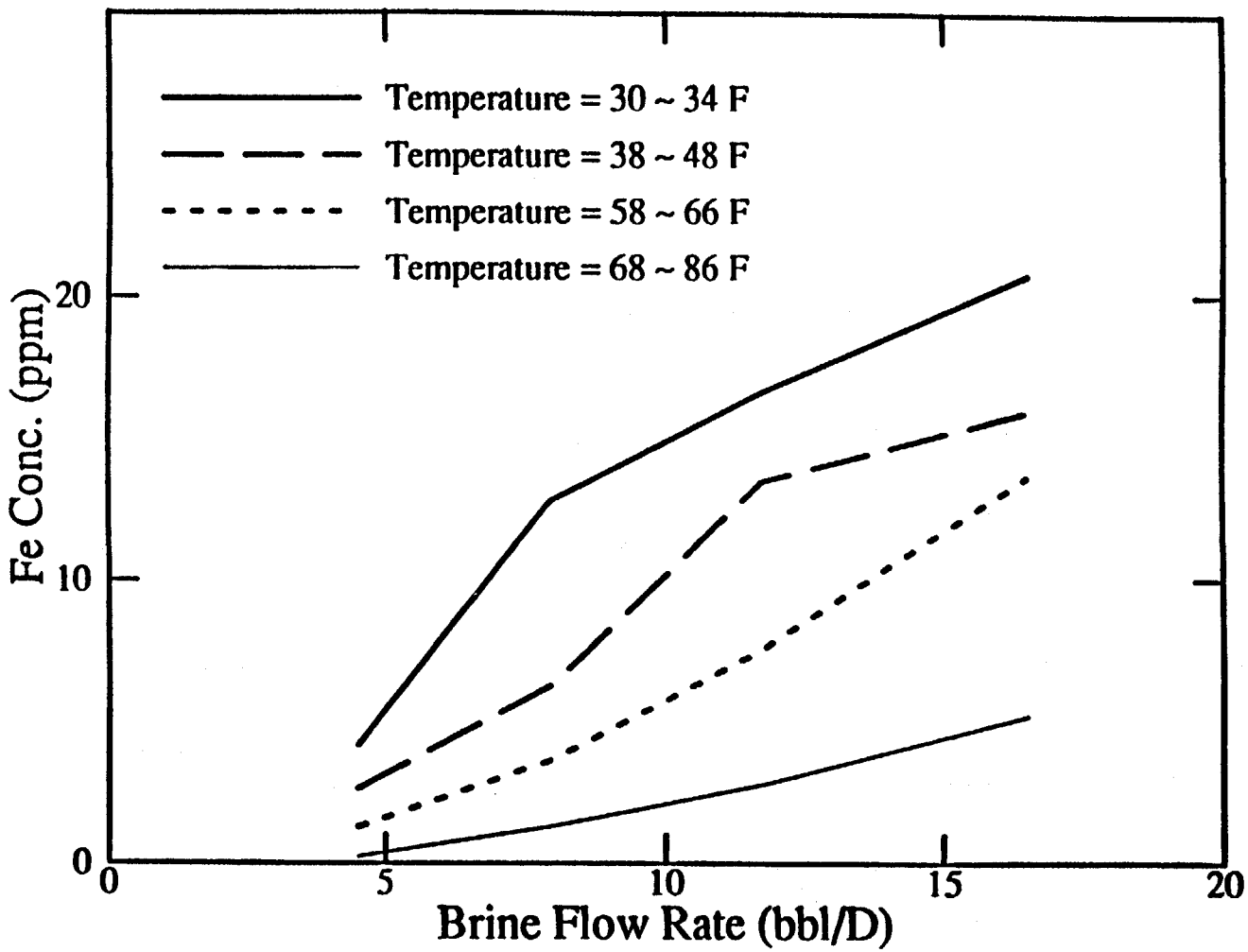


**Figure 6.5. Effect of Flow Rate & Temperature on Brine Treatment (Warren County Brine)**

Table 6.10. Effect of Flow Rate on Iron Removal from Brine
(Bradford Sand Brine)

| Iron Concentration Before and After Treatment | Flow Rate (bbl/d) | | | |
|---|---|---|---|---|
| | 4.5 | 8.0 | 11.8 | 16.5 |
| Inlet Concentration (ppm) | 11.23 | 11.41 | 12.45 | 11.79 |
| Outlet Concentration (ppm) | 0.27 | 0.66 | 0.92 | 1.68 |

## 6.7 - Effect of Temperature

The field experiments of brine treatment were conducted around the year with various weather conditions. From the test results, it seems that no effect on brine treatment would be caused by sunny or cloudy conditions. However, the results show that the temperature does have significant effect on the treatment efficiency, with high temperature helping to increase the efficiency.

Figure 6.5 shows the effects of temperature on brine treatment for Warren County brine. At low flow rate (less than 5 bbl/D), the effect of temperature on the efficiency of brine treatment is small, even through one can observe that high temperature help to remove more iron from the brine. At high flow rate, the effect of temperature is more significant. As expected, the efficiency of brine treatment improves at high temperature.

The average concentrations of iron in Cooper brine is about 13 ppm. Because of the relatively low iron concentration, the effect of the temperature on the brine treatment is not so significant. Table 6.8 summarizes the test results for Cooper brine. Again, it shows that at higher temperature, more iron can be removed with the same flow rate. While the data in Table 6.8 are the statistical results from more than 150 samples taken from the field experiments, Figure 6.6 shows a specific example demonstrating the effect of temperature. The experiment started at noon

and ended at 9:00 PM. The temperature changed from during the test. The curve in Figure 6.6 shows that iron concentration after the treatment increases as the temperature continuously decreases with time. This is an example of the effect of a wide temperature change during one continuous run. For most tests conducted in the field, the temperature did not change as dramatically during the same run, and the efficiency of the treatment is quite stable within one run.

Experiments with Red Valley brine were conducted between November 11, 1991 and March 25, 1992. However, due to the very cold weather, the sand boxes of the filtration unit were frozen most of the time during that period. The results of the experiments conducted while the sand box was frozen are not stable and therefore, are not included in the report. The data shown in Table 6.7 are from the experiments conducted at temperatures around $10^{o}$ F. No effect of temperature can be concluded because of the small temperature variation during these tests. Due to the same reason, no conclusion on the effect of temperature can be made with Bradford Sand brine, which was tested between April 7, 1993 and May 20, 1993.

As for the Kane brine, because of its low iron concentration, the effect of temperature is not so obvious either. The experimental results show that at a temperature above $32^{o}$ F and a flow rate between 4.5 and 16.5 bbl/day, the iron concentration after the treatment is reduced below 0.5 ppm, which means practically all the iron has been removed by the treatment. The only exception to this was a test conducted when temperature dropped below $32^{o}$ F at a flow rate of 12 bbl/day. In this case, the average iron concentration after the treatment is 0.94 ppm.

## 6.8 - Effect of the Angle of Aeration Unit

The effect of the angle of the aeration unit is also investigated. At a constant flow rate, increasing the angle will reduce the thickness of the brine film passing

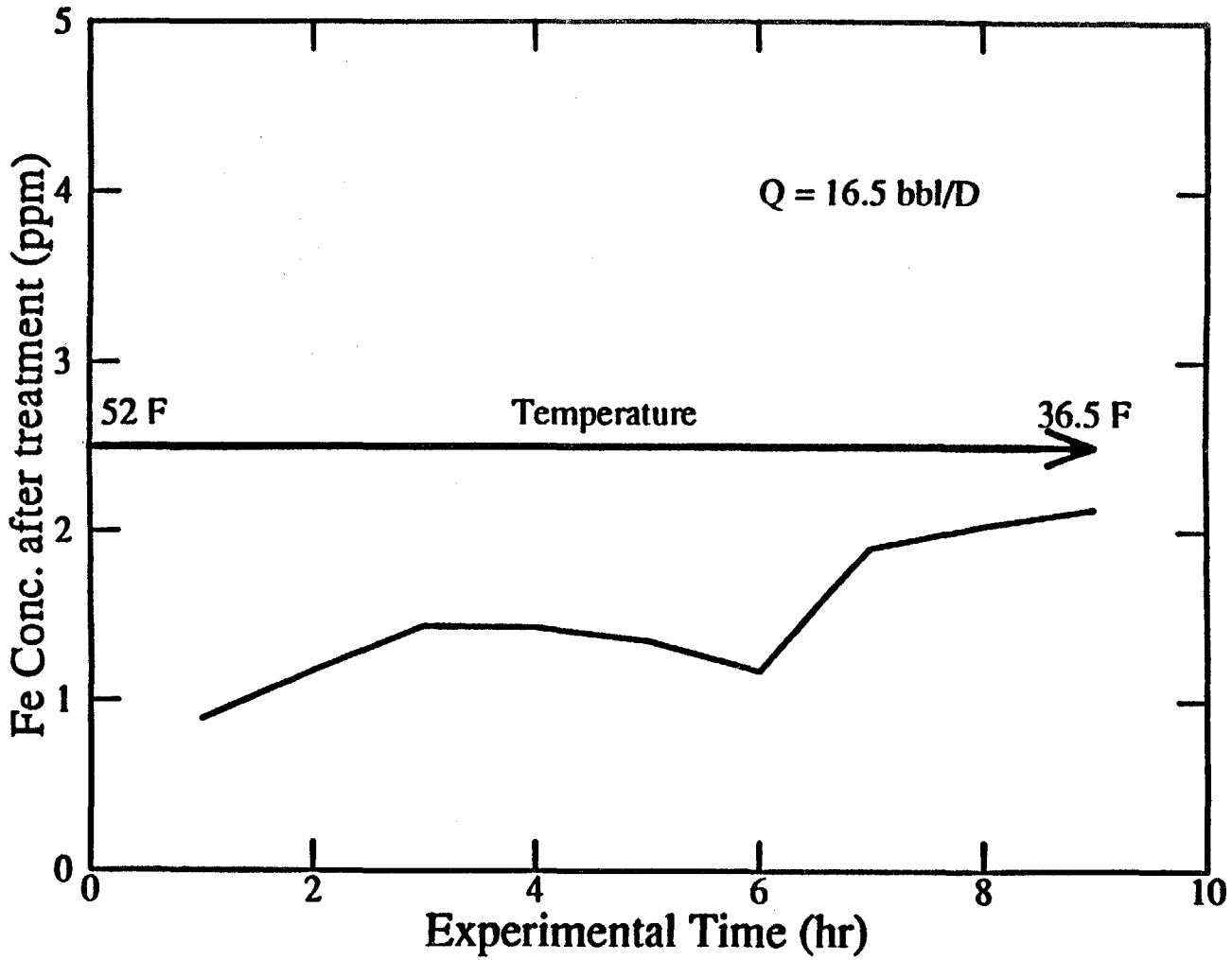


Figure 6.6. Effect of Temperature on Brine Treatment (field unit)

through the aeration unit. However, at the same time, it will also reduce the residence time of the brine in the aeration unit. The effect of the angle of aeration unit could be either way. The aeration unit of the field pilot model was designed with adjustable angle. The angle can be adjusted by adding or taking away the wood block under the unit. Two angles, were tested. The experimental results with the change of the angle are shown in Figure 6.7. Two tests were conducted, one with a flow rate of 16.5 bbl/day and the other with a flow rate of 8.0 bbl/day. Each of the test run up to 8 hours and the angle of aeration unit was changed at the fourth hour without stopping the test. The results show that the effect of the angle of aeration unit on the treatment efficiency is not significant, even though slightly better results were obtained with the smaller angle.

## 6.9 - Analysis for Organics

Organics analyses were conducted for Cooper brine, Kane brine and Bradford Sand brine. The results from the organics analysis show that the brine treatment process can also remove a good percentage of various organics from brine. Tables 6.10 and 6.11 show the typical results for organics removal from brine. A confirmation of the organics analysis is shown in Table 6.12, and two raw chromatograms are given in Figures 6.8 and 6.9. The analysis of organics involves complex procedures. Even though the results obtained so far show good promise of organics removal from brine, more study is needed to qualitatively make any conclusion. The study will be continuing under the research project sponsored by DER.

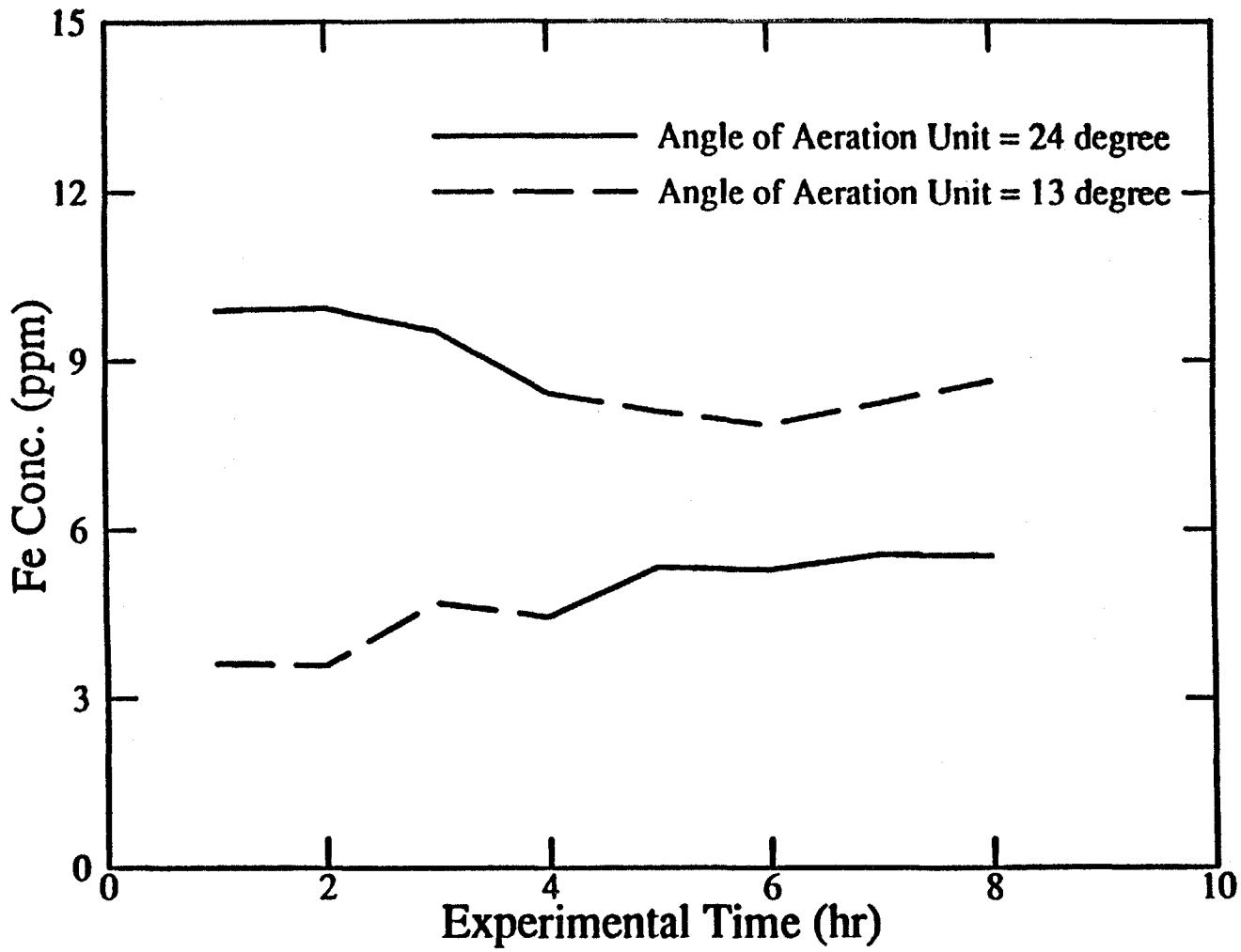


Figure 6.7. Effect of the Angle of Aeration Unit on Brine Treatment (field unit)

Table 6.11. GC/MS Analysis of Organics

| Compound Name | Inlet Sample | Outlet Sample | Percentage Removed |
|---|---|---|---|
| 2-pentanol, 2-methyl | 475 | 87 | 82 |
| 3-pentanol, 3-methyl- | 388 | 161 | 59 |
| toluene | 845 | 209 | 75 |
| 2-hexanone | 206 | 66 | 68 |
| 2-hexanol, 2-methyl- | 560 | 184 | 67 |
| 3-pentanol, 2,3-dimethyl- | 320 | 124 | 61 |
| benzene, dimethyl- | 817 | 133 | 84 |
| hexanol, dimethyl- | 423 | 93 | 78 |
| heptane, 4-methyl | 1577 | 647 | 59 |
| ninane, branch | 505 | 157 | 69 |
| octane, 4-methyl | 590 | 234 | 60 |
| Total | 6949 | 2175 | 69 |

Table 6.12. GC/MS Analysis of Organics for Kane Brine

| Compound Name | Inlet Sample | Outlet Sample | Percentage Removed |
|---|---|---|---|
| Toluene | 505 | 281 | 44 |
| Xylene | 380 | 281 | 39 |
| Octane, branch | 407 | 595 | ? |
| n-$c_{12}$ | 266 | 0 | 100 |
| n-$c_{13}$ | 445 | 0 | 100 |
| n-$c_{14}$ | 818 | 98 | 88 |
| n-$c_{15}$ | 1270 | 0 | 100 |
| n-$c_{16}$ | 1782 | 0 | 100 |
| n-$c_{17}$ | 1680 | 0 | 100 |
| n-$c_{18}$ | 1597 | 0 | 100 |
| n-$c_{19}$ | 1251 | 0 | 100 |
| n-$c_{20}$ | 972 | 0 | 100 |
| n-$c_{21}$ | 544 | 0 | 100 |
| n-$c_{22}$ | 282 | 0 | 100 |
| Total | 12199 | 1205 | 90 |

Table 6.13. GC/MS Analysis of Organics

| Compound Name | MS Area (Inlet) | GC Area (Inlet) | MS Area (Outlet) |
|---|---|---|---|
| 2-pentanol, 2-methyl | 475 | | 87 |
| 3-pentanol, 3-methyl- | 388 | | 161 |
| toluene | 845 | 343 | 209 |
| 2-hexanol, 2-methyl- | 560 | 231 | 184 |
| 3-pentanol, 2,3-dimethyl- | 320 | 131 | 124 |
| benzene, dimethyl- | 817 | 336 | 133 |
| hexanol, dimethyl- | 423 | 199 | 93 |
| heptane, 4-methyl | 1577 | 615 | 647 |
| nonane, branch | 505 | 197 | 157 |
| nonane, branch | 243 | 80 | 96 |
| octane, 4-methyl | 590 | 134 | 234 |
| Total | 6743 | 2282 | 2109 |

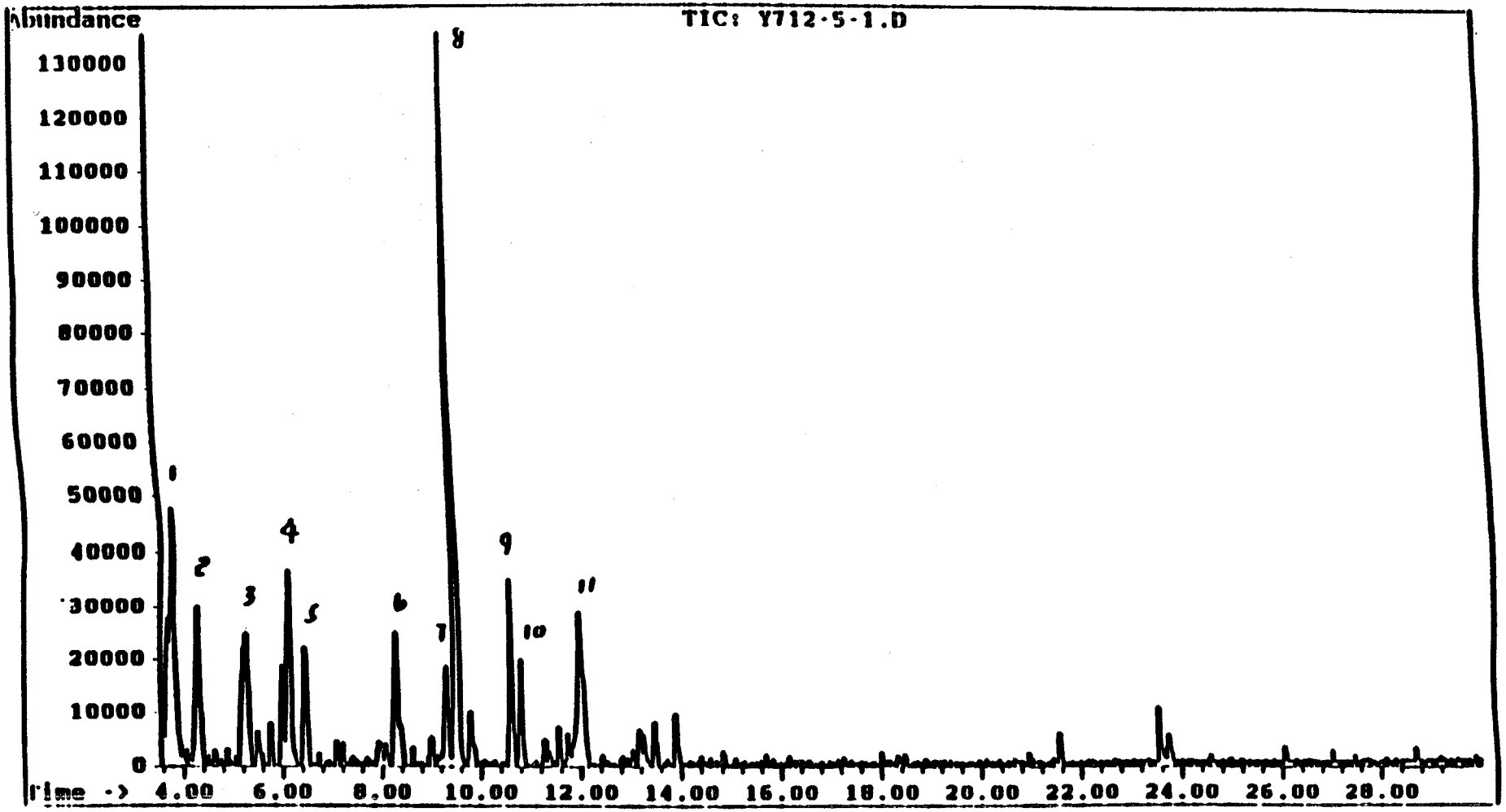


Figure 6.8. Chromatogram of Organic Analysis (using methylene chloroform extraction and GC/MS)

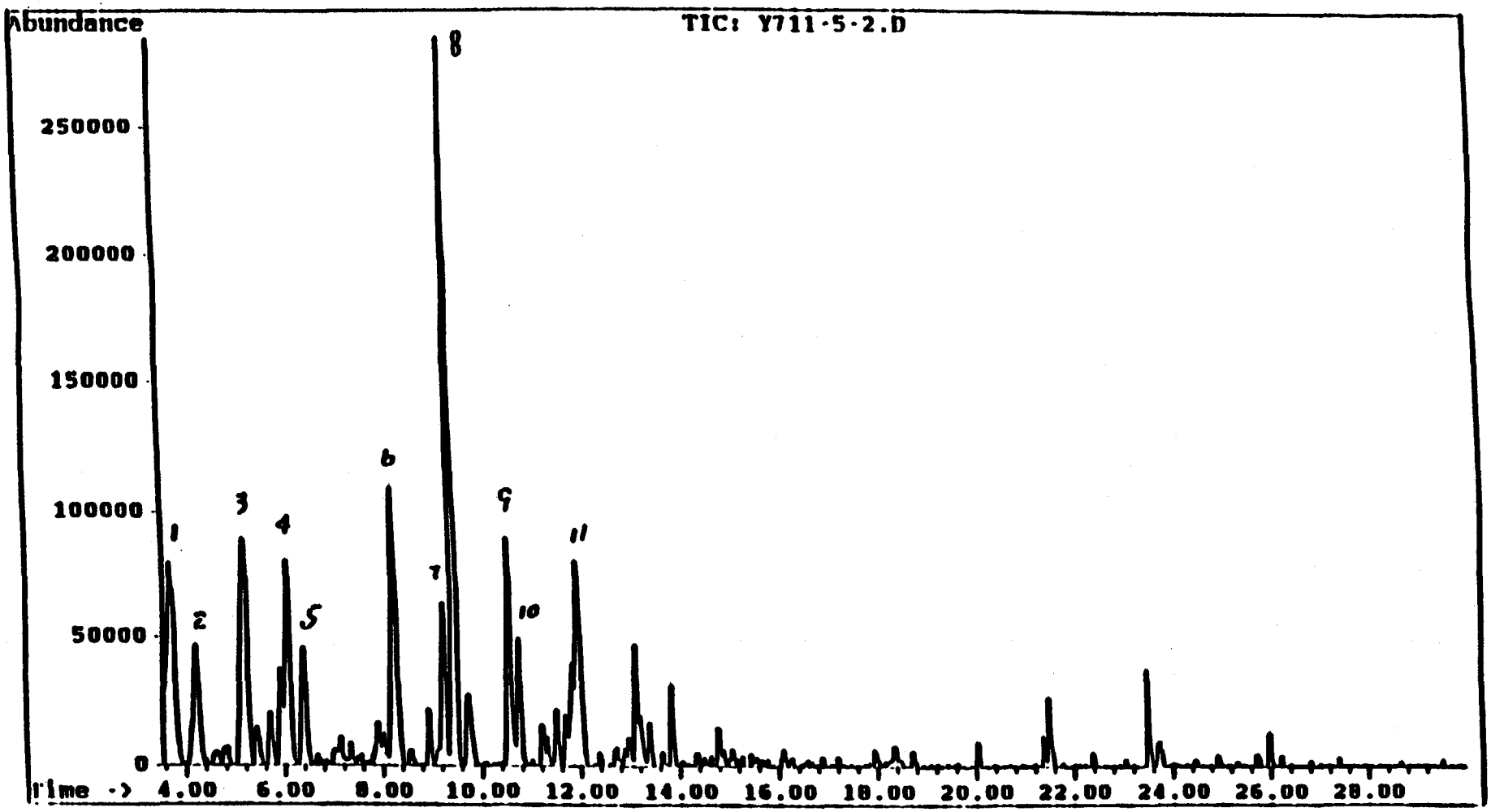


Figure 6.9. Chromatogram of Organic Analysis (using methylene chloroform extraction and GC/MS)

## 6.10 - Development of the Mobile Brine Treatment Unit

In early March 1994, a new idea of constructing a mobile brine treatment facility was conceived. The obvious advantage of such a unit was to ease the transportation of the unit from well site to well site and increase the flexibility and efficiency in conducting field work. Furthermore, there was no need to transport the brine from the field and remote locations to the treatment site. Therefore, a two phase construction plan begun. The first phase of this project included the design of the various components on the unit including their dimensions. The second phase of this project included the actual construction of the mobile unit. A schematic diagram of the constructed mobile brine treatment unit is shown in Figure 6.10. The size and location of each component were designed to conserve space since the working space was limited to 5 x 8-feet (actual size of the purchased trailer). The shaded units in the figure are "stacked" below the other units for this purpose.

In this design a generator was used to provide the power to a pump that drew the brine from the storage tank on the field into a circular separator. From this separator, the brine entered into the pH-adjustment unit with the aim of another pump. pH adjustment unit consisted of three limestone columns, each being 4 inches in diameter and four feet tall. These columns were plumbed in such a way that they could be used individually or in any combination with each other. Fluid from the pH-adjustment unit was directed to the aeration unit. This unit was designed with an adjustable angle to effect the desired brine film thickness. This unit was designed to be 1.5 feet wide, 3 inches deep, and 3 feet long. The aerated brine then entered the retention tank, which was 2.5 feet long, 1.5 feet high, and 1.5 feet wide. The brine was then directed into the sand filtration unit, located directly

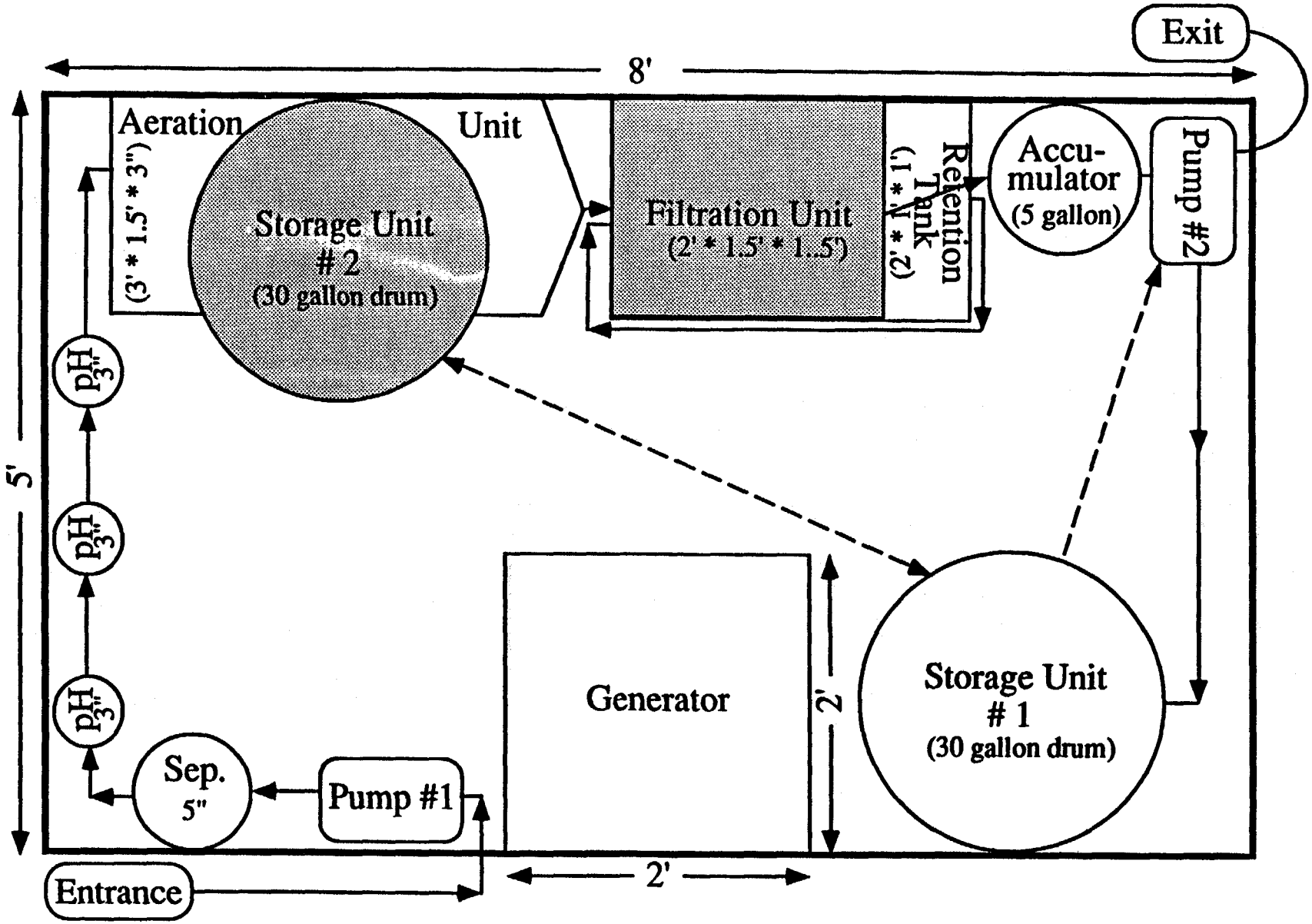


Figure 6.10. Schematic diagram of the Mobile treatment Unit

below the retention tank. The filtration unit was designed to be 2 feet in length and 1.5 feet in height. After completing the treatment process, the brine was guided into a five-gallon accumulation tank. When certain volume of brine was collected in the accumulation tank, an automatic switch was designed to turn on and transfer the treated brine into two 30-gallon storage units, for a total of 60 gallons. When the operation was completed, a second pump discharged the stored treated brine back to the field tank(s). Various sampling ports was constructed through the treatment process so that samples could be collected and shipped to Penn State for analysis and evaluation.

Upon the completion of the mobile unit, a number of sites were designated for further field experimental work. All of these experiments were conducted under the same controlable conditions. For example, the aeration angle and throughput flow rate were kept at 5 degree and one bbl/d, respectively. However, other conditions such as temperature, salinaty of the brine and the inlet concentration of elements were different at each site. The selected sites were: 2nd Venango and Red Valley sands in Venango County, First Venango sand in Clarion County, Cooper sand in Forest County, Grunderville sand in Warren County and Bradford sand in McKean County.

## 6.11 - Analysis of Results

The results of analyses indicated various percentage removal for a number of heavy metals. With the exception of some metals such as iron, the concentration of many heavy metals were very low. Metals such as Beryllium, Chromium, Cadmium, Lead, Nickle, and Strontium were found at extrimely low concentrations and beyond the detection limit of ICP (analytical instrument used for the analyses).

The removal of the other metals which could be detected with ICP were obtained. The percentage removal of aluminum, in the six tested brines, varied from 16% to 84%. The highest removal was obtained from the First Venango formation (inlet aluminum concentration of 257 ppb). The lowest removal was observed in the testing of the Second Venange formation (inlet aluminum concentration of 50 ppb). The percentage removal of iron varied from 61% to almost 100%. The overall removal of iron in the six tested brines was around 90%.

In three out of the six brines, the concentration of copper fell below the ICP detection limit, < 20 ppb. In the other three brines, an average copper removal of around 90% was obtained. The percentage removal of zinc in the six tested brines varied from 0% to 89%. The highest removal was obtained in treating the brine from the Grunderville formation (inlet zinc concentration of 282 ppb). The lowest removal took place treating the brine produced from the Copper formation (inlet zinc concentration of 84 ppb).

Three out of the six tested brines showed very low concentration of titanium (below the ICP detection limit), and a removal between 0% to 56% was calculated for the other three brines. From the tested brines, the highest removal of magnesium, 79%, was achieved in working with Second Venango formation. There was not any reduction on the concentration of manganese treating brine from Red Valley formation. However, the removal of manganese varied between 22% and 79% from the other tested brines. The results of analyses for other heavy metals indicated a 0% to 36% removal of Arsenic, 28% to 83% removal of barium, 4.1% to 59% of magnisium, and 6.7% to 24% of strontium. The results of the inorganic analysis are shown in Tables 6.14 through 6.19. Tables 6.20 through 6.25b present the results of organic analysis for the six tested brines.

Table 6.14. Results of Analysis on Produced Water From Bradford Sand

| Element | Concentration In (ppb) | Concentration Out (ppb) |
|---|---|---|
| Al | 60 | 35 |
| As | < 100 | < 100 |
| Ba | 404 | 67 |
| Be | < 1 | < 1 |
| Cd | < 5 | < 5 |
| Cr | < 2 | < 2 |
| Cu | < 20 | < 20 |
| Fe | 6440 | < 10 |
| Mg | 76700 | 73550 |
| Mn | < 50 | < 50 |
| Ni | < 30 | < 30 |
| Pb | < 50 | < 50 |
| Si | 4610 | 3845 |
| Ti | 41 | 38 |
| Zn | < 10 | < 10 |

| Sampling Ports | pH |
|---|---|
| Inlet | 6.75 |
| After Limestone Column | 6.78 |
| After Aeration Unit | 7.10 |
| After Filtration Unit | 7.00 |

Ambient Temperature ------> 74-79 degree Fahrenhiet

Fluid Temperature ------> ------

Table 6.15. Results of Analysis on Produced Water From Grunderville Sand

| Element | Concentration In (ppb) | Concentration Out (ppb) |
|---|---|---|
| Al | 161 | 78 |
| As | 190 | 190 |
| Ba | 8070 | 2539 |
| Be | < 1 | < 1 |
| Cd | < 5 | < 5 |
| Cr | < 2 | < 2 |
| Cu | 319 | < 20 |
| Fe | 57700 | 3900 |
| Mg | 726300 | 294000 |
| Mn | 5870 | 1800 |
| Ni | < 30 | < 30 |
| Pb | < 50 | < 50 |
| Si | 3440 | 3140 |
| Ti | 21 | 22 |
| Zn | 282 | < 30 |

| Sampling Ports | pH |
|---|---|
| Inlet | 5.88 |
| After Limestone Column | 5.90 |
| After Aeration Unit | 5.87 |
| After Filtration Unit | 6.90 |

Ambient Temperature ------> 72-74 degree Fahrenhiet

Fluid Temperature ------> ------

Table 6.16. Results of Analysis on Produced Water Cooper Sand

| Element | Concentration In (ppb) | Concentration Out (ppb) |
|---|---|---|
| Al | 91 | 68 |
| As | 180 | 115 |
| Ba | 2190 | 1170 |
| Be | < 1 | < 1 |
| Cd | < 5 | < 5 |
| Cr | < 2 | < 2 |
| Cu | 710 | < 20 |
| Fe | 48500 | 4200 |
| Mg | 1295250 | 759750 |
| Mn | 7943 | 4585 |
| Ni | < 30 | < 30 |
| Pb | < 50 | < 50 |
| Si | 2660 | 2315 |
| Ti | < 10 | < 10 |
| Zn | 84 | 84 |

| Sampling Ports | pH |
|---|---|
| Inlet | 5.80 |
| After Limestone Column | 5.85 |
| After Aeration Unit | 5.72 |
| After Filtration Unit | 6.53 |

Ambient Temperature ------> 81-78 degree Fahrenhiet

Fluid Temperature ------> 77-80 degree Fahrenhiet

Table 6.17. Results of Analysis on Produced Water From 2nd Venango Sand

| Element | Concentration In (ppb) | Concentration Out (ppb) |
|---|---|---|
| Al | 50 | 42 |
| As | 140 | 138 |
| Ba | 29400 | 15950 |
| Be | < 1 | < 1 |
| Cd | < 5 | < 5 |
| Cr | < 2 | < 2 |
| Cu | < 20 | < 20 |
| Fe | 34400 | 4680 |
| Mg | 927050 | 860950 |
| Mn | 3245 | 674 |
| Ni | < 30 | < 30 |
| Pb | < 50 | < 50 |
| Si | 2680 | 2030 |
| Ti | 16 | < 7 |
| Zn | 53 | 16 |

| Sampling Ports | pH |
|---|---|
| Inlet | 6.03 |
| After Limestone Column | 6.13 |
| After Aeration Unit | 6.10 |
| After Filtration Unit | 6.43 |

Ambient Temperature ------> 71-71 degree Fahrenhiet

Fluid Temperature ------> 77-71 degree Fahrenhiet

Table 6.18. Results of Analysis on Produced Water From Red Valley Sand

| Element | Concentration In (ppb) | Concentration Out (ppb) |
|---|---|---|
| Al | 101 | 83 |
| As | < 100 | < 100 |
| Ba | 27500 | 20450 |
| Be | < 1 | < 1 |
| Cd | < 5 | < 5 |
| Cr | < 2 | < 2 |
| Cu | < 20 | < 20 |
| Fe | 31900 | 3230 |
| Mg | 1194900 | 966150 |
| Mn | 1900 | 1900 |
| Ni | < 30 | < 30 |
| Pb | < 50 | < 50 |
| Si | 1935 | 1770 |
| Ti | 17 | 17 |
| Zn | 37 | 28 |

| Sampling Ports | pH |
|---|---|
| Inlet | 6.24 |
| After Limestone Column | 6.25 |
| After Aeration Unit | 6.21 |
| After Filtration Unit | 6.53 |

Ambient Temperature ------> 73-79 degree Fahrenhiet

Fluid Temperature ------> 78-78 degree Fahrenhiet

Table 6.19. Results of Analysis on Produced Water From 1st Venango Sand

| Element | Concentration In (ppb) | Concentration Out (ppb) |
|---|---|---|
| Al | 257 | 42 |
| As | 158 | 104 |
| Ba | 2929 | 1486 |
| Be | < 1 | < 1 |
| Cd | < 5 | < 5 |
| Cr | < 2 | < 2 |
| Cu | 175 | 46 |
| Fe | 126356 | 49038 |
| Mg | 1495870 | 1251166 |
| Mn | 4106 | 3190 |
| Ni | < 30 | < 30 |
| Pb | < 50 | < 50 |
| Si | 1532 | 1430 |
| Ti | < 10 | < 10 |
| Zn | 129 | 113 |

| Sampling Ports | pH |
|---|---|
| Inlet | 5.20 |
| After Limestone Column | 5.25 |
| After Aeration Unit | 5.10 |
| After Filtration Unit | 5.75 |

Ambient Temperature ------> 74-71 degree Fahrenhiet

Fluid Temperature ------> 74-72 degree Fahrenhiet

Table 6.20. Results of Organic Analysis on Produced Water From Bradford Sand

| Component | Inlet (ppb) | Before Aeration Unit (ppb) | After Aeration Unit (ppb) | After Filtration Unit (ppb) |
|---|---|---|---|---|
| Benzene | 47 [2] | 18 | 137 [2] | 74 [2] |
| Toluene | 66 [2] | 92 [2] | 278 [2] | 97 [2] |
| Ethyl Benzene | 97 [2] | 82 [2] | 31 [2] | 4.6 |
| M/P-Xylene | 183 [2] | 176 [2] | 99 [2] | 18 |
| O-Xylene | 265 [2] | 232 [2] | 85 [2] | 16 |
| 1, 3, 5-Trimethyl Benzene | 85 [2] | 61 [2] | 22 [2] | 3.2 |
| 1, 2, 4-Trimethyl Benzene | 166 [2] | 139 [2] | 47 [2] | 7.5 |
| Naphthalene | 9.0 | 7.4 | 3.4 | 0.69 |
| Methyl-T-Butyl Ether | 5.6 | 8.1 | 3.9 | 2.0 |
| N-Propyl Benzene | 13 | ----- | 2.3 | ----- |
| N-Butyl Benzene | ----- | ----- | 0.84 | ----- |

1 - Average value obtained from two different dilutions
2 - Estimated amount, value exceeded upper limit of calibration curve
3 - Values obtained from and performed beyond seven-day holding time
4 - Air bubbles in both sample vials

Table 6.21. Results of Organic Analysis on Produced Water From Grunderville Sand

| Component | Inlet (ppb) | Before Aeration Unit (ppb) | After Aeration Unit (ppb) | After Filtration Unit (ppb) |
|---|---|---|---|---|
| Benzene | 80 [2] | 67 [2] | 29 [2] | 38.3 |
| Toluene | 82 [2] | 65 [2] | 27 [2] | 32.5 |
| Ethyl Benzene | 4.5 | 3.2 | 1.1 | ----- |
| M/P-Xylene | 26 [2] | 17 | 6.7 | 9.1 |
| O-Xylene | 31 [2] | 21 | 8.6 | 4.5 |
| 1, 3, 5-Trimethyl Benzene | 12 [2] | 5.8 | 2.3 | ----- |
| 1, 2, 4-Trimethyl Benzene | 31 [2] | 14 | 5.8 | ----- |
| Naphthalene | 7.4 | 3.7 | 1.8 | ----- |
| Methyl-T-Butyl Ether | 1.1 | 0.63 | 0.41 | ----- |
| Isopropyl Benzene | 0.75 | ----- | ----- | ----- |

1 - Average value obtained from two different dilutions
2 - Estimated amount, value exceeded upper limit of calibration curve
3 - Values obtained from and performed beyond seven-day holding time
4 - Air bubbles in both sample vials

Table 6.22. Results of Organic Analysis on Produced Water From 2nd Venango Sand

| Component | Inlet (ppb) | Before Aeration Unit (ppb) | After Aeration Unit (ppb) | After Filtration Unit (ppb) |
|---|---|---|---|---|
| Benzene | 1200 [3] | 920 [3] | 24 | 72 |
| Toluene | 880 [3] | 1100 [3] | 38 | 77 |
| Ethyl Benzene | 46 [2] | 5.9 | ----- | ----- |
| M/P-Xylene | 580 [3] | 630 [3] | 26 | 33 |
| O-Xylene | 180 [3] | 220 [3] | 8.3 | 12 |
| Naphthalene | 11 | 8 | 3.2 | 0.5 |
| 1, 3, 5-Trimethyl Benzene | 82 | 70 [3] | 3.6 | 2.7 |
| 1, 2, 4-Trimethyl Benzene | 190 [3] | 135 [3] | 9.3 | 4.2 |

1 - Average value obtained from two different dilutions
2 - Estimated amount, value exceeded upper limit of calibration curve
3 - Values obtained from and performed beyond seven-day holding time
4 - Air bubbles in both sample vials

Table 6.23. Results of Organic Analysis on Produced Water From Cooper Sand

| Component | Inlet (ppb) | Before Aeration Unit (ppb) | After Aeration Unit (ppb) | After Filtration Unit (ppb) |
|---|---|---|---|---|
| Benzene | 1450 [1,3] | 330 [2,3] | 36 | 10 |
| Toluene | 1600 [1,3] | 460 [2,3] | 48 [2] | 17 |
| Ethyl Benzene | 2.2 | 7.4 | ----- | ----- |
| M/P-Xylene | 740 [1,3] | 410 [2,3] | 24 | 5.6 |
| O-Xylene | 240 [1,3] | 170 [2,3] | 6.7 | 2.4 |
| Naphthalene | ----- | ----- | ----- | ----- |
| 1, 3, 5-Trimethyl Benzene | 5.9 | 56 [2,3] | 2.5 | ----- |
| 1, 2, 4-Trimethyl Benzene | 94 [3] | 99 [2,3] | 4.4 | ----- |

1 - Average value obtained from two different dilutions
2 - Estimated amount, value exceeded upper limit of calibration curve
3 - Values obtained from and performed beyond seven-day holding time
4 - Air bubbles in both sample vials

Table 6.24. Results of Organic Analysis on Produced Water From Red Valley Sand

| Component | Inlet (ppb) | Before Aeration Unit (ppb) | After Aeration Unit (ppb) | After Filtration Unit (ppb) |
|---|---|---|---|---|
| Benzene | 700 [1,3] | 1450 [1,3] | 170 [2] | 156 |
| Toluene | 635 [1] | 1300 [1,3] | 140 [2] | 160 |
| Ethyl Benzene | ----- | ----- | 2.1 | 4.3 |
| M/P-Xylene | 385 [1,3] | 785 [1,3] | 84 [2] | 70 |
| O-Xylene | 160 [3] | 230 [1] | 26 | 25 |
| Naphthalene | ----- | ----- | ----- | 2.1 |
| 1, 3, 5-Trimethyl Benzene | 45 [3] | 72 [3] | 6.6 | 5.8 |
| 1, 2, 4-Trimethyl Benzene | 77 [3] | 130 [3] | 13 | 9.2 |

1 - Average value obtained from two different dilutions
2 - Estimated amount, value exceeded upper limit of calibration curve
3 - Values obtained from and performed beyond seven-day holding time
4 - Air bubbles in both sample vials

Table 6.25a. Results of Organic Analysis on Produced Water From 1st Venango Sand

| Component | Inlet (ppb) | Before Aeration Unit (ppb) | After Aeration Unit (ppb) | After Filtration Unit (ppb) |
|---|---|---|---|---|
| Benzene | 110 [4] | 110 [2,4] | 21 [4] | 3.8 [4] |
| Toluene | 260 [4] | 230 [2,4] | 39 [4] | 6.3 [4] |
| Ethyl Benzene | ----- | 9.3 [4] | 9.6 [4] | ----- |
| M/P-Xylene | 120 [4] | 160 [2,4] | 29 [4] | 2.9 [4] |
| O-Xylene | 42 [4] | 51 [2,4] | 11 [4] | < 2 [4] |
| Naphthalene | ----- | < 2 [4] | ----- | ----- |
| 1, 3, 5-Trimethyl Benzene | < 22 [4] | 16 [4] | ----- | ----- |
| 1, 2, 4-Trimethyl Benzene | 36 [4] | 30 [4] | ----- | ----- |

1 - Average value obtained from two different dilutions
2 - Estimated amount, value exceeded upper limit of calibration curve
3 - Values obtained from and performed beyond seven-day holding time
4 - Air bubbles in both sample vials

Table 6.25b. Results of Organic Analysis on Produced Water From 1st Venango Sand

| Component | Inlet (ppb) | Before Aeration Unit (ppb) | After Aeration Unit (ppb) | After Filtration Unit (ppb) |
|---|---|---|---|---|
| Benzene | 170 [4] | 29 | ----- | ----- |
| Toluene | 390 [4] | 70 [2] | ----- | ----- |
| Ethyl Benzene | ----- | >2 | ----- | ----- |
| M/P-Xylene | 220 [4] | 37 | ----- | ----- |
| O-Xylene | 53 [4] | 12 | ----- | ----- |
| Naphthalene | ----- | ----- | ----- | ----- |
| 1, 3, 5-Trimethyl Benzene | 29 [4] | 5 | ----- | ----- |
| 1, 2, 4-Trimethyl Benzene | 61 [4] | 8 | ----- | ----- |

1 - Average value obtained from two different dilutions
2 - Estimated amount, value exceeded upper limit of calibration curve
3 - Values obtained from and performed beyond seven-day holding time
4 - Air bubbles in both sample vials

# 7. THE PROCESS MODEL

## 7.1 - Objective

The specific objective of this task is to refine and verify a comprehensive mathematical model simulating the treatment process. The model, having been thoughly tested and validated, will form the basic building block for the design software package.

## 7.2 - Process Modeling

In the process of the brine treatment, the oxidization reaction between the oxygen in the air and the iron in the brine occurs at the aeration unit. Aeration is the key for this process to be succeed. In order to achieve optimum performance of the aeration process, a precise reactor design is therefore necessary. A kinetic model has been developed to serve this purpose. For any reactor, the conservation principle requires that the mass of species "i" in the control volume obeys the following statement:

$$\begin{bmatrix}\text{Rate of i Into}\\ \text{Control Volume}\end{bmatrix} - \begin{bmatrix}\text{Rate of i Out of}\\ \text{Control Volume}\end{bmatrix} + \begin{bmatrix}\text{Rate of Production of i}\\ \text{Within Control Volume}\end{bmatrix} = \begin{bmatrix}\text{Rate of Accumulation of}\\ \text{i Within Control Volume}\end{bmatrix}$$

Considering the iron in the brine as the "i" and taking the limit of the control volume, a partial deferential equation can be obtained. Since the flow is one-dimensional in nature, the PDE becomes:

$$\frac{\partial C_{Fe}}{\partial t} = R_{Fe} - \frac{\partial (C_{Fe} v_x)}{\partial x} \tag{1}$$

During brine treatment, if the flow rate keeps constant, the process can be treated as steady state, hence the left term in Equation (1) can be ignored. In

addition, the following two assumptions are made, in order to simplify the calculations.

(1) The brine is distributed evenly on the surface of aeration unit.

(2) The velocity at the contact point between brine and the surface of the aeration unit is zero.

The first assumption indicates that there is no acceleration or deceleration when brine flows through the aeration unit, hence, the velocity of brine along the length of the aeration unit, is constant. The second assumption has been widely accepted in fluid mechanics. Based on the above assumptions, the following equation for calculating the thickness of the brine film over the aeration unit can be derived (detailed deviation of the equation can be found Transport Phenomena by Bird et al., 1960).

$$h = \left[ \frac{3Q\mu}{b\rho \frac{g}{g_c} \sin\theta} \right]^{\frac{1}{3}} \tag{2}$$

The average velocity of brine is defined as:

$$\bar{v} = \frac{Q}{bh} = \left[ \frac{Q^2 \rho \frac{g}{g_c} \sin\theta}{3b^2\mu} \right]^{\frac{1}{3}} \tag{3}$$

The reaction between oxygen and iron can be written as

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$$

where Ferric Oxide ($Fe_2\ O_3$) is the product of the oxidation reaction which will precipitate from the brine as a solid phase. The rate of this reaction depend on several factors such as retention time, brine flow rate, iron concentration in the brine, tem-

perature condition etc.. In a more general form, the rate of the reaction between substances A and B may be written as

$$R_{AB} = KC_A^m C_B^n \tag{4}$$

where $C_A$ and $C_B$ are the concentration of A and B respectively; K is called the specific rate constant and is characteristic of a given reaction but varies with temperature; m and n are the order of the reaction for A and B respectively. In the brine treatment, the change of oxygen concentration in the air can be ignored. Therefore the reaction rate takes the following form.

$$R_{Fe} = K_1 C_{Fe}^m \tag{5}$$

It has been well established in the literature that $K_1$ is a function of temperature and can assume the following form.

$$K_1 = \alpha\, e^{-\frac{\beta}{T}} \tag{6}$$

where $\alpha$ and $\beta$ are constants and need to be determined experimentally. The reaction order, m, should be a constant if the reaction is undergoing at a perfect mixing condition. However, in the case of brine treatment, the direct contact between air and the iron in brine only occurs at the surface of brine film. The reaction rate will be slowed down below the surface. This means that the average reaction rate should decrease quickly as the thickness of brine film increases. Based on this consideration, the reaction order assumes the following form.

$$m = \eta\, e^{-\zeta h} \tag{7}$$

where $\eta$ and $\zeta$ are constants to be determined by experiments. Substituting Equations 3, 5, 6 and 7 into Equation 1, the following analytical equations are derived for the calculation of brine treatment.

$$\frac{\alpha L}{e^{\frac{\beta}{T}}}\left[\frac{3b^2\mu}{Q^2\rho\frac{g}{g_c}\sin\theta}\right]^{\frac{1}{3}} = \begin{cases} \dfrac{C_{Fe,in}^{1-\eta e^{-\zeta h}} - C_{Fe,out}^{1-\eta e^{-\zeta h}}}{1-\eta e^{-\zeta h}} & \eta e^{-\zeta h} \neq 1 \\ \ln(C_{Fe,in}) - \ln(C_{Fe,out}) & \eta e^{-\zeta h} = 1 \end{cases} \tag{8}$$

Equation 8 is derived for steady state flow and under the condition that brine is distributed evenly over the aeration unit. It can be used for the purpose of parametric studies or for design of brine treatment facility.

## 7.3 - Determination of the Constants

In Equation 8, there are four constants, namely $\alpha$, $\beta$, $\eta$, and $\zeta$, which need to be determined before the equation can be used. These constants can be determined from the results of kinetic study as well as the field experimental data. We propose the following method as the constant-determination procedure.

Based on Equation 5, the relation between $\log(R_{Fe})$ and $\log(C_{Fe})$ is linear. The reaction rate, $R_{Fe}$, can be expressed mathematically as $\left[\frac{dC_{Fe}}{dt}\right]$. Therefore, Equation 5 can be rewritten as:

$$\log\left[\frac{dC_{Fe}}{dt}\right] = m\log(C_{Fe}) + \log(K_1) \tag{9}$$

Equation 9 indicates that if drawn in log-log coordinates, the plot of $\left[\frac{dC_{Fe}}{dt}\right]$ vs $C_{Fe}$ is a straight line with a slop of m and an intersection of $\log(K_1)$. The data to draw this kind plots can be obtained from the kinetic study. Note that m is a function of the thickness of the brine film (Equation 7) while $K_1$ is a function of temperature (Equation 6). During the experiments of kinetic studies, oxygen is

pumped passing the brine mixture all through. The contact between oxygen and brine should be well established; hence no effect of thickness is expected. This indicates that the plots of $\log\left[\frac{dC_{Fe}}{dt}\right]$ vs $\log(C_{Fe})$ should have the same slop of m. However, the plots with the kinetic data obtained at different temperature will have different intersection of $\log(K_1)$. From Equation 6, $\log(K_1)$ can be expressed as a function of temperature as:

$$\log(K_1) = \log(\alpha) - \frac{\beta}{T}\log(e) \tag{10}$$

From the previous plots, a set of data in the form of $\log(K_1)$ vs T can be obtained. Using these data, one can draw a straight line on semi-log coordinates as $\log(K_1)$ vs $\frac{1}{T}$ (Equation 10). Thus, the values of the constants, $\alpha$ and $\beta$ in Equation 8 can be obtained from the intersection and the slop of this straight line respectively. Although the value of m can be obtained from the slop of the $\log\left[\frac{dC_{Fe}}{dt}\right]$ vs $\log(C_{Fe})$ plots, the constants, $\eta$ and $\zeta$ may not be determined from the kinetic analysis, since these two constants are the result of the effects of the thickness of brine film in the treatment processing. They must be determined from the treatment processing data. Equation 7 can be expressed as:

$$\eta = me^{\zeta h} \tag{11}$$

Substituting Equation 11 into Equation 8, the constant $\eta$ is eliminated and the constants left in the equation are $\alpha$, $\beta$, m, and $\zeta$ . The values of the first three constants are determined from the kinetic data as discussed above. The only one left in the equation is $\zeta$, which can be determined by substituting the field treatment data into the equation. The above procedure is a fundamental one designed for the

determination of the reaction constants. However, because of the like of sufficient kinetic data at different temperature, this procedure has not been able to apply. Instead, we used the try-and-error method to determine the constants, which best match the field and laboratory experimental data. More kinetic study will be conducted in the near future. The above constant-determination procedure will be applied as soon as there are sufficient data available.

# 8. Using Model for Design Purpose

## 8.1 - Achievements in the Development of the Software

Based on the results we have achieved so far, a software for brine treatment facility design was developed. The software named as BRINE.EXE is a user-friendly, menu-driven program, which can be executed on a personal computer with DOS environment. The software can help the user to design the necessary size of the facility for the treatment of a specified brine. This chapter discusses the basic design strategies. The detailed step-by-step procedure of using the software is described in the USER's MANUAL, which is attached in Appendix B.

The design of the brine treatment facility consists of the design of all the individual units. The designs of oil/brine separator, pH adjustment unit, and settling unit are based on the volume equivalent principle, while the design of filtration unit is based on area equivalent principle. In the design of the oil separator, the pH adjustment unit and the settling unit, the principle of volume equivalent was used. The reason for applying this principle is that if a certain volume of the unit can handle a flow rate of Q, then twice that volume must be able to handle a flow rate of 2Q. In the field tests, it was found out that the sizes of these units are sufficient to handle a flow rate up to 16 bbl/day. Even though the sizes of these unit may be able to handle a flow rate greater than 16 bbl/d, to be on the safe side, we put 16 bbl/day as the maximum capacity of these units. For any flow rate greater than 16 bbl/d, the following formula will be used to calculate the necessary sizes of these units.

$$X_{design} = X_{field} \left(\frac{Q}{16.0}\right)^{\frac{1}{3}} \quad \text{When } Q>16.0$$

where X represents any of the tree dimensions of the unit. The mobile brine treatment facility was tested with field brines at flow rate of 1 bbl/day. The sizes of all the units in the mobile facility have been proved to be adequate to treat brine at least 1 bbl/day. Therefore, for a flow rate of 1 bbl/day, the sizes of these units in the mobile facility are suggested in the software. For any flow rate between 1 bbl/day and 16 bbl/day, the volume interpolation method is used. Let $V_{field}$ represent the volume of a unit in the field prototype facility and $V_{mobile}$ represent the volume of the same unit in the mobile facility. Then, for a flow rate between 1 bbl/day and 16 bbl/day, the required volume for that unit is calculated by the following formula.

$$V = \frac{V_{field} - V_{mobile}}{15} (Q - 1) + V_{mobile} \quad \text{When } 1<Q<16.0$$

The dimensions of the unit is obtained by substituting the required volume into the following equation.

$$X_{design} = X_{field} \left(\frac{V}{V_{field}}\right)^{\frac{1}{3}}$$

In the design of filtration unit, the area-equivalent principle instead of volume equivalent principle was used. This is because of the consideration that an increase in sand thickness will not contribute to the handling of a larger flow rate. The formula used to design the filtration unit is:

$$A_{design} = A_{field} \frac{Q}{16.0} \quad \text{When } Q>16.0$$

where A represents the surface area of the sand in the filtration unit. For a flow

rate between 1 bbl/day and 16 bbl/day, the required surface area of the sand box is obtained through the following formula.

$$A_{design} = \frac{A_{field} - A_{mobile}}{15}$$

In addition, the sand thickness is suggested to be 1.5 feet, even though sand thickness tests conducted in the laboratory shows that a 2.5 inches thickness can do the job. However, a thin sand bed requires frequent sand replacement.

For any flow rate below 1 bbl/day, the sizes of these unit, which were tested with the mobile brine treatment facility in our field experiments, are suggested. This is because the volume or area equivalent principle may not apply when the flow rate is very small. To be on the safe side, it is better to over-design these units rather than under-design them. The most important part of the brine treatment facility is the aeration unit. It is the place where the thin film of brine is created and the oxidation reaction takes place. The length, width and the angle of the aeration unit all affect the efficiency of the brine treatment. Therefore, the design of aeration unit must consider all these three parameters. In addition, one may need to estimate the capacity of an available treatment facility. This includes the calculation of the maximum flow rate that the facility can handle for a given brine, the maximum iron concentration of the brine, and the efficiency of the treatment (the iron concentration after the treatment). Equation (8) is used as the basis for the design and the capacity calculations of aeration unit.

## 8.2 - Length of Aeration Unit

The length of aeration unit is the distance that brine flows in thin film. This distance should provide sufficient contact time between air and the iron in the brine. The thinner the brine film, the less contact time is needed. Therefore, the length of

aeration unit depends not only the iron concentration of the brine, but also the flow rate, and the width of the aeration unit. Generally, smaller flow rate and wider aeration unit will create thinner brine film; hence, require shorter distance (length). However, the relation between the length and the flow rate or width of aeration unit is not linear. For example, doubling the width of the aeration unit may not necessary reduce the length of the aeration unit to half. The relation between these variables is governed by Equation (8), which can be rearranged in the following form.

$$L = \begin{cases} \dfrac{e^{\frac{\beta}{T}}}{\alpha} \left[ \dfrac{Q^2 \rho \frac{g}{g_c} \sin\theta}{3b^2\mu} \right]^{\frac{1}{3}} \dfrac{C_{Fe,in}^{1-\eta e^{-\zeta h}} - C_{Fe,out}^{1-\eta e^{-\zeta h}}}{1 - \eta e^{-\zeta h}} & \eta e^{-\zeta h} \neq 1 \\ \dfrac{e^{\frac{\beta}{T}}}{\alpha} \left[ \dfrac{Q^2 \rho \frac{g}{g_c} \sin\theta}{3b^2\mu} \right]^{\frac{1}{3}} \left[ \ln(C_{Fe,in}) - \ln(C_{Fe,out}) \right] & \eta e^{-\zeta h} = 1 \end{cases} \tag{12}$$

The design of the length of aeration unit is straight forward by using Equation (12). The thickness of brine film, h, in the equation needs to be determined by Equation (2). Figures 8.1 through 8.3 show the examples of length design of aeration unit. In Figure 8.1, The iron concentration of the brine is 50 ppm; the rate needs to be treated is 0.5 gal/min and the operating temperature is set to be 60 F. Two curves are drawn in the figure, for the width of aeration unit of 2 ft and 4 ft, respectively. The angle of aeration unit is $15^o$ for both cases. As the outlet iron concentration decreases, the required length of aeration unit increases. However, as indicated in the figure, the relation is not linear. Furthermore, it can be observed from Figures 8.1 through 8.3 that by doubling the width of aeration unit (from 2 ft to 4 ft), the required length of aeration unit does not necessaryly cut to half. Figure 8.2 is the plot of length of aeration unit vs. inlet iron concentration. At fixed flow rate, outlet iron concentration, temperature and the angle of aeration unit, the

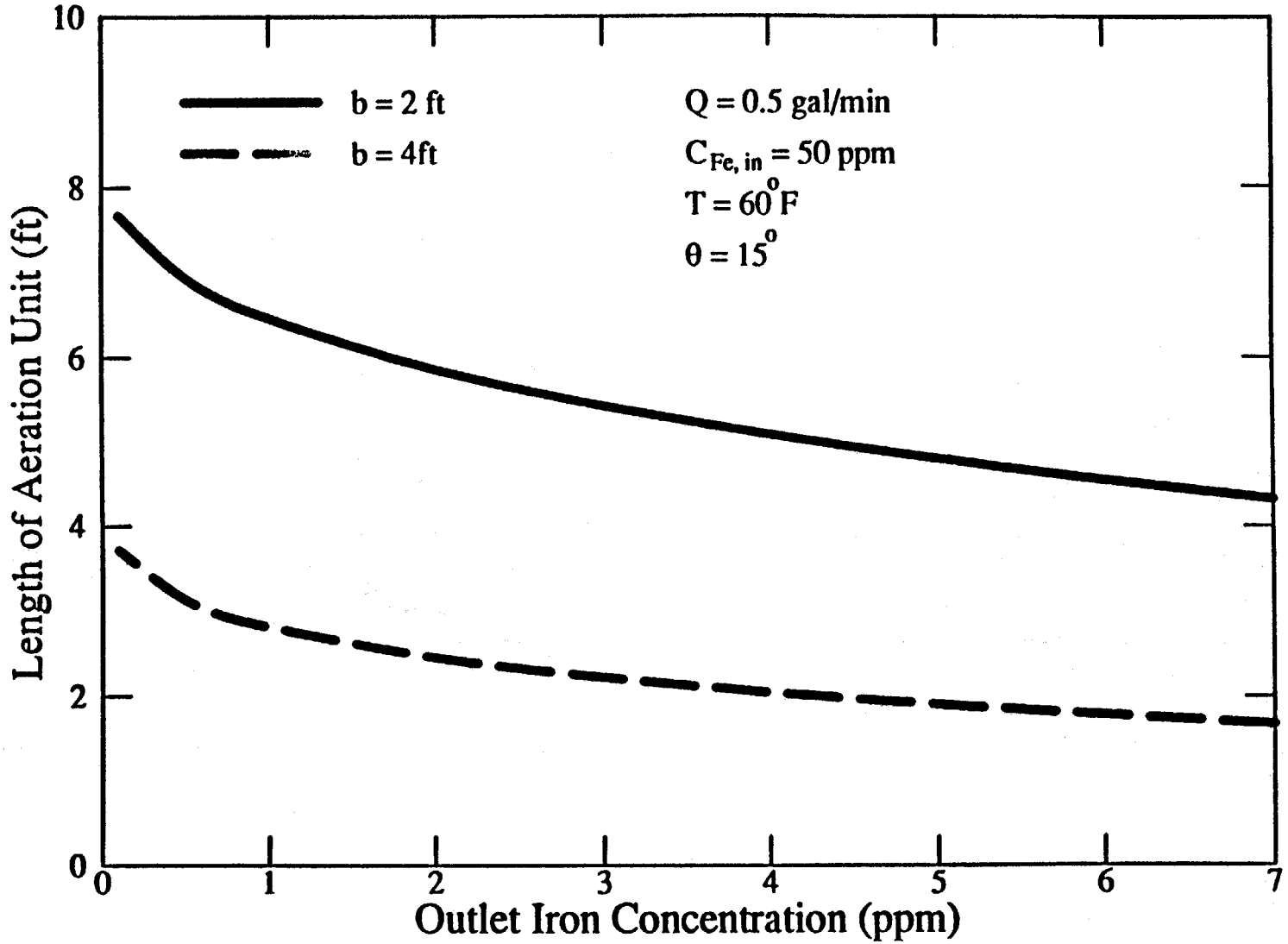


Figure 8.1. Example of Designing Length of Aeration Unit

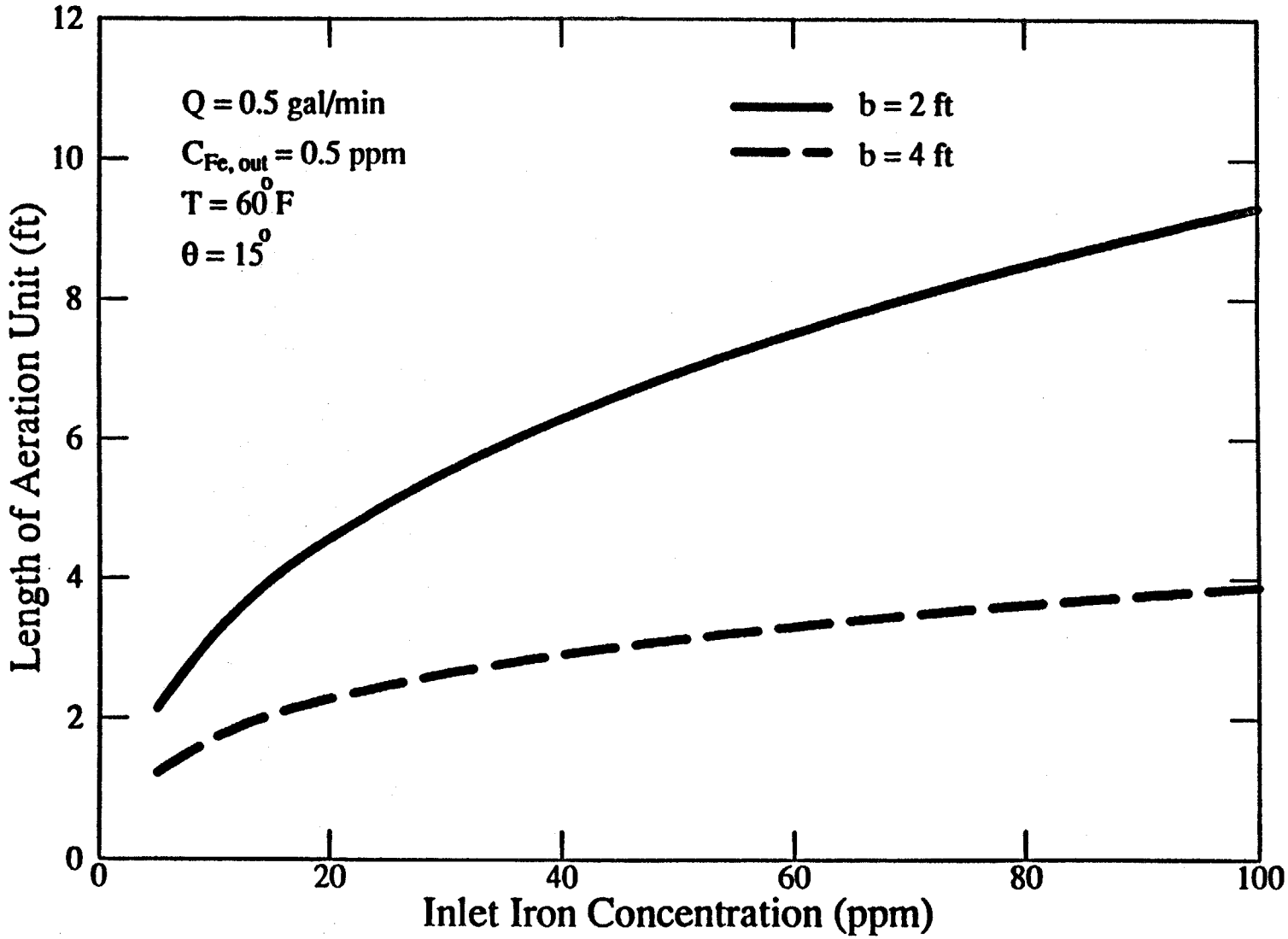


Figure 8.2. Example of Designing Length of Aeration Unit

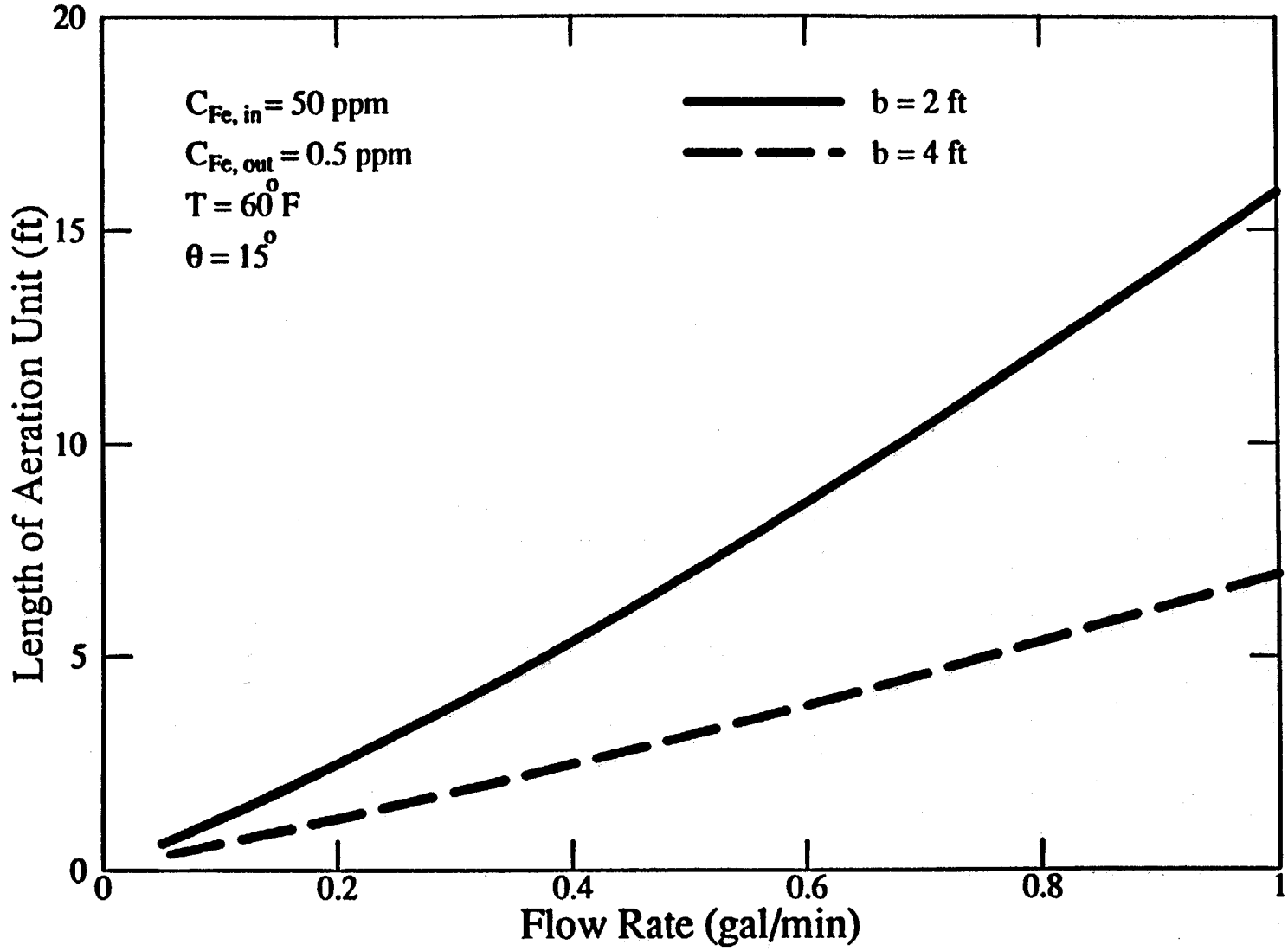


Figure 8.3. Example of Designing Length of Aeration Unit

required length increases as the inlet iron concentration increases. However, the increase is much faster for an aeration unit with a width of 2 ft than that with a width of 4 ft. This is because that with a width of 2 ft, the brine film over the aeration unit is much thicker than the film over a 4 ft width unit. At high iron concentration, it requires much better contact between air and iron in brine; hence the thicker film needs much longer length to provide the necessary contact. Figure 8.3 shows the relation between length of aeration unit and flow rate. When all the other parameters are fixed, longer aeration unit is required at higher flow rate. But, again, the relation is not linear, even though the curves in the figure looks close to straight lines.

## 8.3 - Width of Aeration Unit

In practice, the maximum length of aeration unit could be limited by the available space. If the length of aeration unit called for by the design is too long, one may specify a length which seems feasible and attempt to design the width. It is assumed that the brine flow is evenly distributed over the whole area of the aeration unit. At a constant flow rate, a wider aeration unit will produce a thinner film over the unit. This, in turn, will create a better contact between the oxygen in the air and the iron in brine. The following equation is used for the design of the width of aeration unit.

$$b = \begin{cases} Q\left[\dfrac{\rho\frac{g}{g_c}\sin\theta}{3\mu}\right]^{\frac{1}{2}}\left[\dfrac{e^{\frac{\beta}{T}}}{\alpha L}\dfrac{C_{Fe,in}^{1-\eta e^{-\zeta h}} - C_{Fe,out}^{1-\eta e^{-\zeta h}}}{1-\eta e^{-\zeta h}}\right]^{\frac{3}{2}} & \eta e^{-\zeta h} \neq 1 \\ Q\left[\dfrac{\rho\frac{g}{g_c}\sin\theta}{3\mu}\right]^{\frac{1}{2}}\left[\dfrac{e^{\frac{\beta}{T}}}{\alpha L}\left[\ln(C_{Fe,in}) - \ln(C_{Fe,out})\right]\right]^{\frac{3}{2}} & \eta e^{-\zeta h} = 1 \end{cases} \tag{13}$$

In order to design the width of aeration unit, one must specify the inlet and outlet iron concentrations, the length and angle of aeration unit, and the density and viscosity of brine. Because the calculation of the thickness of brine film needs to know the width of aeration unit (Equation 2), the design of width involves an iteration procedure. The iteration procedure starts with an initial value of width ( $b^{(0)}$ = 2.0 ft in the program). Substituting the initial width into Equation 2, one can calculate the thickness of the thin film, which is needed in Equation 13 for calculating the width of aeration unit in the new iteration level. This procedure continues until the width of aeration unit converges. It was found out during the testing of the program that this iteration procedure may not always converge. In some cases, the values of the calculated width could jump between two numbers forming a repeating circle during the iterations. To solve this problem, a section of program was added to the software. It will monitor the convergency during the iterations. Once the calculated width of aeration unit form a two-number circle, the average value of the two numbers will be used as an initial value to restart the iteration procedure. This new procedure was tested extensively and no convergency problem ever happened. The iteration procedure is quite effective. It usually takes only several iterations to converge. Figure 8.4 shows the relation between the width of aeration unit and the outlet iron concentration while all the other variables are fixed. The shape of the curves in Figure 8.4 is very similar to that in Figure 8.1. It is understandable since both length and width affect the area of aeration unit. It can be observed in the two figures that doubling the width of aeration unit reduces the required length more than half (Figure 8.1), while doubling the length of aeration unit only reduces the necessary width less than half (Figure 8.4), even though the relation between length or width and the area of aeration unit is the same.

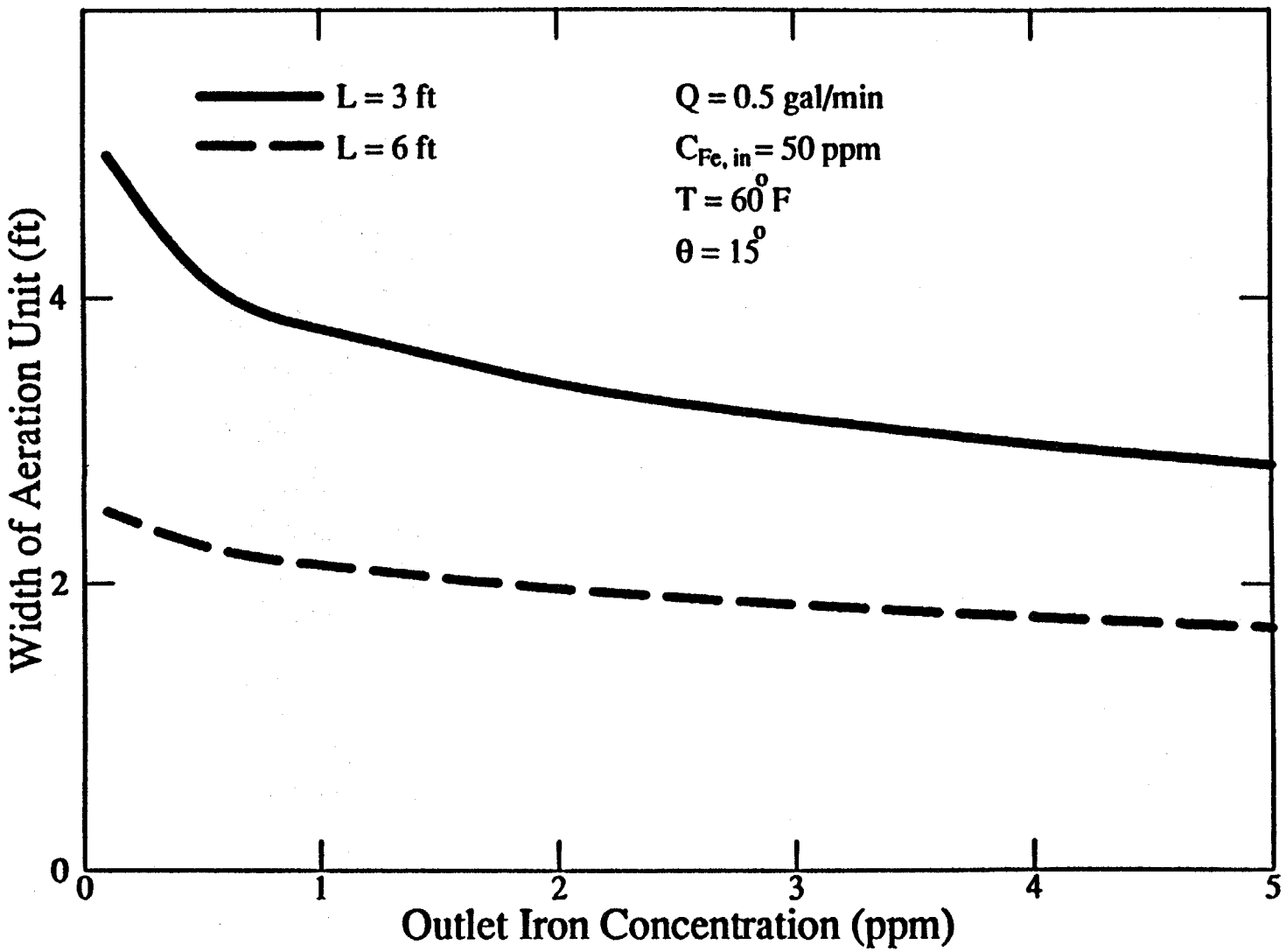


Figure 8.4. Example of Designing Width of Aeration Unit

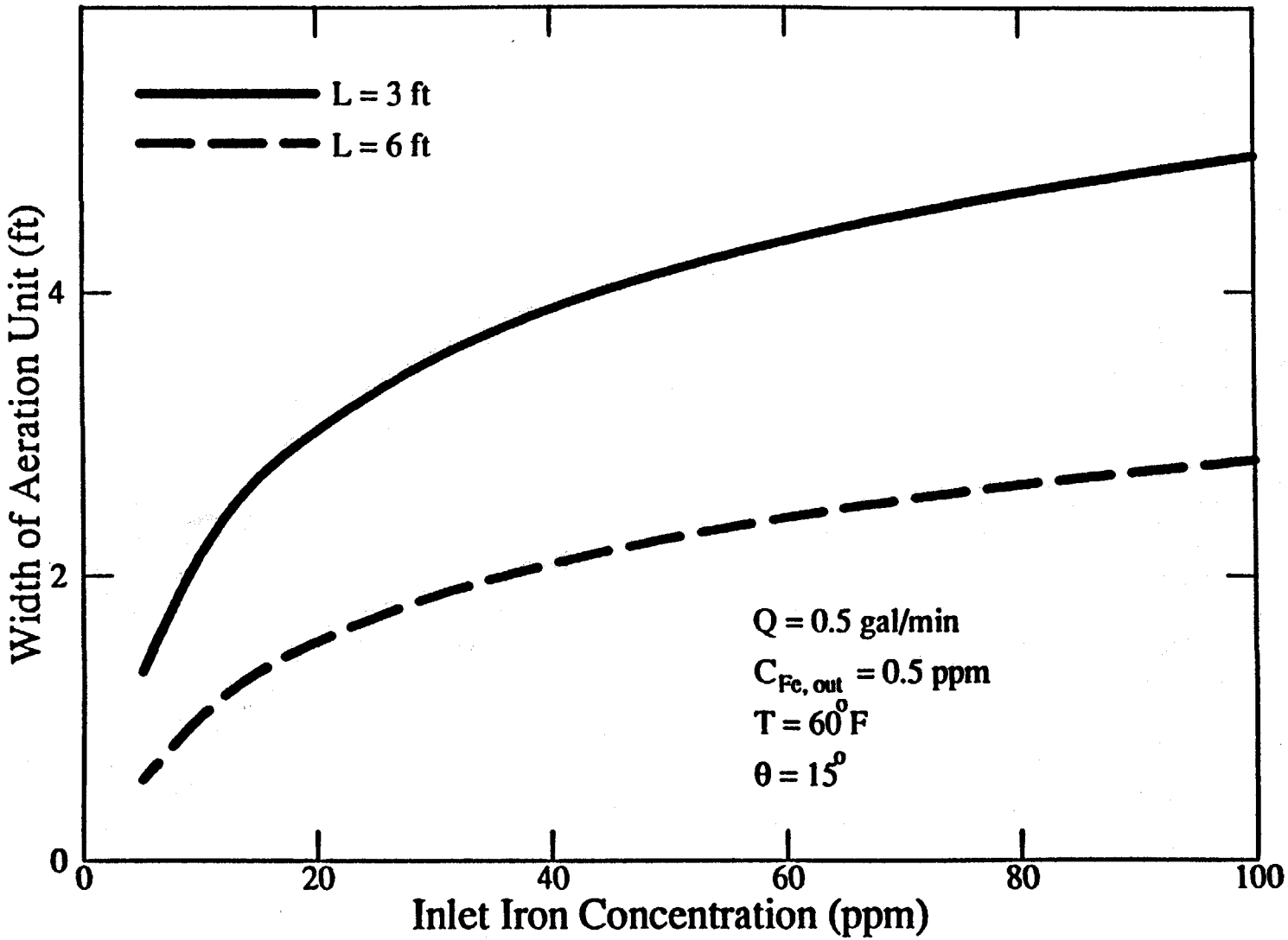


Figure 8.5. Example of Designing Width of Aeration Unit

Figure 8.5 shows the width of aeration unit as a function of inlet iron concentration. As shown in the figure, the required width of aeration unit increase with inlet iron concentration when all the other parameters are fixed. However, the rate of increase varies. If the inlet iron concentration is set equal to the outlet iron concentration, the width of aeration unit should be zero, since no treatment is needed. Starting from the value of outlet iron concentration, the increase of inlet iron concentration results in a sharp increase in the width of aeration unit. However, the rate of increase slows down when the value of inlet iron concentration is greater than 20 ppm. It indicates that the required width of aeration unit is not a simple proportion of inlet iron concentration. The relation between the width of aeration unit and flow rate is linear. This is understandable since the brine flow is evenly distributed on the aeration unit. Proportionly increasing both flow rate and width of aeration unit does not change the thickness of brine film; hence it will not affect the reaction between oxygen in air and iron in brine.

## 8.4 - Angle of Aeration Unit

The effects of the angle of aeration unit are of two-fold, since the oxidation reaction between oxygen and iron is affected by the contact area as well as contact time. When the angle of aeration unit is increased, the thickness of brine film decreases so that the contact between air and brine increases. This will increase the effectiveness of the treatment. However, because of the increased angle, the brine flows faster over the aeration unit, which decreases the contact time, thus decreasing the efficiency of the treatment. Therefore, an optimum angle of the aeration unit may exist when a balance is achieved between these two factors. The following equation should be used when designing the angle of aeration unit.

$$\alpha = \begin{cases} \sin^{-1}\left[\dfrac{3b^2\mu}{Q^2\rho\frac{g}{g_c}}\left\{\dfrac{\alpha L}{e^{\frac{\beta}{T}}}\dfrac{1-\eta e^{-\zeta h}}{C_{Fe,in}^{1-\eta e^{-\zeta h}} - C_{Fe,out}^{1-\eta e^{-\zeta h}}}\right\}^3\right] & \eta e^{-\zeta h} \neq 1 \\ \sin^{-1}\left[\dfrac{3b^2\mu}{Q^2\rho\frac{g}{g_c}}\left\{\dfrac{\alpha L}{e^{\frac{\beta}{T}}}\dfrac{1}{\ln(C_{Fe,in}) - \ln(C_{Fe,out})}\right\}^3\right] & \eta e^{-\zeta h} = 1 \end{cases} \tag{14}$$

Because the calculation of the thickness of brine film involves the angle of aeration unit, an iteration procedure is needed in the design of the angle. The iteration procedure is similar to that of the design of the width. It starts with an assumed initial angle of 10 degree. The iteration procedure will continue by using Equations 2 and 14 alternatively until the angle converges. However, it needs to point out that Equation 14 does not always have a solution. When the value in the [ ] of the right side of Equation 14 is greater than 1.0 or less than 0.0, no reasonable solution can be found from the equation. It indicates that the aeration area (the length and width of the unit) is not properly specified, and there may not be any angle which would be effective for the particular condition. The best way to find an optimum angle is probably to create a table similar to Tables 8.1 and 8.2 using Equation 14. It involves the calculation of the lengths of the aeration unit at various widths and angles with the required flow rate, inlet and outlet iron concentrations. This table is particular useful when one has the flexibility of building the aeration unit at different sizes, so that one can select the combination of the length, width and angle which best suits one's needs. For example, from Table 8.2, one can find the following optimal combination of size and angle of aeration unit. If the width of the unit is 2 ft, one may set the angle between 25° and 36° (the length is 7.4 ft). If the width is 3 ft, then the angle could be better off between 16° and 25° (with a

length of 5 ft). If the length and width are limited to less than 3 and 5 ft respectively, from the table, one can observe that the angle has to be between 9° and 16°.

Table 8.1. Length (ft) of Aeration Unit at Various Width and Angle

| Angle | Width of Aeration Unit (ft)) | | | | | |
|---|---|---|---|---|---|---|
| | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 |
| 1.0 | 20.1 | 10.4 | 6.9 | 5.0 | 3.9 | 3.1 |
| 4.0 | 20.0 | 9.0 | 5.5 | 3.9 | 3.0 | 2.4 |
| 9.0 | 17.6 | 7.6 | 4.7 | 3.4 | 2.6 | 2.1 |
| 16.0 | 15.7 | 6.9 | 4.3 | 3.1 | 2.4 | 2.0 |
| 25.0 | 14.4 | 6.4 | 4.1 | 3.0 | 2.4 | 2.0 |
| 36.0 | 13.6 | 6.2 | 4.0 | 3.0 | 2.4 | 2.0 |
| 49.0 | 13.0 | 6.0 | 4.0 | 3.0 | 2.4 | 2.0 |

* $C_{Fe,in}$ = 50 ppm, $C_{Fe,out}$ = 0.5 ppm, Q = 0.5 gal/min, T = 60° F

Table 8.2. Length (ft) of Aeration Unit at Various Width and Angle

| Angle | Width of Aeration Unit (ft)) | | | | | |
|---|---|---|---|---|---|---|
| | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 |
| 1.0 | 20.3 | 10.6 | 7.0 | 5.1 | 4.0 | 3.2 |
| 4.0 | 20.4 | 9.3 | 5.8 | 4.2 | 3.2 | 2.6 |
| 9.0 | 18.3 | 8.2 | 5.2 | 3.8 | 3.0 | 2.5 |
| 16.0 | 16.7 | 7.6 | 5.0 | 3.7 | 3.0 | 2.5 |
| 25.0 | 15.7 | 7.4 | 5.0 | 3.8 | 3.1 | 2.7 |
| 36.0 | 15.2 | 7.4 | 5.1 | 4.0 | 3.3 | 2.9 |
| 49.0 | 14.9 | 7.5 | 5.3 | 4.2 | 3.5 | 3.0 |

* $C_{Fe,in}$ = 50 ppm, $C_{Fe,out}$ = 0.1 ppm, Q = 0.5 gal/min, T = 60° F

## 8.5 - Efficiency of Brine Treatment

This is to calculate how much iron can be removed from a particular brine by the treatment with an available aeration unit. In order to do so, one must specify the iron concentration in the original brine, the flow rate of brine that needs to be treated, the size and the angle of the aeration unit, as well as the density and viscosity of brine. Equation 8 can be rewritten as an explicit expression of the outlet iron concentration:

$$C_{Fe,out} = \begin{cases} \left[ C_{Fe,in}^{1-\eta e^{-\zeta h}} - \dfrac{\alpha L}{e^{\frac{\beta}{T}}} (1 - \eta e^{-\zeta h}) \left[ \dfrac{3b^2\mu}{Q^2 \rho \frac{g}{g_c} \sin\theta} \right]^{\frac{1}{3}} \right]^{\frac{1}{1-\eta e^{-\zeta h}}} & \eta e^{-\zeta h} \neq 1 \\ \mathrm{EXP}\left[ \ln(C_{Fe,in}) - \dfrac{\alpha L}{e^{\frac{\beta}{T}}} \left[ \dfrac{3b^2\mu}{Q^2 \rho \frac{g}{g_c} \sin\theta} \right]^{\frac{1}{3}} \right] & \eta e^{-\zeta h} = 1 \end{cases} \quad (15)$$

The thickness of brine film over the aeration unit needs to be calculated using Equation (2) before Equation (15) can be applied. The calculation of outlet iron concentration is straight forward. However, for some cases, the calculated value of the outlet iron concentration could be negative. A negative value of outlet iron concentration indicates that the capacity of the aeration unit is not fully utilized at the given conditions and all the iron in the brine can be removed by the treatment. Figure 8.6 shows one of the examples of outlet iron concentration calculation. Two different sizes (one is 3 ft * 2 ft and the other is 4 ft * 3 ft) of aeration unit are considered. Both aeration units have an angle of 15°. The treatment is operated at a temperature of 60° F. The brine flow rate is 0.5 gal/min. The curves in the figure shows the relation between the outlet iron concentration and the inlet concentration.

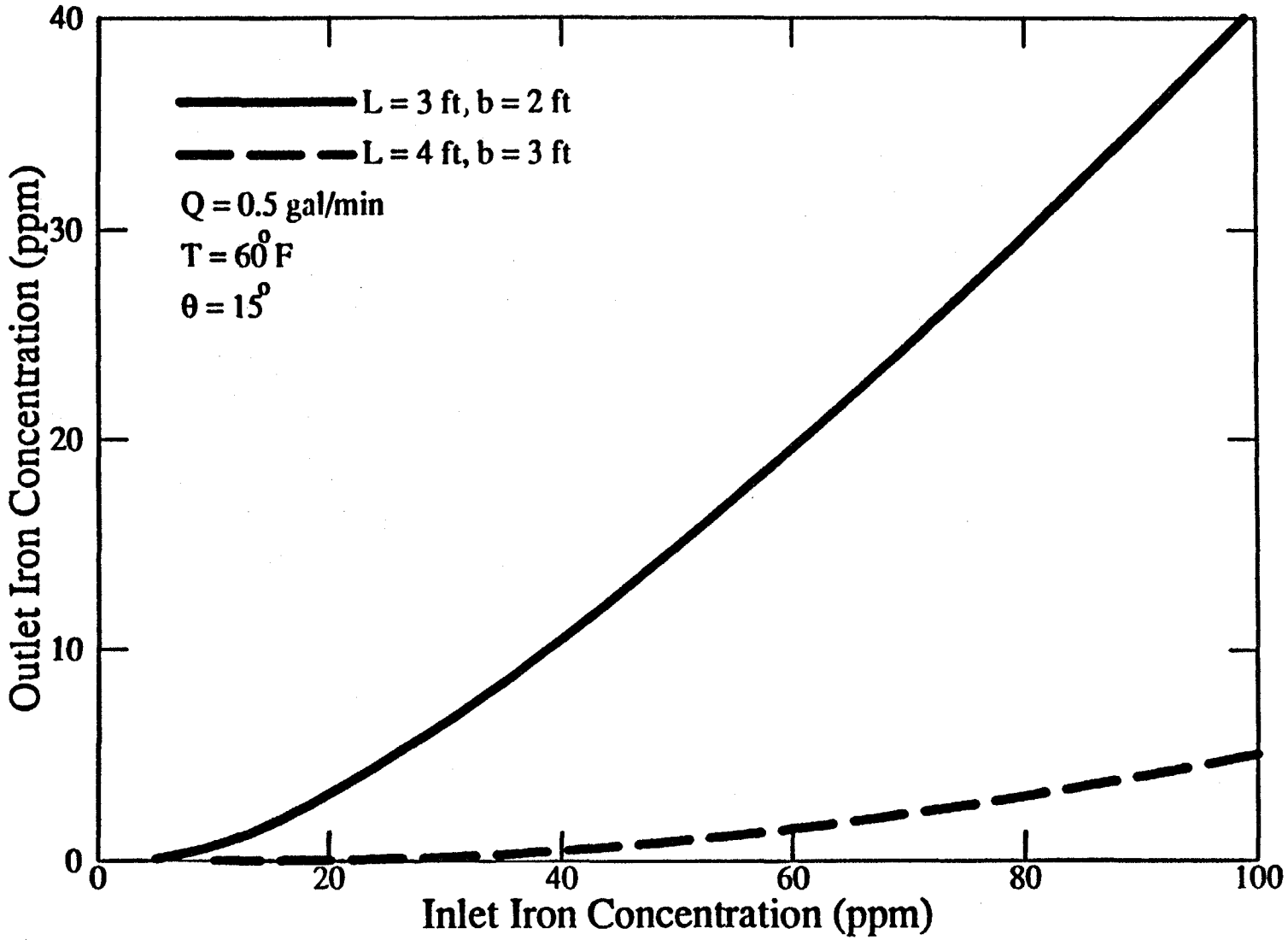


Figure 8.6. Example of Predicting Outlet Iron Concentration

With the flow rate and the size and the angle of aeration unit fixed, the curves indicate that the outlet concentration increases with inlet concentration. When inlet concentration is below 5 ppm, both sizes of aeration unit can essentially remove all the iron from the brine. However, as the inlet iron concentration increases, the larger size unit still removes most of the iron from the brine, while the efficiency of the smaller unit decreases rapidly. The area of the larger unit is only twice of the smaller one. Nevertheless, the efficiency of the brine treatment of the two units is so different.

## 8.6 - Maximum Inlet Iron Concentration

The purpose of calculating the maximum inlet iron concentration is to estimate the worst case that the facility can handle. However, the calculated maximum inlet iron concentration is corresponding to the given flow rate. At a lower flow rate, a higher value could be obtained for the maximum inlet iron concentration with the same facility, while at higher flow rates, the maximum inlet iron concentration should be smaller. The calculation procedure of maximum inlet iron concentration is similar to that of outlet iron concentration. Besides the flow rate, the size and the angle of aeration unit, and the density and viscosity of brine, one needs also specify the required outlet iron concentration.

$$C_{Fe,in} = \begin{cases} \left[ C_{Fe,out}^{1-\eta e^{-\zeta h}} + \dfrac{\alpha L}{e^{\frac{\beta}{T}}} (1 - \eta e^{-\zeta h}) \left[ \dfrac{3b^2\mu}{Q^2\rho \frac{g}{g_c} \sin\theta} \right]^{\frac{1}{3}} \right]^{\frac{1}{1-\eta e^{-\zeta h}}} & \eta e^{-\zeta h} \neq 1 \\ \mathrm{EXP}\left[ \ln(C_{Fe,out}) - \dfrac{\alpha L}{e^{\frac{\beta}{T}}} \left[ \dfrac{3b^2\mu}{Q^2\rho \frac{g}{g_c} \sin\theta} \right]^{\frac{1}{3}} \right] & \eta e^{-\zeta h} = 1 \end{cases} \tag{16}$$

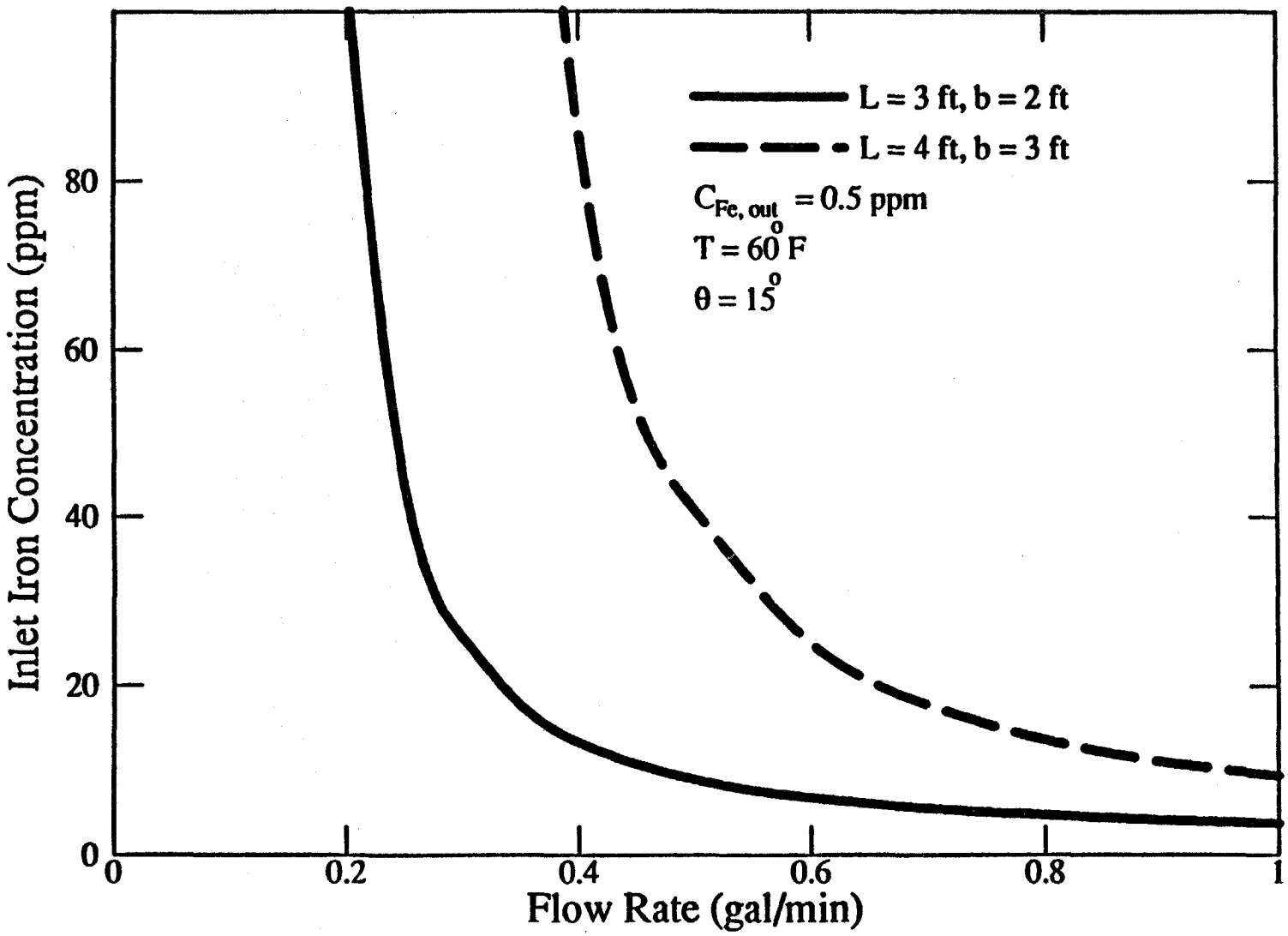


Figure 8.7. Example of Predicting Inlet Iron Concentration

Equation (16) is used for estimating the maximum inlet iron concentration after the thickness of brine film is calculated using Equation (2).

Figure 8.7 shows the example calculation of the maximum inlet iron concentration. Two curves in the figure represent two different sizes of aeration unit. The shape of the two curves is very similar in that each of the curves consists of two straight lines, one near vertical and one close to horizontal. It indicates that there is a critical point which separates two distinguish regimes. In the first regime (the segment near vertical), the thickness of brine film over the aeration unit is a dominant factor of the treatment process. As the flow rate (hence the thickness of the film) increases, the maximum iron concentration that the given aeration unit can handle decreases sharply. It is easy to understand that the larger unit should have a higher critical point, since at the same flow rate, the thickness of the film over the larger unit is much smaller than that over the smaller one. When the thickness of brine film is greater than the critical point (the segment of the curve close to horizontal), the thickness of the film does not have much effect on the treatment process. Therefore, the capability of handling the maximum iron concentration does not change significantly with flow rate. Needless to say, the efficiency of the treatment is very low in the later case.

## 8.7 - Maximum Flow Rate

Quite commonly one may need to determine the maximum flow rate an existing facility can handle and still remove iron effectively. The following equation should be used for this purpose.

$$Q = \begin{cases} b\left[\dfrac{3\mu}{\rho\dfrac{g}{g_c}\sin\theta}\right]^{\frac{1}{2}}\left[\dfrac{\alpha L}{e^{\frac{\beta}{T}}}\dfrac{1-\eta e^{-\zeta h}}{C_{Fe,in}^{1-\eta e^{-\zeta h}} - C_{Fe,out}^{1-\eta e^{-\zeta h}}}\right]^{\frac{3}{2}} & \eta e^{-\zeta h} \neq 1 \\ b\left[\dfrac{3\mu}{\rho\dfrac{g}{g_c}\sin\theta}\right]^{\frac{1}{2}}\left[\dfrac{\alpha L}{e^{\frac{\beta}{T}}}\dfrac{1}{\ln(C_{Fe,in}) - \ln(C_{Fe,out})}\right]^{\frac{3}{2}} & \eta e^{-\zeta h} = 1 \end{cases} \tag{17}$$

In order to determine the maximum flow rate, one must specify all the variables in the right side of Equation (17). However, the calculation of maximum flow rate involves an iteration procedure. This is because that the calculation of brine film thickness (Equation 2) requires the specification of flow rate and the flow rate is unknown in this case. The iteration procedure starts with an initial value of flow rate (0.2 gal/min in the software). Then use Equations (2) and (17) alternatively until the flow rate converges. It was found out during testing the program that this iteration procedure may not always converge. In some cases, the value of the calculated flow rate could jump between two values forming a repeating circle during the iterations. To solve this problem, a section of program was added to the software. It will monitor the convergency during the iterations. Once the calculated flow rates form a two-number circle, the average value of the two numbers will be used as an initial value to restart the iteration procedure. This new procedure has been tested extensively and no convergency problem ever happened. The iteration procedure is very effective. It usually takes only several iterations to converge. Figure 8.8 shows the example of predicting the maximum flow rate. Again, two aeration units are considered. As indicated by the curves in the figure, the larger unit can handle almost twice flow rate as the smaller one with same inlet and outlet iron concentration. The maximum flow rate that a given aeration unit can handle increases gradu-

ally with the outlet iron concentration. However, it is expected that the increase of flow rate will be more sharply as the outlet concentration continuously to increase, since the flow rate will go to infinity as the outlet concentration is close or equal to the inlet iron concentration (Equation 17).

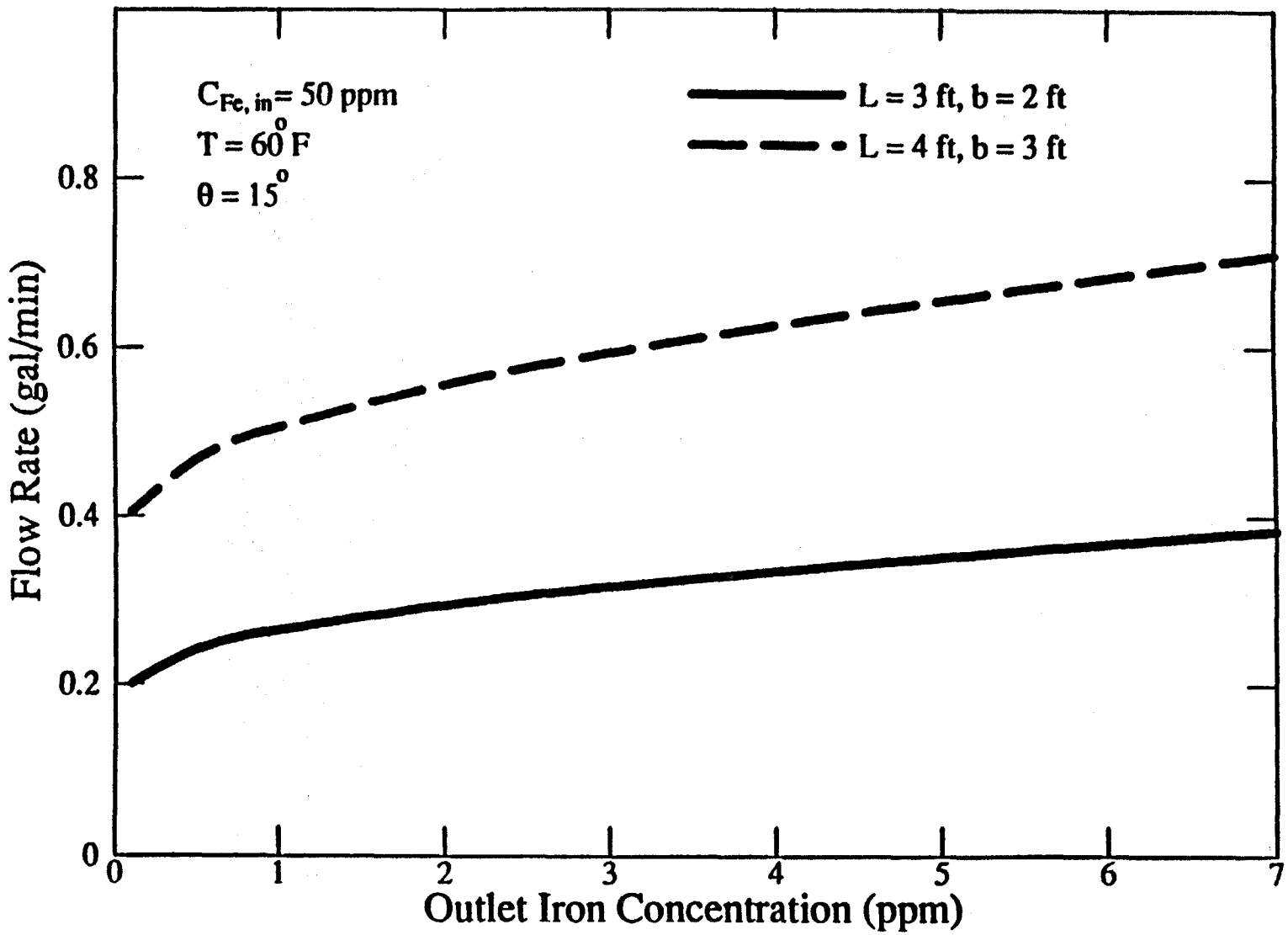


Figure 8.8. Example of Predicting Flow Rate

## Conclusions

Extensive experimental studies, conducted using laboratory and field-based prototype models, indicated that the proposed brine treatment system is capable of removing heavy metals such as iron from the brine. Using Laboratory-base model, the efficacy of the treatment process was tested by varying a number of parameters. Conducted parametric studies led to conclusive results on the effect of flow rate, inlet iron concentration, aeration angle, number of limestone columns, sand thickness and temperature on the treatment process. The results of the experimental studies in laboratory were indicative of a very high efficiency of the process in removing iron from the synthetic brine (100% removal at 1 bbl/d and 92% at 2 bbl/d). Additional experimental work has indicated that the proposed treatment process is able to remove other heavy metals such as copper and aluminum as well.

Experimental work, using field-based model and actual brine, were basically indicative of the same results of that obtained in the laboratory. Five different brines collected from the Western and Central part of Pennsylvania were used for these experiments. The field-based prototype model was constructed to treat the brine for one barrel per day. However, the results of the experimental work on the field showed significant reduction of iron up to 16.5 bbl/d.

Experimental work, using a mobile treatment unit, led to more detailed results regarding the proposed treatment's capability in removal of organics and inorganics in actual brine. These results were indicative of high performance in removal of organics and heavy metals such as iron.

The framework for the process model was initiated by comprehensive laboratory studies on the critical pH and kinetics of elements such as aluminum, copper,

iron, lead, and zinc. Kinetics studies included the single, binary, and multi-element kinetics. Gathered results in these studies were used in a data-base for the development of the software package.

A comprehensive mathematical model, for simulating the treatment process, was developed. The experimental data collected from the laboratory and field studies were incorporated to verify the validity of the developed model. With the aim of the collected data and try-and-error method the necessary constants for the model were obtained.

Based on the results we have achieved so far, a software for brine treatment facility design was developed. This software (BRINE.EXE) could be executed on a personal computer with DOS environment. The software as it stands now can be used to design the necessary size of the facility for the treatment of a specific brine.

Based on this study, the efficiency of the treatment process, both in the laboratory and field conditions, was found to be satisfactory and promising. This study can be used as the framework for further investigations on the efficacy of this process on the removal of the other contaminants. The developed brine treatment process could potentially be considered as an alternative system with high efficiency and low maintenance costs for treating brine.

## Appendix A

# Detail Results of Conducted Experiments

TABLE 1. Effect of flow rate and inlet concentration on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.25 | 50.73 | 50.38 | 49.70 | 50.68 | 50.44 | 50.15 | 50.14 | 50.51 |
| EXIT1 | 41.72 | 49.00 | 48.02 | 49.73 | 50.19 | 50.02 | 50.98 | 50.854 | 49.18 |
| EXIT2 | 41.49 | 47.79 | 47.57 | 48.20 | 48.57 | 50.32 | 51.61 | 49.08 | 47.77 |
| EXIT3 | | | | | 45.92 | 48.18 | 46.20 | 47.38 | 48.30 |
| EXIT4 | | | | | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 |

| Fe II | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.10 | 50.28 | 50.72 | 48.97 | 50.54 | 49.30 | 50.12 | 50.18 | 49.92 |
| EXIT1 | 40.06 | 47.78 | 47.72 | 49.54 | 49.86 | 49.32 | 49.04 | 49.84 | 48.18 |
| EXIT2 | 40.30 | 47.22 | 46.40 | 47.08 | 46.46 | 48.94 | 48.14 | 47.40 | 46.54 |
| EXIT3 | | | | | 35.20 | 36.22 | 37.20 | 38.52 | 39.02 |
| EXIT4 | | | | | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 |

| pH | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.91 | 1.90 | 1.88 | 1.90 | 1.90 | 1.89 | 1.88 | 1.90 | 1.90 |
| EXIT1 | 6.24 | 6.17 | 6.18 | 6.20 | 6.20 | 6.19 | 6.18 | 6.20 | 6.18 |
| EXIT2 | 6.30 | 6.33 | 6.40 | 6.32 | 6.32 | 6.23 | 6.28 | 6.21 | 6.25 |
| EXIT3 | | | | | 6.10 | 6.08 | 6.11 | 6.03 | 6.05 |
| EXIT4 | | | | | 7.44 | 7.26 | 7.18 | 7.26 | 7.25 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 2.163 BBL/DAY
TEMPERATURE = 76° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 2. Effect of flow rate and inlet concentration on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 97.06 | 98.08 | 97.21 | 99.90 | 96.36 | 101.77 | 99.24 | 100.16 | 96.38 |
| EXIT1 | 85.41 | 91.77 | 93.50 | 97.68 | 93.55 | 100.61 | 93.50 | 93.23 | 95.05 |
| EXIT2 | 83.36 | 90.41 | 91.67 | 93.97 | 95.96 | 92.47 | 93.40 | 93.81 | 91.48 |
| EXIT3 | | | | | 88.99 | 89.06 | 92.77 | 89.68 | 90.82 |
| EXIT4 | | | | | < 0.50 | 0.51 | < 0.50 | < 0.50 | 0.59 |

| Fe II | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 92.56 | 93.44 | 93.92 | 92.48 | 92.60 | 98.60 | 92.20 | 93.80 | 92.20 |
| EXIT1 | 84.2 | 90.20 | 94.30 | 93.00 | 93.00 | 93.00 | 92.00 | 93.40 | 90.60 |
| EXIT2 | 81.40 | 86.6 | 93.40 | 92.80 | 93.00 | 93.80 | 93.20 | 92.00 | 90.80 |
| EXIT3 | | | | | 78.00 | 81.20 | 82.40 | 82.40 | 83.80 |
| EXIT4 | | | | | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 |

| pH | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.78 | 1.77 | 1.77 | 1.78 | 1.76 | 1.78 | 1.76 | 1.77 | 1.77 |
| EXIT1 | 6.03 | 6.04 | 6.04 | 6.04 | 6.03 | 6.03 | 6.02 | 6.01 | 6.03 |
| EXIT2 | 6.30 | 6.32 | 6.25 | 6.29 | 6.22 | 6.12 | 6.14 | 6.18 | 6.30 |
| EXIT3 | | | | | 5.95 | 6.02 | 6.10 | 6.00 | 6.08 |
| EXIT4 | | | | | 7.46 | 7.31 | 7.28 | 7.16 | 7.12 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 2.032 BBL/DAY
TEMPERATURE = 69° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 3. Effect of flow rate and inlet concentration on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 153.20 | 152.95 | 155.94 | 155.97 | 155.03 | 153.14 | 155.42 | 155.45 | 155.18 |
| EXIT1 | 145.27 | 151.41 | 153.58 | 150.75 | 153.77 | 152.92 | 155.28 | 156.63 | 152.60 |
| EXIT2 | 142.07 | 152.58 | 151.03 | 153.14 | 152.88 | 153.03 | 152.56 | 154.23 | 152.30 |
| EXIT3 | | | | | 145.18 | 147.78 | 148.90 | 151.09 | 150.25 |
| EXIT4 | | | | | 1.72 | 3.52 | 4.12 | 4.80 | 5.58 |

| Fe II | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 150.88 | 152.68 | 152.40 | 152.80 | 154.00 | 153.26 | 154.00 | 152.40 | 155.20 |
| EXIT1 | 142.00 | 151.72 | 152.00 | 152.00 | 152.80 | 154.06 | 153.20 | 155.20 | 154.04 |
| EXIT2 | 142.04 | 150.40 | 152.00 | 151.20 | 152.80 | 154.29 | 153.60 | 154.00 | 152.80 |
| EXIT3 | | | | | 137.6 | 141.60 | 145.80 | 147.30 | 148.70 |
| EXIT4 | | | | | 1.60 | 3.42 | 4.00 | 4.80 | 5.28 |

| pH | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.87 | 1.99 | 1.88 | 1.85 | 1.88 | 1.89 | 1.90 | 1.89 | 1.88 |
| EXIT1 | 5.93 | 5.89 | 5.92 | 5.93 | 5.93 | 5.90 | 5.90 | 5.89 | 5.85 |
| EXIT2 | 6.00 | 5.92 | 6.04 | 6.09 | 6.04 | 6.00 | 5.96 | 5.95 | 5.96 |
| EXIT3 | | | | | 5.84 | 5.85 | 5.83 | 5.82 | 5.87 |
| EXIT4 | | | | | 6.80 | 6.73 | 6.70 | 6.70 | 6.65 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 2.026 BBL/DAY
TEMPERATURE = 74° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 4. Effect of flow rate and inlet concentration on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 184.30 | 179.93 | 180.04 | 187.71 | 189.75 | 190.51 | 192.02 | 189.22 | 188.46 |
| EXIT1 | 173.92 | 174.89 | 176.40 | 183.40 | 184.80 | 178.77 | 187.17 | 187.06 | 187.92 |
| EXIT2 | 164.77 | 168.85 | 169.94 | 178.98 | 180.28 | 175.43 | 186.09 | 186.20 | 184.80 |
| EXIT3 | | | | | 175.22 | 172.95 | 180.63 | 175.43 | 182.00 |
| EXIT4 | | | | | 6.20 | 13.91 | 11.32 | 16.48 | 21.13 |

| Fe II | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 175.12 | 177.60 | 178.24 | 180.00 | 180.00 | 181.60 | 179.20 | 178.00 | 182.10 |
| EXIT1 | 162.00 | 172.80 | 176.80 | 177.6 | 174.80 | 181.20 | 179.60 | 178.30 | 180.30 |
| EXIT2 | 160.40 | 168.80 | 164.40 | 176.40 | 169.20 | 178.40 | 164.80 | 177.30 | 178.50 |
| EXIT3 | | | | | 152.40 | 157.20 | 160.40 | 163.20 | 164.80 |
| EXIT4 | | | | | 4.40 | 12.40 | 10.00 | 15.20 | 19.12 |

| pH | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:30 | TIME 3:30 | TIME 4:30 | TIME 5:30 | TIME 6:30 | TIME 7:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 2.18 | 2.20 | 2.15 | 2.15 | 2.14 | 2.16 | 2.14 | 2.15 | 2.14 |
| EXIT1 | 5.95 | 5.93 | 5.99 | 5.91 | 5.93 | 5.99 | 5.95 | 5.95 | 5.95 |
| EXIT2 | 6.00 | 6.07 | 6.03 | 6.02 | 6.04 | 6.06 | 6.03 | 6.01 | 6.02 |
| EXIT3 | | | | | 5.72 | 5.82 | 5.89 | 5.89 | 5.92 |
| EXIT4 | | | | | 6.98 | 6.74 | 6.67 | 6.62 | 6.60 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 2.012 BBL/DAY
TEMPERATURE = 69° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 5. Effect of flow rate, inlet concentration, and limestone column on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.35 | 50.60 | 50.55 | 50.02 | 51.02 | 50.46 | 52.26 | 50.32 | 50.63 |
| EXIT1 | 46.32 | 49.07 | 49.05 | 49.73 | 49.10 | 50.19 | 49.63 | 47.87 | 47.12 |
| EXIT2 | 46.46 | 48.66 | 48.83 | 49.06 | 48.87 | 49.10 | 49.53 | 47.70 | 47.21 |
| EXIT3 | | | 40.85 | 41.12 | 42.03 | 42.85 | 41.33 | 41.67 | 41.71 |
| EXIT4 | | | 18.14 | 23.14 | 23.38 | 24.16 | 22.69 | 21.66 | 20.92 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 49.93 | 49.82 | 49.71 | 49.61 | 49.82 | 49.71 | 49.40 | 49.18 | 49.40 |
| EXIT1 | 46.32 | 49.19 | 49.09 | 49.29 | 49.61 | 48.65 | 48.65 | 47.70 | 46.96 |
| EXIT2 | 46.85 | 48.18 | 48.08 | 49.01 | 48.55 | 48.12 | 47.70 | 478.38 | 46.85 |
| EXIT3 | | | 40.70 | 40.70 | 38.80 | 40.92 | 40.92 | 41.02 | 40.60 |
| EXIT4 | | | 18.02 | 23.11 | 22.47 | 23.45 | 22.49 | 21.41 | 20.73 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.92 | 1.93 | 1.92 | 1.94 | 1.93 | 1.93 | 1.92 | 1.93 | 1.93 |
| EXIT1 | 5.78 | 5.72 | 5.80 | 5.78 | 5.78 | 5.79 | 5.78 | 5.78 | 5.79 |
| EXIT2 | 6.01 | 5.82 | 6.04 | 6.04 | 5.96 | 5.95 | 5.98 | 5.95 | 5.93 |
| EXIT3 | | | 6.08 | 6.05 | 6.01 | 6.00 | 6.01 | 5.99 | 5.99 |
| EXIT4 | | | 6.21 | 6.08 | 6.05 | 6.02 | 5.98 | 5.96 | 5.97 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.00 BBL/DAY
TEMPERATURE = 71° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 6. Effect of flow rate, inlet concentration, and limestone column on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 100.18 | 100.29 | 100.67 | 99.71 | 99.07 | 98.12 | 99.94 | 99.32 | 97.24 |
| EXIT1 | 87.16 | 95.97 | 95.14 | 93.41 | 92.42 | 91.55 | 91.88 | 91.65 | 88.40 |
| EXIT2 | 93.40 | 95.00 | 93.12 | 93.09 | 90.42 | 91.57 | 92.51 | 91.57 | 88.23 |
| EXIT3 | | | 78.44 | 81.67 | 83.89 | 92.79 | 83.34 | 85.23 | 83.03 |
| EXIT4 | | | 40.73 | 45.62 | 47.24 | 50.42 | 49.28 | 47.70 | 48.38 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 94.76 | 96.46 | 96.25 | 96.46 | 96.46 | 96.04 | 96.25 | 96.25 | 96.25 |
| EXIT1 | 86.28 | 93.07 | 93.49 | 93.49 | 92.86 | 92.22 | 92.22 | 92.01 | 89.46 |
| EXIT2 | 91.38 | 92.86 | 91.80 | 92.43 | 92.01 | 91.58 | 90.52 | 89.25 | 88.40 |
| EXIT3 | | | 78.02 | 80.56 | 81.62 | 90.23 | 82.47 | 81.83 | 81.62 |
| EXIT4 | | | 40.49 | 46.22 | 47.98 | 50.03 | 49.82 | 47.91 | 47.49 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.97 | 1.96 | 1.96 | 1.95 | 1.96 | 1.97 | 1.96 | 1.96 | 1.96 |
| EXIT1 | 5.75 | 5.77 | 5.78 | 5.77 | 5.75 | 5.72 | 5.74 | 5.74 | 5.74 |
| EXIT2 | 5.95 | 5.98 | 5.92 | 5.88 | 5.90 | 5.83 | 5.92 | 5.92 | 5.89 |
| EXIT3 | | | 5.94 | 5.90 | 5.90 | 5.90 | 5.91 | 5.90 | 5.91 |
| EXIT4 | | | 5.90 | 5.80 | 5.74 | 5.70 | 5.68 | 5.66 | 5.65 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.00 BBL/DAY
TEMPERATURE = 70° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 7. Effect of flow rate, inlet concentration, and limestone column on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 146.05 | 147.48 | 148.00 | 152.99 | 152.83 | 151.48 | 146.29 | 149.67 | 150.52 |
| EXIT1 | 128.56 | 144.34 | 147.67 | 150.99 | 151.82 | 147.75 | 143.87 | 144.53 | 149.19 |
| EXIT2 | 125.46 | 142.20 | 146.06 | 152.35 | 147.39 | 144.27 | 140.61 | 142.61 | 147.04 |
| EXIT3 | | | 130.12 | 136.58 | 135.80 | 134.65 | 133.23 | 134.20 | 137.37 |
| EXIT4 | | | 92.88 | 91.87 | 93.40 | 93.13 | 93.82 | 97.11 | 102.30 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 142.04 | 142.46 | 146.28 | 145.43 | 145.01 | 145.86 | 144.58 | 144.16 | 149.25 |
| EXIT1 | 125.50 | 142.04 | 144.58 | 144.58 | 144.58 | 144.59 | 143.74 | 142.04 | 142.89 |
| EXIT2 | 126.78 | 141.62 | 143.74 | 142.89 | 140.34 | 143.31 | 141.19 | 142.04 | 143.31 |
| EXIT3 | | | 128.47 | 129.32 | 131.44 | 131.44 | 131.02 | 132.71 | 133.56 |
| EXIT4 | | | 89.89 | 89.04 | 91.16 | 92.86 | 94.13 | 95.15 | 97.52 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.95 | 1.97 | 1.98 | 1.97 | 1.97 | 1.97 | 1.99 | 1.97 | 1.98 |
| EXIT1 | 5.74 | 5.71 | 5.67 | 5.65 | 5.65 | 5.66 | 5.65 | 5.65 | 5.65 |
| EXIT2 | 5.89 | 5.90 | 5.77 | 5.77 | 5.72 | 5.75 | 5.856 | 5.82 | 5.83 |
| EXIT3 | | | 5.81 | 5.81 | 5.79 | 5.78 | 5.80 | 5.78 | 5.80 |
| EXIT4 | | | 5.55 | 5.45 | 5.44 | 5.43 | 5.44 | 5.42 | 5.38 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.00 BBL/DAY
TEMPERATURE = 70° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 8. Effect of flow rate, inlet concentration, and limestone column on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 200.99 | 199.15 | 201.20 | 203.36 | 198.79 | 199.59 | 198.85 | 200.90 | 202.79 |
| EXIT1 | 177.09 | 198.45 | 198.28 | 191.56 | 194.81 | 196.52 | 197.97 | 192.05 | 198.87 |
| EXIT2 | 177.00 | 194.71 | 194.39 | 193.29 | 191.84 | 193.57 | 197.42 | 193.36 | 197.50 |
| EXIT3 | | | 191.10 | 190.95 | 191.13 | 193.02 | 195.59 | 192.51 | 193.52 |
| EXIT4 | | | 101.89 | 124.80 | 136.29 | 138.74 | 145.24 | 149.17 | 148.83 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 194.46 | 196.98 | 198.66 | 199.58 | 198.24 | 197.82 | 198.24 | 199.08 | 200.02 |
| EXIT1 | 176.82 | 196.98 | 199.92 | 197.40 | 197.82 | 198.24 | 197.40 | 197.40 | 199.60 |
| EXIT2 | 178.92 | 195.72 | 194.04 | 196.14 | 197.40 | 187.74 | 195.30 | 197.40 | 195.82 |
| EXIT3 | | | 162.96 | 178.92 | 182.70 | 183.12 | 186.06 | 185.22 | 187.90 |
| EXIT4 | | | 101.64 | 128.10 | 137.34 | 141.54 | 144.90 | 145.74 | 147.00 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.96 | 1.95 | 1.95 | 1.96 | 1.95 | 1.96 | 1.96 | 1.97 | 1.95 |
| EXIT1 | 5.70 | 5.71 | 5.69 | 5.69 | 5.62 | 5.64 | 5.63 | 5.64 | 5.60 |
| EXIT2 | 5.89 | 5.85 | 5.83 | 5.84 | 5.80 | 5.81 | 5.78 | 5.78 | 5.77 |
| EXIT3 | | | 5.76 | 5.80 | 5.78 | 5.78 | 5.74 | 5.74 | 5.71 |
| EXIT4 | | | 5.62 | 5.50 | 5.43 | 5.40 | 5.38 | 5.36 | 5.32 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.00 BBL/DAY
TEMPERATURE = 72° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 9. Effect of flow rate and inlet concentration on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.15 | 48.28 | 48.43 | 48.90 | 48.80 | 49.50 | 51.36 | 50.04 | 51.74 |
| EXIT1 | 41.28 | 46.89 | 48.17 | 48.88 | 48.72 | 49.28 | 50.97 | 50.51 | 50.44 |
| EXIT2 | 42.83 | 46.00 | 47.92 | 48.30 | 48.74 | 48.88 | 49.72 | 49.23 | 50.07 |
| EXIT3 | | | | 44.75 | 47.55 | 45.81 | 47.69 | 48.66 | 48.05 |
| EXIT4 | | | | 27.38 | 28.59 | 29.98 | 31.20 | 32.44 | 32.06 |

| Fe II | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 36.18 | 46.63 | 46.74 | 46.63 | 46.74 | 49.11 | 48.14 | 48.24 | 49.32 |
| EXIT1 | 31.77 | 45.55 | 46.74 | 46.95 | 47.49 | 48.03 | 48.14 | 48.24 | 48.78 |
| EXIT2 | 30.26 | 45.12 | 46.52 | 47.17 | 47.38 | 47.60 | 47.81 | 47.17 | 48.03 |
| EXIT3 | | | | 38.98 | 40.28 | 41.89 | 43.38 | 43.72 | 43.78 |
| EXIT4 | | | | 26.17 | 26.60 | 28.21 | 29.83 | 30.80 | 30.28 |

| pH | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 2.16 | 2.16 | 2.15 | 2.16 | 2.16 | 2.15 | 2.16 | 2.16 | 2.15 |
| EXIT1 | 5.97 | 5.78 | 5.75 | 5.75 | 5.74 | 5.75 | 5.75 | 5.77 | 5.74 |
| EXIT2 | 5.97 | 5.95 | 5.95 | 5.94 | 5.93 | 5.95 | 5.96 | 5.92 | 5.93 |
| EXIT3 | | | | 5.98 | 5.97 | 5.98 | 5.95 | 5.91 | 5.91 |
| EXIT4 | | | | 6.25 | 6.16 | 6.10 | 6.04 | 5.90 | 5.88 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 4.01 BBL/DAY
TEMPERATURE = 70° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS =2.5 INCHES

TABLE 10. Effect of flow rate and inlet concentration on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 97.47 | 99.75 | 100.34 | 96.33 | 97.82 | 98.34 | 98.37 | 97.00 | 97.56 |
| EXIT1 | 91.32 | 99.54 | 99.78 | 94.35 | 98.42 | 96.93 | 97.80 | 96.79 | 96.11 |
| EXIT2 | 88.50 | 98.08 | 97.15 | 93.43 | 96.98 | 94.71 | 95.66 | 96.99 | 94.82 |
| EXIT3 | | | | 81.67 | 86.95 | 86.59 | 87.07 | 84.78 | 87.14 |
| EXIT4 | | | | 46.08 | 60.00 | 59.50 | 59.00 | 58.88 | 60.55 |

| Fe II | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 96.28 | 95.64 | 95.85 | 95.72 | 97.34 | 97.77 | 96.70 | 96.28 | 95.85 |
| EXIT1 | 89.25 | 94.36 | 95.85 | 95.85 | 96.28 | 95.42 | 96.06 | 96.06 | 95.64 |
| EXIT2 | 85.63 | 93.93 | 94.79 | 93.21 | 95.42 | 94.79 | 94.28 | 95.85 | 93.72 |
| EXIT3 | | | | 80.94 | 84.14 | 86.90 | 86.40 | 84.76 | 87.54 |
| EXIT4 | | | | 43.45 | 57.72 | 58.36 | 58.58 | 58.15 | 59.21 |

| pH | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 2.02 | 2.05 | 2.03 | 2.04 | 2.05 | 2.03 | 2.02 | 2.03 | 2.02 |
| EXIT1 | 5.76 | 5.82 | 5.84 | 5.81 | 5.77 | 5.73 | 5.74 | 5.75 | 5.73 |
| EXIT2 | 6.03 | 6.04 | 6.04 | 5.96 | 5.93 | 5.90 | 5.86 | 5.84 | 5.84 |
| EXIT3 | | | | 5.98 | 5.92 | 5.91 | 5.91 | 5.90 | 5.90 |
| EXIT4 | | | | 6.12 | 5.82 | 5.76 | 5.72 | 5.72 | 5.69 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 4.01 BBL/DAY
TEMPERATURE = 70° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 11. Effect of flow rate and inlet concentration on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 150.71 | 150.76 | 148.80 | 150.73 | 148.81 | 150.76 | 147.69 | 148.62 | 152.88 |
| EXIT1 | 136.15 | 145.10 | 147.68 | 146.30 | 149.36 | 145.10 | 145.40 | 146.52 | 151.88 |
| EXIT2 | 140.69 | 143.42 | 144.00 | 146.47 | 144.67 | 144.20 | 143.45 | 142.61 | 146.45 |
| EXIT3 | | | | 137.59 | 138.06 | 140.73 | 137.15 | 136.74 | 139.59 |
| EXIT4 | | | | 105.81 | 119.26 | 117.04 | 119.15 | 117.18 | 122.33 |

| Fe II | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 147.84 | 149.06 | 148.80 | 148.80 | 148.00 | 149.88 | 146.80 | 147.29 | 149.88 |
| EXIT1 | 135.21 | 146.00 | 147.60 | 147.60 | 146.00 | 146.40 | 145.32 | 146.00 | 147.36 |
| EXIT2 | 140.40 | 144.04 | 143.00 | 143.00 | 144.60 | 143.60 | 140.60 | 140.32 | 145.20 |
| EXIT3 | | | | 135.60 | 139.20 | 140.00 | 137.60 | 135.00 | 137.00 |
| EXIT4 | | | | 104.00 | 114.80 | 118.00 | 119.20 | 118.00 | 119.20 |

| pH | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 2.00 | 2.01 | 2.00 | 1.99 | 2.00 | 2.01 | 2.00 | 2.00 | 2.00 |
| EXIT1 | 5.50 | 5.55 | 5.55 | 5.55 | 5.50 | 5.49 | 5.47 | 5.50 | 5.49 |
| EXIT2 | 5.72 | 5.75 | 5.75 | 5.68 | 5.72 | 5.67 | 5.56 | 5.64 | 5.60 |
| EXIT3 | | | | 5.76 | 5.73 | 5.71 | 5.68 | 5.68 | 5.68 |
| EXIT4 | | | | 5.78 | 5.66 | 5.62 | 5.59 | 5.54 | 5.54 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 4.01 BBL/DAY
TEMPERATURE = 69° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 12. Effect of flow rate and inlet concentration on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 199.43 | 197.15 | 196.72 | 197.60 | 203.50 | 204.41 | 200.64 | 197.01 | 202.19 |
| EXIT1 | 196.62 | 196.40 | 191.66 | 196.74 | 201.93 | 203.62 | 198.48 | 196.61 | 201.87 |
| EXIT2 | 190.00 | 182.61 | 186.28 | 192.00 | 198.38 | 196.08 | 195.98 | 194.57 | 201.30 |
| EXIT3 | | | | 187.36 | 193.25 | 191.56 | 192.94 | 191.94 | 191.78 |
| EXIT4 | | | | 150.13 | 154.84 | 170.36 | 156.75 | 171.25 | 176.23 |

| Fe II | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 197.38 | 196.18 | 195.22 | 197.46 | 197.85 | 197.85 | 196.56 | 195.69 | 197.42 |
| EXIT1 | 194.41 | 194.26 | 194.93 | 193.16 | 196.13 | 196.99 | 195.69 | 195.26 | 196.56 |
| EXIT2 | 190.36 | 188.83 | 186.32 | 190.73 | 194.40 | 196.77 | 194.83 | 194.83 | 194.83 |
| EXIT3 | | | | 187.49 | 189.21 | 188.78 | 190.51 | 190.94 | 190.51 |
| EXIT4 | | | | 149.47 | 149.20 | 155.09 | 156.23 | 162.43 | 166.32 |

| pH | TIME 0:30 | TIME 1:00 | TIME 1:30 | TIME 2:00 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 2.08 | 2.07 | 2.08 | 2.08 | 2.08 | 2.05 | 2.08 | 2.08 | 2.08 |
| EXIT1 | 5.53 | 5.54 | 5.53 | 5.54 | 5.52 | 5.50 | 5.51 | 5.50 | 5.52 |
| EXIT2 | 5.72 | 5.73 | 5.70 | 5.68 | 5.63 | 5.56 | 5.58 | 5.55 | 5.58 |
| EXIT3 | | | | 5.71 | 5.70 | 5.68 | 5.67 | 5.68 | 5.65 |
| EXIT4 | | | | 5.55 | 5.52 | 5.49 | 5.46 | 5.42 | 4.38 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE SOLID SEPARATOR
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 4.01 BBL/DAY
TEMPERATURE = 70° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 13. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 51.49 | 50.58 | 51.07 | 50.85 | 51.05 | 50.86 | 51.38 | 49.68 | 49.30 |
| EXIT1 | 50.91 | 50.06 | 50.85 | 51.53 | 50.58 | 50.00 | 51.30 | 48.46 | 49.43 |
| EXIT2 | 32.83 | 46.85 | 49.13 | 48.86 | 48.63 | 49.35 | 47.82 | 45.55 | 45.93 |
| EXIT3 | 35.92 | 44.45 | 45.81 | 46.82 | 48.38 | 46.07 | 44.93 | 43.62 | 43.91 |
| EXIT4 | | | 40.90 | 38.48 | 45.38 | 47.66 | 44.11 | 44.42 | 44.58 |
| EXIT5 | | | 17.92 | 22.58 | 21.94 | 21.81 | 19.65 | 18.78 | 17.38 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.10 | 49.50 | 49.50 | 49.44 | 49.60 | 49.50 | 49.80 | 49.60 | 49.20 |
| EXIT1 | 47.90 | 50.50 | 50.10 | 50.80 | 50.80 | 49.13 | 49.10 | 49.24 | 49.36 |
| EXIT2 | 30.50 | 48.10 | 49.30 | 48.90 | 47.90 | 47.10 | 47.80 | 48.00 | 46.90 |
| EXIT3 | 36.00 | 47.10 | 47.60 | 46.60 | 46.30 | 44.50 | 46.90 | 46.30 | 45.50 |
| EXIT4 | | | 40.60 | 38.28 | 40.10 | 40.40 | 41.10 | 40.20 | 39.20 |
| EXIT5 | | | 16.90 | 22.00 | 21.60 | 21.00 | 19.00 | 18.70 | 17.40 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.85 | 1.84 | 1.85 | 1.85 | 1.85 | 1.85 | 1.84 | 1.85 | 1.85 |
| EXIT1 | 5.65 | 5.56 | 5.50 | 5.51 | 5.52 | 5.53 | 5.52 | 5.52 | 5.52 |
| EXIT2 | 6.04 | 5.99 | 5.98 | 5.96 | 5.97 | 6.00 | 5.99 | 6.00 | 6.01 |
| EXIT3 | 6.36 | 6.32 | 6.34 | 6.30 | 6.32 | 6.32 | 6.36 | 6.38 | 6.38 |
| EXIT4 | | | 6.28 | 6.29 | 6.32 | 6.28 | 6.32 | 6.32 | 6.35 |
| EXIT5 | | | 6.75 | 6.52 | 6.47 | 6.42 | 6.36 | 6.33 | 6.30 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.00 BBL/DAY
TEMPERATURE = 72° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 14. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 94.41 | 94.41 | 94.49 | 96.34 | 92.31 | 96.44 | 94.46 | 94.79 | 94.85 |
| EXIT1 | 84.47 | 94.42 | 93.78 | 93.25 | 91.68 | 94.46 | 92.85 | 92.63 | 90.73 |
| EXIT2 | 65.58 | 90.03 | 90.35 | 92.37 | 87.64 | 92.03 | 89.87 | 86.82 | 87.19 |
| EXIT3 | 63.68 | 81.84 | 83.09 | 85.16 | 79.77 | 83.43 | 81.07 | 82.21 | 81.16 |
| EXIT4 | | | 70.63 | 71.88 | 74.77 | 82.85 | 84.21 | 80.02 | 77.93 |
| EXIT5 | | | 8.85 | 19.43 | 22.75 | 23.85 | 24.10 | 24.33 | 27.14 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 93.80 | 93.80 | 94.00 | 93.60 | 93.20 | 94.00 | 93.60 | 94.00 | 94.00 |
| EXIT1 | 84.00 | 93.60 | 94.60 | 94.00 | 91.38 | 93.20 | 92.60 | 92.20 | 90.40 |
| EXIT2 | 64.80 | 90.00 | 91.80 | 90.96 | 90.40 | 90.20 | 89.40 | 88.40 | 87.20 |
| EXIT3 | 63.60 | 80.00 | 82.40 | 84.60 | 80.13 | 82.40 | 80.72 | 81.36 | 80.00 |
| EXIT4 | | | 55.80 | 53.80 | 58.20 | 61.40 | 62.66 | 62.20 | 61.00 |
| EXIT5 | | | 9.40 | 20.00 | 22.40 | 24.00 | 24.00 | 23.60 | 26.30 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.98 | 1.98 | 1.98 | 1.97 | 1.98 | 1.98 | 1.98 | 1.97 | 1.98 |
| EXIT1 | 5.74 | 5.72 | 5.71 | 5.70 | 5.67 | 5.65 | 5.68 | 5.67 | 5.68 |
| EXIT2 | 6.14 | 6.16 | 6.16 | 6.15 | 6.14 | 6.14 | 6.13 | 6.12 | 6.13 |
| EXIT3 | 6.46 | 6.50 | 6.50 | 6.48 | 6.49 | 6.49 | 6.46 | 6.44 | 6.45 |
| EXIT4 | | | 6.29 | 6.24 | 6.25 | 6.24 | 6.23 | 6.25 | 6.23 |
| EXIT5 | | | 6.39 | 6.20 | 6.12 | 6.07 | 6.03 | 6.01 | 5.98 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.00 BBL/DAY
TEMPERATURE = 71° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 15. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 143.56 | 145.82 | 145.21 | 146.74 | 146.89 | 145.61 | 146.55 | 147.66 | 148.73 |
| EXIT1 | 126.12 | 135.51 | 143.53 | 146.18 | 142.61 | 143.08 | 141.99 | 141.89 | 140.94 |
| EXIT2 | 110.40 | 135.42 | 142.60 | 143.96 | 140.98 | 140.02 | 140.92 | 138.11 | 137.33 |
| EXIT3 | 120.95 | 133.14 | 135.23 | 142.18 | 138.82 | 135.37 | 136.56 | 130.69 | 134.08 |
| EXIT4 | | | 128.03 | 129.43 | 130.13 | 134.25 | 130.32 | 130.85 | 128.16 |
| EXIT5 | | | 30.23 | 55.58 | 58.81 | 67.17 | 69.14 | 68.56 | 69.66 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 139.60 | 140.00 | 139.20 | 137.60 | 140.00 | 138.80 | 138.80 | 138.80 | 139.20 |
| EXIT1 | 120.00 | 132.20 | 140.00 | 136.00 | 134.00 | 138.80 | 138.00 | 139.20 | 137.60 |
| EXIT2 | 108.14 | 133.60 | 138.00 | 136.40 | 133.60 | 136.40 | 130.40 | 134.80 | 131.20 |
| EXIT3 | 120.00 | 131.20 | 136.00 | 136.00 | 133.60 | 134.00 | 131.60 | 131.60 | 132.00 |
| EXIT4 | | | 102.00 | 106.00 | 107.60 | 112.40 | 112.80 | 112.80 | 111.60 |
| EXIT5 | | | 30.40 | 55.20 | 57.60 | 65.20 | 62.40 | 66.40 | 68.40 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.97 | 1.98 | 1.97 | 1.97 | 1.97 | 1.96 | 1.97 | 1.97 | 1.97 |
| EXIT1 | 5.67 | 5.63 | 5.63 | 5.60 | 5.58 | 5.60 | 5.63 | 5.60 | 5.62 |
| EXIT2 | 6.75 | 6.14 | 6.12 | 6.11 | 6.09 | 6.10 | 6.10 | 6.09 | 6.10 |
| EXIT3 | 6.60 | 6.40 | 6.37 | 6.38 | 6.37 | 6.37 | 6.39 | 6.38 | 6.38 |
| EXIT4 | | | 6.24 | 6.22 | 6.20 | 6.20 | 6.22 | 6.21 | 6.20 |
| EXIT5 | | | 6.14 | 5.92 | 5.86 | 5.81 | 5.79 | 5.77 | 5.75 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.00 BBL/DAY
TEMPERATURE = 73° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 16. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 186.72 | 189.26 | 185.83 | 190.60 | 198.15 | 194.01 | 189.64 | 190.01 | 192.10 |
| EXIT1 | 170.18 | 186.98 | 182.96 | 185.85 | 194.14 | 193.87 | 187.45 | 187.91 | 190.41 |
| EXIT2 | 145.50 | 178.28 | 180.69 | 182.88 | 188.92 | 191.46 | 186.46 | 186.56 | 187.82 |
| EXIT3 | 144.98 | 172.88 | 177.92 | 180.80 | 188.23 | 187.66 | 185.02 | 183.05 | 185.29 |
| EXIT4 | | | 173.51 | 180.00 | 189.32 | 180.09 | 178.55 | 178.54 | 180.15 |
| EXIT5 | | | 63.90 | 96.72 | 100.83 | 111.11 | 111.16 | 118.46 | 115.62 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 186.00 | 185.60 | 184.00 | 188.80 | 189.60 | 189.80 | 187.20 | 186.80 | 187.20 |
| EXIT1 | 170.20 | 184.00 | 182.00 | 185.20 | 187.40 | 187.60 | 186.40 | 186.00 | 186.64 |
| EXIT2 | 145.20 | 178.80 | 180.02 | 182.60 | 183.80 | 186.60 | 184.00 | 182.40 | 184.64 |
| EXIT3 | 144.00 | 172.20 | 175.60 | 182.20 | 182.60 | 183.20 | 181.60 | 180.00 | 181.46 |
| EXIT4 | | | 153.20 | 152.48 | 155.20 | 160.80 | 163.60 | 164.00 | 163.78 |
| EXIT5 | | | 64.00 | 94.60 | 98.80 | 108.40 | 112.80 | 115.20 | 114.80 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 2.00 | 1.98 | 1.98 | 1.97 | 1.98 | 1.98 | 1.97 | 1.98 | 1.98 |
| EXIT1 | 5.64 | 5.58 | 5.54 | 5.53 | 5.54 | 5.52 | 5.48 | 5.49 | 5.50 |
| EXIT2 | 6.04 | 6.04 | 6.04 | 6.03 | 6.02 | 6.01 | 6.00 | 6.02 | 6.01 |
| EXIT3 | 6.23 | 6.29 | 6.28 | 6.29 | 6.27 | 6.26 | 6.26 | 6.24 | 6.24 |
| EXIT4 | | | 6.17 | 6.13 | 6.12 | 6.10 | 6.11 | 6.11 | 6.10 |
| EXIT5 | | | 5.77 | 5.67 | 5.63 | 5.58 | 5.55 | 5.53 | 5.50 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.00 BBL/DAY
TEMPERATURE = 71° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 17. Effect of aeration angle and retention tank on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 48.75 | 50.34 | 49.51 | 49.85 | 48.08 | 50.52 | 48.65 | 48.69 | 48.17 |
| EXIT1 | 46.18 | 48.96 | 48.76 | 47.77 | 46.81 | 50.11 | 48.58 | 47.66 | 48.03 |
| EXIT2 | 42.10 | 47.32 | 48.44 | 45.58 | 45.61 | 49.97 | 48.44 | 45.45 | 46.93 |
| EXIT3 | 40.73 | 44.28 | 46.09 | 44.45 | 45.18 | 45.99 | 45.11 | 42.93 | 44.07 |
| EXIT4 | | | 41.80 | 40.88 | 43.33 | 42.88 | 44.28 | 39.25 | 43.92 |
| EXIT5 | | | 8.07 | 12.85 | 12.89 | 14.19 | 12.38 | 11.86 | 11.92 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 48.65 | 49.27 | 48.33 | 48.13 | 48.54 | 49.27 | 48.33 | 48.39 | 48.58 |
| EXIT1 | 46.97 | 48.44 | 48.43 | 47.65 | 46.69 | 48.75 | 48.21 | 47.58 | 48.56 |
| EXIT2 | 41.89 | 46.57 | 47.71 | 47.18 | 47.23 | 48.13 | 48.75 | 47.19 | 46.09 |
| EXIT3 | 40.75 | 44.68 | 46.57 | 44.94 | 46.26 | 45.53 | 45.04 | 44.10 | 45.63 |
| EXIT4 | | | 38.98 | 35.96 | 39.08 | 35.96 | 40.33 | 36.07 | 40.64 |
| EXIT5 | | | 8.42 | 12.30 | 12.47 | 13.41 | 12.16 | 12.16 | 11.75 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.93 | 1.94 | 1.94 | 1.94 | 1.95 | 1.94 | 1.94 | 1.94 | 1.94 |
| EXIT1 | 5.72 | 5.60 | 5.55 | 5.55 | 5.54 | 5.55 | 5.54 | 5.55 | 5.54 |
| EXIT2 | 6.10 | 6.02 | 6.00 | 6.01 | 6.00 | 5.99 | 6.00 | 5.98 | 5.99 |
| EXIT3 | 6.36 | 6.32 | 6.32 | 6.31 | 6.30 | 6.30 | 6.30 | 6.29 | 6.30 |
| EXIT4 | | | 6.34 | 6.33 | 6.31 | 6.32 | 6.31 | 6.32 | 6.33 |
| EXIT5 | | | 6.81 | 6.68 | 6.50 | 6.46 | 6.42 | 6.39 | 6.38 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 71° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 18. Effect of aeration angle and retention tank on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 95.24 | 96.42 | 94.72 | 95.85 | 95.76 | 95.81 | 95.76 | 97.82 | 95.08 |
| EXIT1 | 92.37 | 96.14 | 93.91 | 95.17 | 94.72 | 94.91 | 95.06 | 96.88 | 94.56 |
| EXIT2 | 78.22 | 91.70 | 93.60 | 95.02 | 94.69 | 93.35 | 92.32 | 94.26 | 93.22 |
| EXIT3 | 76.56 | 88.66 | 89.95 | 92.68 | 89.91 | 89.32 | 89.82 | 90.81 | 90.07 |
| EXIT4 | | | 87.92 | 86.49 | 88.86 | 88.22 | 89.56 | 87.12 | 84.26 |
| EXIT5 | | | 25.22 | 32.29 | 34.44 | 37.51 | 36.40 | 38.69 | 36.80 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 95.14 | 95.97 | 95.76 | 95.55 | 95.76 | 95.76 | 96.10 | 96.80 | 95.24 |
| EXIT1 | 93.04 | 95.55 | 94.10 | 95.34 | 95.55 | 94.05 | 95.34 | 95.14 | 95.31 |
| EXIT2 | 76.40 | 91.22 | 93.45 | 94.51 | 94.85 | 93.53 | 93.42 | 93.26 | 93.53 |
| EXIT3 | 76.13 | 87.37 | 90.23 | 88.38 | 90.07 | 89.24 | 90.05 | 91.22 | 89.97 |
| EXIT4 | | | 78.90 | 76.82 | 81.19 | 78.90 | 81.60 | 81.19 | 79.94 |
| EXIT5 | | | 25.40 | 32.48 | 35.39 | 38.64 | 37.60 | 37.43 | 35.93 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.87 | 1.87 | 1.87 | 1.87 | 1.87 | 1.87 | 1.88 | 1.88 | 1.87 |
| EXIT1 | 5.54 | 5.50 | 5.45 | 5.43 | 5.44 | 5.42 | 5.43 | 5.43 | 5.44 |
| EXIT2 | 6.00 | 5.95 | 5.92 | 5.91 | 5.90 | 5.91 | 5.90 | 5.91 | 5.92 |
| EXIT3 | 6.25 | 6.21 | 6.19 | 6.19 | 6.18 | 6.18 | 6.18 | 6.20 | 6.22 |
| EXIT4 | | | 6.18 | 6.17 | 6.17 | 6.16 | 6.15 | 6.15 | 6.15 |
| EXIT5 | | | 6.27 | 6.20 | 6.11 | 6.07 | 6.04 | 5.99 | 5.95 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 72° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 19. Effect of aeration angle and retention tank on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 147.11 | 147.19 | 141.71 | 141.63 | 149.88 | 151.80 | 151.45 | 150.91 | 149.60 |
| EXIT1 | 140.20 | 141.81 | 139.83 | 139.90 | 146.88 | 151.44 | 146.73 | 147.17 | 146.22 |
| EXIT2 | 112.92 | 141.18 | 139.60 | 139.34 | 146.57 | 147.02 | 144.19 | 145.14 | 145.10 |
| EXIT3 | 110.51 | 139.82 | 137.21 | 138.26 | 145.46 | 146.99 | 143.49 | 143.71 | 143.53 |
| EXIT4 | | | 102.47 | 138.43 | 145.09 | 146.10 | 142.96 | 141.01 | 140.73 |
| EXIT5 | | | 19.43 | 71.49 | 76.01 | 80.74 | 79.09 | 77.16 | 79.57 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 147.01 | 147.11 | 142.16 | 142.33 | 148.00 | 147.01 | 148.26 | 149.10 | 146.59 |
| EXIT1 | 140.72 | 142.10 | 139.62 | 139.87 | 146.59 | 144.91 | 147.42 | 144.07 | 144.49 |
| EXIT2 | 111.82 | 141.26 | 139.13 | 139.22 | 142.82 | 142.82 | 144.07 | 141.56 | 139.05 |
| EXIT3 | 110.43 | 138.26 | 139.25 | 138.10 | 141.56 | 142.40 | 141.56 | 139.47 | 139.05 |
| EXIT4 | | | 110.15 | 117.69 | 127.32 | 121.88 | 127.74 | 128.49 | 124.39 |
| EXIT5 | | | 19.13 | 69.52 | 72.87 | 77.48 | 77.48 | 82.09 | 77.90 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 2.08 | 2.08 | 2.09 | 2.09 | 2.08 | 2.09 | 2.08 | 2.08 | 2.08 |
| EXIT1 | 5.54 | 5.53 | 5.51 | 5.53 | 5.53 | 5.53 | 5.54 | 5.53 | 5.55 |
| EXIT2 | 6.04 | 6.00 | 5.99 | 6.00 | 6.01 | 6.00 | 6.00 | 6.00 | 6.01 |
| EXIT3 | 6.31 | 6.27 | 6.25 | 6.25 | 6.25 | 6.24 | 6.25 | 6.25 | 6.24 |
| EXIT4 | | | 6.12 | 6.12 | 6.12 | 6.12 | 6.12 | 6.11 | 6.12 |
| EXIT5 | | | 6.11 | 5.93 | 5.78 | 5.70 | 5.66 | 5.62 | 5.57 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 71° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 20. Effect of aeration angle and retention tank on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 199.01 | 201.16 | 201.10 | 198.02 | 203.19 | 201.31 | 199.14 | 198.23 | 201.45 |
| EXIT1 | 185.14 | 201.10 | 197.78 | 195.24 | 200.11 | 197.37 | 198.15 | 196.64 | 199.06 |
| EXIT2 | 162.59 | 199.56 | 196.91 | 194.87 | 197.54 | 195.99 | 197.56 | 196.22 | 194.98 |
| EXIT3 | 158.14 | 196.02 | 193.36 | 193.80 | 192.66 | 194.88 | 194.21 | 194.09 | 191.33 |
| EXIT4 | | | 191.50 | 193.10 | 192.47 | 187.55 | 192.20 | 191.21 | 187.59 |
| EXIT5 | | | 51.16 | 100.19 | 106.38 | 115.80 | 115.96 | 116.27 | 117.49 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 193.89 | 197.65 | 199.33 | 197.65 | 198.49 | 200.17 | 198.91 | 198.07 | 199.75 |
| EXIT1 | 186.14 | 196.40 | 198.49 | 195.73 | 198.07 | 196.40 | 198.25 | 195.56 | 195.56 |
| EXIT2 | 159.13 | 196.40 | 196.73 | 195.05 | 195.98 | 194.72 | 196.82 | 192.42 | 191.79 |
| EXIT3 | 158.10 | 195.56 | 190.70 | 189.98 | 192.63 | 189.28 | 195.14 | 190.12 | 189.28 |
| EXIT4 | | | 162.88 | 164.71 | 169.18 | 165.41 | 171.69 | 170.02 | 166.67 |
| EXIT5 | | | 53.18 | 100.50 | 105.95 | 115.58 | 114.32 | 114.67 | 117.46 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 2.01 | 2.01 | 2.00 | 2.00 | 1.99 | 2.00 | 2.01 | 2.00 | 2.00 |
| EXIT1 | 5.51 | 5.49 | 5.50 | 5.51 | 5.50 | 5.50 | 5.48 | 5.49 | 5.50 |
| EXIT2 | 5.96 | 5.95 | 5.95 | 5.97 | 5.96 | 5.96 | 5.95 | 5.95 | 5.97 |
| EXIT3 | 6.17 | 6.19 | 6.19 | 6.19 | 6.18 | 6.18 | 6.19 | 6.19 | 6.19 |
| EXIT4 | | | 6.04 | 6.05 | 6.05 | 6.05 | 6.05 | 6.05 | 6.04 |
| EXIT5 | | | 5.90 | 5.80 | 5.62 | 5.57 | 5.50 | 5.45 | 5.39 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 74° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 21. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 51.26 | 49.72 | 50.02 | 50.91 | 50.19 | 50.13 | 49.89 | 49.38 | 50.03 |
| EXIT1 | 49.25 | 49.74 | 49.83 | 50.01 | 48.71 | 49.95 | 47.88 | 46.92 | 46.24 |
| EXIT2 | 44.76 | 48.41 | 48.38 | 47.45 | 46.08 | 45.95 | 43.75 | 43.47 | 43.57 |
| EXIT3 | 42.52 | 46.51 | 46.62 | 45.42 | 43.65 | 44.08 | 41.77 | 41.75 | 40.53 |
| EXIT4 | | | 43.33 | 42.95 | 41.05 | 42.37 | 39.05 | 41.27 | 40.51 |
| EXIT5 | | | 6.75 | 10.36 | 11.85 | 11.50 | 10.76 | 9.78 | 9.40 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 51.70 | 50.47 | 50.68 | 49.16 | 49.57 | 49.89 | 49.78 | 49.06 | 49.57 |
| EXIT1 | 49.23 | 49.76 | 49.98 | 49.06 | 49.06 | 49.78 | 49.10 | 46.86 | 48.27 |
| EXIT2 | 43.87 | 48.83 | 47.23 | 47.02 | 46.41 | 46.51 | 43.68 | 43.47 | 42.84 |
| EXIT3 | 42.95 | 46.38 | 46.51 | 45.70 | 44.06 | 45.49 | 43.76 | 43.55 | 41.10 |
| EXIT4 | | | 36.21 | 37.23 | 36.11 | 37.54 | 34.37 | 36.62 | 35.70 |
| EXIT5 | | | 6.02 | 10.20 | 11.73 | 11.32 | 11.00 | 9.69 | 9.18 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.90 | 1.90 | 1.90 | 1.90 | 1.90 | 1.90 | 1.91 | 1.90 | 1.90 |
| EXIT1 | 5.66 | 5.58 | 5.58 | 5.56 | 5.56 | 5.55 | 5.55 | 5.54 | 5.54 |
| EXIT2 | 6.01 | 5.98 | 5.98 | 5.97 | 5.97 | 5.96 | 5.97 | 5.97 | 5.97 |
| EXIT3 | 6.49 | 6.43 | 6.45 | 6.43 | 6.43 | 6.42 | 6.43 | 6.43 | 6.41 |
| EXIT4 | | | 6.41 | 6.40 | 6.40 | 6.39 | 6.41 | 6.39 | 6.39 |
| EXIT5 | | | 6.96 | 6.75 | 6.64 | 6.56 | 6.50 | 6.42 | 6.38 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 71° F
AERATION ANGLE = 10° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 22. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 106.23 | 105.82 | 107.48 | 107.46 | 106.52 | 107.11 | 105.32 | 105.38 | 104.59 |
| EXIT1 | 98.72 | 103.25 | 106.71 | 107.81 | 105.95 | 107.28 | 104.93 | 104.49 | 104.23 |
| EXIT2 | 84.49 | 101.50 | 105.94 | 102.98 | 104.25 | 104.81 | 104.34 | 101.46 | 102.04 |
| EXIT3 | 79.82 | 99.71 | 103.50 | 101.93 | 102.35 | 101.17 | 100.37 | 98.04 | 102.01 |
| EXIT4 | | | 94.47 | 99.40 | 101.67 | 99.14 | 97.96 | 97.54 | 99.31 |
| EXIT5 | | | 31.72 | 36.72 | 43.26 | 45.25 | 46.68 | 46.89 | 48.16 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 105.17 | 105.51 | 106.41 | 105.75 | 104.79 | 106.41 | 106.59 | 105.15 | 105.15 |
| EXIT1 | 98.47 | 104.25 | 106.41 | 105.51 | 104.07 | 105.15 | 104.69 | 103.89 | 104.79 |
| EXIT2 | 83.87 | 101.52 | 104.25 | 103.16 | 104.56 | 103.71 | 104.25 | 101.72 | 102.38 |
| EXIT3 | 81.00 | 100.90 | 102.44 | 101.72 | 102.80 | 102.25 | 102.08 | 99.57 | 102.08 |
| EXIT4 | | | 82.78 | 82.60 | 85.85 | 84.27 | 82.60 | 85.49 | 87.65 |
| EXIT5 | | | 30.48 | 35.53 | 42.20 | 45.07 | 46.52 | 46.16 | 48.32 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 2.05 | 2.05 | 2.05 | 2.05 | 2.05 | 2.05 | 2.05 | 2.06 | 2.05 |
| EXIT1 | 5.67 | 5.61 | 5.58 | 5.57 | 5.57 | 5.55 | 5.56 | 5.55 | 5.55 |
| EXIT2 | 6.08 | 6.03 | 6.04 | 6.03 | 6.02 | 6.03 | 6.02 | 6.02 | 6.03 |
| EXIT3 | 6.47 | 6.42 | 6.41 | 6.40 | 6.40 | 6.40 | 6.40 | 6.40 | 6.39 |
| EXIT4 | | | 6.25 | 6.24 | 6.23 | 6.24 | 6.22 | 6.23 | 6.23 |
| EXIT5 | | | 6.25 | 6.14 | 6.05 | 5.98 | 5.92 | 5.90 | 5.87 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 70° F
AERATION ANGLE = 10° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 23. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 149.67 | 150.28 | 150.06 | 150.49 | 150.19 | 150.69 | 148.86 | 152.01 | 148.30 |
| EXIT1 | 143.29 | 150.12 | 148.90 | 150.83 | 149.63 | 147.65 | 147.55 | 149.41 | 146.65 |
| EXIT2 | 116.04 | 147.35 | 146.03 | 147.44 | 146.52 | 146.86 | 143.53 | 146.51 | 142.69 |
| EXIT3 | 112.97 | 142.73 | 141.67 | 147.24 | 144.85 | 143.04 | 141.04 | 141.75 | 138.11 |
| EXIT4 | | | 134.15 | 144.10 | 134.71 | 140.27 | 138.48 | 139.89 | 137.98 |
| EXIT5 | | | 48.64 | 69.04 | 73.18 | 76.04 | 77.25 | 75.93 | 77.75 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 148.82 | 146.98 | 148.82 | 148.82 | 148.82 | 148.40 | 147.13 | 148.82 | 148.82 |
| EXIT1 | 142.46 | 146.70 | 148.82 | 148.82 | 147.55 | 147.98 | 146.70 | 148.82 | 144.58 |
| EXIT2 | 116.60 | 146.28 | 148.82 | 148.30 | 144.16 | 147.55 | 143.74 | 144.16 | 140.34 |
| EXIT3 | 111.41 | 142.09 | 142.04 | 145.86 | 142.89 | 143.58 | 141.04 | 140.77 | 139.92 |
| EXIT4 | | | 117.45 | 125.08 | 121.69 | 125.76 | 121.69 | 123.38 | 122.96 |
| EXIT5 | | | 47.91 | 67.84 | 73.35 | 76.32 | 75.47 | 75.47 | 76.32 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.95 | 1.95 | 1.94 | 1.94 | 1.95 | 1.94 | 1.94 | 1.94 | 1.94 |
| EXIT1 | 5.55 | 5.50 | 5.48 | 5.46 | 5.45 | 5.44 | 5.43 | 5.42 | 5.42 |
| EXIT2 | 5.99 | 5.92 | 5.92 | 5.91 | 5.90 | 5.91 | 5.91 | 5.90 | 5.91 |
| EXIT3 | 6.38 | 6.26 | 6.28 | 6.28 | 6.27 | 6.28 | 6.27 | 6.28 | 6.27 |
| EXIT4 | | | 6.18 | 6.15 | 6.12 | 6.13 | 6.13 | 6.11 | 6.10 |
| EXIT5 | | | 5.93 | 5.80 | 5.75 | 5.71 | 5.69 | 5.66 | 5.63 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 70° F
AERATION ANGLE = 10° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 24. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 198.81 | 197.11 | 202.54 | 198.40 | 198.61 | 200.63 | 201.51 | 197.19 | 197.29 |
| EXIT1 | 189.08 | 195.10 | 195.18 | 195.68 | 196.79 | 194.66 | 200.82 | 194.51 | 195.31 |
| EXIT2 | 152.49 | 194.29 | 193.48 | 192.82 | 194.95 | 191.97 | 196.82 | 191.30 | 193.27 |
| EXIT3 | 150.69 | 190.09 | 189.00 | 192.48 | 191.21 | 190.70 | 192.20 | 192.63 | 192.49 |
| EXIT4 | | | 185.76 | 183.71 | 190.06 | 190.76 | 189.93 | 189.68 | 189.37 |
| EXIT5 | | | 53.31 | 91.44 | 111.27 | 114.65 | 117.63 | 117.01 | 118.56 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 197.58 | 198.36 | 198.86 | 197.58 | 197.58 | 199.28 | 197.58 | 197.16 | 197.58 |
| EXIT1 | 188.68 | 193.34 | 196.58 | 196.36 | 195.46 | 194.74 | 197.58 | 194.31 | 195.46 |
| EXIT2 | 152.22 | 192.92 | 194.19 | 192.07 | 195.04 | 193.14 | 197.16 | 189.53 | 193.34 |
| EXIT3 | 147.55 | 193.98 | 189.53 | 189.53 | 189.95 | 191.22 | 192.29 | 187.83 | 193.34 |
| EXIT4 | | | 155.18 | 154.76 | 167.48 | 167.06 | 172.57 | 164.09 | 167.27 |
| EXIT5 | | | 57.66 | 91.58 | 110.24 | 113.89 | 117.02 | 116.60 | 118.72 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.94 | 1.93 | 1.94 | 1.93 | 1.93 | 1.93 | 1.93 | 1.94 | 1.93 |
| EXIT1 | 5.50 | 5.46 | 5.41 | 5.40 | 5.38 | 5.40 | 5.39 | 5.39 | 5.38 |
| EXIT2 | 5.97 | 5.93 | 5.90 | 5.89 | 5.88 | 5.88 | 5.90 | 5.88 | 5.89 |
| EXIT3 | 6.27 | 6.25 | 6.22 | 6.23 | 6.22 | 6.22 | 6.23 | 6.23 | 6.22 |
| EXIT4 | | | 6.06 | 6.05 | 6.03 | 6.05 | 6.06 | 6.06 | 6.07 |
| EXIT5 | | | 5.86 | 5.71 | 5.54 | 5.50 | 5.45 | 5.46 | 5.44 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 72° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 25. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.27 | 48.84 | 49.13 | 50.91 | 49.41 | 50.28 | 48.09 | 49.01 | 51.82 |
| EXIT1 | 42.99 | 43.95 | 44.74 | 44.02 | 44.00 | 43.43 | 42.82 | 41.73 | 44.88 |
| EXIT2 | 39.75 | 41.80 | 44.01 | 42.12 | 40.81 | 39.92 | 39.59 | 39.13 | 38.60 |
| EXIT3 | 38.79 | 42.55 | 40.63 | 41.39 | 40.06 | 38.77 | 38.50 | 40.05 | 35.46 |
| EXIT4 | | | 37.68 | 37.70 | 38.50 | 37.72 | 37.79 | 39.00 | 34.06 |
| EXIT5 | | | 2.32 | 4.99 | 5.11 | 4.70 | 4.40 | 4.11 | 4.07 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 48.38 | 48.60 | 48.38 | 47.84 | 48.06 | 48.38 | 48.28 | 48.38 | 48.28 |
| EXIT1 | 42.44 | 44.39 | 44.28 | 43.85 | 43.63 | 43.31 | 42.66 | 42.12 | 42.34 |
| EXIT2 | 39.10 | 41.27 | 42.88 | 41.36 | 41.04 | 39.96 | 39.43 | 39.42 | 38.45 |
| EXIT3 | 36.85 | 42.98 | 40.39 | 40.28 | 39.96 | 38.99 | 38.88 | 38.80 | 37.15 |
| EXIT4 | | | 26.89 | 25.81 | 27.43 | 27.22 | 26.03 | 26.78 | 26.35 |
| EXIT5 | | | 2.80 | 5.08 | 5.40 | 5.08 | 4.43 | 4.43 | 4.54 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.97 | 1.97 | 1.97 | 1.97 | 1.98 | 1.97 | 1.97 | 1.96 | 1.97 |
| EXIT1 | 5.85 | 5.76 | 5.76 | 5.77 | 5.76 | 5.76 | 5.77 | 5.80 | 5.78 |
| EXIT2 | 6.10 | 6.10 | 6.10 | 6.12 | 6.10 | 6.11 | 6.13 | 6.15 | 6.13 |
| EXIT3 | 6.53 | 6.54 | 6.58 | 6.59 | 6.59 | 6.58 | 6.58 | 6.60 | 6.58 |
| EXIT4 | | | 6.45 | 6.47 | 6.48 | 6.47 | 6.48 | 6.47 | 6.47 |
| EXIT5 | | | 6.90 | 6.73 | 6.62 | 6.55 | 6.51 | 6.47 | 6.44 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 70° F
AERATION ANGLE = 40° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 26. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 98.91 | 100.63 | 99.07 | 97.93 | 95.72 | 97.78 | 98.26 | 97.33 | 98.59 |
| EXIT1 | 89.24 | 97.74 | 98.89 | 96.04 | 94.49 | 94.48 | 94.32 | 95.54 | 96.82 |
| EXIT2 | 69.84 | 96.65 | 94.79 | 95.76 | 93.58 | 88.66 | 89.57 | 92.66 | 93.62 |
| EXIT3 | 69.16 | 95.94 | 94.17 | 90.98 | 90.79 | 88.00 | 86.52 | 88.02 | 88.02 |
| EXIT4 | | | 84.18 | 87.69 | 89.17 | 85.27 | 84.44 | 86.98 | 89.74 |
| EXIT5 | | | 16.57 | 25.91 | 27.72 | 27.53 | 27.92 | 28.62 | 28.17 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 97.90 | 99.44 | 99.11 | 97.57 | 96.80 | 97.68 | 94.60 | 97.44 | 96.80 |
| EXIT1 | 89.32 | 94.60 | 96.36 | 96.14 | 94.71 | 95.37 | 93.50 | 93.94 | 95.92 |
| EXIT2 | 69.74 | 97.02 | 93.72 | 96.80 | 93.83 | 89.70 | 90.20 | 92.07 | 92.40 |
| EXIT3 | 72.60 | 97.13 | 90.97 | 90.20 | 98.10 | 88.00 | 86.35 | 88.22 | 89.10 |
| EXIT4 | | | 66.44 | 74.64 | 70.64 | 68.31 | 68.64 | 68.53 | 66.68 |
| EXIT5 | | | 14.74 | 24.20 | 25.52 | 26.40 | 28.38 | 28.60 | 27.94 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.97 | 1.97 | 1.96 | 1.96 | 1.98 | 1.97 | 1.97 | 1.96 | 1.96 |
| EXIT1 | 5.75 | 5.66 | 5.64 | 5.63 | 5.64 | 5.62 | 5.63 | 5.63 | 5.64 |
| EXIT2 | 6.09 | 6.04 | 6.04 | 6.03 | 6.03 | 6.03 | 6.03 | 6.02 | 6.03 |
| EXIT3 | 6.54 | 6.45 | 6.44 | 6.44 | 6.43 | 6.43 | 6.42 | 6.42 | 6.42 |
| EXIT4 | | | 6.19 | 6.18 | 6.16 | 6.15 | 6.14 | 6.14 | 6.13 |
| EXIT5 | | | 6.29 | 6.17 | 6.10 | 6.04 | 6.01 | 6.00 | 5.96 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 70° F
AERATION ANGLE = 40° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 27. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 150.73 | 148.58 | 148.81 | 150.24 | 153.43 | 152.75 | 149.36 | 148.76 | 148.52 |
| EXIT1 | 142.19 | 147.69 | 147.66 | 145.26 | 154.10 | 150.35 | 144.87 | 146.33 | 145.58 |
| EXIT2 | 121.10 | 141.70 | 145.77 | 144.45 | 149.94 | 148.53 | 141.48 | 145.38 | 143.83 |
| EXIT3 | 128.06 | 142.20 | 143.54 | 143.53 | 145.90 | 144.41 | 138.35 | 143.19 | 143.94 |
| EXIT4 | | | 132.81 | 133.15 | 135.85 | 145.64 | 130.96 | 139.40 | 136.98 |
| EXIT5 | | | 39.47 | 57.05 | 63.33 | 69.10 | 64.19 | 66.03 | 67.70 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 148.29 | 147.00 | 148,93 | 147.43 | 148.71 | 147.86 | 147.86 | 147.86 | 147.61 |
| EXIT1 | 142.29 | 147.86 | 147.21 | 145.07 | 146.14 | 146.57 | 147.96 | 147.43 | 145.71 |
| EXIT2 | 121.39 | 141.54 | 145.82 | 144.00 | 144.86 | 144.86 | 142.29 | 144.39 | 144.64 |
| EXIT3 | 125.57 | 142.50 | 143.14 | 142.24 | 142.71 | 142.71 | 140.14 | 141.86 | 141.43 |
| EXIT4 | | | 107.57 | 111.00 | 113.57 | 116.14 | 116.14 | 118.03 | 118.29 |
| EXIT5 | | | 37.29 | 52.29 | 59.57 | 67.29 | 66.43 | 67.29 | 67.71 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.86 | 1.86 | 1.85 | 1.86 | 1.85 | 1.85 | 1.85 | 1.85 | 1.86 |
| EXIT1 | 5.62 | 5.55 | 5.55 | 5.54 | 5.53 | 5.53 | 5.52 | 5.53 | 5.53 |
| EXIT2 | 5.94 | 5.94 | 5.94 | 5.94 | 5.93 | 5.92 | 5.93 | 5.92 | 5.92 |
| EXIT3 | 6.37 | 6.38 | 6.34 | 6.32 | 6.32 | 6.30 | 6.31 | 6.30 | 6.29 |
| EXIT4 | | | 6.10 | 6.10 | 6.09 | 6.09 | 6.09 | 6.08 | 6.07 |
| EXIT5 | | | 5.93 | 5.87 | 5.83 | 5.79 | 5.78 | 5.76 | 5.75 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 71° F
AERATION ANGLE = 40° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 28. Effect of aeration angle on iron removal

| TOTAL IRON | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 201.58 | 206.01 | 200.31 | 200.81 | 204.12 | 198.75 | 199.67 | 196.03 | 201.27 |
| EXIT1 | 193.60 | 204.28 | 200.32 | 199.70 | 202.02 | 196.11 | 194.87 | 196.64 | 196.25 |
| EXIT2 | 169.71 | 197.84 | 197.02 | 196.15 | 198.31 | 198.52 | 190.95 | 194.61 | 195.94 |
| EXIT3 | 167.73 | 193.54 | 193.82 | 195.88 | 195.40 | 189.75 | 186.65 | 191.60 | 191.27 |
| EXIT4 | | | 179.63 | 185.88 | 179.19 | 191.82 | 180.97 | 185.94 | 192.95 |
| EXIT5 | | | 89.01 | 102.75 | 101.74 | 104.61 | 112.47 | 117.11 | 117.49 |

| Fe II | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 201.43 | 202.30 | 203.83 | 200.99 | 202.74 | 198.38 | 200.12 | 196.20 | 201.21 |
| EXIT1 | 194.13 | 204.48 | 199.69 | 200.12 | 201.65 | 196.20 | 194.67 | 196.85 | 196.74 |
| EXIT2 | 169.17 | 198.38 | 197.07 | 196.20 | 198.38 | 192.13 | 191.62 | 194.89 | 196.31 |
| EXIT3 | 171.00 | 193.15 | 193.58 | 195.98 | 196.20 | 191.84 | 187.48 | 191.62 | 192.06 |
| EXIT4 | | | 156.52 | 161.32 | 163.94 | 171.35 | 166.99 | 170.04 | 171.35 |
| EXIT5 | | | 89.38 | 102.84 | 102.02 | 114.67 | 113.36 | 117.89 | 118.16 |

| pH | TIME 0:30 | TIME 1:30 | TIME 2:30 | TIME 3:00 | TIME 3:30 | TIME 4:00 | TIME 4:30 | TIME 5:00 | TIME 5:30 |
|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.92 | 1.91 | 1.91 | 1.92 | 1.92 | 1.91 | 1.91 | 1.91 | 1.91 |
| EXIT1 | 5.59 | 5.54 | 5.55 | 5.54 | 5.54 | 5.52 | 5.52 | 5.52 | 5.52 |
| EXIT2 | 5.95 | 5.93 | 5.93 | 5.93 | 5.93 | 5.92 | 5.91 | 5.91 | 5.91 |
| EXIT3 | 6.23 | 6.20 | 6.20 | 6.19 | 6.20 | 6.20 | 6.19 | 6.18 | 6.19 |
| EXIT4 | | | 5.93 | 5.95 | 5.96 | 5.96 | 5.95 | 5.95 | 5.94 |
| EXIT5 | | | 5.60 | 5.58 | 5.56 | 5.51 | 5.49 | 5.49 | 5.47 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SOLID SEPARATOR
EXIT 5 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 71° F
AERATION ANGLE = 40° DEGREE
SAND THICKNESS = 5.0 INCHES

TABLE 29. Effect of angle of aeration unit on iron removal

| TOTAL IRON | TIME 1.00 | TIME 1:20 | TIME 1:40 | TIME 2:00 | TIME 2:20 | TIME 2:40 | TIME 3:10 | TIME 3:30 | TIME 3:50 | TIME 4:10 | TIME 4:30 | TIME 4:50 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.30 | 51.81 | 49.42 | 49.61 | 50.71 | 49.98 | 50.20 | 49.53 | 50.75 | 51.11 | 50.89 | 49.29 |
| EXIT1 | 43.42 | 49.19 | 47.26 | 48.33 | 47.89 | 47.06 | 48.49 | 46.98 | 47.81 | 50.48 | 49.93 | 48.08 |
| EXIT2 | 27.41 | 39.91 | 41.31 | 42.88 | 44.13 | 43.51 | 46.52 | 43.27 | 46.07 | 45.13 | 44.81 | 43.88 |
| EXIT3 | 26.85 | 39.36 | 41.29 | 42.50 | 42.91 | 43.20 | 44.15 | 43.24 | 45.90 | 45.27 | 44.72 | 42.44 |
| EXIT4 | 2.05 | 5.67 | 8.22 | 8.48 | 8.16 | 8.62 | 10.57 | 11.42 | 12.30 | 12.05 | 12.72 | 12.68 |
| Aeration Angle = 45 ° | | | | | | | Aeration Angle = 1 ° | | | | | |

| pH | TIME 1.00 | TIME 1:20 | TIME 1:40 | TIME 2:00 | TIME 2:20 | TIME 2:40 | TIME 3:10 | TIME 3:30 | TIME 3:50 | TIME 4:10 | TIME 4:30 | TIME 4:50 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.99 | 2.00 | 1.98 | 1.99 | 1.99 | 1.99 | 1.99 | 1.99 | 2.00 | 2.00 | 1.99 | 2.00 |
| EXIT1 | 5.71 | 5.66 | 5.65 | 5.64 | 5.64 | 5.64 | 5.63 | 5.62 | 5.62 | 5.64 | 5.64 | 5.63 |
| EXIT2 | 6.14 | 6.08 | 6.07 | 6.07 | 6.07 | 6.08 | 6.08 | 6.09 | 6.08 | 6.08 | 6.10 | 6.09 |
| EXIT3 | 6.69 | 6.66 | 6.65 | 6.65 | 6.65 | 6.65 | 6.38 | 6.40 | 6.39 | 6.40 | 6.41 | 6.40 |
| EXIT4 | 6.45 | 6.35 | 6.29 | 6.22 | 6.17 | 6.12 | 6.10 | 6.09 | 6.06 | 6.02 | 6.03 | 6.02 |
| Aeration Angle = 45 ° | | | | | | | Aeration Angle = 1 ° | | | | | |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 68° F
SAND THICKNESS = 2.5 INCHES

TABLE 30. Effect of angle of aeration unit on iron removal

| TOTAL IRON | TIME 1.00 | TIME 1:20 | TIME 1:40 | TIME 2:00 | TIME 2:20 | TIME 2:40 | TIME 3:10 | TIME 3:30 | TIME 3:50 | TIME 4:10 | TIME 4:30 | TIME 4:50 | TIME 5:10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 97.50 | 100.97 | 99.01 | 101.11 | 100.70 | 100.35 | 97.37 | 98.95 | 100.33 | 99.35 | 97.92 | 100.50 | 100.19 |
| EXIT1 | 96.58 | 98.68 | 96.97 | 99.04 | 97.44 | 97.66 | 97.35 | 97.34 | 97.47 | 98.96 | 97.63 | 100.19 | 98.46 |
| EXIT2 | 88.63 | 94.29 | 96.72 | 98.49 | 95.48 | 96.56 | 97.84 | 96.97 | 97.82 | 98.54 | 96.66 | 98.10 | 98.73 |
| EXIT3 | 88.52 | 92.68 | 94.32 | 98.24 | 95.34 | 96.81 | 96.27 | 95.25 | 96.04 | 97.04 | 96.49 | 98.66 | 96.80 |
| EXIT4 | 19.15 | 34.72 | 39.35 | 41.25 | 45.93 | 46.86 | 40.77 | 38.45 | 38.10 | 37.27 | 39.88 | 38.02 | 39.76 |
| Aeration Angle = 1 ° | | | | | | | Aeration Angle = 45 ° | | | | | | |

| pH | TIME 1.00 | TIME 1:20 | TIME 1:40 | TIME 2:00 | TIME 2:20 | TIME 2:40 | TIME 3:10 | TIME 3:30 | TIME 3:50 | TIME 4:10 | TIME 4:30 | TIME 4:50 | TIME 5:10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.53 | 1.52 | 1.53 | 1.55 | 1.55 | 1.54 | 1.54 | 1.53 | 1.53 | 1.53 | 1.53 | 1.54 | 1.53 |
| EXIT1 | 5.26 | 5.20 | 5.14 | 5.16 | 5.16 | 5.15 | 5.13 | 5.12 | 5.11 | 5.11 | 5.10 | 5.10 | 5.10 |
| EXIT2 | 5.72 | 5.70 | 5.67 | 5.67 | 5.66 | 5.65 | 5.63 | 5.61 | 5.61 | 5.60 | 5.60 | 5.59 | 5.60 |
| EXIT3 | 6.07 | 6.05 | 6.04 | 6.04 | 6.03 | 6.03 | 6.35 | 6.36 | 6.36 | 6.35 | 6.34 | 6.35 | 6.35 |
| EXIT4 | 6.17 | 6.02 | 5.98 | 5.98 | 5.85 | 5.83 | 5.78 | 5.72 | 5.71 | 5.71 | 5.72 | 5.74 | 5.72 |
| Aeration Angle = 1 ° | | | | | | | Aeration Angle = 45 ° | | | | | | |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 68° F
SAND THICKNESS = 2.5 INCHES

TABLE 31. Effect of angle of aeration unit on iron removal

| TOTAL IRON | TIME 1.00 | TIME 1:20 | TIME 1:40 | TIME 2:00 | TIME 2:20 | TIME 2:40 | TIME 3:10 | TIME 3:30 | TIME 3:50 | TIME 4:10 | TIME 4:30 | TIME 4:50 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 147.31 | 148.32 | 149.98 | 149.44 | 150.22 | 150.89 | 149.19 | 150.85 | 148.14 | 150.07 | 151.51 | 151.01 |
| EXIT1 | 144.69 | 145.50 | 148.11 | 147.58 | 148.58 | 148.78 | 148.00 | 148.46 | 146.72 | 147.04 | 149.10 | 149.07 |
| EXIT2 | 133.63 | 143.78 | 146.55 | 146.21 | 148.11 | 148.31 | 146.43 | 144.59 | 143.41 | 144.55 | 143.95 | 144.03 |
| EXIT3 | 133.15 | 141.05 | 144.70 | 143.73 | 146.15 | 142.87 | 143.05 | 144.16 | 140.64 | 141.57 | 139.35 | 143.77 |
| EXIT4 | 45.28 | 68.56 | 73.77 | 76.12 | 80.49 | 77.93 | 80.98 | 84.68 | 85.27 | 86.64 | 82.96 | 84.71 |
| Aeration Angle = 45 ° | | | | | | | Aeration Angle = 1 ° | | | | | |

| pH | TIME 1.00 | TIME 1:20 | TIME 1:40 | TIME 2:00 | TIME 2:20 | TIME 2:40 | TIME 3:10 | TIME 3:30 | TIME 3:50 | TIME 4:10 | TIME 4:30 | TIME 4:50 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.77 | 1.77 | 1.78 | 1.78 | 1.77 | 1.78 | 1.77 | 1.78 | 1.78 | 1.77 | 1.77 | 1.78 |
| EXIT1 | 5.29 | 5.26 | 5.25 | 5.25 | 5.25 | 5.25 | 5.23 | 5.24 | 5.25 | 5.24 | 5.24 | 5.24 |
| EXIT2 | 5.76 | 5.75 | 5.76 | 5.77 | 5.77 | 5.77 | 5.80 | 5.80 | 5.80 | 5.80 | 5.79 | 5.79 |
| EXIT3 | 6.42 | 6.41 | 6.39 | 6.37 | 6.37 | 6.36 | 6.10 | 6.10 | 6.10 | 6.10 | 6.10 | 6.10 |
| EXIT4 | 5.58 | 5.56 | 5.52 | 5.47 | 5.44 | 5.44 | 5.46 | 5.45 | 5.45 | 5.42 | 5.41 | 5.40 |
| Aeration Angle = 45 ° | | | | | | | Aeration Angle = 1 ° | | | | | |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 68° F
SAND THICKNESS = 2.5 INCHES

TABLE 32. Effect of angle of aeration unit on iron removal

| TOTAL IRON | TIME 1.00 | TIME 1:20 | TIME 1:40 | TIME 2:00 | TIME 2:20 | TIME 2:40 | TIME 3:10 | TIME 3:30 | TIME 3:50 | TIME 4:10 | TIME 4:30 | TIME 4:50 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 197.02 | 201.73 | 198.23 | 199.92 | 199.19 | 201.41 | 198.90 | 201.60 | 199.36 | 196.33 | 198.85 | 198.74 |
| EXIT1 | 196.30 | 198.66 | 197.23 | 199.36 | 200.22 | 198.56 | 198.30 | 200.69 | 199.76 | 197.27 | 196.70 | 197.46 |
| EXIT2 | 194.15 | 193.05 | 194.25 | 195.38 | 196.36 | 197.52 | 193.90 | 198.71 | 196.56 | 194.93 | 195.66 | 193.08 |
| EXIT3 | 189.24 | 189.01 | 191.18 | 188.55 | 194.84 | 194.48 | 190.26 | 189.34 | 195.87 | 192.19 | 189.10 | 193.08 |
| EXIT4 | 123.14 | 133.73 | 136.09 | 135.91 | 139.96 | 141.01 | 135.85 | 134.13 | 135.23 | 129.84 | 131.01 | 131.42 |
| Aeration Angle = 1 ° | | | | | | | Aeration Angle = 45 ° | | | | | |

| pH | TIME 1.00 | TIME 1:20 | TIME 1:40 | TIME 2:00 | TIME 2:20 | TIME 2:40 | TIME 3:10 | TIME 3:30 | TIME 3:50 | TIME 4:10 | TIME 4:30 | TIME 4:50 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.69 | 1.70 | 1.70 | 1.69 | 1.70 | 1.69 | 1.69 | 1.70 | 1.70 | 1.69 | 1.69 | 1.70 |
| EXIT1 | 5.19 | 5.16 | 5.14 | 5.13 | 5.14 | 5.14 | 5.12 | 5.11 | 5.12 | 5.12 | 5.12 | 5.12 |
| EXIT2 | 5.73 | 5.72 | 5.71 | 5.71 | 5.72 | 5.72 | 5.70 | 5.69 | 5.69 | 5.70 | 5.70 | 5.69 |
| EXIT3 | 6.06 | 6.04 | 6.04 | 6.04 | 6.04 | 6.03 | 6.34 | 6.33 | 6.34 | 6.33 | 6.34 | 6.33 |
| EXIT4 | 5.29 | 5.25 | 5.23 | 5.24 | 5.27 | 5.23 | 5.23 | 5.24 | 5.23 | 5.25 | 5.26 | 5.26 |
| Aeration Angle = 1 ° | | | | | | | Aeration Angle = 45 ° | | | | | |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE SECOND LIMESTONE COLUMN
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 68° F
SAND THICKNESS = 2.5 INCHES

TABLE 33. Effect of sand thickness on iron removal

| TOTAL IRON | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 48.48 | 49.25 | 50.21 | 49.48 | 95.47 | 95.33 | 96.65 | 96.50 | 142.96 | 143.15 | 147.62 | 147.00 | 172.19 | 178.57 | 179.71 | 177.02 |
| EXIT1 | 48.75 | 47.87 | 48.48 | 48.86 | 93.63 | 91.72 | 94.96 | 95.58 | 138.24 | 143.94 | 146.49 | 145.83 | 171.81 | 178.01 | 178.44 | 176.83 |
| EXIT2 | 42.51 | 43.51 | 45.55 | 46.25 | 92.16 | 91.96 | 93.88 | 93.07 | 137.36 | 142.25 | 143.77 | 143.98 | 172.19 | 173.92 | 175.07 | 174.48 |
| EXIT3 | 42.66 | 42.03 | 43.39 | 45.10 | 88.83 | 91.12 | 90.95 | 92.87 | 134.53 | 142.25 | 142.01 | 142.53 | 167.60 | 174.75 | 175.38 | 174.83 |
| EXIT4 | 24.10 | 25.35 | 26.95 | 28.36 | 58.39 | 64.65 | 67.00 | 69.10 | 104.04 | 107.88 | 111.58 | 110.57 | 123.97 | 128.73 | 128.01 | 130.46 |

| pH | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.80 | 1.80 | 1.79 | 1.80 | 1.73 | 1.72 | 1.73 | 1.72 | 1.68 | 1.68 | 1.68 | 1.68 | 1.55 | 1.54 | 1.54 | 1.54 |
| EXIT1 | 5.49 | 5.46 | 5.44 | 5.44 | 5.38 | 5.38 | 5.37 | 5.37 | 5.29 | 5.29 | 5.29 | 5.30 | 5.18 | 5.18 | 5.17 | 5.17 |
| EXIT2 | 5.91 | 5.90 | 5.90 | 5.88 | 5.80 | 5.80 | 5.80 | 5.79 | 5.74 | 5.74 | 5.74 | 5.73 | 5.62 | 5.62 | 5.63 | 5.61 |
| EXIT3 | 6.26 | 6.26 | 6.24 | 6.23 | 6.16 | 6.15 | 6.15 | 6.15 | 6.09 | 6.09 | 6.09 | 6.09 | 6.00 | 6.01 | 6.00 | 5.99 |
| EXIT4 | 6.31 | 6.27 | 6.23 | 6.22 | 6.16 | 6.14 | 6.12 | 6.10 | 6.04 | 6.02 | 6.02 | 6.00 | 5.96 | 5.95 | 5.92 | 5.91 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 68° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 34. Effect of sand thickness and retention tank on iron removal

| TOTAL IRON | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.91 | 47.95 | 49.48 | 49.35 | 95.03 | 95.91 | 93.88 | 97.15 | 142.49 | 143.35 | 144.38 | 146.34 | 181.79 | 183.23 | 174.12 | 184.69 |
| EXIT1 | 48.30 | 48.51 | 48.75 | 48.14 | 94.56 | 95.19 | 93.03 | 95.73 | 141.20 | 143.11 | 142.91 | 141.55 | 178.34 | 179.28 | 173.91 | 182.37 |
| EXIT2 | 46.35 | 44.97 | 46.05 | 47.44 | 93.47 | 93.04 | 93.29 | 94.04 | 141.88 | 143.76 | 140.07 | 139.65 | 178.05 | 173.62 | 173.71 | 179.56 |
| EXIT3 | 45.85 | 45.20 | 45.83 | 47.10 | 91.65 | 89.85 | 92.87 | 93.04 | 139.28 | 141.12 | 141.03 | 137.76 | 176.85 | 171.15 | 171.40 | 176.10 |
| EXIT4 | 21.39 | 23.13 | 25.61 | 29.05 | 53.90 | 59.65 | 65.33 | 68.60 | 92.87 | 99.44 | 106.96 | 106.57 | 117.04 | 124.38 | 126.66 | 129.23 |

| pH | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.63 | 1.64 | 1.63 | 1.64 | 1.60 | 1.60 | 1.60 | 1.60 | 1.62 | 1.61 | 1.61 | 1.61 | 1.60 | 1.60 | 1.60 | 1.60 |
| EXIT1 | 5.41 | 5.38 | 5.37 | 5.38 | 5.31 | 5.32 | 5.32 | 5.33 | 5.32 | 5.32 | 5.32 | 5.31 | 5.24 | 5.22 | 5.23 | 5.24 |
| EXIT2 | 5.77 | 5.78 | 5.76 | 5.76 | 5.70 | 5.70 | 5.70 | 5.70 | 5.68 | 5.68 | 5.68 | 5.68 | 5.65 | 5.65 | 5.65 | 5.65 |
| EXIT3 | 6.08 | 6.09 | 6.09 | 6.09 | 6.03 | 6.03 | 6.01 | 6.01 | 6.00 | 6.00 | 6.00 | 6.01 | 6.00 | 6.00 | 6.00 | 5.99 |
| EXIT4 | 6.28 | 6.24 | 6.23 | 6.20 | 6.08 | 6.05 | 6.03 | 6.01 | 6.00 | 6.01 | 5.98 | 5.97 | 5.94 | 5.92 | 5.90 | 5.90 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 68° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 5 INCHES

TABLE 35. Effect of sand thickness and retention tank on iron removal

| TOTAL IRON | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 49.06 | 50.51 | 50.39 | 49.42 | 95.97 | 96.38 | 98.34 | 97.66 | 144.32 | 147.51 | 150.01 | 147.71 | 179.64 | 184.14 | 183.49 | 186.28 |
| EXIT1 | 48.33 | 50.04 | 49.75 | 50.57 | 94.71 | 95.21 | 94.80 | 94.90 | 142.29 | 143.12 | 145.76 | 143.65 | 178.66 | 179.77 | 181.14 | 182.84 |
| EXIT2 | 43.04 | 43.45 | 43.57 | 46.68 | 91.32 | 91.82 | 90.49 | 90.07 | 141.48 | 143.43 | 145.61 | 138.75 | 174.93 | 178.35 | 179.51 | 178.07 |
| EXIT3 | 41.93 | 41.29 | 42.59 | 44.25 | 90.49 | 89.42 | 89.61 | 88.86 | 137.09 | 140.95 | 142.41 | 138.73 | 172.88 | 175.60 | 179.15 | 177.88 |
| EXIT4 | 22.87 | 24.37 | 26.73 | 27.36 | 52.30 | 60.15 | 64.52 | 67.73 | 95.78 | 97.20 | 109.74 | 107.46 | 120.20 | 124.04 | 128.43 | 128.10 |

| pH | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.90 | 1.90 | 1.89 | 1.90 | 1.83 | 1.83 | 1.82 | 1.81 | 1.75 | 1.75 | 1.74 | 1.74 | 1.68 | 1.67 | 1.67 | 1.67 |
| EXIT1 | 5.52 | 5.52 | 5.52 | 5.52 | 5.43 | 5.43 | 5.42 | 5.43 | 5.34 | 5.35 | 5.35 | 5.35 | 5.26 | 5.24 | 5.25 | 5.24 |
| EXIT2 | 5.96 | 5.96 | 5.96 | 5.96 | 5.88 | 5.89 | 5.90 | 5.90 | 5.82 | 5.82 | 5.82 | 5.82 | 5.73 | 5.73 | 5.73 | 5.74 |
| EXIT3 | 6.33 | 6.33 | 6.31 | 6.32 | 6.25 | 6.25 | 6.25 | 6.24 | 6.18 | 1.18 | 6.18 | 6.18 | 6.12 | 6.12 | 6.12 | 6.11 |
| EXIT4 | 6.68 | 6.60 | 6.54 | 6.50 | 6.43 | 6.39 | 6.37 | 6.35 | 6.23 | 6.23 | 6.21 | 6.20 | 6.08 | 6.06 | 6.02 | 6.00 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 68° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 5 INCHES

TABLE 36. Effect of sand thickness on iron removal

| TOTAL IRON | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.41 | 53.24 | 51.17 | 51.36 | 98.23 | 99.32 | 98.56 | 97.14 | 145.96 | 148.54 | 151.27 | 147.24 | 185.13 | 182.22 | 184.34 | 185.31 |
| EXIT1 | 50.38 | 51.47 | 49.96 | 50.59 | 97.39 | 96.87 | 96.87 | 93.14 | 144.79 | 147.04 | 145.08 | 145.30 | 182.99 | 181.04 | 183.18 | 182.75 |
| EXIT2 | 42.95 | 45.60 | 45.69 | 45.31 | 93.33 | 93.73 | 91.80 | 90.23 | 142.56 | 140.94 | 142.52 | 141.90 | 177.03 | 177.57 | 178.68 | 177.32 |
| EXIT3 | 43.49 | 40.51 | 43.16 | 44.52 | 92.74 | 92.05 | 90.01 | 90.52 | 141.56 | 141.38 | 140.10 | 140.71 | 170.84 | 177.68 | 177.18 | 176.22 |
| EXIT4 | 24.01 | 26.04 | 25.43 | 26.92 | 58.52 | 62.70 | 63.01 | 66.32 | 101.68 | 104.06 | 107.09 | 108.99 | 119.67 | 128.88 | 127.89 | 128.43 |

| pH | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.78 | 1.78 | 1.76 | 1.76 | 1.74 | 1.74 | 1.74 | 1.74 | 1.70 | 1.70 | 1.69 | 1.68 | 1.64 | 1.64 | 1.64 | 1.64 |
| EXIT1 | 5.44 | 5.40 | 5.39 | 5.37 | 5.30 | 5.30 | 5.30 | 5.31 | 5.27 | 5.27 | 5.27 | 5.27 | 5.20 | 5.19 | 5.18 | 5.18 |
| EXIT2 | 5.91 | 5.88 | 5.88 | 5.88 | 5.83 | 5.83 | 5.83 | 5.83 | 5.78 | 5.78 | 5.78 | 5.78 | 5.72 | 5.71 | 5.71 | 5.71 |
| EXIT3 | 6.34 | 6.34 | 6.33 | 6.32 | 6.26 | 6.27 | 6.27 | 6.27 | 6.23 | 6.23 | 6.23 | 6.23 | 6.16 | 6.16 | 6.16 | 6.16 |
| EXIT4 | 6.40 | 6.41 | 6.40 | 6.38 | 6.28 | 6.26 | 6.25 | 6.25 | 6.18 | 6.19 | 6.16 | 6.15 | 6.08 | 6.06 | 6.04 | 6.04 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 68° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 37. Effect of temperature on iron removal

| TOTAL IRON | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 49.32 | 48.19 | 51.37 | 51.76 | 97.43 | 94.23 | 100.49 | 96.22 | 141.88 | 143.44 | 145.81 | 142.60 | 175.13 | 180.79 | 174.91 | 178.44 |
| EXIT1 | 47.76 | 47.38 | 49.87 | 48.79 | 97.16 | 94.47 | 96.65 | 94.46 | 139.57 | 140.91 | 141.14 | 141.09 | 174.49 | 173.69 | 171.56 | 172.67 |
| EXIT2 | 47.02 | 46.19 | 48.20 | 49.89 | 93.17 | 92.31 | 97.20 | 93.78 | 138.75 | 141.15 | 141.90 | 141.67 | 172.54 | 171.15 | 171.80 | 172.00 |
| EXIT3 | 46.32 | 45.75 | 47.66 | 46.96 | 91.83 | 92.13 | 95.01 | 93.73 | 137.46 | 140.58 | 138.60 | 139.23 | 170.87 | 169.55 | 171.00 | 171.56 |
| EXIT4 | 32.00 | 34.12 | 37.59 | 37.76 | 73.93 | 73.03 | 79.42 | 82.39 | 117.10 | 122.75 | 126.40 | 123.74 | 156.05 | 157.05 | 156.68 | 157.56 |

| pH | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.89 | 1.88 | 1.88 | 1.88 | 1.82 | 1.82 | 1.82 | 1.82 | 1.76 | 1.75 | 1.76 | 1.76 | 1.71 | 1.71 | 1.71 | 1.70 |
| EXIT1 | 5.40 | 5.39 | 5.38 | 5.38 | 5.29 | 5.29 | 5.28 | 5.28 | 5.21 | 5.21 | 5.21 | 5.20 | 5.13 | 5.13 | 5.12 | 5.12 |
| EXIT2 | 5.75 | 5.75 | 5.74 | 5.75 | 5.67 | 5.67 | 5.67 | 5.67 | 5.60 | 5.60 | 5.60 | 5.60 | 5.56 | 5.56 | 5.55 | 5.55 |
| EXIT3 | 6.09 | 6.08 | 6.07 | 6.07 | 6.02 | 6.02 | 6.02 | 6.03 | 5.95 | 5.95 | 5.96 | 5.96 | 5.92 | 5.92 | 5.92 | 5.92 |
| EXIT4 | 6.36 | 6.31 | 6.28 | 6.25 | 6.13 | 6.14 | 6.13 | 6.13 | 6.05 | 6.05 | 6.05 | 6.04 | 6.00 | 6.00 | 5.99 | 6.00 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 44° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 38. Effect of temperature on iron removal

| TOTAL IRON | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 49.58 | 47.78 | 48.78 | 49.19 | 99.07 | 102.87 | 102.31 | 103.43 | 146.44 | 145.82 | 146.71 | 145.64 | 186.68 | 185.32 | 186.14 | 183.39 |
| EXIT1 | 46.96 | 47.18 | 47.91 | 48.21 | 98.81 | 100.66 | 101.12 | 101.68 | 146.04 | 146.34 | 143.22 | 143.44 | 186.09 | 184.57 | 185.27 | 184.57 |
| EXIT2 | 44.59 | 44.98 | 45.91 | 45.43 | 98.36 | 100.54 | 100.19 | 100.89 | 145.00 | 143.37 | 145.20 | 144.33 | 183.34 | 181.98 | 183.38 | 180.37 |
| EXIT3 | 44.31 | 44.10 | 45.57 | 44.84 | 96.39 | 100.61 | 98.97 | 97.70 | 144.06 | 141.16 | 142.52 | 141.92 | 181.84 | 180.42 | 182.78 | 181.69 |
| EXIT4 | 24.05 | 25.71 | 26.71 | 27.01 | 63.03 | 67.19 | 70.13 | 70.80 | 107.39 | 105.80 | 107.43 | 106.37 | 137.23 | 139.81 | 140.25 | 139.32 |

| pH | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.92 | 1.93 | 1.92 | 1.91 | 1.85 | 1.85 | 1.85 | 1.84 | 1.82 | 1.82 | 1.82 | 1.82 | 1.77 | 1.76 | 1.77 | 1.76 |
| EXIT1 | 5.52 | 5.50 | 5.48 | 5.48 | 5.36 | 5.37 | 5.36 | 5.36 | 5.32 | 5.32 | 5.32 | 5.30 | 5.24 | 5.24 | 5.24 | 5.23 |
| EXIT2 | 5.92 | 5.90 | 5.90 | 5.90 | 5.82 | 5.81 | 5.81 | 5.81 | 5.76 | 5.76 | 5.76 | 5.76 | 5.71 | 5.71 | 5.71 | 5.72 |
| EXIT3 | 6.29 | 6.29 | 6.30 | 6.29 | 6.22 | 6.22 | 6.21 | 6.21 | 6.17 | 6.17 | 6.17 | 6.17 | 6.12 | 6.12 | 6.12 | 6.12 |
| EXIT4 | 6.55 | 6.53 | 6.52 | 6.50 | 6.36 | 6.35 | 6.34 | 6.34 | 6.25 | 6.24 | 6.25 | 6.24 | 6.15 | 6.14 | 6.15 | 6.15 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 54° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

TABLE 39. Effect of temperature on iron removal

| TOTAL IRON | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 50.33 | 53.30 | 48.91 | 49.37 | 98.93 | 98.09 | 98.73 | 99.56 | 143.90 | 144.16 | 145.90 | 147.10 | 180.32 | 181.35 | 180.17 | 180.27 |
| EXIT1 | 50.83 | 53.23 | 49.90 | 48.45 | 98.59 | 98.95 | 98.42 | 99.12 | 140.64 | 144.36 | 142.53 | 144.76 | 179.49 | 180.18 | 179.21 | 176.92 |
| EXIT2 | 49.48 | 52.13 | 48.27 | 47.65 | 98.33 | 97.32 | 98.00 | 96.99 | 138.83 | 142.62 | 142.87 | 142.43 | 175.09 | 178.59 | 177.85 | 175.73 |
| EXIT3 | 49.78 | 46.01 | 47.65 | 47.66 | 96.34 | 95.73 | 94.96 | 94.86 | 138.15 | 141.34 | 136.62 | 140.67 | 175.90 | 177.28 | 173.39 | 175.32 |
| EXIT4 | 23.91 | 22.36 | 25.84 | 27.37 | 61.71 | 61.58 | 64.58 | 66.37 | 98.14 | 100.63 | 100.09 | 103.13 | 130.00 | 130.81 | 131.79 | 130.87 |

| pH | TIME 0.50 | TIME 1:00 | TIME 1:10 | TIME 1:20 | TIME 2:10 | TIME 2:20 | TIME 2:30 | TIME 2:40 | TIME 3:30 | TIME 3:40 | TIME 3:50 | TIME 4:00 | TIME 4:50 | TIME 5:00 | TIME 5:10 | TIME 5:20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INLET | 1.82 | 1.82 | 1.81 | 1.81 | 1.79 | 1.79 | 1.79 | 1.78 | 1.75 | 1.75 | 1.76 | 1.75 | 1.67 | 1.68 | 1.67 | 1.67 |
| EXIT1 | 5.45 | 5.43 | 5.42 | 5.41 | 5.34 | 5.35 | 5.34 | 5.35 | 5.29 | 5.29 | 5.28 | 5.29 | 5.21 | 5.21 | 5.21 | 5.22 |
| EXIT2 | 5.82 | 5.82 | 5.80 | 5.80 | 5.75 | 5.75 | 5.75 | 5.75 | 5.70 | 5.70 | 5.71 | 5.71 | 5.65 | 5.65 | 5.65 | 5.65 |
| EXIT3 | 6.18 | 6.18 | 6.17 | 6.18 | 6.12 | 6.12 | 6.12 | 6.14 | 6.09 | 6.09 | 6.10 | 6.10 | 6.05 | 6.05 | 6.06 | 6.05 |
| EXIT4 | 6.58 | 6.54 | 6.49 | 6.47 | 6.31 | 6.30 | 6.29 | 6.29 | 6.20 | 6.20 | 6.20 | 6.19 | 6.11 | 6.10 | 6.10 | 6.09 |

EXIT 1 - AFTER THE FIRST LIMESTONE COLUMN
EXIT 2 - AFTER THE AERATION UNIT
EXIT 3 - AFTER THE AERATION UNIT
EXIT 4 - AFTER THE SAND FILTRATION UNIT
FLOW RATE = 3.014 BBL/DAY
TEMPERATURE = 64° F
AERATION ANGLE = 1° DEGREE
SAND THICKNESS = 2.5 INCHES

## Appendix B

# Brine Treatment Facility Design Software

# *BRINE.EXE*

## *Brine Treatment Facility Design Software*

**USER'S MANUAL**

**by**

**Brine Treatment Research Group**
**The Pennsylvania State University**
**202 Hosler Building**
**University Park, Pennsylvania 16802**

**DISCLAIMER**

*The design software described in this manual was developed by Penn State University under research programs sponsored by Ben Franklin Advanced Technology Center (Ben Franklin Program), Pennsylvania Oil & Gas Association, Pennsylvania Energy Development Authority, Penn Grade Crude Association and the U.S. Department of Energy. The model upon which this design software is based was developed using the best available scientific knowledge, both laboratory and field data. However, neither the Pennsylvania State University nor the investigators take responsibility for the use and/or misuse of this software and hence, no guarantees are given. The Pennsylvania State University and/or its staff shall not be liable for any consequences arising from the use of this software.*

## INTRODUCTION

Brine.exe is a user-friendly, menu-driven program which can be executed on a personal computer with DOS environment. The purpose of this program is to design a brine treatment facility. The brine treatment research group at Penn State has been conducting research both in the field pilot unit and in the laboratory on brine treatment for several years and has developed a mathematical model to simulate the treatment process. Based on the results of this research, this program has been developed and tested to design a treatment facility to remove iron from brine. This program is the first step in developing a comprehensive design software for brine treatment facilities. More functions for addressing other needs, such as removal of organics (oil and grease) and metals other than iron, will be added to the program as additional experimental and field results become available. Figure 1 shows the flow chart for the program. This manual details the step-by-step procedure for using brine.exe.

## STARTING THE PROGRAM

In order to run this program, you must have a personal computer or workstation, with a DOS environment. At the DOS prompt, type in 'brine' and then press the return key, and the program will start to run. The first message appearing on the screen is an introduction to this program. Press the return key for the program to continue.

## THE MAIN MENU - AN OVERVIEW

At this time, the main menu will show on the screen. It has five choices: (0) help, (1) create a new data file, (2) modify a existing data file, (3) design the brine treatment facility, and (4) quit from the program. Option (0), the help screen, is provided to allow the operator to obtain additional information and further explanations of the choices presented. This option (0) is made available both in the main menus as well as the submenus, and throughout the entire design procedure. While the program is running (apart from the main menus and submenus), the help screen can be reached by entering a question mark (?).

In order to design a brine treatment facility, you must provide some basic information to the program. This is done through the data file, which should be under the name of "brine.dat". You may create the data file by any method, which will be discussed in next chapter, or you may choose to create the data file from the main menu. To do so, press '1' and then the return key.

The second option from the main menu is to modify a data file. If you already have a data file and want to change few numbers in the data file for another design, you may find this option very useful. It will ask you to input only the data you want to change and make the changes in your existing data file. To choose this option, press '2' and the return key.

The next option is to design the size of the brine treatment facility according to the requirements specified in your data file. The brine treatment facility consists of five units. Each unit has a different function and needs to be designed individually. Therefore, this option will lead you to a submenu -- the design menu. To proceed with the design, press '3' and press the return key.

The last option in the main menu is to quit from the program. Pressing '4' and the return key will return you back to the DOS prompt.

## THE DATA FILE

In order to design any facility, one needs to specify the requirements for that particular facility. For instance, to design the size of any equipment, we need to specify what capacity the equipment should have. We specify this type of information or requirements in the data file, which must be of the name of "brine.dat". The data specified in the data file must follow certain format. There are several ways to put your data file into the required format. These are described below.

Perhaps the easiest way to create a data file is to choose option 1 from the main menu, Create a New Data File. If you choose this option, the computer will ask you for all of the

required input values one at a time. Be sure to enter all the required information in the form of a real number (i.e., a number with a decimal point; e.g., enter **2.0** instead of **2**); otherwise, the program will ask you to re-type the number. When all values have been typed in, the computer will save the data file on the disk with the values you just entered and will return you to the main menu. Your new data file will automatically be put into the correct format required by the program.

Another simple way to create a data file is to modify an existing data file, which is done through option 2 on the main menu. Details on using this option are discussed in the next section.

Finally, it is possible for the user to create a data file by using any editor that runs under DOS or WINDOWS environment. However, the file must conform to the standards described below.

The data file consists of 13 lines. The first three lines are simply a heading. The last line is a footer line. The remaining eleven lines are in a table format. The left part of the table indicates the name of each variable and the right part gives the values of each variable. Figure 2 shows an example of the data file. The variables in the file must be listed in the same order as shown in Figure 2. The names of the variables (the character field) must occupy 49 columns and the values of these variables must be in the form of real number (a number with a decimal point) and must occupy a maximum of 10 columns in the file (the number field)*. In order for brine.exe to use the data file you are creating, you must save the data file under the name, "brine.dat". If you are creating your own data file from an editor, it may be helpful to look at the sample data file that has been included on the disk, called "brine.dat".

* For users who may be familiar with FORTRAN, the data file has been set up using the following format: 5X,41A,3X,F10.4.

The units of the variables are also included in the data file (see Figure 2). If you are using units different from Figure 2, you need to convert them to the proper units. For example, if your flow rate value is in gal/min, you need to do a simple calculation to convert the value into bbl/day before entering the value into the input file. (The conversion factor for these particular units is 1 gal/min=34.24 bbl/day.) Common unit conversions are provided in the help screen. Theoretically, the values of these variables could be any number greater than zero, with the exception of the angle of the aeration unit. By definition, the angle of the aeration unit is the angle between the length of the unit and a horizontal plane (see Figure 5). Hence, the value of this angle is restricted to a number between 0 and 90. However, based on our experience, an angle between 0° and 50° is more practical. The values specified in the data file are the user's choice, based on his/her situation.

When preparing a data file, some basic rules need to be kept in mind:

1. The program will design only one parameter at a time. For example, if one wants to design the length of the aeration unit, he/she must specify all the variables in the data

```
-------------------------------------------------------------
      THE INPUT DATA FOR BRINE TREATMENT DESIGN
-------------------------------------------------------------
Brine Flow Rate (bbl/day)                  =      2.0000
Inlet Iron Concentration (ppm)             =     40.0000
Outlet Iron Concentration (ppm)            =      5.0000
pH Value of the Brine                      =      6.0000
Operation Temperature (F)                  =     50.0000
Length of Aeration Unit (ft)               =      3.0000
Width of Aeration Unit (ft)                =      2.0000
Angle of Aeration Unit (degree)            =     24.0000
Diameter of Limestone Column (inches)      =      7.5000
-------------------------------------------------------------
```

Character field
49 columns

Number Field
10 columns
(maximum)

Figure 2. Sample data file

file except the length. The value in the data file for length can be any number, since it is the variable being calculated by the program. Since the values of specific gravity and viscosity may not be readily available to the user, default values have been set for these parameters (specific gravity=1.0, viscosity=$0.235 \times 10^{-4}$ lb-sec/ft$^2$). These default values are for pure water, since the specific gravity and viscosity of brine should be reasonably close to that of pure water.

2. A higher value of flow rate will require a larger treatment unit; therefore, you should specify in the data file the maximum flow rate you will encounter. Do not use an average value to design your facility if the flow rate varies seasonally.

3. A higher value of inlet iron concentration also requires a larger facility. To be on the safe side, you might want to slightly increase the value of inlet iron concentration, since it would be better to over-design the facility than to under-design.

4. The outlet iron concentration needs to be specified according to the requirements of the governmental regulations. A smaller value of outlet iron concentration will result in a larger facility.

5. The value of pH will only affect the design of the limestone columns. A higher pH requires fewer limestone columns. If the pH value is greater than 7.0, no limestone column is needed for the treatment process.

6. The operation temperature is a very important parameter in the design of the brine treatment facility. A lower temperature requires a larger unit. It would be best to specify in the data file the lowest temperature you think will be encountered in the field. However, if the temperature falls below the freezing point, the brine may freeze. The treatment process obviously will not work if the brine cannot flow through the treatment unit.

7. The length, width and angle of aeration unit are all related to each other in the design of the unit. For example, if you choose to build a longer aeration unit, the required width of the unit should be smaller. Therefore, you must specify two of these variables in order to design the third one. However, in the program, there is an option to design length, width and angle together (see page 12). With this option, you do not need to specify any of these parameters for the aeration unit. The output will be a table showing different combinations of length, width and angle. You can choose any of these combinations for your needs.

8. The choice of the diameter of the limestone column is only limited to the sizes of columns available. A smaller diameter will result in a longer limestone column. If various diameters of columns are available, you may want to design the length of the limestone column at various diameters and choose the combination of length and diameter that best suits your needs.

## MODIFY A DATA FILE

As mentioned earlier, you may choose to create your data file by modifying a data file already in existence. This is accomplished by selecting option 2 from the main menu. This will lead you to a submenu, which lists all the variables in the data file. You can select a variable you wish to modify by typing in the number corresponding to that variable and press the return key. The computer will ask you to enter the value of that variable from the keyboard by a prompt on the screen. You may select all the variables one at a time to create a new data file or you may select only the variables you want to change. All the other variables will keep the original values in the existing data file. After you have done all the modifications needed, select the quit option by typing in '12' and press the return key, which will return you to the main menu.

## BRINE TREATMENT DESIGN

After you have prepared the data file, you are ready to design your brine treatment facility. From the main menu, select the design option by typing '3' and press the return key. This will lead you to a design submenu. From the design submenu, you may select to design oil separation unit, pH adjustment unit, aeration unit, solids settling unit, or filtration unit by typing in '1', '2', '3', '4', or '5' respectively and press the return key. Or you may select the option of designing all the units by typing in '6' and press the return key. The quit option (type '7' and press return key) from this menu will return you to the main menu.

## DESIGN OF OIL SEPARATION UNIT

The function of this unit is to separate oil from brine. Oil separation unit is a box with several plates inside the box as shown in Figure 3. The design of the oil separation unit will provide you with the size of the box needed based on the brine flow rate encountered. The size given by this program should be considered as the **minimum** size. A larger size box will provide a better capacity for separating oil from brine. Therefore, you may build a box greater than or equal to the length, width and height given by this program. The length, width and height of the oil separate unit will be displayed on the screen as well as written in the output file named "brine.out". You can print out this file on a printer after you exit this program. After the design is done, the computer will ask you if you want to make another design. If you answer yes (type 'Y' and press return key), the program will return to the subdesign menu; if you answer no (type 'N' and press the return key), it will exit the program.

## DESIGN OF pH ADJUSTMENT UNIT

The pH adjustment unit consists of limestone columns. Higher pH value of brine helps to accelerate the oxidation reaction between the brine and the air. The function of the pH adjustment unit, as its name indicated, is to increase the pH value of the brine to above 6.0. This is done by flowing the brine through the limestone column. The efficiency of the pH adjustment is dependent

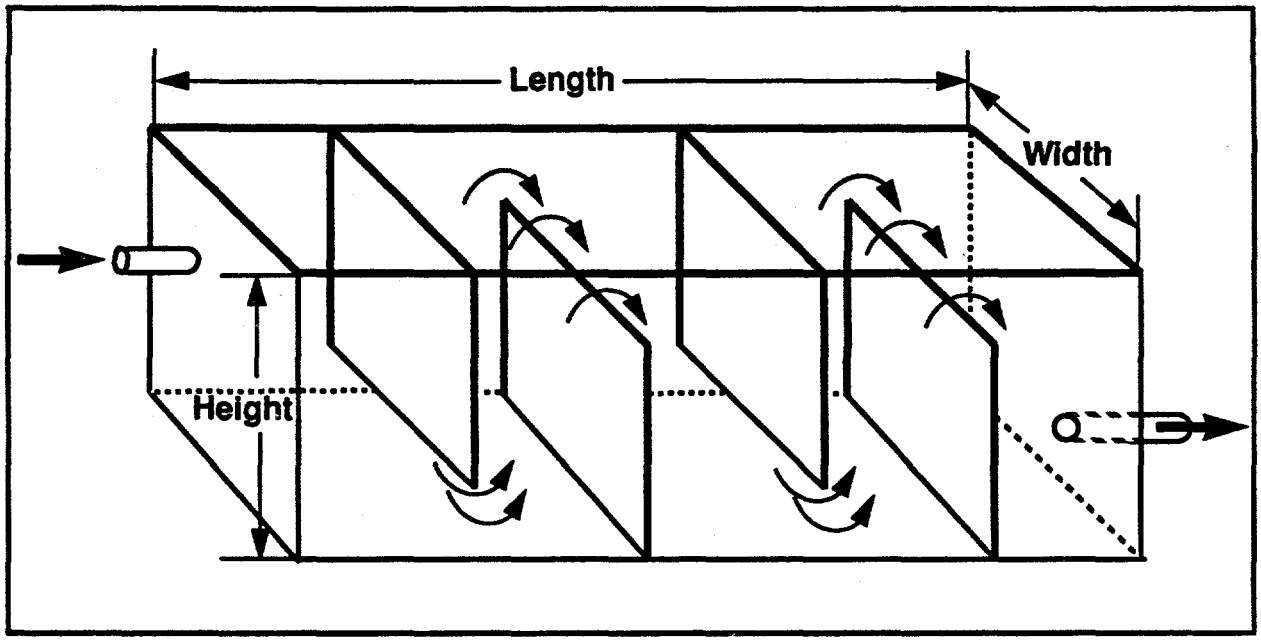


Figure 3. Oil separation unit

on the contact time between brine and limestone. A larger limestone column will permit longer contact time. Although the limestone column could be any shape, the cylindrical column is considered to be the best and hence is strongly recommended. At this time, brine.exe addresses the design of cylindrical limestone columns only. In order to design the pH adjustment unit, the user must specify the diameter of the limestone column in the data file. The program will calculate the total length of the column accordingly. The user can divide the total length into several columns to make the construction easier. As long as the total length of these columns is greater than or equal to the value given by this program, the pH adjustment unit should work properly. Whenever multiple limestone columns are used, the flow must always be such that it is upward in each column. Figure 4 shows an example of a 3-column system indicating the flow directions. The purpose of this configuration is to achieve maximum contact between brine and limestone chips. This flow configuration is achieved by building the oil separation unit at a higher elevation than the limestone columns so that the gravity potential is great enough to drive the brine through all the columns.

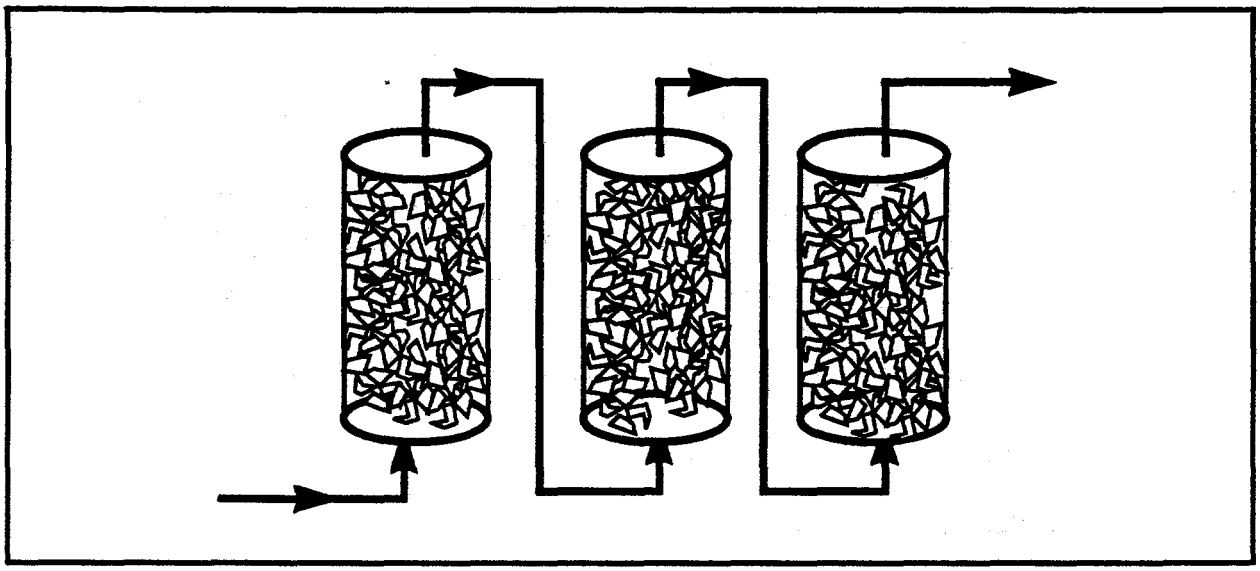

Figure 4. Flow direction for multiple-column pH adjustment unit

The total length of the pH adjustment unit will be displayed on the screen as well as written in the file named "brine.out." The total length is calculated based on the specified pH value of the brine and the diameter of the limestone column in the data file. This value should be regarded as the minimum length. Theoretically, the pH value could be any number between 0 and 14. However, our studies indicate that the maximum value of pH that can be obtained by installing limestone columns is 7.0. Hence, if the brine already has a pH of at least 7.0, no limestone columns are needed.

After the design is done, the computer will ask you if you wish to make another design. Answering yes (type 'Y' and press the return key) will return you to the design submenu while answering no (type 'N' and press the return key) will exit the program.

## DESIGN OF AERATION UNIT

Aeration unit is the most important part of the brine treatment facility. It is the place where the thin film of brine is created and the oxidation reaction takes place. The length, width and the angle of this unit (as defined in Figure 5) all affect the efficiency of the treatment. Choosing the

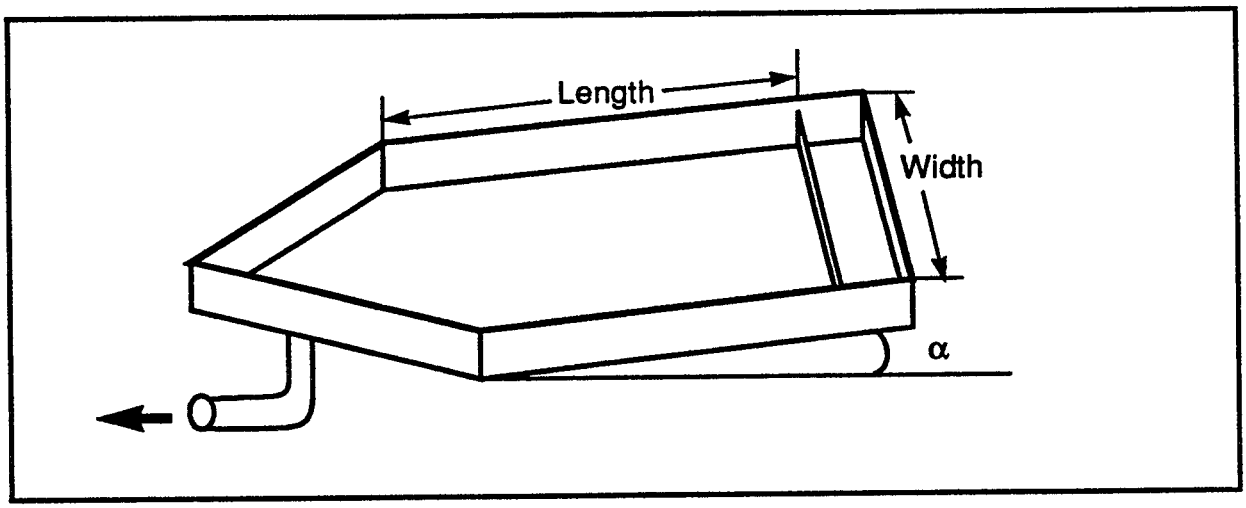


Figure 5. Aeration unit with dimensions

design of aeration unit from the design submenu will lead you to another submenu -- let us call it the aeration submenu (see Figure 6). The aeration submenu gives you 7 options, which are divided into two parts, the parameter design and the capability calculation. The following discusses the 7 options in detail.

```
SIZE DESIGN:
   (1) LENGTH OF AERATION UNIT
   (2) WIDTH OF AERATION UNIT
   (3) ANGLE OF AERATION UNIT
   (4) ALL THE ABOVE PARAMETERS

CAPACITY CALCULATIONS:
   (5) OUTLET IRON CONCENTRATION
   (6) MAXIMUM INLET IRON CONCENTRATION
   (7) MAXIMUM FLOW RATE

   SELECT ONE NUMBER (1-7):
```

Figure 6. Aeration submenu

## Length of aeration unit

The length of aeration unit is the distance that brine flows in thin film. This distance should provide sufficient contact time between air and the iron in the brine. This program

calculates the minimum length required to provide the contact time based on the width, angle, flow rate, inlet and outlet iron concentration, viscosity and gravity you specified in your data file. Remember, this is the **minimum** length required. You may create a longer aeration unit to provide more effective treatment of the brine. If the length of aeration unit called for by this program is too long for practical purposes, you may specify a length which seems feasible and attempt to design the width by selecting the next option (see next section).

### Width of aeration unit

In the design, we assume that the brine flow is evenly distributed over the whole area of the aeration unit. At a constant flow rate, a wider aeration unit will produce a thinner film over the unit. This, in turn, will create a better contact between the oxygen in the air and the iron in brine. The width of aeration unit is calculated based on the length, angle, flow rate, inlet and outlet iron concentration, viscosity and gravity you specified in your data file. The value provided by this program should be treated as the **minimum** width required. You may build several aeration units with the total width greater than or equal to the designed value. However, these units must be installed in **parallel** and brine flow should be distributed evenly to each of them.

### Angle of aeration unit

The effects of the angle of aeration unit are of two-fold, since the oxidation reaction between oxygen and iron is affected by the contact area as well as contact time. When the angle of aeration unit is increased, the thickness of brine film decreases so that the contact between air and brine increases. This will increase the effectiveness of the treatment. However, because of the increased angle, the brine flows faster over the aeration unit, which decreases the contact time, thus decreasing the efficiency of the treatment. Therefore, the optimum angle of the aeration unit occurs when a balance is achieved between these two factors. However, it is the **area** of the aeration unit that provides the contact between air and brine. If the aeration area (the length and width of the unit) is not properly specified, there may not be any angle which would be effective

for your particular conditions. In this case, the program will write a message on the screen, telling you that no angle can be found.

On the other hand, if the aeration area is sufficiently large, any angle between 0° and 50° should work for the conditions you specified in your input data file. In this case, the program will write a message on the screen telling you that any angle would work. There are also some situations where only a single angle or a small range of angles would work. In this case, the output of the program will be a single value for the angle or two values indicating the upper and lower limits of the range of acceptable angles.

**Design length, width and angle together**

This is probably the best way to obtain an optimal design for the aeration unit. With this option, you do not need to specify the length, width or angle of the aeration unit. The program will calculate the length of the aeration unit for different combinations of width and angle based on the flow rate and the inlet and outlet iron concentration. The program will output the results in the form of a table. This option is most useful when you have the flexibility of building the aeration unit at different sizes, so that you can select the combination of the length, width and angle which best suits your needs. Again, the values of the length and width should be regarded as the **minimum** values and they will be displayed on the screen as well as written in the output file.

**Outlet iron concentration**

This part of the program makes a capacity calculation that applies to the situation where you already have a treatment facility in place and need to use it for a different brine. In this case, you need to specify the size and the angle of the aeration unit, the inlet iron concentration and the flow rate. Based on this information, the program calculates the outlet iron concentration (after the treatment). If the outlet concentration is too high, it means that this facility does not have the capacity to handle the flow rate you specified. You may want to specify a smaller flow rate and run the program again. The software has been designed such that if the outlet iron concentration

exceeds the limits imposed by the governmental regulations, a warning message will appear on the screen alerting the operator that the present design will not be adequate and new parameters should be entered for more satisfactory results. Generally, with the same facility, a lower flow rate will increase the efficiency of the treatment. All the calculated values will be appear on the screen as well as in the output file.

### Maximum inlet iron concentration

If the required outlet iron concentration is specified, you can use this option to obtain the maximum inlet iron concentration that the existing facility can handle at a specified flow rate. Any brine whose inlet iron concentration is below the value given by this part of the program can be treated by the existing facility. Again, if the iron concentration of your brine is higher than the maximum value, you may decide to treat it at a lower flow rate.

### Maximum flow rate

Quite commonly, one may need to determine the maximum flow rate that an existing facility can handle and still remove iron effectively. In order to determine the maximum flow rate, you must specify the values for all the variables in the data file except the flow rate. The program will calculate the maximum flow rate and display it on the screen and in the output file. This value should be considered the **maximum** flow rate for the facility to effectively treat the brine.

After using any of these options under the aeration submenu, you will be asked if you want another design. Answering yes (type 'Y' and press the return key) will return you to the design submenu and answering no (type 'N' and press the return key) will exit the program.

## SOLIDS SETTLING UNIT

Settling unit is a box similar to the oil separation unit as shown in Figure 3. The design of these two units is very similar. The program will provide you with the size of the box based on the brine flow rate that you specified in your data file. The function of this unit is to provide sufficient

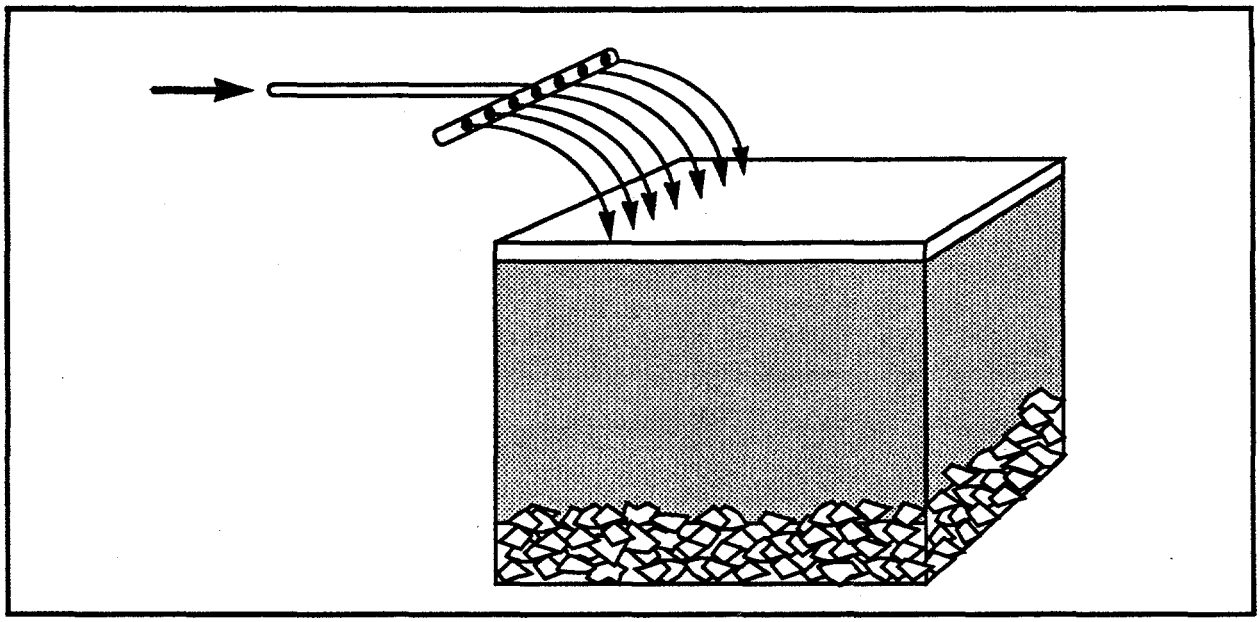

Figure 7. Filtration unit.

retention time to remove precipitated solids. The size given by this program should be regarded as the **minimum** size. A larger size box will provide better capacity for removing the solids. The size of the unit given by this program (including length, width and height) will be displayed on the screen as well as written in the output file named as "brine.out". After the design is done, the computer will ask you if you want to make another design. If you answer yes (type 'Y' and press return key), the program will return to the design submenu; if you answer no (type 'N' and press the return key), it will exit the program.

## FILTRATION UNIT

The filtration unit is another important part of the brine treatment facility. The structure of this unit is very simple (see Figure 7). It is a box with a layer of limestone chips spread over the bottom and filled with sand. The function of this unit is to remove the suspended solids which have by-passed the solids settling unit. It serves the additional purpose of neutralizing the treated brine prior to discharge. It has been observed in our experiments that most of the solids, in fact, are removed in this unit. The design of the filtration unit includes the surface area of the sand box (length * width), the depth of sand and the depth of limestone chips. Although our experimental

results indicated that it may not be necessary to distribute the brine over the entire sand surface, we do suggest you try to spread the brine over as much surface area as possible by using a spreader. A simple design such as the one shown in Figure 7 has been found to be adequate. It consists of a short pipe with several evenly distributed, small holes drilled in it. The width of the spreader be almost as wide as the sand box. The holes can be drilled with a one-inch drill bit and the holes spaced one inch apart. The function of the spreader is simply to distribute the brine over the entire surface of the filtration unit. While we do recommend the use of this kind of spreader, the most important part of this phase of the treatment process is the size of the sand box. The output results will be shown on the screen as well as written in the output file. Again, the dimensions specified in the results should be considered the **minimum** dimensions necessary for effective treatment.

## DESIGN ALL THE UNITS

If you are designing a new facility, this is the option you may want to choose (type '6' and press the return key from the design submenu). This option will go through all the design procedures as if you had already selected options 1 - 5 in the design submenu. The output results will be displayed on the screen as well as written in the output file.

## EXIT THE DESIGN SUBMENU

The last option in the design submenu is to return to the main menu. By typing '7' and pressing the return key, the program will display the main menu on the screen. From the main menu, you can chose to modify the data file, run another case, or exit this software.

## OBTAIN A HARD COPY OF DESIGN RESULTS

Throughout the running of this program, all the information will be displayed on the screen and also will be written to the output file named "brine.out." After exiting the program, the user can review the output results on the screen by using the "TYPE" command or any editing software to look at "brine.out." However, there exists an option that allows the operator to save

the output under any name. If no file name is specified, the output will be saved as "brine.out." It is also possible to obtain a hard copy of the results by printing the output file on a printer. The output file is in ASCII format; please refer to the appropriate manual for your computer or check with your system administrator to determine how to send the output file to a printer.

## GUIDELINES FOR CONSTRUCTING AND OPERATING THE TREATMENT FACILITY

As was mentioned previously, the primary function of the design software is to provide the operators with the proper and adequate sizing of the principal components of the brine treatment system. The actual construction of the system is left to the operators; however, we would like to suggest some construction guidelines. Some of the recommendations which might be considered when constructing the facility are listed below.

1. PVC pipes must be used for constructing the pH adjustment unit (limestone columns). These pipes come in various diameters and can be purchased at local hardware stores.

2. It is possible to build the separator, aeration, retention tank and filtration unit with wood. However, we do recommend using plastic for these (see #3 below). When using wood to construct these units, one must take special care to seal the units in order to prevent any leaks. We recommend applying plastic coating and fiberglass resin to the inner surface of the units for adequate sealing.

3. Since the brine treatment facility will be operating outdoors, it is subject to seasonal changes, such as sun, rain, and a wide temperature range. These changes will eventually affect the integrity of the wooden units. Therefore, it is recommended that plastic be used to construct units such as the separator, retention tank and filtration unit. These plastic containers come in different sizes and under normal conditions will eliminate the possibility of leakage. Our experimental work with the field model

proved that in the long run it is more cost-effective to use plastic instead of wood for these units.

4. The units should be constructed such that they could be easily disconnected and reconnected. This would allow the operator to repair the system more easily and quickly.

5. In order to provide sufficient surface area for the brine that comes in contact with the limestone, it is recommended to use limestone chips of grade 1-B that are approximately 1/4" in size. This limestone can be purchased through local mining companies.

6. Sand and gravel used in the filtration unit can be purchased locally through garden stores such as Agway. We have used yellow creek stone and landscaping stone as large as 1/2-inch or even 1-inch in our field and laboratory work.

7. Since the top layer of sand in the filtration unit becomes contaminated first, it is recommended to agitate the surface of the sand occasionally in order to prolong the effectiveness of the sand in the filtration process.

8. We always recommend over-designing the components of the treatment facility in order to be on the safe side.



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