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Full Name of Author — Nom complet de l'auteur

JAYARATNAM NAGENDRAN

Date of Birth — Date de naissance

June 6, 1951

Country of Birth — Lieu de naissance

SRI LANKA

Permanent Address — Residence fixe

8626 - 24 AVE
EDMONTON, ALBERTA
CANADA T6K 1Y1

Title of Thesis — Titre de la these

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S.E. HRUDEY

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FEASIBILITY OF ELECTROLYTIC FLOTATION FOR THE TREATMENT OF PRODUCTION RECYCLE WATER AT HEAVY OIL EXTRACTION FACILITIES

by

© JAYALINGAM NAGENDRAN B.S., P.Eng.

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

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IN

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CIVIL ENGINEERING

EDMONTON, ALBERTA

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled FEASIBILITY OF ELECTROLYTIC FLOTATION FOR THE TREATMENT OF PRODUCTION RECYCLE WATER AT HEAVY OIL EXTRACTION FACILITIES submitted by JAYALINGAM NAGENDRAN B.S., P.Eng. in partial fulfilment of the requirements for the degree of MASTER OF SCIECE in ENVIRONMENTAL ENGINEERING.

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Supervisor

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Date....April 16, 1980.....

ABSTRACT

One current technology for extracting heavy oil from underground formations is a method of steam stimulation. This process generates a large volume of oil-in-water emulsion. For economic and environmental reasons, it is necessary to treat this emulsion wastewater so that the clarified water can be reused for steam production and reinjection into the formation.

The in-situ heavy oil extraction facility in Cold Lake, Alberta, Canada presented the opportunity to obtain actual heavy oil-in-water emulsions for experimental work on a bench scale. The primary objective was to evaluate the electrolytic flotation process for technical and economic viability in treating heavy oil-in-water emulsions.

Using electrolytic flotation for heavy oil-in-water emulsion treatment was a new application for this process and presented many uncertainties. Numerous trials were conducted to determine the capability of this process and under varying operating conditions. The major variables in the experiment were, current density, electrode material, residence time in the reactor and chemical dosage.

The results confirm the technical feasibility of the electrolytic flotation process for the destabilization of oil-in-water emulsions from heavy oil extraction facilities. The cost for 90 to greater than 99 percent treatment efficiency was 0.22¢/bbl of synthetic crude produced for power consumption and 3.56¢/bbl for chemical consumption.

Treating the same wastewater with chemical coagulation alone to obtain equivalent treatment would cost 5.56¢/bbl of synthetic crude produced. The cost per barrel calculations were based on 141,000 barrels of synthetic crude produced per day with a production recycle water rate of 38.2 x 10^3 m^3/d. In addition, the required residence time in the electrolytic flotation cell was 15 minutes compared to 1 to 4 hours required for chemical coagulation alone. The reduced residence time allows for smaller reactor size and therefore reduced capital cost.

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GLOSSARY

API Gravity -- The gravity of fuel oils as measured with a hydrometer and expressed in °API (American Petroleum Institute) at 60°F. The API gravity is an empirical unit related to specific gravity in the following manner:

$$\text{Degrees API gravity at } 60°F = \left(\frac{141.5}{\text{Sp. gravity at } 60°F} - 131.5 \right)$$

Asphaltene -- A crude oil base classification referring to oil at the heavy end of the range (15° API gravity and lower). Asphaltic crude oils contain a large proportion of high boiling point hydrocarbons.

Hydrocarbons -- An organic compound made up of atoms of carbon and hydrogen. Because many of these compounds are present naturally in crude oil and natural gas, and as the carbon atoms each have four valence bonds, by which they can attach to other atoms, many hundreds of hydrocarbon compounds have been identified.

Resins -- Resins represent a complex mixture of aliphatic and cyclic organic compounds, such as terpenes and oxyterpenes, resin alcohols, and resin acids. Resins are as a rule wholly or partly soluble in alcohol, ether or

volatile oils and in this respect are distinct from gums.

I. INTRODUCTION

In an era of depleting non-renewable resources and higher energy costs, the recovery of untapped heavy oil is necessary and has recently become economically viable. Berry (1979) has reported a world wide heavy oil reserve of over 4,000 billion barrels in place, whereas recoverable light crude is estimated at only 2,000 billion barrels. Heavy oils are differentiated from standard light crude oil on the basis of their relative gravities and viscosities. Heavy oils, typically have API gravities between 10° and 20° and a viscosity range of between 40 and 2,000,000 centipoise at 15.6°C. In contrast, light oils have API gravities of 35° or more and viscosities usually under 10 centipoise at 15.6°C.

The known heavy oil reserve in Alberta is associated with the oil sand deposit. There is also recent evidence of more heavy oil in some carbonate formations, however very little is known about this potential reserve.

The Alberta oil sands are amongst the largest deposits of their kind in the world and are estimated to contain about 1,000 billion barrels of bitumen in-place. The four major deposits are Athabasca, Cold Lake, Peace River and Wabasca (Figure 1). These deposits underlie an area of approximately 70,000 km² in eastern and northern Alberta and vary in depth from surface outcrops to beds covered with more than 750 meters of overburden.

The Cold Lake oil sands are made up of four separate deposits each covered by overburden extending from 300

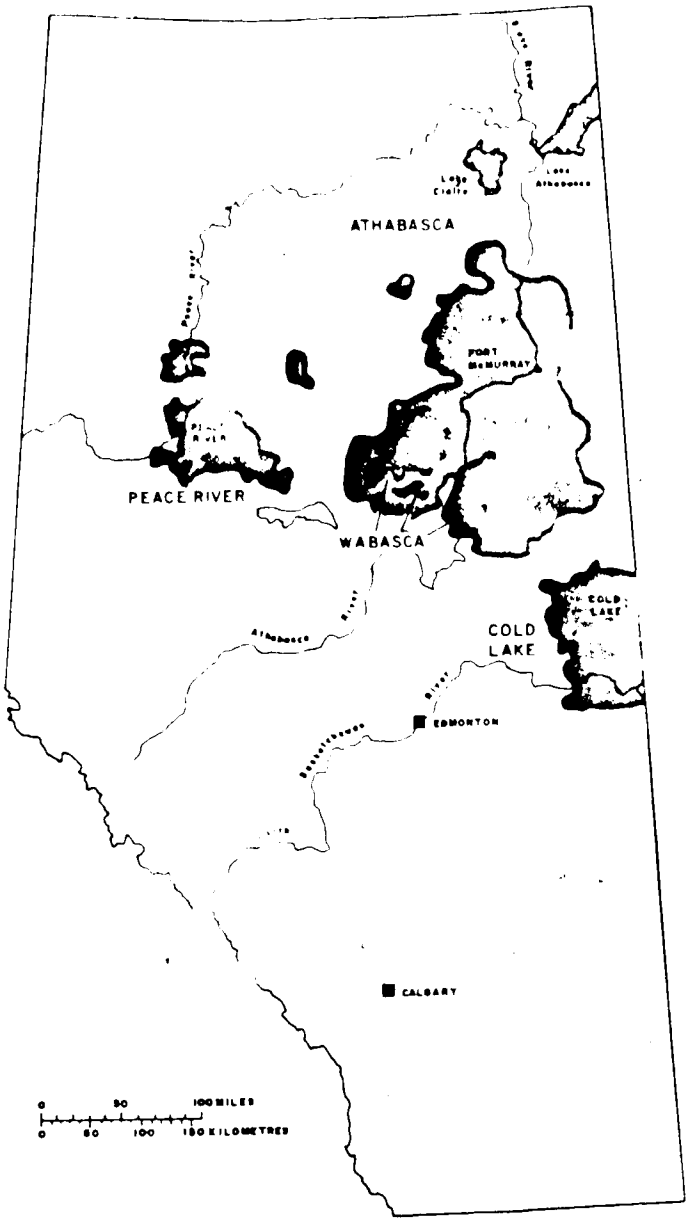


FIGURE 1 LOCATION IN ALBERTA OF THE FOUR MAJOR OIL SANDS DEPOSITS

meters to a depth of 600 meters. The crude bitumen occurs in beds of sand, usually partly cemented together, and in porous carbonate rocks. The sand grains are usually covered with a film of water, and bitumen occupies part of the pore space, along with fine clay particles, other mineral matter and occasionally some natural gas.

An experimental oil extraction project has been operating for 12 years at Cold Lake, Alberta and a full scale, permanent facility will be constructed pending Government approval. The facility is expected to recover 160,000 barrels per day of crude bitumen which would be upgraded and treated to produce 141,000 barrels per day of synthetic crude oil (EIA, 1979).

Montgomery (1980) has reported the API gravity of the Cold Lake heavy crude to be between 10° and 14°. Heavy crude also contains greater quantities of sulphur, nickel and vanadium than conventional crude. The carbon to hydrogen ratio of heavy crude is relatively high and the percent recovery of bitumen from the formation is low. A breakdown of the Cold Lake heavy crude is presented in Table 1.

Heavy oil in its natural state is too viscous to flow freely. Therefore, a method of steam stimulation is employed to reduce the viscosity and enable the oil to flow. However this process generates a large volume of oil-in-water emulsion. It is economically and environmentally essential to treat this oil-in-water emulsion, firstly to recover the oil and secondly to use the hot water for steam generation

TABLE 1

Average Class Composition of Bitumen from the Cold Lake Deposits (Strausz, 1979)

Components	Weight %
Hydrocarbons:	40
Saturated	21
Aromatic	19
Asphaltene:	16
Resins:	44
Acidic	15
Basic	7
Neutral N-Compounds	1
Neutral	21

for re-injection.

The produced oil-in-water emulsion for experiments in this study was obtained from the ESSO Resources Canada Limited, experimental in-situ heavy oil production plant at Cold Lake, Alberta. A process called electrolytic flotation was tested as a possible method of destabilizing and separating this relatively stable oil-in-water emulsion. The experimental electrolytic flotation process consisted basically of an electrode grid placed at the bottom of a batch reactor cell. The emulsion contains predominantly negatively charged colloidal globules of oil. Due to the repulsion of like charges the oil globules are prevented from coagulating, contributing to the stability of the emulsion. Current passing from the electrode grid through the emulsion may neutralize charged particles and thereby destabilize the emulsion and promote floc formation. The bubbles created due to the electrolysis of water then carry the flocs to the surface to effect phase separation.

The effects of electrode material, current density, residence time and chemical addition on the electrolytic flotation process were investigated. Treatment efficiency at an economically viable energy input was also investigated.

II. OBJECTIVES

The electrolytic flotation process has been proved successful in treating many types of industrial wastewater. However, this process has not been used in treating oil-in-water emulsions from heavy oil extraction facilities. Therefore as a first stage of experimental work in this process application, the following objectives were set:

1) To evaluate the feasibility of the electrolytic flotation process for separating oil from oil-in-water emulsions originating from production recycle water at heavy oil extraction facilities.
2) To evaluate the sensitivity of the electrolytic flotation process to relevant wastewater characteristics.
3) To consider the process variables that seem most probable to have a significant effect on electrolytic flotation process performance.
4) To identify the suitable process conditions within the framework of the parameters (variables) chosen and compare the cost of electrolytic flotation to that of chemical coagulation.
5) Based on the findings of this experimental study, to consider the applicability of the electrolytic flotation process to oil removal from other industrial oily wastewaters.

III. EMULSION THEORY AND SCOPE OF THE ELECTROLYTIC FLOTATION PROCESS

A. EMULSION THEORY

Emulsion refers to a mixture of a liquid in another liquid in which it is immiscible. The phase which is present in finely divided droplets is called the disperse or internal phase and the phase forming the medium in which these droplets are suspended is called the continuous or external phase. Becher (1965) defined an emulsion as a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameter, in general exceeded 0.1 μ.

There have been many emulsion theories published over the years. These publications included theories with respect to the orientation of molecules, phase volume, emulsion type, nature of the interfacial film, interfacial viscosity, dimensions of the interfacial film, droplet diameter, electrical charge, etc.. In this study dealing with electrolytic treatment of emulsion wastewater, it is convenient to begin the discussion with the electrical theories of emulsion.

Becher (1965) summarized the work done by Helmholtz, Gouy and Stern and has pointed out the complexity of interfacial interactions due to the existence of surface charges. In an attempt to explain this phenomena, Helmholtz introduced the concept of the electrical double layer.

Helmholtz assumed that the charge on the particles of a hydrophobic colloid was due to an unequal distribution of ions at the particle-water interface. Further, Helmholtz pointed out that if ions of one charge were closely bound to the particle, ions of opposite charge will line up parallel to them, forming a double layer of charges (Figure 2). Helmholtz' theory requires that the potential drop at the interface be sharp and considering the mobility of ions, it is doubtful that the regular orientation of ions which is needed to form the true Helmholtz layer are achievable. To overcome this shortcoming in the Helmholtz theory, Gouy proposed that the double layer is diffuse, with the outer ionic layer possessing an electrical density falling off exponentially. Stern on the other hand proposed a compromise theory between Helmholtz and Gouy which dealt with a two part double layer with one layer, approximately a single ion in thickness fixed to the interfacial surface. In this layer, there is a large drop in potential (Helmholtz layer) at the interface. The second layer extends some distance into the liquid dispersing phase and is diffuse (Gouy layer), with a gradual fall in potential into the bulk of the liquid. The potentials at an oil-water interface according to the three theories are illustrated in Figure 3.

Introduction of the potential knowing the properties assumed by Gouy into the Poisson equation leads to several interesting results. One of these as reported by Becher (1965) is the existence of the parameter,

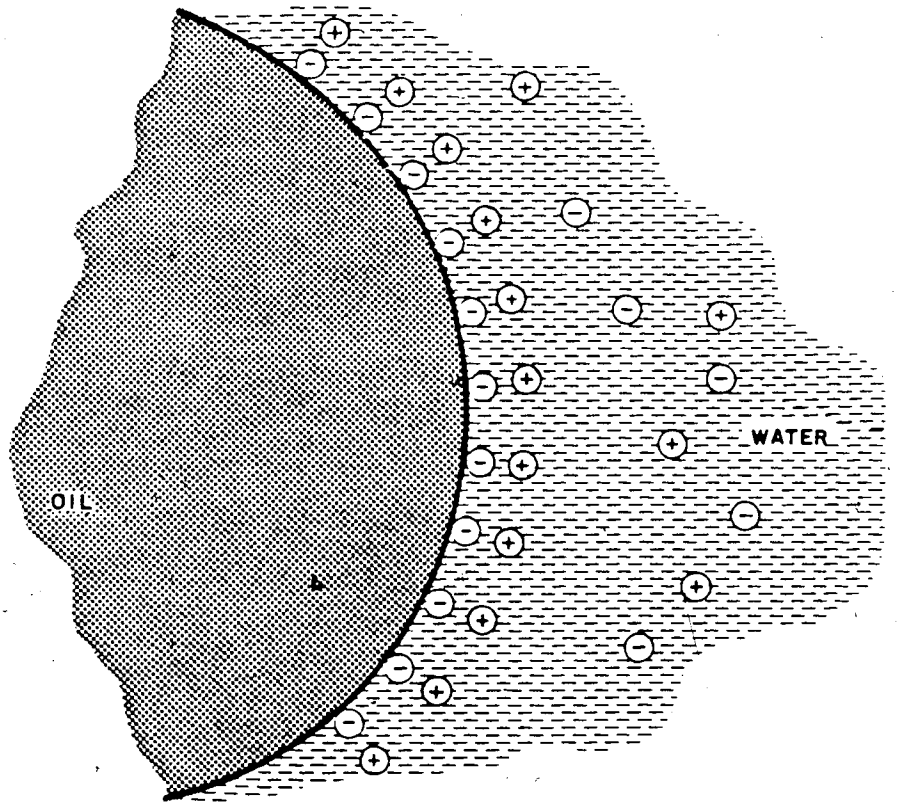


FIGURE 2 IDEALIZED REPRESENTATION OF THE ELECTRICAL DOUBLE LAYER AT AN OIL-WATER INTERFACE (BECHER 1965)

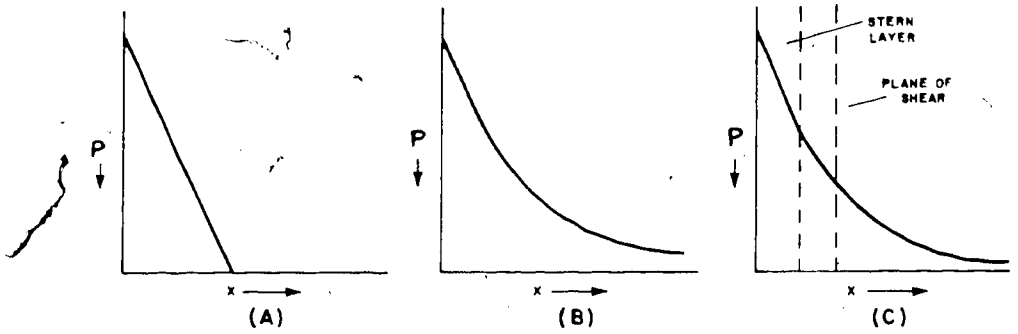


FIGURE 3 POTENTIAL AT AN OIL-WATER INTERFACE ACCORDING TO (A) THE SIMPLE HELMHOLTZ THEORY (B) THE GOUY DIFFUSE DOUBLE-LAYER THEORY (C) THE STERN DIFFUSE DOUBLE-LAYER THEORY. THE POTENTIAL MEASURED AT THE PLANE OF SHEAR IS THE ZETA-POTENTIAL. (BECHER 1965)

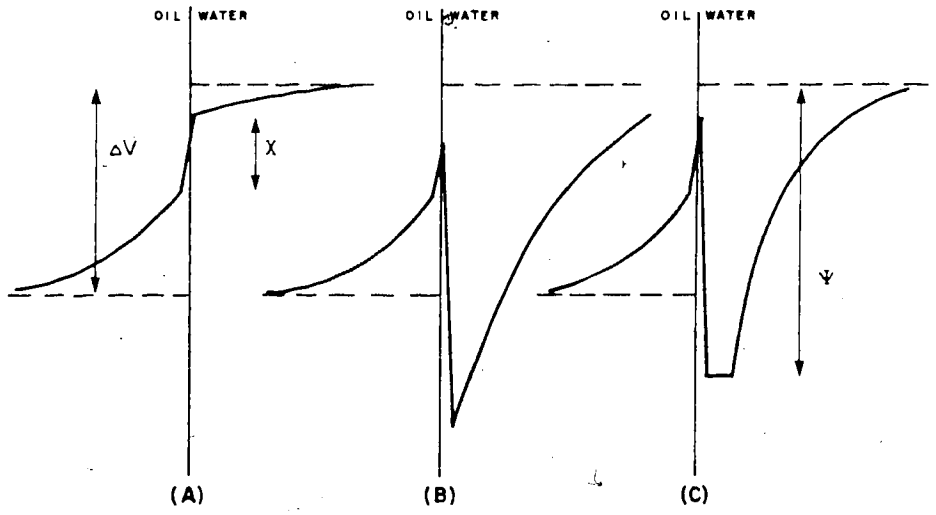


FIGURE 4 THE DOUBLE LAYER AT THE OIL-WATER INTERFACE IN EMULSIONS. (A) IN THE ABSENCE OF SURFACE-ACTIVE COMPOUNDS. (B) IN THE PRESENCE OF SURFACE-ACTIVE COMPOUNDS. (C) IN THE PRESENCE OF A LARGE CONCENTRATION OF ELECTROLYTE IN THE WATER PHASE, IN ADDITION TO THE SURFACE-ACTIVE COMPOUND. (VAN DEN TEMPLE 1953)

$$K = \left(\frac{8 \pi n Z^2 e^2}{\epsilon K T} \right)^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where:

Z = the valence of the ions of opposite charge to the surface charge;

n = the number of ions oppositely charged to the surface charge per cm^3 in the solution at a distance from the double layer (i.e. the gross concentration);

e = the elementary charge on the particle (1.6×10^{-19} C);

ϵ = the dielectric constant (unitless);

K = the Boltzman's constant (1.38×10^{-23} $J.K^{-1}$);

T = the absolute temperature °K; and

K = the reciprocal of the distance from the particle of a plane containing most of the charged particles (cm^{-1}).

Therefore 1/K is the effective diameter of the particle, and the thickness of the double layer is seen to be proportional to $n^{-1/2}$, i.e. to the concentration of the ionic species which constitutes the ions of opposite charge to the surface charge. This fact has important consequences for the theory of the coagulation of emulsions as will be shown subsequently when discussing liquid-liquid interfaces.

The foregoing theories have dealt predominantly with particles rather than droplets because most theoretical work has concerned itself with the solid-liquid interface. Becher (1965) cited Verwey's work which states that the principal

difference between the solid-liquid interface and the liquid-liquid interface is the possiblity of a double layer existing on both sides of the interface.

Van den Temple (1953) illustrated the existence of the two sided double layers (Figure 4A). As can be seen, the potential on both sides of the interface is appreciable. In the oil-in-water emulsions the smallest part of the double layer potential occurs in the outer aqueous phase (in the absence of emulsifying agents). Such a system will have a strong tendency towards coalescence and hence be an instable emulsion. The addition of surface active agents (surfactants), concentrated at the interface, changes the potential pattern significantly. The magnitude of the potential difference between the interiors (ΔV) of the two phases remains unchanged, so long as the ionic concentrations in the bulk phase are not affected by the adsorption process. The initial change in the potential difference caused by the adsorption of the surface-active ions is compensated for by a rearrangement of the dissolved ions across the interface. This is shown in Figure 4B. As is evident, the major portion of the charge is now concentrated in the aqueous phase, and the zeta-potential is sufficiently large so that a stable oil-in-water emulsion can result. Moore (1972) defined the zeta potential at the interface as the effective potential across the double layer. Basically this refers to the potential at the interface, as illustrated in Figure 3 and Figure 4. Figure 4C illustrates

the changes in the potential pattern caused by the addition of a large amount of electrolyte in the water phase in addition to the surface active agent. As would be expected from Equation 1, the effective radius of the diffuse double layer is decreased by this addition. The ions of the opposite charge to that of the surface charge move in among the surface-active ions, producing a thin layer of uniform potential.

Since there are many types of emulsions, it is necessary to classify emulsions into some uniform categories. A convenient way to classify emulsions is to divide them into two categories on the basis of the nature of the external phase. The two categories of interest to this discussion are oil-in-water (o/w) and water-in-oil (w/o) emulsions. The terms "oil" and "water" are very general. Almost any highly polar, hydrophilic liquid can be termed as "water" and hydrophobic, nonpolar liquids can be termed as "oil".

Lissant (1974) classified emulsions by dividing the two major categories above into three classes, based on the volume percentage of the internal phase, or the internal phase ratio. Emulsions with less than 30 percent internal phase form the first class. Emulsions with about 30 to 74 percent internal phase fall into the second class and those with more than 74 percent internal phase fall into the third class. The two categories and the three classes of emulsions lead to six different groups of emulsions (Table 2).

TABLE 2

The Six Major Classes of Emulsions

GROUP	Internal-phase ratio (IPR)		
	30%	30 to 74%	74%
Water in oil	Low-IPR w/o	Medium-IPR w/o	High-IPR w/o
Oil in water	Low-IPR o/w	Medium-IPR o/w	High-IPR o/w

Becher (1965) reported Alexander and Johnson's work which indicates that the charge on particles in colloidal systems, can generally arise in three different ways:

a) ionization;

b) adsorption; and

c) frictional contact.

In the case of emulsion droplets, the difference between the first two mechanisms is blurred. In connection with the charge arising from a possible frictional mechanism, Becher (1965) cited Coehn's empirical rule which states that a substance having a high dielectric constant is positively charged when in contact with another substance having a lower dielectric constant. Since water has a dielectric constant much higher than most of the substances which are likely to be the other phase of the emulsion, including oil, it appears that droplets of an oil-in-water emulsion will probably have a negative charge, whereas the water droplets in a water-in-oil emulsion will probably be positively charged.

Based on the literature review thus far, the production recycle water obtained from Cold Lake, Alberta, used in this experimental study can be categorized as a Low Internal Phase Ratio, oil-in-water emulsion with emulsion droplets that are most probably negatively charged. The treatment of this emulsion to effect phase separation requires the

destabilization of the emulsion. Destabilization and phase separation usually occur in a two step process. The first step is *coagulation* and the second step is *flocculation*. Therefore it is important to consider the processes of coagulation, flocculation and other methods of destabilizing the emulsion wastewater.

B. DESTABILIZATION OF EMULSIONS

Kemmer (1979) defined coagulation as the destruction of the emulsifying properties of the surface-active agent or neutralization of the charged oil droplet and defined flocculation as the agglomeration of the neutralized droplets into large, separable globules. WPCF (1977) defined flocculation as the coalescence or agglomeration of finely divided suspended matter by physical or chemical coagulant aids. Coagulation and flocculation processes have commonly been used for pretreatment of wastewater.

As reported in WPCF (1977), the flocculation process may be a self-flocculation process which occurs through mixing only or an induced flocculation consisting of chemical addition followed by mixing. Some agglomeration of colloids will begin immediately because of Brownian movement in the liquid. This is referred to as perikinetic flocculation as contrasted with orthokinetic flocculation, which is accomplished by particle collisions induced by hydraulic or mechanical means. It is the orthokinetic flocculation that is of interest to us in this study. Some

of the significant fundamental theories of particle aggregation to flocculation have been developed by Camp (1955) and Hudson (1965).

Camp (1955) revealed that the completion of the chemical reactions in a coagulation or softening process is almost instantaneous after the chemicals are fully dissolved. The precipitates first formed are crystals of molecular size. The initial increase of size of these colloidal crystals is caused by true diffusion or Brownian motion. At this stage the particles are still too small to be seen by the naked eye. The completion of the coagulation process requires gentle turbulent mixing of the suspension. The rate of coagulation depends on the number of particles, the rate of collision, the size of particles, ability of particles to adhere to each other, detention time and degree of mixing (mean velocity gradient). Camp (1955) proved that the rate of collision of particles at any given particle concentration is proportional to the absolute velocity gradient or the space rate of change of velocity at any point.

Velocity gradients are created in fluids by energy input. Such energy is dissipated by the creation of shear forces that are equal at any point to the product of the fluid viscosity and the velocity gradient. The rate of power dissipation (the work of shear per unit of volume per unit of time at a point) is known as the "dissipation function". The mean value of the dissipation function W, is equal to

the total power dissipation divided by the volume of the flocculation chamber. The root-mean-square velocity gradient, G is defined by the following equation:

$$G = \left(\frac{W}{\forall}\right)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

in which $\forall$ is the absolute viscosity of the fluid.

Since the rate of floc formation is directly proportional to the velocity gradient G, it should follow that the greater the magnitude of G the less should be the time required to form the floc. Hence, for economy in the size of flocculation chambers, the velocity gradients should be made as large as practicable. The practical limit however, of the velocity gradient for any flocculation process is determined by the size of the floc particles required because there is a maximum size of floc particles associated with each velocity gradient. This is best exemplified by examining the viscosity of the fluid.

By definition, the viscosity of a fluid is the proportionality constant between the unit shearing force, τ, and the velocity gradient, G', at a point.

$$\forall = \frac{\tau}{G'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

It is evident from equation 3 that the higher the velocity gradients become, the greater will be the shearing forces in a fluid. As floc particles grow they become weaker and are

more easily sheared apart. Thus, to form small floc particles, relatively high velocity gradients may be necessary and for large floc particles lower velocity gradients may be required. Overly violent mixing in flocculation chambers will prevent the formation of floc particles that are large enough to settle out effectively. WPCF (1977) concluded that pilot and bench scale work are invaluable in determining the flocculation method and G value requirements for particular wastewater streams. The value of G measured as S^{-1}, is used as a measure of the intensity of turbulence created. In general, a very gentle mixing would be related to a G of 20 and a vigorous mixing would be related to a G of 100.

In view of Camp's (1955) finding that the coagulation step is almost instantaneous, the rate determining step in this process would be the slower flocculation process. Becher (1965) reported that increasing the concentration of the oil phase in the emulsion will result in a slowly increasing rate of coagulation but a much faster increasing rate of flocculation. Consequently, in highly concentrated emulsions, the coagulation step can be the rate determining step.

Even in dilute emulsions, coagulation can be made the rate determining step by the addition of surface-active agents. These agents may have little or no effect on the rate of flocculation but can inhibit coagulation considerably (Becher, 1965).

Having considered the two stage process of coagulation and flocculation that occurs while demulsifying an emulsion, some of the methods that have been used for demulsifying emulsions need further consideration.

Emulsions may be broken by chemical, electrolytic, or physical methods. Emulsion breaking can also be termed as "resolution" of an emulsion. Kemmer (1979) reported many common forms of breaking emulsions. Chemicals are used extensively to destabilize emulsions and enhance mechanical treatment. Sulphuric acid has been used in oily wastewater treatment plants as a first step in emulsion breaking. Chemical coagulating agents, such as salts of iron or aluminum have also been used successfully. However, the hydroxide sludges of aluminum and iron are difficult to dewater. Even though acids are more effective than coagulant salts, the resulting acidic wastewater has to be neutralized prior to disposal or reuse.

Kemmer (1979) also reported that organic demulsifiers such as polyamines, alkyl substituted benzene sulfonic acids and their salts, alkyl phenolic resins, etc., are extremely effective emulsion breaking agents, giving more consistent results and generally producing better effluent quality than inorganic chemical treatments.

The main chemical coagulant used in this study was ferric chloride ($FeCl_3$). Ferric chloride is one of three iron compounds used in wastewater treatment as a coagulant. Commercially, ferric chloride is available as liquid,

anhydrous and hydrated crystals. The anhydrous form is granular while the crystalline form is irregular lumps. Liquid ferric chloride is a dark brown solution in water. WPCF (1977) reported that ferric chloride is very hygroscopic and therefore it has to be shipped in air-tight containers. Because of the hygroscopic and corrosive nature of anhydrous ferric chloride, it is recommended that stock solutions be prepared for use in treatment processes. It must also be noted that heat is generated when this chemical goes into solution. The iron salt reacts with the natural alkalinity of the wastewater to form a hydroxide precipitate that coagulates suspended and colloidal material. Two representative formulae are as follows:

$$2\ FeCl_3 + 3\ Ca(HCO_3)_2 \longrightarrow 2\ Fe(OH)_3\downarrow + 3\ CaCl_2 + 6\ CO_2$$

$$FeCl_3 + 3\ NaOH \longrightarrow Fe(OH)_3\downarrow + 3\ NaCl$$

Mechanical oil-in-water emulsion treatment methods currently in established use are air flotation (AF), dissolved air flotation (DAF), vacuum flotation (VF), ultra filtration (UF) and activated carbon adsorption (AC).

Air flotation, dissolved air flotation and vacuum flotation have been discussed by Metcalf and Eddy (1972). These different types of air flotation alone are not capable of destabilizing a stable emulsion. However, once the emulsion is destabilized, air flotation methods are capable of effecting phase separation. In air flotation, air bubbles

are formed by introducing the gas phase directly into the liquid phase through a revolving impeller or through diffusers. Such flotation alone is usually not effective for phase separation of oil-in-water emulsions. In dissolved air flotation, air is dissolved in wastewater under a pressure of several atmospheres and is followed by the release of the pressure to the atmospheric level. This is more effective than the air flotation process for phase separation. Finally in vacuum flotation, the wastewater is saturated with air and a partial vacuum is applied, which causes the dissolved air to come out as bubbles. This process is not as effective as the dissolved air flotation process for phase separation.

Kemmer (1979) described ultra filtration as a method of forcing an oily emulsion to pass through very small pores (less than 0.005 microns) in a membrane. Only water and dissolved low molecular weight materials can pass through the pore structure of the membrane, leaving a concentrate of the emulsified oil droplets and suspended particles. Plugging does not occur as it can in ordinary filtration because particulates are much larger than the pores and cannot enter the membrane structure.

Activated carbon is usually employed to clean up wastewater containing less than 100 mg/L of soluble and emulsified organics. This is usually a polishing step. Activated carbon, when contacted with water containing organic material, will remove these compounds selectively by a combination of adsorption of the less polar molecules,

filtration of larger particles and partial deposition of colloidal material on the exterior surface of the activated carbon. WPCF (1977) reported that the removal of soluble organics by adsorption depends on the diffusion of the particle to the external surface of the carbon, and then within the porous absorbent. For colloidal particles, internal diffusion is relatively unimportant because of the small particle size. Adsorption is partially the result of forces of attraction at the surface of a particle that cause soluble organic materials to adhere to that surface when they contact it, and partially the result of the limited water solubility of many organic substances. The fact that activated carbon has a large and highly active surface area per unit weight makes it an efficient adsorptive material. The large surface area and the activity of this surface is the result of the activation process that produces numerous pores within the carbon particle and creates active sites on the surface of the pores.

Having considered the theory of emulsions and various methods of destabilizing emulsions, electrolytic flotation will be specifically considered as a method for emulsion destabilization.

C. ELECTROLYTIC FLOTATION

Electrolytic flotation, as the name may suggest, is a means of flotation which uses electrolysis to effect the treatment. Holderness (1966) defined electrolysis as the

decomposition of a compound molten or in solution, by the passage of electric current. For electrolysis, a source of direct current is required. The current is conveyed to the electrolyte by electrodes. The electrode(s) connected to the positive pole of the source of current is the anode and the electrode(s) connected to the negative pole of the source is the cathode. The conventional current enters the electrolyte by the anode and leaves by the cathode.

Holderness (1966) reported that all other factors being constant, the order of discharge of ions will be that of the electrochemical series. The least electropositive elements (or groups) will tend to discharge first (i.e., most electropositive ions remain ionized in solution longer than the least electropositive ions). The order of ascending electropositivity is as follows:

CATIONS

$Pt^{4+} < Ag^{+} < Cu^{++} < H^{+} < Pb^{++} < Sn^{++} < Fe^{++} < Zn^{++} < Al^{3+} < Mg^{++} < Na^{+} < Ca^{++} < K^{+}$

A similar phenomena occurs with electronegative ions to that of the electropositive ions. The order of ascending electronegativity is as follows:

ANIONS

$OH^{-} < I^{-} < Br^{-} < Cl^{-} < NO_3^{-} < SO_4^{--}$

The order of discharging ions according to their discharge potential becomes complicated when the relative

concentration of ions are dissimilar. For ions whose discharge potentials are close together, such as OH^- and Cl^-, the order of discharge is reversed if the concentration of Cl^- is much greater in solution than that of OH^-. However, this effect would not be felt, for example, between OH^- and SO_4^{--} owing to the great difference in their electronegativity.

The nature of the electrode can also influence the ionic discharge. The most important example is, if a common salt solution is electrolyzed with a platinum cathode, H^+ from water discharges first.

$$2\ H^+ + 2\ e^- \longrightarrow H_2$$

If, however, a mercury cathode is used, the energy of discharge of the sodium ion is much reduced and it discharges to form a sodium amalgam and no hydrogen is liberated under these conditions.

$$Na^+ + e^- \longrightarrow Na$$

$$Na + Hg \longrightarrow NaHg$$

Masterton and Slowinski (1969) reported the cathodic reductions and anodic oxidations that take place in a water solution. At the cathode, the cation may be reduced to the corresponding metal or the water molecule may be reduced to generate elementary hydrogen.

$$2\ H_2O + 2\ e^- \longrightarrow H_2(g) + 2\ OH^-$$

At the anode, the anion may be oxidized to the corresponding non-metal or the water molecule may be oxidized to generate elementary oxygen.

$$H_2O \longrightarrow 1/2\ O_2(g) + 2\ H^+ + 2\ e^-$$

The important and necessary requirement for a successful electrolytic flotation operation is the generation of oxygen gas at the anode and the hydrogen gas at the cathode. It is these gas molecules that are solely responsible for carrying the flocs formed in this process to the surface of the reactor cell. The passage of current is also responsible for neutralizing charged particles and droplets in solution enabling the emulsion droplets to coagulate and flocculate prior to the flotation process.

The electrolytic flotation process has found wide application outside North America for the treatment of industrial wastewaters. In North America, the food processing industry has found this process a valuable means of treating their wastewaters. The majority of technical information on the electroytic flotation process appears in foreign language journals or patents. Translations of some of the important foreign language publications and available publications in English have been used as the source of background information in this investigation.

Snyder and Willihnganz (1976) reported electrolytic flotation as being attractive for oily emulsions because it breaks up the emulsion, separates the oil in a floating

layer and requires no chemical addition. However, Dubois (1976) reported that electrolytic flotation has very little effect on emulsions and as a result this process cannot be used on emulsions unless combined with chemical coagulation-flotation treatments. On the other hand, Beck, et al. (1974) reported that electroflotation can provide relatively rapid flotation and compaction of floc and can be used alone or in conjunction with flocculants. Ramirez, et al. (1976) went a step further and stated that electrolytic flotation can be used with or without coagulants, but the process should be carried out in two sequential steps. The first step being electrocoagulation and the second step being electroflotation.

Chambers and Cottrell (1976) recommended electrolytic flotation especially for low flow rates (less than 25 m^3/h). Choffel (1976) reported electrolytic flotation as being very efficient but rather costly and its application limited to waste volumes under 100 m^3/h. Genkin and Belevtsev (1978) indicate the process being applicable to relatively concentrated wastewater discharged in small volumes. Ramirez, et al. (1977) studied a commercial operation performing efficiently at flow rates a little over 100 m^3/h. Clayton and Noble (1974) reported better than 99% removal of settleable matter from a potato crisp factory having an effluent flow of 200 m^3/h.

There are many electrode materials that can be used. It is even possible to use different electrodes for the anode

and the cathode. Depending on the electropositivity of the metal used for the anode, the dissolution of metals is variable during the electrolysis of water. Therefore, the type of anodes used is very significant, for it will dictate the frequency of electrode replacement and resultant operating and maintenance cost. To circumvent this problem, researchers have experimented with numerous stable electrode materials (Table 3). Snyder and Willihnganz (1976) used gold for the anode and stainless steel for the cathode to prevent the dissolution of the anode. On the other hand, in operations where chemical addition is necessary prior to electrolytic flotation, it is at times preferable to have sacrificial electrodes such as iron and aluminum. Genkin and Belevtsev (1978) listed the main advantages of using a electrocoagulation process over a coagulation with chemical addition as follows:

- the apparatus for electrocoagulation is more compact and its operation is simple;
- detention periods are shortened;
- chemical feeding equipment is reduced or absent;
- the liquid phase in sludge produced is reduced giving a reduced volume of sludge;
- electrocoagulation takes place analogous to coagulation with iron and/or aluminum but with the added advantage of the liquid not being enriched with anions and the salt content does not increase due to precipitation of the metal hydroxides.

TABLE 3

Types of Electrode Material Used in the Electrolytic Flotation Process

1. Iron [Kaliniichuk, et. al. (1976)]
2. Aluminum [Barrett (1976), Chamers and Cottrell (1976), Kaliniichuk, et al. (1976)]
3. Stainless steel [Snyder and Willihnganz (1976)]
4. Platinum [Mikheeva et al. (1974)]
5. Graphite carbon [Genkin and Belevtsev (1978)]
6. Dioxide of lead [Chambers and Cottrell (1976), Genkin and Belevtsev (1978)]
7. Manganese and ruthenium deposited on titanium [Genkin and Belevtsev (1978)]
8. Lead coated titanium [Lewin and Forster (1974)]
9. Stainless steel cathode, gold anode [Snyder and Willihnganz (1976)]
10. Duriron [Ramirez, et al. (1977)]

The utility of the electrotytic flotation process is evident by the number of successful applications undertaken by various industries. The types of industries using this technique on wastewater have been summarized by Clayton and Noble (1974) as follows:

1. Emulsions: Mineral or Synthetic oils
2. Water containing fats: Slaughterhouses, Milk Industry, Cream Manufacturers
3. Textile Industry: Finishing and Dyeing
4. Painting: Coloured waters
5. Chemical Industry: Polymers, Colourants
6. Pharmaceutical Industry: In particular if the water contains biological poisons.
7. Papermills: Coating, printing waters
8. Sulphite or Kraft Pulp production
9. Wood Industry: Fiberboard and Plywood
10. Glass Industry: Elimination of Silicates
11. Clay and Porcelain Industry
12. Food Industries
13. Mixed or Municipal Wastewaters

Genkin and Belevtsev (1978) reported the capability of the electrolytic flotation process to remove the following dissolved impurities: cyanides, rhodamides, nitro-compounds, amines, alcohols, aldehydes, ketones, azo dyes, sulphides, mercaptans and anthraquinone derivatives. However, no

explanation was given for the mechanism of removal.

In addition to the versatility of the electrolytic flotation process, there are also many other advantages to this process over conventional treatment methods such as chemical coagulation and gravity settling and dissolved air flotation. The major apparent advantage of electrolytic flotation over other flotation oil removal processes is its ability in some circumstances to remove *emulsified oils*. Beck, et al. (1974) summarized the advantages of the electrolytic flotation process as follows:

- The process almost always surfaces the floc, keeping the floc together in one place for easy skimming.
- Surfaced floc contains less water than conventional floc.
- The combination of chemical and electrochemical inputs drastically cuts chemical costs for water treatment because of their synergistic effect.
- The process can handle light and heavy wastewater loads without requiring a change of sequence.
- Detention time is very short, allowing smaller treatment tanks and reduced space requirements.
- The overall cost of the process is low.
- Effluent waters often have better than 90 percent reduction in chemical oxygen demand, biochemical oxygen demand, suspended solids and oil and grease.

Chambers and Cottrell (1976) reported the following additional advantages:

- The electrode grids can be arranged to provide good coverage of the flotation tank's surface area, so uniform mixing between the effluent and the gas bubbles is achieved.
- A large amount of very small bubbles is formed with minimum turbulence.
- The electric-field gradient between the electrodes aids flocculation of existing solids.
- Gas production and residence time are easily controlled.

The most important aspect in the investigation undertaken was the ability of the electrolytic flotation process to remove oil from wastewater. A summary of the oil removal performance reported in the literature for this process is provided in Table 4.

The operating parameters that affect the performance of the electrolytic flotation process are:

a. current density;

TABLE 4. PERFORMANCE CHARACTERISTICS OF ELECTROFLOTATION

Influent Oil Concentration mg/L	Effluent Oil Concentration mg/L	% Oil Removal	pH	Chemical Usage	Electrical Input	Electrode Material	Reference
1,300	1	99%	5	-	30 mA/cm^2 @ 15 V	Al	Ohtsugi and Kai (1974)
1,350	3.5	99.7%	-	-	40 mA/cm^2	Al cathode Pb anode	Mizusaki (1975)
10,000	1	99.99%	5.8	-	@ 30 V	Al	Ayuzawa, et al. (1975)
500	20	96%	-	$CaCl_2$	50 mA/cm^2	Ferrite	Nakayama (1977)
4,800	4	99.9%	-	NaCl $CaCl_2$	-	-	Itagaki and Yajima (1977)
5-15	2.5	-	-	-	30 mA/cm^2 .25 KW hr/m^3	Fe	Bedrin, et al. (1377)
23,000	10	99.99%	5	-	-	Pt/Ta anode Cu cathode	Naruse, et al. (1976)
150	10	93-95%	-	-	-	-	Stelmach and Wisniewski (1976)
10-20,000	20-40	99%	8	$Al_2(SO_4)_3$ 1500-2500 mg/L		Al	Petrova, et al. (1973)
25-200	15-20	-	-	-	30-40 mA/cm^2	Steel	Mikheeva, et al. (1974)

NOTE: Electrical input in mA/cm^2 means milli Amperes per centimeter squared of horizontal electrode surface area.

b. applied voltage;

c. electrode material; and

d. residence time.

Current density is defined as the amperes of current per centimeter squared of horizontal electrode surface area. Therefore, for a given current input, the following variations will increase the current density:

i) fewer electrodes;

ii) shorter electrodes; and

iii) smaller diameter electrodes.

For a given electrode system, current input is directly proportional to the applied voltage (ie. when the applied voltage increases current input increases). However, when maintaining a constant current input, increasing the number of electrodes will decrease the voltage across the electrode grid. For better electrolytic flotation treatment performance, greater current densities and voltages are advantages. The limiting factor in increasing these variables is operating power costs. Hence, cost-effective current density and voltage should be derived within the constraints of acceptable and reasonable power cost. In liquid effluents where the oil emulsions can be easily broken, current densities as low as 30 mA/cm^2 have been

found to be adequate (Table 4).

The electropositivity of electrodes is a very important variable in the electrolytic flotation process. Electrodes with greater electropositivity, as indicated earlier, tend to ionize into solution rapidly and thereby act as a coagulating agents. This enhances the performance of the process but at the same time frequent anode replacement is necessary. For continuous, uninterrupted operation, electrodes with low electropositivity are required. Also, greater current densities have a greater ionizing effect on electropositive anodes. Depending on the anode material, this could also be considered a limiting factor on how high the current density could be increased.

Longer residence times, give rise to better treatment efficiencies provided constant destabilization of the emulsion is taking place. However, longer residence time requires larger reactor volume, resulting in a much larger capital cost for the same volume of wastewater treated. Also, longer residence time with continuous treatment means greater power cost. Therefore, residence time should be minimized.

IV. EXPERIMENTAL METHODOLOGY

The analytical and experimental work were done in two phases. The first phase involved an exploratory stage to establish a combination of analytical and experimental procedures that would indicate the capability of the electrolytic flotation process to treat the specific wastewater at hand. Having established the analytical method and the experimental conditions necessary to produce meaningful results, the second stage involved generating data adequate for statistical validation and verification of the performance capability of the electrolytic flotation process. One significant difference in the analytical method between Phase 1 and Phase 2 was in the method of sample handling prior to the oil and grease analysis. In Phase 1 all samples were filtered using a Whatman No. 40 filter paper. However, with further experimental work it was found that the centrifuged samples provided a better indicator of the actual emulsified oil and grease left in the sample. Therefore all oil and grease analyses in Phase 2 were performed on centrifuged samples (Table 5).

A. ANALYTICAL

Total organic carbon (TOC) was analysed by the combustion infrared method 505 (APHA, 1975) using a Beckman model 915 A Total Carbon Analyzer. The maximum deflection of the chart recorder was set at 100 mg/L carbon for a 20 µL sample injection of 100 mg/L standard. The filtered sample

TABLE 5

A Comparison of Filtered vs Centrifuged Samples for Oil and Grease Analysis (analysis performed on untreated raw samples)

O & G concentration of filtered samples mg/L	O & G concentration of centrifuged samples mg/L
240	1750
270	1900
340	1980
Mean: 280	1850

was diluted five fold prior to analysis. TOC was measured by first analyzing for total carbon and then for inorganic carbon and the difference between the two was calculated to be TOC.

The pH of the samples was measured with a glass combination electrode and a Hach portable pH meter which was standardized with pH 4.0 and pH 9.0 buffer solutions.

Total alkalinity was measured by titration of a 25 mL sample with 0.02 N sulphuric acid to a pH 4.5 endpoint according to method 403 (APHA, 1975). The endpoint was detected when the colour changed from blue to pink using bromocresol green-methyl red indicator.

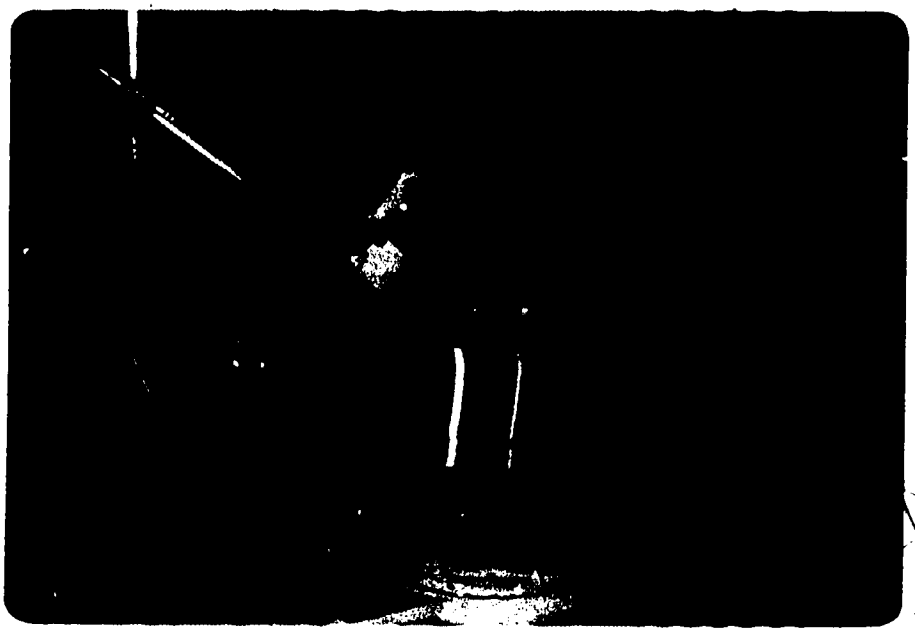
Electrical conductivity was read directly off a Hach conductivity meter after standardizing the instrument with a 0.0100 M standard potassium chloride solution.

Oil and grease concentration was considered to be the most important experimental parameter and as such considerable time was allocated to the establishment of an accurate method of analysis.

The solvents evaluated for the oil and grease extraction were limited to Freon 113 (1, 1, 2 - trichloro - 1, 2, 2 trifluoroethane) and methylene chloride (CH_2Cl_2). Freon is the solvent recommended and used in method 502 (APHA, 1975). Thus it was hoped that the Partition-Infrared Method could be used to measure the oil and grease concentration. A series of three successive extractions were made with 25 mL volumes of methylene chloride per extraction

using twenty two (22) different emulsion samples. Once extracted the methylene chloride was evaporated using a "Buchi" Rotavapor R rotary evaporater (Plate 1) The extracted oil concentration was quantified by a method similar to the partition-gravimetric method 502A (APHA, 1975). Then, 100 mL of Freon 113 was added to the distilling flask containing the oil and the flasks were shaken to aid in redissolving the oil in the solvent. The distilling flask with the Freon 113 was allowed to sit for over 12 hours. The Freon 113 with the extracted oil was poured into another preweighed clean distilling flask and again the procedure of method 502A (APHA, 1975) was followed. The resulting oil concentration was recorded. Knowing the concentrations of oil extracted by methylene chloride and Freon 113, it was possible to find by difference the percent of oil extracted by Freon 113 with respect to the concentration extractable by methylene chloride. It was found that the mean of the percent extractable by Freon 113 is 46.5% of that extractable by methylene chloride using a sample population of 22. The standard deviation was calculated to be 25% (Table 6). Therefore it was concluded that methylene chloride was a more efficient solvent in extracting emulsified oils originating from heavy oil extraction facilities.

The next stage of the oil and grease analysis was to find the optimum number of extractions needed using methylene chloride. Again a sample population of 22 was



ROTARY EVAPORATOR USED IN OIL EXTRACTION.

PLATE 1

TABLE 6

EXTRACTION EFFICIENCY OF FREON IN THE OIL & GREASE ANALYSIS

Sample #	Mass of Extracted O&G with CH_2Cl_2 mg	Mass of CH_2Cl_2 Extract Dissolving in 100mL of Freon, mg	% Extracted by Freon
1.	652	244	37.42
2.	696	312	44.83
3.	144	136	94.44
4.	144	94	65.28
5.	9	1	11.11
6.	9	1	11.11
7.	14	4	28.57
8.	13	1	7.69
9.	6	4	66.67
10.	49	40	81.63
11.	8	4	50.00
12.	13	5	38.46
13.	84	64	76.19
14.	6	4	66.67
15.	9	5	55.56
16.	13	7	53.85
17.	18	12	66.67
18.	6	4	66.67
19.	58	6	10.34
20.	10	3	30.00
21.	13	5	38.46
22.	9	2	22.22

mean: $\bar{x} = 46.54$

Std. Dev.: $S = 25.13$

used. Three successive 25 mL volume extractions were done with methylene chloride and the oil concentration was determined, again using the partition volumetric method similar to method 502A (APHA, 1975). Then a fourth 25 mL extraction with methylene chloride was done on the already extracted sample and the concentration of oil was determined. It was found that the mean percent of oil extracted by the fourth extraction was small compared to that extracted by the first three extractions (Table 7). In view of the relatively low recovery by the fourth extraction, the added benefit of this extraction is negligible. This is justified when considering that the precision of the oil and grease analysis was observed to be of similar magnitude. Therefore three methylene chloride extractions were considered to be sufficient.

Once methylene chloride was selected as the solvent, the partition-infrared method 502 B (APHA, 1975) was no longer feasible. The chemical structure of methylene chloride, unlike Freon 113 has two C-H bonds which would interfere and mask the wave length range of 2700 to 3100 cm^{-1} which is the same range used to determine the oil and grease concentration. The peak wave length used for oil and grease analysis is 2930 cm^{-1}. Hence it was necessary to use a method similar to the partition-gravimetric method 502A (APHA, 1975) with the exception of using methylene chloride instead of Freon 113 and the following procedure was followed:

TABLE 7

4th EXTRACTION EFFICIENCY OF METHYLENE CHLORIDE IN THE OIL & GREASE ANALYSIS

Sample #	O & G Concentration with 3 Extractions mg/L	O & G Concentration on the 4th Extraction mg/L	% Extracted on the 4th Extraction
1.	16	2	12.5
2.	720	0	0
3.	47	0	0
4.	66	0	0
5.	70	0	0
6.	29	3	10.3
7.	245	10	4.1
8.	40	0	0
9.	67	7	10.4
10.	422	6	1.4
11.	29	0	0
12.	43	0	0
13.	67	0	0
14.	31	0	0
15.	65	0	0
16.	46	0	0
17.	292	0	0
18.	48	0	0
19.	188	0	0
20.	49	0	0
21.	46	0	0
22.	45	0	0

o/o Extracted on 4th Extraction

Mean of all values = 1.76
Mean for values showing results = 7.74
Fraction having zero values = 0.77

Where possible 200 mL of sample volume was pipetted into a modified flask (Plate 2). The sample volume was reduced to 100 mL when analyzing highly concentrated samples such as the untreated raw sample. The sample was acidified to a pH of less than 2 with a 1+1 solution of hydrochloric acid and extracted three times with methylene chloride. The modified flask in Plate 2 was designed to replace the separatory funnel in method 502A (APHA, 1975) for a two fold purpose. The first purpose was to reduce the manpower requirement in vigorously shaking the separatory funnel in view of the many oil and grease analyses that were performed in this study. The second purpose was to achieve more consistent results with the modified flask arrangement than with the separatory funnel. A magnetic bar was introduced into the modified flask and all the mixing was done with the aid of magnetic stirrers. All samples were stirred for two minutes and the magnetic bars were rotated at the same velocity. The oil laden methlyene chloride was funneled into a clean, pre-weighed round bottom distilling flask as per method 502A (APHA, 1975). The distilling flask was then connected to the rotary evaporator. When all the methylene chloride was evaporated and only the residual oil and grease remained in the distilling flask, it was removed from the rotary evaporator and put in an oven at 103°C for 5 minutes. From the oven the distilling flask was transferred to desicator for one hour prior to weighing it and calculating the oil and grease concentration.

OIL EXTRACTION USING MODIFIED ERLENMEYER FLASKS

PLATE 2

B. EXPERIMENTAL

The samples for this study were obtained from the experimental insitu heavy oil recovery plant in Cold Lake, Alberta, Canada. The plant is owned and operated by ESSO Resources Canada Ltd. The oil-in-water emulsion samples were trucked in 25 gallon plastic lined barrels. The samples were transported in two batches. The first batch consisted of 10 drums and the second batch consisted of 15 drums. The samples were stored at room temperature and the sample age used in the experiments varied from two days to two months.

All samples used were pumped from the 25 gallon barrels into a plastic container (Plate 3). The plastic container had a tap near its bottom from which the samples were transferred to the electrolytic flotation cell. By drawing the sample off the bottom of the container, floating non-emulsified oil was not transferred to the reactor. This allowed the assessment of the treatment efficiency for emulsified oil alone. A heating coil was placed in the plastic container to raise the temperature of the sample to approximately 50°C to 60°C.

The electrolytic flotation cell was constructed from transparent acrylic plastic. The cell was cylindrical in shape with an internal diameter of 15 cm and a height of 91 cm (Plate 4). The cell was fitted with four sampling ports. The bottom sampling port was placed 15 cm above the bottom of the cell and each subsequent sampling port was spaced 20

RAW WASTEWATER BARRELS AND CONTAINER
USED FOR PREHEATING THE WASTEWATER

PLATE 3

ELECTROLYTIC FLOTATION CELL

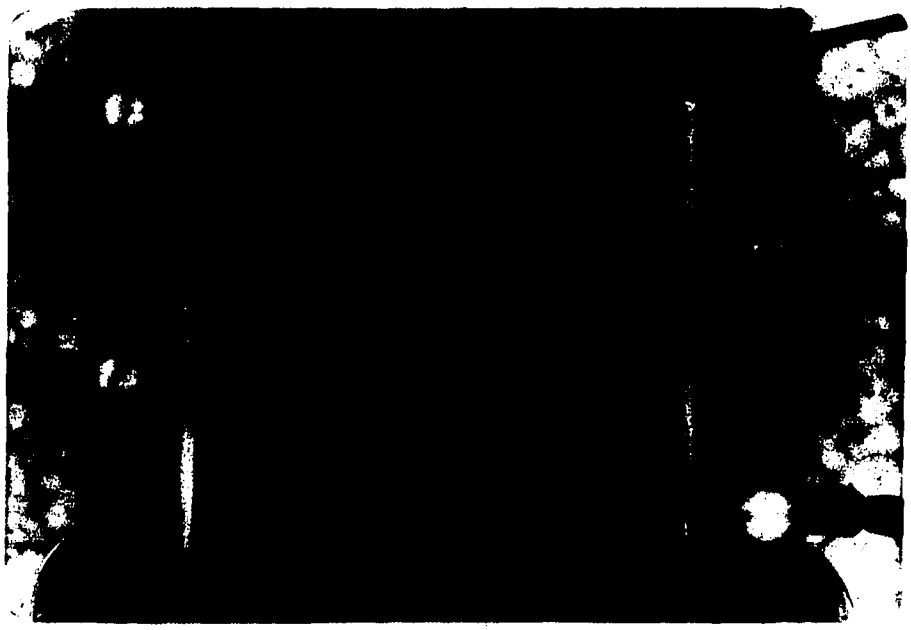
PLATE 4

cm apart. The sampling ports were designed such that the sample could be drawn off anywhere within the cross section of the reactor in the plane of the sampling port. This was built into the system to avoid wall effects influencing the quality of sample collected. The electrolytic flotation cell had a detachable coupling 22 cm above the bottom to enable easier handling and cleaning when necessary.

The first phase of the experiment was conducted with 12 liter sample volumes and the second phase was conducted with 5 liter sample volumes. Four electrolytic flotation cells were constructed each equipped with a heating coil and insulation material surrounding the exterior to maintain the sample at a constant temperature.

Initially eight electrode grids were constructed, the first four containing 2 pairs of electrodes spaced 2 cm apart and the next four containing 4 pairs of electrodes spaced 1 cm apart. The electrode materials used initially were iron and aluminum. Each electrode was 7.5 cm in length and 0.32 cm in diameter. Later, 7.5 cm long stainless steel electrodes with a diameter of 0.32 cm and 7.5 cm long platimum electrodes with a diameter of 0.16 cm were used.

The electrodes were fitted into a 10 cm by 10 cm square electrode grid (Plate 5) and were held in place with plastic screws. With these detachable screws, the replacing or changing of electrodes in the electrode grid was easily accomplished. Separate wires were welded to each electrode. The wires leading to the anode were brought together and



ELECTRODE GRID CLEARLY SHOWING CORRODED ANODES

PLATE 5

welded to a single wire leading to the power supply. Similarly the wires leading to the cathode were welded together with a single wire to the power supply.

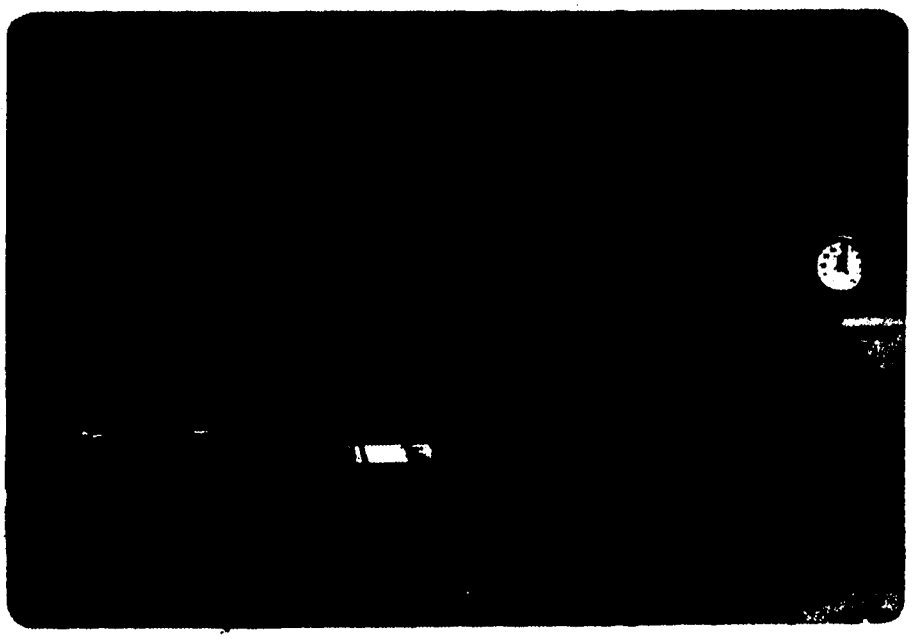
Two different variable, direct current power supplies were used (Hewlett-Packard Model 10438 B variable current and voltage, direct current power supply and a Sorenson Model DCR 60-T8B variable current and voltage, direct current power supply).

The experimental procedure consisted of transferring the heated wastewater sample from the plastic container into the electrolytic flotation cell. The electrode grid was placed at the bottom of the cell and the two wires leading out were connected to the positive and negative terminals of the power supply (Plate 6). When chemical addition was desired, it was added and agitated prior to turning on the power supply. At predetermined time intervals, samples were collected from the bottom sampling port, in the vicinity of the center of the horizontal cross section of the cell in order to avoid wall effects.

Coagulation tests were conducted in 1 L beakers using 800 mL sample volumes. A Model 300 Phipps and Bird, Inc., six paddle stirrer was used to mix the flocculating agent, ferric chloride ($FeCl_3$), into the sample (Plate 7).

EXPERIMENTAL APPARATUS WITH POWER SUPPLY, INSULATED REACTOR WITH HEATING COILS, TIMER AND ELECTRODE GRID

PLATE 6



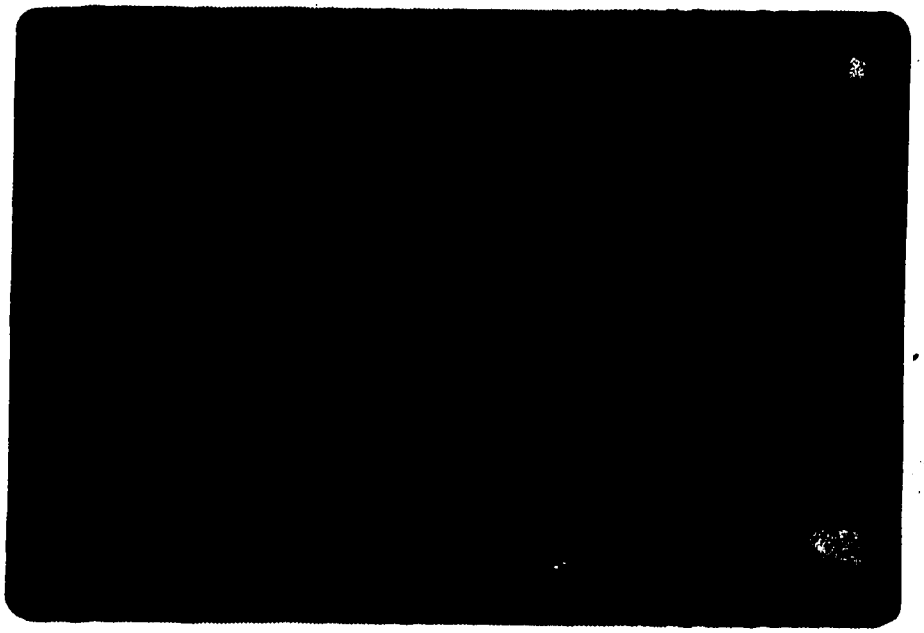
CHEMICAL COAGULATION TEST APPARATUS

PLATE 7

V. RESULTS AND DISCUSSION

The primary objective of this study, was to evaluate the feasibility of the electrolytic flotation process for separating oil from oil-in-water emulsions originating from production rec[illegible]r at heavy oil extraction facilities. To achieve this [illegible] it was necessary to establish the technical f[illegible] of this process prior to developing a cost analysis. The technical feasibility of the electrolytic flotation process on many industrial wastewaters excluding emulsified wastewater from heavy oil extraction facilities is known and has been discussed previously. Therefore, the initial approach taken in establishing the technical feasibility of treating emulsion wastewater from the heavy oil extraction facility was to apply process conditions already established in treating other types of wastewater.

On this basis, the experiments were conducted with iron and aluminum electrode grids. Sample volumes of 12 liters were used at room temperature and current densities ranging from 50 mA/cm^2 to 400 mA/cm^2 over a period of up to 1.5 hours were applied. Even though some visible clarification took place at 1.5 hours, the anodes were highly corroded (Plate 8) and they had to be replaced prior to each experiment. The high electropositivity of aluminum and iron, caused them to have a high affinity to enter solution and made these electrode materials unsuitable for this experiment. The high rate of anode dissolution created some doubt as to whether the sample clarification was due solely



HIGHLY CORRODED ELECTRODES

PLATE 8

to the electrolytic flotation process or whether it was due to a combination of chemical coagulation, flocculation and electrolytic flotation. In order to eliminate metal ions from the anodes from entering the solution and masking the effect of the electrolytic flotation process, it was necessary to use, for the anode material, a less electropositive metal which would not dissolve into solution easily. New electrode grids were made with stainless steel electrodes, to determine if stainless steel would be more stable than iron or aluminum. Contradictory to Anon. (1969) which stated that stainless steel electrodes had a one year operating life, it was evident that stainless steel was also not a satisfactory anode material. Even though the rate of anode dissolution under similar conditions was considerably less than that of iron and aluminum, it was still significant. To substantiate this, the anodes were weighed before and after each run. Calculations showed that approximately 350 mg/L to 700 mg/L of metal entered the solution at current densities varying from 130 mA/cm^2 to 200 mA/cm^2 over a 1.5 hour operating period. Hence, stainless steel was considered an unsuitable anode material and its use was discontinued. These results indicated that the anode material had to be very stable, i.e., the anode material had to be very low in electropositivity. Therefore a noble metal, platinum, was considered.

There were two ways to use the platinum electrodes. One was to make the anodes out of platinum and use a less

expensive metal for the cathodes. The second alternative was to use platinum for the entire electrode grid. Both these modes of operation, though potentially viable yielded unsatisfactory treatment results. The power supply indicated that the current dropped towards zero within 15 minutes of operation. Upon examining the electrodes, it was evident that the anodes were coated with a black precipitate. The characteristics of this precipitate will be discussed later. To overcome this problem the experiment was run by manually alternating the polarity of the electrodes every 10 minutes. Alternating the polarity had the effect of self cleansing the anodes and therefore allowing continuous operation. The use of platinum for the anodes and another more electropositive metal for the cathodes was then not possible, because when the polarity was alternated the cathodes became the anodes. Once the utility of this procedure was established, an automatic timer was built which altered the polarity of the electrodes every 10 minutes.

Electrode grids were constructed with platinum electrodes and with the aid of the automatic timer, continuous operation was possible. The electrochemically stable platinum anodes did not dissolve into solution and therefore electrode replacement was not necessary. However, in the absence of any chemical addition, there was no visible treatment taking place. This result suggested that some chemical addition was necessary to treat the production

recycle water using the electrotytic flotation process. Even though Dubois (1974) was not dealing with heavy oil emulsions, this is in keeping with his conclusion that electrolytic flotation without chemical addition has very little effect on emulsions. However, this is contradictory to Snyder and Willihnganz (1976) who reported that chemical addition was unnecessary in the electrolytic flotation process. It is also contradictory to Beck, et al. (1974) and Ramirez, et al. (1976) who reported that this process can provide emulsion breaking and clarification with or without chemical addition.

When attempting to establish a suitable metal for the electrodes, simultaneous chemical coagulant dosages were also tried. It was hoped that when the electrolytic flotation process alone failed to treat the emulsion wastewater a combination of chemical coagulation and electrolytic flotation would work. Initially alum was selected and dosed at 25 mg/L. In all, seven trials were performed with iron, stainless steel and platinum electrodes with current densities varying from 65 mA/cm^2 to 100 mA/cm^2. The two trials with platinum electrodes showed no visible clarification after 1.5 hours of operation. Two similar trials with calcium hydroxide were tried at dosages of 25 mg/L and 50 mg/L using stainless steel electrodes at a current density of about 150 mA/cm^2 without any success over 1.5 hours. Another trial with 500 mg/L of humic acid and stainless steel electrodes did not provide any treatment.

Using the stainless steel electrodes again a frothing agent cetyl trimethyl ammonium bromide was tried at 20 mg/L and current density of 500 mA/cm² and no visible treatment occurred. Finally the reactor sample was acidified with sulphuric acid to a pH less than 4.5, visible flocs formed but no clearing of the effluent took place.

These preliminary unsatisfactory results necessitated that alternative operating conditions be considered. The recycle water at the Cold Lake pilot plant was generated at approximately 90°C. Based on the work of Vold and Mittal (1965), higher operating temperatures offered some promise. They studied the effects of temperature on the stability of Nujol-Water emulsions and found that the emulsions were all found to be less stable at higher temperatures. Therefore the samples were heated to between 50°C and 60°C. This was regarded as the maximum feasible temperature for the experimental set up available.

With heated samples and chemical coagulants (alum and later ferric chloride) the electrolytic flotation process provided visible clarification. The results of these experiments are summarized in Table 8 and Table 9. These results will be discussed later in this section. Thus, the technical feasibility of the electrolytic flotation process was established. The economic feasibility will also be discussed later.

The second objective was to evaluate the sensitivity of the electrolytic flotation process to relevant wastewater

TABLE 8: INFLUENCE OF ALUM DOSAGE, RESIDENCE TIME AND CURRENT DENSITY ON ELECTROLYTIC FLOTATION

				INITIAL				FINAL				
Expt. #	Alum Dosage mg/L	Residence Time hrs.	Current Density ma/cm^2	ph	Electrical Conductivity Micromhos/cm	Alkalinity as $CaCO_3$ equiv. mg/L	O&G mg/L	ph	Electrical Conductivity Micromhos/cm	Alkalinity as $CaCO_3$ equiv. mg/L	TOC mg/L	O&G mg/L
1	20	1.5	198	7.0	5750	240	3480	7.9	5000	380	129	720
2	20	1.5	330	7.0	5750	240	3480	8.6	6000	320	97	46
3	20	1.5	99	7.0	5750	240	3480	8.4	6500	320	92	70
4	20	1.5	165	7.0	5750	240	3480	8.1	6750	360	92	29
5	20	1.5	99	7.0	5750	240	3480	8.1	6750	420	84	245
6	20	1.5	132	7.0	5800	340	3180	7.5	6000	336	107	67
7	20	1.5	99	7.0	5800	340	3180	7.5	6000	330	109	422
8	10	1.5	132	7.0	5800	340	3180	7.6	6500	348	111	67
9	10	1.5	99	7.0	5800	340	3180	8.5	6500	370	102	292
10	10	1.5	165	7.0	5800	340	3180	8.6	6500	360	125	65
11	10	1.5	66	7.2	6000	360	2890	8.2	6500	350	103	188
12	0	1.5	165	7.2	6000	360	2890	8.4	6250	320	83	46
13	0	1.5	132	7.2	6000	360	2890	8.0	6500	352	94	52
14	0	1.5	99	7.2	6000	360	2890	8.0	6500	352	93	176
15	0	1.75	99	7.2	6000	360	2890	7.6	6500	360	103	82
16	0	2	99	7.2	6000	360	2890	7.6	6500	360	80	390
17	0	1.25	132	7.0	6900	330	2084	7.4	6900	370	40	356
18	0	1.25	198	7.0	6900	330	2084	7.6	700	380	94	180
19	0	1.5	198	7.0	6900	330	2084	7.6	6500	360	90	800
20	10	1.5	198	7.0	6900	330	2084	7.6	7000	370	105	1300
21	0	1.5	264	7.0	6900	330	2084	7.8	7500	368	65	94

Sample volume for all experiments = 12 litres

Temperature of sample = 55°C ± 5°C

TABLE 9

ELECTROLYTIC FLOTATION: To Assess Treatment Performance With Ferric Ion Dosage

	Fe^{3+} Concentration mg/L					
	0	80	0	100	0	125
Oil & Grease Concentration mg/L	626 488 508 610 615 676 705 684 563 742 806 884 1175 880 882 936	101 97 88 74 79 108 84 105 83 114 95 118 136 162 135 121	645 448 492 455 464 488 508 610 615 676 705 684 563 742 884 1175	52 47 54 54 61 69 51 60 54 48 63 62 60 68 67 69	464 880 882 936 786 786 897 897 834 834 868 868 808 808 856 856	36 46 51 49 34 38 39 38 43 49 49 51 47 50 41 57
Avg.	736.25	106.3	644.7	58.4	821.1	44.9
Std. Dev.	181.64	24.1	187.55	7.13	132.77	6.6

NOTE:
Sample volume: 5L
Electrodes: Pt
Residence time: ½ hour
Temperature: 55°C ± 5°C
Current: 1 Amp
Volts: 6 V

characteristics. In the early phase of the experiment, while attempting to obtain a suitable electrode material, the most troublesome wastewater characteristic was the sulphur compounds which were in solution. This was evident when using platinum electrodes. Within fifteen minutes of turning the power supply on, the current dropped towards zero. Upon examining the electrodes a black precipitate was visible. Mikheeva, et al. (1974) reported this to be a sulphide precipitate caused by sulphur containing organic compounds present in wastewater. This problem was overcome by automatically switching the polarity of the electrodes as has already been discussed.

The relative stability of the emulsion wastewater was evident when comparing the current densities that were required to treat this emulsion wastewater as reported in Table 8 (up to 330 mA/cm^2) to that of the typical current densities that were required to treat other emulsion wastewaters as reported in Table 4 (up to 50 mA/cm^2). A possible reason for this added stability may have to do with the presence of surfactants in the emulsion wastewater under study. Swisher (1970) reported that surfactants have a strongly hydrophobic group and a strongly hydrophilic group linked together in the same molecule. The hydrophilic group tends to orient towards the water phase and the hydrophobic group tends to orient towards the oil phase. This promotes dispersion and emulsification. The most hydrophobic group is the hydrocarbon radical having a total of from about 10 to

20 carbon atoms. Swisher (1970) also reported that the hydrophobic groups contributed by the petroleum industry are principally hydrocarbons, deriving originally from the paraffins of crude oil. Typical hydrophilic groups are sulfonates, sulphates and carboxylates. Strosher and Peak (1978) reported that of 16 chemical groups investigated from samples of oil sands (Athabasca formation) upgrading plant effluent and associated effluents, the most abundant organic constituents were the hydrocarbons, organic sulphur compounds, organic nitrogen compounds and oxygenated organic compounds. A previous study done by Strosher and Peak (1976) reports that 92% of the extractable carbon from oil sands plant tailing pond dike filter drainage was in the form of oxygenated compounds, including organic acids, phenols, ketones, aldehydes, organic acid esters, amides, quinones, organic sulphur compounds, organic nitrogen compounds and hydrocarbons. Montgomery (1980) confirmed the presence of the compounds found above to also be present in the Cold Lake heavy oil formations. However, he indicated the relative concentrations of the compounds to be different between the Cold Lake and Athabasca formations. Therefore, one could speculate that the surfactant properties of polar organic compounds, such as those reported above, could contribute to the stability of the oil-in-water emulsions produced from Cold Lake heavy oil.

Another characteristic that may be a relevant indicator of the sensitivity of the electrolytic flotation process is

electrical conductivity. As reported in Table 8, the range of electrical conductivity in the emulsion wastewater was between 5000 micromhos per centimeter and 7500 micromhos per centimeter. This is far greater than the typical electrical conductivity of other wastewaters treated successfully by electrolytic flotation. Ramirez, et al. (1976) reported the electrical conductivity of wastewater originating from a meat processing plant without dehairing liquor to be between 950 micromhos per centimeter and 1500 micromhos per centimeter. Das Gupta and Mohanta (1976) reported the electrical conductivity of Kraft mill effluent as 578 micromhos per centimeter. The higher electrical conductivity is indicative of a higher dissolved solids concentration.

The third objective was to consider the process variables that seem most likely to have a significant effect on electrolytic flotation process performance.

The rate of mixing of the reactor sample could be a significant process variable. As cited previously Camp (1955) showed that the rate of collision of particles at any given particle concentration is proportional to the absolute velocity gradient or the space rate of change of velocity at any point. However as velocity increases the shearing forces will also increase and as floc particles grow, higher velocities can break them down again. Therefore, it was decided to apply gentle mixing to the reactor sample to increase the probability of particle collision and thus the rate of coagulation. The possible presence of surface active

agents in the sample could have a slowing down effect on the rate of coagulation and it was felt that gentle mixing could overcome such problems as have already been discussed. A motor with a long shaft and three propellers was used to mix the reactor contents. However, at this stage of the experimental development, sufficient chemical addition was not used and even though coagulation may have taken place to some degree, clarification of the effluent did not take place. The mixing device was used only for 15 minutes of each experiment. The heavy motor sitting on top of the reactor and the impellers catching the wires leading out of the electrodes caused some practical problems. In subsequent experiments the reactor volume was reduced and further use of the mixer was not possible without great modifications. Therefore, establishing the contribution of mixing to the process was not pursued.

Initial evaluation of other process variables was conducted at a stage when samples were being heated to between 50°C and 60°C, but using stainless steel electrodes and alum dosage. This was also a stage in the experimental development when the oil and grease sample analysis was done without centrifuging the sample prior to analysis. However, the information obtained showed some important trends. The process variables that were tested were current density, residence time in the reactor and alum dosage. These results are tabulated in Table 8. Owing to the lack of confidence with the oil and grease analysis in these experiments the

total organic carbon concentrations were used as an alternate indicator. The total organic carbon analysis was done on filtered samples. Therefore all the dissolved organic carbon is represented by this analysis. If it can be assumed that a fixed proportion of this total organic carbon is contributed by the oil and grease, we can plot total organic carbon versus current density and alum dosage to get some idea of the performance. These are plotted in Figure 5 and Figure 6. The effects of increasing current density on the oil and grease concentration is plotted in Figure 7.

From Figure 5 it is evident that alum dosage up to 20 mg/L has no significant effect on the electrolytic flotation process. However, subsequent experiments in which the stainless steel electrodes were weighed before and after each run showed that between 350 mg/L and 700 mg/L of the stainless steel electrode was entering solution. Therefore the effect of the alum dosage was totally masked by the high electrode metal dosage. Theoretically the maximum rate of iron that could be dissolved for the test conditions employed (assuming that all the electrons in the process are supplied by the ionization of iron to the ferric ion) is 783 mg/L (9,400 mg) (Appendix B). The relationship between total organic carbon and current density is not very well established as illustrated in Figure 6. However, Figure 7 seems to indicate a possible reduction effect on oil and grease concentration with increasing current density.

From this point on all oil and grease samples were

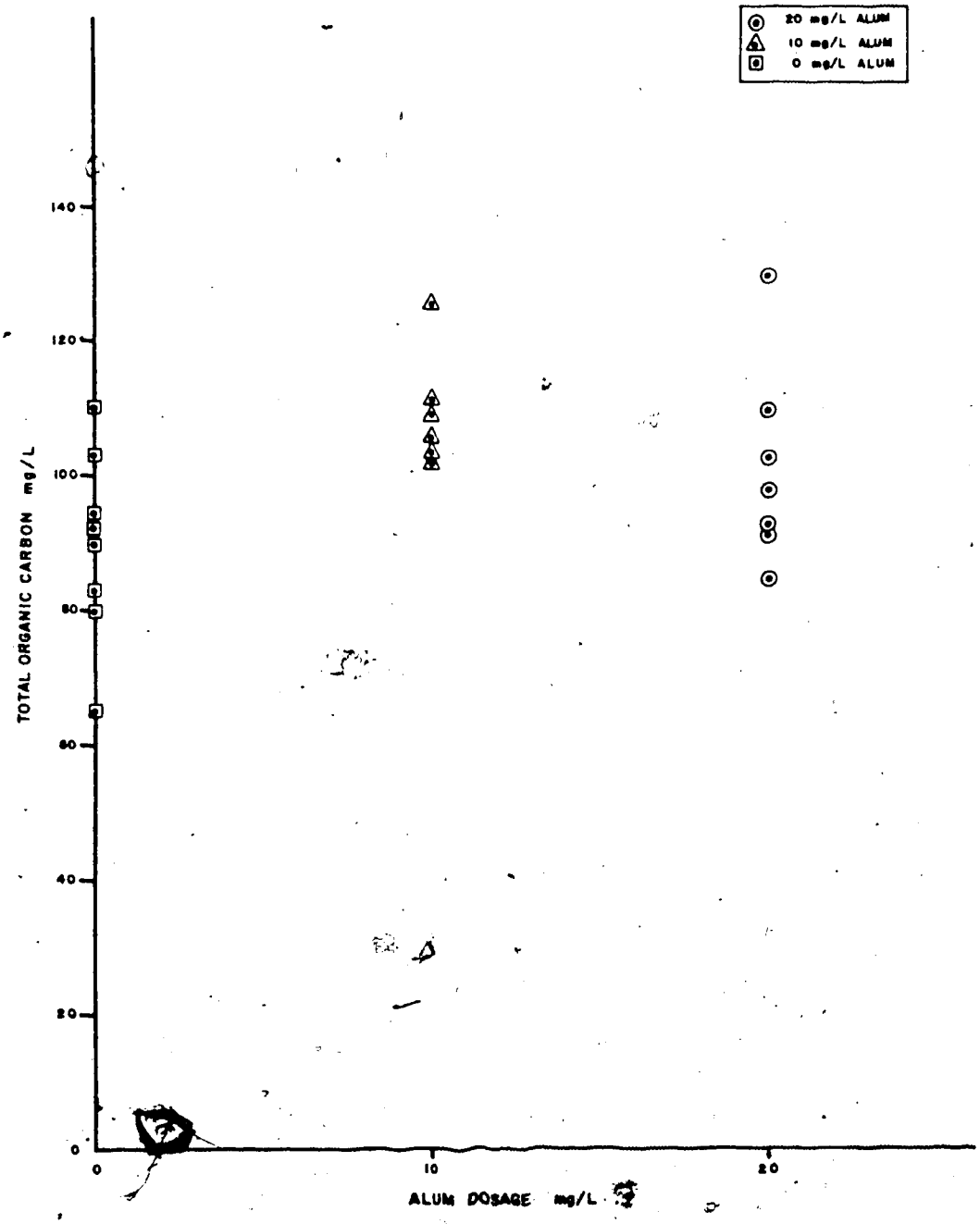


FIGURE 5 THE EFFECT OF ALUM DOSAGE ON TOTAL ORGANIC CARBON AT VARYING CURRENT DENSITIES (TABLE 8)

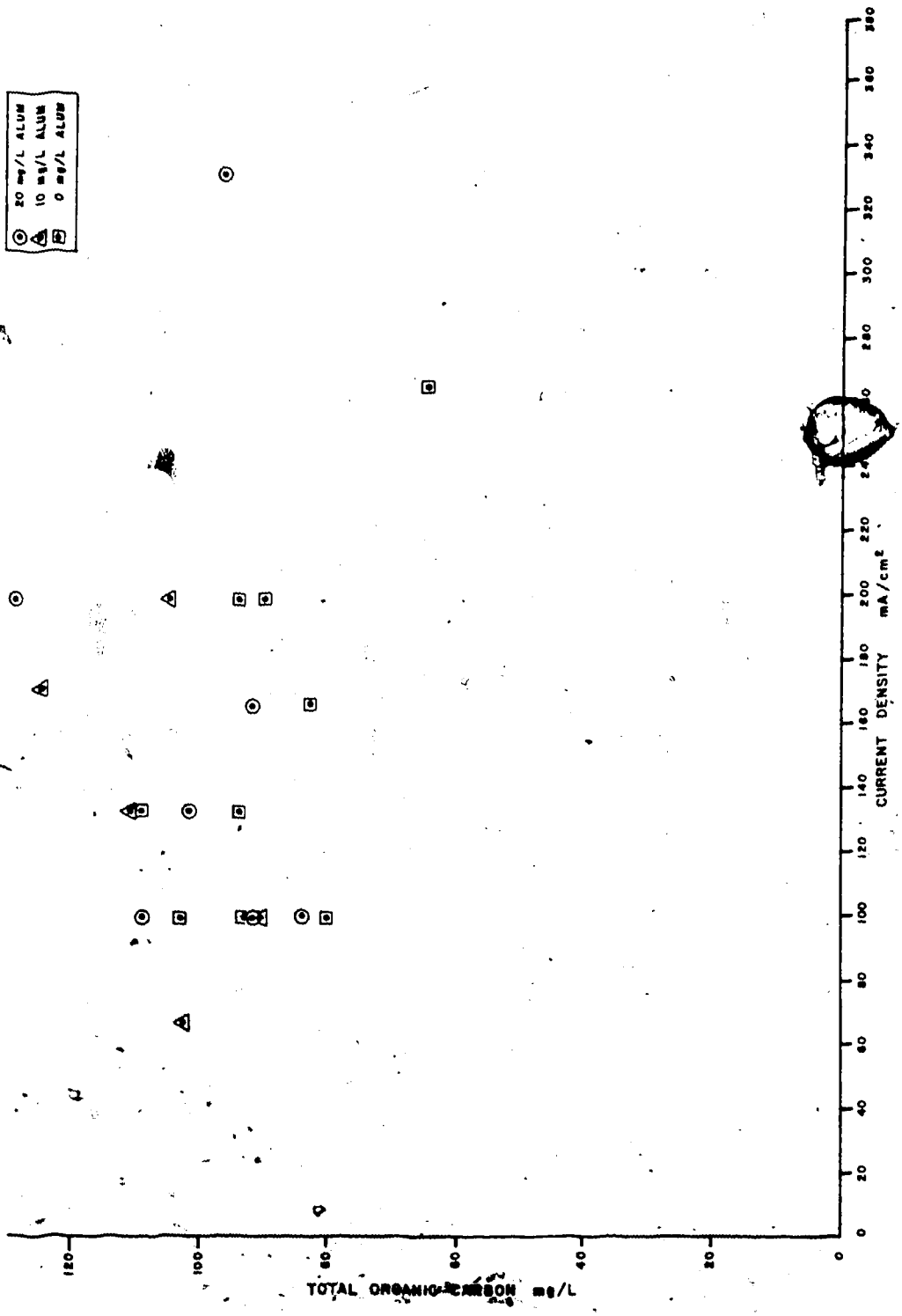


FIGURE 6 THE EFFECT OF CURRENT DENSITY ON TOTAL ORGANIC CARBON

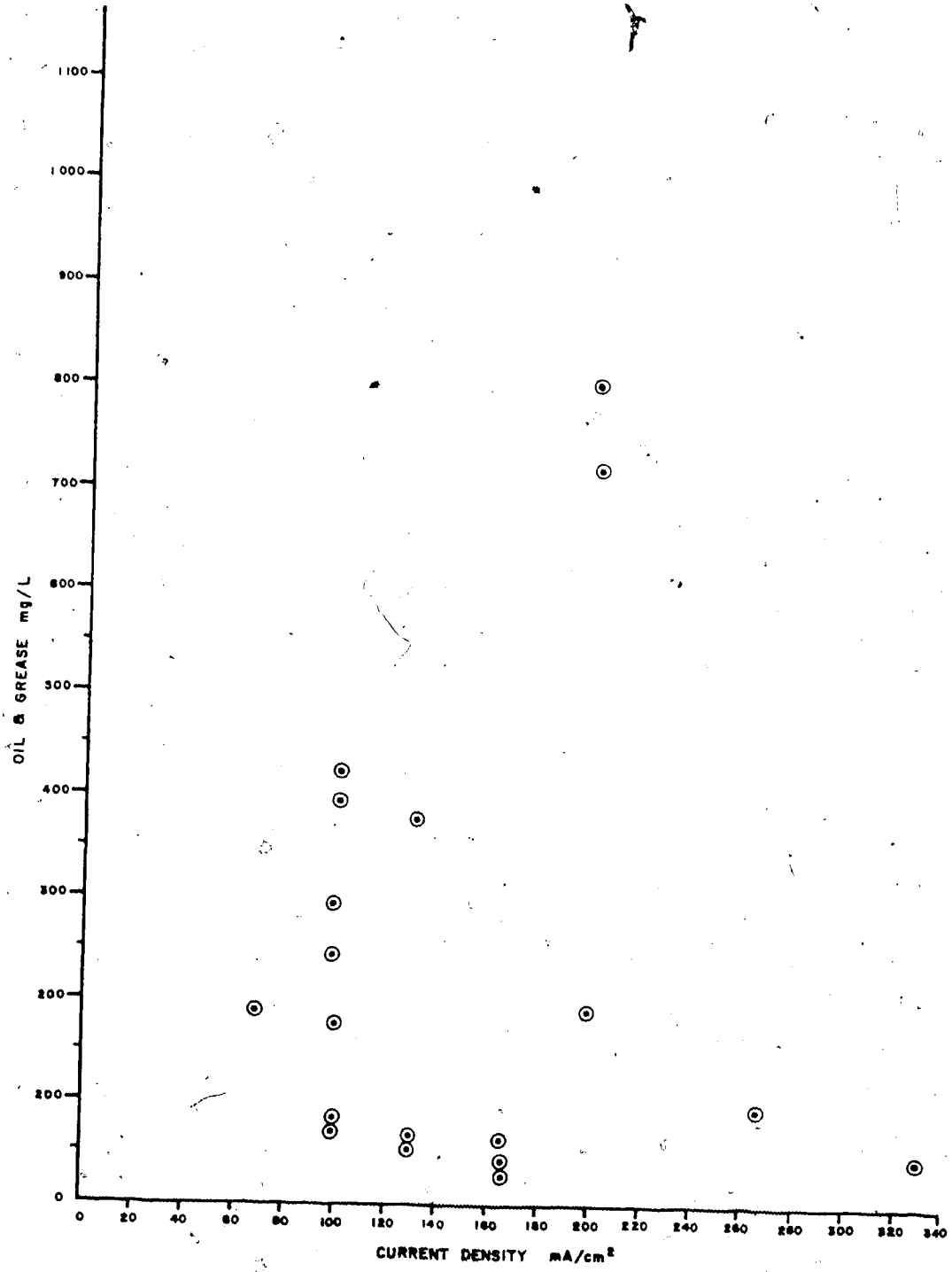


FIGURE 7 THE EFFECT OF CURRENT DENSITY ON OIL & GREASE

centrifuged and more consistant and reliable oil and grease analysis was possible. Also, all the experiments on the electrolytic flotation process were conducted with platinum electrodes.

The fourth objective was to identify the suitable process conditions within the framework of the parameters (variables) chosen and to compare the cost of electrolytic flotation to that of chemical coagulation. Having established the need for chemical coagulation in conjunction with electrolytic flotation, the stategy here was to first assess the chemical requirement to break the emulsion without using the electrolytic flotation process. This would then be used to compare the chemical requirement for the electrolytic flotation process to show the benefit of using the electrolytic flotation process.

Ferric chloride ($FeCl_3$) was selected as the chemical coagulating agent on the basis of preliminary trial with a variety of chemicals (lime, ferric sulphate, alum, etc.). The concentration of the ferric ion (Fe^{3+}) was varied from 0 mg/L to 156 mg/L. Each series of tests contained six one liter beakers containing 800 mL of sample. Twenty such series of experiments were conducted. The results of these are tabulated in Table 10. It must be noted that the initial 15 series of six beaker tests were conducted on the original batch of sample brought from Cold Lake, and the final 5 series of experiments were conducted on the second batch of sample brought from Cold Lake. The oil and grease

TABLE 10: COAGULATION TEST RESULTS

Fe^{3+} Dose mg/L	Oil & Grease Concentration mg/L																				$\bar{x}$	σ
Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20		
0	1680			4214	6664	3870	3050	3084	3516	3692	4036	3584	4566	5692	3060	608	622	479	686	622	2995	1695
31.25	1380																				3984	733.86
62.5	1070																				564	74.92
93.75	540																					
105.25		540		906	818				331													
110.75		305	109	66	279	286	301	104	321	432						119	98	118	116	110	193	107.66
125.0	106	86	80	47	68	181	152	129	135	111	78	104	121	98	38	81	83	91	101	63	102	30.36
138.25		32	51	39	24	53	148	71	71	65	49	42	53	61	63	83	83	85	93	59	63	20.34
137.5											30	32	31	37	33	76	72	89	79	56	54	22.87
143.75		29	38	18	22	33	50	39	29	30	31	28	29	29	40	59	54	75			37	14.66
156.25	30	23				40	48	37		30	32	24	32	19	22				46	33	32	9.47

NOTE: All samples were heated to 55° C ± 5° C

Run 1 to 15: $\bar{x}$ & σ from Run 4 Run 15 : 3984 733.86

Run 16 to 20: $\bar{x}$ & σ from Run 16 Run 20: 564 74.92

concentration of the untreated samples in the first batch was on the average approximately seven fold higher than the oil and grease concentration in the second batch of samples. This is typical of the operating fluctuations at the plant and hence the experimental system should be capable of handling these fluctuations. Experimental results showed that the range of initial concentrations from 500 mg/L to 5500 mg/L, did not affect the concentration of the treated samples significantly. To substantiate this finding the mean of the first 15 treated samples were compared to the mean of the last 5 treated samples after treatment with 125 mg/L of ferric ions. The t-test statistic showed that the two means did not differ significantly at the 10% significance level (Appendix 1).

Having established the concentration of ferric ions needed for clarification by the coagulation test, it was essential to compare the ferric ion concentration needed to obtain equivalent clarification using the electrolytic flotation process. It was also important to operate the electrolytic flotation process at an economically viable rate of energy consumption. It was calculated that if 1 ampere of current and 7 volts were applied for one hour it would cost approximately $33.00 per 1000 m^3 of wastewater treated. Reducing retention times to one-half hour or fifteen minutes would reduce this cost to $16.50 and $8.25 respectively for each 1000 m^3 treated (Appendix 2). Based on these calculations, the electrolytic flotation process was

limited to a maximum of 1 ampere of current input. The electrolytic flotation experiments were conducted at ferric ion concentrations varying from 50 mg/L to 125 mg/L with 5 liter sample volume and at a temperature of 55°C ± 5°C. After the initial experiments the ferric ion concentrations were limited to 80 mg/L, 100 mg/L and 125 mg/L. The results of these experiments are summarized in Table 9. These results indicate the treatment achieved with 80 mg/L ferric ion concentration in the electrolytic flotation process is equivalent to the treatment achieved with 125 mg/L of ferric ion concentration in the chemical coagulation experiments at the 10% significance level (Appendix 3). The overall performance of the chemical coagulation versus electrolytic flotation process is plotted in Figure 8 and shows clearly the superior performance of the electrolytic flotation process over chemical coagulation alone.

In order to eliminate any sample variances due to the age of the sample and other experimental factors that may change from day to day, simultaneous electrolytic flotation and chemical coagulation experiments were conducted. In the electrolytic flotation experiments samples were collected at 15 minute and 30 minute intervals. In the chemical coagulation experiments, stirring was continued for 30 minutes and the flocs formed were allowed to settle for a minimum of four hours. These results are tabulated in Table 11. Both the electrolytic flotation and the chemical coagulation tests were conducted at 125 mg/L of ferric ion

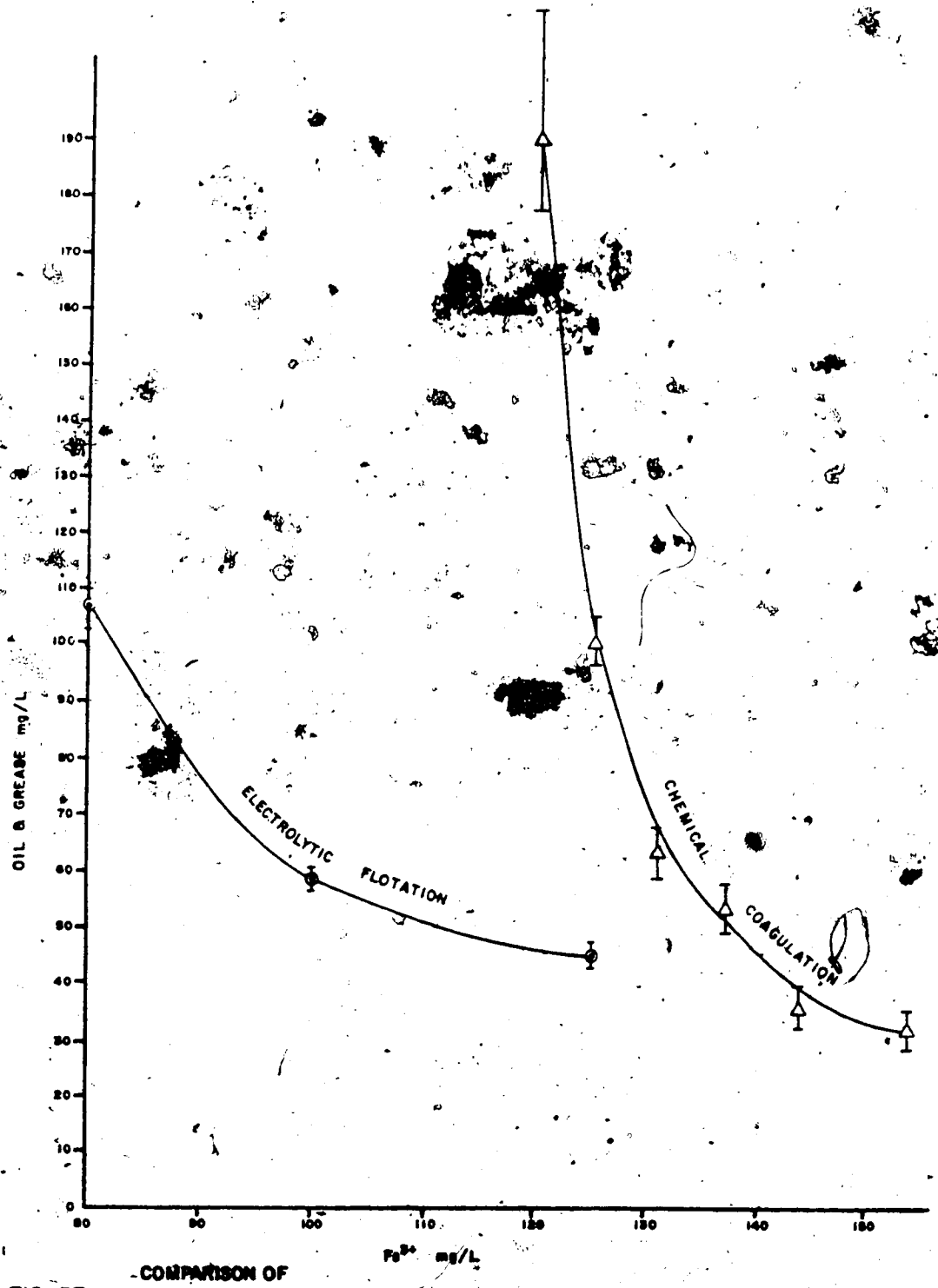


FIGURE 8 COMPARISON OF THE CHEMICAL REQUIREMENT FOR ELECTROLYTIC FLOTATION VS. COAGULATION

TABLE

SIMULTANEOUS ELECTROLYTIC FLOTATION AND CHEMICAL COAGULATION TESTS

Oil & Grease Concentration (mg/L)			
Expt. #	Electrolytic Flotation 1 amp. 6 volts		Coagulation
	15 min.	30 min.	30 min.
1.	41	34	88
2.	41	45	84
3.	41	47	82
4.	43	37	89
5.	41	42	82
6.	44	44	88
7.	40	42	70
8.	53	42	64
9.	56	46	67
10.	50	44	73
11.	50	47	79
12.	47	48	89
Ave.	45.6 = μ1	43.2 = μ2	79.6 = μ3
Std. Dev.	5.5	4.2	9.0

Note: All these experiments were conducted with a Ferric ion concentration of 125 mg/L and at 55°C.

concentration. A one way analysis of variance of the three sets of results (two from electrolytic flotation and one from chemical coagulation) was done (Appendix 4). The results confirm a highly significant difference ($P<0.001$) between the three means. However, when the means of the two electrolytic flotation process results were compared using the Duncan's multiple-range test, it showed that the treatment of samples obtained after 15 minute residence time and 30 minute residence time did not differ significantly (Appendix 5).

These findings clearly show that the electrolytic flotation process is superior to chemical coagulation a[illegible]. In summary the best process conditions obtained for electrolytic flotation were a current density of 132 mA/cm^2, a residence time of 15 minutes, a ferric ion dosage of 80 mg/L. These process conditions were obtained at an operating temperature of 55°C ± 5°C.

Though the treatment cost of the electrolytic flotation process is less than that of chemical coagulation, the relative cost of the two processes is of vital importance to the industrial operator. Cost analysis was based on a 350 pound drum of ferric chloride costing $90.00 and a daily production rate of 141,000 barrels of synthetic crude with a produced water recycling rate of 38.2 x 10^3 m^3/d (Appendix 2 and 6). On this basis the chemical cost for the electrolytic flotation process (at 80 mg/L ferric ion concentration) was estimated at approximately 3.56¢ per bbl. of synthetic crude

produced. Adding the cost of power estimated at 0.22¢ per bbl. of synthetic crude produced for 15 minutes of operation, at 1 ampere and 7 volts, make the cost of treatment 3.78¢ per bbl. of synthetic crude produced. It was hoped that the rate of hydrogen production during electrolysis would off set some of the power and chemical costs. However, calculations performed (Appendix 9) showed a hydrogen production volume of only 0.4 L per ampere per hour during the electrolytic flotation process. Therefore the cost benefit of recovering hydrogen was negligible. On the other hand the chemical cost of treating the wastewater by chemical coagulation at 12[illegible] mg/L of ferric ion concentration in order to obtain the equivalent treatment obtainable by electrolytic treatment is approximately 5.56¢ per bbl. of synthetic crude produced. This plus the gentle stirring for half a hour increases the cost to approximately 5.96¢ per bbl. of synthetic crude produced. As residence time was from 1 to 4 hours in chemical coagulation treatment, the size of the coagulation chamber would have to be 4 to 16 times larger than the equivalent electrolytic flotation unit. This larger reactor size would add substantially to the capital cost for chemical coagulation treatment.

As reported in EIA (1979) the ESSO Resources Canada Limited, Cold Lake, heavy oil extraction facility will produce wastewater for recycling at the rate of 38.2 x $10^3 m^3/d$ (8.4 x 10^6 Imp. gallons per day). Van Note, et al. (1975) illustrated graphically that the operating and

maintenance cost of a 1000 m^3/d primary sedimentation unit with ferric chloride addition was \$14.98 per 1000m^3 of wastewater treated. They have also shown the operating and maintanance cost for 1000 m^3/d activated sludge plant with ferric chloride addition is \$24.23 per 1000 m^3/d wastewater treated. Assuming a 100% increase in operating and maintenance cost since 1975, these costs will translate to \$29.96 and \$48.46 per 1000 m^3 respectively. The cost of treating 1000 m^3/d with the electrolytic flotation process using a 80 mg/L of ferric ion concentration and current densities sufficient to achieve a treatment efficiency of between 90% and 99% or better is \$139.60. Sewage treatment costs cannot be directly related to the electrolytic flotation process costs estimated by this study due to differences in wastewater characteristics and in the nature of the processes, however, comparisons do provide a gross indicator of the relative magnitude of treatment costs.

Based on the economic cost evaluations, it is apparant that the electrolytic flotation process would be very attractive if less expensive means of chemical treatment could be applied. Also, the cost of ferric chloride sludge handling has not been assessed and this could present a further drawback to the application of this technology. However, in view of the technical feasibility of electrolytic flotation, the use of this process is still conceivable particularly if other treatment processes prove to be uneconomically or technically unfeasible.

The fifth objective, on the basis of the findings of this study, was to consider the applicability of the electrolytic flotation process to oil removal from other industrial oily wastewaters. Based on the higher rate of anode dissolution when using metals of higher electropositivity (iron, aluminum, stainless steel, nickel, etc.), this process will be very useful in short term or intermittent operations. Spills and emergency situations as well as operations where small volumes of wastewater are collected over a period of time and then discharged periodically fall under the intermittent operations category. In such operations, replacing the electrodes does not cause operating delays. Therefore, sacrificial electrodes are ideally suited. Sacrificial electrodes have the advantage of supplying metal ions at a constant rate, thereby eliminating the necessity for chemical coagulant addition. This also eliminates the need for chemical storage tanks and equipment for injecting and mixing the chemicals. Also, the rate of metal addition can be controlled by the current input to the electrodes. The electrolytic flotation process has the advantage of floating the sludge layer for easy skimming. A floating sludge layer is usually more compact (less water content) than a settled sludge layer. Since the buoyancy forces move the sludge to the surface and the gravitational forces of the floc particles already at the surface act opposite to the buoyancy forces, a more compact sludge layer is formed. An electrolytic flotation

unit is light and compact and therefore is easily portable for emergency requirements. The simplicity of operating an electrolytic flotation unit and the treatment efficiency of the process makes this an attractive alternative in emergency situations.

VI. CONCLUSIONS AND RECOMMENDATIONS

The results indicate that the electrolytic flotation process is technically feasible and a process superior to chemical coagulation in treating production recycle wastewater from heavy oil extraction facilities. The electrolytic flotation process under the best conditions tested was found to be quick and efficient producing a thick floating sludge layer. Further work is needed to determine if chemical usages can be reduced or if alternate less expensive chemicals can be used. Under the conditions tested the treatment costs were considered higher than would be desirable for full scale implementation.

Increasing the current density increased the treatment efficiency. The best current density and residence time conditions were fixed by limiting the power cost of treating 1000 m^3 to less than $20.00. Based on this limitation it was found that the current density was 130 mA/cm^2 (1 ampere, 7 volts). 15 minutes of residence time was found to be adequate and treatment was possible within the cost objective for power consumption. Heating the sample above room temperature was vital in obtaining better treatment efficiency and chemical addition was necessary to obtain emulsion destabilization and phase separation. The experimental temperature was selected to be 55°C ± 5°. This was however not based on the best performance but rather on the maximum practicable temperature for the given experimental set up. Further work on accurately maintaining

the temperature and studying its effect on the treatment efficiency with each incremental increase of 10°C would be useful. It was found that 80 mg/L of ferric ion concentration was necessary to obtain an oil and grease concentration of less than 50 mg/L in the treated sample. The initial oil and grease concentrations before treatment varied from 500 mg/L to over 5500 mg/L. Therefore the treatment efficiency varied from 90 percent to over 99 percent.

The electropositivity of the electrode material must be very low to prevent rapid dissolution of the anode into solution and thereby necessitating frequent replacement of electrodes. Platinum was found to be a suitable electrode material, but an automatic timer was required to alter the polarity and prevent electrode fouling.

More experimental work should be done on increasing the current density while decreasing the chemical addition in order to establish the interplay between these two variables. A temperature as close to the actual operating temperature (90°C) as possible may reduce the chemical requirement drastically.

A better characterization of the wastewater with respect to the presence of emulsifiers and demulsifiers would be useful. As a first stage, synthetic crude prepared in the laboratory with known characteristics may help better define the interdependence of various chemical components in solution. It is very likely that sample age may have a

bearing on the particle size distribution and hence the stability of the emulsion. The experimental results did not seem to show any change in performance characteristics with time, however a more definitive study is warranted with respect to aging of the wastewater.

It is also recommended that a two stage process be tried, with the first stage being chemical coagulation and the second stage being electrolytic flotation. Mixing of the sample to enhance flocculation should also be studied, to determine to optimum mixing velocity. Finally, the height of the wastewater column above the electrode grid could be a significant parameter. That is, the current density per unit volume of wastewater treated should receive attention.

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APPENDIX

APPENDIX 1

From Table 10:

For 125 mg/L Fe^{3+}:

Run 1 - 15	Run 16 - 20
$\bar{X}_A = 107.6$	$\bar{X}_B = 83.8$
$S_A = 32.29$	$S_B = 14.04$
$\Sigma A_j = 1614.0$	$\Sigma B_j = 419.0$

Standard error of the mean $\bar{d}$ between the two sets of samples:

$$SS_A = \sum_j^{15} X_{Aj}^2 - (\sum_j^{15} X_{Aj})^2/15 = \sum_j^{15} X_{Aj}^2$$

$$= (106^2 + 86^2 + \ldots + 138^2) - \frac{1614^2}{15}$$

$$= 188.266 - \frac{1614^2}{15} = 14599.6$$

$$S_A^2 = \frac{14599.6}{n_A - 1} = \frac{14599.6}{14} = 1042.83$$

$$SS_B^2 = 35901 - \frac{419^2}{5} = 788.8$$

$$S_B^2 = \frac{788.8}{n_B - 1} = \frac{788.8}{4} = 197.2$$

$$F = \frac{S_A^2}{S_B^2} = \frac{1042.83}{197.2} = \underline{5.29}$$

$$F_{0.025\ (14,4)} = \underline{14.25}$$

Since the calculated F value is smaller than the critical F value there is no significant difference in the variances and therefore the variances can be pooled.

Therefore,

$$S^2 = \frac{\Sigma X_{Aj}^2 + \Sigma X_{Bj}^2}{(n_A-1) + (n_B-1)} = \frac{14599.6 + 788.8}{14 + 4}$$

$$= 854.91$$

$$S_{\bar{d}} = S^2 \frac{n_A + n_B}{n_A n_B} = 854.91 \frac{15 + 5}{15 \times 5}$$

Therefore,

$$S_d = 15.1$$

Two Tailed t-Test

H_o: $\mu_1 = \mu_2$

H_1: $\mu_1 \neq \mu_2$

$$t = \frac{X_A - X_B}{S_d} = \frac{d}{S_d}$$

$$= \frac{107.6 - 83.8}{15.1} = \underline{1.58}$$

$t_{0.05}$ (for 18 degrees of freedom) = 2.101

$t_{0.10}$ (for 18 degrees of freedom) = 1.734

The experimental value of t lies within the critical tabular value, therefore, the hypothesis H_o : $\mu_1 = \mu_2$ is accepted and is claimed that $\bar{X}_A$ does not differ significantly from $\bar{X}_B$ at the 10% significance level.

APPENDIX 2

1 Ampere 7 volts for 1 hour of operation.

Watts = 7 X 1 = 7 in 5 liters of solution.

Therefore,

$\frac{\text{Watts}}{L} = \frac{7}{5} = 1.4 = 0.0014$ kW/L

Since 0.0014 kW/L is applied for one hour, we have

= (0.0014) (1)

= (0.0014) kWh/L

Cost of 1 kWh = 2.3 cents.

0.0014 kWh/L = 1.4 kWh/m^3

Cost of treating one million gallons (4546 m^3) for 1 hour

$= 4.56 \frac{L}{g} \times 1{,}000{,}000 g \times 0.0014 \frac{kWh}{L} \times 2.3 \frac{\text{cents}}{kWh}$

= 14683 cents = \$146.83 = <u>\$33.00/1000 m^3</u>

Therefore, cost of treating for 1/2 hour

= \$73.42 = <u>\$16.50/1000 m^3</u>

Therefore, cost of treating for 15 minutes

= \$36.71 = <u>\$8.25/1000 m^3</u>

Therefore, cost per bbl. of synthetic crude produced (based on 141,000 bbl produced and a recycle rate of 8.4 X 10^6 gal)

$= \frac{36.71}{10^6} \times \frac{8.4 \times 10^6}{141{,}000} =$ <u>0.22 cents</u>/bbl

APPENDIX 3

Oil and Grease Concentration (mg/L)	
80 mg/L Fe^{3+} Electrolytic Flotation	125 mg/L Fe^{3+} Coagulation
101	106
97	86
88	80
74	47
79	68
108	161
84	152
105	129
83	135
114	111
95	78
118	104
136	121
163	98
135	138
121	81
	83
	91
	101
	63
$\bar{X}$ 106.3	102
Std.Dev. 24.1	30.4
n (# of data points) 16	20
1700.8	2040.0

Calculation of the standard error of the difference, $\bar{d}$:

$$SS_A = \sum_j^{16} X_{Aj}^2 - (\sum_j^{16} X_{Aj})^2/16 = \sum_j^{16} X_{Aj}^2$$

i.e.,

$$SS_A = (101^2 + 97^2 + \ldots + 135^2 + 121^2) - \frac{1700.8^2}{16}$$

$$= 189,581 - 180,795^2 = 8,785$$

Therefore, $SS_A = 8785$

$$s_A^2 = SS_A/n_{A-1} = \frac{8785}{15} = 585.7$$

$$SS_B = (106^2 + 86^2 + \ldots + 101^2 + 63^2) - \frac{2040^2}{20} = \sum_j^{20} X_{Bj}^2$$

$$= 224,167.0 - 208,080.0 = 16,087$$

Therefore,

$$SS_B = 16,087$$

$$s_B^2 = SS_B/n_{B-1} = \frac{16,087}{19} = 846.7$$

$$F = \frac{s_B^2}{s_A^2} = \frac{846.7}{585.7} = 1.45$$

$$F_{0.01}(16,20) = 3.26$$

Since the calculated F value is smaller than the critical F value, there is no significant difference in the variances, therefore, the variances can be pooled.

$$s^2 = \frac{\Sigma X_{Ai}^2 + \Sigma X_{Bi}^2}{(n_A-1) + (n_B-1)} = \frac{8785 + 16087}{(15 + 19)}$$

i.e.,

$$s^2 = 731.53$$

$$s_{\bar{d}} = \sqrt{s^2 \frac{n_A + n_B}{n_A n_B}} = \sqrt{731.53 \frac{16 + 20}{16 \times 20}}$$

i.e.,

$$s_{\bar{d}} = 82.3$$

Two-Tailed t - Test

$$t = \frac{(\bar{X}_A - \mu_A) - (\bar{X}_B - \mu_B)}{s_d}$$

H_o: $\mu_1 = \mu_2$

H_1: $\mu_1 \neq \mu_2$

$$t = \frac{\bar{X}_A - \bar{X}_B}{s_{\bar{d}}} = \frac{\bar{d}}{s_{\bar{d}}}$$

$$t = \frac{106.3 - 102}{82.3} = 0.052$$

$t_{0.10}$ ([15 + 19] degrees of freedom) = 1.692

The experimental value of t lies well within the critical tabular value. Therefore, the hypothesis

H_o : $\mu_1 = \mu_2$ is accepted at the 10% significance level.

APPENDIX 4

Null Hypothesis:

$H_o : \mu_1 = \mu_2 = \mu_3$ (from Table II)

Analysis of Variance Calculations:

Total Sum of Squares (TSS)

$$TSS = \sum_{i}^{12} \sum_{j}^{3} X_{ij}^2 - X^2/36$$

i.e.,

$$TSS = (41^2 + \ldots + 89^2) - \frac{(2020^2)}{36}$$

i.e.,

$$TSS = 124,704 - 113,344.44$$

Therefore,

$$TSS = 11,359.56$$

Experimental Sum of Squares (CSS):

$$CSS = \sum_{i}^{12} X_i^2/3 - \frac{X^2}{36}$$

$$= \sum_{i}^{12} \frac{(163^2 + \ldots + 184^2)}{3} - \frac{(2020^2)}{36}$$

i.e.,

$$CSS = \frac{340,798.0}{3} - 113,344.44$$

Therefore,

$$CSS = 254.89$$

Error Sum of Sequence (ESS):

ESS = TSS - CSS

= 11,359.56 - 254.89 = 11,104.67

Mean Sequence

$$MS_C = \frac{CSS}{\text{degs. of freedom}} = \frac{254.89}{12 - 1} = 23.17$$

$$MS_E = \frac{ESS}{\text{degs. of freedom}} = \frac{11,104.67}{(36 - 3) - 1} = \frac{11,104.67}{32}$$

Therefore,

$MS_E = 347.02$

Calculated F Value

$$F = \frac{MS_E}{MS_C} = \frac{347.02}{23.17} = 14.98$$

Critical F-Value (from tables)

degs. of freedom = $\frac{32}{11}$

$F_{0.05}(32,11) = 2.57$

$F_{0.01}(32,11) = 3.94$

$F_{0.001}(32,11) = 6.68$

Analysis of Variance Summary

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F
Treatments	11	255	23.17	14.98
Error	32	11,105	347.02	
Total	43	11,360		

There is a highly significant difference between the experimental type means, therefore, the hypothesis is rejected.

APPENDIX 5

Duncan's Mutiple-Range Test

Experiment	Electrolytic Flotation = 30 min.	Electrolytic Flotation = 15 min.	Chemical Coagulation
Mean	43.2	45.6	79.6

Variance of sample means,

$$S_{\bar{x}} = \left(\frac{\text{error mean square}}{\text{\# of experiments}}\right)^{\frac{1}{2}} = \left(\frac{347.02}{12}\right)^{1/2}$$

$$= 5.38$$

p means	2	3	
r_p (from Duncan's multiple range test tables)	2.89	3.03	For 32 degrees of freedom (see previous ANOVA table)

Multiplying each value of r_p by $S_{\bar{x}} = 5.38$, we have

p	2	3
R_p	15.55	16.30

R_p - Least significant range.

To test for significant differences among two adjacent means, we obtain ranges of (45.6 - 43.2) = 2.4 and (79.6 - 45.6) = 34.0 respectively. Since the first of these values does not exceed $R_2 = 15.55$, the difference between the means is not significant. Since the second of these values exceeds $R_3 = 16.30$, the difference between the means is significant.

43.2	45.6	79.6

APPENDIX 6

$90.00 for 350 lb $FeCl_3$

M.W. of $FeCl_3$ = 162.206 g

i.e., every 162.206 g of $FeCl_3$ has 55.847 g of Fe^{3+}

Therefore,

in 350 lb. $FeCl_3$ the weight of Fe^{3+}

$$= 350 \times \frac{55.847}{162.206} = 120.5 \text{ lb. } Fe^{3+}$$

If 80 mg/l is needed

1×10^6 gal = 4.54×10^6 L

Therefore,

in 4.54×10^6 L we need (80) (4.54×10^6) mg of Fe^{3+}

$= 3.632 \times 10^8$ mg

= 363.2 kg

= 799 or 800 lb/10^6 gal of Fe^{3+}

$$800 \text{ lb } Fe^{3+} = \frac{800}{120.5} \times 350 = 2,323.6 \text{ lb } FeCl_3$$

For electrolytic flotation

at $90.00 for 350 lb

cost of $FeCl_3$ per 10^6 gal = $\frac{2324}{350} \times 90 = \$597.60/10^6$ gal

For coagulation

Need approximately 120 lb. Fe^{3+} for 10^6 gal

$$1250 \text{ lb. } Fe^{3+} = \frac{1250}{120.5} \times \frac{350}{\text{lb } Fe^{3+} \text{ in } 350 \text{ lb } FeCl_3} = 3630.7 \text{ lb } FeCl_3$$

at \$90.00 for 350 lb.

Cost of $FeCl_3$ per 10^6 gal = $\frac{3630.7}{350}$ X 90 = \$933.61

160,000 bbl of crude bitumen is upgraded to produce 141,000 bbl of synthetic crude oil

8.4×10^6 gallons (38.2×10^3 m^3/d) of water is to be recycled.

Therefore,

gal/bbl of synthetic crude produced = $\frac{8.4 \times 10^6}{141,000}$ = 59.57 gal/bbl

Chemical cost of electrolytic flotation = \$597.60/10^6 gal

Therefore,

chemical cost per bbl of synthetic crude produced

$$= \frac{597.60}{10^6} \times 59.57 = 3.56¢/bbl$$

Chemical cost of coagulation = \$933.61/10^6 gal

Therefore,

chemical cost per bbl of synthetic crude produced

$$= \frac{933.61}{10^6} \times \$59.57 = 5.56¢/bbl$$

APPENDIX 7

Current Density Calculations

Length of electrode = 7.5 cm

Diameter of electrodes:

Fe = 0.32 cm

Al = 0.32 cm

Stainless Steel = 0.32 cm

Pt = 0.16 cm

Horizontal surface area of

Fe, Al and stainless steel electrodes = $2\pi rh$

$$= (2)(\pi)\frac{(0.32)}{2}\ 7.5 = 7.54\ cm^2$$

Therefore, 2 anodes = $7.54 \times 2 = 15.1\ cm^2$

Horizontal surface area of Pt electrodes

$$= 2\pi rh$$

$$= (2)(\pi)\frac{(0.16)}{2}(7.5) = 3.78\ cm^2$$

Therefore 2 anodes = $7.6\ cm^2$

Pt (for 2 anodes)

$$1\ Amp = \frac{1\ Amp}{7.6\ cm^2} \times 1000 = 132\ mA/cm^2$$

$$2\ Amp = \frac{2}{7.6} \times 1000 = 263\ mA/cm^2$$

$$3\ Amp = \frac{3}{7.6} \times 1000 = 395\ mA/cm^2$$

Al, Fe, Stainless Steel (2 anodes)

1 Amp = $\frac{1}{15.1}$ X 1000 = 66 mA/cm^2

2 Amp = $\frac{2}{15.1}$ X 1000 = 132 mA/cm^2

3 Amp = $\frac{3}{15.1}$ X 1000 = 199 mA/cm^2

4 Amp = $\frac{4}{15.1}$ X 1000 = 265 mA/cm^2

5 Amp = $\frac{5}{15.1}$ X 1000 = 331 mA/cm^2

Al, Fe, Stainless Steel (4 anodes)

1 Amp = $\frac{1}{30.2}$ X 1000 = 33 mA/cm^2

2 Amp = $\frac{2}{30.2}$ X 1000 = 66 mA/cm^2

3 Amp = $\frac{3}{30.2}$ X 1000 = 99 mA/cm^2

4 Amp = $\frac{4}{30.2}$ X 1000 = 132 mA/cm^2

5 Amp = $\frac{5}{30.2}$ X 1000 = 166 mA/cm^2

APPENDIX 8

Theoretical Rate of Iron Dissolution

Assuming that all the current in the system was conducted through electrons obtained from the ionization of iron, i.e.:

$$Fe^{\circ} \text{ ----- } Fe^{3+} + 3e^{-}$$

Assume,

For 1 Amp over 1 hour of operation

$$1 \text{ Amp} = 1 \frac{\text{coulomb}}{\text{sec}}$$

Therefore,

$$\# \text{ of coulombs needed} = 1 \frac{\text{coulomb}}{\text{sec}} \times 1 \text{ hour} \times (60 \times 60 \frac{\text{sec}}{\text{hr}})$$

$$= 3600 \text{ coulombs}$$

but, 1 coulomb = 6.25×10^{18} electrons.

Therefore,

$$\# \text{ of electrons needed} = (3600)(6.25 \times 10^{18})$$

$$= 2.25 \times 10^{22} \text{ electrons}$$

$$6.023 \times 10^{23} \frac{\text{electrons}}{\text{mole}}$$

Therefore,

$$\# \text{ of moles} = \frac{2.25 \times 10^{22}}{6.023 \times 10^{23}} = 0.0374 \text{ moles}$$

1 mole Fe° weighs = 55.84 grams/mole

Therefore,

grams Fe° = 55.847 X 0.0374 = 2.089 grams

= 2089 mg Fe° per Amp per hour.

Therefore,

at 2 Amp for 1.5 hours = 2089 X 2 X 1.5

= 6267 mg

At 3 Amp for 1.5 hours = 2089 X 3 X 1.5

(200 mA/cm^2) for stainless steel electrodes = 9,400 mg

12 liter sample volume was used.

Therefore, concentration of Fe^{3+} in solution

$$= \frac{9400}{12\ L}\ mg = 783\ mg/L$$

APPENDIX 9

Hydrogen Generation Rate

$H^+ + H^+ + 2e^- \longrightarrow H_2$

i.e., need 2 electrons per molecule of H_2 generated.

Assume: 1 Amp for 1 hour

$1 \text{ Amp} = 1 \frac{\text{coulomb}}{\text{sec}}$

Therefore,

1 Amp over 1 hour = $1 \times 60 \times 60 = 3600$ coulombs

1 coulomb = 6.25×10^{18} electrons

Therefore,

3600 coulombs = $(6.25 \times 10^{18})(3600)$

= 2.25×10^{22} electrons

Need $2e^-$ per molecule

Therefore,

Number of molecules = $\frac{2.25 \times 10^{22}}{2} = 1.125 \times 10^{22}$

1 mole = 6.23×10^{23} molecules.

Therefore,

Number of moles = $\frac{1.125 \times 10^{22}}{6.23 \times 10^{23}} = 0.0181$ moles

1 gram mole at S.T.P. occupies 22.4 Liters

Therefore,

0.0181 gram mole = 0.4054 Liters = 405.4 mL volume

i.e., 405.4 mL volume of hydrogen will be produced per each ampere per hour.