TREATMENT

OF

REFINERY CRUDE OIL TANK SLUDGE

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Abstract

The treatment and disposal of oil refinery tank sludge is a critical issue among oil refineries. This is because of the hazardous nature of the sludge due to high levels of oil and heavy metals, which must be removed prior to disposal. This study was carried out to investigate the removal of crude oil and heavy metals to allow the design of an appropriate disposal treatment that could meet the environmental regulations for this type of waste.

A typical emulsified crude oil tank sludge, produced from tank cleaning operations was characterised and was shown to contain approximately 41%, 16%, 25%, and 8% of solids (sand), oil, water and volatile materials, respectively. The sludge also contained high level of metals, of which more than 98% resided in the solids fraction. The heavy metals analysed were copper, nickel and zinc with average values of 3,955mg/kg, 443 mg/kg and 13,851 mg/kg of raw sludge, respectively.

The crude oil fraction of the sludge was removed by solvent washing with kerosene which resulted in emulsion breakdown. A model which optimises the removal of crude oil was developed and validated against experimental data. The model predictions agreed well with experimental trials using kerosene as the solvent. A 2:1 solvent to sludge ratio is adequate to remove the oil (> 98%) in the sludge after two washing stages. This resulted in oil-free/metal-rich solids. Kerosene washing reduced the volume by 76% and mass by 59 %, which allows easier handling and disposal.

Heavy metals reduction was achieved by acid washing using 8N nitric acid and a 10:4 mixture of 2.4N hydrochloric and 8N nitric acids. Approximately 99% of the metals were removed using a 10:1 acid to solids ratio, at pH <1 and ambient conditions, making the sludge suitable for land application and meeting the appropriate disposal guidelines for oil and metal levels.

The solvent washing process was shown to be industrially feasible for volume and mass reduction of the sludge. However, heavy metal reduction by acid washing requires further optimisation before it can be applied on an industrial scale.

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Nomenclature

δ_b = bulk density of raw sludge [kg/m^3]

W_b = bulk mass of raw sludge [kg]

V_b = bulk volume of raw sludge [m^3]

δ_p = particle density of washed solids [kg/m^3]

W_p = mass of washed solids [kg]

V_k = volume of kerosene at ambient temperature [m^3]

V_f = final volume (kerosene + washed solids) [m^3]

x = concentration of oil in raffinate/feed stream [kg oil/kg (oil + solvent)]

X = concentration of oil in solvent/extract stream [kg oil/kg (oil + solvent)]

y = concentration of solids in raffinate/feed stream [kg solids/kg (oil + solvent)]

Y = concentration of solids in solvent/extract stream [kg solids/kg (oil + solvent)]

w = concentration of water in raffinate/feed stream [kg water/kg (oil + solvent)]

W = concentration of water in solvent/extract stream [kg water/kg (oil + solvent)]

R = mass of raffinate/feed stream [kg (oil + solvent)]

S = mass of solvent stream [kg (oil + solvent)]

E = mass of extract stream [kg (oil + solvent)]

m = mass of mixture [kg (oil + solvent)]

x_{mn} = concentration of oil in mixture [kg oil/kg (oil + solvent)]

y_{mn} = concentration of solids in mixture [kg solids/kg (oil + solvent)]

w_{mn} = concentration of solids in mixture [kg water/kg (oil + solvent)]

C = concentration of oil [kg oil/kg solvent]

RI = refractive index [dimensionless]

Chapter 1

Introduction

1.1 Background of the problem

The New Zealand Refining Company Ltd. (NZRC) generates an average of 100 tonnes of crude oil tank sludge annually from tank maintenance operations. This sludge was found to contain heavy metals at levels exceeding those set out by Public Health Guidelines, (NZ Dept. of Health 1992) for disposal by land application. Heavy metals found in the sludge were mercury, chromium, cadmium, lead, nickel, zinc and copper. The type of sludge being produced by NZRC is an oil/water/sand emulsion that makes it difficult to handle (Gozan *et al.* 1996).

NZRC has been using landfarming as the mode for disposal of their oily refinery wastes. However, the adverse effect on the environment of heavy metals accumulation makes this practice unsustainable. Analysis of soil samples taken from the landfarming site (Gozan *et al.* 1996) has shown that it exceeded the heavy metal concentration set by the Public Health Guidelines (NZ Dept. of Health 1992). For this reason an alternative treatment methodology is required.

At present, NZRC sludge has been disposed through co - landfill. However, this system is recognised as a short-term solution and is subject to increasing restrictions and criticisms by regulatory authorities.

1.2 Objective of the study

This study is aimed at developing an alternative method of treatment that can be applied industrially to stabilise crude oil tank sludge. This method will be aimed at making the sludge suitable for land application. This study aims to:

- Remove the crude oil from NZRC tank sludge.
- Reduce the heavy metal concentration in NZRC sludge.

- Investigate the feasibility of the method for industrial application.

Achieving these aims would provide the solution for treatment and disposal of oil refinery sludge and could be used in oil refineries globally.

Chapter 2

Review of Literature

2.1 Introduction

The treatment and disposal of oil refinery tank sludge is a global problem among oil refineries, because of the tightening of environmental legislation on land application of hazardous wastes. The hazardous nature of the sludge is due to high oil and heavy metals content, which must be removed prior to disposal. Before stabilisation could be carried out in an attempt to make it suitable for disposal, knowledge about emulsion phenomena, heavy metal chemistry and the nature of the sludge are essential. This is to provide the basic information required to design and implement an appropriate disposal treatment.

2.2 Characteristics of refinery sludge

Petroleum refineries generate oily sludges which can be characterised as an oil/water/solid emulsion (Engelder and Spearman 1993). Oily sludges are stable emulsions formed through emulsification of oil with water, usually in the presence of suspended fines. The mechanism responsible for the formation of sludge is thought to be the adsorption of asphaltenes to hydrophilic solid particles at the oil-water interface (Fromm and White 1995).

Emulsions are encountered at nearly every step of the petroleum production and recovery operations, viz. within the underground porous media (reservoir), at wellheads, in phase separators, in flotation units, in crude oil transport facilities and at various stages of the refining process. The emulsification of oil and water is believed to occur mostly in the well bore where the velocity gradients are very high (Raghavan and Marsden 1971). The source of emulsifying agents in the emulsions produced, is the crude oil itself, which contains a variety of surface-active agents such as polycyclics and long-chain fatty acids (Steinhauff 1962 and Lissant 1976). Finely divided solids such as clay and sand are also present in the crude oil and these are well-known stabilizing agents for emulsions.

2.3 Characteristics of NZRC oil sludge

Oil sludge at the New Zealand Refining Company (NZRC) is generated from five main sources. These sludge streams came from the tank bottoms of crude and residue tank cleaning, gravity separators, effluent wastewater treatment, de-oiled sludge from desalter effluent water and the algae biomass sludge of the retention basin (Gozan *et al.* 1996). Among these streams it was found that the bulk of the heavy metals were found in the crude oil tank sludge. An average of 100 tonnes of this sludge is generated each year.

A previous study has shown that the oil sludge consists of an emulsion of heavy crude oil, water and sand. The type of sludge produced is a water in oil emulsion. This sludge contains mercury, chromium, cadmium, lead, nickel, zinc and copper. The average composition of the sludge is 52% water, 35% crude oil and 13% sand (White 1997).

Among the heavy metals present, copper, nickel and zinc were highest in concentration. Significant levels of these metals have been measured in the sludge which was found to contain 957 mg/l, 21.2 mg/l, 101 mg/l and 1,716 mg/l of copper, mercury, nickel and zinc, respectively (Gozan *et al.* 1996). White (1997) found that NZRC crude oil tank sludge contained 495 mg/kg, 144 mg/kg and 1,463 mg/kg of copper, nickel and zinc, respectively.

2.4 The hazards of oil sludge

In general terms, a hazardous substance is a material with a substantial potential to pose a danger to living organisms, materials, structures or the environment. Such dangers may include explosion or fire hazards, corrosion, toxicity to organisms or other detrimental effects. A hazardous waste is a toxic substance that has been discarded or otherwise designated as a waste material, or one that may become harmful by interaction with other substances. In a simple sense, hazardous waste is a material that has been left where it should not be and that may cause harm to you if you encounter it (Manahan 1990).

A waste or any substance is considered hazardous, as defined under the authority of the Resource Conservation and Recovery Act (RCRA) the United States Environmental Protection Agency (EPA), in terms of the characteristics of ignitability, corrosivity, reactivity and toxicity (Identification and Listing of Hazardous Wastes 1986). These characteristics are defined as follows.

a. Ignitability - if a waste has an organic layer or one which exerts a high vapor pressure and a flash point less than 140 °F.

b. Corrosivity - if a waste has a pH less than 2 or greater than 12.5

c. Reactivity - if a waste can generate toxic gases when exposed to extreme pH conditions. Wastes containing sulfides or cyanides are examples of this type.

d. Toxicity – if a waste has been found, through laboratory studies, to have a carcinogenic, mutagenic or teratogenic effect on human or other life forms.

Oil sludge generated from the petroleum refineries are considered hazardous (Engelder and Spearman 1993). Crude oils, regardless of origin, mainly consist of hydrocarbons mixed with variable amounts of sulfur, nitrogen and oxygen compounds. Heavy metals in the form of inorganic salts or organometallic compounds are present in the crude mixture in varying trace amounts depending on the source. Although heavy metals in crude oils are found in trace amounts, their presence is harmful (Matar and Hatch 1994).

The hydrocarbons may exist as alkanes, alkenes and arenes, depending upon the kinds of bonds between carbon atoms. The presence of elements other than hydrogen and carbon in organic molecules greatly increases the diversity of chemical behaviour. As organometallic compounds enter the environment, they are biologically synthesized by bacteria. Some of these compounds are particularly toxic because of their mobility in living systems and ability to cross cell membranes (Manahan 1990).

2.5 Disposal of refinery sludges

Disposal of refinery sludge is becoming a critical issue for the refining industry due to its hazardous nature (Bryant and Moores 1991). Refinery sludges can be disposed through different routes after being pretreated for volume reduction. These are discussed below.

2.5.1 Landfill

Hazardous waste landfills are disposal pits, usually below ground level. Pits constructed under more modern regulations require a synthetic lining material, an appropriate cap when closed and a leachate collection system (Manahan 1990). Waste is often pretreated by dewatering (volume reduction) or solidification (prevent leaching) before disposal to landfill (Concawe 1995). Secure landfills for hazardous waste disposal are now equipped with double liners, leakage detection, leachate monitoring and collection and groundwater monitoring systems (Blackman 1993).

The greatest environmental concern with landfill of hazardous wastes is the generation of leachate from infiltrating surface water and groundwater with resultant contamination of groundwater supplies (Manahan 1990).

2.5.2 Landfarming

Landfarming is the treatment of oily or biological sludges by controlled application to a specially prepared area of soil so that the micro-organisms present in the soil can biodegrade the organic components of the sludge as rapidly as possible (Concawe 1995). The greatest application of this treatment is found in the petroleum industry for the biodegradation of waste petroleum solids and sludges (Manahan 1990).

NZRC sludge used to be disposed through landfarming. However, landfarming has not been continued because of heavy metals accumulation in the soil (Gozan *et al.* 1996). Since the ceasing of landfarming operations, NZRC sludge has been disposed of at contaminated landfills.

2.5.3 Incineration

Incineration is high temperature oxidation which converts oily sludges and etc. into gaseous products and solid residues (ash) which are less voluminous than the original material (Concawe 1995). This process involves oxidative conversion of combustible materials to harmless gases suitable for atmospheric release. Undesired gaseous products such as HCl, SO_2, NO_x must be removed prior to release. Residual solids such as ash are landfilled (Theodore *et al.* 1987).

Materials which are basically hydrocarbons can be burned in modified boilers as fuel. Alternatively, oily materials are incinerated in power station boilers or cement kilns. However, less combustible materials or more hazardous materials may require the use of a support fuel and/or the installation of expensive flue gas scrubbing/solids removal equipment to meet air pollution regulations. The economics of incineration are unfavourable and the technique is not always in the best interest of energy conservation (Concawe 1995).

2.5.4 Composting

Composting of hazardous wastes is the biodegradation of solid or solidified materials in a medium other than soil. Bulking material, such as plant residue, paper, municipal refuse, or sawdust may be added to retain water and enable air to penetrate to the waste material. This process can be carried out in a container, often with air pumped through it to aid biodegradation. Alternatively, the waste material may be placed in open piles or rows (windrows) which are reformed periodically to facilitate penetration of air (Manahan 1990).

Gozan (1998) conducted composting trials for NZRC sludge using a vented (aeration) rotating drum bioreactor and sawdust as the bulking agent. It resulted in the decomposition of oil to more than 70% after 50 days of composting. Although the process was shown to be feasible, it still requires further optimisation before industrial implementation.

2.6 Emulsion chemistry

An emulsion is a "signinificantly stable" suspension of particles of liquid of a certain size within a second, with immiscible liquid (Rosen 1978). It is a two phase oil/water system where one of the phases is dispersed as droplets in the other. The phase which is present in the form of droplets is referred to as the "dispersed phase" and the phase which forms the matrix in which these droplets are suspended is called the "continuous phase".

The droplets in emulsions usually exceed 0.5µm in diameter so that they are visible under an optical microscope. Emulsions also contain a third component called the emulsifying agent or emulsifier, which has two principal functions : (1) to decrease the interfacial tension between oil and water; (2) to stabilize the dispersed phase against coalescence once it is formed (Pal 1994).

Emulsions can be classified into three broad groups:

(a) Water-in-oil emulsions, designated as " W/O emulsions" ;

(b) Oil-in-water emulsions, designated as "O/W emulsions" ;

(c) Multiple emulsions

The W/O emulsions are consist of water droplets dispersed in a continuum of oil, and is more commonly encountered in the petroleum industry and therefore are referred to as "regular emulsions". The O/W type of emulsions consist of oil droplets dispersed in water, and are called reverse emulsion in the petroleum industry, being the reverse of the more common W/O types. Multiple emulsions consist of one or more small water droplets entrapped within large oil droplets. These are in turn suspended in a continuum of water. Multiple emulsions are not as common as binary emulsions (Pal 1994).

2.6.1 Formation of emulsion

Emulsification is the formation of an emulsion from two immiscible liquid phases. The emulsion is formed when one of the two immiscible liquids is broken up into particles that are dispersed in the second liquid. Since the interfacial tension between two immiscible pure liquids is always greater than zero, the dispersion of the inner liquid (which produces a tremendous increase in the area of the interface between them) results in a correspondingly large increase in the interfacial free energy of the system. Consequently, the emulsion produced is highly unstable thermodynamically, relative to the two bulk separated by a minimum area interface. The presence of an emulsifying agent, stabilises the basically unstable system for a sufficient time so that it can perform such a function (Rosen 1978).

There are many ways to produce an emulsion from liquid phases that are mutually insoluble or only slightly soluble. It is usually achieved by applying mechanical energy. First, the interface between the two phases is deformed to such an extent that droplets form. These droplets are mostly far too large and are subsequently broken up or disrupted into smaller ones. The disruption of droplets is a critical step in emulsification.

A suitable surfactant called an emulsifier is needed to produce a stable emulsion. The role of the surfactant is complicated but essential, and depends on its nature and concentration. Droplets may coalesce again after being formed, and this may be another critical step. Unfortunately, coalescence mechanisms are only partly understood, and whether and how fast coalescence will happen cannot be predicted in the complicated situation during emulsification. The surfactant is of paramount importance. It largely determines which phase is going to be the continuous one: it is commonly the one in which the surfactant is soluble (Bancrof's rule). These processes will occur simultaneously and their rates depend on several factors, including concentrations and nature of surfactants, amount of energy applied and temperature (Walstra 1983).

In primary oil production operations, W/O emulsions are more commonly encountered. O/W emulsions usually occur when a given oil field becomes old and produces a greatly increased amount of water (Jenkins 1977). In enhanced oil recovery operations, both O/W and W/O emulsions are produced (Pal 1994).

A stable emulsion is formed when mechanical energy has been applied into a mixture of oil and water to form droplets that can be dispersed in the oil phase. These droplets will collapse against each other (coalesce) and form successively larger droplets which eventually settle out as a result of natural convection motion. The presence of a surfactant (emulsifier) will provide a molecular coating around each water droplet. The molecules of this film are polarized in such a manner that the droplets repel each other and are maintained in a disperse state, thus forming a stable dispersion. No amount of heating, settling, pulling or waiting will cause them to separate unless a demulsifier is added in trace amounts to balance the stabilising forces of the emulsion (Delchad 1990).

2.6.2 The role of surfactants

Surfactants are surface active because they concentrate at interfacial regions such as air-water, oil-water and solid-liquid interfaces. The surface activity of surfactants derives from their amphiphilic structure, meaning that their molecules contain one soluble and one insoluble moiety. In aqueous systems, a surfactant has a polar or ionic hydrophilic moiety and a nonpolar hydrophobic moiety, referred to as the head and tail groups, respectively (West and Harwell 1992).

There are three basic concepts which need to be understood in order to explain the majority of observed phenomena about the mode of action of surfactants. These are solubility, adsorption of a surfactant at a surface, and the formation of micelles in solution. Three phenomena differentiate a surfactant from other chemical entities. It is the abnormal solubility characteristics of surfactants that give adsorption and form micelles. It is adsorption at surfaces that gives the surface active effects of foaming, wetting, emulsification, dispersing of solids and detergency. It is the micellar properties that give the solution and bulk properties of surfactants such as viscosity and solubilisation. There is increasing evidence that the micellar properties are necessary in functional effects such as emulsification and detergency (Porter 1994).

A surfactant can be pictured as a long straight hydrophobic group and a small round hydrophilic group which can be oriented in various ways. Surfactants absorb because of these two groups in the molecule : a hydrophobic (water hating) group and a hydrophilic (water liking) group as shown in Figure 2.1.

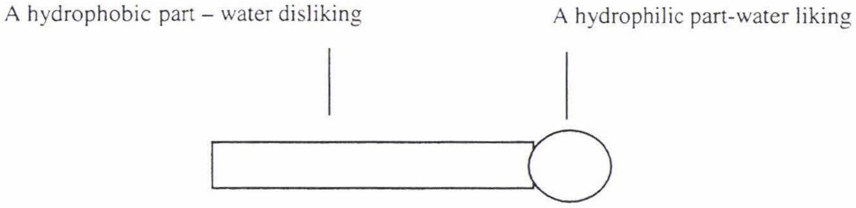


Figure 2.1 Basic structure of a surfactant (Porter 1994).

The aqueous solubility of a lone surfactant molecule will depend upon the relative strength of the hydrophobic and hydrophilic effects. They are not independent, since both rely on the structure of the hydrogen bonds around the hydrophilic and hydrophobic groups. The adsorption of a surfactant from solution onto a surface depends upon the concentration.

Figure 2.2 shows the effect of increasing surfactant concentrations. At very low concentrations (I and II), there is no orientation and the molecule lies flat on the surface. As the concentration increases (III), the number of surfactant molecules on the surface increases. There is not enough room for them to lie flat so they begin to reorientate, the orientation depending upon the nature of the hydrophilic group and the surface. At concentration IV, the number of surfactant molecules available is now sufficient to form a unimolecular layer. This particular concentration is of importance and is known as the critical micelle concentration (CMC). The surfactant molecules in the solution will form an ordered structure known as a micelle so long as the concentration is above the CMC.

At concentration V (above IV), there is no apparent change in adsorption at hydrophobic surfaces, but at hydrophilic surfaces more than one layer of surfactant molecules can form ordered structures on the surface of the solid (Porter 1994).

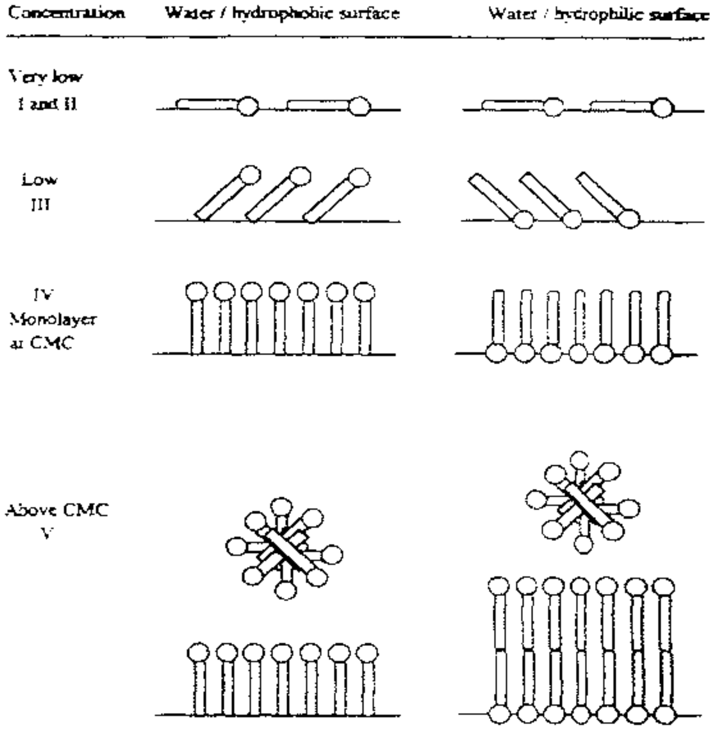


Figure 2.2 Effect of surfactant concentration on surface adsorption (Porter, 1994).

2.6.3 Classification of surfactants

Surfactants are classified according to the nature of the hydrophilic portion of the molecule. These are anionic, cationic, nonionic and amphoteric surfactants. Anionics are surfactants where the surface-active part of the molecule carry a negative charge, cationic surfactants carry a positive charge, nonionic surfactants carry no charge and amphoteric surfactants can carry a positive charge or both, depending upon the conditions e.g. pH (Porter 1994).

2.6.4 Breakdown of emulsions

An emulsion is broken if its two phases are completely separated. Breaking an emulsion is an irreversible separation and can be looked upon as the reversie of the process of emulsification. An emulsion can break for a number of reasons including insufficient quantity of emulsifying agent in the formula, decomposition of the agent, the presence of electrolytes or antagonistic ions and abrupt changes of the temperature (Sutheim 1947).

Menon and Wasan (1985) broadly categorized the phenomenon of emulsion separation into three different processes. These are outlined below.

2.6.4.1 Creaming

Creaming is a phenomenon by which the emulsion separates into two emulsions, one richer and the other poorer in the dispersed phase. The mechanism of creaming appears to be due to slow sedimentation of the emulsified droplets (Menon and Wasan 1985). Creaming is not de-emulsification, but rather the creation of two emulsions, one floating on top of the other. The creaming phenomenon obeys Stoke's Law governing the rate of gravitational sedimentation (Bennett *et al.* 1968).

2.6.4.2 Inversion

Inversion is a process of the simultaneous switching of the internal and external phases of the emulsion (Bennett *et al.* 1968). It is the sudden change of a water-in-oil (W/O) emulsion to an oil-in-water (O/W) emulsion and vice versa. This is termed phase inversion. This instability is dependent on a variety of factors, such as the nature and concentration of the emulsifier, temperature, volume fractions of the two phases and the physical properties of the phases (Menon and Wasan 1985).

2.6.4.3 Demulsification

Demulsification is the agglomeration and coalescence of droplets of the dispersed phase, eventually resulting in a breakdown of the emulsion into two separate phases A wide variety of materials has been used to accelerate the coalescence of emulsions. Numerous patents have been granted and methods described for demulsifying the crude oil emulsions (Sunder Ram and Shah 1984).

2.6.5 Techniques for emulsion separation

Many situations arise where the separation of the two phases of an emulsion is desired (Ross and Morrison 1988). The recent increase in environmental consciousness has created interest in breaking sludges and emulsions prior to its disposal due to stringent environmental regulations.

The breaking of water in crude oil emulsions is a necessary operation in the production of much of the world's oil before refining can take place (*Cairns et al.* 1976). Consequently, factors affecting the stability of such emulsions are of considerable importance. Water in crude oil emulsions are frequently stable over long periods. This stability is partly dynamic due to the high bulk viscosity of the draining oil. However, there are many cases in which stable emulsions exist when the oil has a relatively low bulk viscosity. Stability in such cases is primarily the result of adsorption phenomena and the consequent interface rheology in the presence of surface active agents or surfactants (Cherkasov *et al.* 1965).

The problem of separating two immiscible liquids when one is dispersed within the other is frequently encountered in petroleum technology (Sunder Ram and Shah 1984). There are several methods on how to break an emulsion. Some of these processes are discussed below.

2.6.5.1 Chemical method

Chemical method is the addition of chemical demulsifiers to break the emulsion by destabilising the interfacial layer. The resistance of the emulsion to coalescence is determined by the structure and physical properties of the chemicals adsorbed at the interface (Menon and Wasan 1985). An emulsion will often break if the emulsifying agent is chemically altered. Emulsions stabilised with alkalai-metal soaps are broken on adding acid or metal ions, such as iron or calcium, which convert soaps to water-insoluble fatty acids or metallic salts.

Emulsions stabilised with anionic agents can be broken by adding a cationic detergent, such as a quaternary ammonium salt, which converts the agent to a water-insoluble complex.

Another way to separate a stable emulsion is to replace the emuslifying agent with a surface-active solute of greater adsorptive potential but less stabilising effect. In the same manner, emulsions stabilised with adsorbed solid particles can be broken by the addition of a solvent that wets the particles and removes them from the interface. Among the chemical methods to destabilise emulsions is the addition of electrolyte to increase the ionic strength of the medium, thus reducing the repulsion between droplets of an electrostatically stabilised emulsion (Ross and Morrison 1988).

2.6.5.2 Physical or mechanical method

Gravity settling is one of the oldest techniques known for the separation of two phases in which one phase is dispersed in the other. Separation can be achieved through the use of gravity settlers such as batch holding tanks, continues-flow baffled units, and/or parallel or corrugated plate separators phases (Menon and Wasan 1985). The rate of demulsification can also be promoted by agitation which is sensitive to high shear that throws the droplets into one another with consequent coalescence.

Centrifugation is another mechanical method to accelerate creaming or breaking of emulsions (Ross and Morrison 1988). The idea of using a centrifugal field to separate fluids of differing densities is not new. High speed centrifugal separators, such as the ultracentrifuge, accelerate gravity-driven creaming as well as accelerating coalescence of droplets, thus leading to eventual separation of the phases (Menon and Wasan 1985).

Filtration using fine filters such as fritted glass or filter cakes of infusorial earth will reduce the water content of oil field emulsions to as little as 0.2 % (Sunder Ram and Shah 1984).

Thermal separation can also be used since most emulsions are less stable at higher temperatures, as the adsorption of the stabiliser decreases with temperature. In some cases the emulsifying agent is thermally decomposed (Ross and Morrison 1988). Lowering the temperature of the emulsion below the freezing point of water causes the water to change into ice. The ice expands and thereby breaks the oil envelope (Menon and Wasan 1985). The separation of water as ice allows the electrolytes in the aqueous medium to become concentrated, thus reducing the electrostatic repulsion between droplets. The freeze-thaw cycle usually needs to be done slowly and repeatedly for best results (Ross and Morrison 1988).

2.6.5.3 Electrical Method

The imposition of high potentials on emulsions bearing a charge leads to the coagulation of the water droplets (Sunder Ram and Shah 1984). In most systems where one phase is dispersed in the other phase, the droplets often possess an electric charge with respect to the continuous phase. If electrodes are placed in such a system and an electric field is set up, the droplets tend to move toward the electrode of opposite charge. The droplets then coalesce by collision with each other and with the electrodes. Electrically induced coalescence techniques are gaining prominence because electricity is much cheaper than most other energy sources (Menon and Wasan 1985).

2.7 Industrial methods for oil separation

The main purpose of pretreatment processes is to reduce the sludge to the lowest possible volume. It is common to separate the solid materials from the hydrocarbons and the water. It can be a simple treatment (e.g. decanting) or a more sophisticated process (e.g. mechanical dewatering). The technique used for sludge reduction is the reduction factor (weight of sludge to pretreatment divided by the weight of sludge after pretreatment) and may vary between refineries. Pretreatment of the sludge is necessary to be able to modify the physical, chemical or biological properties of the waste (oil sludge) in order to render it less or non-hazardous (Concawe 1995).

There are a number of pretreatment processes utilised to reduce the volume of the sludge prior to its disposal or treatment. The following are brief descriptions of these unit operations or systems.

2.7.1 Centrifugation

Centrifugation exploits the difference in density between solids and liquids (or two liquid phases) to separate them by applying centrifugal force (Concawe 1990). This process in principle is very much like gravity settling, but with the force of gravity increased many times using centrifugal force. It is frequently used in applications where gravity settling would be considered but would take too long. Example situations include low density difference between phases to be separated, small particle size of the dispersed phase, or high viscosity of the continuous phase. The multiplication of gravity by centrifugal force makes these applications possible in a reasonable length of time (Long 1995). The application of high speed centrifuges is generally not suitable for sludges containing oils, due to the tendency to form oil/water emulsions which are difficult to treat when returned to the refinery waste treatment system (Bryant and Moores 1991).

This process has been used by NZRC as part of its sludge treatment operations. The bottom stream from the centrifuge is the final sludge that needs treatment and disposal management (Gozan 1998).

2.7.2 Filtration

Filter presses and related systems, mechanically dewater sludges by pressure. This has benefits of high volume reduction and recovery of the oil from oily sludges. In most cases, filter aids are needed to enhance dewatering and prevent clogging of the filter, but result in increased waste volume. Heating and the use of flocculants may also be used to enhance performance (Concawe 1995).

2.7.3 Drying

Drying is a process which normally involves the removal of a liquid from a solid by evaporation. Drying is a thermal process involving heat-transfer and vaporization (Long 1995). Non-mechnical means of sludge drying (e.g. sludge drying beds) are not generally used because they are labour intensive, require an arid climate, and tend to emit odours from volatile organic compounds (VOCs) (Bryant and Moores 1991).

2.7.4 Demulsification

This process of pretreatment of the refinery sludge is made through the addition of demulsifying agents in trace amounts. These balance out the stabilising forces of the emulsification in the shortest possible time and permits natural settling. Alternatively, a mechanical system can be used to improved separation of the emulsified sludge (Delchad 1990).

Deemulsification is used for dewatering of NZRC tank sludges. 50-75% of the water is removed and hence the sludge volume is reduced (Gozan 1998).

The use of surfactants has been developed in the oil industry to enhance oil recovery from reservoirs (Peters *et al.* 1992). Surfactant enhanced remediation of organic contaminants is fairly well understood (Nivas *et al.* 1996). Several studies have been conducted to mobilize organic pollutants from the soil for decontamination using surfactant solutions. Rickabaugh *et al.* (1986) used different types of surfactants to promote solubilization of chlorinated hydrocarbons from a contaminated soil. It was found that the use of blends of nonionic-cationic or nonionic-anionic surfactants generally gave better removals compared to any type of surfactants used alone at different concentrations. Cationic surfactants, when used alone, generally gave lower removals than anionic or nonionic surfactants used alone.

The effect of anionic and nonionic surfactants on the sorption and micellar solubilization of monocyclic aromatic compounds (e.g. benzene, chlorobenzene and styrene), which are considered non-aqueous phase liquids (NAPLs), in soil-free and soil-water systems have been investigated. Results of the study demonstrated that surfactants can be effectively used as chemical ammendments to minimize the volatilities of monocyclic aromatic compounds and enhance sorption and solubilization in soil environments contaminated by proper selection of surfactant type and concentration (Doong *et al.* 1996).

Yeom *et al.* (1996) investigated the dissolution of polycyclic aromatic hydrocarbons (PAHs) from weathered soil contaminated with coal tar, using nonionic surfactants. They found that mass transfer of the PAHs was greatly enhanced by the surfactant used. This could not be attributed to its solubility enhancement by surfactant micelles, but rather increased diffusivity of PAH in the tar matrix. This changed the physical properties of the medium through penetration of the organic matrix of the soil, swelling the medium and creating more space for PAH's diffusion.

Peters *et al.* (1992) conducted a preliminary screening of 22 surfactants to be used for leaching undisturbed soil cores that had been contaminated with diesel fuel. The chosen surfactants resulted in 87% to 97% removal of the diesel fuel during batch extraction.

2.7.5 Solvent extraction

Solvent extraction is a process in which a substance is transferred from solution in one solvent to another without any chemical change taking place (Manahan 1990). When solvent extraction is applied to solid materials it is called leaching (Long 1995).

In pollution prevention, this process is usually applied to the removal of organics, mostly oil and grease, from aqueous solutions or from oily sludges. For solvent extraction to be effective, the species to be removed should have high solubility in the solvent and the solvent should have high selectivity for the species to be removed relative to other materials in the feed. Furthermore the solvent should have low solubility in the feed material or solution. Once a suitable solvent is found, it is necessary to be able to easily separate the species from the solvent after the extraction is done. It is usually difficult to meet all the above criteria in an economical manner (Palepu *et al.* 1995).

A complete extraction system consists of a multistage extractor (e.g., rotating-disk contactors or mixer-settlers or packed columns) and equipment to separate the solvent from the extract. Most commercial uses of this process in pollution prevention are not for recovery and reuse of components but for the decontamination of solutions, soils and sludges (Palepu *et al.* 1995).

Since sludges and emulsions are frequently encountered in industrial processing and petroleum refining, two new processes have been developed that can break oil sludges and emulsions and allow recovery of the oil present leaving clean solids and water for disposal. These processes are called B.E.S.T (basic extraction sludge treatment) and the CFS liquid propane extraction process.

The B.E.S.T. process, which was developed by the Resources Conservation Company (Seattle, WA) takes advantage of the unusual miscibility properties of aliphatic amines such as triethylamine in water. Below 68°F, triethylamine and water are completely miscible, while above 68°F the solution splits into two phases. When using this process, the feed sludge and the amine are mixed at a temperature of about 40°F with a solvent to sludge ratio of approximately 2:1. This dissolves all the liquid components and breaks any emulsions or stable suspensions. Since the solution is alkaline, heavy metals in the sludge precipitate as hydrated oxides and are removed along with the solids fraction. The released solids can be removed by any solid-liquid separation process, such as filtration or centrifugation above 68°F. Approximately 99% solid matter can be achieved (Long 1995).

The CFS process which was developed by Critical Fluid Systems, Inc. for breaking oily sludges and emulsions uses subcritical liquid propane as the extraction solvent. The oil in the sludge dissolves in the propane, separating the sludge into two liquid phases and one solid phase. The oil-propane phase is separated from the water-solids slurry by decanting and the solids are removed from the water layer by filtration. Propane is recovered by distillation using vapor compression of the distillate vapor to minimise the heat requirement. The CFS system has been designated by the EPA as the best demonstrated available technology (BDAT) for treating refinery wastes (Long 1995).

2.8 Heavy metals chemistry

"Heavy metals" also known as trace metals, is a collective term applying to the group of metals and metalloids with an atomic density greater than 6 g/cm. It is a loosely defined term which is widely recognised and is usually applied to the elements such as cadmium, chromium, copper, mercury, nickel, lead and zinc. These metals are commonly associated with pollution and toxicity problems (Alloway and Ayres 1993).

Heavy metals are divided into two classes: essential and non-essential to life. Essential elements follow the general trend that an undersupply to an organism leads to deficiency, sufficient supply results in optimum conditions, and oversupply results in toxic effects and possibly death. Non-essential elements can never result in deficiency but at low concentrations can be tolerated by organisms. At higher concentrations they become toxic. In general, all heavy metals are potentially toxic (Smith & Williamson 1986).

The concentrations of heavy metals available to terrestial, aquatic and marine organisms (i.e. their bioavailability) are determined by their solubilization and the release of metals from rock-forming minerals through adsorption and precipitation reactions which occur in soils and sediments (Alloway and Ayres 1993).

2.8.1 Toxic effects of heavy metals

The sensitivity of organisms to metal toxicity varies widely both between and within species of plants and animals. Many factors can modify the response to a toxic dose of metals. Some individuals are genetically adapted to tolerating anomalously high concentrations of certain metals. It is therefore difficult to generalise about toxicity (Alloway and Ayres 1993).

As for the mechanisms of toxicity, the most relevant is certainly the chemical inactivation of enzymes. All divalent transition metals readily react with the amino, imino and sulfhydryl groups of proteins. Some of them (e.g. Cd, Hg) may compete with essential elements such as zinc and displace it in metalloenzymes. Some metals may also damage cells by acting as antimetabolites or by forming precipitates or chelates with essential metabolites (Forstner 1995).

2.8.2 Fate of heavy metals in soils

Soil reaction is the primary factor controlling the chemical behaviour of metals and other important processes in the soil. The chemical equilibria of soil can be characterised by dissolution, diffussion, sorption and precipitation of metals. Depending on the variability in the physical and chemical characteristics of metals, affinity to soil components govern speciation. Soluble, exchangeable and chelated species of heavy metals are most mobile in soils and this governs their migration and phytoavailability. The behavior reflected in their speciation depends greatly upon the ionic form as well as the soil conditions. The main soil variables involved in the metal status are pH, organic matter, hydrous oxides, clays, carbonates and salt contents (Kabata-Pendias 1995).

Solid species tend to be less mobile than colloidal or dissolved forms. Labile complexes are in equilibrium with their local environment while inert complexes are not. The identification of such classes of metal species can have great implications in the understanding of the behaviour of heavy metals in natural and polluted systems (Bourg 1995).

The most important chemical processes affecting the behaviour of metals in soils are those concerned with the adsorption of metals from the liquid phase onto the solid phase. Several mechanisms are involved in the adsorption of metal ions. These include cation exchange (or non-specific adsorption), specific adsorption, organic complexation and co-precipitation. Although, the extent of adsorption can be measured and isotherms calculated, (described by either the Langmuir or the Freundlich adsorption isotherm equations) it is frequently difficult to be precise about which particular process is responsible for the retention of metals in any particular soil. In general, heavy metals cations are most mobile under acidic conditions (Alloway 1990).

This explains the high removal efficiency of heavy metals under decreasing pH levels conducted by Tuin and Tels (1990) using 1 N hydrochloric acid on a contaminated clay soil.

Selectivity of clay, mineral and hydrous oxide adsorbents in soils and sediments for divalent metals generally follows the order Pb > Cu > Zn > Ni > Cd. However, some differences occur between minerals and with varying pH conditions (Alloway and Ayres 1993).

2.8.3 Fate of heavy metals in receiving water

In aquatic environments, heavy metals are either dissolved (dissociated) or particulate. The sediment fractions that may interact with toxic metal compounds are where precipitated metals reside and include fine and organic particulate. Solids clay and organic particulates have a high sorptive capacity for many chemicals and act as the contaminant transport medium in aquatic system (Evans 1989).

The solubility of metal ions in solution will depend on the concentration of anions and chelating ligands present in the water, its pH, redox status and the presence of adsorbent sediments (Alloway and Ayres 1993).

Dissolved metal ions can form a wide variety of complexes. In heterogeneous systems the chemistry of metals is further complicated by adsorption onto sediments (suspended or bottom), colloids, plant materials and also by the formation of co-polymers (Smith and Williamson 1986).

Although the chemistry of metals in natural waters is very complex, it is possible to derive some broad generalisations, such as that the pH level of the water plays a vital role on the speciation of metals. In essence, speciation of metals is determined by the environment and changes in speciation are responses to alterations (Moore and Ramamoorthy 1984).

2.8.4 Heavy metals in crude oil (hydrocarbons)

Many heavy metals are found in crude oil. Some of the more abundant are nickel, vanadium and iron. They are present in the form of organometallic compounds, such as those of nickel and vanadium as in porphyrins. Vanadium and nickel are poisons to many catalysts. Most of these heavy metal compounds are concentrated in the heavy residues (Matar and Hatch 1994). Organometallic compounds, which differ from complexes and chelates, are bound to the metal by a carbon-metal bond (Manahan 1990).

The relative amounts of usable fractions obtained from crude oil do not coincide with commercial needs. The qualities of the fractions obtained directly by distillation of the crude oil seldom meet the required specifications for various applications. Each fraction must be upgraded in the petroleum refinery to meet the requirements for its end-use application. Major hydrocarbon refining and conversion processes include cracking, dehydrogenation (reforming), alkylation, isomerization, addition, substitution, oxidation-oxygenation, metathesis, oligomerization and polymerization (Olah and Molnar 1995).

Some of these processes can not be performed without using some of the heavy metals as catalysts in the process. The catalysts that are able to perform these reactions are metal oxides (molybdena, chromia and alumina), noble metals and zeolites. Many metals (nickel, palladium and platinum) have long been known to catalyze the dehydrogenation of cyclohexane to benzene. Platinum on charcoal was the first catalyst known to bring about skeletal isomerization of saturated hydrocarbons. The process observed is the transformation of butyl and pentylcyclopentanes to the corresponding alkylarenes that must involve C_5-C_6 ring enlargement.

Besides platinum, other metals (Pd, Ir, Ru, Au) also exhibit some although substantially lower activity. The main transformation using these metals is hydrocracking. The possible isomeration reactions are chain branching, substituent migration and C_5-C_6 ring interconversion. These transformations usually take place in the presence of hydrogen and they are often called hydroisomerizations. Several mechanisms were proposed to interpret the bond shift isomerization, each associated with some unique feature of the reacting alkane or the metal. Metals differ in their ability to catalyze isomerations. (Olah and Molnar 1995).

Hydrocarbons with suitably acidic (allylic, propargylic and acetylenic) hydrogens can be transformed to organometallic derivatives, which can then react with alkylating agents to yield alkylated products. This process is called alkylation through organometallics. The reactivity of different hydrogens to participate in metalation decreases in the order primary > secondary > tertiary. Alkalai metal alkyls, particularly n-butyl lithium, are the reagents most frequently used to form metalated intermediates (Olah and Molnar 1995).

2.9 Extraction of heavy metals

Decontamination of soil polluted with heavy metals in the environment is a worldwide problem. The extent of this problem has only been felt recently and a great effort has to be made to arrest these problems. Extractions of these metals make use of the specific differences between the properties of contaminants or contaminated particles and the properties of the environment where the metal resides. Several factors have to be considered, such as type and concentration of the contaminants, physical state of contaminants and their interactions with the environment (Rulkens *et al.* 1995).

There are several ways that heavy metals can be extracted. A number of reagents, including acids, bases, salts, and complexing agents, may be useful in extracting metals. Sequential chemical-extraction techniques, when applied to determine the metal distribution in wastewater sludge was, found to be of greater value than techniques based on a single extractant (Stover *et al.* 1976). Although more time consuming, sequential chemical-extractions provide detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of heavy metals (Tessier *et al.* 1979).

Techniques for removing metals from soil generally involve contacting the soil with an aqueous solution. Metal contamination is generally found on the finer solid particles since metals are often preferentially bond to clays and humic materials. Thus, separating out the finely-divided material may substantially reduce the heavy metal content of the bulk soil (Peters and Shem 1995). Separating out the fines from the course fraction removed 90% of the metals but only 30% of the total dredged material on a study of a contaminated soil (Werther *et al.* 1986).

Solid/liquid separation processes represent a preliminary step in the remediation of contaminated soil. However, metals are still bound to a solid phase in a much more concentrated form (Peters and Shem 1995) and therefore a special aqueous solution is needed for extraction, depending on the physical and chemical state of the metals.

Extraction of heavy metals from the contaminated soil can be performed either using in situ techniques or on-site extraction. For in situ extraction, the aqueous extractant is allowed to percolate through the soil to promote metal mobilization. On site extraction following excavation can be performed either batchwise, semi-batchwise or continuous. The soil is first pre-treated for size reduction and classification. The contaminated soil is then contacted with the extractant and the soil is separated from the spent extractant. The eluant is further recycled to decomplex and precipitate the metals from solution. Alternatively it is treated using electrodeposition techniques to recover the metals (Peters and Shem 1995).

Tessier *et al.* (1979) identified 5 fractions/phases in soil where heavy metals are likely to reside and be affected by their environmental conditions. These fractions/phases are; exchangeable, bound to carbonates, reducible, bound to organic matter and the residual fractions/phases. Therefore, knowing the possible state or form of the metals present in the soil is very crucial in determining what type of extractant will be used.

From the application point of view, the type and concentration of an extractant (complexing ligands) and the system pH are the operational parameters that can be controlled (Peters and Shem 1995).

Several methods used for the industrial scale reduction in heavy metals are discussed below.

2.9.1 Simple aqueous extraction

The removal of heavy metals using water has been employed to investigate the occurrence of water-soluble heavy metals in sewage sludges (Lake *et al.* 1984). Water-soluble forms comprise metals which exist in ionic, molecular or colloidal form in the sludge-solution phase (Mathews 1984). However, Bloomfield and Pruden (1975) suggested that solubility reduction of metals following successive percolation with distilled water was attributed to the development of anaerobic conditions.

Extraction of heavy metals from an air-dried digested sewage sludge with tap water resulted in <1% of lead and aproximately 2% of copper being leached, while up to 11% of cadmium and 36% of zinc were water soluble (Lagerwerff *et al.* 1976).

Considerable variations in metal solubility have been reported from different sludges because of the differences in properties (Lake 1987).

2.9.2 Chloride/acetate extraction

Chloride/acetate solutions have been used to extract exchangeable forms of metals from sediments and soils (Gibson and Farmer 1986; Tessier *et al.* 1979 and Mingot *et al.* 1995). The mechanism of extraction involves displacement of metals loosely held on negatively charged exchange sites by calcium, barium, magnesium or sodium ions which saturate these sites (Lake 1987). These solutions have been employed to liberate exchangeable metals in the soil or sediment.

McLaren and Crawford (1973) prefered calcium chloride ($CaCl_2$) than the frequently used ammonium acetate (NH_4OAc) for extracting exchangeable cations from soil, because it has less effect on the natural pH and extracts less organic matter. Tessier *et al.* (1979) found that $MgCl_2$ treatment does not affect silicates, sulfides and organic matter.

2.9.3 Acid extraction

Extraction techniques based on acidification have been applied to sludges and sludge soil matrices (Lake 1987). The extraction process is based on leaching of heavy metals from soil particles, or the complete dissolution of heavy metals.

During leaching with acids, low pH values have to be applied for the efficient removal of most heavy metals. This requires special materials in order to prevent corrosion of equipment (Rulkens *et al.* 1995).

Tuin and Tels (1990) found that between 80% and 90% of cadmium, copper, lead and zinc could be extracted from a contaminated clay soil with repeated batchwise extractions with 0.1N hydrochloric acid or a single extraction with 2N hydrochloric acid. Nickel extraction percentages varied between 45% and 80%. An acid concentration above 0.1N HCl was necessary to clean the contaminated clay soil to a level that met the maximum tolerable metal levels.

Mingot *et al.* (1995) conducted a sequential extraction of copper, chromium, nickel, lead and zinc from an urban sewage sludge with different types of acids (HCl, HNO_3 and H_2SO_4, at pH 1.5). They found that acid treatment can mobilize part of the cation content of all fractions including the residual fractions. The reductions of the two most labile fractions were great. The extraction efficiency sequence of the different acids have the following general trend: Cr : $H_2SO_4 = HNO_3 > HCl$; Cu : $HNO_3 > HCl = H_2SO_4$; Zn : $HCl > H_2SO_4 = HNO_3$; Pb : $HNO_3 > HCl = H_2SO_4$; Ni : $H_2SO_4 > HNO_3 = HCl$.

The liquid to solids ratio (extractant to clay weight ratio, L/S) influences the removal efficiency of nickel and copper when hydrochloric acid is used as extractant, although the effect is much less than the pH (Tuin and Tels 1990).

Sreekrishnan and Tyagi (1994) found that acid requirement, expressed in grams H_2SO_4 per gram of dry sludge, is not a constant even for the same sludge type, but rather depends on the sludge solids concentration when H_2SO_4 was applied to sewage sludges. Although extractions were highly dependent on pH, the acid requirement per unit dry weight of sludge was related to the sludge solids concentration. It was further reported that acid requirement per unit dry weight of sludge decreased as the concentration of solids increased. Though higher concentration of sludge solids is beneficial to reduce the acid consumption, thicker sludge can result in lower efficiency of mixing or the need for more power for the mixing (Sreekrishnan and Tyagi 1994).

Tuin and Tels (1991) tested extraction of heavy metals on a laboratory scale using a stirred tank reactors (CSTR) and countercurrent processes with 0.2-0.3M hydrochloric acid solutions in an attempt to develop a continuous treatment process. The countercurrent process gave greater efficiencies than CSTR but the difference was only small. It was suggested that the residence time required for CSTR could be short (15-30 minutes) while it should be as long as possible in the column. Thus a combination of the two seemed to be promising. An extraction in a stirred tank followed by a second extraction in a countercurrent column was trialed. However, it was suggested that the most powerful tool to get the necessary greater extraction efficiencies seemed to be the use of stronger acid solutions. Since complete neutralization of the hydrochloric acid solution did not occur after one single treatment, there was a possibility of recycling the extractant, which would reduce the cost of chemicals used in the process.

2.9.4 Chelation/complexation extraction

Extraction based on chelation involves the coordination ot two or more donor atoms present in the chelating ligand to the same metal ions in such a way as to form a heterocyclic ring termed a chelate. Ethylenediaminetetraacetic acid (EDTA), for example, is a sexadentate ligand (see Figure 2.3) (ie, contains six donors atoms capable of coordination into a single metal ion) which forms five chelate rings when all donor atoms are coordinated to a metal (Lake, 1987).

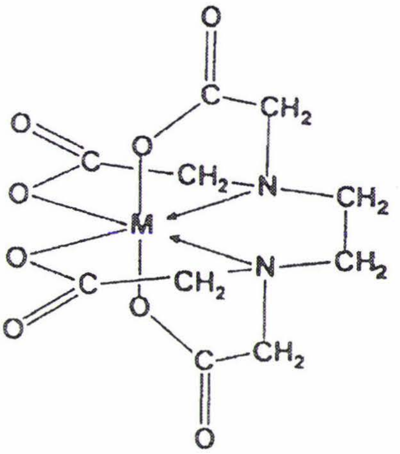


Figure 2.3 – Chelation of a metal ion (M) by EDTA (Lake 1987).

The major effect of complexation is the dramatic increase in solubility of heavy metal ions, especially for strong complexing agents such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) (Peters and Ku 1987).

The ability of chelating agents to form stable metal complexes makes these materials such as EDTA and NTA (nitrilotriacetic acid) an extractant for treatment of heavy metal-polluted soils (Wagner 1989). Although complexation is the major mechanism responsible for the metal solubilization, the overall release process depends on the proton concentration and the system's ionic strength (Elliot and Peters 1995).

The release of cadium, chromium, copper, lead and nickel from a contaminated soil sample using EDTA alone and EDTA followed by hydroxylamine hydrochloride at pH 6 to reduce iron oxides in the soil has been observed. The use of EDTA alone removed over 90% of the lead and cadmium. Chromium removal was approximately 25% and lead removal was strongly pH insensitive (Peters and Shem 1995).

EDTA forms very stable complexes in aqueous solutions and it offers good possibilities to be recuperated and recycled (Tuin and Tels 1990).

White (1997) used Na_2-EDTA in removing the heavy metals for NZRC oil sludge. Reduction was not successful with an approximate removal of only 10% of the heavy metals content. The reduction is not enough to lower the heavy metals content to a level suitable for land application. Poor extraction was due to oil coatings around the sand particles which prevented the metal ions to be mobilised by Na_2-EDTA solution. It was suggested that the use of EDTA with the addition of a surfactant might improve the removal efficiency.

2.9.5 Surfactant enhanced extraction

The role of surfactants in the remediation of subsurface metal contamination is less well understood. Extraction of chromium from chromate-contaminated subsurface environments using batch experiments demonstrated that surfactant used alone enhanced the extraction of chromate 2.0 – 2.5 times greater than water. When a complexing agent, diphenyl carbazide, was solubilized by aqueous micelles, the system was able to enhance the chromate elution by 9.3 to 12 times greater than water (or 3.7 – 5.7 times greater than surfactant without the complexing agent). Column studies of this showed that when surfactants were used along with the complexing agent, 213 % of Cr (VI) can be removed compared to deionized water in less than 20 pore volumes, whereas deionized water took 35 pore volumes to reach the baseline removal (Nivas *et al.* 1996).

Hayes *et al.* (1995) conducted a study on the effect of Quarternary Ammonium Surfactant on sorption of Cu (II) and Sr (II) onto soil, which has three soil constituents (quartz, kaolinite and montmorillonite). Quarternary Ammonium Compounds (QACs) are a class of cationic surfactants. Once introduced into soil environments, it may cause sorbed cationic metal ions to be released to the soil solution. The result of the study was that QACs did not have much of an effect on trace metal ion mobilization, particular on strongly bonding cations like Co (II) for soils that have their reactivity dominated by surface hydroxyle site bearing minerals. In the case of Sr (II), desorption of metal ions was possible for clay minerals like kaolinite or montmorillonite. The amount of desorption and trends with pH, depended on the relative amount of metal ion sorbed to these site types and the metal cation type.

The effect of water soluble surfactants on the uptake of copper, zinc, cadmium, or lead ions by three types of clay (kaolinite, illite and a montmorillonite) over the pH range of 3 – 10 was studied by Beveridge and Pickering (1983). Results of this study showed that charged surfactants influenced the phase distribution process when present at low concentrations (< 0.005 % W/V) but much higher levels of nonionic species (> 0.1 % W/V) were required to produce observable effects. The cationic surfactants reduced metal ion uptake in montmorillonite suspensions by competing for surface sites, but with illite and kaolinite, the added organic cations had much smaller effects on the equilibrium position. The addition of anionic surfactants led to increased metal losses from solution. This was the case, particularly in the presence of an alkyl benzene sulphonate and precipitation of sparingly soluble metal-surfactant species was considered as the controlling process.

Woller *et al.* (1996) showed that technical oil-soluble surfactants with complexing properties were able to lower the content of simultaneously present heavy metals by approximately two or three orders of magnitude, starting at 10 – 100 mg/l by applying commercially available quinolines (such as LIX 26) and oximes (such as LIX 84). These oil-soluble surfactants were used as extractants for heavy metals treating real landfill leachates without any pretreatment. The experiments were carried out successfully in a countercurrent mixer-settler. The importance of the result is a possible application for extraction process even in cases with extremely unfavourable electrolyte conditions. For as long as the right conditions are met, it is possible to extract the heavy metals nonselectively from wastewater down to a concentration of micrograms per litre.

2.9.6 Membrane separation

There are several types of membranes used for metal separations: electrodialysis, reverse osmosis, donnan membrane, ultrafiltration and several kinds of special liquid membranes (Brooks 1991). The process of separation is through filtration by a membrane that will separate soluble from insoluble species based on the commonly accepted size definition. These membrane-based separation processes are attracting considerable attention in recent years due to their potential for low capital cost and energy efficiency. Ultrafiltration and reverse osmosis have demonstrated industrial utility (Borwankar *et al.* 1987).

Membrane separation processes are most appropriate for dilute solutions such as rinse waters. Most membranes are mechanically fragile and vulnerable to degradation by corrosive and strongly oxidative systems such as concentrated chromic acid. Separation efficiency also requires elimination of insolubles and suspended solids which block the membrane surfaces (Brooks 1991).

2.9.7 Biosorption removal

The term biosorption refers to many modes of non-active metal uptake by (microbial) biomass which may even be dead. Metal sequestration by different parts of the cell can occur through complexation, coordination, chelation of metals, ion exchange, adsorption and inorganic microprecipitation. Any one or a combination of these metal-binding mechanisms may be functional to various degrees in immobilizing one or more metallic species on the biosorbent. Metallic cations are attracted to negatively charged sites at the surface of the cell. The (bio) sorptive metal uptake can be quantitatively evaluated from experimental biosorption equilibrium isotherms similar to those used for the performance evaluation of activated carbons (Volesky 1990).

Cells of algae, fungi and bacteria exhibit higher sortive capacities for different metal ions in aqueous solutions. This phenomenon has been well documented for both living and non-living cells (Greene *et al.* 1987).

2.9.8 Electrowinning

Electrowinning is a mature technology and has been used extensively for separation and recovery of metals from solutions. A wide variety of waste systems ranging from the heap leachates of extractive hydrometallurgy, mine leachate, plating wastes, sludges and others have been applied using this process (Brooks 1991). Separation of heavy metals is based on the electrokinetic phenomena using electric current through an electrode. These phenomena, despite the applied potential, includes adsorption, complexation, precipitation, acid-base reactions and diffusion of metals from solution.

2.10 Conclusions

Based on the literature, there are several ways to extract oil and heavy metals from soils, leacheates and sludges which can be used for NZRC oil sludge. Each method has a specific application depending on the type of waste or soil to be treated or remediated. However, because NZRC sludge is an emulsified water in oil sludge (W/O), pre-treatment is necessary in breaking the emulsion before stabilisation can be made. The presence of crude oil makes the extraction of heavy metals more difficult. Thus, there is a need to address this problem first before the extraction of the heavy metals can be attempted.

Theoretically, centrifugation is a potential pre-treatment for oily sludges. However, for industrial application, this process is not feasible due to the volume of sludge to be treated and the tendency to form oil/water emulsions at higher speed which have been found even more difficult to address.

Though pressure filtration, drying and the addition of demulsifying agent have been extensively used in the pre-treatment of refinery sludge, these processes are only effective for sludge volume reduction (dewatering) and do not totally break the emulsified NZRC sludge.

Solvent extraction offers a promising solution for the breakdown of the component of the sludge. The availability of a complete commercial extraction systems makes this process suitable for emulsion breaking. Once the right solvent has been found, oil removal can therefore be achieved.

Once the crude oil is removed from the sludge through the breaking of emulsion, there are several potential methods that can be applied for metal extraction as outlined in Section 2.9.

The simple aqueous extraction used to remove metals from sewerage sludges, can not be applied to NZRC oil sludge. In general, the solubility of metal ions in water is also very limited for the majority of the metals present in the sludge.

The use of chloride/acetate solutions for the extraction of heavy metals from the NZRC sludge is not a suitable reagent since most of the metal ions are in the organic and residual fractions of the sludge's inorganic matter. These types of extractants are only effective if the metal ions are in the exchangeable and carbonate fractions.

Membrane separation is a proven technology. However, this method cannot be applied since it is only appropriate for metals in solutions.

Exploitation of the biosorption phenomena of heavy metal extraction has gained a lot of interest in the industrial world today. One of the major advantages in the deployment of biosorbent materials are their low anticipated price and good metal uptake capacities. However, there is still a need to have more technical data and information regarding the assessment of the economics of biosorption process for large-scale applications. The source of biosorbent biomass needs to be secured as a raw material. Metal selectivity and physiocochemical properties of biosorbent materials as well as regenaration techniques are still the focus for demanding scientific investigations of interdisciplinary nature (Volesky 1990).

One of the methods used in electrowinning is electroreclamation. The transport phenomena involved are electro-osmosis, electrophoresis and electrolysis. This is suitable for the removal of heavy metals from soil. Although it has been demonstrated successfully for the removal of heavy metals from clay soils, in practice, treatment cost estimation is high. The use of electrical energy and handling of excavated soils makes this process expensive for treating NZRC oil sludge.

Extraction through chelation/complexation is also a proven method to remove heavy metals from the sludges and soil. However, this method is only effective if the metals to be extracted are solubility limited. The use of chelating agents can cause dramatic increase in solubility of heavy metal ions. Using this method for NZRC sludge does not offer good removal efficiencies due to the nature of the sludge.

Mineral acids have been widely used (Tessier *et al.* 1979; Tuin and Tels 1990; Mingot *et al.* 1995) for the extraction of heavy metals in sludges and soils and have provided the best results. The use of mineral acids offer a good potential extractant to reduce the metal content of the sludge considering the nature of the waste sample. The ability of mineral acids to leach and dissolve heavy metals with high extraction efficiencies makes this a good candidate for the removal of heavy metals in NZRC sludge. However, acid extraction needs large amounts of acid in order to extract the heavy metals in the sludge. The problems of its hazardous nature and non-recovery of concentrated acids makes this method expensive.

To conclude, the best way to break the emulsified sludge is through solvent washing to remove crude oil. The use of mineral acids is a potential extractant for the reduction of heavy metals to a level that would meet the limits set by the Public Health Guidelines (NZ, Dept. of Health 1992).

Chapter 3

Sludge Characterisation

3.1 Introduction

Characterisation of an oily sludge was required before any disposal treatment method could be carried out. This provided the information needed to design and implement an appropriate disposal treatment, which would meet the stringent environmental regulations for oily wastes from oil refineries. In many instances, oil sludge wastes fall under the definition of " hazardous wastes " (Bryant and Moores 1991).

The aim of this characterisation was to identify the major composition of a typical crude oil tank sludge. A second objective was to determine the heavy metals content and its speciation within the sludge. Knowledge of these basic properties then provided a guide for the design of specific disposal treatments that could be applied industrially.

3.2 Sludge source/background

A typical crude oil tank sludge was supplied by New Zealand Refining Company (NZRC) from tank cleaning operations. The visual appearance of the sludge is shown in Figure 3.1. The sludge sample had been de-emulsified to reduce water content. The sludge was taken from the tanks used for southeast asian crudes, which typically have low mercury and sulfur levels. The sediments present in the sludge were likely to have been derived from crude oil wells and corrosion of tank walls.

The NZRC crude oil tank sludge produced is a water in oil emulsion. The sludge contains crude oil and heavy metals (e.g. copper, nickel and zinc) at levels exceeding those set out by Public Health Guidelines (NZ, Dept. of Health 1992) for disposal by land application (Gozan *et al.* 1996 and White 1997).

Figure 3.1 – Photograph of a raw NZRC crude oil tank sludge.

3.3 Overall composition of crude oil tank sludge

The overall sludge composition was determined using a combination of the Dean & Stark and Soxhlet extraction procedures (Whitman *et al.* 1974) to quantify its water, oil and solid fractions. A kerosene washing method was also used to measure the sludge composition. Details of each method and the results obtained are given below.

3.3.1 Dean and Stark/Soxhlet extraction

The entire sludge sample was mixed thoroughly prior to the separation of water, oil and solid fractions using a modified electric drill mixer to achieve homogeneity (USEPA 1992). Pre-treatment mixing of the sludge was found to be essential in obtaining a representative sample for the determination of its composition and at least five replicates were made in obtaining data.

A combination of Dean & Stark and Soxhlet extraction procedures was used to measure the water, oil and sand fractions (see Figure 3.2). A known weight of sample was placed in a paper thimble that was suspended above a refluxing organic solvent (toluene), which is immiscible with water. Upon heating, water in the sample is co-distilled with the solvent vapours and the distillate will form a two – phase mixture of solvent and water. The water from the condensed distillate was continuously separated in a graduated Dean and Stark trap, designed so that the denser water phase collects at the bottom, while the solvent (lighter phase) is recycled back through the thimble. This dissolves the oil present in the sample and carries it to the bottom of the kettle. The solids are retained in the thimble.

The water content was determined directly from the graduated trap and the solids content was determined through air drying at ambient conditions. Drying the solids above ambient temperature caused spontaneous combustion due to the presence of pryoric compounds in the sediment fraction. Because of this effect, a modified drying procedure was used. A thin layer of solids was left at ambient conditions overnight.

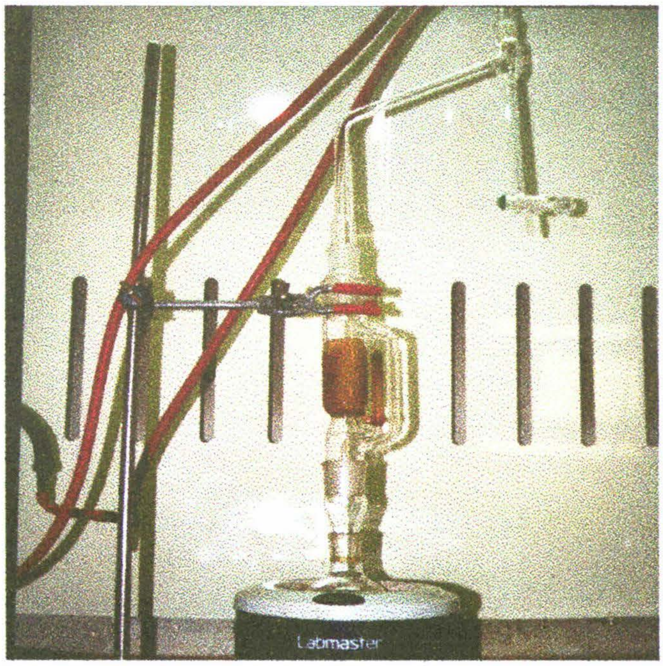


Figure 3.2 – Photograph of combined Dean & Stark/Soxhlet extraction apparatus used.

The oil content was determined by vacuum evaporation, using a rotavator (Buchi model No. R110). The initial water bath temperature of the rotavator was set at a low temperature (between 40-50°C) while stripping the solvent. Once the solvent was largely reduced, the water bath temperature was increased to 70°C for complete toluene removal. After solvent removal, the oil fraction was determined gravimetrically (Pal 1994). Appendix A-1 shows the detailed procedure for the combined Dean & Stark/Soxhlet extraction method used in this work.

Initial results from the analysis showed that the sludge was 25% water, 25% oil and 42% solids. An average of 8% weight loss was noted when mass balances were performed from each fraction. These losses were thought to be due to the presence of a volatile fraction in the sludge that was lost during the extraction process. A simple experiment was designed to prove this.

A known weight of raw sludge in a beaker was exposed in ambient condition for 24 hours. The original weight was decreased by about 7.5% which proved the presence of the volatile fraction in the raw sludge. This volatile fraction could be increased if the raw sludge is completely dried.

Finely divided solids were noticed in the toluene/oil mixture before vacuum evaporation. The calculated oil fraction was therefore the oil plus the fine solids that leaked from the thimble during reflux. The greater the sludge volume used for analysis the more fine solids got washed through. For this reason, a modified Dean & Stark and Soxhlet extraction method was designed in which the solvent was filtered through #1 Whatman filter paper prior to solvent evaporation. Using this method, the oil fraction was found to be 16% of the total sludge.

The presence of finely divided solids in the sludge has an impact on the subsequent design of oil recovery operations. The presence of these solids would require longer settling times or the use of centrifugation to separate them from the solvent during washing operations. For this reason, a kerosene washing method was devised to allow the characterisation of oil and fine/coarse particles in the sludge.

3.3.2 Solvent washing with kerosene

Solvent washing takes advantage of the high solubility, fast dissolution of crude oil and the settling characteristics of the solids of the sludge. Raw sludge was treated with kerosene at solvent to sludge ratio of 2 to 1 at ambient temperature for at least 3 minutes with constant mixing, to dissolve the oil. The solids were allowed to settle and the liquid was decanted. The solids were washed again with fresh solvent and mixed for 1 minute. Three to five seconds after mixing, the liquid was decanted, before any fine solids were able to settle out. This was repeated until no visible suspended solids were found in the solvent.

All the decanted solvent with fine solids were combined and allowed to settle. The clear solvent was decanted off and the resulting fine solid particles were dried at 105°C for 1 hour to remove any entrained solvent. The oil/solvent mixture (from the first washing) and the fine solids were separated by filtration using #1 Whatman filter paper, dried and the solids were determined gravimetrically. Kerosene was chosen because this was used for later solvent washing work. It had the further advantage that the kerosene washed solids did not ignite when dried at 105°C.

A fine/coarse solid ratio of 0.52 was found after solvent washing. This corresponds to 14% fine and 27% coarse solids in the original sludge.

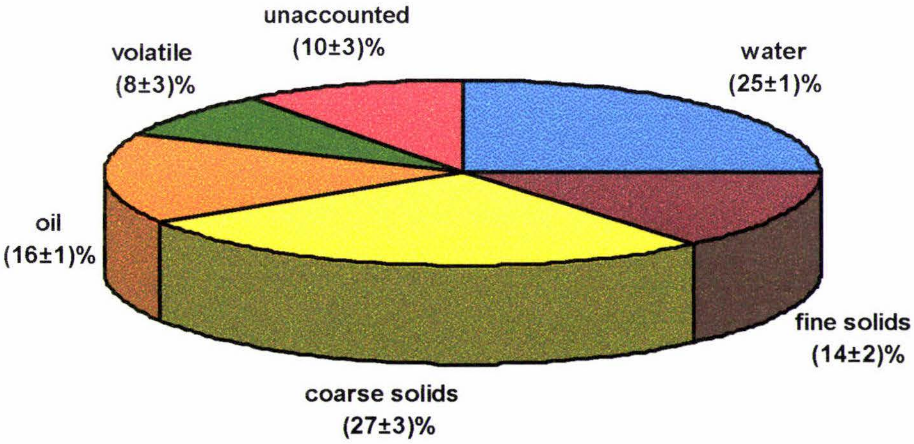


Figure 3.3 – Overall composition of the raw sludge (total basis).

Figure 3.3 shows the overall composition of the sludge after averaging all the data obtained from different methods and eliminating all possible sources of errors. The solid fraction (both fine and coarse) obtained from solvent washing method was used rather than the combined Dean & Stark and Soxhlet extraction method due to problems in drying the solids in the oven at 105°C. The oil and water fractions were calculated using the modified combined Dean & Stark and Soxhlet extraction method. The volatile fraction was 8%. 10% of the raw sludge was unaccounted for when mass balances were performed. This includes any experimental errors that had been encountered in the analysis. Table 3.1 shows the overall sludge composition expressed on a dry basis.

Water $g_{water}/(g_{oil}+g_{sand})$	Sand $g_{sand}/(g_{oil}+g_{sand})$	Oil $g_{oil}/(g_{oil}+g_{sand})$	Others $g_{others}/(g_{oil}+g_{sand})$
0.44	0.72	0.28	0.32

Table 3.1 – Composition of NZRC crude oil tank sludge (dry basis).

Table 3.2 shows the comparative analysis obtained from this work and the previous studies made for the crude oil tank sludge from different storage tanks. These results show that the composition of the sludge in the different batches varies greatly. This can be seen by the variation of water fractions. The solids and oil fraction obtained from this study can not be compared with Gozan *et al.* (1996) and White (1997) because of the discrepancy in the methods in obtaining these fractions. The presence of fine solids in the oil fraction after extraction and the volatile components were not considered by the previous studies.

Composition, (% wt.) (kg/total raw sludge)	This Study (Tank – 04)	Gozan *et al* (1996) (Tank – 03)	White (1997) (Tank – 09)
oil	16 %	44 %	35 %
water	25 %	16 %	52 %
solids	41 %	43 %	13 %
volatile matter	8 %	no data	no data
unaccounted	10 %	no data	13 %

Table 3.2 – A comparative NZRC crude oil tank sludge analysis.

3.4 Sludge density measurement

The physical characteristics of the sludge before and after treatment were necessary information for future handling and design purposes. Measurements of the bulk and particle density were conducted, to determine the mass and volume reduction achieved by the proposed treatment operations.

Bulk density (δ_b) is the ratio of bulk mass (W_b) and the volume occupied by the sludge (V_b). It was measured by filling a known volume of a pre-weighed container with raw sludge and the weight was measured. The bulk density of the sludge was determined using Equation (3.1) below. Care was taken to ensure no air was trapped in the volumetric cylinder used for the measurement. This method was used to determine the bulk density of the raw sludge and the solids fraction after Dean & Stark/Soxhlet extraction. The average bulk density of the well-mixed raw sludge and the solids fraction is 1,259 kg/m^3 and 1,167 kg/m^3, respectively.

$$\delta_b = \frac{W_b}{V_b} \tag{3.1}$$

Particle density (δ_p) is related to the specific particle and is dependent on the chemical and physical properties of the material. It was measured using the displacement method. A known weight (W_p) of washed solids was placed in a graduated cylinder with a known volume (V_k) of kerosene at ambient temperature. The final volume (V_f) was measured and used to calculate the particle density of the washed solids using Equation (3.2) shown below. This method was used to quantify the particle density of sand fraction after water and oil removal. The average particle density of the resulting washed solids was 2,333 kg/m^3.

$$\delta_p = \frac{W_p}{(V_f - V_k)} \tag{3.2}$$

3.5 Heavy metal levels in crude oil tank sludge

Different heavy metals had been previously identified in the sludge. This has been outlined in Section 2.3. The speciated ions of these metals in the different fractions of the sludge had also been determined. White (1997) had identified that approximately 94% of copper, 77% of nickel and 78% of zinc resided in the sand fraction of the sludge. Approximately 85% of the total metals resided in the solids fraction.

The aim of this section was to measure the heavy metals in the water, oil, fine and coarse solids fractions and the total sludge to determine how they were distributed within the sludge.

3.5.1 Heavy metals analysed

Although several heavy metals were identified in the previous studies (Gozan *et al* 1996), the heavy metals being measured in this study were limited to copper, nickel and zinc since these were identified at significant levels. NZRC sludge was also found to contain mercury. However, a lack of laboratory equipment and its volatile nature prevented analysis of this element. Heavy metal analysis from each fraction (water, oil and sand) and the raw sludge were determined using an Atomic Absorption Spectrophotometer (AAS) (Model no. GBC 933AA) as shown in Figure 3.4. Prior to any metal analysis being done, collection and pre-treatment of the samples were performed to avoid possible errors (Gorsuch 1970; USEPA 1992; Stoeppler 1992; Tschopel 1992). Standardization and calibration of the instrument were also performed to ensure precision of results (GBC Scientific Equipment Ltd. 1993). The specific details are outlined below.

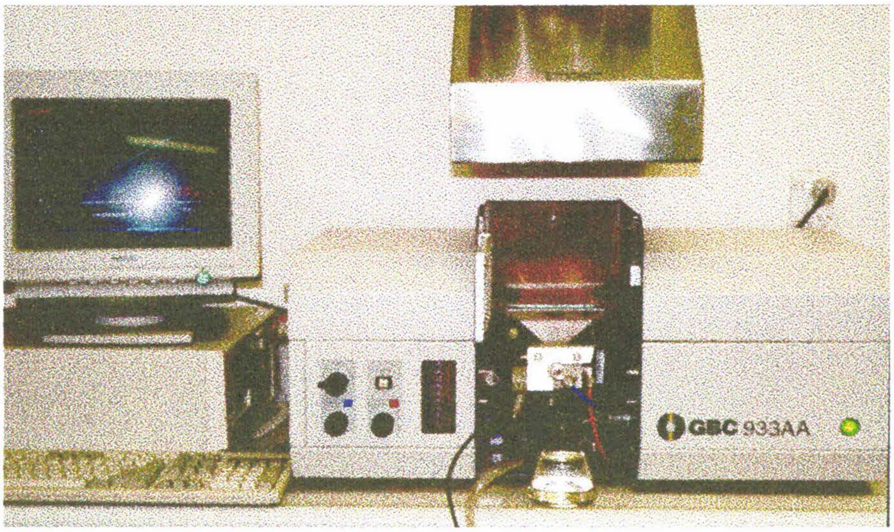


Figure 3.4 – Photograph of the atomic absorption spectrophotometer (AAS) (Model no.GBC 933AA).

3.5.2 Sample collection and preparation

In order to accurately measure the heavy metal levels in each fraction it was important to separate the sludge in a way that did not change the distribution of heavy metals in the sludge. Several methods were considered for obtaining samples of each fraction. Solids and oil fractions separated using the modified Dean and Stark/Soxhlet extraction method were used as sampling materials. Solids, both fine and coarse, obtained from solvent washing method were also used for heavy metal analysis. For the water fraction, a centrifugation method was carried out because the water fraction derived from the combined Dean & Stark/Soxhlet extraction method contains no heavy metal brought about by the distillation effect. All components derived from this method were analysed for heavy metals.

Centrifugation is a commonly used laboratory technique for the determination of water and oil contents of emulsions. Both oil/water and water/oil emulsions, with or without solids, can be analysed over a wide range of water concentrations (Pal 1994).

A known weight of sample of raw sludge, between 50-100g, was added to a centrifuge tube in which centrifugation was carried out at 5000rpm – 6000rpm for at least 20 minutes. When separation of the three components (water, oil and sand) had occurred, each fraction was recovered for heavy metal analysis. The water was immediately acidified to pH < 2 with (1 part concentrated acid + 1 part distilled water) nitric acid for sample stability by preventing adsorption of heavy metals into the walls of the vessel. This was particularly important for diluted concentrations (Gorsuch 1970 and USEPA 1992). This centrifugation was repeated with more raw sludge until a considerable amount of water sample (at least 400ml) was obtained for analysis.

3.5.2.1 Solids fraction

Solids samples were obtained from the modified Dean & Stark/Soxhlet extraction, centrifugation and solvent washing procedures and were treated separately for heavy metal analysis. Total solids obtained from each method were mixed thoroughly to achieve homogeneity before any sampling was made. Solid samples from the centrifugation and solvent washing methods were dried at 105°C for 1 hour prior to sampling and analysis. Solid samples from the modified Dean & Stark/Soxhlet extraction method were only air dried overnight at ambient conditions, due to ignition problems caused by the presence of pryoric compounds. All samples were stored at 4°C prior to analysis.

3.5.2.2 Oil fraction

Oil fractions were obtained from the modified Dean & Stark/Soxhlet extraction and the centrifugation method. The oil fractions obtained from each batch were combined and mixed thoroughly to achieve homogeneity and then dried at 105°C for 1 hour prior to any sampling and analysis. The samples were stored at 4°C.

3.5.2.3 Water fraction

All acidified water fractions recovered from each centrifugation batch were combined and mixed thoroughly to achieve homogeneity prior to any sampling and analysis being made. The sample was stored at 4°C.

3.5.3 Heavy metal analysis

A multistage procedure was used for the determination of heavy metal levels in the solid and oil samples. The procedure included pretreatment, destruction of organic matter in the sample, dilution of the elements of interest to a suitable analysis range and the determination of the analytes (Tschopel 1992).

3.5.3.1 Dry ashing technique

The dry ashing technique was used for the destruction of oils and other organic compounds present in the sample, to minimise any interference in the analysis of heavy metals (Gorsuch 1970). Except for the water sample, all samples were dry ashed. This involved the evaporation of moisture, volatile materials and progressive oxidation of the non-volatile residue, until all organic matter was destroyed.

About 1-2 g of sample was placed into a crucible made of silica. The sample was charred periodically using a bunsen burner. The crucible was then placed in a muffle furnace overnight at 450-500°C to ensure total destruction of any organic matter in the sample. The solubilisation of the metals in the ashed sample was achieved using the acid digestion technique described below.

3.5.3.2 Acid digestion

A mixture of nitric and hydrochloric acid (USEPA 1992) was used to ensure total mineralisation of organic material and conversion of inorganic material (residues from dry ashing) into completely soluble compounds (Tschopel 1992).

The residue obtained from the dry ashing technique was transferred to a beaker and 4ml of 8N nitric acid and 10ml of 2.4N hydrochloric acid were added. The crucible was rinsed with the same amount of acid mixture and this was also added into the beaker. The mixture was heated under reflux at a temperature approximately but not higher than 85°C for 30 minutes by covering the beaker with a watch glass. Care was taken to avoid vigorous boiling to prevent the loss of hydrochloric acid – azeotrope. The sample was allowed to cool and was then quantitatively transferred to a 100-ml volumetric flask and diluted to an appropriate level with distilled water (USEPA 1992). The sample was analysed for heavy metals of interest. Further dilution was applied if the resulting aqueous sample solution was out of range to allow optimal determination (Tschopel 1992).

3.5.3.3 Preparation of water samples

The water fraction derived through centrifugation was the only sample tested for heavy metals. This is because water from the Dean & Stark method contains no heavy metals due to it being distilled from the sludge sample. The acid preserved water sample was directly digested using a slightly different procedure than used for the solid and oil samples (USEPA 1992). 50-ml aliquot of sample was transferred into a 250-ml beaker. 1ml of concentrated nitric acid and 0.5ml of concentrated hydrochloric acid were then added. The sample was heated on a hot plate at 85°C until the volume had been reduced to approximately 10ml. Care was taken to ensure that the sample did not boil. After reaching the 10ml volume, the beaker was covered with a watch glass and allowed to reflux for 30 minutes. The sample was allowed to cool and quantitatively transferred to a 100ml volumetric flask and diluted to an appropriate level with distilled water. The sample was then allowed to stand overnight at 4°C to separate insoluble material (USEPA 1992) before the metal analysis was performed.

3.5.3.4 Standard preparation, calibration and measurement

At least three standard solutions and a blank were freshly prepared for each metal analysis, to calibrate the Atomic Absorption Spectrophotometer (AAS) (Model No. GBC 933AA). The calibration standards used were 1.000, 2.000, 3.000, 4.000 and 5.000 mg/l for copper; 2.000, 4.000, 6.000 and 8.000 mg/l for nickel; 0.500, 1.000 and 1.500 mg/l for zinc as suggested by the manufacturer of the instrument (GBC Scientific Equipment Ltd. 1993). These calibration standards were used prior to metal analysis to ensure precision of measurements.

The calibration was performed using the blank solution to zero the instrument. The calibration standards for each metal of interest were then analysed with the lowest concentration first. The absorbance was plotted against the concentration through an on-line computer, to produce a typical calibration curve. Unknown samples were then analysed to determine the concentration based on the calibration curve. If the unknown sample did not fall within the range of the calibration standards, pre-concentration or dilution of the sample was necessary to obtain precision results.

Glass and plastic apparatus were only used to avoid possible contamination. All reusable labwares were thoroughly washed with laboratory-grade detergent and tap water. The labwares were then rinsed with tap water and soaked overnight in a mixture of dilute nitric and hydrochloric acids (1 part concentrated nitric + 2 parts concentrated hydrochloric + 9 parts distilled water) (USEPA 1992). This was followed by rinsing with distilled water and oven drying at 35°C.

3.5.4 Heavy metal levels

The samples analysed in this work allowed the characterisation of heavy metals in the whole sludge and the components that make up the sludge. These results are discussed below.

3.5.4.1 Total sludge analysis

Results for total sludge (raw sludge) analysis showed an average concentration of 1,681 mg/kg, 180 mg/kg and 6,066 mg/kg for copper, nickel and zinc, respectively. The results of this study are summarised with those of Gozan *et al.* (1996) and White (1997) in Table 3.3. The results in this study are higher compared with the average metal levels obtained by Gozan *et al.* (1996) and White (1997) working with the same type of sludge. The reason for this difference is likely to be the heterogeneity of the sludge samples and the different crude oil tanks that the sludge was sourced from at the New Zealand Refining Company.

Metal (mg/kg raw sludge)	This Study	Gozan, (1996)	White, (1997)
copper	1,681	957	495
nickel	181	101	144
zinc	6,066	1,716	1,463

Table 3.3 – Comparative metal levels in raw NZRC crude oil tank sludge.

3.5.4.2 Solids fraction

Solids from different separation methods were analysed and it was found that the bulk of the heavy metals in the raw sludge were in the sand fraction. These findings conform to literature on soil chemistry which have found that heavy metals reside in the sand, rather than in oil or water (White 1997; Peters and Shem 1995; Alloway 1990; Evans 1989 and Tessier *et al.* 1979). Several different mechanisms can be involved in the absorption of metal ions into the soil, including cation exchange, specific adsorption, organic complexation and co-precipitation (Alloway 1990).

Metal (mg/kg dry solids)	Centrifuged solids	Dean & Stark solids	Washed Solids		
			Combined fractions	Coarse fraction	Fine fraction
copper	2,142	2,699	3,817	2,845	1,677
nickel	219	493	374	300	326
zinc	6,055	11,478	10,035	10,587	10,914

Table 3.4 – Heavy metals in the solids derived using different separation method.

Table 3.4 shows a comparative analysis of the metal levels in solids obtained by the different separation methods. The concentration of heavy metals in the centrifuged solids was lower compared with the results obtained from kerosene washed and combined Dean & Stark/Soxhlet derived solids. The presence of significant oil in the centrifuged solids was the cause of this difference. Except for copper, the metal levels of both the fine and coarse solids were similar. The copper concentration in the fine solids was 46% lower than observed in kerosene washed and combined Dean & Stark/Soxhlet derived solids samples.

3.5.4.3 Oil fraction

The oil fractions from the centrifugation method and oil (filtered and unfiltered) from the combined Dean & Stark/Soxhlet separation method, were analysed for metal concentrations. Table 3.5 shows the average metal levels in the oil fractions obtained from different methods of separation. Metal levels in oil fractions derived from the combined Dean & Stark/Soxhlet and centrifugation separations were similar except for copper. The metal levels in unfiltered oil fraction were generally high compared to the filtered and centrifuged oil fractions. The anomaly between the filtered and unfiltered oil fractions was caused by the presence of fine solids in the unfiltered oil fraction. These fine solids contain high metal levels as discussed in Section 3.5.4.2, which indicates that the metals in the unfiltered oil fraction were actually the fine particles. This explains the lower metal levels speciated in the solids fraction (85%) reported by White (1997) as the oil fraction analysed for metal levels was not filtered after separation using the combined Dean & Stark/Soxhlet method. This therefore increases the metal levels present in the oil fraction.

Metal (mg/kg dry oil)	Centrifuged oil	Filtered oil	Unfiltered oil
copper	54	27	133
nickel	34	39	95
zinc	477	520	2,488

Table 3.5 – Metal levels in oil fractions derived using different separation methods.

3.5.4.4 Water fraction

The water phase is the least probable destination of the heavy metals in the sludge. In this case the heavy metal concentrations in the water phase were practically negligible as compared to the concentrations obtained from the solid fraction. Copper, nickel and zinc concentrations were 1mg/kg, 2mg/kg and 15mg/kg of water, respectively. Further consideration of the heavy metals in the water fraction was therefore not necessary.

3.5.4.5 Overall mass balance of heavy metals in sludge

An overall mass balance for copper, nickel and zinc concentrations from each fractions gave total sludge concentrations of these metals at 3,955mg/kg, 443mg/kg and 13,851mg/kg, respectively. These concentrations are 135%, 145% and 128% higher for copper, nickel and zinc, respectively, than the raw sludge levels. The reason for this is thought to be due to the losses of sample encountered during charring (dry-ashing). The presence of water and volatile fractions trapped within the sludge caused several explosions in the crucible due to their lower boiling point compared with the oil. This resulted in some weight losses. In spite of this, the results for the raw sludge and its constituent fractions agreed reasonably well.

Figure 3.5 illustrates how the metals are distributed within the raw sludge. Nearly all of the metals are present in the solids fraction. In this study the heavy metal levels in the oil were lower than found by White (1997) due to the discovery that fine particulates become entrained in the oil fraction extracted using the combined Dean & Stark/Soxhlet method. Filtering to remove these results in very low heavy metal levels in the oil fraction. These results also show that the metals remain in the solids fraction if the oil is separated using kerosene washing as discussed in Section 3.5.4.2. Oil removal will expose the solids surface and allow easier access to the heavy metal binding sites by solubilising agents such as mineral acids.

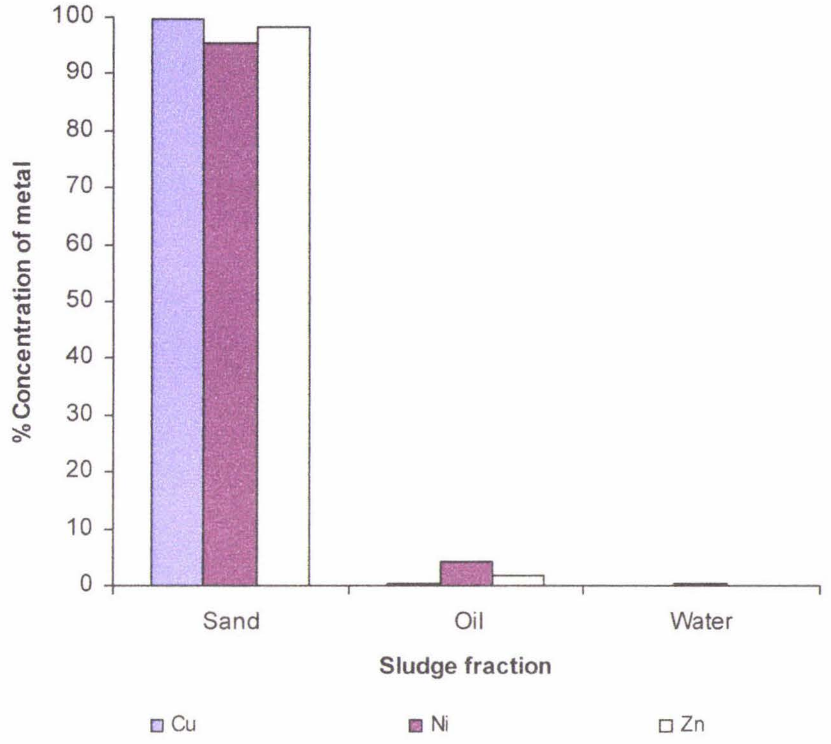


Figure 3.5 – Distribution of heavy metals within the sludge.

3.6 Conclusion

Several separation processes were utilised to characterise the crude oil tank sludge. A combined Dean & Stark/Soxhlet extraction technique was used to determine the oil and water fractions. A modified procedure was used in determining the oil fraction due to the presence of fine solids in the oil. The solvent/oil mixture was filtered prior to oil measurement.

Complete drying of the solids using the combined Dean & Stark/Soxhlet extraction method was difficult due to the presence of pryoric compounds which ignite upon drying at 105°C. Therefore the solids fraction was determined using the solvent washing technique. The solids derived from the solvent washing did not ignite when dried at 105°C.

The solids, oil, water and volatile fractions were found to be 41%, 16%, 25% and 8%, respectively. The total solids fraction was found to be 41% with a fine to coarse solid ratio of 0.52. A volatile fraction of 8% was measured through drying at ambient temperature. Approximately 10% of the original sludge sample was not accounted for by the characterisation experiment.

An average concentration of 3,955mg/kg, 443mg/kg and 13,851mg/kg of copper, nickel and zinc, respectively, were determined for total sludge using the Atomic Absorption Spectrophotometry (AAS) technique. The bulk of the heavy metals (> 98%) resided in the solid fraction. This provides an opportunity to isolate the metals in the solids. Average concentrations of 3,120mg/kg copper, 334mg/kg nickel and 10,754mg/kg zinc were found in the solids fraction.

These results show that significant volume reduction is possible if the oil and water fractions are removed. This can be achieved using washing with kerosene, which will break the emulsified crude oil tank sludge. This will allow recovery of the oil for reprocessing in the oil refinery. If a metal-free oil fraction is required, then care must be taken to separate the fine particles from the recovered oil.

After oil recovery, the remaining solids will be high in heavy metals as greater than 98% of the metals reside in the solids fraction. The metals could then be extracted from the solids using conventional acid leaching procedures.

Both solvent washing and acid leaching of the sludge were investigated and are summarised in the following chapters of this report.

Chapter 4

Solvent Washing

4.1 Introduction

Based on the results of the literature search and sludge characterisation, the best pre-treatment option for NZRC crude oil tank sludge is to break the emulsion and separate the oil and water from the solids. Breaking of W/O (water in oil) emulsions can be achieved through solvent washing, which provides oil removal, solids separation and volume reduction in treating the oily sludge. Since the bulk of heavy metals reside in the solids fraction, it is believed that solvent washing therefore offers a good potential solution for stabilising the crude oil tank sludge.

However, before we can apply the solvent washing process, there is a need to optimise the washing operation for industrial application. Hence, it is necessary to validate the feasibility of solvent washing in treating the NZRC sludge. The approach taken in this research was to establish a theoretical mass balance for a multi-stage washing process and then validate the model against experimental data. This model was then used to determine the feasibility of an industrial scale operation.

4.2 Theoretical washing stage analysis

Solvent extraction or solvent washing is a process in which a substance is transferred from one solvent to another without any chemical changes taking place (Manahan 1990).

Washing stage analysis is based on a three – component system containing pure solvent, insoluble carrier solid and soluble solute (Treybal 1980). In this study, kerosene, sand and oil were considered as solvent, insoluble solids and solute, respectively.

For kerosene to be an effective leaching solvent, it must fulfill two major functions. Firstly, it must be able to desorb the desired solute from the surface of the solids and, secondly, it should be able to disperse the released solute to keep it from being mechanically remixed with feed solids and trapped in the matrix during the phase separation (Long 1995).

When enough kerosene is added to the oil sludge and adequately mixed to attain equilibrium, the resulting mixture is a slurry of sand immersed in a solution of oil in kerosene. The sand fraction can be separated through settling or filtration to constitute a one stage washing operation. Since the initial oil content of the sludge was determined in Section 3.3.1, a theoretical estimate can be made to determine oil removal through solvent and solute (solid-free) mass balances.

4.2.1 Theoretical mass balance for a single stage washing experiment

A general washing operation is shown in Figure 4.1, which gives the basic terminology used for solid-liquid extraction. The circle represents the entire operation of a single n^{th} stage, including the mixing of oil sludge and kerosene and the separation of the resulting insoluble solids by filtration or settling. The number of stages can be increased to achieve the level of oil removal required. The streams entering the extraction unit are the feed and solvent, while the streams leaving the extractor are the extract and raffinate. These streams are defined as follows:

- Feed Stream (F) – solid/liquid mixture or solution to be extracted/separated.
- Solvent Stream (S) – the liquid solvent or solution to which the feed is contacted/mixed.
- Extract Stream (E) – solvent-rich phase containing the components extracted from the feed.
- Raffinate Stream (R) – refined product from which materials have been extracted.

To allow a mass balance to be performed in the washing or leaching operation, several assumptions must be made. The major assumptions made for the mass balance were:

- Equilibrium for oil dissolution is attained during mixing.
- No preferential absorption of either solvent or solute by the solids.

- Uniform concentration throughout the vessel – complete mixing.
- Solubility of oil in solvent is not limiting.
- All oil fractions dissolve in the solvent.
- No solvent losses by evaporation during phase separations.
- No solids in the solvent and extract streams.
- Solvent/solids ratio after each separation is constant
- Water is dispersed evenly throughout the solvent.

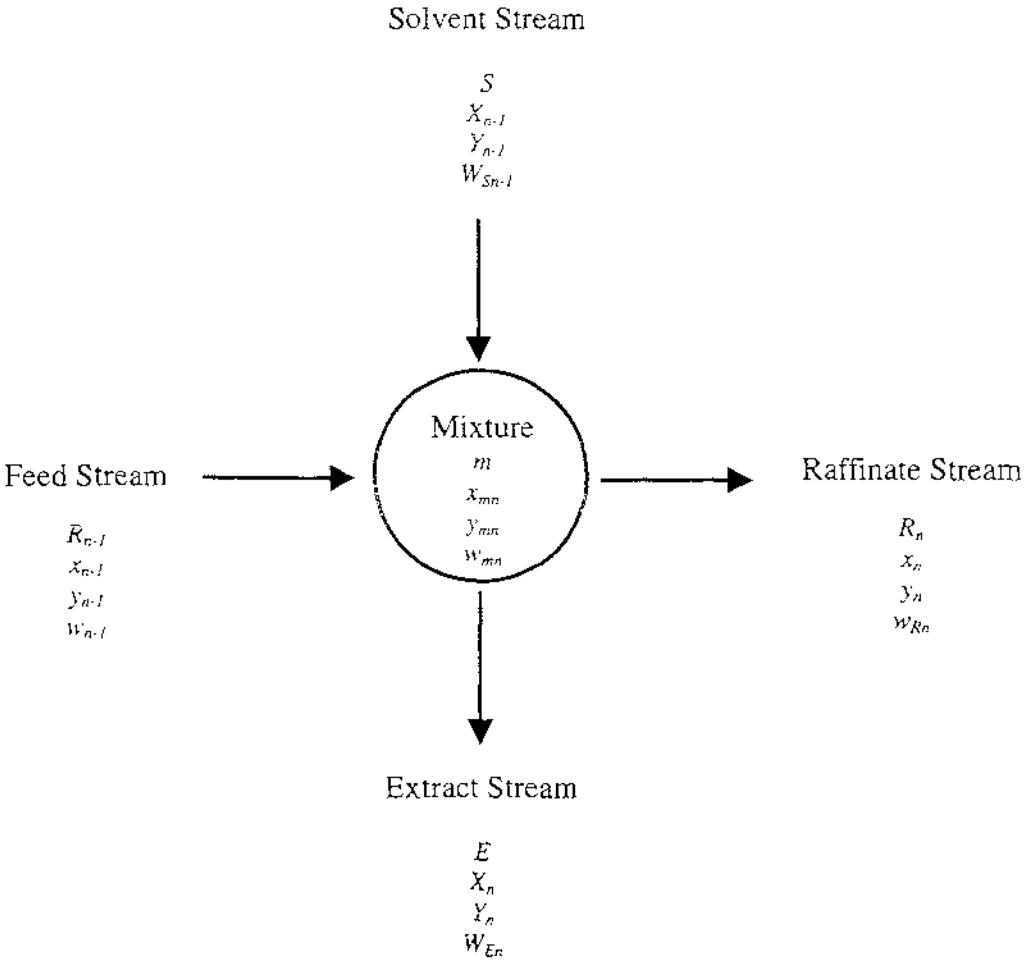


Figure 4.1 - A general nth stage washing operation.

where:

x = concentration of oil in raffinate/feed stream, kg oil/kg (oil + solvent).

X = concentration of oil in solvent/extract stream, kg oil/kg (oil + solvent).

y = concentration of solids in raffinate/feed stream, kg solids/kg (oil + solvent).

Y = concentration of solids in solvent/extract stream, kg solids/kg (oil + solvent).

w = concentration of water in raffinate/feed stream, kg water/kg (oil + solvent).

W = concentration of water in solvent/extract stream, kg water/kg (oil + solvent).

R = mass of raffinate/feed stream, kg (oil + solvent).

S = mass of solvent stream, kg (oil + solvent).

E = mass of extract stream, kg (oil + solvent).

m = mass of mixture, kg (oil + solvent).

x_{mn} = concentration of oil in mixture, kg oil/kg (oil + solvent).

y_{mn} = concentration of solids in mixture, kg solids/kg (oil + solvent).

w_{mn} = concentration of solids in mixture, kg water/kg (oil + solvent).

Theoretically, since it is assumed that there are no (oil and solvent) losses during the washing operation, a total oil and solvent balance gives,

$$S + R_{n-1} = m = E + R_n \tag{4.1}$$

Because there are no solids losses in the extract, a total solids balance gives,

$$SY_{n-1} + R_{n-1}y_{n-1} = m\, y_{mn} = EY_n + R_n y_n \tag{4.2}$$

Because of no oil losses, a total oil balance is given by

$$SX_{n-1} + R_{n-1}x_{n-1} = mx_{mn} = EX_n + R_n x_n \tag{4.3}$$

From the assumption that water is evenly distributed in the solvent, a water balance can be expressed as,

$$SW_{sn-1} + R_{n-1}w_{n-1} = mw_{mn} = EW_n + R_n w_n \tag{4.4}$$

Since the initial values and composition of feed and solvent streams are known e.g. S, R_{n-1}, X_{n-1}, Y_{n-1}, W_{n-1}, x_{n-1}, y_{n-1} *and* w_{n-1}, at equilibrium (all the oil is dissolved in the solvent) then,

$$x_n = X_n = x_{mn} \tag{4.5}$$

By combining the result of Eq. (4.5) with Eq. (4.3) and Eq. (4.1) and rearranging gives,

$$x_n = \frac{SX_{n-1} + R_{n-1}x_{n-1}}{S + R_{n-1}} = x_{mn} = X_n \tag{4.6}$$

By rearranging Eq. (4.2) and using Eq. (4.1), it can be shown that,

$$Y_{mn} = \frac{SY_{n-1} + R_{n-1}y_{n-1}}{S + R_{n-1}} \tag{4.7}$$

Rearranging Eq. (4.1) gives,

$$E = S + R_{n-1} - R_n \tag{4.8}$$

Consequently, by combining the oil balance of Eq. (4.3) and Eq. (4.5) and rearranging for R_n gives,

$$R_n = \frac{SX_{n-1} + R_{n-1}x_{n-1}}{x_n} - E \tag{4.9}$$

By substituting Eq. (4.8) into Eq. (4.9) for E gives,

$$R_n = \frac{SX_{n-1} + R_{n-1}x_{n-1}}{x_n} - (S + R_{n-1}) + R_n \tag{4.10}$$

Solving for R_n gives,

$$R_n = \frac{SX_{n-1} + R_{n-1}x_{n-1}}{2x_n} - \frac{(S + R_{n-1})}{2} \tag{4.11}$$

From Eq. (4.2),

$$EY_n + R_n y_n = SY_{n-1} + R_{n-1} y_{n-1} \tag{4.2}$$

At this stage it is necessary to define how the solids material is separated between the raffinate and extract streams. It is therefore possible to define a value for either y_n or Y_n. Usually it is assumed that there is no solids in the extract (i.e. $Y = 0$) and so it is best to then solve Eq. (4.2) to find the value for y_n.

$$y_n = \frac{SY_{n-1} + R_{n-1} y_{n-1} - EY_n}{R_n} \tag{4.12}$$

4.2.2 Model predictions

The above equations were used to construct a spreadsheet for co-current washing of the oil sludge. These equations were used to calculate the oil removal after three washing stages at different solvent to sludge ratios, assuming a constant raffinate composition of $Y_{mn} = 3$, using the actual oil concentration of the sludge of $x = 0.28$ (see Chapter 3) and there is no solids found in the extract stream ($Y = 0$). The theoretical oil removal was predicted using the spreadsheet after the first, second and third stage washings, as shown in Figure 4.2. The Spreadsheet is included on disk in Appendix A-5.

It can be seen that the model predictions are sensible, although the assumptions made in its development must be tested. The model was therefore validated against experimental data and several of the assumptions made in the development of the model were tested.

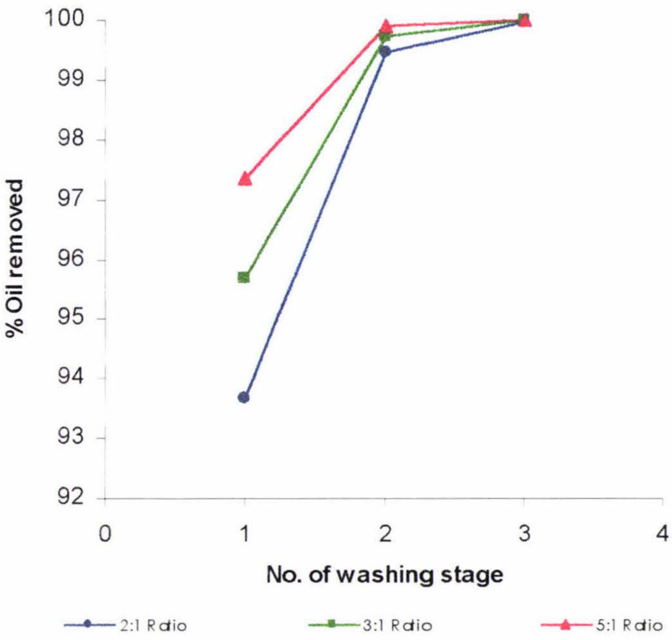


Figure 4.2 – Theoretical oil removal at different solvent to sludge ratio after 3 washing stages.

4.3 Solvent selection

Before validation of the model was carried out, the solvent was chosen based on its feasibility in industrial application. Several factors were considered in deciding what type of solvent to use. Table 4.1 shows how a suitable solvent was selected for treating NZRC sludge.

Solvent type	Emulsion breakdown	Availability in the refinery	Boiling point	
			Initial °C	Final °C
light tops	+	+	32	78
naphthalene	+	+	99-102	170-175
kerosene	+	+	145	300

Table 4.1 – Basis of solvent selection.

All the three solvents listed are capable of breaking the sludge emulsion and readily available as a process stream in oil refineries. However, due to differences in boiling points, kerosene was chosen because it has the highest boiling point. Therefore the solvent will not immediately evaporate at ambient conditions during washing operations. In using light tops and naphtha, a closed vessel would be required since these type of solvents are more volatile and therefore problems of evaporation and explosions are possible. Capital cost requirements would also be greater if a pressure vessel is required.

4.4 Experimental model validation

Validation of the model with experimental data was necessary before an industrial scale operation could be designed. This included testing of how long it takes for the system to attain equilibrium and the settling properties of the solids. To achieve this, determination of the oil concentration dissolved in kerosene for each extraction stage over a range of sludge to solvent ratios was required.

4.4.1 Oil Concentration Measurement

Measurement of the oil concentration in the solvent was required before any experimental measurements could be made. It was necessary that the oil concentration measurement should be fast, accurate and only a small amount of sample used, to avoid losses of materials during the experiment.

Centrifugation and distillation (e.g. Dean & Stark Method) are the most commonly used methods for estimating oil concentration in sludges. Centrifugation is not effective for separating miscible solutions, e.g. oil being dissolved in the solvent. This means that steam distillation is the only proven method used to measure the oil concentration. However, this method requires longer times, a large amount of sample and it is only effective for samples of high oil concentrations. For a gram of sample with 10% oil, this method needs to weigh 0.01g of oil to have an accurate oil concentration estimate. Achieving this amount of oil after performing the distillation process is highly susceptible to errors and thus is not applicable for oil measurement in solvent washing operation. Hence, there is a need to develop another method which is fast, accurate (even below 5%) and that only requires a small amount of sample for analysis.

To meet these requirements, a new method based on the refractive index of the solvent was developed. All materials have refractive indexes greater than unity which depend on the substance and the wavelength of the light (Sears *et al.* 1987). When dissolved in the solvent, the sludge oil exhibits a refractive displacement of the light that travels through that medium. The deviation will depend on the composition or concentration of the oil present in the solvent. The oil concentration measurement method used in this work took advantage of this phenomenon.

Figure 4.3 – Photograph of the refractometer used (RFM 340 model).

A series of standardised oil/solvent solutions (kg oil/kg solvent) was prepared using the crude oil extracted from the NZRC sludge through the modified Dean & Stark/ Soxhlet extraction method used during the characterisation of sludge. In a COD tube, an oven dried (105°C) known weight of oil (0.0300-0.3000g) was mixed manually (10-15 minutes shaking) with a known weight of kerosene (0.9000-8.0000g). Care was taken to ensure that the oil was totally dissolved in kerosene. An oil concentration range from 0-10% was prepared and left overnight prior to refractive index measurement. The refractive index was taken for each concentration using a RFM 340 model refractometer (see Figure 4.3) under controlled temperature (22°C), by circulating water from a constant temperature water bath. A minimum of 5 seconds was required before taking any refractive index measurement to ensure temperature stability and at least three readings were taken. It was found that the refractive index of the solvent changed linearly with increasing oil concentration. A plot of the refractive index versus oil (sludge oil) concentration resulted in Figure 4.4.

$$C = 14.939RI - 21.703 \qquad (4.13)$$

where:

C = concentration of oil, kg oil/kg solvent

RI = refractive index of the solution

Equation 4.13 was fitted to this data and used to back-calculate the oil concentration from the measured RI in future analyses. This relationship allowed the quick and easy measurement of oil concentration.

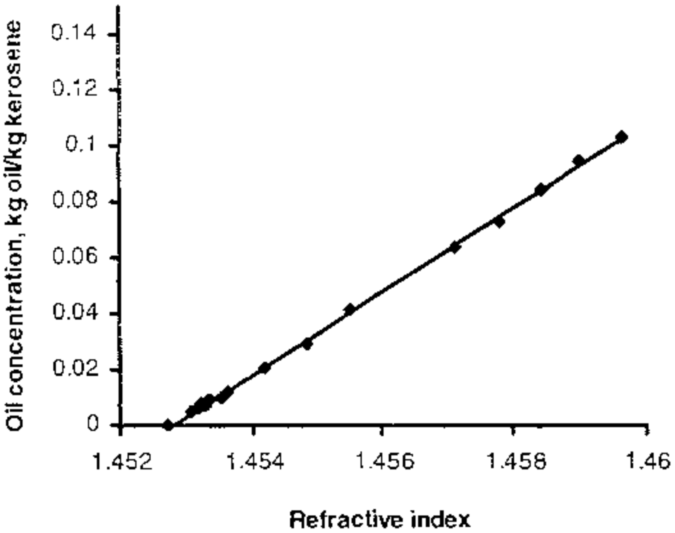


Figure 4.4 – Correlation of refractive index vs. oil concentration.

It was found that it was important to measure the refractive index of the mixture at the same temperature as that used in the derivation of the standard curve. This was because the refractive index measurement is very sensitive to the effect of temperature (see Figure 4.5). This correlation, therefore, is only effective if oil measurement is performed at the reference temperature. This technique was then used in subsequent analyses to validate the theoretical washing model.

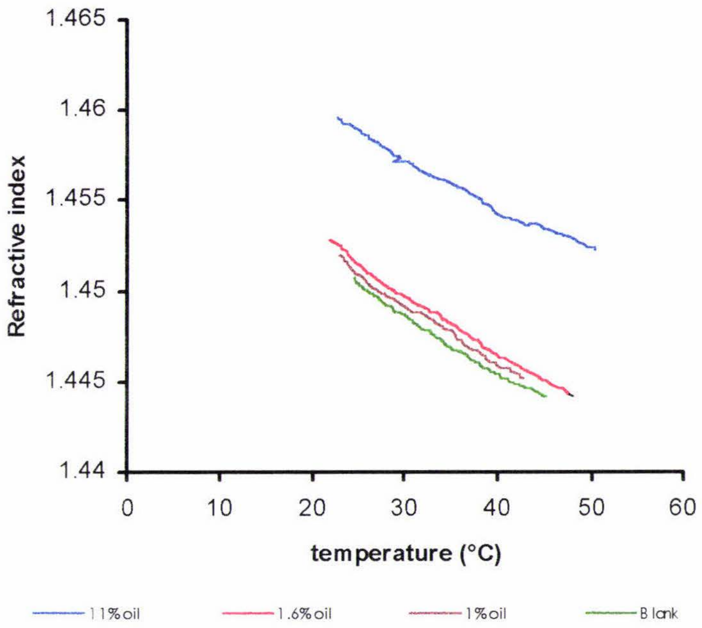


Figure 4.5 – Effect of temperature on the refractive index.

4.4.2 Equilibrium measurement

In washing operations where the solvent dissolves the solute, equilibrium between the solvent and solid phases is necessary before separation is carried out. This was one of the key assumptions used in the development of the mathematical model. In the case of oil sludge washing, where the oil dissolves into the solvent, there is a need to determine how long it takes for the oil concentration in the solvent to reach steady state.

This was determined by combining a known sludge sample to the solvent (kerosene) in the ratio of 2:1 under constant mixing. Using an automatic pipette, one ml. of sample was taken every 10 seconds until the mixture became homogeneous. The refractive indexes of these samples were then measured under controlled temperature conditions as outlined in Section 4.4.1.

A continuous flow sampling system for refractive index measurement with an on-line computer attached had been tried for better sampling efficiency. However, inaccurate results were experienced due to the accumulation of very fine solids in the prism cell of the refractometer. For this reason collection of samples was done manually.

The resulting refractive index data was converted into concentration units using the standard curve (Eq. 4.13) and then plotted (see Figure 4.4). As shown in Figure 4.6, equilibrium conditions were attained in less than three minutes under constant mixing at ambient temperature with 2:1 solvent to sludge ratio.

It was also found that the rate of the dissolution of oil follows a first order rate relationship (see Figure 4.7), which is typical for mass transfer from a surface. This and the fast rate of dissolution shown, indicated the absence of inter particle oil diffusion. This experiment shows that a contact time of at least 3 minutes is required in washing operations under normal conditions. For this reason, at least 3-minutes contact time was used before commencing the settling phase of all subsequent experiments.

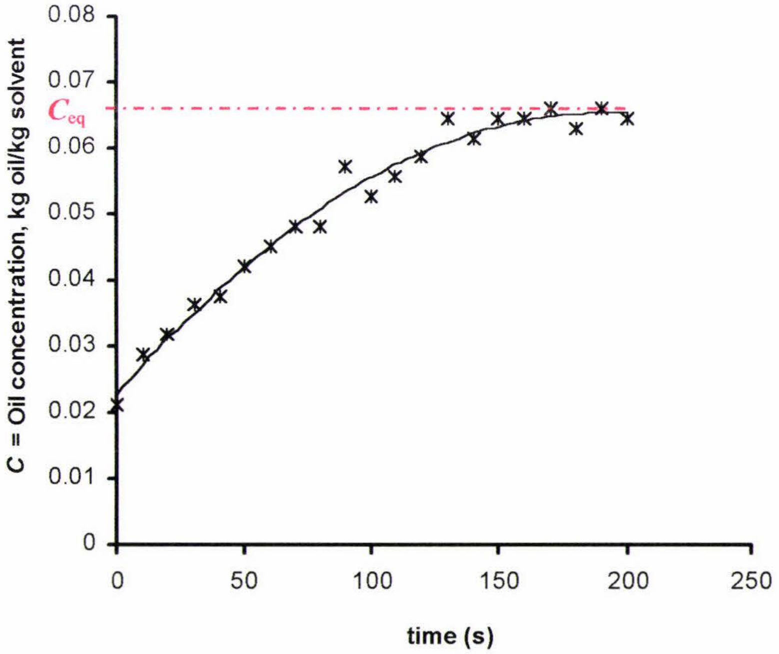


Figure 4.6 – Oil dissolution kinetics for 2:1 solvent to sludge ratio.

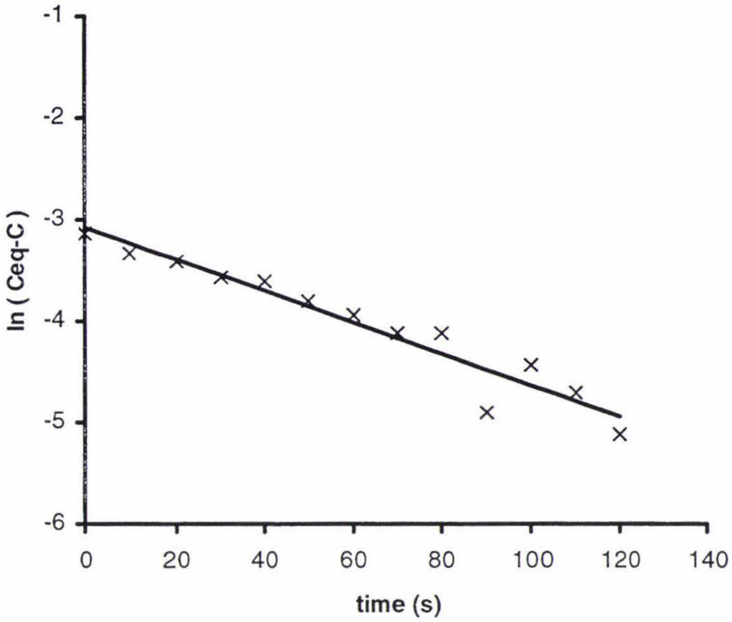


Figure 4.7 – ln (C_{eq} - C) vs time graph for oil dissolution kinetics.

4.4.3 Solvent washing

Based on the solvent selection criteria discussed in Section 4.3, kerosene was used for solvent washing. The use of kerosene took advantage of the high solubility and fast dissolution of the oil and the good settling characteristics of the solids in the mixture. In addition to this, the ready availability of the solvent as process stream in oil refineries makes it an ideal choice for use in the treatment of the oil sludge.

A well-mixed sludge sample was air-dried by spreading it in a thin layer on aluminum foil and leaving in fume-hood overnight before washing. The pre-dried oil sludge was then mixed with the solvent at a ratio of 2:1. Constant mixing using a magnetic stirrer was continued for at least 5 minutes to dissolve the oil and allow the sample to reach equilibrium.

After equilibrium was achieved, the solids were allowed to settle for 10-15 minutes. The extract (solution) was decanted to the lowest level above the solid/liquid interface, weighed and filtered to determine the amount of solids present. All weights were determined to allow a complete solvent, solids and total mass balance to be calculated.

The refractive index of the oil/solvent mixture was measured during each mixing stage and used to calculate the oil concentration as described in Section 4.4.1. Refractive indexes were measured at the same temperature as the correlation was derived (22°C) using a constant temperature water bath to regulate the refractometer cell temperature.

The remaining solids were washed a further two times using an equal amount of fresh solvent in the same way as described above. The final raffinate (solids) was oven-dried at 105°C for one hour to determine the amount of solids and solvent left. The above measurements provided all the necessary information to allow a full mass balance to be carried out over the system.

This experiment was then repeated for four different sets of solvent to sludge ratios (2:1, 3:1, 4:1 and 5:1) to validate the theoretical oil removal predictions discussed in Section 4.2.2. A 1:1 solvent to sludge ratio was not used in this study since the amount of kerosene is not enough to allow adequate mixing and equilibrium could not be attained. During initial trials it was observed that raw (wet) sludge was easier to wash compared to the dried one. This was due to the difficulties in achieving mixing of the solvent with the dried sludge. Inspite of this, an air-dried sludge was preferred in this work to minimise weight measurement discrepancies caused by the presence of volatile compounds that were lost from the wet sludge through evaporation during washing. A weight loss of about 18 % was observed when a raw sludge was dried overnight prior to solvent wash. This amount will correspond to the volatile fraction measured during the characterisation of the sludge (Chapter 3) if the volatiles plus the unaccounted fractions were added together. It is also possible that water evaporation may have occured during the air-drying.

Drying the sludge before kerosene washing does not give any industrial scale advantages. Instead, an added difficulty in mixing had been encountered due to the hardening of the material upon drying. In industrial situations, it would be preferable to wash the raw sludge directly to increase oil recovery yield and to aid in mixing with the kerosene. The presence of water in the sludge would help to reduce the solvent required for the washing operation.

The coarse solids in the sludge settle immediately as soon as the mixer stops, while it takes at least an hour before complete settling of fine solids was obtained. For this reason, the extract after each washing stage was filtered to determine the extent of solids separation.

The presence of fine solids in the extract will pose some industrial problems that should be considered. If the fines are not removed from the oil stream they will travel through the distillation process during the reprocessing of the solvent and crude oil. The settling time should therefore be taken into account before an industrial scale design is made.

A plastic washing vessel was used instead of glass, since the fine solids of the sludge stuck to the glass material due to its high surface energy. Using a glass vessel resulted in difficulties in measurement of the settling time, since the whole vessel was covered with fine solids making it hard to see through the solution.

The theoretical mass balance assumed that water was evenly distributed in the solvent due to rapid mixing. The bulk of this would be removed after the first washing. It was also assumed that any water present in the sludge does not affect the refractive index measurements. It was found experimentally that most of the water settled with the solids, due to its higher density compared to kerosene. Though the assumption made was not true, the presence of water does not significantly affect oil removal efficiencies. In an industrial scenario, it is most likely that water will stay with the solids after draining the solvent mixture and does not pose any problem.

One of the assumptions made in the development of the model was to obtain constant solvent retention in the solids after each washing stage. It was found that in these experiments, the amount of kerosene retained after each washing stage was not constant. In spite of this, the experimental data showed that over 98% oil removal was achieved at different solvent retention (raffinate). Based on the theoretical mass balance, kerosene retention in the solids after each washing stage should be less than 50% to achieve a minimum of 98% oil removal using 2:1 solvent to sludge ratio.

Two methods were used to calculate oil removal efficiencies at different solvent to sludge ratios, after each of the three washing stages. The first method utilised the refractive index correlation to determine the amount of oil removed using the measured weights of extract obtained from each washing stages, less the amount of solids present in it. The total amount of oil was derived from the sum of oil removed from each washing stage plus the amount of oil that was left in the raffinate. The removal oil efficiencies were calculated using the summarised equations below.

$$Total\ oil\ removed = \sum_{1}^{n} \left[(Conc.of\ oil\ in\ E_n) \times (kg\ of\ E_n - kg\ of\ solids\ in\ E_n \right] \qquad (4.14)$$

$$\begin{aligned} Total\ oil \quad = \quad & \sum_{1}^{n} \left[(Conc.of\ oil\ in\ E_n) \times (kg\ of\ E_n - kg\ of\ solids\ in\ E_n \right] \ + \\ & \left[(kg\ of\ R_n - kg\ of\ solids\ in\ R_n) \times (Conc.of\ oil\ in\ R_n) \right] \end{aligned} \qquad (4.15)$$

$$\%\ Oil\ removed \quad = \quad \frac{Total\ oil\ removed}{Total\ oil} \ \times \ 100 \qquad (4.16)$$

Results of the oil removal efficiencies using this method after each of these washing stages are shown in Figures 4.8, 4.9 & 4.10, respectively.

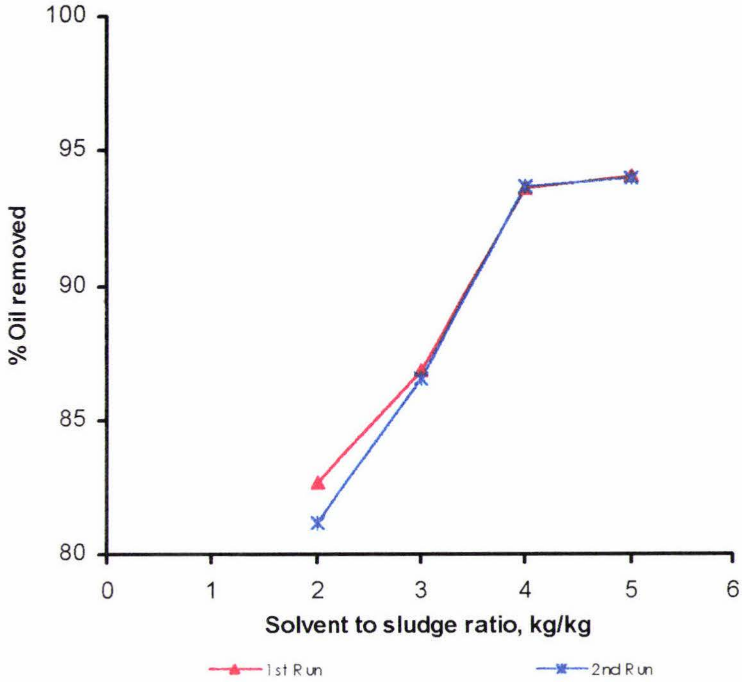


Figure 4.8 – Experimental oil removal after the first washing stage calculated using the refractive index correlation.

Figure 4.9 – Experimental oil removal after the second washing stage calculated using the refractive index correlation.

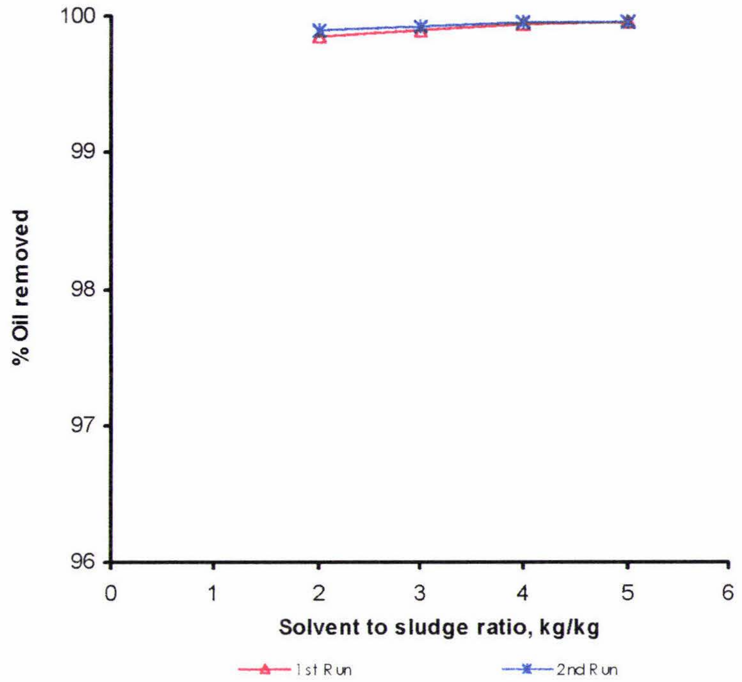


Figure 4.10 – Experimental oil removal after the third washing stage calculated using the refractive index correlation.

The second method used to calculate the experimental oil removal efficiencies was based on the weights obtained from the extract less its solids, and the raffinate from each washing stage. The total amount of oil in the feed was based on the compositions obtained through the modified Dean & Stark and Soxhlet extraction outlined in Chapter 3, using the same air-dried sludge sample. The total solids used in the calculations were obtained from the final raffinate stream in the washing experiment. Experimental oil removal efficiencies using the mass balance are shown in Figures 4.11, 4.12 & 4.13 after each of the three washing stages.

The experimental results using these two methods were found to agree well with the theoretical values. Although there were some variations, these clearly followed the same trend, especially after the second washing stage as shown in Figures 4.14, 4.15, 4.16 & 4.17.

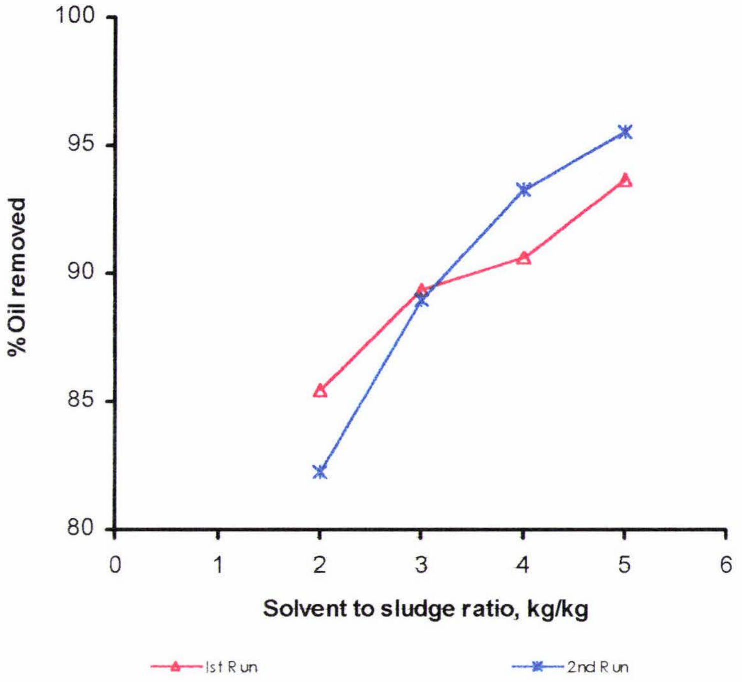


Figure 4.11 – Experimental oil removal after the first washing stage using the spreadsheet.

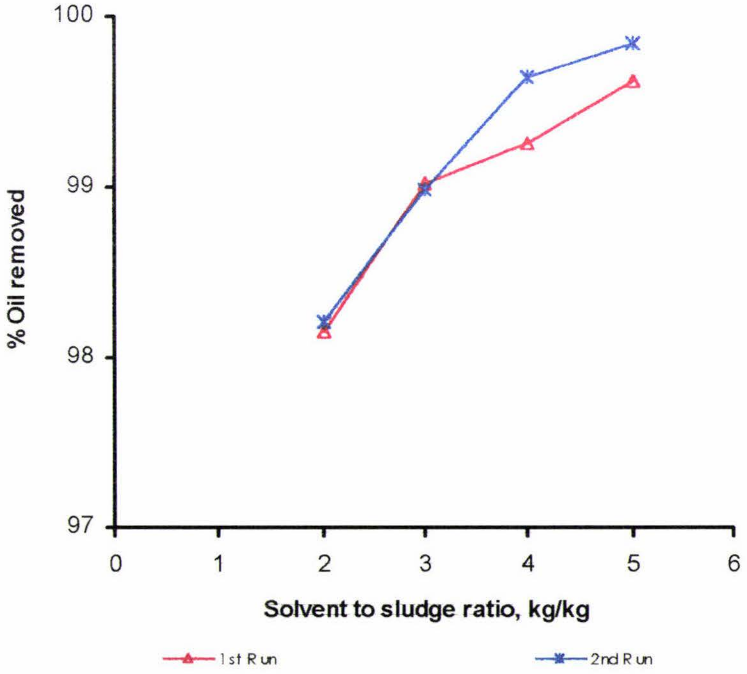


Figure 4.12 – Experimental oil removal after the second washing stage using the spreadsheet.

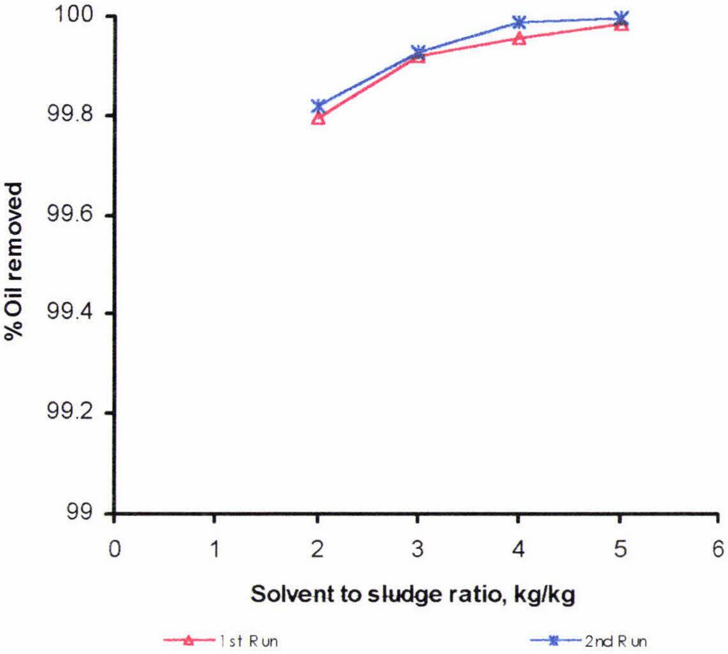
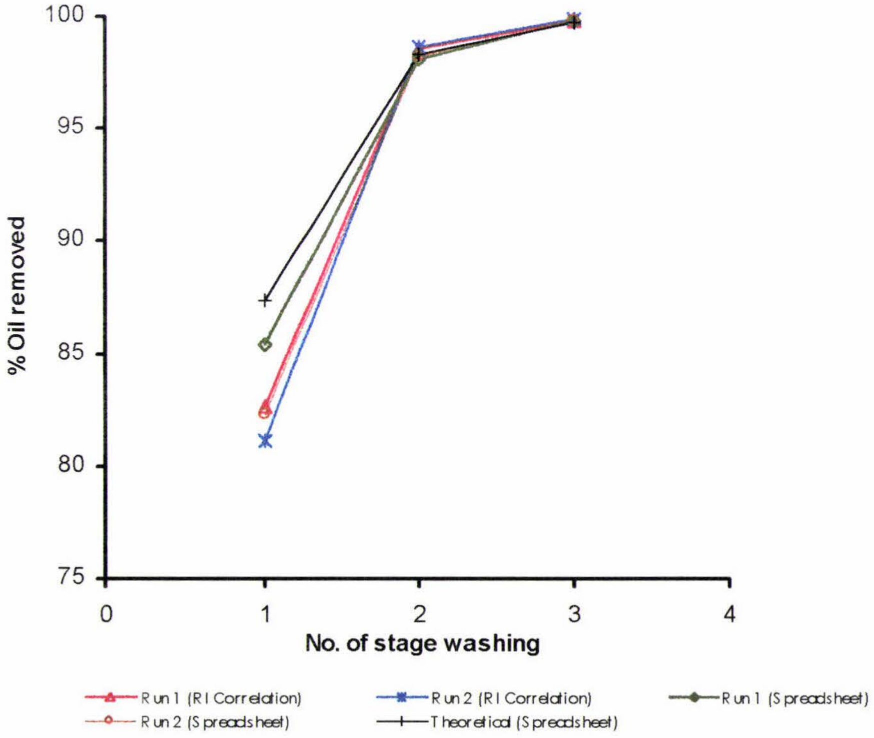


Figure 4.13 – Experimental oil removal after the third washing stage using the spreadsheet.



Figures 4.14 – Comparative oil removal for 2:1 solvent to sludge ratio.

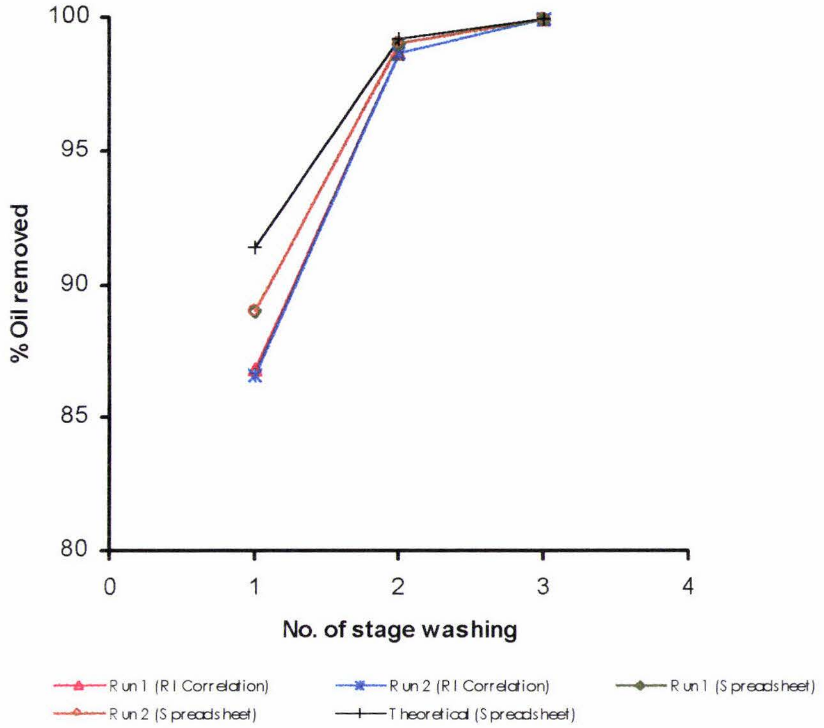


Figure 4.15 – Comparative oil removal for 3:1 solvent to sludge ratio.

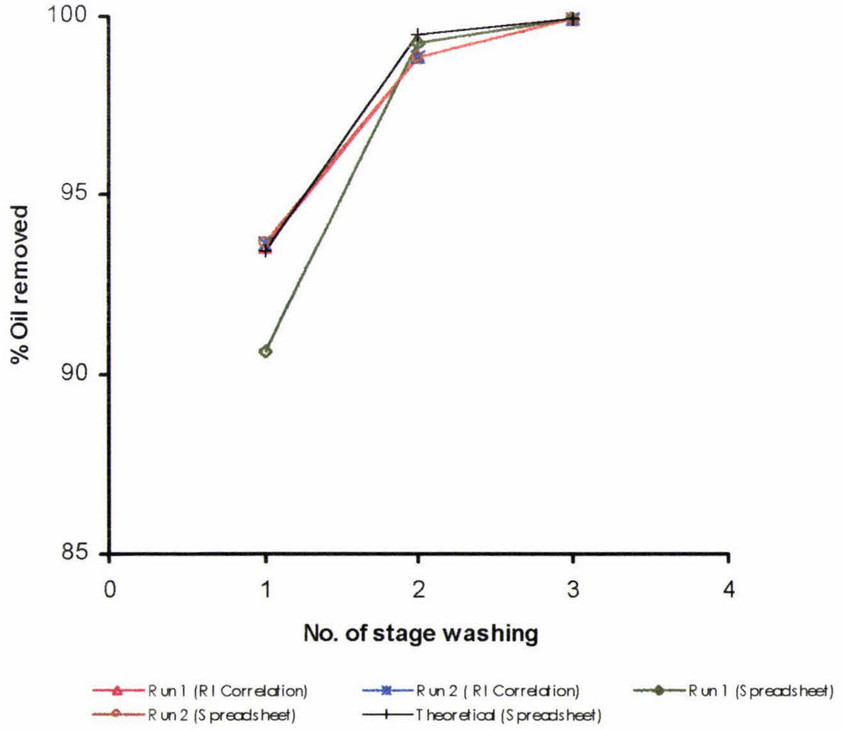


Figure 4.16 – Comparative oil removal for 4:1 solvent to sludge ratio.

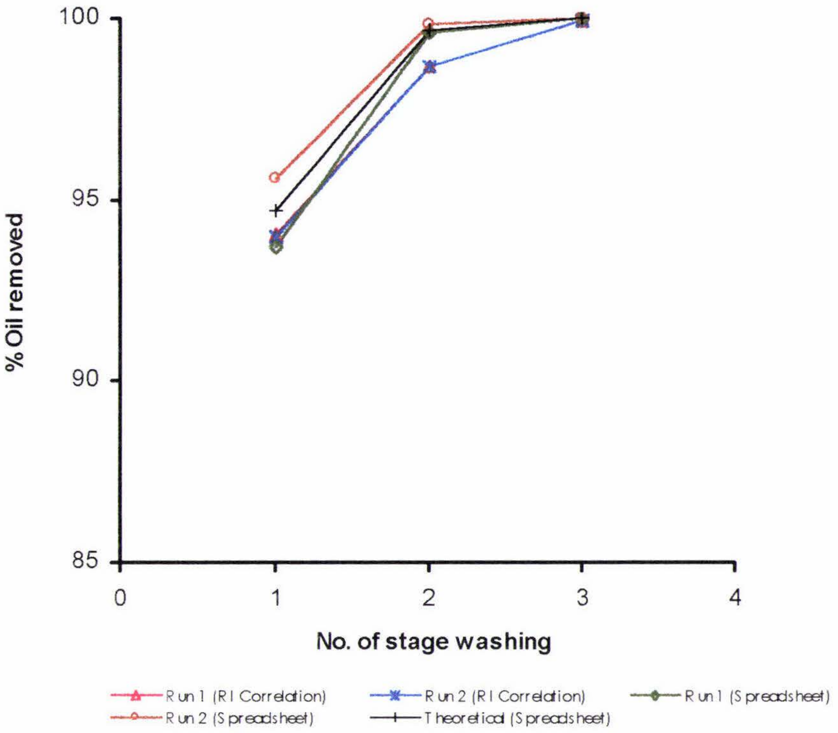


Figure 4.17 – Comparative oil removal for 5:1 solvent to sludge ratio.

To further check the validity of the two experimental methods, the oil concentration from each washing stage measured using the refractive index correlation was compared against the oil concentration calculated using the spreadsheet method. Figures 4.18, 4.19, 4.20 & 4.21 show that the oil concentrations derived from different solvent to sludge ratios through the refractive index correlation agreed well. The first washing stages of the refractive index method were a little higher than the spreadsheet method, although the data fall within an acceptable margin of error.

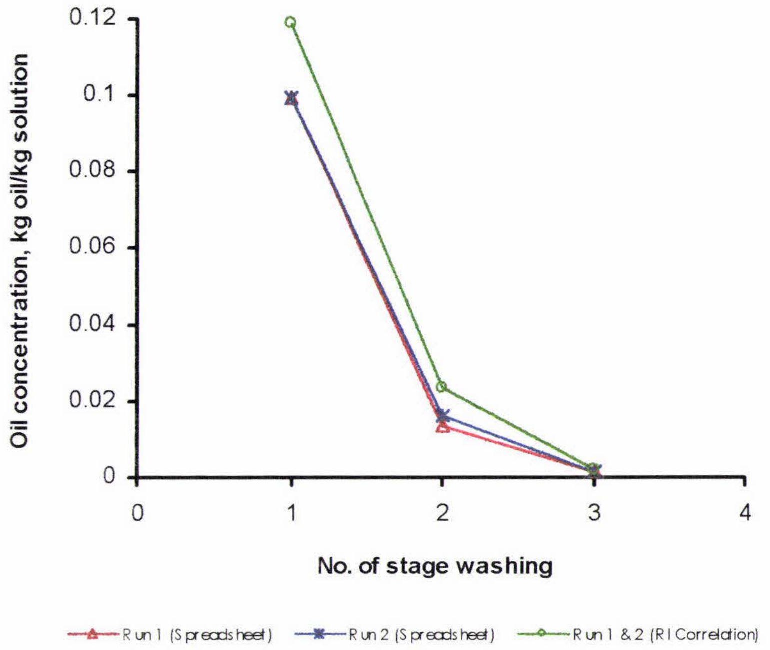


Figure 4.18 – Comparative oil concentration measurement for 2:1 solvent to sludge ratio.

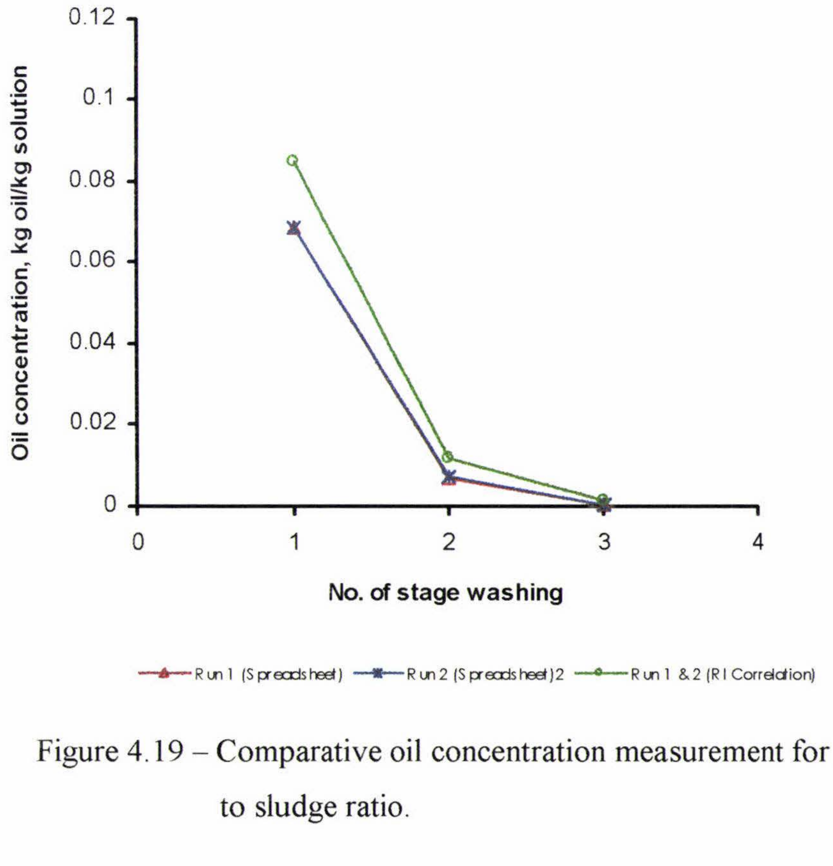


Figure 4.19 – Comparative oil concentration measurement for 3:1 solvent to sludge ratio.

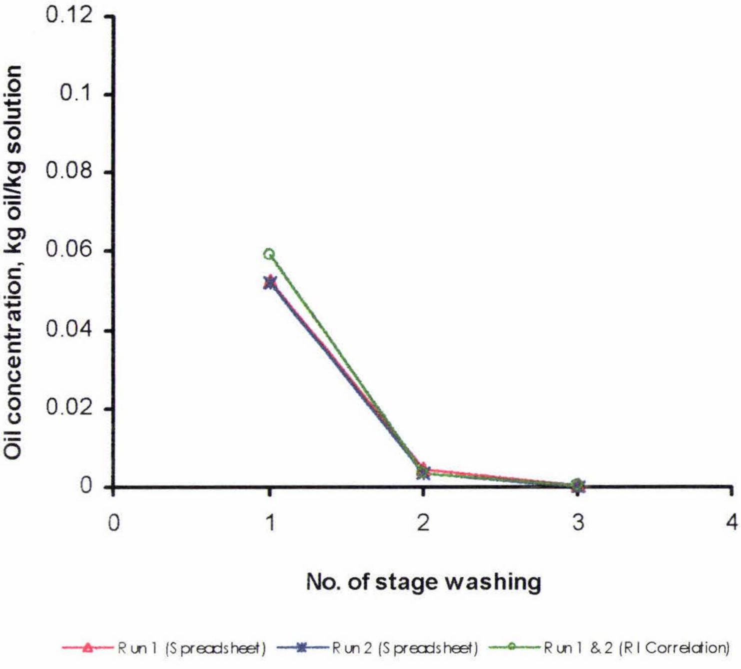


Figure 4.20 – Comparative oil concentration measurement for 4:1 solvent to sludge ratio.

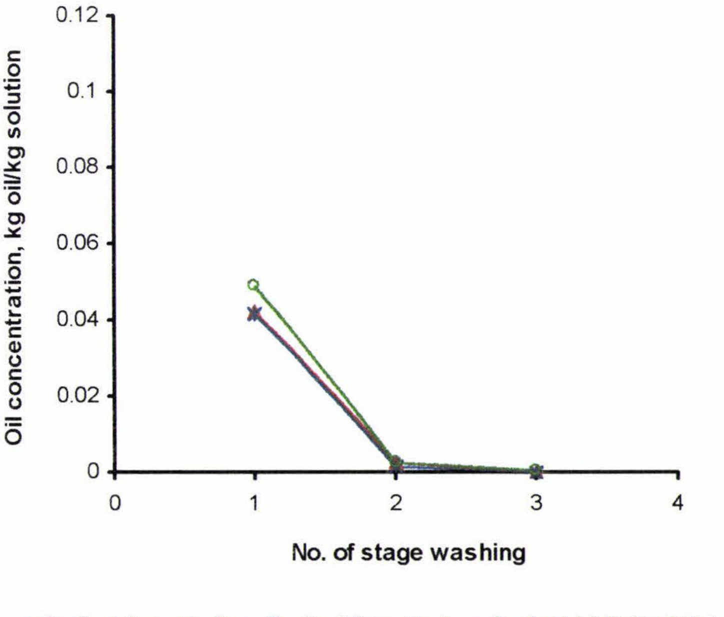


Figure 4.21 – Comparative oil concentration measurement for 5:1 solvent to sludge ratio.

The experimental oil removal efficiency using both the refractive index correlation and the spreadsheet methods were found to agree well with the theoretical removal efficiencies given by the mass balance outline earlier in this section. This mass balance can be applied to model alternative sludge/solvent ratios, solids separation techniques and stage efficiencies in treating NZRC crude oil tank sludge. The experiments outlined here show that the assumptions made in the development of the mass balance are valid for the range of conditions used in the experimental work described in this report.

The results of this study suggest a solvent to sludge ratio of 2:1 and minimum of 2 washing stages were adequate to achieve over 98% oil removal. Kerosene washing provides a volume reduction of 76% and mass reduction of 59%. This leaves an oil-free/metal-rich solids fraction that is easy to manage and dispose. The physical appearance of the washed sludge is shown in Figure 4.22.

Figure 4.22 – Photograph of NZRC sludge after kerosene washing.

The NZRC washed sand also provides opportunity for further treatment for its disposal through solidification or removal of the heavy metals through acid washing. This will be studied further in Chapter 5. Kerosene washing also allows the recovery of oil from the sludge. This could result in up to 16 tonnes/year, based on an average of 100 tonnes/year generation of crude oil tank sludge at NZRC.

4.4.4 Sensitivity analysis of the solvent washing process

Based on the theoretical and experimental calculations presented, only two washing stages were required to remove the crude oil in the sludge. A minimum of 98 % oil removal efficiency was achieved, resulting in oil-free/metal-rich solids fraction. However, further theoretical calculations were performed to optimise the process of kerosene washing of the oil sludge.

Using the experimental sludge composition data obtained in Section 3.3.2, it was possible to predict the removal efficiencies at different solvent to sludge ratios, at varying oil concentrations and separation efficiencies. The effect of the initial oil concentration in sludge is shown in Figures 4.23, 4.24 & 4.25. These graphs are drawn assuming the raffinate stream contains 50% w/w of solvent after the separation.

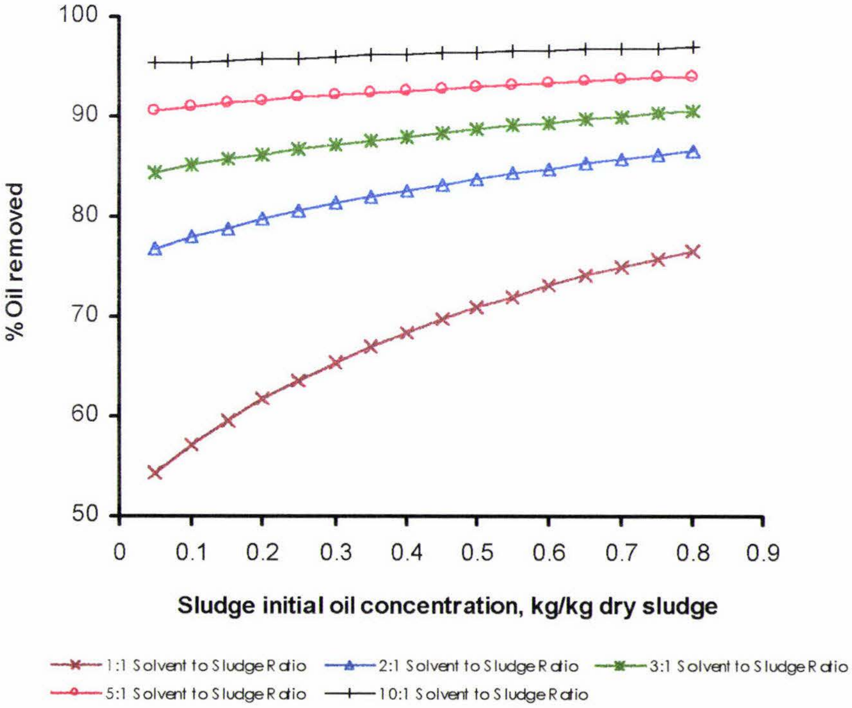


Figure 4.23 – Effect of varying initial sludge oil concentration on the removal efficiency after the first washing stage.

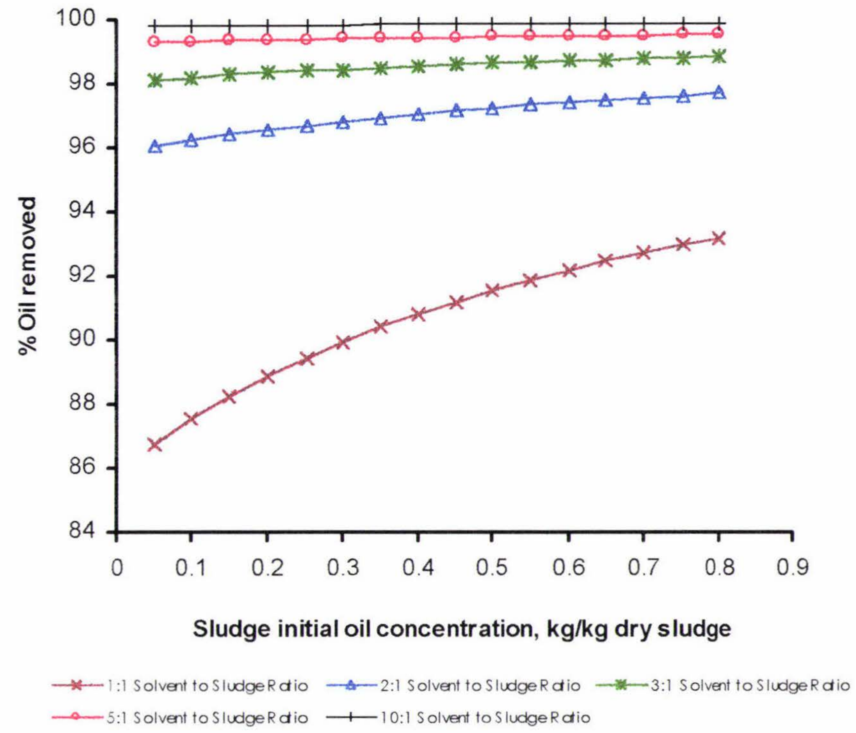


Figure 4.24 – Effect of varying initial sludge oil concentration on the removal efficiency after the second washing stage.

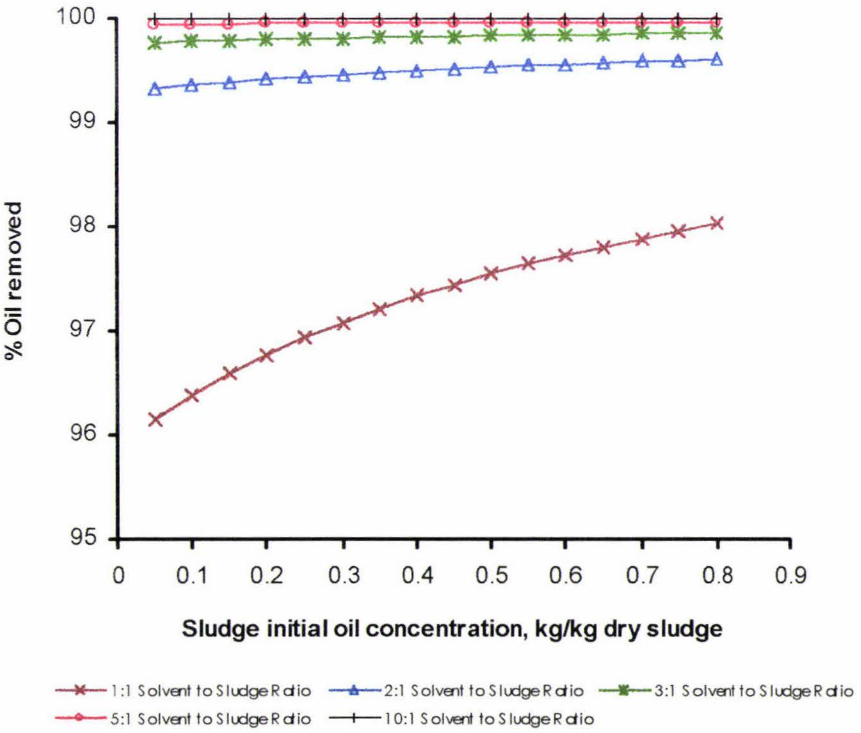


Figure 4.25 – Effect of varying initial sludge oil concentration on the removal efficiency after the third washing stage.

It can be seen in Figures 4.23, 4.24 & 4.25 that the oil concentration in the sludge does not significantly affect overall removal efficiencies at different solvent to sludge ratios except for the 1:1 ratio. Although the removal efficiency for 2:1 ratio is below 98% after the second washing stage (Figure 4.24), the reason for this is due to assumption of high solvent retention (50%) in the raffinate. These results mean that natural variations in sludge composition will not cause difficulties in achieving oil removal in the industrial situation.

Figures 4.26, 4.27 & 4.28 show the effect of the efficiency of the solvent separation step on oil removal after one, two and three washing stages. For these graphs it was assumed that the initial sludge oil concentration was 0.28 kg/kg (see Table 3.1).

The solvent to sludge ratio was not a critical factor to achieve good oil removal, as long as the raffinate was maintained with less than 50% w/w solvent (see Figure 4.27). An oil removal of 98% could still be achieved theoretically at a 1:1 solvent to sludge ratio if the raffinate is separated to achieve a maximum of 33% w/w solvent after the second washing stage. In practice it is not possible to achieve this since the amount of solvent is insufficient to achieve adequate mixing to obtain equilibrium.

The critical parameter to be considered in designing the washing process is therefore the solids separation efficiency after settling. The higher the residual kerosene/solids ratio, the lower the oil removal efficiency the washing operation can achieve. The effect of dryness of the raffinate therefore determines the efficiency of the washing. Figure 4.27 shows that the raffinate should contain a maximum of 50% solvent on a weight basis to achieve over 98% oil removal after the second washing stage with a minimum solvent to sludge ratio of 2:1. The efficiency of separation of solids from the solution should therefore be considered in the design of an industrial scale oil removal treatment facility for crude oil tank sludge.

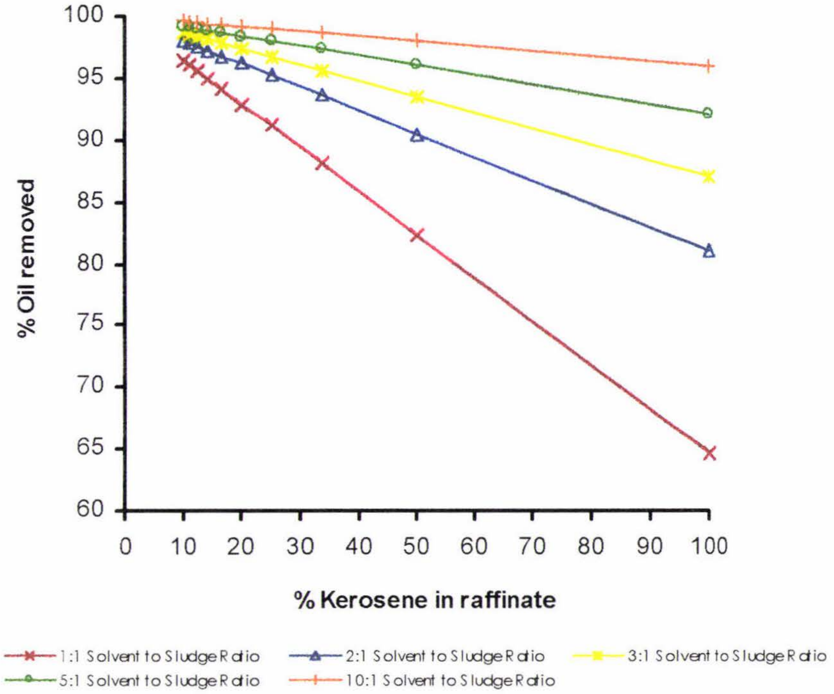


Figure 4.26 – Effect of solvent retention in raffinate on removal efficiency after the first washing stage.

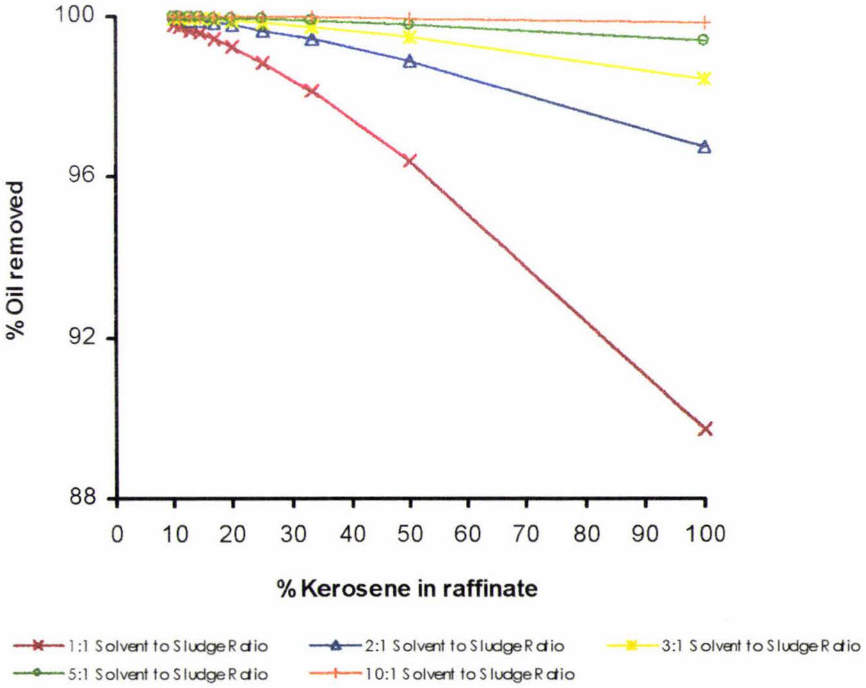


Figure 4.27 – Effect of solvent retention in raffinate on the removal efficiency after the second washing stage.

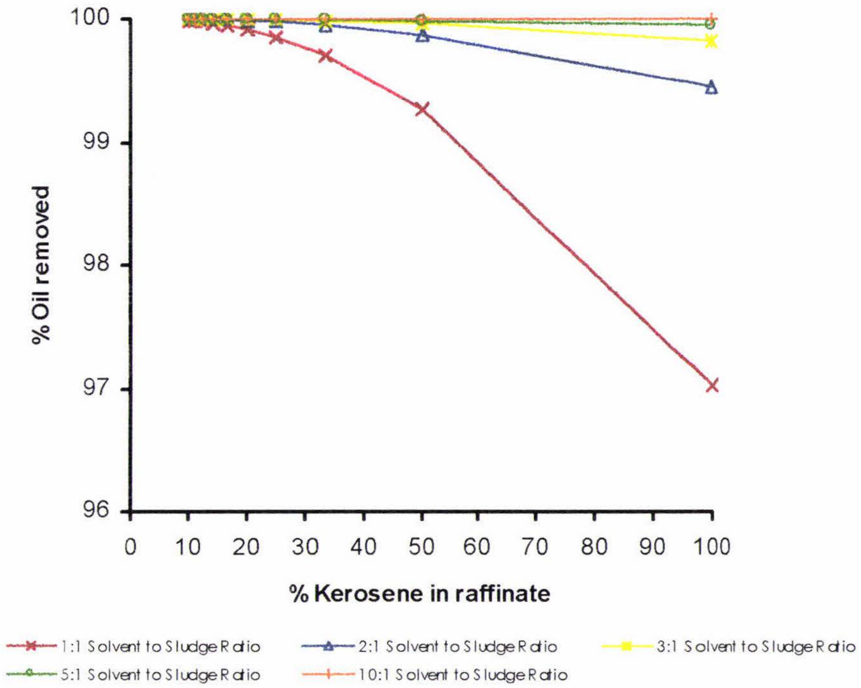


Figure 4.28 – Effect of solvent retention in raffinate on the removal efficiency after the third washing stage.

4.4.5 Reusability of solvent (extracts)

In any washing operation, the recovery of solvent is important since operating costs are closely related to the type and the quantity of solvent used. The less solvent used the more economical the process would be. The possibility of reusing the solvent (extract solution) prior to solvent recovery was investigated to further optimise the washing operation, by reducing the amount of solvent needed to treat the NZRC sludge. Reuse of extract solutions can be achieved using batch-wise or counter-current washing systems.

4.4.5.1 Batch-wise operation

This system reuses the first and second extracts from a previously washed sludge to treat a new batch of raw sludge, to optimise the use of the solvent prior to solvent recovery. A theoretical mass balance was performed using a spreadsheet to determine the oil extraction efficiency. A considerable amount of oil can still be removed by reusing the extracts following the same washing stage from it was previously used. This is shown in Figure 4.29. Fresh solvent was added in the solids first washing stage of each batch, to make-up for the solvent loss caused by the retention in the solids. The addition of fresh solvent is necessary to avoid mixing problems as discussed in Sections 4.4.3 and 4.4.4. The optimum extraction efficiency of the solvent is therefore dependent on the oil removal required.

By reusing the extract for washing a new batch of raw sludge, the minimum solvent to sludge ratio of 2:1 can further be reduced to 1:1 ratio for each stage, if 98% oil removal is required after the second batch. This means that reduction of solvent use is possible. This results in lower operating costs for the treatment of the sludge.

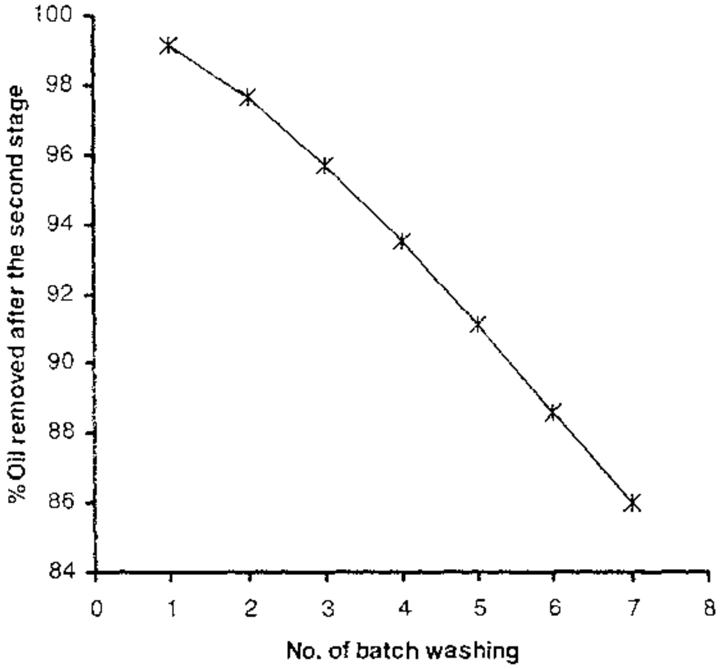


Figure 4.29 – Reusability of 1st and 2nd extracts for a batch- wise system.

4.4.5.2 Counter-current operation

In this system, the second extract (solvent solution) from a previously washed sludge is used as a first stage extractant to treat a raw sludge. Fresh solvent is added to the second stage. A theoretical mass balance was performed using the spreadsheet, to determine the extent of oil removal after the second stage for this mode of operation. This resulted in above 99% oil removal as shown in Figure 4.30. These results show that the second extract can be reused perpetually and still achieve the desired removal efficiency. This would therefore decrease the requirements for solvent.

In this theoretical calculation, any solvent losses were compensated by the addition of fresh solvent. This was to avoid mixing problems. It was also assumed that a constant raffinate composition of 50% w/w solvent was achieved in each washing stage after solvent separation.

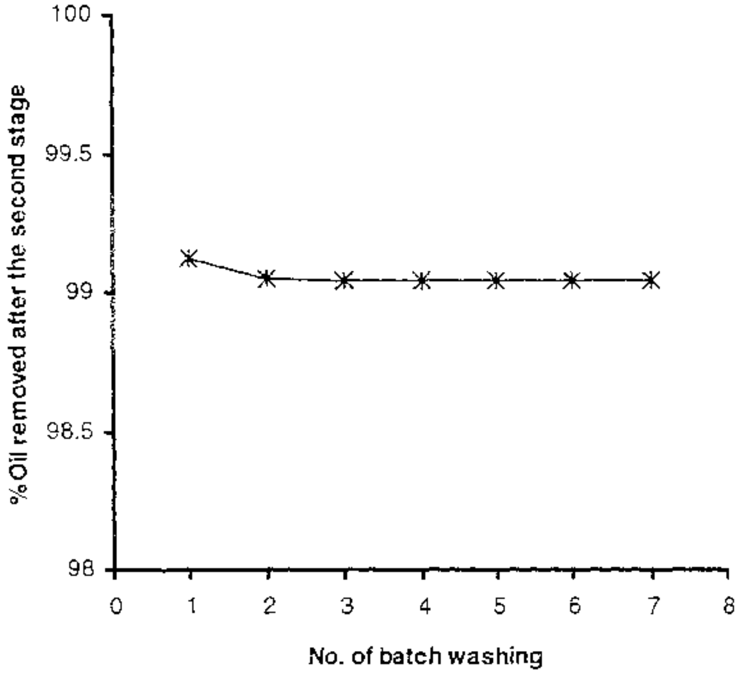


Figure 4.30 – Reusability of second extract under counter- current system.

Results of the theoretical calculation on the reusability of the solvent prior to recovery using both methods have shown an opportunity to increase the efficiency of the washing process. The counter-current method was specifically designed to determine the minimum solvent to sludge ratio that could be used in treating the sludge, without meeting the limitation of inhibited mixing. The counter-current operation can give an overall solvent requirement of 2:1 solvent to sludge ratio.

4.5 Design and economic analysis of an industrial scale washing operation

Based on the discussions above, removal of crude oil using kerosene washing is a feasible option. Two stage counter-current and two stage batch-wise systems are the best possible methods to optimise the washing process to reduce the sludge volume and recovery of crude oil and kerosene. Either mode of operation resulted in an overall solvent requirements equal to twice the mass of sludge treated. It is therefore necessary to determine whether these two systems have any cost advantages over the existing disposal method of the sludge.

In order to compare the cost of the solvent washing treatment, it was necessary to design and cost an industrial scale washing facility.

4.5.1 Washing operation

Based on the result of this experimental work and the information gathered from NZRC, several unit operations had been identified for the design of an industrial scale washing operation using a batch type system. A simple flow diagram of the washing operation is presented in Figure 4.29. Each unit operation has been numbered and is outlined below.

Step 1:Tank Filling (1 hr)

> The tank would be filled with crude oil tank bottom sludge that is produced during maintenance operations. Solvent would be added and mixed with the sludge to achieve the desired solvent to sludge ratio.

Step 2: Mixing (1/3 hr.)

> When the tank is full, a further 15 minutes of mixing is necessary to ensure equilibrium is reached.

Step 3: Settling (1 hour)

The mixer is turned off and left to settle the solids for an hour.

Step 4: Extract Separation (1/2 hr.)

Draining of solvent mixture to the level above solid/solvent interface to achieved desired raffinate composition (below 50 % solvent).

Step 5: Solvent Filling (1/2 hr.)

Addition of equal amount of solvent for the second stage wash. The mixer is turned on when the tank is half full to facilitate mixing.

Step 6: Mixing (1/3 hr.)

When tank is full, another 15 minutes of mixing is required to ensure that equilibrium is reached for the second washing.

Step 7: Settling (1hr.)

The mixer is turned off and allowed the solids to settle again.

Step 8: Extract Separation (1/2 hr.)

The solvent mixture is drained to the level above solid/solvent interface and the desired raffinate composition (below 50 % solvent).

Step 9: Solids Removal (1/2 hr.)

The washed solids are removed from the washing vessel for disposal or further treatment to remove heavy metals.

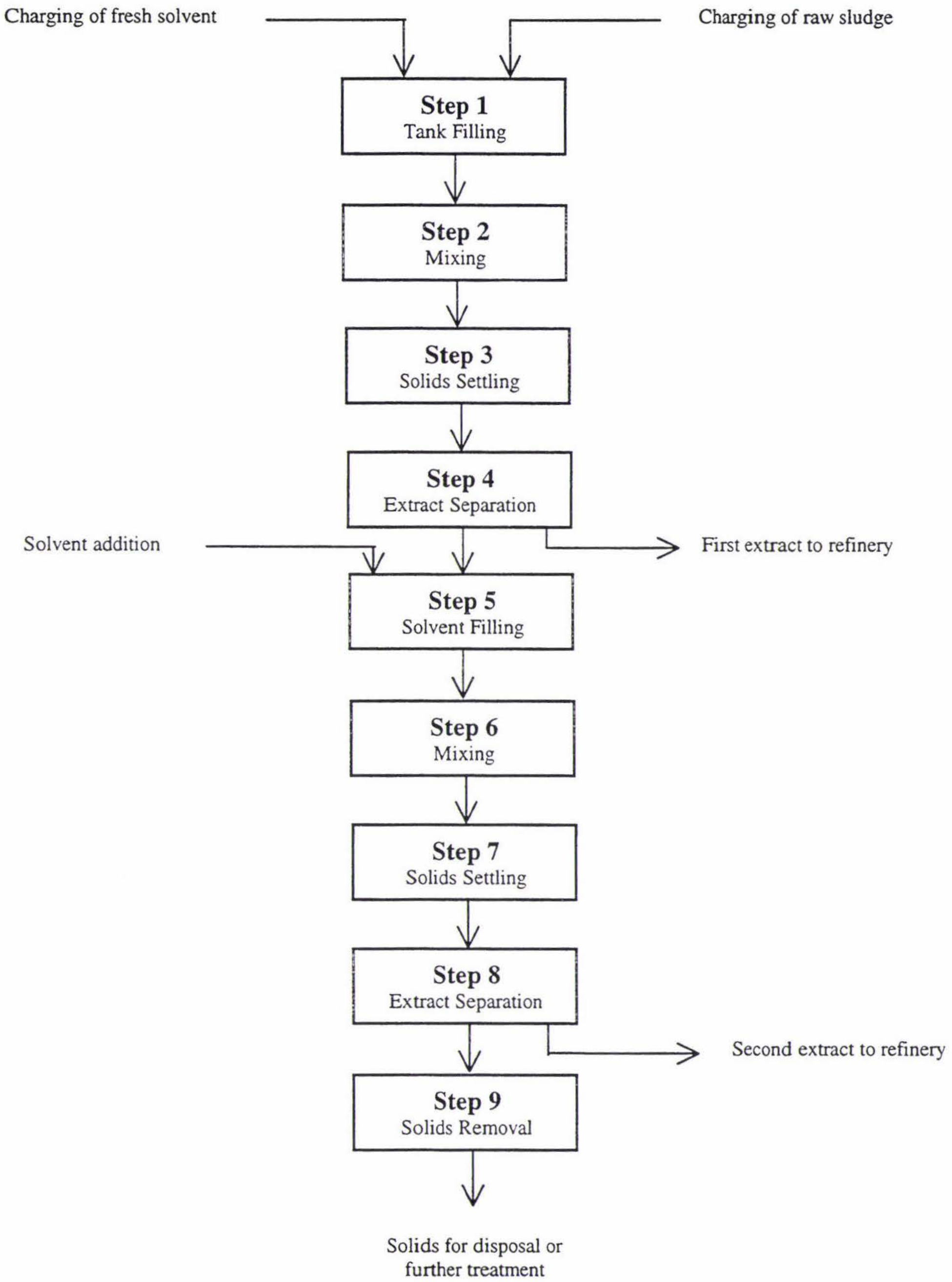


Figure 4.31 – Process flow design of solvent washing operation.

4.5.2 Design of washing vessel

Based on the process flow diagram outlined above, the equipment design is primarily for the washing vessel. Ulrich (1984) suggested that design of equipment is necessary to assess the capital cost needed for the washing operation. The design of the washing vessel was based on the assumptions outlined below.

Assumptions:

- 100 tonnes/year of crude oil tank bottom sludge is produced.
- The sludge is only generated during one month of cleaning and maintenance operations.
- The washing operation takes 5 hrs. and can operate for 10 hrs per day.
- Washing with 2:1 solvent to sludge ratio.

4.5.2.1 Washing vessel capacity and shape

Since the sludge is generated on a daily basis, a batch system vessel is best to treat the NZRC sludge. The estimated volume for the vessel is based on the amount of sludge generated per day during cleaning and maintenance operations. This also avoids storage costs and minimises the accumulation of a large volume of sludge prior to treatment or disposal.

Based on the assumptions above and as suggested by Ulrich (1984) and McCabe *et al.* (1993), a 6m^3 cylindrical washing vessel was calculated to treat all the sludge generated in one day. This is based on a two-batch per day (5-hr per batch) using a two stage (2:1 solvent to sludge ratio) washing operation. A 3kW motor is necessary to drive a 6-blade pitched turbine to completely mix the sludge with solvent. The impeller and power requirement is based on achieving vigorous mixing considering the nature of materials to be mixed. To achieve vigorous mixing, a 4-baffled washing vessel is necessary.

A cylindrical vessel with conical (45 - 60° angle) shape at the bottom is necessary to facilitate the collection and removal of washed solids after washing the sludge. The conical section at the bottom should have a 0.5m^3 capacity to accommodate the maximum solids that can be separated from the extract after settling. Figure 4.32 shows a schematic diagram of the 6m^3 capacity washing vessel based on the recommendations suggested by Ulrich (1984) and McCabe *et al.* (1993). All design parameters were calculated and are shown in Appendix A-4.

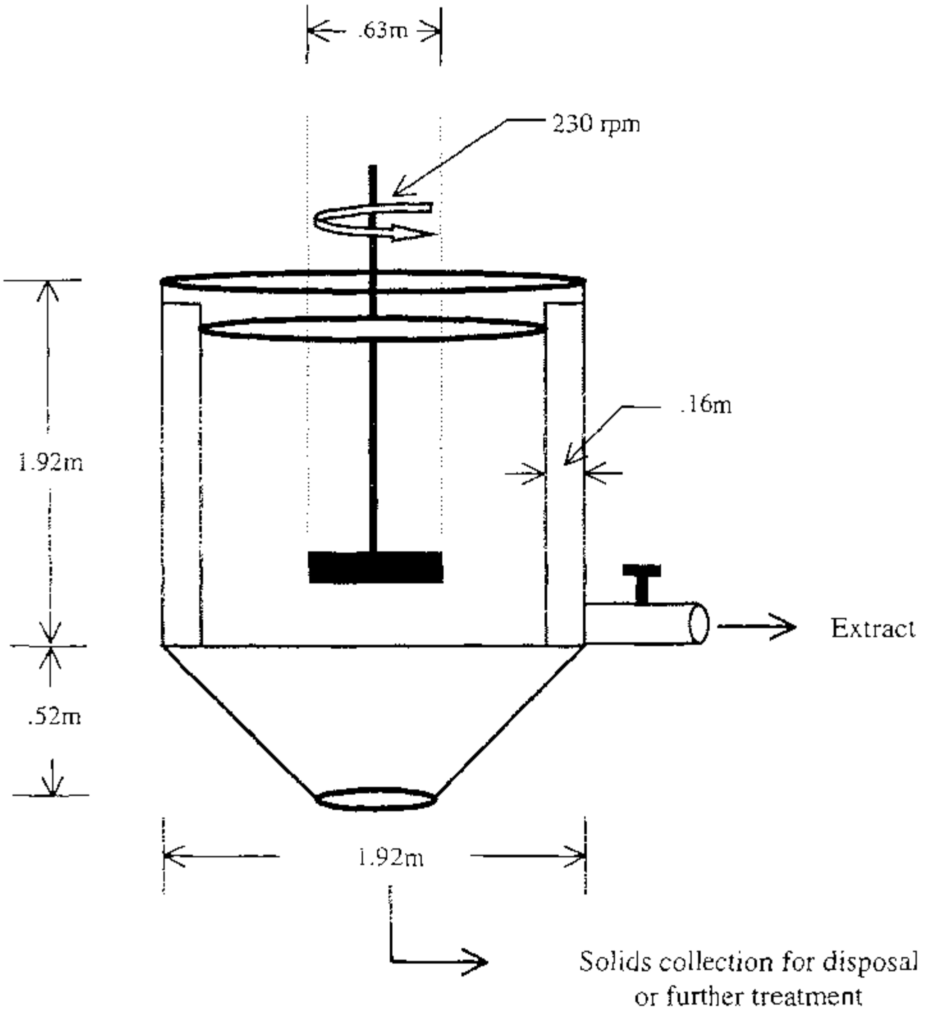


Figure 4.32 – Schematic diagram of a washing vessel.

4.5.3 Cost and economic analysis

Ulrich (1984) suggested that an economic evaluation of any project should be executed prior to implementation. Determination of the basic capital cost, operating costs and other economic benefits must be considered to determine if the washing process is financially feasible.

4.5.3.1 Capital cost estimate

The capital cost for the washing operation is focused on the design of the washing vessel. Total cost estimate and its breakdown is shown in Table 4.2. Derivation of this cost is also shown in Appendix A-4. The estimated costs of each piece of process equipment were based from Jebson and Fincham (1994).

Item	Estimated cost (NZ$)
6 m^3 cylindrical tank (3m high)	25,000
stirrer (3kW power consumption)	13,200
pump & motor	5,000
total capital cost	43,200

Table 4.2 – Estimated capital cost for a $6m^3$ washing capacity vessel.

4.5.3.2 Operating costs

Labour and power costs for this process have been assumed minimal as these are likely to be less than currently used in the cleaning and maintenance programme. The only cost to be considered in this process is the reprocessing of kerosene (NZ $ 16.00/tonne). Based on the average of 100 tonnes/year sludge generation, a total of 200 tonnes per year of kerosene will be used to treat the sludge on a 2:1 solvent to sludge ratio at two batches per use of kerosene. A maximum of 190 tonnes of kerosene can be reprocessed since some of the solvent will be lost due to retention in solids (at 25% retention). Table 4.3 shows the itemized operating cost and the calculation is shown in Appendix A-4.

Item	Cost (NZ $)
reprocessing of kerosene	3,040
cost of kerosene (Lost)	6,400
total Operating Costs	9,440

Table 4.3 – Estimated operating costs.

4.5.3.3 Recovery savings

The recovery of oil and volatile from the extract is an added benefit for the treatment of crude oil tank sludge. It is assumed that the oil and the light tops are also recovered during reprocessing of kerosene that goes through the normal process of the crude oil distillation. A maximum of 16 and 8 tonnes of crude oil and light tops, respectively, can be recovered based on the result on the characterisation of the sludge in Section 3.3.2. However, the savings associated with the recovery of the light tops was not included due to the volatility of the material and the difficulty in quantifying how much would be recovered in an industrial situation.

Washing the sludge would save on disposal costs due to the mass reduction achieved. A maximum of 59% mass reduction can be achieved, based on solids fraction of the sludge (Section 3.4). This would mean savings in terms of handling, hauling and landfill disposal costs. Table 4.4 shows the itemized savings that can be generated through solvent washing. Calculations are shown in Appendix A-4.

Item	Savings (NZ $)
crude oil (16 tonnes @ NZ$195/tonne)	3,120
disposal savings (handling,hauling & landfill @ $200/tonne)	11,800
total savings	14,920
overall net savings (total savings -total operating costs)	5,480

Table 4.4 – Estimated overall net savings.

4.3.3.4 Cost benefit analysis

Based on the assumptions made above, the total cost of investment of an industrial scale washing facility would be about NZ$ 43,200.00. This washing process would generate an annual overall net savings of NZ$ 5,480.00, which makes the treatment attractive. However, based on the financial analysis, the return of investment (ROI) is only 9.4% per annum with the assumption of 15-year life expectancy of the equipment at no salvage value. The ROI is probably less than the minimum attractive rate based on the prevailing market in New Zealand. The washing operation will break even but the decision to go ahead with industrial scale operation would depend on the continued availability of landfill sites and the benefits of onsite treatment of trade wastes.

4.6 Conclusion

The treatment and disposal of refinery crude oil tank sludge can be achieved through kerosene washing, which provides oil removal and volume reduction by an average of 76 %. This process takes advantage of the high solubility and rapid dissolution of the oil in kerosene. Equilibrium can be attained in less than three minutes and practically all the oil present is dissolved with constant mixing under ambient conditions.

The settling characteristics of the solids in the solvent and the availability of kerosene in oil refineries make it an obvious choice for washing operations. A minimum of 2:1 solvent to sludge ratio is required to be able to effectively attain equilibrium conditions and avoid mixing problems due to insufficient solvent. Based on a sensitivity analysis made on a theoretical mass balance of the system, the variation of the initial oil concentration of the sludge does not significantly affect the removal efficiency. However, solvent retention in the raffinate must be less than 50% w/w to achieve above 98% removal of the oil in the sludge. It is also possible to reuse the kerosene extracts and still produce an oil-free and metal- rich solids after extraction.

The recovery of oil, solvent and volatiles make this attractive. The effect of oil removal and volume reduction will also provide opportunity for easy waste management and disposal handling.

Although the treatment is less attractive economically based on the financial analysis, assessment of the feasibility of the process should not be limited in terms of its economic viability but also the cost to the environment and the company image.

The further treatment of the washed solids to remove heavy metals is the subject of the following chapter.

Chapter 5

Removal of Heavy Metals

5.1 Introduction

In the characterisation of the sludge outlined in Chapter 3, it was shown that the bulk of the heavy metals remain in the solid fraction after solvent washing. Removal of heavy metals is essential to meet the solids disposal land requirement for heavy metal concentrations if the sludge is to be ultimately discharged to land (NZ Dept. of Health 1992). Several opportunities for treatment to remove these metals prior to disposal exist. The metal rich solids fraction could be dried and used as a construction material through solidification with cement. This would isolate the heavy metals from the environment. Alternatively, extraction of heavy metals from soils has shown to be possible by leaching, using acids or chelating agents (Tuin and Tels 1990; Tessier *et al.* 1979; Allen and Chen 1993; Gibson and Farmer 1986 and Peters and Shem 1995).

This chapter investigates the effectiveness of heavy metal removal by acid washing. The heavy metals investigated were copper, nickel and zinc since they were found beyond acceptable levels for land disposal (Gozan *et al.* 1996 and White 1997). The effectiveness of heavy metal removal by the washing operation was assessed for varying acid-to-solid ratios, concentrations and type of acids. The amount of metals removed and final metal concentrations were measured.

5.2 Metal extraction using hydrochloric acid

Batch extractions were carried out using 1N hydrochloric acid to remove heavy metals from NZRC kerosene washed solids. The general procedure followed for the extraction of heavy metals is outlined below.

A known sample (2-10g) of NZRC kerosene washed solids sludge was oven-dried at 105°C for 1 hour. It was then placed in an Erlenmeyer flask which had been pre-soaked overnight with a mixture of dilute nitric and hydrochloric acid (1 part concentrated nitric acid + 2 parts concentrated hydrochloric acid + 9 parts distilled water) (USEPA 1992). A weight of 1N hydrochloric acid, depending on the desired acid-to-solid ratio (kg/kg), was added and shaken overnight in a Lab-Line® Incubator-shaker set at 140 rpm at a constant temperature of 20°C. The resulting acid solution was decanted and filtered with a pre-weighed # 41 Whatman filter paper. The filtrate was collected and directly tested for copper, nickel and zinc metals using the Atomic Absorption Spectrophotometer (AAS) following the standard method given by the USEPA (1992), which is also outlined in Section 3.5.3.4.

The filtered solids were oven dried at 105°C for 1 hour, and the final weight was taken to determine the weight loss caused by acid washing. The heavy metal concentration was measured in the acid washed solids by following the procedure for dry ashing and acid digestion method as discussed in Sections 3.5.3.1 and 3.5.3.2 above, to determine the remaining heavy metals after acid washing.

5.2.1 Extraction of heavy metals using different acids and concentrations

Different types of acids were evaluated to extract the heavy metals from the solvent washed NZRC sludge. Extraction of heavy metals using 1N hydrochloric acid, 1N sulfuric acid, 1N nitric acid, a 10:4 mixture of 1N hydrochloric & 1N nitric acids, 2.4N hydrochloric acid, 8N nitric acid and a 10:4 mixture of 2.4N hydrochloric & 8N nitric acids were performed to compare their removal efficiencies. The use of 2.4N hydrochloric acid, 8N nitric acid and acid mixtures was based on the procedure for the determination of total recoverable elements in solid samples (USEPA 1992). A combination of oxidising and non-oxidising mineral acids (HNO_3 & HCl) should ensure high metal release in the solution. The same general procedure as presented in Section 5.2 was followed to determine the heavy metals in the acid solution and the acid washed solids.

5.3 Results and discussion

The experiments outlined above enabled the investigation of the effectiveness of acid washing of the solvent washed sludge. Several different factors which could potentially influence the heavy metal solubilisation were assessed. These included acid-to-solid ratios, acid concentrations, type of acid and mixtures of acids. These are discussed in detail below. The key parameters used to assess the success of the acid washing were the extent of heavy metal removal and the final concentration of heavy metals in the solids after washing.

5.3.1 Effect of acid-to-solid ratio

Determination of the optimum acid-to-solid ratio was achieved by extracting heavy metals from the sludge using a 1N hydrochloric acid at different acid-to-solid ratios over the range 2:1 to 100:1 kg/kg. Three replicate sets of experimental trials were performed.

The amount of metals extracted by the acid divided by the total amount (metals extracted by acid + metals left in solids after acid leaching) was used to calculate the heavy metal removal efficiency. The removal efficiencies for copper, nickel and zinc are shown in Figures 5.1, 5.2 and 5.3, respectively. These figures demonstrate that an acid-to-solid ratio of 10:1 is necessary to achieve maximum removal of metals using 1N hydrochloric acid. Approximately constant removal efficiencies were achieved with acid-to-solid ratios greater than 10:1, with average removal efficiencies of 18%, 70% and 80% of copper, nickel and zinc, respectively.

The variability of the removal efficiencies is thought to be due to the variations of initial metal concentrations used for each sample. Similar observations were reported by Tuin and Tels (1990).

These figures show that increasing the acid-to-solid ratio above 10:1 does not give any advantage in terms of metal removal. Rather, it would increase the cost of extraction process due to the extra amount of acid required.

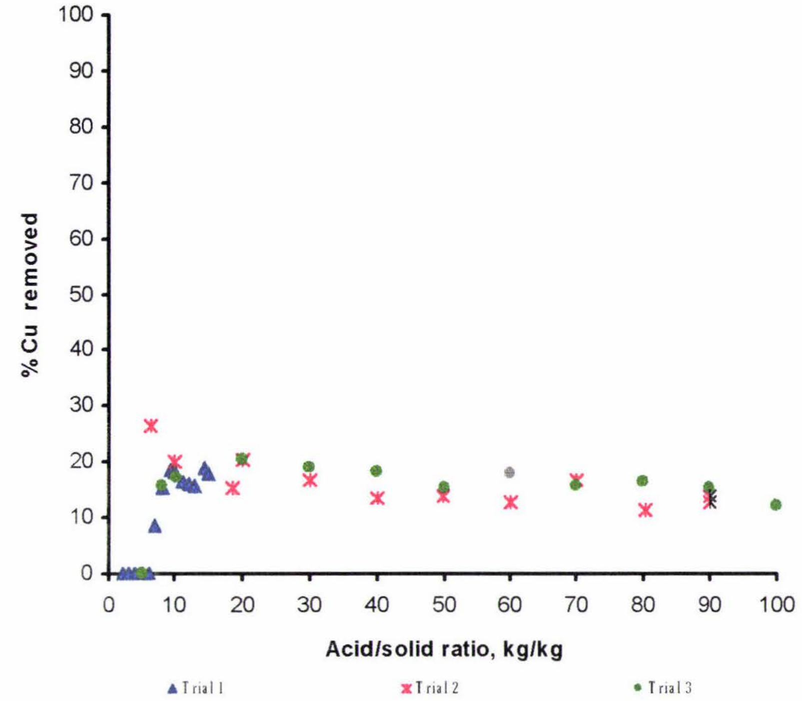


Figure 5.1 – Removal efficiency of copper in 1N hydrochloric acid solution.

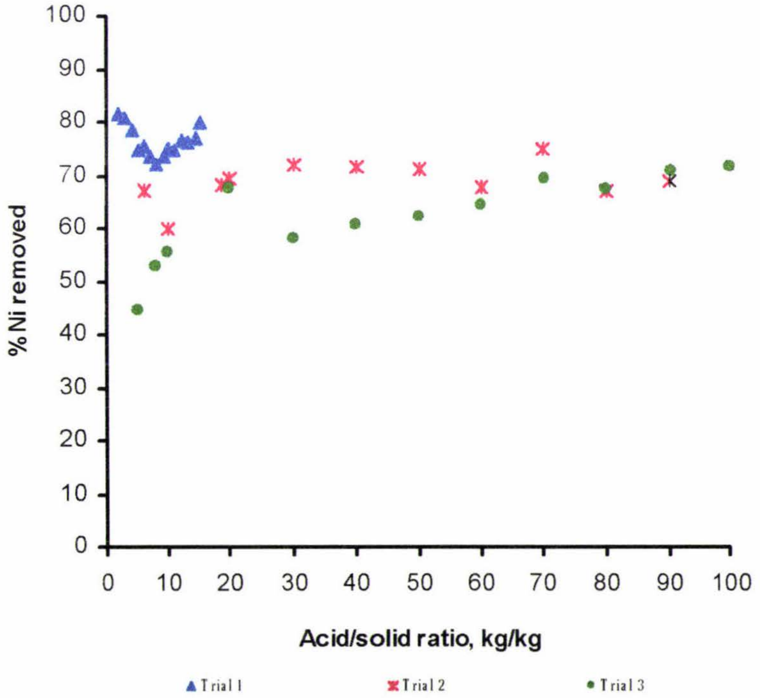


Figure 5.2 – Removal efficiency of nickel in 1N hydrochloric acid solution.

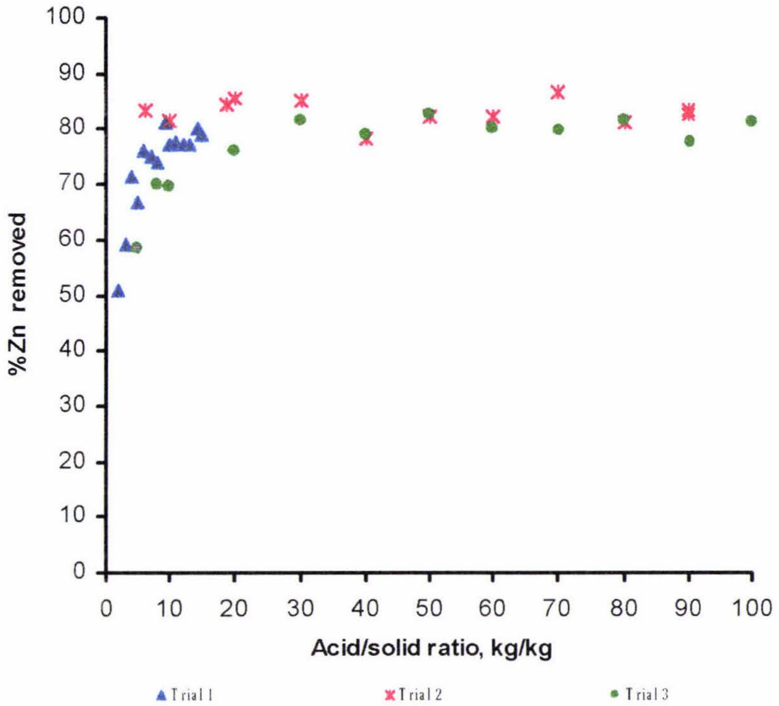


Figure 5.3 – Removal efficiency of zinc in 1N hydrochloric acid solution.

The use of 1N hydrochloric acid will allow removal of most of the zinc and nickel present in the solids. It is not as effective at solubilising copper from the solids. One possible reason for this is the reaching of the solubility concentration of copper and the other metals in the acid solution. This was checked by looking at the concentration of each metal in the acid solution.

With increasing acid-to-solid ratio and the pH maintained at <1, the concentration of copper, nickel and zinc in the acid solution at equilibrium is shown in Figures 5.4, 5.5 and 5.6. These clearly show that the effect of increasing the acid-to-solid ratio is the dilution of the solution.

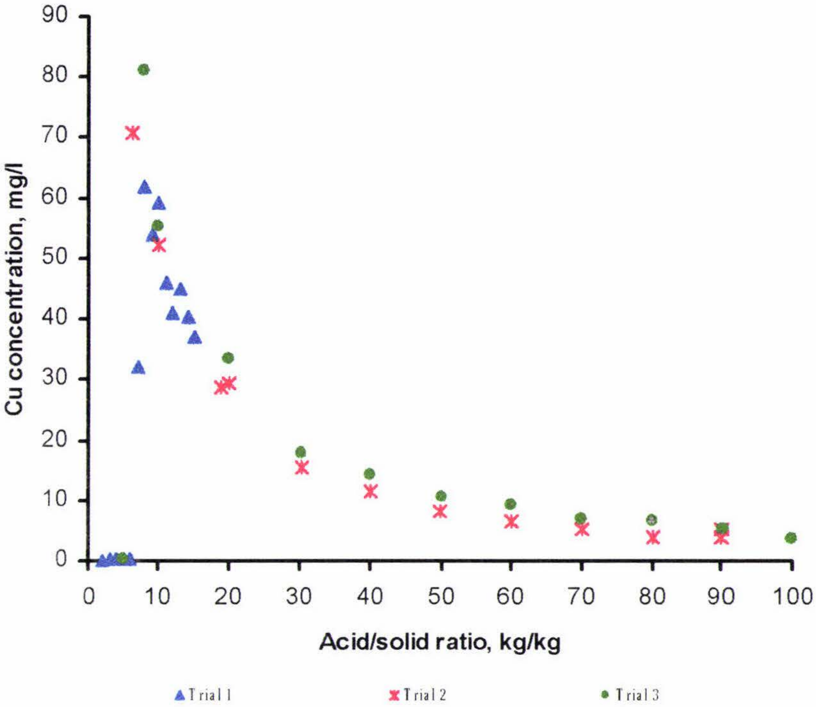


Figure 5.4 – Copper concentration in 1N hydrochloric acid solution.

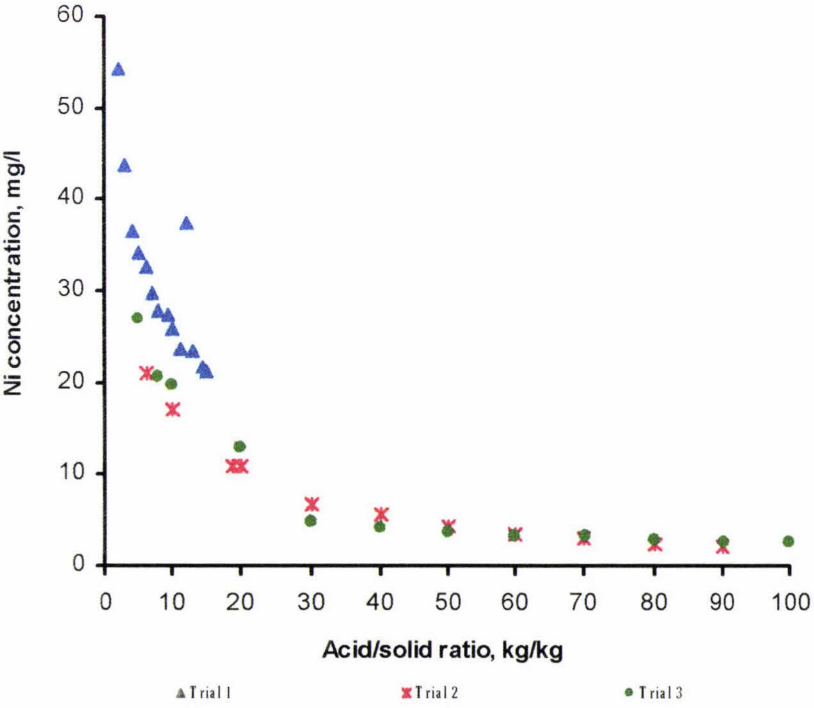


Figure 5.5 – Nickel concentration in 1N hydrochloric acid solution.

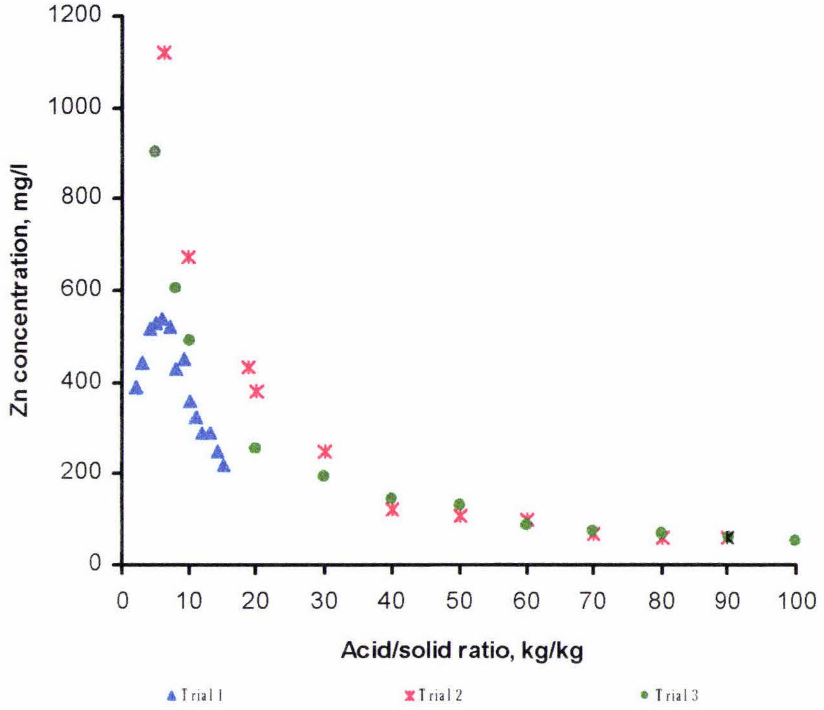


Figure 5.6 – Zinc concentration in 1N hydrochloric acid solution.

Another way of proving that increasing the acid-to-solid ratio does not solubilise any more of the metals contained in the sludge is by plotting the total amount of metals extracted into solution against the acid-to-solid ratios for copper, nickel and zinc. These are shown in Figures 5.7, 5.8 and 5.9, respectively. This is the maximum amount of copper, nickel and zinc that can be extracted using 1N hydrochloric acid per kg of solid material. These graphs show that the extraction of copper, nickel and zinc was not limited by its solubility at acid-to-solid ratios greater than 10:1. Release of the metals is solubility dependent below the 10:1 acid-to-solid ratio.

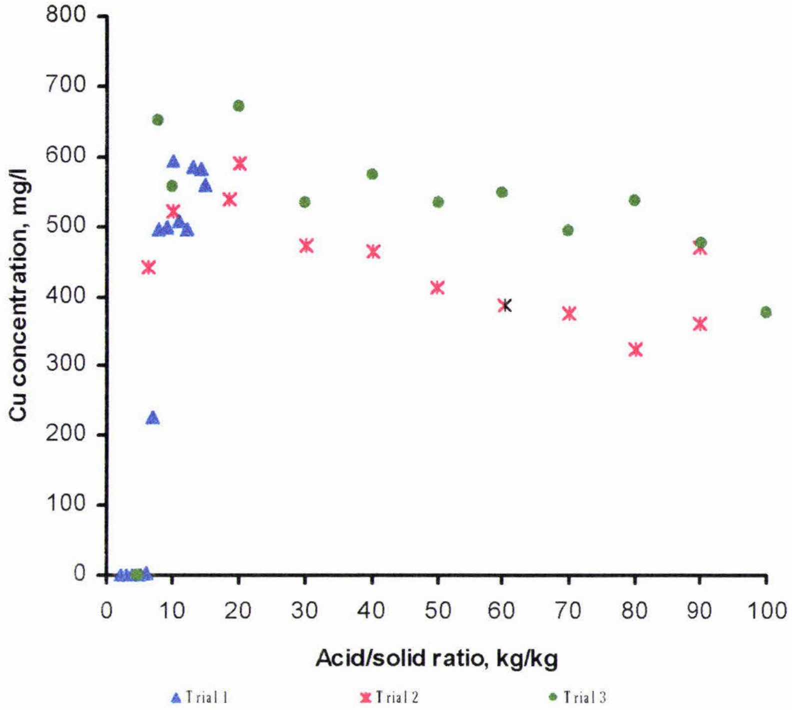


Figure 5.7 – Amount of copper solubilised per kg solids in 1N hydrochloric acid solution.

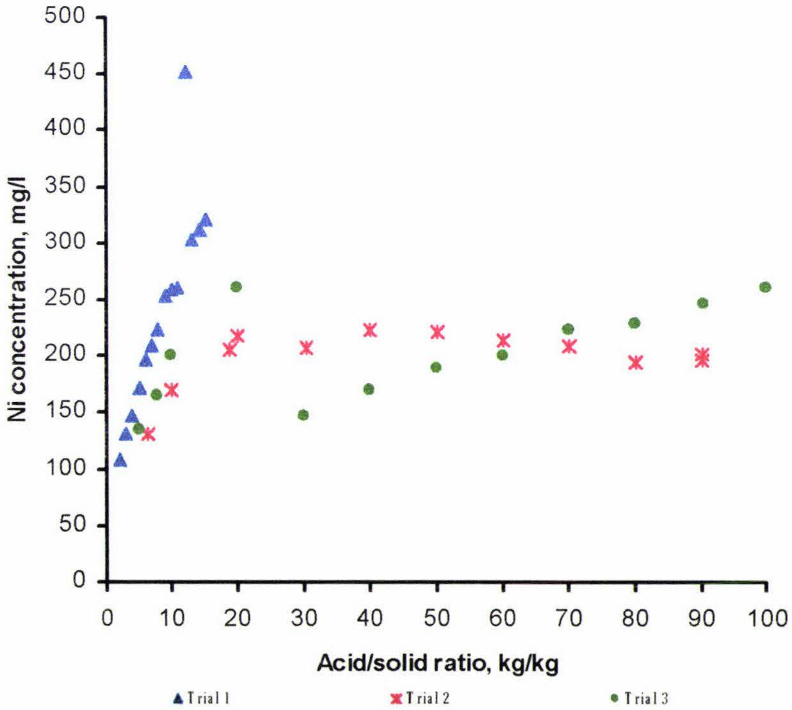


Figure 5.8 – Amount of nickel solubilised per kg solids in 1N hydrochloric acid solution.

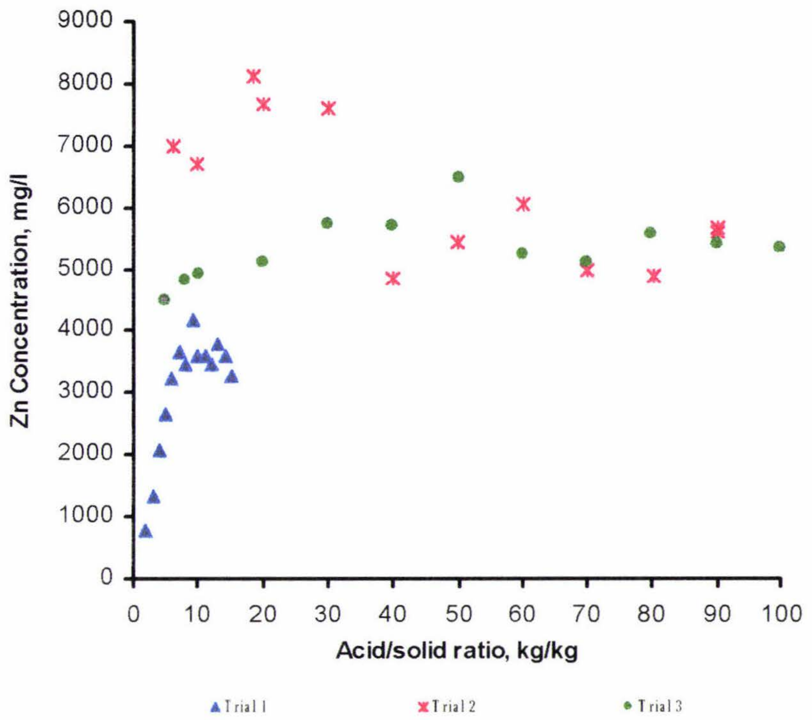


Figure 5.9 – Amount of zinc solubilised per kg solids in 1N hydrochloric acid solution.

Since the extraction of these heavy metals in general was not solubility dependent after 10:1 acid-to-solid ratio, the use of a chelating agent will not aid the metal removal process because the problem is in getting the metals into a water soluble form. Increasing the extraction temperature is not likely to help dissolve the remaining insoluble metals in the sludge. It will only speed up the dissolution processes and therefore allow shorter contact times (< 4 hrs.) to be used to attain equilibrium (Ireland 1998). These results also suggest that multi-step extractions will not give any advantage in terms of increasing metal removal efficiencies.

The average copper removal was 18% which was the lowest compared to 70% and 80% for nickel and zinc, respectively, as shown in Figures 5.1, 5.2 and 5.3. One possible reason for this could be that copper in general is unaffected by non-oxidising or non-complexing dilute acids in the absence of air. Hydrochloric acid is an example of this type of acid (Cotton and Wilkinson 1980; Brady and Humiston 1986). By using hydrochloric acid as an extractant, there is a possibility that copper metals might precipitate in the solution in the form of halide compounds (Cotton and Wilkinson 1980). This could therefore explain why copper compounds were solubilised during the total heavy metal measurement performed on the solids, using the dry ashing and acid digestion methods. This analysis uses both hydrochloric and nitric acids (a combination of non-oxidising and oxidising mineral acids). The solid samples were also oxidised in the furnace overnight using the dry ashing technique (Gorsuch 1970) for the destruction of all organic matter present in the solids prior to the acid digestion. This oxidation step and the combination of oxidising and non-oxidising acids most likely allowed all the copper compounds to be solubilised in the acid solution.

As expected, extraction of approximately 70% and 80% for both nickel and zinc shows removal efficiencies for these metals were high. This is consistent with most literature reports where hydrochloric acid solutions were used as extractants (Tuin and Tels 1990). Most compounds of these metals dissolve readily in non-oxidising mineral acids (Cotton and Wilkinson 1980; Brady and Humiston 1986). The formation of soluble metal-chloride complexes may contribute to the good extraction results using hydrochloric acid (Tuin and Tels 1990).

Therefore, the extractability of the three metals from the NZRC solvent washed sand using a 1N hydrochloric acid as extractant can be summarised as Zn > Ni > Cu. The use of a combination of oxidising and non-oxidising mineral acids presented the most likely method to improve the process and achieve greater removal efficiencies for copper from the solids.

5.3.2 Effect of metal extraction using different acids, mixture of acids and concentrations

Table 5.1 shows the comparative removal efficiencies using different types of acids, mixtures of acids and different concentrations. These experiments were aimed at showing the effectiveness of the individual acids (hydrochloric, nitric and sulfuric acid) at removing the metals from the solid material. Dilute acids (1N) were trialed as these would be preferred in industrial scale operations to reduce operating costs. The high concentration acid trials were performed to allow comparison of extraction effectiveness to the analytical digestion method.

Type of acid and concentration	% Zn removed	% Cu removed	% Ni removed
1N HCl	94	44	67
1N H_2SO_4	89	21	55
1N HNO3	91	39	64
10:4 mixture of 1N HCl & 1N HNO_3	96	42	70
2.4N HCl	94	51	78
8N HNO_3	99	99	89
10:4 mixture of 2.4N HCl & 8N HNO_3	99	95	89

Table 5.1 – Removal efficiency using different acids, mixtures and concentrations.

Based on the extraction efficiencies using different low strength (1N) acids, hydrochloric acid performed the best with an average removal of 44%, 67% and 94% for copper, nickel and zinc, respectively. This was followed by nitric acid, with an average removal of 39%, 64% and 91% for copper, nickel and zinc, respectively. Sulfuric acid had the lowest average of 21%, 55% and 89% for copper, nickel and zinc, respectively.

The removal efficiencies of zinc and copper using 1N hydrochloric acid were higher than achieved at the same acid-to-solid ratio in the previous experiment (see Section 5.2). The nickel removal was within the range of the extraction efficiencies achieved in the previous experiment. This increase in zinc and copper removal is thought to be caused by the heterogeneity of the sludge sample used and slight changes made in the procedure for acid extraction.

The solid sample used in this experiment came from a different batch of kerosene washed NZRC sludge as compared to the previous experiment and could therefore have different solids composition and initial metal concentrations. Although the entire raw sludge sample used in this study was completely mixed prior to any analyses being made, it did not guarantee a uniform solid composition after washing with kerosene. The amount of solid sample used in this experiment was also doubled compared to the previous experiment and therefore results obtained were more accurate.

The acid washed solids were rinsed with distilled water to remove the acid solution after filtration. This could remove error due to the retention of solubilised metals in the solids and the filter paper. Assuming that the moisture content of the filtered solids material is 25%, an error of 3% could occur because metals that are solubilised are retained in the solids fraction during sample drying. By rinsing the solids after acid washing, this error was avoided. This could further explain the difference for the removal efficiencies of the metals from the previous experiments that were performed without rinsing.

The removal efficiency using a mixture of 1N hydrochloric acid and 1N nitric acid (10:4 HCl-to-HNO_3 ratio) is shown in Table 5.1. The results were similar to using only 1N hydrochloric acid or 1N nitric acid. It should be noted that this mixture gives a total acid concentration of 1 molar but the actual concentration in the mixture is 0.7N hydrochloric acid and 0.3N nitric acid.

The use of 2.4N hydrochloric acid increased the average removal efficiencies for copper and nickel to 51% and 78%, respectively. However, the average zinc removal efficiency was not improved.

Using 8N nitric acid removed practically all the zinc and copper metals from the solids while nickel removal efficiency was increased to 89%. Using a mixture of 2.4N hydrochloric and 8N nitric acids (10:4 ratio), removal efficiencies of zinc and nickel were similar to using only 8N nitric acid. Copper removal was decreased from 99% to 95%. This was due to the dilution effect of combining the acids. The final concentration of acids in the mixture was 1.7N hydrochloric acid and 2.3N nitric acid.

The differences of using this mixture in metal extraction from the analytical procedure for the determination of total recoverable elements in solid samples (USEPA 1992) are outlined below.

- destruction of organics through the dry ashing technique (Appendix A-2).
- oxidation of inorganic compounds at 450-500°C (Appendix A-2).
- heating the acid mixture under reflux for 30 minutes at 85°C (Appendix A-3).

The oxidation process achieved by the dry ashing is likely to be the cause of the solubilisation of the remainder of the metals.

Further trials should be undertaken to find the optimal acid mixture and strength to achieve copper and nickel removal from the sludge. It is suggested that a combination of hydrochloric and nitric acid at concentrations between those investigated in this study could be effective.

5.3.3 The effect of acid washing to solids

Acid washing can cause severe damage to soil or sand structure. Tuin and Tels (1990) reported a weight loss of up to 13% of the total solids that had dissolved in hydrochloric acid during leaching experiments. Muller (1986) reported a weight loss of up to 20% in a similar operation.

In this study, the dissolution of the solids during acid washing was determined. A maximum of 59% dissolution of the original weight of the solids was observed. Figure 5.10 shows the extent of solids dissolution at a range of acid-to-solid ratios. A dramatic increase in weight loss was observed up to 30:1 acid-to-solid ratio. Beyond this, an average of 59% weight loss was observed, as shown in Figure 5.10.

The averaged weight loss observed using different types of 1N acids and the mixture of hydrochloric and nitric acids at 10:1 acid-to-solid ratio was 45% (see Table 5.2). This was higher compared with the result of the previous experiment of 36% at the same acid-to-solid ratio (see Figure 5.10). The reason for this was thought to be the variation of solids composition. The sample came from a different batch of kerosene washed NZRC sludge and the amount of sample used was greater. Hence greater accuracy during weighing was achieved.

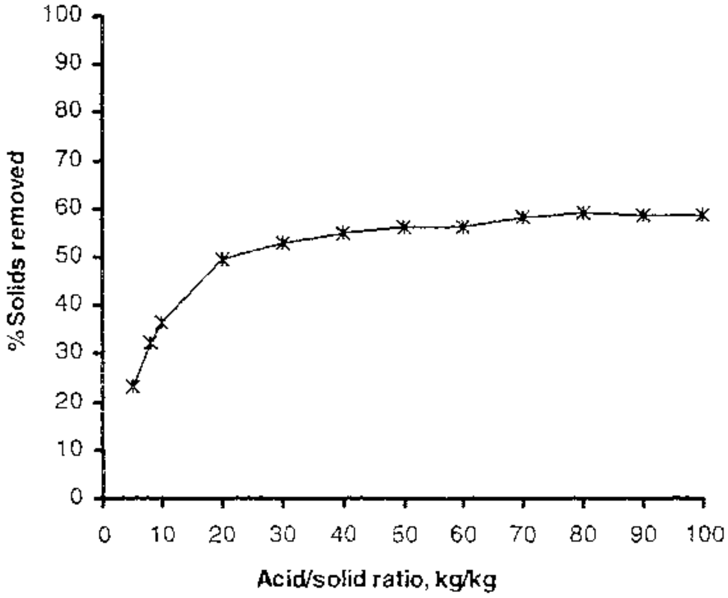


Figure 5.10 – Weight loss during acid washing with 1N hydrochloric acid.

An average of 63% solids loss was observed after acid washing using 2.4N of hydrochloric acid, 8N nitric acid and their mixtures, compared with an average 45% weight loss using different 1N acid concentrations as shown in Table 5.2. Although it was higher than observed in the previous experiment (average of 59%), this result is comparable with the weight loss observed at higher acid-to-solid ratios using 1N hydrochloric acid beyond 30:1 ratio as shown in Figure 5.10.

The organic material in the solids would be dissolved in the acid solution during the washing operation (Tuin and Tels 1990). To check this explanation of the solids lost, the kerosene washed NZRC solids were oxidised in the furnace overnight at 450 - 500°C. The physical appearance of the oxidised sludge can be seen in Figure 5.11. An average weight loss of 20% was observed. Therefore, only 33% of the solids lost during acid washing can be attributed to the organic content of the solids.

Based on this observation, weight reduction is not only due to the organic content that dissolves in the acid solution, but also the dissolution of inorganic compounds present in the solids.

Type of acid and concentration	**% wt. Loss**
1N HCl	45
1N H_2SO_4	44
1N HNO_3	45
10:4 mixture of 1N HCl & 1N HNO_3	45
2.4N HCl	63
8N HNO_3	63
10:4 mixture of 2.4N HCl & 8N HNO_3	63

Table 5.2 - Percent weight loss using different acid and concentration.

This solids reduction has three major impacts on an industrial washing process. Firstly, the mass of the treated solids is reduced by 60%. This means less final solids require disposal. Secondly, after extraction the acid solution contains significant amount of organic and inorganic compounds. This will affect the acid reusability and must be considered during the treatment and disposal of the spent acid solution. Thirdly, as some of the solid material is removed, the metals concentration in the remaining solids will be higher than expected with the metal removal efficiencies allowed. This is discussed in the next section.

Figure 5.11 – Oxidised kerosene washed sludge at 450-500°C.

5.3.4 Metal concentration in solids after acid extraction

Metal analyses were performed in the solids after acid washing with 1N hydrochloric acid. These results are given in Figures 5.12, 5.13, and 5.14.

Because of the effect of the solids loss, the concentration of the metals left in the washed solids was higher than expected. This was the reason why copper concentrations in the solids after acid washing were higher than the total copper measurement of the unwashed solids.

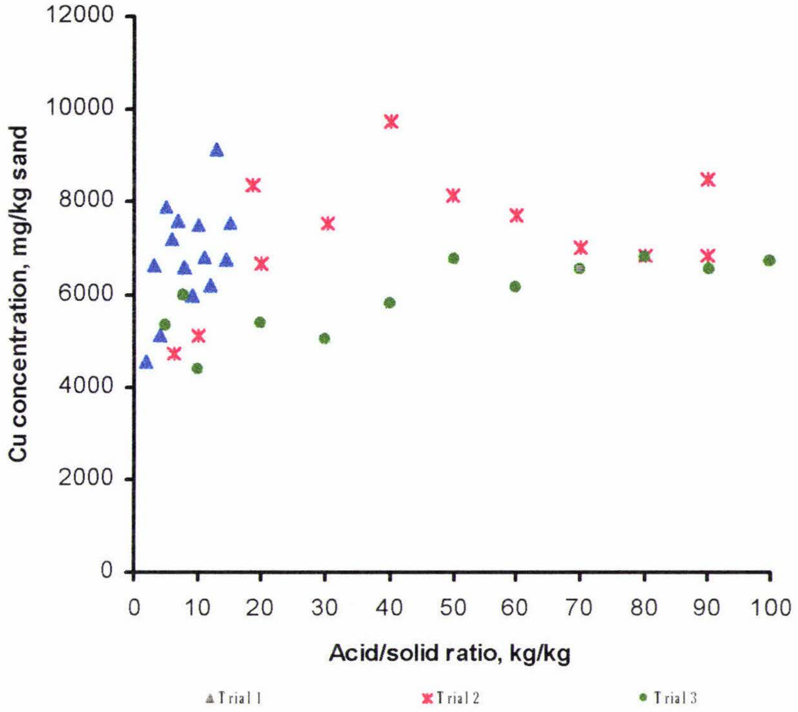


Figure 5.12 – Copper concentration in sand after acid washing.

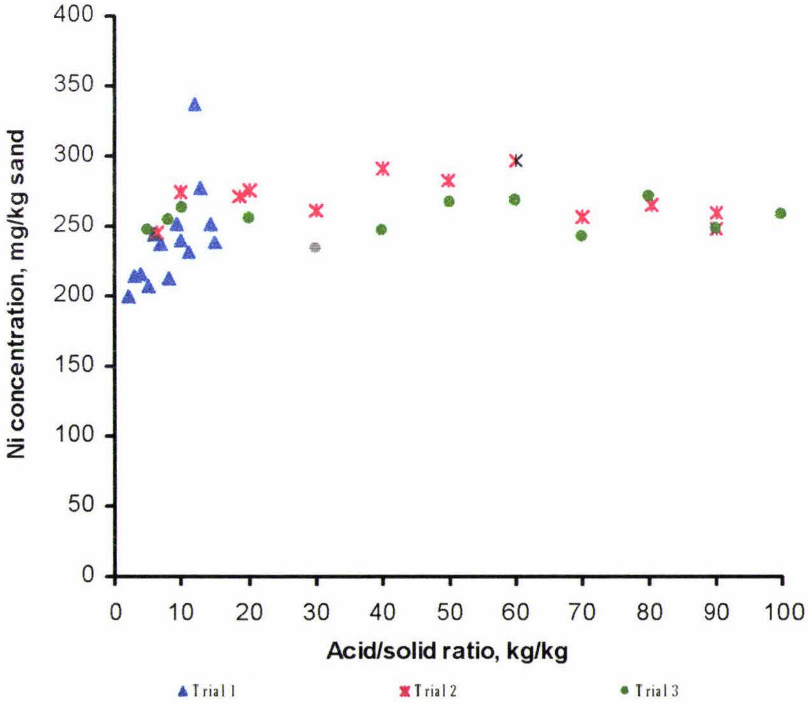


Figure 5.13 – Nickel concentration in sand after acid washing.

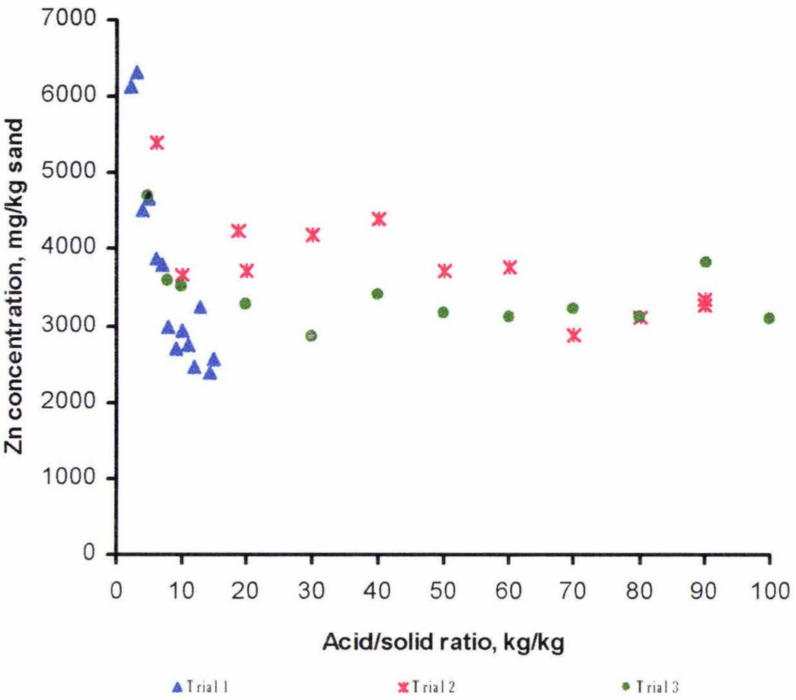


Figure 5.14 – Zinc concentration in sand after acid washing.

The average initial concentrations of copper, nickel and zinc in the solids before acid washing were 2,704 mg/kg, 150 mg/kg and 3,385 mg/kg, respectively obtained from the total of metals in solution and acid washed solids. Metal concentrations in the solids after acid washing with different 1N acid concentrations, mixtures, and 2.4N hydrochloric acid increased except for zinc, as shown in Table 5.3.

Both copper and nickel concentrations were reduced, only after using 8N nitric acid and a mixture of 2.4N hydrochloric & 8N nitric acids. Based on the results in Table 5.3, in order to meet the guidelines for sludge disposal defined by NZ. Dept. of Health (1992) (Cu < 1,000 mg/kg, Ni < 200 mg/kg and Zn < 2,000 mg/kg), 8N nitric acid or a mixture of 2.4N hydrochloric and 8N nitric acids was necessary. Although zinc can be reduced to the acceptable level using only 1N hydrochloric acid, the problem lies with copper and nickel. Using high acid concentrations will increase treatment cost and should be considered before any industrial application. More work is required to show the optimum acid strength and mixture needed to achieve effective copper and nickel removal.

Type of acid and concentration	Zn mg/kg	Cu mg/kg	Ni mg/kg
Kerosene washed sludge	3,385	2,704	150
1N HCl	763	4,745	206
1N H_2SO_4	1,177	6,536	205
1N HNO_3	1,331	4,930	195
10:4 mixture of 1N HCl & 1N HNO_3	615	5,998	182
2.4N HCl	1,096	6,855	198
8N HNO_3	137	84	86
10:4 mixture of 2.4N HCl & 8N HNO_3	168	981	97

Table 5.3 – Metal concentration after washing with different acids and concentration.

5.4 Conclusion

The extraction efficiency using different types of 1N acids follows in the order of HCl > HNO_3 > H_2SO_4. The extractability of the three metals from the NZRC kerosene washed sand using different types of 1N acids as extractants follows the order of Zn > Ni > Cu. The minimum effective acid-to-solid ratio was found to be 10:1. Increasing this ratio does not improve removal efficiencies since the release of copper, nickel and zinc in the acid solution is not solubility dependent above this ratio.

The acid washing process dissolved a significant portion of the solid fraction (up to 59% of its original weight). At higher acid concentrations and a lower acid-to-solid ratio (10:1 ratio), solids dissolution of 63% was observed after acid extraction.

The impact of weight loss during acid washing should be taken into consideration because instead of decreasing the concentration of heavy metals in the final waste product, it can result in raising the concentration. This occurred in the experiments for copper and nickel. Using 1N different acids or 2.4N hydrochloric acid did not reduce the metal concentration of copper and nickel but rather increased it. Zinc concentration was reduced to a level that meets the land disposal guidelines. Acid washing with 8N nitric acid and a mixture of 2.4N hydrochloric & 8N nitric acids reduces the three metal concentrations to levels within the acceptable guidelines for land application set by the NZ. Dept. of Health (1992).

Oxidation through incineration of the NZRC crude oil tank sludge prior to acid washing is possible to remove the organic content of the sludge. Though the presence of the crude oil serves as the fuel for combustion and could facilitate easy removal of heavy metals during acid extraction, this is not an option due to air emission problems in burning the sludge.

It is suggested that future experimental work be undertaken to identify the optimum acid mixture and strength to meet the disposal requirements, but still minimise acid utilisation. Further investigations are required to determine the potential of acid reuse in an industrial scale operation. Once this information is available, an economic feasibility of the treatment process can be undertaken. However, it should be noted that economic viability should not be the only basis for decision. It should be viewed in the total context of the environment and include consideration of the expected availability of contaminated landfill sites.

Chapter 6

Closure

6.1 Conclusions

This study has identified several alternative treatment processes to achieve the stabilisation of refinery crude oil tank sludge. The sludge's physical and chemical properties were studied and identified.

A model which optimises the kerosene washing of the sludge was developed and validated against experimental data. The model took advantage of the high and rapid solubility of the oil in kerosene. It was found that a minimum of 2:1 solvent to sludge ratio was required to effectively remove the oil in the sludge. Based on the sensitivity of the washing operation to the process variables, the initial oil concentration of the sludge did not significantly affect the removal efficiency. The retention of solvent in the raffinate must be under 50% w/w to achieve above 98% oil removal efficiency.

The effect of kerosene washing reduced the sludge volume and mass by 76% and 59%, respectively. The removal of oil by solvent washing left an oil-free and metal-rich solids fraction of the sludge. It was shown that an industrial scale operation is possible as an alternative treatment for oily sludge in oil refineries.

The oil-free and metal-rich washed solids provided an opportunity to remove the heavy metals using mineral acids. It was found that extraction efficiency using different 1N acids followed the order of HCl > HNO_3 > H_2SO_4. The extractibility of the three metals from the NZRC kerosene washed sand using different 1N acids as extractants followed the order of Zn > Ni > Cu. The minimum effective acid-to-solid ratio was 10:1.

It was also found that the acid washing process had significantly dissolved the solids fraction (up to 59% of the original weight). The impact of dissolution of solids into the acid solution resulted in even higher metal concentration in the final waste product than present in the raw sludge. The use of 8N nitric acid and a 10:4 mixture of 2.4N hydrochloric and 8N nitric acids successfully reduced the metal concentrations to levels within the acceptable guidelines set by the NZ Dept. of Health (1992) for land application.

6.2 Suggested future study

This study has identified several areas which require further investigation before industrial application can be made for the stabilisation of refinery crude oil tank sludge. These are outlined below;

- Improve the settling time of the solids during solvent washing to reduce washing time.
- Improve solvent separation in the solids after solvent washing to minimise solvent losses and attain higher removal efficiencies.
- Investigate the drying time of kerosene in the washed NZRC solids.
- Investigate the possibility of using the oil-free and metal rich solids as a construction material to isolate the heavy metals from contamination to the environment.
- Investigate the maximum efficiency for the reuse of used solvent (extracts) for further optimisation.
- Investigate the optimum acid mixture and strength to effectively reduce the heavy metals and still meet the disposal requirement set by the regulatory authorities.

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Appendix A-1

Dean and Stark method

Introduction:

This test covers the determination of water in soil by the Dean and Stark method. The material to be tested is heated under reflux with a water immiscible solvent, which co-distils with the water sample. Condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and the solvent returning to the still.

Apparatus: Quickfit round bottom flask (500ml)
Heating mantle
Water trap (10ml)
Condenser (400mm)

Reagents: Petroleum distillate solvent (e.g. light tops)
5% boiling 90-100°C and 90% boiling below 210°C

Procedure:

Measure 100 ± 1g of sample into a 500ml round bottom flask. Add 100ml of solvent carrier to the flask. Connect flask, trap and condenser together as illustrated in the experimental. Turn heat to full until boiling, then reduce heat setting to 9. Continue distillation until no water is visible in any part of apparatus except in the trap, and the volume of water remains constant for 5 minutes. When evolution of water is complete, allow trap and contents to cool. Dislodge any water adhering to the sides of the trap with a wire rod and transfer them into the water phase. Read the volume of water to the nearest scale division.

Appendix A-2

Dry ashing method

A dry ashing procedure varies for a wide range of samples, the procedure following is satisfactory method for the use on oil sludges.

Procedure:

1.Weigh 5 to 10g of dried sample into a suitable crucible: it is desirable for the sample to be thinly spread over a fairly large area. Silica is probably the most generally useful construction material for the ashing vessel.

2. Add the ashing aid if appropriate (see note below).

3. Dry and thoroughly char the sample. This is best carried out with an infra red lamp, but heating on a hot plate or very careful heating with a burner can be used alternately. The sample must not be allowed to ignite, and if a burner is used, care must be taken to avoid local overheating.

4. Introduce the ashing vessel into a furnace heated about 450°C. Slightly higher temperatures – about 500°C may be used in some cases.

5. Heat overnight, or for a similar period. If unoxidized organic matter remains moisten the residue with water, or diluted nitric acid (1+2), evaporate to dryness on a water bath and return to the furnace for a further period.

6. When a suitable ash has been obtained, cool the basin, and moisten the contents with a little water. Very carefully add 10ml of (1+1) HCl and evaporate to dryness on a water bath. Take up the residue in very dilute HCl (1+9) or other suitable solvent.

The elements to be determined remain in the residue of the flask, and can be treated further as appropriate.

Note: It is most convenient to add the ashing aid as a large volume of diluted matrial so that all parts of the sample are thoroughly wetted. Typical concentrations and amounts would be 10ml of 10% sulphuric acid solution or 10ml of 7% $Mg(NO_3)_2.6H_2O$ solution, for 5 g sample. When the addition has been made, the ashing vessel is heated gently to drive off the added water, and then the ashing proceeds as described above.

Appendix A-3

Acid digestion techniques

A. Sample collection, preservation and storage

1. Prior to sample collection, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration, acid preservation, etc. should be performed at the time of sample collection or as soon thereafter as practically possible.

2. For the determination of dissolved elements, the sample should be filtered through a 0.45-μm membrane filter. Use a portion of the sample to rinse the filter assembly, discard and then collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to a pH of less than two.

3. For the determination of total recoverable elements in aqueous samples, acidify with (1+1) nitric acid at the time of collection to a pH of less than two. The sample should not be filtered prior to analysis.

4. Solid samples usually require no preservation prior to analysis other than storage at 4°C.

Note: Samples that cannot be acid preserved at the time of collection because sampling limitations or transport restrictions, should be acidified with nitric acid to $pH < 2$ upon receipt in the laboratory (normally, 3ml of (1+1) nitric acid per liter of sample is sufficient for most ambient and drinking water samples). Following acidification, the sample should be held for a minimum of 16 hr before withdrawing an aliquot for sample processing.

B. Sample preparation – for dissolved elements

For the determination of dissolved elements in drinking water, wastewater, ground and surface waters, take a 100ml (± 1ml) aliquot of the filtered acid preserved sample, add 1ml of concentrated nitric acid. The sample is now ready for analysis. Allowance should be made in the calculations for the appropriate dilution factors.

Note: If a precipitate is formed during acidification, transport or storage, the sample aliquot must be treated using the procedure in A.

C. Sample preparation – for total recoverable elements

C.1

For the determination of total recoverable elements in water or waste water, take a 100ml (± 1ml) aliquot from a well mixed, acid preserved sample and transfer it to a 250ml Griffin beaker. Add 1ml of concentrated HNO_3 and 0.5ml of concentrated HCl. Heat the sample on a hot plate at 85°C until the volume has been reduced to approximately 20ml, ensuring that the sample does not boil (A spare beaker containing 20ml of water can be used as a gauge).

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered beaker containing 50ml of water located in the center of the hot plate can be maintained at approximately but no higher than 85°C. Evaporation time for 100ml of sample at 85°C is approximately 2hr with the rate of evaporation rapidly increasing as the sample volume approaches 20ml.

Cover the beaker with a watch glass and reflux for 30 minutes. Slight boiling may occur but rigorous boiling should be avoided. Allow to cool and quantitatively transfer to either a 50ml volumetric or a 50ml class A stoppered graduated cylinder. Dilute to volume with ASTM type I water and mix. Centrifuge the sample or allow to stand overnight to separate insoluble material. The sample is now ready for analysis. Prior to the analysis of samples the calibration standards must be analysed and the calibration verified using a Quality Control sample. Once the calibration has been verified, the instrument is ready for sample analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterised, samples should be analysed as soon as possible after preparation.

C.2

For the determination of total recoverable elements in solid samples (sludges, soils, and sediments), mix the sample thoroughly to achieve homogeneity and weigh accurately a 1.0 ± 0.01g portion of the sample. Transfer to a 250ml Phillips beaker. Add 4ml (1+ 1) nitric acid and 10ml (1+4) HCl. Cover with a watch glass. Heat the sample on a hot plate and gently reflux for 30 min. Very slight boiling may occur, however, vigorous boiling must be avoided to prevent the loss of the HCl azeotrope.

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50ml of water located in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C.

Allow the sample to cool and quantitatively transfer to either 2 - 100ml (± 1ml) volumetric flask or a 100ml class A stoppered graduated cylinder. Dilute to volume with ASTM type I water and mix. Centrifuge the sample or allow to stand overnight to separate insoluble material. The sample is now ready for analysis. Prior to analysis of samples the calibration standards must be analysed and the calibration verified using a Quality Control sample. Once the calibration has been verified, the instrument is ready for sample analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterised, samples should be analysed as soon as possible after preparation.

Note: Determine the percent solids in the sample for use in calculations and for reporting data on a dry weight basis.

Appendix A-4

Calculations

A. Design of washing vessel

A.1 Washing vessel capacity

Assumptions

- 100 tonnes/month generation.
- Washing operation takes 5 hrs. and can operate for 10 hrs. per day.
- Washing with 2:1 solvent to sludge ratio.
- 2 batches per day operation

Sludge properties

- 41% = solids fraction of raw sludge.
- 1,259 kg/m^3 = bulk density of raw sludge.
- 2,333 kg/m^3 = particle density of washed solids.
- 780 kg/m^3 = density of kerosene.

A.2 Total volume estimate per batch

Sludge volume per batch

100 tonnes/month x 1month/30 days) x 1 day/2 batch x 1000 kg/1tonne

= 1,667 tonnes/batch

Solving for the volume;

V_b = 1,667 kg/1,259 kg/m^3

= 1.32 m^3

Volume of kerosene

For a 2:1 solvent to sludge ratio and solving for the volume;

$Vs = (1{,}667\ \text{kg} \times 2)/780\ \text{kg/m}^3$

$= 4.27\ \text{m}^3$

Total volume $= 1.32\ \text{m}^3 + 4.27\ \text{m}^3$

$= 5.6\ \text{m}^3$ (This will correspond to the working tank volume = V_t)

A.3 Dimensions of cylindrical vessel

Estimate of vessel diameter

Since $D_t = H_t$ as suggested by Ulrich (1984) & McCabe *et al* (1993).

Using the general formula for a cylindrical shape ($V = \pi D^2 h/4$) and substituting $H_t = D_t$;

$$D_t = \frac{(5.6\ \text{m}^3)^{1/3}\ (4)}{\pi}$$

$= 1.92\ \text{m}$

Estimate of impeller diameter and baffle width

As suggested by Ulrich (1984) and McCabe *et al* (1993), $D_{\text{impeller}} = 1/3\ D_t$ and

baffle width = $1/12\ D_t$

Therefore:

$D_{\text{impeller}} = 1/3\ (1.92)$

$= .63\ \text{m}$

baffle width = 1/12 (1.92)

$= .16\ \text{m}$

Volume estimate for the conical section

Since 41% of raw sludge is solids;

Weight of solids = 1,667 (.41)

= 683 kg/batch

Using the formula for density;

Volume of solids = 683 kg/2,333

= $.3\ m^3$ say $.5\ m^3$

Height estimate for the conical section

Using the general formula for the volume of a cone and solving for H_c
$H_c = V(3)(4)/\pi D^2$

$= (.5)(3)(4)/\pi(1.92)^2$

$= .52$ m

Type of impeller

McCabe *et al.* (1993) suggested that to attain vigorous liquid/liquid mixing containing solids, a 6 pitched turbine impeller is required to achieve complete mixing. A pitched blade will generate an axial force towards the bottom of the tank to disperse the solids particle.

A.4 Estimate of power requirement

An empirical method is used to calculate the power requirement as suggested by Ulrich (1984). For a vigorous liquid/liquid mixing, it is suggested that power requirement can be estimated using the formula;

$P = 0.8\ V_t^{\ 0.8}$

where:

P = power requirement
V_t = working tank volume

Substituting values;

$P = .8\ (5.6)^{0.8}$

$= 3$ kW

Using the formula for Power Number; (Ulrich, 1984 and McCabe *et al*, 1993);

$P_N = P/N^3 \delta_s\ D_i^5$

Where:

P_N = power number
N= speed of rotation
δ_s = density of kerosene
P = power requirement

At high Re; $P_N = 4$ and substituting values and solving for N;

$N = 3000/(4)(780)(.63)^5$

$= 3.84$ rps

Solving for Re, using the empirical formula (Ulrich, 1984 and McCabe et al,1993);

$Re = N\delta_s\ D_i^2/\mu$

$= (.62)^2\ (780)\ (3.84)/1.4 \times 10^{-3}$

= 849,139, therefore it is turbulent.

Checking the assumed P_N using the graph form Foust (1990);
The assumed P_N falls in the turbulent region.

B. Cost estimates

B.1 Capital cost estimate

Tank: 6 m3 @ 3 m high x 2 m diameter = NZ $ 25,000 (NZ$ 1994)

Stirrer: Power Consumption = 3 kW

NZ$ 6,000 x 2.2 to get stainless steel = $ 13,200

Pump and motor = $ 5,000

Total capital cost = $ 43,200

B.2 Operating cost

- $16/tonne to reprocess dirty kerosene (Source: Personnel Communication Dept., NZRC, Ltd, Whangarei.)

- use of 2:1 solvent to sludge ratio at 2 batches/use of solvent.
- 190 tonnes kerosene/year @ $16/tonne = $ 3,040
- 10 tonnes of kerosene lost due to solids retention @ $640/tonne = $ 6,400/year

Total operating Cost = $ 9,440

B.3 Savings

Crude oil recovery savings:

- $ 195/tonne (Source: NZRC) @ 16% of 100 tonnes/year = $ 3,120

Disposal Savings:

- Reduction of sludge mass by 59%, assuming disposal cost = $ 200/tonne for transport, packaging and landfill cost.

- 100 tonnes/year x .59 x 200/tonne = $ 11,800

Overall Savings = 11,800 + 3,120 - 9,440 = $ 5,480

Appendix A-5

Spreadsheet on disk

Appendix A-5 is on floppy disk. The disk contains the theoretical and experimental mass balances for the washing operation. It also contains the metal extractions data. Below are the list of data that can be found in the disk with its corresponding filename using Excel 97.

Description of Data	Filename
Theoretical Oil Removal Prediction	Theoretical mass balance
Experimental oil removal using Refractive Index (Run 1 and 2)	Refrac 1 and Refrac 2
Experimental oil removal using spreadsheet (Run 1 & 2)	Spreadsheet 1 and spreadsheet 2
Metal extractions data	Metal extractions

Errata

The mass balance given on pages 4.4 - 4.6 is incorrect. This was an error made during the writing of the chapter but the mass balance used during the data analysis and that contained on the accompanying spreadsheet is correct. The subsequent discussion and conclusions are also correct.

The mass balance on page 4.4 – 4.6 should be as follows.

A total mass balance over stage n gives;

$$S + R_{n-1} = m = E + R_n \qquad [4.7]$$

Assuming no solids in the extract stream a solids balance over stage n gives;

$$S\,Y_{n-1} + R_{n-1}\,y_{n-1} = m\,y_{mn} = R_n y_n \qquad [4.8]$$

An oil balance over each stage n gives;

$$S\,X_{n-1} + R_{n-1}\,x_{n-1} = m\,x_{mn} = E\,X_n + R_n\,x_n \qquad [4.9]$$

A water balance over each stage n gives;

$$S\,W_{n-1} + R_{n-1}\,w_{n-1} = m\,w_{mn} = E\,W_n + R_n\,w_n \qquad [4.10]$$

The variables S, R_{n-1}, X_{n-1}, Y_{n-1}, x_{n-1}, y_{n-1} and w_{n-1} are all know for each stage (n).

At equilibrium; $x_n = X_n = x_{mn}$ and $w_n = W_n = w_{mn}$

Rearranging equation [4.9] gives;

$$x_n = \frac{SX_{n-1} + R_{n-1}x_{n-1}}{S + R_{n-1}} \qquad [4.11]$$

Rearranging equation [4.7] for the mass of extract (E) gives;

$$E = S + R_{n-1} - R_n \qquad [4.12]$$

Rearranging equation [4.8] for the raffinate mass (R_n) gives;

$$R_n = \frac{SY_{n-1} + R_{n-1}y_{n-1}}{y_n} \qquad [4.13]$$

Rearranging equation [4.10] for the water concentration (w_n) gives;

$$w_n = \frac{SW_{n-1} + R_{n-1}w_{n-1}}{S + R_{n-1}} \qquad [4.14]$$

It is then necessary to state how much solvent (with dissolved oil) remains with the raffinate stream after separation (y_n). This depends on the separation method used to separate the extract from the raffinate streams. For the experiments carried out in this work it was found that $y_n = 3$ kg solids/kg (oil+solvent).

Equations 4.11-4.14 can be used to solve for the unknown variables, w_n, R_n, E and x_n.