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Heavy Metals Removal from Oil Sludge Using Ion Exchange Textiles

Ziyad Muslat

A Thesis
in
The Department
of
Building, Civil, and Environmental Engineering

Presented in partial Fulfillment of the
requirements for the degree of Masters of Applied
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Abstract

Heavy Metals Removal from Oil Sludge Using Ion Exchange Textiles

Ziyad Muslat

The oily sludge consume considerable amount of refiner's budget, since it is recognized as a hazardous material. A series of regulations had been adopted worldwide restricting the disposal of petroleum wastes and forced the search for new treatment methods. Heavy metals content in oil sludge limit choices for recycling oily sludge and prevent its use in other industrial processes or as fuel oil. In this research, ion exchange textiles were used for the first time for the removal of heavy metals from oil sludge. The target metals which were tested for their removal are cadmium, vanadium, nickel, copper, zinc, and iron.

Ion exchange textiles were applied directly to oil sludge to assess the performance of ion exchange process in oil sludge without using a pre-treatment stage. Then, two different pre-treatments methods were developed to enhance ion exchange in oil sludge; first pretreatment method included pretreatment of oil sludge with organic solvent. The second pretreatment method used pretreatment with aqueous solution (solvent extraction) before applying ion exchange textiles.

Results showed that all metals responded positively to pre-treatment with acetone. Using this technique, vanadium was removed from oil sludge below detection limit; other metals such as cadmium, zinc, nickel, iron, and copper was removed at 99 %, 96 %, 94%, 92 %, and 89 % respectively..

The process developed by this work, provides a new economic technology for the treatment of oil sludge with regard to heavy metals removal.

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Finally I would like to dedicate my work to my parents whom are the source of my pride, for their passionate support and endless love.

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Chapter One

Chapter 1: Introduction

1.1 Statement of the problem

The increasing global demand for oil as a source of energy has caused increase of crude oil excavation and processing. Petroleum refineries are burdened with the problem of handling large sludge quantities which is generated from all refinery facilities. It is estimated that more than 28,000 tons per year of petroleum oily sludge are being generated from each Petroleum refinery. This oily sludge is now recognized as hazardous waste under the Resource Conservation and Recovery Act (RCRA) (EPA, 1998).

Old practices for dumping oil sludge have resulted in serious pollution effects on the environment and humans. Around the world there are thousands of pits which were used as dumping sites for oil sludge. Oil sludge in these sites contaminates ground water by leaching through the soil, and contaminated soil migrates due to dust weathering. Light hydrocarbons evaporate from these sites causing contamination of air which adds to green house gases. Finding new sustainable technologies would permit reduction of oil sludge dumping and the environmental problems associated with it.

One of the problems preventing oil sludge from being recycled or utilized as fuel oil or in roads pavement is that their heavy metals content. Metals content in oil sludge can reach high concentrations; vanadium, for example, can reach more than 1500 mg/l. These metals content would cause damages to the catalyst used for thermal cracking of heavy oil fractions to lighter fractions, and if used as fuel oils heavy metals will migrate with exhaust gases to precipitate later in the surrounding areas, which as was found by some investigations to migrate hundreds of miles before settle down (Silva *et al.*, 1998).

Metals which are found to have high concentrations in oil sludge are vanadium, nickel, zinc, cadmium, copper, and iron.

Implementation of new sustainable technologies is always challenged by the economical aspects. To date most of developed technologies are costly, which discourage refineries to adopt them as an integral part of their processes, especially in the developing countries where environmental laws are not that strict, and nearly there is no monitoring for environmental pollution.

Credits are given to the English scientist H.S Thompson who was the first to lay down modern scientific terminologies for ion exchange phenomenon in 1850, since then enormous developments has been done regarding the production of synthetic materials capable to exchange ions in solutions (Harland, 1994).

To date water and wastewater treatment is the prevailing domain for ion exchange processes. It is still didn't find its way to petroleum refining industry. Part of the problem is that very little is known about the behavior of ions in non aqueous media. When applying ion exchange theory in non aqueous media it is always expected that it will behave in the same it as if it is in aqueous media. Another sources for difficulty is the poor polarity for most of hydrocarbon compounds (Wachinski and Etzel, 1997).

Successful application of ion exchange theory for removal of heavy metals from oil sludge allows a sustainable technique that is also economically feasible, which will help to attract refineries to adopt this new technology.

Ion exchange textiles have been developed, as ion exchangers, in the second half of the twenty's century. They are made from non woven textile grafted with ion exchange

polymers. This type of textiles has great potential for applications in different domains were other types of ion exchangers are difficult to be applied.

1.2 Objectives

The main objective of this work is to assess the feasibility of heavy metals removal from oil sludge by the application of ion exchange process using ion exchange textiles (IET) as the exchanger material.

In doing so, secondary objectives were adopted as follows:

- Investigate the IET performance in non aqueous media (oil sludge phase)
- Investigate the effect of organic solvent properties on the ion exchange process
- Investigate the effect of complexes formation on the extraction of metals from oil phase to the aqueous solution
- Investigate the effect of strong electrolyte presence on the extraction of metals in solvent extraction process.

Chapter Two

CHAPTER 2: Literature Review

2.1. Heavy metals in environment

The heavy metals are a group of elements between copper and mercury on the periodic table of the elements -- having atomic weights between 63.546 and 200.590 and specific gravities greater than 4.0. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc, but excessive levels can be detrimental to the organism (Chesters, 1987).

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent, they enter our bodies via food, drinking water resources, and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain (Bockris, 1977).

Heavy metals are dangerous because they tend to bio-accumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted (Nordberg *et al.*, 1985).

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

2.2. Heavy metals and their impact on the environment and health

In the following text a description of some heavy metals and their impact on environment and human health.

2.2.1. Cadmium

Problems associated with cadmium have only accelerated in 1950s. Since the cadmium consumption in the last forty years is estimated to be more than eight times of the cadmium consumption in the entire history of man kind (Foulker, 1990).

Physical and chemical properties

In 1817, cadmium was discovered by Strohmeyer by accidentally through his investigation of zinc carbonate, thus its name was derived from Greek word Kadmeia, which means zinc ore calamine.

Cadmium is ductile metal; it is relatively soft, which is improved by alloying.

Table 2-1 lists some main characteristics of Cadmium.

Table 2-1 Cadmium physical properties

Melting point	320.9 °C
Boiling point	767 °C
Density (@20°C)	8.64 g/ml
Color	Silver-White
Atomic number	48
Atomic mass	112.4
Isotopes	^{110}Cd , ^{113}Cd , ^{116}Cd , ^{106}Cd , ^{108}Cd , ^{114}Cd , ^{112}Cd , ^{111}Cd
Electrochemical potential (Cd^{+2}/Cd)	-0.40 V
Oxidation state	+2

Cadmium is readily soluble in nitric acid, but slowly soluble in hydrochloric acid and sulfuric acid, but non soluble in basis.

Cadmium sources and emissions to environment

Cadmium is produced as an inevitable by-product of zinc (or occasionally lead) refining, since these metals occur naturally within the raw ore. However, once collected the cadmium is relatively easy to recycle (Merian, 1990).

The most significant use of cadmium is in nickel/cadmium batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and electrical stress. Cadmium coatings provide good corrosion resistance, particularly in high stress environments such as marine and aerospace applications where high safety or reliability is required; the coating is preferentially corroded if damaged. Other uses of cadmium are as pigments, stabilizers for PVC, in alloys and electronic compounds. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products (Harrison, 1980).

In the general, non-smoking population the major exposure pathway is through food, via the addition of cadmium to agricultural soil from various sources (atmospheric deposition and fertilizers application) and uptake by food and fodder crops. Additional exposure to humans arises through cadmium in ambient air and drinking water (Foulkes, 1990).

Effects of cadmium on the environment

Cadmium derives its toxicological properties from its chemical similarity to zinc an essential micronutrient for plants, animals and humans. Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted.

In humans, long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer, although data concerning the latter are difficult to interpret due to compounding factors.

Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals, although most human data do not support these findings.

The average daily intake for humans is estimated as 0.15µg from air and 1µg from water. Smoking a packet of 20 cigarettes can lead to the inhalation of around 2-4µg of cadmium, but levels may vary widely (Merian, 1991).

2.2.2. Copper

Copper is very easily complexed and is involved in many metabolic processes in living organisms some of which involve in the redox potential of Cu (I)/Cu (II).

Physical and chemical properties

Table 2-2 summarizes main properties of copper:

Table 2-2 Properties of copper

Melting point	1083 °C
Boiling point	2590 °C
Density (@ 20°C)	8.93 g/ml
Color	red
Atomic number	29
Atomic mass	63
Isotopes	69.1% ⁶³ Cu, 30.9% ⁶⁵ Cu
Electrochemical potential (Cu(II)/Cu(I))	+0.34 V
Oxidation state	+2

Copper is the best common conductor of heat and electricity after Silver. Compounds and complexes of copper have very different properties than the metal alone

Sources of copper and emissions to environment

Copper is mostly always extracted from ores in underground or open pit mines. The most important ores contains besides copper as a metal, Copper sulfate, Copper sulfide, Copper oxide, and copper bicarbonate. The global demand on copper is increasing, although the recycling of copper now days provide the source of about 30% of present copper quantities.

Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. Copper can be present in oil also naturally

from rocks in the oil field, or from the storage and transportation vessels. It can also from the oil processing equipment in the refinery (EPA, 1996a).

Also it can reach ground water from rocks containing copper. Waste coming out from copper mining industries usually ends up contaminating the surface soil and during raining seasons this waste is carried with the run off ending up in nearby lakes and rivers (Merian, 1991).

Effects of copper in the environment

The evolutionary process, in selecting copper to carry out specific physiological roles, has avoided its toxic potential in three mechanisms:

- Developing an active process for eliminating any excess copper ingested in the diet.
- Reducing the thermodynamic activity of copper ions virtually to zero by utilizing the metal as a prosthetic element tightly bound to specific copper proteins.
- Interaction between zinc and copper.

Copper can only become toxic to humans and animals if one of these mechanisms becomes defective, because of either genetic or acquired causes.

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk for health effects from overexposure to copper.

To most bacteria and Viruses, copper is toxic. For many decades copper sulfide has been used as a fungicide.

In normal cases plants seems to have some regularity mechanisms to limit copper content at about 20mg/l (Buck, 1977). How ever toxic copper can alter the growth of

plants roots. Generally, copper is hardly available for bioprocesses, because of its strong complex-bound in the soil (Merian, 1991).

2.2.3. Iron

With regard to its biological activity, iron is the most versatile of all the elements. The unique properties of iron have led to its key role in the catalysis of metabolic processes. All organisms require a mechanism for its assimilation so as to avoid the ill effects that result from iron deficiency, which affects millions of people in the world, especially, children and menstruating women. However, excess iron can be toxic.

Physical and chemical properties of iron

Table 2-3, provides properties for iron;

Table 2-3 Iron physical properties

Melting point	1535 °C
Boiling point	3000 °C
Density (@20°C)	7.9 g/ml
Color	White
Atomic number	26
Atomic mass	58.8
Isotopes	92% ⁵⁶ Fe, 6% ⁵⁴ Fe, 2% ⁵⁷ Fe
Electrochemical potential	
(Fe(II)/Fe)	-0.44 V
Fe(III)/Fe(II)	+0.77 V
Oxidation state	+2,+3, +4 (very rare)

Iron is malleable and a ferromagnetic metal, but it loses its ferromagnetic properties and displays a paramagnetic behavior at 770 °C. Although iron is reactive, but it is stable in dry air and water free of carbon dioxide due to coating of iron oxide. In aqueous solutions iron is found in the form of iron (II), or iron (III), under normal aerobic conditions and at pH approaches neutrality, all ferrous iron is oxidized and converted to ferric form which is more stable, the ferrate form (iron (IV)) can be found in oxoanion form which can be obtained using strong oxidizing agents in strongly alkaline media, it can also be obtained by oxidizing iron (III) bound to certain strongly stabilizing ligands.

Sources of iron and emission to environment

Iron is extracted from ores, of which hematite, magnetite, limonite, pyrite, and bornite.

Technically advanced processes for steel making generate more suspended solids and somewhat less dissolved ferrous sulfate. Large wastes amounts containing iron hydroxide are produced during aluminum extraction process from bauxite. This ferric oxide is called red mud, and in most of the cases it ends up in nearby lakes, although it is now used as a landfill after being filtered through sand. As for other basic manufacturing industries, it produces atmospheric, water-borne and solid wastes. Although dust extraction plants associated with basic oxygen furnaces have largely eliminated the traditional brown smoke associated with steel works, some of the highly toxic fumes produced during steel making still escape.

Effects of iron in the environment

Iron is a low toxicity metal, it was found to be toxic at concentrations exceeding 200 mg/l of nutrient solution, and 200mg/day were found to be toxic to mankind. There is

no clear data for iron toxicity on microorganisms which live in lakes and rivers, for plants it was found that plants can tolerate the iron concentration, and have the ability to control its concentration in the plants by the production of certain chelating agent. In fact iron deficiency in humans, animals, and plants was found to have more serious problems than that caused by its excess availability.

2.2.4. Nickel

The bioavailability and biological effects of nickel depends on the type of nickel compounds present. Divalent nickel compounds are relatively non toxic. The inorganic water soluble nickel compounds can cause respiratory irritation and asthma, skin dermatitis and a troubling affliction of the general population (especially for women).

Water insoluble inorganic nickel compounds causes respiratory tract cancers. While nickel carbonyl is extremely toxic vapor, it is also carcinogenic.

Chemical and physical properties of nickel

Nickel is hard, malleable, ductile, ferromagnetic metal, and relatively resistant to corrosion. It loses its ferromagnetic properties at 358 °C. Complexing with peptides enables the formation of stable nickel (III) and reduces the electric potential from 4.2 to 0.7-1. V. Table 2-4 lists the main chemical properties of nickel metal.

Table2-4 Physical properties of nickel

Melting point	1453 °C
Boiling point	2732 °C
Density (@20°C)	8.91 g/ml
Color	Silver- White
Atomic number	28
Atomic mass	58.71
Isotopes	⁵⁸ Ni, ⁶⁰ Ni, ⁶¹ Ni, ⁶² Ni, ⁶⁴ Ni
Electrochemical potential (Ni(II)/Ni)	-0.24 V
Oxidation state	-1, +1, +2, +3 (usually not stable), +4(very rare)

Sources of nickel and emissions to environment

Nickel is mainly obtained from its sulfides ores, and to lesser extent from its oxides ores. Nickel enters groundwater and surface water from dissolution of rocks and soils due to biological cycles, atmospheric fallout, and modern Industrial processes. Also it comes from leached nickel from dump sites, compost, and sewage sludges. Acid rains has very strong tendency to mobilize nickel from soils to the groundwater, since nickel is readily soluble in solutions of pH less than 6.5, while it forms insoluble hydroxides at ph higher than 6.7.

Atmosphere gets nickel from natural sources, such as, volcanic activities, and rocks and soils weathering dusts, and from human activities, such as, wastes incineration,

fossil fuel combustion, emissions from mining and refining processes, and from metal consumption in industrial processes (Isacson *et al.*, 1985).

Effects of nickel on the environment

Small amounts of nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. The EPA does not currently regulate nickel levels in drinking water. Nickel can accumulate in aquatic life, but its presence is not magnified along food chains (Isacson *et al.*, 1985).

2.2.5. Vanadium

(Scandinavian goddess, Vanadis) vanadium was first discovered by Del Rio in 1801. Unfortunately, a French chemist incorrectly declared that Del Rio's new element was only impure chromium. Del Rio thought himself to be mistaken and accepted the French chemists's statement.

The element was rediscovered in 1830 by Sefstrom, who named the element in honor of the Scandinavian goddess, Vanadis, because of its beautiful multicolored compounds. It was isolated in nearly pure form by Roscoe, in 1867, who reduced the chloride with hydrogen. Vanadium of 99.3% to 99.8% purity was not produced until 1922.

Physical and chemical properties of vanadium

Because of its numerous oxidation states, vanadium forms a great number of compounds. Most of the organic vanadium compounds are unstable. Metallic vanadium reacts with oxygen, nitrogen, and carbon at relatively low temperatures (<300°C).

Vanadium is most commonly available as vanadium pentoxide and as ferrovanadium (iron-vanadium alloy containing 40-80% vanadium by weight). Some physical and chemical properties of vanadium and of some of its compounds are given in Table 2-5. Vanadium pentoxide (V₂O₅) is the most common commercial form. It dissolves in water to form acidic solutions and dissolves in acids. It reacts with bases to form vanadates. Vanadium trioxide (V₂O₃) is basic in solution and dissolves in acids to give the green hexa-aquo ion (V(H₂O)₆)⁺³. In solution, V⁺³ is a strong reducing agent and slowly attacks water with the production of hydrogen.

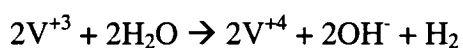


Table 2-5 Vanadium properties

Melting point	1890 °C
Boiling point	3000 °C
Density (@20°C)	6.11 g/ml
Color	greyish
Atomic number	23
Atomic mass	50.94
Isotopes	99% ⁵¹ V, 1% ⁵⁰ V
Electrochemical potential (V(II)/V)	-1.20V
Oxidation state	-1, +2, +3,+4(most stable), +5

Sources of vanadium and emissions to the environment

Metallic vanadium does not occur in nature. Over 70 vanadium minerals are known, carnotite and vanadinite being the most important from the point of view of mining. Production of vanadium is linked with that of other metals such as iron, uranium, titanium, and aluminum. As rich minerals rarely occur in large deposits, ores with low vanadium content, which exist in large amounts, are important. Extraction of vanadium from fossil fuels, including vanadium-rich oil and coal, tars, bitumens, and asphaltites, is important in several countries.

Vanadium from all sources is ultimately deposited on soils or surface waters. There is little migration of vanadium in soils, except via uptake by living organisms and redeposition. Vanadium tends to be trapped by, and move with, trivalent iron. Most vanadium in surface waters is suspended and becomes incorporated in sedimentary deposits in oceans.

Effects of vanadium on the environment

The uptake of vanadium by humans mainly takes place through foodstuffs, such as buckwheat, soya beans, olive oil, sunflower oil, apples and eggs. Vanadium can have a number of effects on human health, when the uptake is too high. When vanadium uptake takes places through air it can cause bronchitis and pneumonia.

The acute effects of vanadium are irritation of lungs, throat, eyes and nasal cavities. Other health effects of vanadium uptake are:

- Cardiac and vascular disease
- Inflammation of stomach and intestines
- Damage to the nervous system

- Bleeding of livers and kidneys
- Skin rashes
- Severe trembling and paralyses
- Nose bleeds and throat pains
- Weakening
- Sickness and headaches
- Dizziness
- Behavioral changes.

The health hazards associated with exposure to vanadium are dependent on its oxidation state. This product contains elemental vanadium. Elemental vanadium could be oxidized to vanadium pentoxide during welding. The pentoxide form is more toxic than the elemental form. Chronic exposure to vanadium pentoxide dust and fumes may cause severe irritation of the eyes, skin, upper respiratory tract, persistent inflammations of the trachea and bronchi, pulmonary edema, and systemic poisoning. Signs and symptoms of overexposure include; conjunctivitis, nasopharyngitis, cough, labored breathing, rapid heart beat, lung changes, chronic bronchitis, skin pallor, greenish-black tongue and an allergic skin rash.

Vanadium can be found in the environment in algae, plants, invertebrates, fishes and many other species. In mussels and crabs vanadium strongly bioaccumulates, which can lead to concentrations of about 10^5 to 10^6 times greater than the concentrations that are found in seawater.

Vanadium causes the inhibition of certain enzymes with animals, which has several neurological effects. Next to the neurological effects vanadium can cause

breathing disorders, paralyses and negative effects on the liver and kidneys. Laboratory tests with test animals have shown, that vanadium can cause harm to the reproductive system of male animals, and that it accumulates in the female placenta. Vanadium can cause DNA alteration in some cases, but it cannot cause cancer with animals.

The growth of some aquatic plants is stimulated by trace quantities of vanadium (1-10 µg/litre), but concentrations above 100 µg/litre are toxic. Some marine invertebrates, such as the tunicates, accumulate vanadium levels of up to 0.3% dry weight. Invertebrates are generally less sensitive to vanadium than fish.

2.2.6. Zinc

Zinc is a natural element which is essential for man and most living organisms. Indeed, zinc deficiency is now recognized as a human health problem. Zinc emissions resulting from industrial activity have decreased significantly in recent decades and present-day zinc levels do not pose a risk to the environment. Recent concern about the risk of zinc ecotoxicity in the aquatic environment is not supported by scientific fact.

Localized sites where historical contamination has occurred, however, require proper management.

Physical and chemical properties of zinc

Zinc is brittle, but it becomes ductile at about 120 °C, and can be rolled. Other physical properties of zinc are presented in Table 2-6.

Zinc has strong tendency to react with acidic, alkaline, and inorganic compounds. In dry air zinc oxidizes, and in wet air conditions zinc carbonate is formed, thereby protecting the metal from further corrosion. Zinc chloride, zinc chlorate, zinc sulfates and

nitrates are readily soluble in water, while the oxides, sulfides, carbonate, phosphates and silicates, and organic complexes are not (Bockris, 1977).

Table 2-6 Zinc properties

Melting point	419.58 °C
Boiling point	907 °C
Density (@20°C)	7.14 g/ml
Color	Bluish-white
Atomic number	30
Atomic mass	65.39
Isotopes	48.6% ⁶⁴ Zn, 27.9% ⁶⁶ Zn, 4.1% ⁶⁷ Zn, 18.8% ⁶⁸ Zn, 0.6% ⁷⁰ Zn
Electrochemical potential (V(II)/V)	-0.76 V
Oxidation state	+2

Zinc sources and emissions to the environment

Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing.

The world's zinc production is still rising. This basically means that more and more zinc ends up in the environment.

Zinc is a very common substance that occurs naturally. Many foodstuffs contain certain concentrations of zinc. Drinking water also contains certain amounts of zinc, which may be higher when it is stored in metal tanks. Industrial sources or toxic waste

sites may cause the zinc amounts in drinking water to reach levels that can cause health problems.

Water is polluted with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. This wastewater is not purified satisfactorily. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters.

Effects of zinc on the environment

Zinc is a trace element that is essential for human health. Shortage of zinc can cause a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects (Chesters, 1987).

Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc chloride can cause respiratory disorders.

In the work place environment zinc contagion can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity.

Zinc can be a danger to unborn and newborn children. When their mothers have absorbed large concentrations of zinc the children may be exposed to it through blood or milk of their mothers.

Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways. When zinc enters the bodies of these fish it is able to bio magnify up the food chain.

Large quantities of zinc can be found in soils. When the soils of farmland are polluted with zinc, animals will absorb concentrations that are damaging to their health. Water-soluble zinc that is located in soils can contaminate groundwater (Merian, 1991).

Zinc cannot only be a threat to cattle, but also to plant species. Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils.

On zinc-rich soils only a limited number of plants has a chance of survival. That is why there is not much plant diversity near zinc-disposing factories. Due to the effects upon plants zinc is a serious threat to the productions of farmlands. Despite of this zinc-containing manures are still applied.

Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The breakdown of organic matter may seriously slow down because of this (Chesters, 1987).

2.3 Metals in oil

The behavior of a metal depends on its physical and chemical properties and on the Environment in which the metal is present (Choudhury, 1998).

Crude oil contains three different fractions: paraffinic, naphthenic, and aromatic which also contain sulfur and nitrogen. The second part of the crude oil is the resins coating the asphaltene fraction so that it can be peptized into the crude oil. The resins are a brown, sticky hydrocarbon which contain nitrogen, oxygen, and sulfur, are soluble in n-

pentane but insoluble in propane, and have molecular weights greater than 3000. The asphaltenes contain the chelated metals, vanadium, nickel, and possibly some calcium along with sulfur, oxygen, and nitrogen. During crude oil distillation, the asphaltenes are not volatilized and remain in the vacuum reduced crude along with most of the resin fraction.

Crude oils typically contain trace amounts of metals with vanadium and nickel being the most common. Usually they are in an oil-soluble form, not removable by water-washing or filtration, and in conventional refining processes they become concentrated in the residual fuel oil fractions as shown in Table 17. Vanadium may occur in crude oil at concentrations up to 400 ppmv, and often causes severe corrosion problems with high-temperature metal surfaces in steam generators. The metals also tend to form particulate emissions in the sub-micron range.

The presence of metals in crude oil and heavy fractions is highly undesirable because oil products such as fuels will have a low yield, produce toxic oxides when burned, cause corrodibility and produce ashes that can damage engines. A reduction in the amount of metals in the oil is accomplished by the process of hydrodemetallation (HDM), where the molecules that contain metals lose these atoms by reactions of hydrogenation. The products of HDM reactions can accumulate in the catalyst pores, causing the formation of deposits which end up obstructing those pores irreversibly, blocking access to the catalyst sites and leading to a progressive loss of catalytic activity (Wei, 1991). These deposits are metal sulfides and active demetallation catalysts, which are less active than the original catalyst (Pereira, 1990).

All crude oil contains trace metals with nickel (Ni) and vanadium (V) generally being the predominant elements. These trace metals were formerly only considered a concern from the perspective of the fuel cracking process. The metals are generally complexed as porphyrins (Stencel, 2000).

Heavy oils require a substantial amount of cracking in order to be economically refined to produce usable products. One major problem affecting the economics of refining heavy oils is the fact that many of these oils contain metal compounds which poison the catalysts used to crack the oil. "If heavy oils could be upgraded without sacrificing the usable product yield or without adversely affecting the economics of oil refining as catalyst poisoning does, many new sources of oil products could be developed in the western hemisphere" (Pereira, 1990).

Metal compounds accumulate in the heavier fractions. The vanadium and nickel are in the crude oil as porphyrins or metal chelates. Originally the metals were probably magnesium (chlorophyll) and iron (hemoglobin). The ratio of the metals to each other is due to when and how they were buried. Some of the vanadium and nickel can be loosely held between the asphaltene molecules (intercalation). The other metals are complexed onto the water droplets and probably were due to the structure that the oil migrated through. Crude oils such as the Paraffinic Pennsylvanian crude contain very small amounts of asphaltenes. It is possible that the asphaltenes dropped out of the oil phase but are still down in the formation (Silva *et al.*, 1998).

Vanadium is present in high concentrations in the Boscan crude oil, and a significant amount of this metal exists in the crude in the form of vanadyl porphyrin chelates. Since porphyrins are detectable in crude oils even at low concentrations using

ultraviolet-visible spectrum analysis, and since the vanadyl porphyrins are notorious for their stability and survivability, vanadyl porphyrin behavior and atomic vanadium balances can be used to determine the metal's behavior in the refining of Boscan crude oil (Wei, 2000).

An alternative oil source that could be used to provide oil products is tar sands. However, the tar sand resources generally produce a heavy oil product that also requires significant upgrading to produce usable products. The high costs of mining the tar sand, extracting the raw tar sand bitumen, and refining the tar sand bitumen to produce salable products are major economic obstacles to be overcome before commercial development of most tar sand resources can occur (Jensen, 1977).

The inhibitory effects of heavy metals can also influence biodegradation of organic materials. The presence of heavy metals in oil sludge, motor oil, and used crankcase oil may have deleterious effects on the hydrocarbon oxidizers in decomposing petroleum hydrocarbons (Frankenberger 1992). Jensen (1977) studied the effects of lead on biodegradation of oily waste in soil and found that the presence of lead caused certain changes in the population of soil microbiota. Reduction in the bacterial population was evident, particularly at the highest lead concentration of 5,000 ppm. Measurements of oxygen consumption revealed increased microbial activity after the addition of oil to soils, but the presence of lead markedly reduced this activity with a prolonged lag phase in the biodegradation of oil sludge. Other elements of concern include zinc, copper, chromium, nickel, and cadmium. With repeated applications of oily sludge to a landfarming operation, heavy metals may accumulate at levels in which biodegradation may be reduced.

A recent risk evaluation of the presence of metals in crude oils indicated that they are unlikely to be a major risk management consideration at crude oil spill sites (Magaw *et al.*, 1999a; Magaw, *et al.*, 1999b). The evaluation involved a total of 26 crude oils that were analyzed and found to contain very low levels of metals.

Evaluation of the human health risk associated with soil containing these crude oils showed that the potential risk due to the presence of the metals was not significant at total crude oil concentrations in soil above 10,000 mg/kg, measured as total petroleum hydrocarbons (TPH). The amount of metals in 10,000 mg/kg TPH would also be protective of soil invertebrates, plants, and soil microbial communities as defined by published ecological soil screening levels (Magaw, *et al.*, 1999b).

2.4 Petroleum oily sludge

Oily sludge is a waste dumped by petroleum refineries. Oily sludge is one of the major industrial wastes that require treatment in refineries and petrochemical industries (Silva, *et al.*, 1998).

Oily sludge wastes generated in refineries were estimated to be nearly 30,000 tons per year per refinery (EPA, 1991). Hydrocarbon residue is collected from various sources, such as (Burbridge *et al.*, 2001):

- Cleaning of crude oil, asphalt, low sulfur heavy stock (LSHS), furnace oil, and intermediate storage tanks;
- American petroleum institute (API) separator sludge;
- Cleaning of accidental heavy oil spillage on the ground;
- Cleaning of surge ponds in wastewater treatment plant;

- Dissolved air flotation (DAF) scum;
- Chemical sludge;
- Biological sludge.

Hydrocarbons form nearly 70% of oily sludge content; they are mostly paraffines and asphaltenes, other oily sludges constituents include clay, inorganic matter, heavy metals, water which almost 25% of the oil sludge, etc. Oily Sludge contains large amount of combustible material which have high heating values (Shie *et al.*, 2000). Oily sludge contains high level of oil and grease, corrosion products, and sulfur (Mukarji, 2000). Table 2-7 provides typical characteristics of purified refinery sludge

Table 2-7 Characteristics of purified refinery sludge (Hydrocarbon fraction) (Kuriakose and Manjooran, 2001)

Density @ 15 °C(g/ml)	0.957
Pour point (°C)	+42
Flash point (°C)	>200
Kinematic viscosity @ 100 °C	30.33
Acidity (mg KOH/g)	4.3
Asphaltenes (%wt)	7.8
Wax (%wt)	6.00
Total Sulfur (%wt)	3.43
Ash content (%wt)	4.8

To date there is no technique or combination of techniques that provide a complete solution from the economic point of view. The difficulty in finding such a solution arises from several factors. Major problem comes from the variable composition of the petroleum waste which is affecting the efficiency of the various steps of any treatment technology. Even in relatively homogeneous petroleum waste, the variability of

the composition can adversely affect greatly the efficiency of impurities separation from the petroleum waste (Ripley *et al.*, 1998). Another problem is associated with oil sludge that comes from the crude oil bottom storage tanks, since crude oil usually contains 3% to 5% by volume oil in the globular form which settles down in the bottom of storage tanks forming thick layer of globular oil commonly known as crude oil sludge or crude oil tank bottoms. Periodically Refineries take some of the crude oil storage tanks out of service and clean out the bottoms. The removed materials may be sent to landfill or may be incinerated (Silva *et al.*, 1998).

Disposal of oily sludge is indeed a major environmental problem for refineries. Oily sludge is generally disposed of in an open ground. In many developing countries no measures are taken to prevent soil contamination or the spreading of the waste, also no monitoring of the sludge liquids leakage to the surrounding soils and underground is monitored. As a result thousands sites around the globe are posing a serious environmental problem for so many years, “Bahrain pitch” is one of these sites in which petroleum refinery used to dump its residues during 1938 to 1942. Over the years, and due to natural forces some changes have been induced such as dusting over by desert sands, evaporation by heat, deposition of rain water, and migrated seawater (Ripley *et al.*, 1998).

2.5 Oil sludge treatment techniques

There are three factors that affect the evaluation and selection of a treatment method or technology for hazardous oily waste and sludge; these factors are:

- Economic benefits (cost of the process)
- Environmental benefits

- Time saving.

The efficiency of any process is evaluated in terms of what the removal success in accordance of the cost involved. Moreover, until now, the main challenge is to find a new technology with high working efficiency and very low cost, that it would make it acceptable to the private sectors.

Alternative treatment methods available for hazardous oily waste and sludge are categorized as:

- Incineration processes.
- Physical & chemical processes, such as: liquid-liquid extraction, steam stripping, and distillation.
- Biological treatment
- Thermal treatment technologies
- Catalytic treatment methods
- Land farming

There are some other methods, which are intended for the recovery of metals, especially valuable metals, from oil wastes. Fly ashing is one of these processes, in which oil is burned to ashes at high temperatures in presence of oxygen, then metals are recovered from the ash by acid leaching, metals are then recovered by either ion exchange or electric deposition (Tokuyama *et al.*, 2002). In case of trace metals present, this method is not cost effective.

2.5.1 Incineration processes

In this method oil sludge or oil waste is incinerated to give ash, flue gases, and energy, the energy is usually used for the production of steam for steam turbines, or

heating, and it is used as a heating source for the waste oil reclaiming unit. The resulted ash is sent to a landfill, While gases are discharged to the atmosphere, after being subjected to electrostatic precipitator, and being scrubbed by acid (sulfuric acid or hydrochloric) to remove suspended materials and dust. Usually fuel oil is used as incineration starter.

Mainly the Rotary-Kiln incinerator type is used for its ability to be used for multipurpose and for promoting good firing and burning. Usually an incineration system contains a variable rotary-Kiln to provide a wide combustion range for water-oil-solids mixtures. The typical incineration temperature is around 850 °C (Silva *et al.*, 1998).

The main problems with this method are;

- i)* Older units may need additional control equipment to meet future air pollution emission standards.
- ii)* Some incinerators are not compatible with solid fuels or solid waste, as these materials will start to burn too high in the furnace, also energy consumed is more than energy produced.
- iii)* Treatment of the waste at the exhaust means that you are dealing with low specific weights and large volumes, which means that equipment must be huge.
- iv)* The feedstock is also low in Btus and the material handling equipment to load the feedstock must be large.
- v)* It may also take longer to obtain air permits than alternative technologies.
- vi)* There are significant community concerns about incineration.
- vii)* When heavy metals are present in oil sludge or oil waste, other problems will rise regarding the emission of these metals to the air. Even with the use of electrostatic

precipitators metals can still escape to the atmosphere which is then carried to precipitate in the surrounding areas. In studies carried around refineries sites found that the concentration of metals in the soil in nearby areas where dramatically high due to incineration processes which evolve these metals in flue gases coming out of these refineries (Kotoky, 2003).

viii) This method is considered expensive, and it has problems with the public acceptance for incineration.

2.5.2 Thermal treatment technologies

2.5.2.1 Pyrolysis and gasification

Pyrolysis is a form of incineration that chemically decomposes organic materials by heat in the absence of oxygen. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C (800 °F). In practice, it is not possible to achieve a completely oxygen-free atmosphere. Because some oxygen is present in any Pyrolysis system, a small amount of oxidation occurs. If volatile or semi-volatile materials are present in the waste, thermal desorption will also occur.

Organic materials are transformed into gases, small quantities of liquid, and a solid residue containing carbon and ash. The off-gases may also be treated in a secondary thermal oxidation unit. Particulate removal equipment is also required. Several types of pyrolysis units are available, including the rotary kiln, rotary hearth furnace, and fluidized bed furnace. These units are similar to incinerators except that they operate at lower temperatures and with less air supply.

Pyrolysis and gasification, like incineration, are options for recovering value from waste by thermal treatment. The basic technology concepts are not novel but, recently, several new proprietary processes have been developed. This brief note provides an independent overview of this subject and aims to answer some of the most common questions about the use of pyrolysis and gasification to process wastes.

Both pyrolysis and gasification turn wastes into energy rich fuels by heating the waste under controlled conditions. Whereas incineration fully converts the input waste into energy and ash, these processes deliberately limit the conversion so that combustion does not take place directly. Instead, they convert the waste into valuable intermediates that can be further processed for materials recycling or energy recovery.

Pyrolysis and gasification offer more scope for recovering products from waste than incineration. When waste is burnt in a modern incinerator the only practical product is energy, whereas gases, oils and solid char from pyrolysis and gasification can not only be used as a fuel but also purified and used as a feedstock for petrochemicals and other applications. Many processes also produce a stable granulate instead of an ash, which can be utilised easily and safely. In addition, some processes are targeted at producing specific recyclables such as metal alloys and carbon black. From waste gasification, in particular, it is feasible to produce hydrogen, which many see as an increasingly valuable resource. The reaction temperature can reach around 360 °C to 550 °C, and gas carrier temperature is usually around 800 °C (Shie *et al.*, 2000). Generally, pyrolysis is intended for recycling wastes oils without regarding heavy metals content in the waste. Some processes are claimed to remove metals from oils in a high efficiency. A process of such, is used for metals removal with presence of hydrogenating compound containing N rings

(1,2,3,4-tetrahydroquinoline) at a temperature of around 420 °C, then the mixture was cooled, residues were separated from pyrolysis products by filtration, the vanadium removal is claimed to be 83% (Kashima Oil Co. Ltd., 1983).

While this type of recycling is rarely economically attractive under current market conditions, these technologies do offer the scope for increasing recycling rates to achieve government targets or address environmental concerns.

Factors that may limit the applicability and effectiveness of the process include:

- There are specific feed size and materials handling requirements that affect applicability or cost at specific sites
- Highly abrasive feed can potentially damage the processor unit
- High moisture content increases treatment costs
- Treated media containing heavy metals may require stabilization.

The main disadvantages of this method are that:

- i)* Overall cost is substantial, process is capital intensive and some by-products may have limited or no value. The overall cost is expected to be approximately \$300 per metric tonne
- ii)* Oil produced is generally high in tar and asphalt components with low viscosity
- iii)* Both pyrolysis and gasification have poor heat transfer properties and consequently do not heat evenly. Therefore, process products vary greatly. There are a high number of components with low quantities available for recovery
- iv)* Pyrolysis is not effective in either destroying or physically separating inorganic compounds from the contaminated medium. Volatile metals may be removed as a

result of the higher temperatures associated with the process, but they are not destroyed. By-products containing heavy metals may require stabilization before final disposal (Shie *et al.*, 2000)

v) When the off-gases are cooled, liquids condense, producing an oil/tar residue and contaminated water. These oils and tars are hazardous wastes, requiring proper treatment, storage and disposal (Shie *et al.*, 2000).

2.5.2.2 Coking

This method can only be applied under the 40CFR 261.6 exception, which states that a refinery with a coker can use hazardous waste that contains oil as a feed to stoke a coker only, if this waste is generated at the facility where the coker is located, and if the resulting coke does not have hazardous characteristics.

Oil wastes that can be received by a coker include:

- Tank bottom sludge
- Bio sludge
- DAF float (K048)
- Slop oil emulsion solids (K049)
- API separator sludge (K051).

This method is being used in the industry; it seems to be effective in recycling the formerly mentioned wastes (Leeman, 1988).

Never the less it is considered expensive, and it does not consider removal of heavy metals. However, a method described for purifying coke fuel by contacting oil residue to a molten anhydrous alkali metal hydroxide at high temperature and relatively

long time sufficient for extraction substantially all heavy metals and recovering the coke products (Ohsol *et al.*, 1999).

2.5.2.3 Retech/ Tetral process

Retech/ Tetral process is based on high temperature thermal desorption. The first step involves drying the sludge. The second step is to heat the dried sludge to 500 °C - 600 °C by a heat transfer fluid, in order to prevent oil combustion. Next step will be the condensation and separation of oil and water. Then oil will be recycled, treated solids are cooled and disposed, while uncondensed vapor portions are treated in an off-gas recovery system. Due to high-energy consumption, this method is considered expensive, and it is not suitable when metals are present in sludge (Silva *et al.*, 1998).

2.5.2.4 Sealtech process

Sealtech Inc. offers Sealtech process. It is a combination of centrifuge and drying processes to produce a cement kiln fuel from sludge. Depending on the sludge type, the centrifuge can be vertical or horizontal; this process separates water and oil. Water will be sent to wastewater treatment plant, and oil is sent to the refinery. The concentrated sludge is then, processed in a high temperature-mixing tank; the recovered oil is remixed with the solids to produce the kiln fuel. The homogenized slurry is then dried in an agitated tank, which is equipped with steam coils. Water content in the slurry is reduced to less than 10%. Blending is needed as final step to achieve the specification of a particular kiln customer. Oil and water vapors are separated by gravity. Oil is sent to be recycled and water is sent to the wastewater treatment plant (Bishop, 1995).

This method is high energy consumption. It does not consider metals removal.

2.5.2.5 Thermal conversion

The Thermal Conversion Process (TCP) copies the geological and geothermal processes of nature. The technology emulates what occurs daily in the earth's subduction zones, but uses an accelerated process (Sorbal *et al.*, 2003).

Thermal conversion process (TCP) consists of the following steps

- Slurrying the organic and inorganic materials with water
- Heating the slurry under pressure to the reaction temperature (between 380 °C to 450 °C).
- Separation of Light oils and formed gases are separated through flashing the mixture.
- Removed of solids from the reactor bottom.
- Separation of water vapours by heating the oil.
- Light oil is recycled, and water is cooled and sent to waste water plant.

This process require high energy consumption, high energy consumption due to water vaporizing, it is also doesn't consider treatment for heavy metals in oily sludge.

2.5.2.6 Molten tin process

Residual oil is treated with molten tin or molten tin alloys sprayed with argon at a temperature of 500 °C. Oil is sprayed at the bottom of the molten tin. Molten tin absorbs heavy metals in the residual oil, metals removal in this process was found to achieve about 90% for copper (Miyadera *et al.*, 1975).

No data is available for this process cost, it can be applied for light oil sludges, heavier oil sludges have to be diluted with organic solvents in order to be sprayed.

2.5.2.7 Molten Salt oxidation

A Molten Salt Oxidation (MSO) process is available for waste destruction (halogenated, hazardous, radioactive). It can be used for Syn Gas production from wastes. Also it can be applied for metals recovery from organic waste (Ag, Au, Ni, etc.) surface cleaning (removes organics and inorganics), and salt recovery (organic contaminated: Na, K, Ca, Ba, Li, and Mg). Organic waste or salt stream with organic contaminants (usually air) are introduced into the bottom of a vessel containing a molten bed of salt. As the feed stream moves up through the bed of salt, organics are oxidized into CO₂ and H₂O. The reaction is usually exothermic (Hsu *et al.*, 2002).

A molten salt process may also be used for waste pyrolysis. In molten-salt oxidation (MSO), combustible waste is oxidized in a bath of molten salts (at 500–950°C). There is no direct flame, which prevents problems associated with incineration. Shredded solid waste is injected with air under the surface of a molten salt bath. Hot gases rise through the molten salt bath. The salt, being alkaline, scrubs acids from gases. The heat of molten salt degrades and melts waste material. Because the salt bath is liquid, it also removes some particles in the gas. By-products are retained in the melt. Gases exiting the salt bath are treated by an emission cleanup system before discharge to the atmosphere. Spent molten salt is tapped from the reactor, cooled and placed in a landfill. The molten salt is usually recycled in the reactor chamber.

Depending on the waste treated (especially inorganics) and the amount of ash, spent molten salt may be hazardous and require special care in disposal.

2.5.3 Biological treatment

In this method, oil sludge is processed in a decanter centrifuge as a first step, most of the oil separated after this step can be returned to the refinery, water coming out of this separator is sent to the wastewater treatment plant.

Residue coming from the decanter has to be diluted with water prior to bioprocessing. Following this process, comes the chemical treatment for solids stabilization in the final waste, which is then dewatered and then can be landfilled. This process generates vent gases that may require further treatment.

This method has shown success with API separator sludge and DAF float from refinery operations. The treated residue meets EPA's best-demonstrated available technology standards (BDAT), and it can be landfilled in a RCRA permitted landfill.

The estimated cost of this process is \$ 400/t for flow rate of 9000 tons/y of diluted waste (10 % solids, 30% oil and grease).

Presence of heavy metals can inhibit the bioactivity. Depending on metals, content in sludge the bioactivity can be dramatically reduced. In addition, the process is difficult to control, performance is difficult to verify and proper airflow must be maintained to provide oxygen if using aerobic bacteria. Bacteria, which may have been developed to consume specific compounds, will, when placed, activate alternative enzyme systems to eat the easiest available compounds (Cookson, 1999).

Microorganisms need incubation period to adapt to the waste stream, and waste loads have to be assigned carefully since high loads can cause a shock to these microorganisms leading to inhibit its growth and sometimes result in killing them.

2.5.4 Landfarming

Landfarming is a bioremediation treatment process performed in the upper soil zone. Sludge, sediments, or contaminated soils are integrated into the soil surface and periodically turned over to aerate the mixture, in order to enhance the biodegradation of the wastes and so the hazardous materials will be eliminated. This technique was used in oily sludge disposal and for other petroleum refinery wastes, but it is forbidden in Europe and in Quebec (Cookson, 1999).

The degradation rate is affected by the molecular size of the compounds to be degraded, i.e. the higher molecular weight of the organic compounds, the slower the degradation rate will be. In addition, presence of chlorinated, nitrated compounds makes the biodegradation more difficult. In addition, the shape orientation of a molecule can ease or complicate this biodegradation process.

Several factors limit the applicability of this process such as:

- Space requirement;
- Uncontrolled biodegradation conditions, which may increase the time required for biodegradation to complete, especially for recalcitrant compounds;
- The possibility of releasing particulate matters due to the operations.
- Inorganic compounds are non biodegradable;
- The presence of heavy metals can alter the process, since some of these metals can poison the microorganisms. And the possibility of these metals to migrate downward and reach groundwater (EPA, 1996).

The cost of such method range from \$ 45 to \$ 105/m³ of the waste (Cookson, 1995).

2.5.5 Physical Treatment

2.5.5.1 Propane solvent extraction

Propane solvent extraction (PSE) is a multistage extraction and decanting process (Figure 2-1), in which liquid propane is used as the solvent. In this process liquid propane is mixed with sludge oil and solvent, and then is overhead to solvent recovery flash unit. The separated oil can be recycled to the refinery and solvent is reused. The bottom products which are water and solids are pumped to filtration unit to separate solids from water. Water is then processed in wastewater treatment plant while solids are disposed.

EPA as BDAT standard for refinery hazardous wastes K048- K052 classifies this processed.

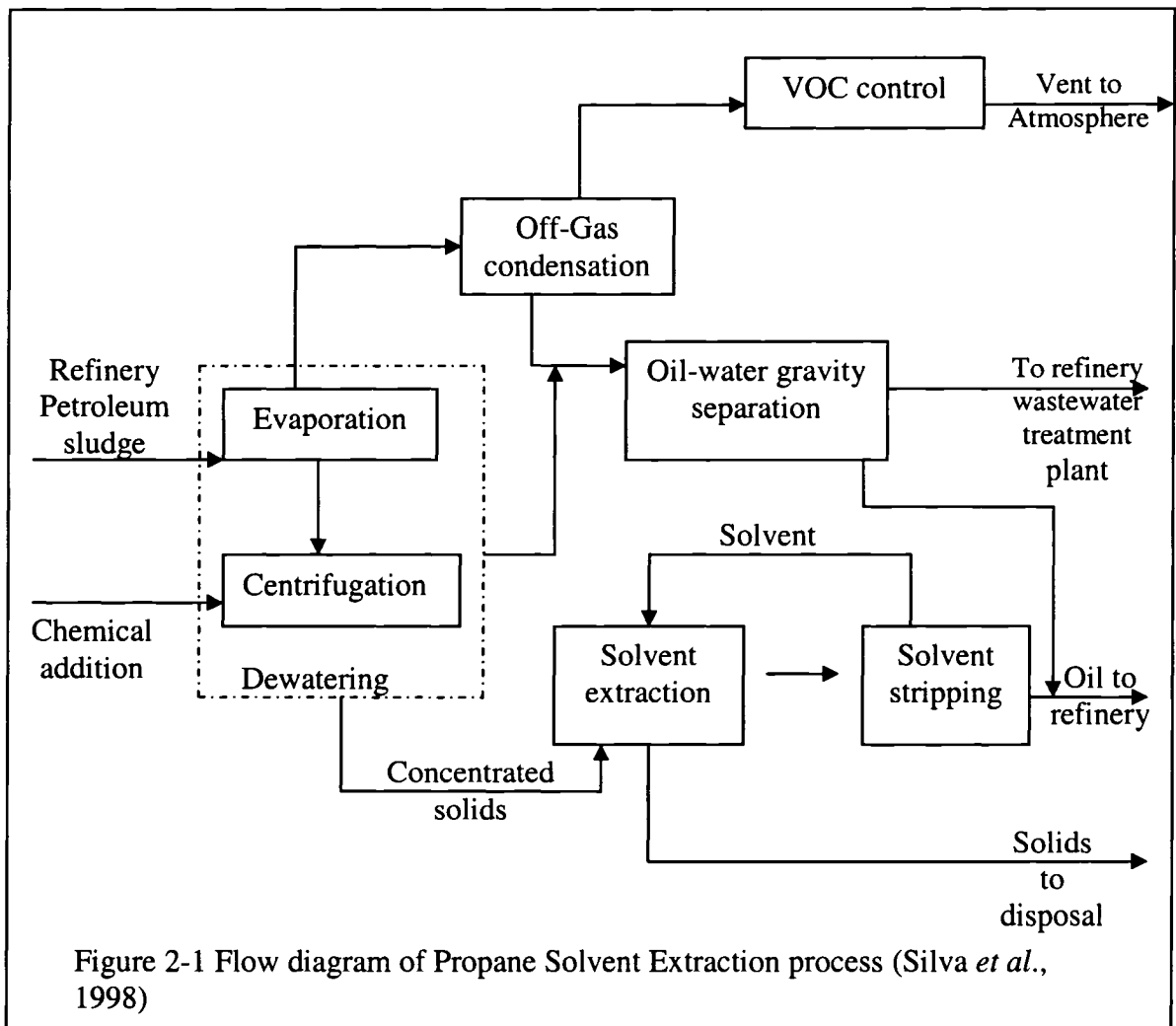
Operating temperature is 30°C to 50°C, and at an operating pressure of 20 atm (Filippi and Markiewicz, 1991).

Advantages of this process:

- Reduce volume of residue for disposal;
- Recycling of Oil recovered,
- Using a closed extraction system, i.e. no emissions to atmosphere.

While the disadvantages are:

- High initial capital investment;
- Propane availability and transportation;



2.5.5.2 Carver- Greenfield process

Carver- Greenfield process was developed by Charles Greenfield and has been used for different industrial wastes; from food processing wastes to petroleum sludge. It is a combination of evaporation, centrifugal separation, and solvent extraction.

The method utilizes steam, solvents, and evaporation equipment to remove all the water from wet oily sludge. The final residue produced by this method can be completely dry and totally, hydrocarbons free. Therefore, this residue can be disposed as non-hazardous waste.

Fuel oil is usually used as a solvent. This solvent is introduced in the first stage of the treatment process to allow water to be evaporated without production of residues that cannot be pumped. Another advantage to the use of solvent is related to the extraction of petroleum out of solids in the liquid phase.

The specific composition of the sludge, (i.e. water content) affects the type of evaporator to be used. Multi-effect evaporators are more efficient for high water content sludges. While single-stage evaporator is used for sludges with about 30% water content.

Evaporated water is condensed along with light distillates in the second stage, and then water is separated from these light distillates by gravity. Water is then sent to wastewater treatment plant. Oil is separated from the solvent in the centrifuge, while solids from the in the bottom are heated and purged with steam or inert gas such as nitrogen for further oil recovery. The recovered oil in this stage is sent along with oil separated from the centrifuge to the distillation tower for solvent recovery.

This method is considered highly expensive and complicated. It also requires high energy consumption. This method does not consider metal removal (Habibi, 2004).

2.5.5.3 Ohsol process

Ohsol process was developed by Uni Pure Corporation and consists of evaporation, and centrifugation for refinery wastes. In the first stage, surfactant is added to the waste to enhance emulsion, then the mixture will be pressurized and heated to about 10 atm, and 150 °C, and then the mixture will be rapidly flashed to break the emulsion, and to evaporate water and light oils. The remaining waste will be separated in a three-phase centrifuge (Rhodes, 1994).

This process involves high energy consumption, and it doesn't deal with heavy metals separation. There is a risk of forming dioxins at this temperature that will create more problems for the treatment process.

2.5.5.4 Sarex process

Separation and Recovery Systems, Inc. offer Sarex process commercially. It uses low temperature drying, centrifuge, and high temperature thermal desorption.

First sludge is indirectly preheated to around 65 °C using steam, then it is centrifuged, chemicals might be added when de-emulsifying of waste is needed.

Oil and water are sent to the wastewater treatment plant for the recovery of oil and treatment of the wastewater. Solids are carried from the centrifuge using an enclosed screw conveyor and are sent to be further dried at a temperature of 80 °C to 300 °C to ensure the removal of water and light hydrocarbons. Water and organic vapor are condensed and, separated, and recovered separately.

The final step is that solids are conveyed to thermal desorber, in which solids are heated to a temperature of 300 °C for a final removal of hydrocarbons. Hydrocarbons separated from the desorber and the dryer are collected on granular activated carbon for disposal (Miller *et al.*, 1994).

This method is very expensive, incurring high capital cost. It does not account for heavy metals presence in oily sludge wastes.

2.5.5.5 SoilTech process

SoilTech process has been used originally for treatment of contaminated soil. It includes some treatment stages for hazardous organics such as PCBs, which are not commonly found in petroleum refinery sludges. It has developed a thermal desorption system, a method that can be used for both contaminated soil, and petroleum sludges (Silva *et al.*, 1998).

2.5.5.6 Waste- Tech process

Known as waste- Tech Services Inc.'s desorption and recovery unit, it is a two – stage thermal desorption system. The first stage entails heating the sludge to around 300 °C in order to dry it using a thermal screw process which removes water and light oils. The volatiles are later condensed, while solids from this step will be sent by gravity to the next stage (Rasmussen, 1994).

In next stage, the sludge is heated to around 500 °C, so that all remaining hydrocarbons will be volatilized. This stage features a paddle mixer with high surface area that can be heated by electric heaters in the sealed molten salt-filled hollow paddles.

Oil condensed from the two systems will be recycled to the refinery, water will be sent to the wastewater treatment plant, and uncondensed vapors will be treated or oxidized before being released to the atmosphere, while remaining solids will be disposed after, being cooled (Rasmussen, 1994).

This process is complex, expensive, and requires high energy consumption. It does not consider removal of heavy metals from oil sludge.

2.5.5.7 TaBoRR process

Western Research Institute has offered TaBoRR process that complies with standards for tank bottom recovery and remediation, so it is more frequently used for tank bottoms from oil field production than refinery K-listed wastes. In this process, water and light hydrocarbons are evaporated in order to concentrate the solids. While water vapors and light hydrocarbons are then condensated and separated. Solids from bottom tank are fed to a screw conveyer where it is subjected to a hot stripping gas generated in a furnace in which fuel oil is combusted, for further hydrocarbons stripping. The remaining solids are then heated to about 550 °C to crack any remaining hydrocarbons. Solid materials are finally collected and cooled for disposal (Johnson *et al.*, 1993).

This method is high energy consumption which limits its applications, and it is not recommended for treating small facilities. Treating heavy metals containing sludges can create problems related to metals emissions and solids disposal.

2.5.5.8 Centech process

Offered by Centech Inc., Centech process is a three phase centrifugation. It is also more frequently used for tank bottoms from oil-field production (Silva *et al.*, 1998).

As the previous method, it is also require high energy consumption, and does not consider the presence of metals.

2.5.5.9 Hydrothermal processes:

Several hydrothermal processes have been introduced for oil sludges separation. The generalized process flow diagram is shown in Figure 2-2.

And some of these methods include:

- i) Emulsion breaking process is one of these methods, which includes heating the emulsion under autogenous pressure to temperatures between 230 °C to 370 °C. After cooling the mixture, four separable phases are formed. The generated gas is vented, and oil is decanted, while solids are filtered from water.

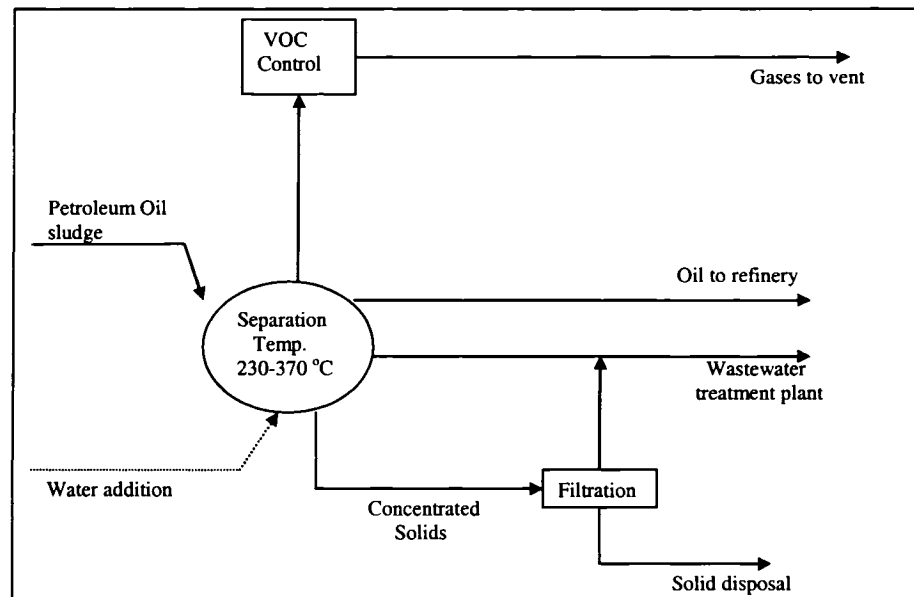


Figure 2-2: Process flow diagram for hydrothermal treatment. (Silva *et al.*, 1998)

- ii) Heating the emulsion to 400 °C and pressure between 200 to 440 atm. The supercritical fluid that is formed under these conditions can be removed and after being cooled and depressurized oil can be separated from water by gravity. Solids are removed from the reactor for disposal.
- iii) De-oiling and dewatering of the sludge, in which oil sludge is diluted with recycled oil and then pumped into a distillation column. Steam is injected into the column to distill the water and oil. Solids are removed from the bottom of the

column, while water and oil are collected from the top of the column and then cooled and separated by settling.

iv) Petroleum sludge treatment that separates emulsion into three distinctive layers; oil, water, and solids. In this method temperature is raised to 300 °C to 350 °C, and pressure should be between 100 to 200 atm. High pressure is applied to ensure water and oil evaporation prevention. The immediate removal of the distinctive layers at process conditions is the dominant factor for achieving high separation efficiency. Separation time can range from few minutes to hours. Continuous operation can permit the recovery of most of the energy input into the liquid-liquid heat exchanger. In this method at least 97% of oil can be recovered and then recycled to the refinery, separated water is found to have high COD (around 5000 ppm) due to dissolved organics but no visible oil can be seen, so it is sent to the wastewater treatment plant. Wet solids are found to have a moisture content of about 50%, and 1-2% oil. Initial tests indicate that these solids comply with EPA's BDAT standards for land disposal. The main advantage of this process is that it is held in one vessel, but water generated by this process needs more treatment processes.

Generally hydrothermal processes require high energy, and these processes are normally very expensive. Heavy metals are not considered in these methods.

2.5.5.10 Adsorption

Reactive adsorption is a fixed bed process. This method is originally proposed for mercury removal from any hydrocarbon stream including naphtha and crude oil and

condensate. It is based on high temperature chemisorption for selective adsorption of mercury. It uses a special adsorbent, CuS and activated carbon as the adsorbent support, the process is carried at 450°F (285 °C), and 220 psig (1516.85 kpa). The adsorbent life range is around one year, but might be extended to 2 years at contemplated operating conditions. The efficiency of this method is believed to be around 99%, lab tests indicate that concentration of mercury in hydrocarbon streams can become as low as 1 ppb (Muneyoshi *et al.*, 1999).

Regeneration of the adsorbent is not economically advised since it requires high temperatures of about 500 °C, which reduces the activity of the adsorbent significantly (Yan, 1987). The adsorbent has to be disposed after recovering the mercury adsorbed. One of the methods suggested is burning the adsorbent and activated Carbon, which generate high temperatures at burning, this will cause decomposition of mercury compounds into mercury vapor which is then condensed and recovered as a metal, and adsorbent can be sent to disposal (Yan, 1990). Oil can be further recovered from the catalyst by exposing the catalyst to steam at a temperature range from 100 °C- 400 °C, heavy metals desorption is suppressed, and only oils are purged and recovered from the adsorbents (Muneyoshi *et al.*, 1999).

This method is designated for mercury removal only, and not tested for other metals. It is also involves energy consumption, and problems with spent adsorbent.

A patented Japanese method used a spent hydrogenating catalyst for metals adsorption from hydrocarbons at 400 °C and a pressure of 130 Kg/cm², the removal achieved 70 %, and the spent catalyst lasted for almost three months (Masaaki *et al.*, 1974).

2.5.5.11 Supercritical Solvent Extraction:

Supercritical fluid extraction has been applied in diverse domains as a newly developed separation technology. It is considered as an effective method to process fossil fuel in that the extract, residues, and extraction solvent separate easily (Figure 2-3). In addition, the extraction production rate and composition can be controlled by adjusting extraction conditions (i.e., temperature, pressure, solvent, etc.)

- One of the oldest methods suggested the addition of mineral acid or mixture of mineral acids to the oil waste in order to combine with metals in the waste oil and separate into the aqueous phase, steam or compressed air can be used for the agitation. The aqueous phase is then separated from oil and sent for metals to be recovered. While waste oil can be recycled or used as fuel oil (Rothberg, 1916).
- One of these processes uses toluene as the extracting solvent. The operating pressure is about 70 atm, and temperature of 420 °C. In this process oil will be extracted and metals will be lift in the aqueous phase which is sent to waste water treatment plant for the recovery of metals, while oil and toluene are separated and oil is recycled and toluene is reused. Lab tests showed the metals removal could reach 99% (Hao-quan *et al.*, 2000).

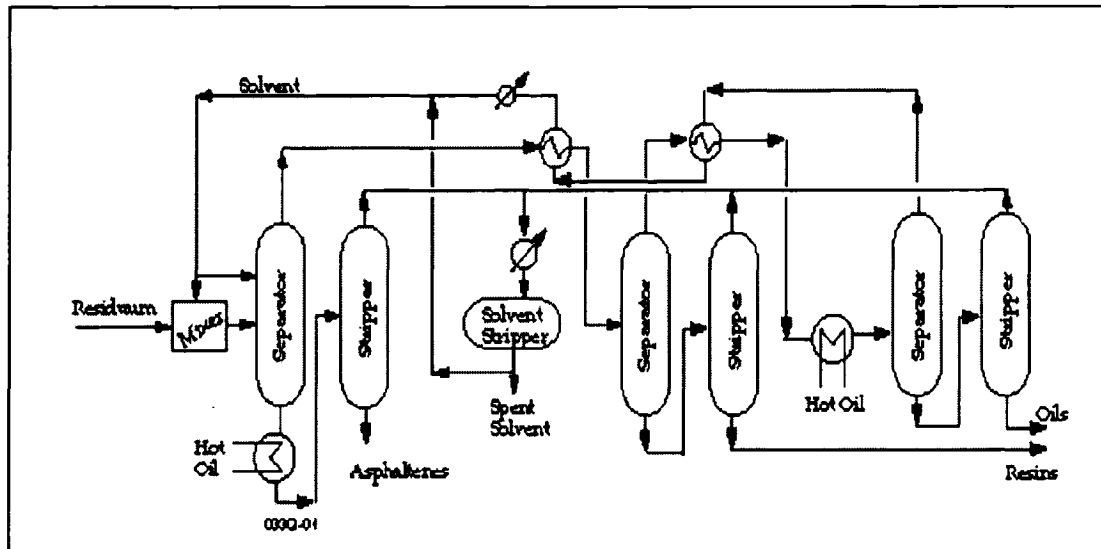


Figure 2-3: Supercritical Extraction Process Flow Diagram (Hao-qan *et al*, 2000)

- Another method comprises establishing an aqueous flux solution of water cyanide, zinc, lead acetate, and hydrochloric acid; scrubbing the solution and oil together to cause the flux to combine with metals in oil and establish a fuse, then separating oil from the solution and fuse. The flux solution is prepared by dissolving lead and zinc acetate in water with the addition of small amounts of cyanide and hydrochloric acid to ease the dissolution of the acetate salt into the solution. The addition rate of the flux solution is adjusted in a way to allow the fuse formation rate to be higher than the phase separation rate (Bell, 1973).
- Another process applied anionic surfactant to oil waste at a temperature range of 65 °C to 80 °C to remove water and metals in a form of insoluble salts (Salusinszky, 1980).
- A method was developed lubricating oil refining involves addition of organic solvent to dissolves base oil and flocculates the major part of additives and particulate matter. This solvent is basically prepared from potassium hydroxide and

2-propanol. A pilot plant was made for this process showed that it can produce recycled oil with properties similar to virgin oil (Alves dos Reis, 1991).

- Another method suggested alkaline treatment for waste oils by the addition of almost 7.5% of NaOH-Na₂CO₃ (2:1) for removal of Zn, Fe, Rb (Jimenez *et al.*, 1990).
- Another method used hexane as a refluxing solvent for residual oils under high temperatures ranging from 360 °C to 420 °C, and showed a complete vanadium removal from residual oils (Yasuhiro *et al.*, 1979).
- An old process uses diluted sulfuric acid (10%) as an extractive solvent for heavy metals from waste oils, the problem with this method is the acidic residues that is formed by this process, so it is suggested to add an alkaline agent to the mixture of the oil and acid and then emulsified with hot water, and then the mixture is sent to settle and allow for the aqueous and oil phases to separate. Then oil phase is sent to be processed and aqueous phase is sent to wastewater treatment plant (Ray *et al.*, 1957).

Supercritical solvent extraction methods are considered expensive and consume high energy. It also requires good control since it is done under highly pressurized conditions and, sometimes, high temperatures.

2.5.5.12 Precipitation

Precipitation of dissolved heavy metals in waste effluents is achieved with the addition of a solution of sodium polythiocarbonate. The precipitate is a stable unleachable, extremely insoluble metallic polythiocarbonate particle.

In this method waste oil is thoroughly mixed with sodium polythiocarbonate solution and then left to settle. Using gravity or filtration, the formed salt and aqueous layer are removed. Oil can then be recycled or burned as fuel oil. The aqueous solution is settled for separation of the removal of the precipitate.

This method is useful in the following applications:

- Removal of dissolved heavy metals from waste oils;
- Conversion of hazardous metal hydroxides into a non-hazardous material;
- Reduction of chlorine to chlorides;
- Removal of dissolved heavy metals from industrial wastewaters;
- Stabilization of hazardous waste dumpsites to prevent continual leaching of dissolved heavy metals in the ground water.

Metallic polythiocarbonates are used in wood preservatives. And can be used as source for metal reclamation processes (Legare *et al.*, 1988).

Other processes involve using other compounds such as disodium carboxyl-methyl trithiocarbonate (DCT), or disodium trithiocarbonate, to precipitate lead and chromium as metal sulfides (Bresson *et al.*, 1984). This method showed it could remove up to 80% percent of metals presented in oil sludge (Effendi *et al.*, 1994).

2.5.6 Catalytic treatment methods

Heavy metal compounds can be removed from oil with reduction of the metal contents if a specific type of catalyst is employed.

- A catalytic process uses a mixed catalyst bed from zirconium oxide, which is known for its stability at the relatively high temperatures, and potassium carbonate. It

showed that the removal of nickel and vanadium achieved 99%, at a temperature of 480 °C and a pressure of 225 atm, the residence time was almost 30 minutes and the oil feed rate (LHSV) was 100 ml/h.

Main advantage of this method is that metals removal is accomplished without the need to concentrate these metals in the heavy fractions of the out flowing oil. And no coke formation is observed (Andersen, 1999).

- Other process uses carbon black and activated Alumina powder as a shaped hydrogenation catalyst for desulfurization of heavy oils, and removal of metal compounds at a temperature range of 300 °C to 450 °C, and hydrogen pressure of 50 to 200 kg/cm², the liquid hourly space velocity is 0.3 to 5 h⁻¹. This catalyst has been shown to have long life than other types. (Kageyama *et al.*, 1982)
- Another process involves the use of bio-catalysts for the removal of nickel and vanadium from asphaltenes. This method indulges the use of enzymes or different hemoproteins for biocatalytical fractionation of asphaltenes. It was found that this method was useful to remove about 53% of total heavy metals from asphaltenes (Mogollon *et al.*, 1998).
- Another process comprises hydrogenation for removal of heavy metals by treating slurries, which contain powder catalysts containing ferromagnetic substances, and heavy oils containing heavy metals in presence of hydrogen at temperatures from 300 °C to 500 °C, and pressure from 10-250 kg/cm². In order to deposit heavy metals on the catalyst, and settling the slurries to remove most of the powder catalyst. The remaining powder is removed magnetically. Oil is forwarded for hydrogenation, while catalyst is disposed as a spent catalyst (Ino, 1995).

2.5.7 Conclusion

Main advantages and disadvantages of previously mentioned oil sludge treatment methods are summarized in Table 2-8

Table 2-8: Summary of main advantages and disadvantages of oil sludge treatment methods

Treatment Method	High Cost	long processing time	High energy consumption	Metals removal	comments
Incineration processes	X		X		Gas emissions can create problems
Thermal treatment technologies	X		X	X	
Biological treatment		X			
Land farming		X			Not allowed in Quebec
Physical treatment	X		X		
Catalytic treatment methods	X		X	X	Depending on catalyst type

There are many commercial methods available for reducing or concentrating metals in heavy oils. These methods are usually subdivided into thermal methods, and catalytic processes.

In thermal methods, temperatures of more than 500 °C are needed; furthermore, these methods lead to the production of great amounts of coke. In the thermal methods, metals become concentrated in the coke being formed. In catalytic methods, the need for hydrogen under high pressure is very great, and costs for plants are therefore equally high. Since the metals are precipitated predominantly onto the catalysts, the consumption of catalysts is also very high.

In pyrolysis when the off-gases are cooled, liquids condense, producing an oil/tar residue and contaminated water. These oils and tars are hazardous wastes, requiring proper treatment, storage and disposal. Also incineration is not cost effective or environmentally accepted due to the need to deal with NO_x, SO_x, CO₂, CO, and heavy metals emissions (Ripley *et al.*, 1998).

Landfarming, which is a natural degradation process, it is very slow, expensive, and space demanding, and requires complicated mechanisms of control, and this method can easily fail to meet the requirements for reduction of high molecular weight hydrocarbon (Conway, 1999). Also pollutants can leach into water table below (Santos, 1999). Land farming is prohibited in quebec.

Although biotreatment is often applied, it has many limitations, such as the choice of microorganisms, type of biosurfactant, quantity of additives, period of growt, and the right temperature profile.

In the treatment of heavy oils with water, as the supercritical solvent, there is one limiting factor, because heavy oils contain compounds that form coke very rapidly. The upper temperature limit must therefore as a rule be below 440 °C, to prevent excessive coke formation, which would lead to stopping up of the reactor systems (Hao-quan, 2000).

In removing or concentrating metal compounds from heavy oils in the presence of water near the critical point, metals from the unprocessed heavy oil are typically present, after the treatment, in unconverted form. Usually in the heaviest portion of the outflowing oil product. This can be ascertained from the refraction properties of the organometallic compounds (Hao-quan, 2000).

The cost of processed sludge with current technologies was reported in 1998 to range from \$100 to \$800 per tonne; these costs include labour cost, capital recovery, and disposal of residues (Silva *et al.*, 1998).

There is accordingly still a demand for methods removal of metal compounds from oily sludges that overcomes the problems of the previously known methods.

2.6 Ion exchange textiles and resins

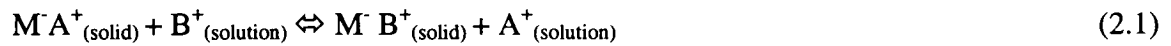
The ion exchange phenomenon observations date from the ancient times. Thompson and Way first established the mechanism of the reaction in 1850. The main domain for ion exchange was devoted to water treatment. Every day the demand for high quality water is increasing in several sectors of industry.

Ion exchange textiles (IET) and resins have wide applications in water and wastewater treatment, even though the ion exchange textiles some how considered very new compared to resins. Neither ion exchange resins nor IET have been applied to oil or oil sludge for heavy metals removal.

2.6.1 Ion exchange theory

An ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase, the ion exchanger is the solid phase meaning, that it is insoluble in the medium in which the exchange is carried out.

A simplified equation to describe the ion exchange reaction might be defined as follows:



Where: M^- is the ion exchanger, A^+ is ion originally attached to the ion exchanger, B^+ is the cation in the solution .

A^+ , B^+ are usually referred to as the counter-ions, while M^- is called the insoluble fixed anion, while the anions in the solution which have the same charge as the fixed anion are called co-ions and they are known not to take part in the exchange reaction to any considerable extent.

The anionic exchange reaction the equation will be as follows:



Where: M^+ fixed cation, A^- is ion originally attached to the ion exchanger; B^- is the cation in the solution (Harland, 1994).

The most important characteristics of an exchanger are:

- A reversible and rapid exchange rate
- Hydrophilic structure of regular and reproducible form
- Effective and controlled ion exchange capacity
- Chemical stability towards electrolyte solutions
- Physical stability in terms of mechanical strength and resistance to attrition
- Thermal stability

- Consistent particle size and effective surface area compatible with the hydraulic design requirements for industrial scale plant
- The type of exchanger, which enable to select either cation or anion.

The cost of modern ion exchange resins is high; therefore, important consideration is given to exchanger properties, which prolong resin life, and minimize the volumes of exchanger required (Wachinski and Etzel, 1997).

2.6.2 Ion exchangers

Ion exchange materials are generally classified into two broad categories:

- Inorganic ion exchange materials
- Organic ion exchange resins

Inorganic ion exchange materials are related to natural clay soils while organic forms are generally formed through the copolymerization procedures of styrene and divinylbenzene (Harland, 1994).

2.6.2.1 Inorganic ion exchange materials

Natural inorganic exchangers can be classified into three main categories: zeolites, oxides, and clay minerals. Synthetic inorganic exchangers can be classified into the following categories: zeolites, hydrous oxides, acidic salts of polyvalent metals, salts of heteropoly acids, hexacyanoferrates and other ionic compounds (Iagrega, 1994). Inorganic exchangers have no applications for waste management in the hydrometallurgic industry, but they have interesting properties such as, resistance to decomposing in the presence of ionizing radiation or at high temperatures, which have made them interesting

for the treatment of nuclear waste. There are also examples of their high selectivity towards certain ions (Komarneni *et al.*, 1988, Lehto *et al.*, 1990), which indicates that they may be suitable for certain hydrometallurgical applications.

Zeolites and clay minerals are crystalline aluminosilicates. The structure of zeolites is based on tetrahedral SiO_4 and AlO_4 units, which are connected by shared oxygen atoms (Figure 2-9). This kind of three-dimensional structure has small pores where the exchangeable ions are located and where the ion exchange reaction takes place. Silicon is tetravalent and aluminium is trivalent, which results in negatively charged framework structures and thus each mole of aluminium produces one equivalent of cation exchange capacity for the zeolite framework. In contrast to zeolites, clay mineral exchangers have two-dimensional layered structures.

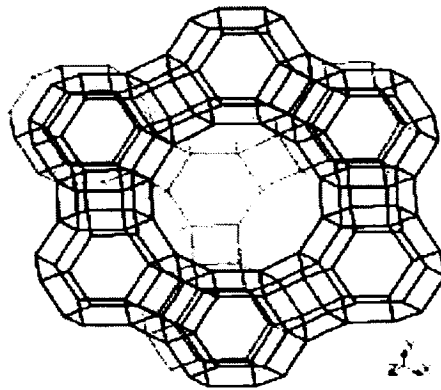


Figure 2-5: Zeolite structure

Zeolites have a rigid pore structures, but the layered structures of clay minerals may have some elasticity depending on the ionic form in which the mineral exists. The ion exchange properties of zeolites and clay minerals are mainly based on the charge density and pore size of the materials.

Some studies of natural zeolites and some hydrous oxides have been made for their profitable use in waste treatment. Clinoptilolite and chabazite have been investigated for the separation of transition metals from mixed metal contaminated effluents, also phlogopite mica and mordenite have been studied for Cs and Sr sorption (Liang, 1993, Komarneni, 1988). Clinoptilolite has been rather extensively used in radioactive waste decontamination (Hutson, 1996).

Synthetic inorganic exchangers form heterogeneous groups but there are a few selective hydrous oxides, hexacyanoferrates and zeolites which play an essentially part in nuclear waste management. Investigations of modified titanates (synthetic hydroxyapatite) and hexacyanoferrates (Lehto *et al.*, 1990, Lehto *et al.*, 1991) have been targeted to find a method for the selective separation of Sr, Cs and Ag from nuclear wastes. Nuclear waste management is very expensive compared to waste management in the hydrometallurgic industry, so, very expensive synthetic exchangers can be used if the over-all process is still cost-effective. On the other hand, there are some studies to find inexpensive selective inorganic materials, which can compete with chelating exchangers: Modified titanates and composite of iron oxyhydroxides and gypsum. Granular hexacyanoferrate has been utilized in several industrial scale applications for Cs separation (Harjula *et al.*, 1998)

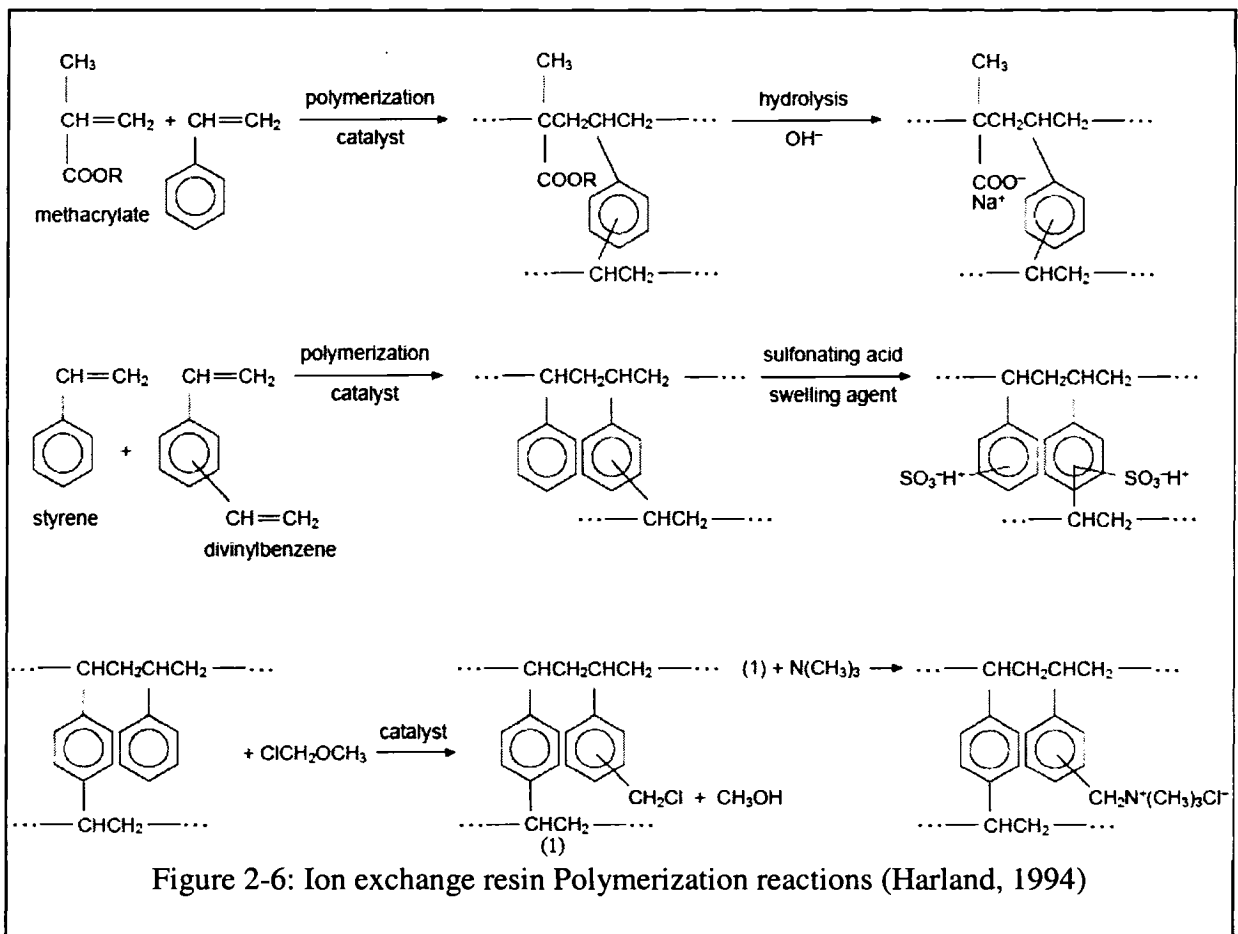
2.6.2.2 Organic ion exchange resins

Organic resins are produced through a specific type of polymerization reaction known as addition or vinyl polymerization. This consists of free radical induced polymerization between reactants (monomers) carrying ethenyl (or vinyl) double bonds (

-CH=CH₂). Figure 2-5 shows the reaction in two steps for simplicity, but in reality, the reaction occurs simultaneously.

Ion exchange resins are divided into groups based on their function (cationic or anionic), and the activation solution of the resin. So the ion exchange resins are classified into four groups as follows:

- Styrenic cation exchange resins (strong and weak acid)
- Styrenic anion exchange resins (strong and weak base)
- Acrylic cation exchange resins (strong and weak acid)
- Acrylic anion exchange resins (strong and weak base).



2.6.2.2.1 Styrenic cation exchange resins

This type of exchanger is made through the free radical copolymerization of two monomers, ethylbenzene (styrene) and diethylbenzene (divinylbenzene, DVB) in an aqueous suspension media, due to its high exothermic energy involved in the reaction, and dispersed as spherical droplets throughout the reacting medium (Harland, 1994).

Activation of the copolymer depends on the activation solution. Strong acid styrenic resins are activated by sulfonation of the copolymer with hot sulfuric acid which results in introducing the sulfonic functional group onto the matrix, this group gives the copolymer its strong acidic cation exchange resin. The matrix is then subsequently treated with brine or sodium hydroxide solution to produce the sodium sulfonate salt form (RSO_3Na).

Weak acidic styrenic resins are the result of copolymer treatment using carboxylic acid derivative instead of sulfuric acid.

Styrene cation polymers are used in water and wastewater treatment for so many years.

2.6.2.2.2 Styrenic anion exchange resins

They have the same styrene-DVB matrix as the cationic resins, but copolymer is subject to two synthesis steps:

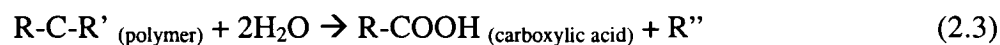
- Chloromethylation: to introduce the chloromethyl groups ($-\text{CH}_2\text{Cl}$) onto the styrene nuclei through a catalyzed reaction between the copolymer and chloromethoxymethane.

- **Amination:** in this step either Trimethylamine ((CH₃)₃N) is added to produce quaternary benzyltrimethyl-amonium chloride functional group which gives the resin its strong base anion exchange properties. The addition of methylamine or dimethylamine will produce the weak base anion exchange resin.

2.6.2.2.3 Acrylic cation exchange resins

Propenic (acrylic) monomers are the base for the copolymerization of these resins instead of ethylbenzene.

For example methylacrylic- divinylbenzene which is a weak acidic cation exchanger is the result of copolymerization of DVB and methylpropenoic acid. The remaining step as in the styrene resins is the acid hydrolysis to add the carboxylic acid group. The reaction is given by the following equation:



Some researches now are being conducted to produce resins which have both strong acid and weak acid groups simultaneously.

2.6.2.2.4 Acrylic anion exchange resins

Compared with styrenic structure, acrylic anion exchange resins demonstrate beneficial exchange equilibria and kinetics towards large organic ions. This is because the aliphatic skeletal structure of the acrylic matrix has greater hydrophilic nature. This

would mean weaker van der Waals type attraction between the resin matrix and the hydrocarbon structure of an organic counter ion.

Methyl propenoate is used to copolymerize with DVB for the formation of the resin matrix. This formed matrix is relatively flexible due to the fact that it can be used in three ways according to functionality (Streat, 1988)

- **Weak Base Functionality:** by amination with dimethyl aminopropylamine (DMAPA) which introduces a tertiary amine functional group.
- **Strong Base Functionality:** employing chloromethane on the weak base product will convert it into strong base quaternary ammonium resin.
- **Bifunctionality:** mixing the weak base with the strong base resin will produce allow obtaining this bifunctionality.

2.6.3 Ion exchange textiles

Textile materials made of polymers with chemically active functional groups have a unique combination of properties. On one hand, they can fulfill functions of conventional textile materials such as cloths, non-woven fabrics, filters etc., on the other hand, they can function as chemical agents, such as ion exchangers, complexions, reductants or oxidants, or catalysts (Soldatov *et al.*, 1999).

Each new physical form of ion exchangers (granule, membrane, and liquid ion-exchange extractants) requires new technological processes. Introduction of ion exchangers and complexones in the form of textiles into water treatment practice will influence the development of new technologies based on their specific properties (Soldatove *et al.*, 1999).

2.6.3.1 Features of ion exchange textiles

Important features of fibrous ion exchangers are (Yeon *et al.*, 2004)

- their extremely high osmotic stability allowing their multiple drying and moistening as well as conversion from one ionic form to the other without destruction of their filaments.
- The filtering layers of ion-exchange fabrics do not significantly change their volume and permeability upon changing swelling of the filaments, accompanied by variation of degree of ion exchange and ionic form.
- Selective to heavy metal ions, fibrous ion exchangers exhibited a high efficiency in purification of potable water.

Ion-exchange textile materials can provide all benefits offered by shallow bed technology RECOFLO and can be used in similar systems. At the same time, they offer further progress in ion exchange technologies because they allow the reduction of the height of the filtering beds by a power of magnitude without losing their efficiency. They also open new possibilities in construction of another apparatus unsuitable for granular ion exchangers (Yeon *et al.*, 2004).

2.6.3.2 Preparation of ion exchange textiles

IET are obtained by a radiochemical grafting of acid functional groups onto a non-woven matrix (80% viscose, 20% polyester). The general preparation of the non-woven sheet consists in the initial separation of viscose fibres which then are mixed by carding to make a thick fibrous layer. Various layers are bound to form a sheet with a

thickness of about 2 mm. The grafting process is the next step: The C–OH groups of fibres are transformed into C–O^d radical with a continuous electron beam. Energy of 350 keV allows a homogeneous penetration inside the material. The fibers are then impregnated with an aqueous solution of polymerisable vinylic monomers containing functional groups. The C=C opening allows the grafting onto the radicals created by irradiation. The grafted textile sheet is finally rinsed with deionised water in order to eliminate the unreacted monomers, and dried (yeon *et al.*, 2004).

Two types of matrices appeared most practical for syntheses of fibrous ion exchangers. The first is polypropylene (PP) industrial fibers modified by radiochemical grafting of polystyrene (ST) or its copolymer with divinylbenzene (DVB). These fibers can undergo the same chemical conversions as usual ST–DVB polymers (Yeon *et al.*, 2004).

The polypropylene matrix remains practically unaffected in these processes and such fibers are very close analogues of ST–DVB resins. Nevertheless, in some cases they exhibit markedly different behavior and may not be considered a mechanical combination of PP and the ST–DVB-based ion exchangers (Soldatov *et al.*, 1990). They contain domains of pure polypropylene and ST–DVB structure with the size reaching 20nm. The PP–ST–DVB matrices have been used as a basis for the preparation of a variety of different ion exchangers: sulfonic, carboxylic and phosphonic acid cation exchangers; several types of strong base anion exchangers with different functional groups; and weak base anion exchangers. The other family of fibrous ion exchangers has been obtained on the basis of industrial polyacrylic fibers. Their mechanical properties are sufficient to allow their textile processing. The most common textile form of these ion exchangers

tested and used in air purification processes has been non-woven needle puncture fabric with a thickness of 10 mm and a mass of about 1 kg/m² (Lacour *et al.*, 2004).

2.6.3.3 Ion exchange textiles versus ion exchange resins

A unique combination of properties of textile ion-exchange materials determines their advantages compared to granular ion exchangers in many processes (Lacour *et al.*, 2004). A small diameter of their monofilaments (5–50 µm) and uniformity of thickness provide a high rate and efficiency of ion-exchange processes. They are similar to micro spherical ion exchangers used for analytical properties. The application of such resins in large-scale processes is hardly possible due to high resistance of the filtering layers to water flow. This difficulty is eliminated when fibrous ion-exchange materials are used because their bed resistance is easily controlled by the packing density of fibrous materials in accordance with technological requirements in each specific case. Along with conventional column processes, ion-exchange textile materials can be applied in a form of continuous moving bands, in apparatuses with tangential flow of liquid relative to the layer of ion exchange material, thin layers, apparatuses combining functions of mechanical and ion-exchange filters etc (Lacour *et al.*, 2004).

The ion exchange, non-woven fabrics have a continuous uniform structure allowing their installation in absorbers with filtering area of the ion exchanger 50–30 m²/m³ if the filtering bed thickness, h , is 10–20 mm. Such values of h provide a high efficiency of ion-exchange process, and theoretical productive capacity of the ion exchange absorber is much higher than an apparatus of comparable size with granular ion exchangers (Yeon *et al.*, 2004).

Ion exchange textiles (IET) allow the reduction filtering beds height of the by a power of magnitude without losing their efficiency (Yeon *et al.*, 2004).

2.6.4 Selective ion exchangers

Specific ion exchangers exhibit an ability to uptake one or a few particular ions. This selectivity is due to the tendency of these ions to form strong complexes with, or are precipitated by certain class of compound. Such exchangers have great potential in analytical chemistry and commercial recovery or purification processes.

Resins with iminodiacetate or ethylenediaminetetraacetic acid as a functional groups shows high affinity towards many polyvalent and transitional metal cations.

2.6.5 Selection of an ion exchange material

In selecting an ion exchange material, a comparison between organic and inorganic ion exchange material, should be applied in conjunction with comparison of the resins within the organic category. Knowledge related to the applicability, lifespan, and various advantages and limitations is paramount to the selection successfulness of the appropriate resin for the particular application.

2.6.6 Applications of ion exchangers

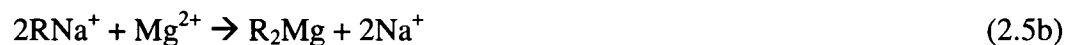
Since the early 1900s, ion exchange resins have been used in separation applications ranging from soluble material recovery to the purification of process or wastewater streams. It wasn't until the mid-1980s, however, that their full potential was realized through the development of a truly continuous process system — ISEP®. Calgon

Carbon Corporation's Engineered Solutions commercialized that system, later expanding its application capabilities by developing CSEP®.

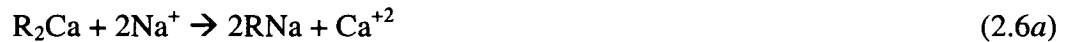
The current uses of ion exchange are long and numerous, and although one can't go into all of them here, it worth to point out several important applications:

2.6.6.1 Water softening

Water softening accounts for the major tonnage of resin sales. Hard waters, which contain principally calcium and magnesium ions, cause scale in power plant boilers, water pipes and domestic cooking utensils. Hard waters also cause soap precipitation which forms an undesirable gray curd and a waste of soap. Water softening involves the interchange of hardness for sodium on the resin. Typically, hard water is passed through a bed of a sodium cation exchange resin and is softened.



Regeneration of the exchanger involves the passage of a saturated solution of sodium chloride through the resin.



2.6.6.2 Dealkalization

Many industrial processes require that hardness and be removed from raw water before the water is used in the process. Two main processes involving ion exchange are used for dealkalizing;

- Dissolved solids are removed to the extent of the alkalinity in the raw water by passing the raw water through a bed of weak acid cation resin in the hydrogen form.

The 100 percent utilization of regenerant acid that is characteristic of this process decreases operating costs and greatly minimizes the waste disposal problem. A weak acid cation resin creates no free mineral acidity in the effluent when regenerated at a level of not more than 105-110 percent of the theoretically required amounts for the cations picked up.

- Chloride anion dealkalinizing involves passing the raw water through an anion exchange resin that is in the chloride form to remove alkalinity.

2.6.6.3 Demineralization

Ion exchange demineralization is a two-step process involving treatment with both cation and anion exchange resins (Weber, 1972). Water is passed first through a column of strong acid cation exchange resin that is in the hydrogen form (RH^+) to exchange the cation in solution for hydrogen ions:



Where, C^+ represents common cations, for example; Ca^{2+} , Mg^{2+} and Na^+ .

This effluent is passed to a column of anion exchange resin in the hydroxide form ($R OH^-$) to replace anions in solutions with hydroxide:

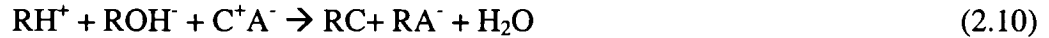


Where, A^- represents common anions, for example, Cl^- , SO_4^{2-} and NO_3^- .

The hydrogen ions from the cation resin neutralize the hydroxide ions from the anion resin:



The net effect is the removal of electrolytes and a yield of purified water. Alternatively, the impure water may be passed through an intimately mixed bed of cation and anion exchange resins where both types of exchange occur simultaneously:



The choice of the ion exchange system for demineralization depends on the water quality desired, operating and capital economics, and composition of the raw water (Applebaum, 1968).

2.6.6.4 Condensate polishing

Single or mixed bed ion exchange resins are used in deep bed filter demineralizers for reduction of particulate matter and dissolved contaminants in utility power plant condensates.

2.6.6.5 Ultra pure water

Ultra pure water (UPW) is essential to the proper fabrication of integrated circuit boards in the semiconductor industry. As the degree of integration becomes increasingly more complex, the semiconductor industry requires higher levels of water purity. Single beds, mixed beds and also reverse osmosis are used in the production of ultra pure water.

2.6.6.6 Nitrate removal

Ion exchange is used for the removal of nitrates from nitrate polluted waters. Strong base anion exchange resins operating in the chloride ion form (salt solution regenerated) have been successfully used for this service (Sheinker and Cudoluto, 1977).

2.6.6.7 Waste treatment

Radioactive Radiation waste systems in nuclear power plants include ion exchange systems for the removal of trace quantities of radioactive nuclides from water that will be released to the environment. The primary resin system used is the mixed bed.

2.6.6.8 Chemical processing – catalysis

Since ion exchange resins are solid, insoluble, (but reactive) acids, bases, or salts, they may replace alkalis, acids, and metal ion catalysts in hydrolysis, inversion, esterification, hydration or dehydration, polymerization, hydroxylation and epoxidation reactions. The advantages of ion exchange resins as catalysts include easy separation from the products of reaction, repeated reuse, and reduction of side reactions and lack of need for special alloys or lining of equipment.

2.6.6.9 Purification

Purification by ion exchange is used to remove contaminating acids, alkalis, salts, or mixtures from non-ionized or slightly ionized organic or in-organic substances. Examples include formic acid removal from 50 percent formaldehyde solutions, removal of amines from methanol, removal of iron from steel pickling operations, purification of aluminum bright dip baths and removal of iron in the purification of hydrochloric acid (Kraus and Moore, 1949).

Metal Extraction, Separation and Concentration; In aqueous or solvent mixtures containing large amounts of contaminants and small amounts of a desired solute, ion exchange resins can be used to selectively isolate and concentrate the desired solute, for example, the recovery of uranium from sulfuric acid leach solution with strong base

anion resins. Other specific chelating resins can be used for metals recovery such as copper, nickel, cobalt, and precious metals (Kraus and Moore, 1949).

2.6.6.10 Desiccation

Ion exchange resins, particularly strong acid cation exchange resins in the dry state, are useful as desiccants (Wymore, 1962). Ion exchange resins show their greatest capability as desiccants in the drying of hydrophobic solvents, for example, hydrocarbons and chlorinated hydrocarbons, Sugar Separations and Purifications. Ion exchange resins are used as an integral part of corn syrup, highfructose corn syrup (HFCS) processing and other starch based syrups. In sucrose processing, the resins are often used for softening feed streams, recovering sugar from molasses streams, or decolorization. They are also used in the production of non-nutritive sweeteners such as sorbitol or mannitol.

Resins and adsorbents are used in four major unit processes in corn sweetener processing: deashing, chromatographic separation of glucose and fructose, mixed bed polishing and color removal. In deashing, a bed of weak base anion resin typically follows a bed of strong acid cation resin. The resins used are macroporous, as their large porous structure allows syrup components to move freely into the bead.

2.6.6.11 Chromatographic separation

Chromatographic separation is a manufacturing process using ion exchange resins to separate one dissolved component from another (Khym, 1974). It is applied in the sugar industry for the purification of compounds such as sucrose, glucose, fructose, oligosaccharides, sorbitol and mannitol. It can be used to separate salt from glycerol and in purifying amino acids and various organic acids. Most industrial chromatography

today utilizes simulated moving bed (SMB) technology to minimize solvent use, leading to a significantly reduced cost of operation when compared to traditional batch chromatography.

2.6.6.12 Pharmaceuticals and fermentation

Ion exchange resins are useful as carriers for medicinal materials and in slow release applications. In some cases, the ion exchange resin has the medicinal affect desired, for example, Cholestyramine, a dried and ground strong base anion resin used to bind bile acids for reducing blood cholesterol. Ion exchange resins also are used in a variety of fermentation and biotechnology processes, such as the isolation and purification of lysine, streptomycin and neomycin and other similar antibiotics.

2.6.7 Ion exchange in non-aqueous media

Principles of ion exchange in non-aqueous solutions continue to be hotly debated.

To date, Environmental and Power Technologies has more than 1,000 equipment years of absolute success at solving the problems associated with other media.

The most common problem associated with the use of resins in oils is the false assumption that resins are water-treatment technology and therefore must behave the same in the oil environment. In the oil environment, water is not produced and acid neutralization does not take place. The requirement of water in the resin is critical because it activates the ion exchange reaction.

Non-aqueous exchange kinetics are slower so adequate contact time must be available.

Dow, which is an ion exchange resins manufacturer, has reported the use of ion exchange resins for removal of acids and metal salts from organic solvents in applications such as color control (shelf life improvement) and precious metal catalyst recovery. Nevertheless, a few simple adjustments are required (Samuelson, 1963).

Most ion exchangers are normally delivered as a water-wet product. Since water and organic solvents do not mix, an interface will exist at the water-solvent boundary that will inhibit ion mobility into and out of the resin beads. Drying the ion exchange resin will allow solvents to permeate fully the media so the chemistry is fully utilized.

Ion exchange resins can be dried either in an oven at 95°C to 100°C (200°F to 212°F) or via chromatographic displacement using a dry, polar solvent, methanol, ethanol, isopropanol, acetone, etc. (Buchwald and Wood, 1953). For critical applications, where water must be completely excluded, it is wise to verify that the resin is dry using a Karl-Fisher titration.

When water is removed from ion exchange resins, they typically shrink in size. Care should be taken if they are re-hydrated as they will swell creating high pressures that can damage the resin beads and equipment.

Dehydrated beads are "tighter" or more kinetically inhibited. Ion exchange processes are therefore slower and longer contact times or slower flow rates may be required.

Dry macro porous resins will contain air that will prevent contact between the resin and the solvent. The beads can be degassed by pulling a slight vacuum on the resin solvent mixture (DOW, 2001).

2.6.8 Conclusion

Applications for ion exchange have many current forms, and some of these could expand as increased awareness of ion exchange processes continues. In addition, as the field of materials engineering continues to produce an ever-increasing variety of substances, the potential for creating new, useful ion exchange materials grows.

Furthermore, the explosive growth in computer power during the last 15 years helps materials engineers work much more efficiently in developing useful compounds. If virtual reality technology materializes as its proponents profess, materials development could be in for another burst of growth.

The use of ion exchange resins and textiles in the treatment of water and wastewater containing metals has been the predominant domain. In recent years the usage of ion exchange was expanded numerously to include new domains such as soil remediation gases treatment, food and pharmaceutical industry.

In literature review performed, there was a clear lack for the application of ion exchange resins and textiles in the field of oil sludge treatment and oil purification. This fact presents the need for further research to be conducted on oil purification and oil waste and sludge treatment.

Some limitation and difficulties do exist regarding the application of ion exchange textiles in oil waste and sludge. As an example, in oil environment, water is not produced, which is critical because water activates the ion exchange reaction. In addition, non-aqueous exchange kinetics are slower so adequate contact time must available. However, its application provides a potentially effective method for removing heavy metals from oil and oil wastes and sludge. So far, ion exchange was never used in oil or oil

waste treatment. As the demand for oil is increasing which will eventually force to utilize heavy fractioned oils, and with the need to obtain methods for further recycling oil wastes, these resins will find their way to be used in oil industry.

There is a need to investigate the feasibility and effectiveness of ion exchange textiles application in oil and oil sludge treatment. Especially its use in combination with other processes and methods.

2.7 Ethylenediaminetetraacetic acid (EDTA) for heavy metals removal

2.7.1 Characteristics:

EDTA was patented in Germany in 1935 by F. Munz. The molecule is a substituted diamine (Figure 2-7) usually marketed as its sodium salts. It is a powerful complexing agent of metals and a highly stable molecule, offering a considerable versatility in industrial and household uses (Hu, 1998).

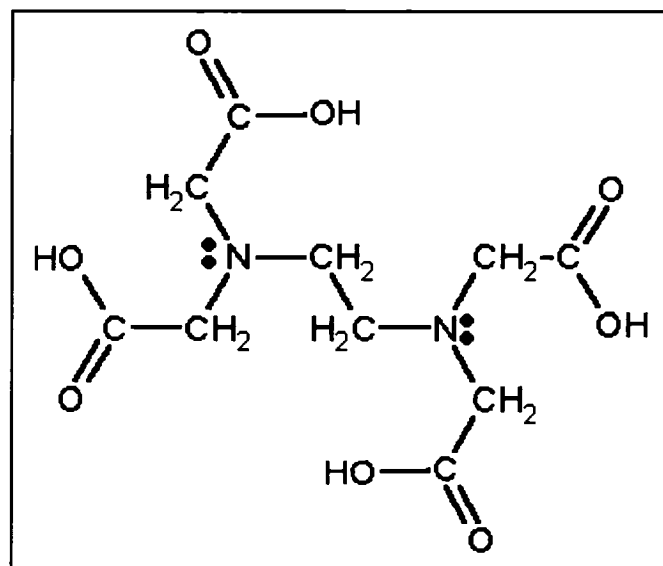


Figure 2-7: EDTA structure

EDTA is a multidentate ligand. That is, it can coordinate to a central metal using up to 6 electron pairs (2 on N and 4 on COO-) (Tai *et al.*, 2003).

EDTA has four COOH functionalities and 2 NH₂ functionalities. Each of these groups can complex with a metal, so this one molecule usually acts as a multidentate molecules to form a 1:1 complex with metal thus Formation Constant K_f usually looks very simple. The K_f for most multivalent metals and EDTA are very large, 10¹⁰-10³⁰ (Tai *et al.*, 2003).

EDTA specific gravity is 0.86, and its molecular weight is 292.25 g/mol. It partially water soluble, and usually it exists as a white odorless crystal. EDTA is commonly abbreviated as H₄Y where Y denotes the EDTA⁻⁴ ion. It dissociate in water into different forms of ions such as H₃Y⁻, H₂Y⁻², HY⁻³, and Y⁻⁴. The respective values of pKa are given in Table 2-8 (Furia, 1972).

EDTA has been extensively in removal of metals from water and soils due to its ability to form strong water soluble chelates with most metals (Yeung and Menon, 1995).

Table 2-9: EDTA Speciation and pKa values at 20 °C and presence of 0.1 M KNO₃

Ionic form	pKa
H ₃ Y ⁻	2.00
H ₂ Y ⁻²	2.66
HY ⁻³	6.16
Y ⁻⁴	10.26

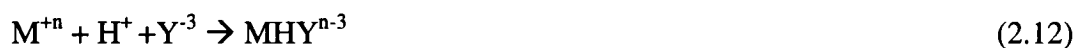
2.8.2 Metal-EDTA complexation theory

A variety of complexes can form when a metal ion encounter an EDTA ion.

MY complex can be found as in the following equation:



A protonated MHY complex can also be seen:



Or hydroxo complex $MY(OH)_n$;



Also a mixed complex MYX can be formed, where X is a unidentate ligand (Yeung and Menon, 1995)

Table 2-10 lists values for metal- EDTA constants at 20 °C and pH 7.

Table 2-9 metal EDTA constants at 20 °C and pH 7

Element	K_{MY}
Cd	2.9×10^{16}
Cu	6.3×10^{18}
Fe	2.1×10^{14}
Ni	4.2×10^{18}
V	(II) 5.0×10^{12} (III) 7.9×10^{25}
Zn	3.2×10^{16}

Very low stability constant numeric values (between negative values and 1) mean that the metal-ligand is not only soluble in water but readily dissociates into the metal

ionic form shown and the ligand, yielding essentially all metal in ionic form at pH as low as pH 2 to as high as pH 7.4.

The values of formation constants for these metals indicates that the complexes formed between these metals ions and EDTA will be water soluble and EDTA is potentially useful for enhancing mobilization of heavy metals. However, these formation constants are based on aqueous solution as the containing media, and no data is yet established for metals-EDTA complexes formation in non-aqueous media such as the oil sludge media. It would be a good contribution to knowledge to investigate the ability of EDTA to capture metals from oily sludge medium and the behavior of EDTA-metals complexes with IET.

Chapter Three

CHAPTER 3: Materials and methodology

3.1 Introduction

While detection and analysis of metals in oil and oil sludge methods are well documented, there was nearly no data available for ion exchange in oil or oil sludge, suggesting that no work has been done yet in this domain. This is may be due to the assumption that ion exchange is only applicable in aqueous media where water is very much available.

The main problem faced this research work was to develop a method in which ion exchange process can work. This lead to the concern whether oil sludge sample needs to be pre-treated or not, and what type of pre-treatment has to be applied. So it was determined to investigate the applicability of ion exchange in oil sludge sample to proceed in three ways. First, IET was chosen as the ion exchange medium because of the advantages it would provide to the experiment, which is previously mentioned in chapter two (section 2.6.3.1). In the next step, characterizing oil sludge sample, various oil sludge samples were performed.

First stage of the investigation is the direct application of IET to oil sludge sample as a starting point. The results from stage one permitted to assess the possibility of enhancing ion exchange process through pretreatment of oil sludge sample with an organic solvent before subjecting it to IET. In this step, the effect of solvent polarity was also investigated.

In the third stage, it was decided to use an aqueous solution to extract heavy metals from the sample and then apply the IET to the aqueous solution instead of oil

sludge sample to overcome the problem of oil sludge presence. In this extraction stage, two aqueous solutions were used; EDTA solution was used and a diluted nitric acid solution was used. Figure 3-1 is an illustration for the experimental methodology applied to this research.

The arrangement of this methodology was set in such to achieve the objectives of the research. It involves the following stages:

- Perform literature review to determine the target metals
- Oil sludge characterization;
- Preparation of oil sludge samples for analysis using microwave digestion;
- Analysis of oil sludge samples, using atomic absorption spectrometer for determination of metals content in these samples;
- Preparation of sludge samples to achieve an accurate concentration of target metals;
- Choice and preparation of ion exchange textiles produced by Institut Textiles de France, in Lion, for metals removal from oil sludge;
- Find a pre-treatment method for facilitating ion exchange process in non aqueous solutions;
- Assessing the metals removal from oil sludge based on the developed methods.

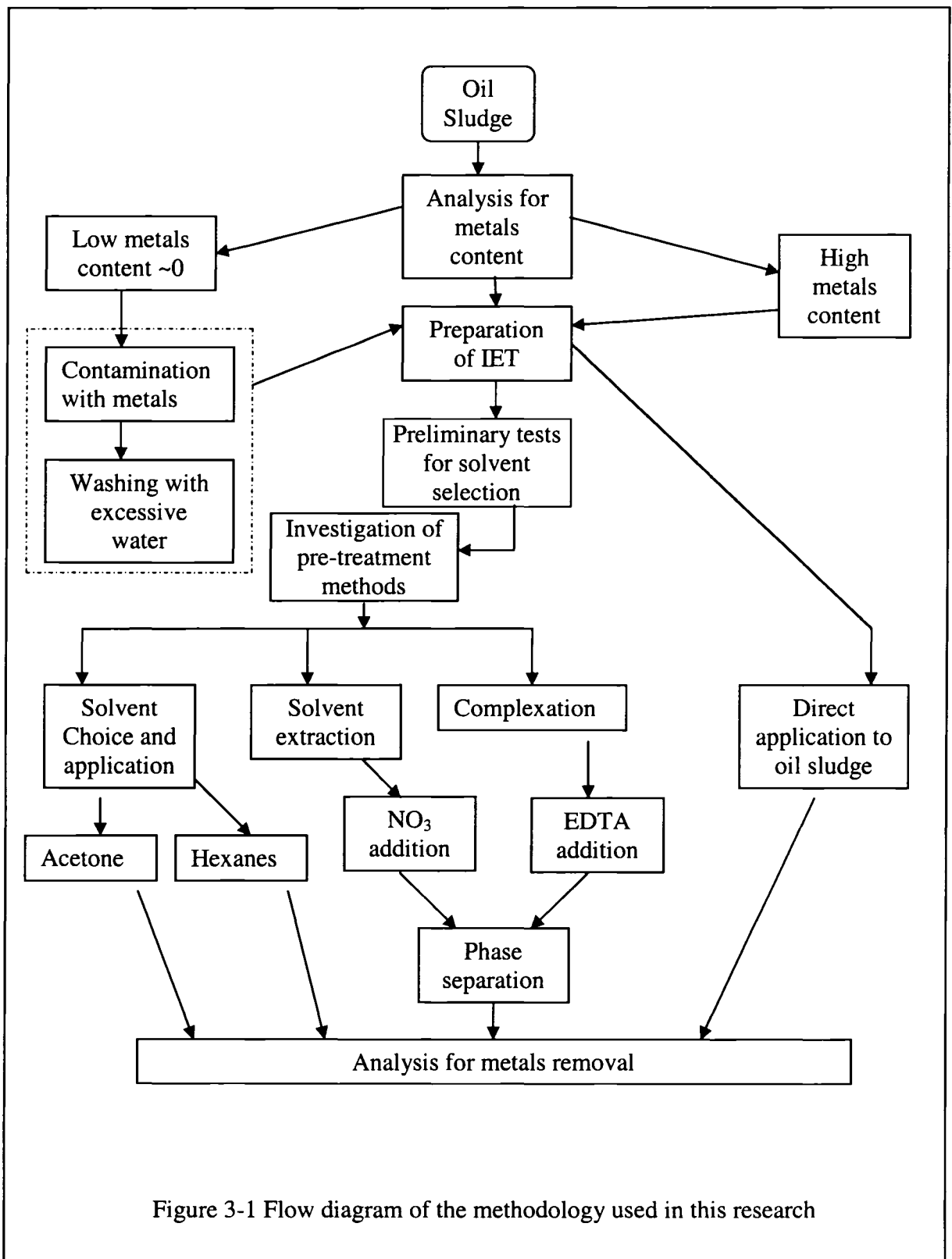


Figure 3-1 Flow diagram of the methodology used in this research

3.2 Oil sludge

Initially three types of oil sludge samples were used for analysis of metals content, and the fourth sample was the completely liquid phase that was decanted from the top of the oil sludge container after a gravimetric separation of phases.

- The first type of samples was oil sludge brought from the bottom of crude oil storage tanks in Shell Canada refinery located in Montreal (Figure 3-2). This oil sludge consisted, due to long storage period, of the completely liquid phase at the top of the container (Figure 3-3), and the semi solid sludge at the bottom.



Figure 3-2 Semi solid sludge that is used in this research



Figure 3-3 Oil sludge Liquid phase

- The second type of samples was the oil sludge (Figure 3-4) that was previously subjected to a new electrokinetic separation technology for recovery of the liquid phase, solid phase and water using DC current (Elektorowicz *et al.*, 2003a, 2003b, Habibi *et al.*, 2004, Habibi 2003).



Figure 3-4 Oil sludge after Electrokinetic process

- The third type was oil sludge (Figure 3-5) mixed with surfactant and then exposed to the new electrokinetic technology mentioned above (Elektorowicz et al., 2003a, 2003b, Habibi *et al.*, 2004 Habibi, 2003).



Figure 3-5 Oil sludge with surfactant after Electrokinetic process

These three types were analyzed for their metals content in order to determine which one of them has the highest metals content and to see if there is any probable effect of the application of the electrokinetic process as it was a possibility to combine both processes in the future. Also the decanted liquid phase was analyzed for its metals content to assess whether liquid oil will have more metals content than the semi solid sludge.

3.3 Target metals

Literature review shows that the most abandoned metals in most of crude oil are; cadmium, copper, iron, nickel, vanadium, and zinc (Magaw *et al.*, 1999). Table 3-4

shows the average and maximum concentrations of these metals in residual oil tank sludge (EPA, 1999).

Based on these findings from literature review, it was decided to proceed with these metals as the target metals for this research.

Table3-1: Average and maximum concentrations of target metals in residual oil tank sludge

Metals	Average content in residual oil tank sludge (mg/l)	Maximum content in residual oil tank sludge (mg/l)
Cd	64	100
Cu	45.3	84.0
Fe	6300	11000
Ni	247	410
V	940	1400
Zn	138	200

3.4 Analysis for metals

The initial samples analysis for metals, involve preparation of samples to be analyzed for metals content using atomic absorption spectrometer. And then use the atomic absorption spectrometer for the analysis of metals content.

3.4.1 Microwave digestion Procedure

The microwave digestion unit used through out the research experiments is illustrated in Figure 3-6. It was found that the maximum sample size for an oil sample to

be digested is 1g with an amount of 17 ml concentrated nitric acid, and a three stage digestion at a pressure of 100psig (689.48 Kpa), 150 psig (1034 Kpa), and 190 psig (1310 Kpa), when the pressure inside the vessel reached 200 psig (1379 Kpa), the process went under aggressive conditions of rapid gas evolution which raised the pressure inside the digestion vessel above 600 psig (4137 Kpa) and caused the rupture of the safety membrane of vessels.

After the digestion process was completed, the resulting solutions were clear brownish with little sediments as shown in Figure 3-7. The solutions were ventilated to allow for remaining gases to escape and the sediments to precipitate, and then the liquid phase was decanted and analyzed with the AAnalyst 100, Perkin-Elmer.

The settled sediments were placed in the furnace at 550 °C and were found to be inorganic solids.



Figure 3-6: Microwave digestion unit



Figure 3-7 Digested oil sludge samples

3.4.2 Atomic absorption analysis

3.4.2.1 Atomic absorption spectrometer (AAS)

The PerkinElmer AAnalyst 100 system consists of a high efficiency burner system with a Universal GemTip nebulizer and an atomic absorption spectrometer, (Figure 3-8). The burner system provides the thermal energy necessary to dissociate the chemical compounds, providing free analyte atoms so that atomic absorption occurs. The spectrometer measures the amount of light absorbed at a specific wavelength using a hollow cathode lamp as the primary light source, a monochromator and a detector. A deuterium arc lamp corrects for background absorbance caused by non-atomic species in the atom cloud.



Figure 3-8: AA Analyst 100 used in the research work

Flame atomic absorption spectrometry has been used extensively for a number of years to study trace wear metals in used engine oil, and lubricating oils.

There are three sample preparation methods presently being employed prior to determination of metals by flame atomic absorption (Hassan, 1984):

- Dilutions of the oil sample in an organic solvent such as xylene or methyl isobutylketone (MIBK) followed by direct aspiration or injection into the flame.
- Total acid digestion or ashing of the oil sample and dissolution with an appropriate acid.
- Digestion of the oil sample by an acid such as hydrochloric acid or nitric acid.

Each method of sample preparation has advantages and disadvantages and the choice depends on the requirements of the wear metals program. The dissolution of the oil sample in an organic solvent and comparison with a known set of organometallic standards made up in the organic solvent is simple and fast. However the method has been shown not to measure the total metal content since not all the particulate metal

aspirated is atomized (Mostyn *et al.*, 1967). The organic solvent acts as combustible fuel which can disturb the flame conditions. Disruption of flame conditions can, however, be reduced by using an adjustable uptake nebulizer and flame microsampling techniques (Perkin Elmer, 1997).

Sample treatment by ashing is very time-consuming and although total metal content for iron, copper and chromium are determined accurately, volatile metals such as lead are lost during the ashing process.

Digestion of oil by an acid such as hydrochloric acid or nitric acid is also time consuming. A strong vacuum pump and heating of the oil sample is required to ensure that a large enough sample is filtered for determination. The use of microwave digestion method has enabled to overcome these problems, however, the gas evolution from the digestion process limits the digestion sample size since the evolved gases can increase the pressure in the vessels and might cause damage of the unit.

Both the ashing and digestion methods permit aqueous standards to be used for calibration, but if sulfuric and phosphoric acid are used during sample treatment, a standard addition method or a set of matched matrix standards incorporating these acids is required for calibration. The greatest disadvantage to the digestion and ashing methods is that they rely heavily upon strict sampling programs. The particulate metal will settle out very quickly from oil and any deviation from the sampling program can give anomalous results.

In this research, acid digestion was selected based on the hypothesis that this method will allow for metals detection at accuracy higher than other methods since there will be no need to reduce the atomic absorption spectrometer sample aspiration which

reduces the sensitivity for metals detection. The other reason is to overcome the viscosity matching for the standards and the oil sludge sample, and to ensure no metal loss since the digestion is carried in a sealed vessels.

3.4.2.2 AAS procedure

The method used here in this research was the acid digestion of oil samples with concentrated nitric acid.

Table 3-1, shows the settings of the AAnalyst 100 that were used for metals content in the digested oil samples.

Table 3-2 AAnalyst 100 settings

Metals	Wt, volume of oil sample (g,ml)	Volume of tested sample (ml)	Wave length (nm)
Fe	1	17	252.3
Cu	1	17	324.8
Zn	1	17	213.9
Ni	1	17	352.6
Cd	1	17	228.8
V	1	17	318.4

3.5 Method Development

3.5.1 Ion exchange textiles (IET) characteristics and preparation

Ion exchange textile used in this research was viscosis non woven-textile grafted with ion exchange polymer of cationic strong- acid type consisting of a sulfonic group (-

HSO_3^-) as its primary functional group. This IET was used for all the stages except for EDTA experiment. This IET has a total exchange capacity of 0.5 meq/g, and works in a pH range of 7 to 14. In EDTA experiment a strong anionic IET of quaternary ammonium ($-\text{NH}_4^+$) was used. This IET has a total exchange capacity of 0.4 to 1 meq/g and works in a pH range of 1 to 8. The use of anionic IET with EDTA was because EDTA-metals complexes usually have negative charges (see section 2-7 in literature review). The textile sheets were obtained from L'Institut Textile de France.

Each textile was cut into a circular shape matching the inner diameter of the perforated Buckner funnel, so that it covers the entire perforated surface of the funnel, the diameter of each IET sheet was almost 3 cm. Figure 3-9 shows a sample of the ion exchange textile used in this project.

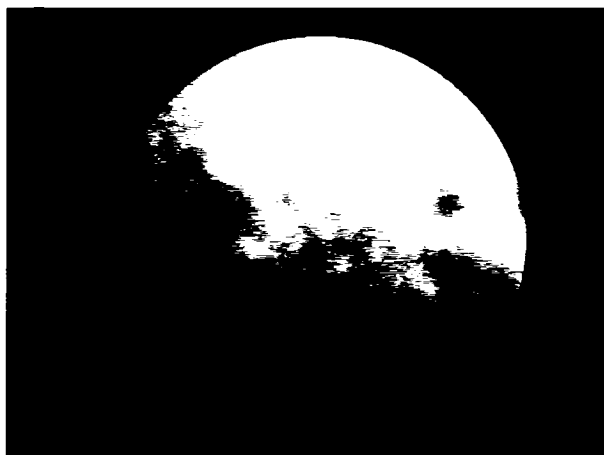


Figure 3-9 Ion exchange textile used in the project

It was found that better ion exchange results in the oil (non aqueous) medium were achieved when textiles were placed in 10 % sulfuric acid in order to transform the sulfonic cation part from sodium ion to hydrogen ion. The acid traces have to be removed

from the textile texture by washing with excessive distilled water. Textiles were then conditioned with different solvent type according to the experiment stage, as follows;

- Stage one: oil sludge only; IET sheet was conditioned with liquid phase of oil sludge sample.
- Stage two:
 - i)* Hexanes experiment set; IET was conditioned with 10 ml of hexanes;
 - ii)* Acetone experiment set; acetone was the conditioning solvent for IET sheet
- Stage Three:
 - i)* EDTA experiment set; distilled water was the conditioning solvent;
 - ii)* Nitric acid experiment set; 10% nitric acid was the conditioning solvent

3.5.2 Apparatus

The apparatus showed in Figure 3-10 was used for the application of ion exchange between the conditioned IET and the treated oil sludge samples and aqueous phases.

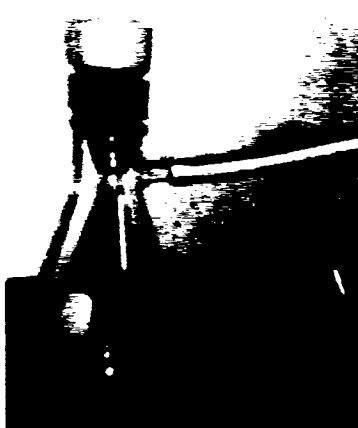


Figure 3-10 Apparatus used for the ion exchange process

The IET sheet is placed in the perforated Buckner funnel, oil sample or the aqueous phase will be forced to pass through the IET and Buckner funnel by vacuum filtration to volumetric funnel. Water current is used as the vacuum source

3.5.3. Oil sludge characteristics

The oily sludge was collected from crude oil storage tanks bottom in Shell® Canada refinery which is located in Montreal. Sludge was collected and stored in sealed containers (Said, 2004). During the storage, the sludge has separated into two phases; the liquid phase, and the semi solid sludge (Figure 3-2), the liquid phase was decanted, and the semi solid sludge was found to have the characteristics summarized in Table 3-2.

Table 3-3 Oil sludge sample properties (Habibi, 2004)

Component	Content (%wt)
Water content	18.06
Light Hydrocarbons	55.87
Non-VOC	23.47
Solid material	2.6

Analysis for metals content in this sample using AAS showed very little metals content (Table 3-3). There for, for the research purposes, an increase of target metals content was decided. The calculations of metals concentration in oil sample for all the experiments are listed in appendix B

Table 3-4 Metals content in oil sludge sample before contamination

Metals	Conc. in AAS sample (mg/l)				Concentration in oil sample (mg/l)
	1 st Run	2 nd Run	3 rd Run	Average	
Fe	2.6	2.6	2.6	2.60	42.60
Cu	0	0	0	0.00	0.00
Zn	0	0	0	0.00	0.00
Ni	0	0	0	0.00	0.00
Cd	0	0	0	0.00	0.00
V	0.8	0.8	0.8	0.80	13.60

3.6 Speciment preparation

3.6.1. Oil sludge contamination with metals

Oil sludge sample of 275 g was mixed with 250 ml of solution containing metals each of 1000 mg/l concentration in the solution.

The mixture was stirred vigorously on a shaker at a speed of 100 rpm, for two days, and then was left to settle in a separatory funnel for another two days, in order to allow the oil phase to separate from the aqueous phase.

The oil sludge sample was then washed with 300 ml of distilled water, to remove excess metals solution that was trapped in the oil without being removed in the separatory funnel. The excess water was removed in the separatory funnel, and oil sludge sample was ready to be tested by the ion exchange textiles.

Analysis for metal content in oil sample after contamination with a solution of these metals ions showed the metals concentration in the oil sludge sample as listed in Table 3-5

Table 3-5 Metals content in the contaminated oil sludge sample before IET application

Metal	Volume of oil sample (ml)	Volume of tested sample (ml)	Conc. in AAS sample (mg/l)				Conc. in oil sample (mg/l)
			1 st Run	2 nd Run	3 rd Run	Average	
Fe	1	17	22.0	21.9	22.3	22.1	375.1
Cu	1	17	27.0	27.0	27.0	27.0	459.0
Zn	1	17	21.0	21.3	21.0	21.1	358.7
Ni	1	17	22.9	22.9	23.0	22.9	389.9
Cd	1	17	24.7	24.6	24.7	24.7	419.3
V	1	17	24.0	24.0	24.0	24.0	408.0

3.6.2 Oil sludge and IET experiments sets

In preparation for ion exchange textiles, based on previous works, Oil sludge sample was divided into three main groups:

- Oil sludge only: in which only oil sludge was exposed to the IET
- Pre-treatment with organic solvent: three experiments were conducted, in each experiment oil sludge was mixed with an organic solvent and then the mixture was passed through IET which was conditioned with same type of organic solvent.
- Extraction solvent: under this category, oil sludge was pre-treated with EDTA, and nitric acid in two separate experiments, then the emulsion was allowed to settle and the separated aqueous solution was passed through the IET.

In the first group, only oil sludge was introduced to the ion exchange textile directly.

In the second group, an organic solvent was added to the oil sludge sample and then was passed through the ion exchange textile for metals removal. Several solvents were tested for solubility with oil sludge. The tested organic solvents were:

- Acetone
- Hexanes
- 1-Octanol
- Benzene
- Methanol

Based on the solubility of the oil sludge in these solvents it was decided to proceed in further research with acetone and hexanes.

In the third group, extraction solvent was mixed with oil sludge sample and then left to settle for layers separation. Then the aqueous layer was passed through the ion exchange textiles for metals removal.

EDTA and nitric acid were selected as the extraction solvents (section 2-7).

3.6.2.1 Stage one: Oil sludge only

Procedure

A sample of 10.01g of oil sludge semi solid was mixed with 10 g of the oil liquid phase which was separated from the semi solid oil sludge phase, and then was placed on the shaker for three days. Finally, it was allowed to pass through the IET for 30 minutes.

Analysis for metals

Samples were taken from the oil sludge portion that passed through the IET and the residue which remained on the IET. These samples were digested with nitric acid and analyzed in the atomic absorption spectrometer for metals content.

3.6.2.2. Second stage: pre-treatment with organic solvent

- **Pre-treatment with hexanes**

Procedure

Ten milliliters of hexanes was to added to 10.09 g of oil sludge sample weight in order to dissolve the oil sludge sample, and then the another 10 ml of hexanes was added to the same sample to complete dissolving the oil sludge sample. The solution was left to mix properly in the shaker at a speed of 130 rpm, for one day.

Then the sample was introduced to the treatment with IET. The sample was circulated through the textile three times; each run took approximately ten minutes to be completed. Hexanes were then removed by evaporation from the oil sample.

A remaining sludge of about 1 g was left without being dissolved by hexanes; the existence of this sludge has increased the time for the second and third run to twenty minutes from ten minutes in the first run. This remaining sludge neither was immiscible even with the addition of another 2 ml of hexanes nor was miscible in benzene.

Analysis for metals

Samples of 1 ml of the separated hexanes, and oil sludge, and the remained sludge on the textile were digested with 15ml concentrated nitric acid in the microwave following the same procedure used previously in the analysis of the original oil sludge.

- **Pre-treatment with acetone**

Procedure

In this experiment, acetone was used as the pre-treatment of the oil sludge sample.

An amount of 10 ml of acetone was added to the 10.01 g of oil sludge, and was placed on the shaker for almost one day on a speed of 130 rpm.

The solution was then allowed to circulate through the ion exchange textile was circulated three times. Amount of residue left on the IET surface in this experiment was nearly 0.5 g and was almost like very fine particles.

Acetone was, then, removed by evaporation from the oil sludge sample.

Analysis for metals

A sample of one milliliter of the oil sludge was digested with 15 ml of concentrated nitric acid in the microwave digester, and almost 0.2 g of the remaining sludge was digested in the microwave with 5 ml Nitric acid concentrated. Then both samples were analyzed for metals with AAS.

3.6.2.3 Third stage: pre-treatment with aqueous solutions

- **Pre-treatment with EDTA**

Procedure

An amount of 10.6 g of oil sludge was mixed with 20 ml of 20% EDTA solution, and the mixture was placed on the shaker for about two days at a speed of 90 rpm. The mixture was, then, placed in a separatory funnel for two days to allow the EDTA to separate from the oil sludge sample, as shown in Figure 3-12.



Figure 3-11 Separation of phases in solvent extraction process

EDTA solution was collected at the bottom of the funnel, and was taken to be circulated through the ion textile for about twenty runs. There was some fine particles suspended in the solution but were trapped by the textile.

Analysis for metals

The treated EDTA solution was analyzed using the AAS spectrometer to determine the amount of metals remained in the solution. In addition, one gram of the oil sludge remained in the separatory funnel was digested with ten milliliter of concentrated nitric acid in the microwave in order to determine the amount of metals remained in the sample.

- **Pre-treatment with nitric acid**

Procedure

An amount of 10.07g of oil sludge sample was mixed with 10 ml of 20 % nitric acid. The mixture was placed on the shaker at a speed of 90 rpm for two days. The mixture was then allowed to separate in the separatory funnel for two days. The nitric solution was separated from the bottom of the funnel, while oil sludge was the upper layer in the funnel. The same system showed in Figure 3-12 was used for nitric acid and oil separation.

The separated aqueous solution was then passed through the ion exchange textile for about twenty runs each run lasted for about 10 seconds.

It was noticed that although only 10 milliliters of 20 % nitric acid was added to the oil sludge sample, 12 ml of aqueous solution was collected in the separatory funnel.

Analysis for metals

The treated solution was tested for metal content with atomic absorption spectrometer. A one gram of the remaining sludge in the funnel was digested with 10 ml of concentrated nitric acid (68%) in the microwave digestion unit. Then, it was analyzed for its metals content.

The above illustrated series of experiment tests permitted for the first time assess the feasibility of applying IET to remove metals from oil sludge.

Chapter Four

CHAPTER 4: Results and Discussion

Atomic absorption analysis indicated that metals were mostly present in the semi solid fraction of the original petroleum oil sludge. The other fractions have been shown to be metals free. Subsequently, they were excluded from being used in tests; since whatever results coming out from the semi solid fraction would apply to the entire oil sludge.

4.1 Experiment stages

4.1.1 Stage one: oil sludge only addition experiment

The objective from this experiment was to assess removal of metals from oil sludge without applying any a conditioning liquid or pre-treatment. The results obtained from this experiment are listed in Table 4-1. The calculations equations for the metals concentrations are shown in appendix B.

Table 4-1 Oil only experiment: metals content in oil sludge sample after direct application to IET

Metals	Conc. in AAS sample (mg/l)				Conc. in oil sludge sample (mg/l)	Removal %
	1 st Run	2 nd Run	3 rd Run	Average		
Fe	18.3	18.3	18.2	18.27	365.3	2.7
Cu	21.5	21.4	21.5	21.47	429.3	6.5
Zn	17.8	17.8	17.8	17.80	356.0	0.8
Ni	17.7	17.7	16.8	17.40	348.0	10.7
Cd	20.5	20.7	20.6	20.60	412.0	1.7
V	24.0	19.8	19.8	18.00	360.0	11.8
					Over all %	5.7

Results show a low metals removal. This might be because of poor contact between oil sludge sample and IET. Oil sludge sample contained liquid oil, and dense oil residues which accumulated on the IET forming a cake layer that prevented further liquid oil from penetrating IET sheet, thus trapping metals in liquid oil on the IET sheet. Another reason might be because of poor ion exchange between oil sludge sample and IET. Ion exchange works better in polar media rather than non polar media. since oil sludge is considered nonpolar, it would be expected that ion exchange will not be of great amount in such case. Metals removed here might be the metals dissolved in water droplets that are trapped in the oil sludge matrix and which were able to reach ion exchange textile sheet. Never the less, the highest removal was for vanadium and nickel (nearly 11%), while zinc showed the least removal percentage at almost 1%. Iron removal also was not high as vanadium but was still better than zinc and cadmium. Copper removal from oil sludge was almost 7%.

4.1.2 Stage two: Pre-treatment with organic solvent

The sought target from this experiment set was to observe the effect of reducing oil sludge residues through the addition of an organic solvent to dissolve this residue. The choice of organic solvent was based on the solubility of oil sludge in the organic solvent. Polarity of the solvent was also taken into consideration. Based on those two reasons was the selection of acetone, which has slight polarity properties and hexanes, which is non-polar organic solvent. Both solvent have relatively low boiling point, which facilitated solvent recovery from oil sludge.

4.1.2.1 Pre-treatment with hexanes

It was noticed that the semi solid fraction of oil sludge (residue) which was non soluble in hexanes was less than 1 g. Analysis for metals content of oil sludge-hexanes liquid phase sample after IET application and oil sludge residue are shown in Tables 4-2 and 4-3 respectively.

Table 4-2 Pre-treatment with hexanes: metals content in liquid phase sample after IET

Metals	Conc. in AAS sample (mg/l)				Average conc. in liquid oil phase (mg/l)
	1 st Run	2 nd Run	3 rd Run	Average	
Fe	13.10	13.10	13.20	13.13	197.00
Cu	9.00	9.00	9.00	9.00	135.00
Zn	18.00	18.10	18.00	18.03	270.50
Ni	16.00	16.00	13.00	15.00	225.00
Cd	4.10	4.10	3.90	4.03	60.50
V	0.30	0.20	0.30	0.27	4.00

The lowest concentration was found for vanadium then for cadmium while the highest concentration was that of zinc and nickel. Iron and copper obtained concentrations were also high but less than zinc and nickel.

Table 4-3: Pre-treatment with hexanes: metals content in the oil sludge residue

Metals	Conc. in AAS sample (mg/l)				Average conc. in residue (mg/l)
	1 st Run	2 nd Run	3 rd Run	Average	
Fe	9.8	9.8	9.8	9.8	294.0
Cu	3.0	3.1	3.0	3.0	90.5
Zn	2.0	2.0	1.9	2.0	59.0
Ni	5.0	5.0	5.0	5.0	150.0
Cd	2.5	2.6	2.4	2.5	75.0
V	1.3	1.3	1.2	1.3	38.0

Iron had the highest concentration, followed by nickel while zinc and vanadium had the lowest.

Metals content in oil sludge residue were expected to be higher than what was found here; as metals usually accumulate in heavy oil fractions, especially in resinous-asphaltene complexes (Galimov *et al.*, 1990).

Oil sludge residue did not prevent dissolved oil sludge from passing through IET, but it did slow its rate.

When hexanes solvent was evaporated, some of light oil fractions came out with the solvent due to their close boiling point to that of hexanes which might caused metals concentration to get higher when analyzed for their content, but the error resulted from

this would not affect the overall process results, since the quantity of these light hydrocarbons was very low compared to oil sludge sample.

Metals removal

In order to determine the exact metals removal percentage, it was necessary to carry out mass balance for metals (appendix B.2.2), to find out the metals content in liquid oil sludge fraction before applying IET. Table 4-4 shows concentrations of metals in liquid oil sludge sample before IET application. Table 4-5 presents summary of metals removal percentages.

Table 4-4 Hexanes addition experiment: metals concentration in liquid fraction of oil sludge-hexanes sample before IET application

Metal	Conc. in liquid fraction of oil sludge-hexanes (mg/l)
Fe	379.34
Cu	478.25
Zn	374.36
Ni	402.43
Cd	437.29
V	427.33

Table 4-5: Pre-treatment with hexane: metals removal

Metal	Concentration in liquid fraction of oil sludge sample (mg/l)	Average conc. in oil sample after IET (mg/l)	Removal %
Fe	379.34	197.00	48.07
Cu	478.25	135.00	71.77
Zn	374.36	270.50	27.74
Ni	402.43	225.00	44.09
Cd	437.29	60.50	86.16
V	427.33	4.00	99.06
Over all %			62.8

Except for vanadium and cadmium it was noticed that the efficiency of metals removal was relatively low, particularly zinc. It was expected that the removal of zinc would be low, since zinc tends to form complexes with organic materials making its removal more difficult (Merian, 1991). The other cause is probably referred to the non-polarity of hexanes, which may did not increase ion exchange process.

4.1.2.2 Pre-treatment with acetone

Addition of Acetone resulted in relatively complete oil sludge dissolution. Amounts of oil residue left behind were very small to be considered. Metals removal in this experiment set, as being shown in Table 4-8, was almost complete.

Table 4-6: Acetone addition experiment: metals content after the IET

Metals	Conc. in AAS sample (mg/l)				Removal %
	1 st Run	2 nd Run	3 rd Run	Average	
Fe	2.1	2	1.9	2.0	92.0
Cu	3.5	3.4	3.4	3.4	88.8
Zn	1	0.9	1	1.0	96.0
Ni	1.7	1.7	1.6	1.7	93.6
Cd	0.4	0.4	0.4	0.4	98.6
V	0	0	0	0.0	100
Over all %					94.8

Metals removal in this experiment was almost complete for most of the metals of interest, and was quietly high for the rest. This is probably due to the polarity of acetone as a solvent that provided favorable conditions for ion exchange process. Oil sludge was completely dissolved in acetone, which provided better contact between metals ions and IET.

Vanadium was totally removed; the removal of zinc was almost 96 %; removal of copper was nearly 89 %; cadmium removal was very close to vanadium removal at 99 %; iron and nickel removal was nearly 92 and 93 % respectively.

The addition of acetone also provided the process, other advantages. Acetone has low boiling point, so its use required less energy and time for solvent recovery; in addition, its low boiling point resulted in less light hydrocarbons escape with solvent during evaporation process.

4.1.3 Stage three: Pre-treatment with aqueous solvent extraction

In this experiment set, the effect of pre-treatment of oily sludge with a strong electrolyte (such as NO_3^-) and a complexation agent (such as EDTA) was investigated. Subsequently nitric acid and EDTA were used for metals extraction in the first and second series of tests.

Results showed that the real factor affecting both of the experiment sets was the metals extraction yield from oil sludge phase to liquid phase. Therefore, for both of these experiments the removal efficiency, which includes the metals removal from liquid phase, and equal to the overall efficiency in which the effect of extraction is included.

4.1.3.1 Pre-treatment with EDTA

Metals removal in this experiment depended on their capability to form complexes with EDTA, and on the separation yield between EDTA aqueous phase and oil sludge phase.

Results for metals content after application of IET aqueous phase treated with EDTA are shown in Table 4-7

Table 4-7 pre-treatment with EDTA: metals content in aqueous phase treated with EDTA after IET application

Metals	Conc. in AAS sample (mg/l)				Conc. in aqueous phase (mg/l)
	1 st Run	2 nd Run	3 rd Run	Average	
Fe	0.01	0.01	0.01	0.01	0.30
Cu	0.05	0.05	0.06	0.05	1.60
Zn	0.02	0.01	0.01	0.04	1.34
Ni	0.02	0.02	0.02	0.02	0.67
Cd	0.01	0.00	0.01	0.01	0.20
V	0.00	0.00	0.00	0.00	0.00

Metals removal from EDTA aqueous phase was almost complete. The concentrations of all metals were less than two mg/l. This was the typical medium for a ion exchange process to take place, since the process was held in an aqueous solution. Vanadium, cadmium, and iron had the next lowest concentrations. Copper and zinc had higher values, but they were still less than two mg/l, which would comply with any regulation for wastewater disposal. In order to know exactly how efficient the removal was in this experiment, it was necessary to assess the extraction yield of metals from oil sludge by EDTA, which would require a mass balance for metals in oil sludge layer and metals in /EDTA solution (appendix B.2.2). The mass balance equations are listed in appendix B 2.3

Metals content in the remained oil sludge phase after treatment with EDTA are shown in Table 4-8.

Table 4-8: EDTA addition experiment: metals content in oil sludge

Metals	Conc. in AAS sample (mg/l)				Conc. remained in oil sludge phase(mg/l)
	1 st Run	2 nd Run	3 rd Run	Average	
Fe	3	3.2	2.8	3.00	60.00
Cu	4.9	5	4.9	4.93	98.67
Zn	11.6	11.6	11.5	11.57	231.33
Ni	2.3	2.3	2.3	2.30	46.00
Cd	13.1	13.2	13.1	13.13	262.67
V	12.9	12.9	12.7	12.83	256.67

In general concentrations of metals remained high in oil sludge fraction after EDTA extraction which may indicate that metals-EDTA complexes formation was less strong than metals-Oil complexation. Vanadium, cadmium, and zinc concentrations were of the highest while nickel had the lowest concentration.

Metals remained in oil sludge shows a low metals transfer from oil sludge matrix to EDTA solution.

Based on mass balance for metals in oil sludge and EDTA aqueous phase, it was found that metals such as copper, nickel and iron had the higher transfer than other metals (Table 4-9).

Table 4-9 pre-treatment with EDTA: metals content in EDTA aqueous phase

before IET application

Metal	Metals in aqueous phase conc. (mg/l)
Fe	157.55
Cu	180.17
Zn	63.69
Ni	171.95
Cd	78.32
V	75.67

Metals removal

Metals removal efficiency from the aqueous phase is given in Table 4-10.

Table 4-10 Pre-treatment with EDTA: removal of metals from aqueous phase

Metals	Concentration in aqueous phase before IET (mg/l)	Conc. in aqueous phase after IET (mg/l)	Removal %
Fe	157.55	0.30	99.81
Cu	180.17	1.60	99.11
Zn	63.69	1.34	97.90
Ni	171.95	0.67	99.61
Cd	78.32	0.20	99.74
V	75.67	0.00	100.00
		Over all %	99.4

Metals removal by IET from the aqueous phase was found to be quite high due to a typical ion exchange conditions, i.e. the ion exchange process was in aqueous medium. Another contribution might come from the size of formed complexes, which helped trapping these complexes on the surface of IET or within its texture.

The efficiency of the process depended on the extraction yield. Metals extraction yield, which is considered as the overall process efficiency is given in Table 4-11.

Table 4-11 Extraction (process overall efficiency)

Metal	Conc. in original sample before EDTA pre-treatment (mg/l)	Conc. remained in oil sludge after EDTA treatment (mg/l)	Extraction %
Fe	375.10	60.00	84.00
Cu	459.00	89.67	80.46
Zn	358.70	231.33	35.51
Ni	389.90	46.00	88.20
Cd	419.30	262.67	37.36
V	408.00	256.67	37.09
		Over all %	60.4

4.1.3.2 Pre-treatment with nitric acid

It was noticed during this experiment that the aqueous phase separation was faster than in the use of EDTA case. It also seemed that there was more aqueous solution quantity than the original quantity added to the oil sludge sample. This indicated that the 20% nitric acid addition helped liberating more aqueous liquid from oil sludge matrix. Metals contents in the aqueous phase after the IET treatment are shown in Table 4-12.

Table 4-12 Metals content in nitric acid aqueous phase after IET treatment

Metals	Conc. in AAS sample (mg/l)				Conc. in nitric acid aqueous phase after IET (mg/l)
	1 st Run	2 nd Run	3 rd Run	Average	
Fe	1.20	1.20	1.20	1.20	2.4
Cu	0.10	0.10	0.10	0.10	0.2
Zn	0.70	0.70	0.70	0.70	1.4
Ni	0.20	0.20	0.20	0.20	0.4
Cd	0.05	0.05	0.05	0.05	0.1
V	0.00	0.00	0.00	0.00	0.0

Metals removal was determined by their transfer from oil matrix to the aqueous phase. Metals contents remaining in oil sludge phase are found to be as in Table 4-13.

Table 4-13 Metals content remaining in the oil sludge phase after phase separation

Metal	Conc. in AAS sample (mg/l)				Conc. remained in oil sludge after nitric acid pre-treatment(mg/l)
	1 st Run	2 nd Run	3 rd Run	Average	
Fe	9.4	9.4	9.4	9.4	188.0
Cu	19.1	19.0	19.1	19.1	381.3
Zn	8.9	8.6	8.8	8.8	175.3
Ni	19.2	19.2	19.3	19.2	384.7
Cd	12.8	12.7	18.6	14.7	294.0
V	18.0	18.0	18.0	18.0	360.0

Based on mass balance, metals concentrations in the aqueous phase before IET treatment was found to be as shown in Table 4-14.

Table 4-14 Metals conc. in nitric acid aqueous phase before IET treatment

Metal	Conc. of metals in Aqueous Phase before IET (mg/l)
Fe	93.55
Cu	38.85
Zn	91.70
Ni	2.60
Cd	62.65
V	24.00

Nickel concentration in nitric acid aqueous phase was exceptionally low while iron and zinc had the high concentrations in nitric acid. The extraction efficiency of metals using nitric acid is shown Table 4-15

Table 4-15 Pre-treatment with nitric acid: extraction efficiency

Metal	Conc. in oil sludge before pre-treatment (mg/l)	Conc. remained in oil sludge after pre-treatment(mg/l)	Extraction %
Fe	375.10	188.00	49.88
Cu	459.00	381.30	16.93
Zn	358.70	175.30	51.13
Ni	389.90	384.70	1.33
Cd	419.30	294.00	29.88
V	408.00	360.00	11.76
Over all %			26.82

Metals removal

Metals removal efficiencies from aqueous phase are shown in Table 4-16.

Table 4-16: Pre-treatment with nitric acid: IET metals removal from nitric acid aqueous phase

Metal	Concentration in nitric acid aqueous phase before IET treatment (mg/l)	Conc. in nitric acid aqueous phase after IET treatment (mg/l)	Removal %
Fe	93.55	2.40	97.43
Cu	38.85	0.20	99.49
Zn	91.70	1.40	98.47
Ni	2.60	0.40	84.62
Cd	62.65	0.10	99.84
V	24.00	0.00	100.00
		Over all %	96.64

Metals removal from the aqueous phase was very high. Vanadium was completely removed; other metals were almost removed, except for nickel, which yielded the lowest removal percentage. High polarity of the nitric acid aqueous layer provided good ion exchange conditions between IET and the aqueous layer.

4.2 Effectiveness of ion exchange textile application: evaluation of methods

IET removal efficiency varied with the experimental methods applied and type of metal. Figures 4-1 through 4-6 show comparisons between these methods regarding their removal efficiency for each of target metals.

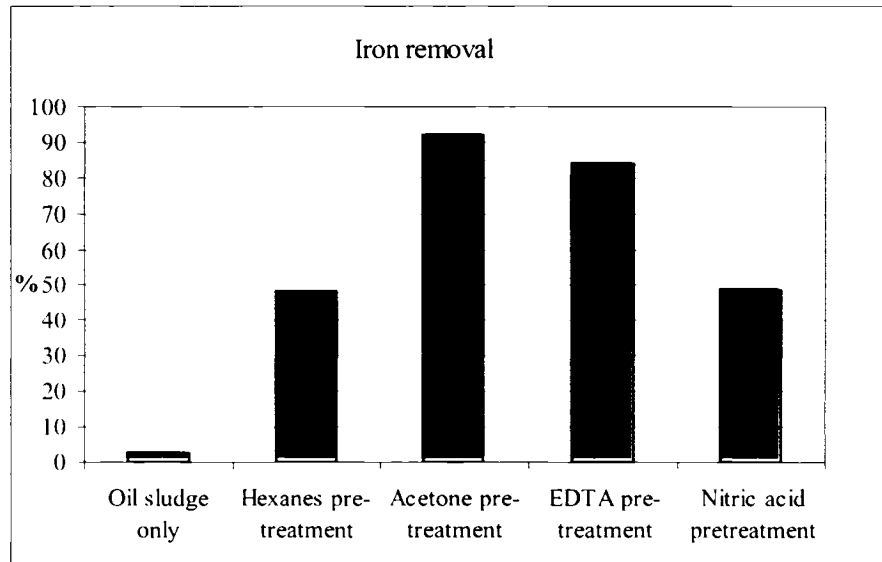


Figure 4-1 Iron removal comparison of the pretreatment methods

As indicated by Figure 4-1, pretreatment with acetone addition experiment showed the highest removal for iron. When EDTA was added to oil sludge, it gave better performance than in nitric addition and even better than when hexanes was applied. As it was previously shown, oil sludge alone had the lowest iron ion exchange.

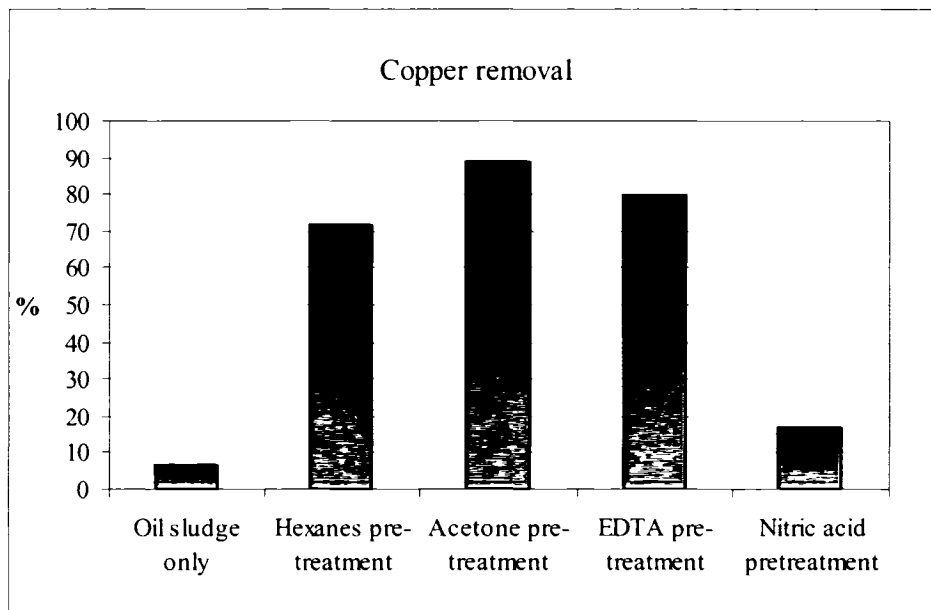


Figure 4-2 Copper removal comparison of pretreatment methods

Ion exchange of copper ions had the best results when acetone was used in the pre-treatment of oil sludge sample. Hexanes gave results close to EDTA pretreatment while nitric acid pre-treatment results were less than both hexanes and EDTA, but it was still better than when oil sludge was used alone with IET.

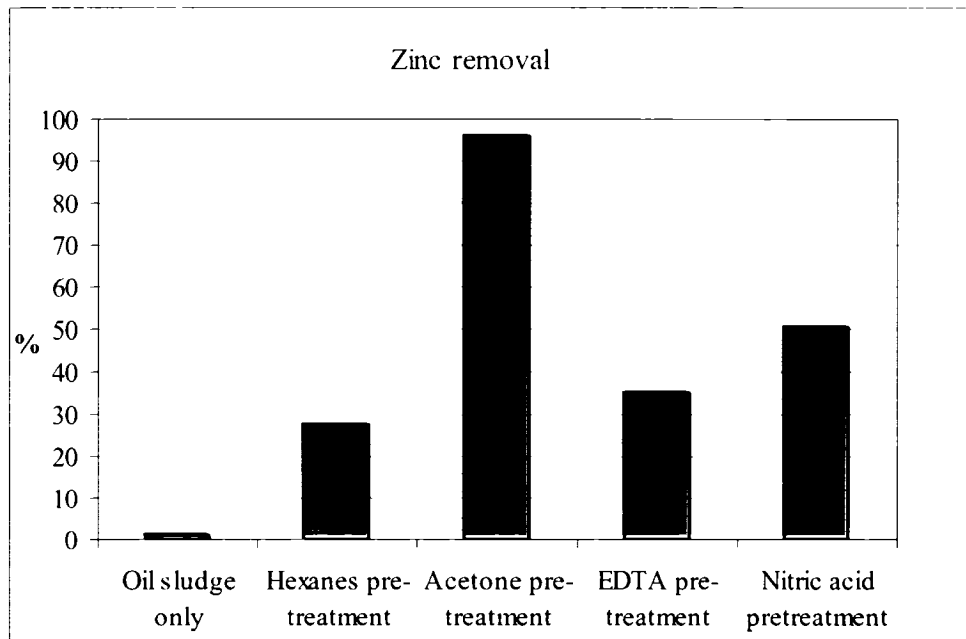


Figure 4-3 Zinc removal comparison of pretreatment methods

Pre-treatment with acetone had the best zinc removal results than any of the other three pre-treatment methods. When nitric acid was used, IET removed nearly half of zinc that was removed when acetone was applied. EDTA and hexanes results were close in removal of zinc from oil sludge.

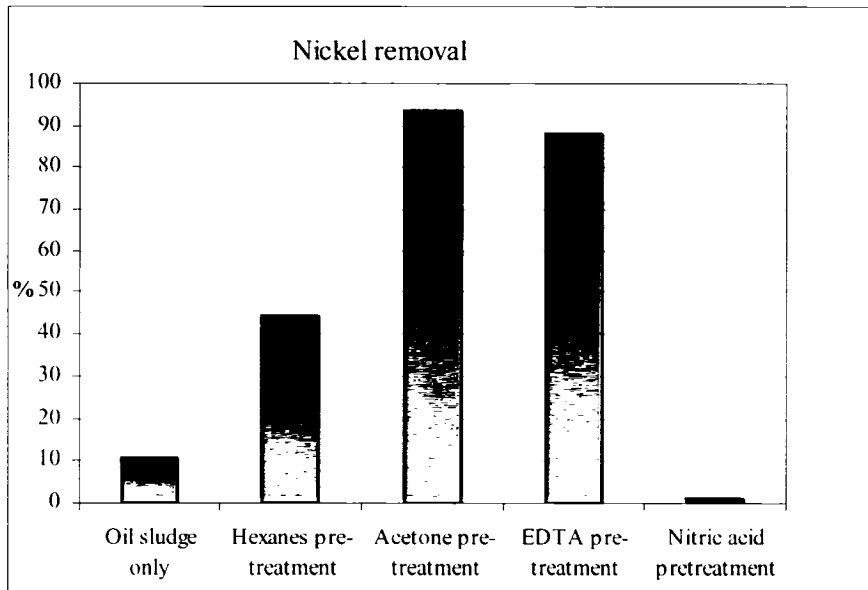


Figure 4-4 Nickel removal comparison of pretreatment methods

Highest removal of nickel was achieved with acetone pre-treatment. However, pretreatment with EDTA gave results close to acetone experiment. Hexanes permitted removal of only 40% of copper, but this removal was far better than the case of pre-treatment with nitric acid, which gave lowest removal results.

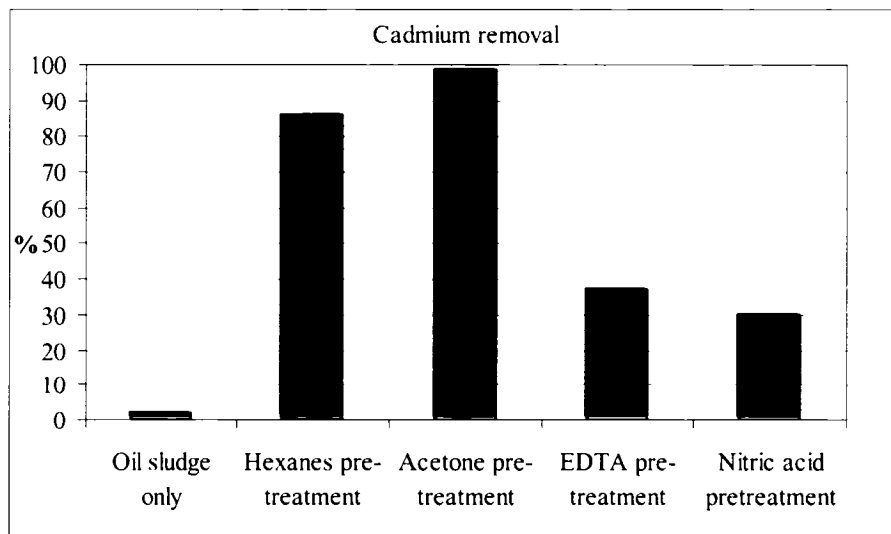


Figure 4-5 Cadmium removal comparison of pretreatment methods

The pre-treatment with acetone had also the best performance for cadmium removal using ion exchange process. While the use of oil sludge only obtained the lowest results, pre-treatment with nitric had results close to EDTA experiment. Hexanes addition has achieved removal results better than both EDTA and nitric acid experiments.

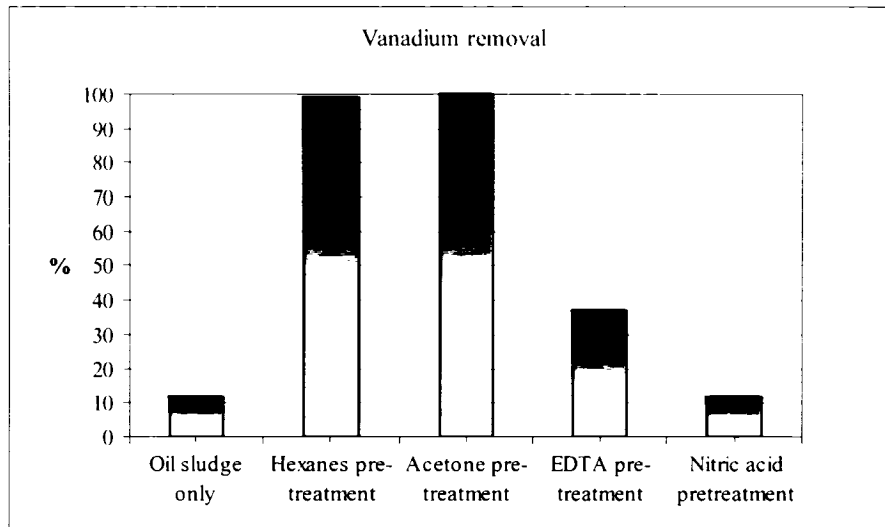


Figure 4-6 Vanadium removal comparison of pretreatment methods

Vanadium was totally removed, in both pre-treatment with hexanes and acetone. EDTA pre-treatment had helped to remove nearly 40% of vanadium. The addition of nitric acid did not have clear advantages over the tests of oil sludge without pre-treatment.

A comparison of metals extraction from oil sludge by the application of nitric acid and EDTA solution was made in Figure 4-7, showed that except for zinc, EDTA solution has done better metals extraction than nitric acid solution.

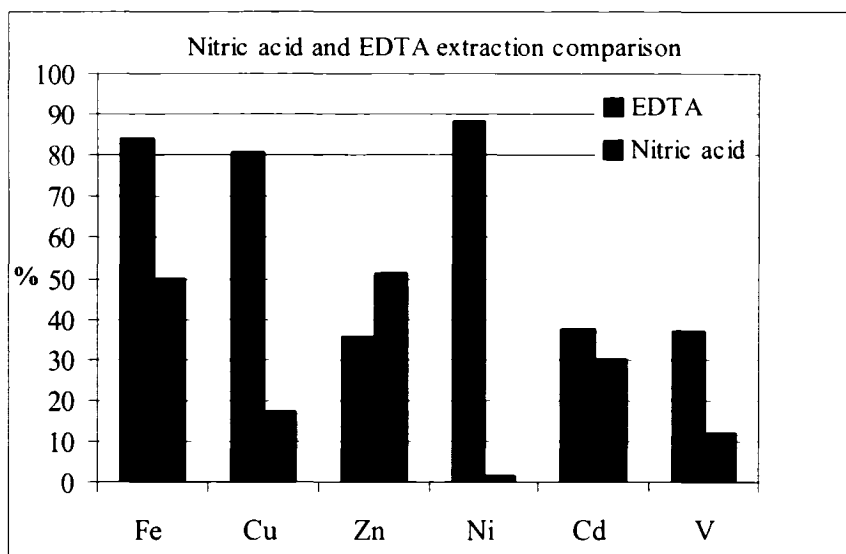


Figure 4-7 Metals extraction comparison between nitric acid and EDTA

Comparison of the five experiments for metals removal had shown clearly that best results were obtained when acetone was used, with an overall efficiency of 95 %; while the lowest values were obtained when IET was applied directly to oil sludge sample, which had an efficiency of 5.7%. Overall efficiencies for the rest of methods applied were; Hexanes 63 %, EDTA 60 %, and nitric acid 26%.

Chapter Five

CHAPTER Five: Conclusions and Recommendations

5.1 Conclusions

This thesis has dealt with development of a new technology for metals removal from oil sludge through the application of ion exchange technology. Ion exchange phenomenon has been known for centuries and has vast applications in water and wastewater treatment, and so many different industries. However, to my knowledge it has never been applied to oil waste treatment. This research would

In this research, ion exchange textiles were used for the ion exchange process applied for removal of metals from oil sludge. Three different approaches were followed during this research to assess the feasibility and applicability of ion exchange in oil sludge medium.

1. The application of these different approaches has permitted to generate the following conclusions:
 - The exposure of IET to oil sludge directly has led to poor ion exchange results due to the low polarity of oil sludge, as well as the high volume of residues in oil sludge, which did not allow for better contact between IET and oil metals in oil sludge.
 - The application of hexanes and acetone as organic solvents to dissolve oil residues prior to treatment with IET showed that polar the oil sludge is the better ion exchange result can be obtained.
 - The effectiveness of nitric acid and EDTA pretreatment was greatly affected by the extraction yield of metals from oil phase to the aqueous phase. Although ion

exchange process worked very well in both aqueous solutions, the overall process yield kept less than the acetone addition experiment due to the extraction limitation. However, the process showed better results for pretreatment with EDTA rather than with nitric acid.

2. The performed investigation showed a feasibility application of ion exchange process into oil sludge treatment method.
3. The application of IET with pretreatment permitted for a high removal of target metals from oil sludge:
 - Vanadium, major component in oil, was completely removed;
 - Cadmium removal efficiency was nearly 99 %
 - Zinc removal was also high at almost 96 %
 - Nickel removal was about 94 %
 - Iron was removal was nearly 92 %
 - Copper had a removal efficiency of almost 89 %.
4. Results showed that treatment using IET medium is an efficient method for oil sludge treatment regarding metals removal
5. Results also showed that the IET can be considered as an extension step in oil sludge treatment technology after phase separation, (including electrokinetics separation of phases)
6. These investigations made a contribution to new technologies along with present guidelines on sustainable development
7. Ion exchange textiles have potential to applied to other types of sludge with higher water content .

5.2 Contribution

The main contribution of this work is that the development of a new technique for treatment of oil sludge for removal of heavy metals. This method overcomes disadvantages of other technologies currently available, with regard to simplicity and affordability.

Other contributions made by this work include:

- This is the first work done to apply ion exchange textiles to oil sludge treatment for heavy metals removal,
- For the first time, the ion exchange process in oil sludge has been assessed,
- First application of acetone in the pretreatment of oil sludge before ion exchange was used,
- Hexanes has been applied for the first time to oil sludge pretreatment prior to ion exchange process,
- For the first time, EDTA has been used as a complexing agent in oil sludge treatment for heavy metals extraction from oil phase to aqueous solution phase before applying ion exchange textiles,
- Heavy metals response to various pre-treatment methods of oil sludge has been assessed, by this work, for the first time,
- First work to establish protocols and equipment for ion exchange textiles preparation and testing in oil sludge treatment.

5.3 Recommendations for future work

- Additional work should be performed to investigate the possibility and the efficiency of ion exchange textiles regeneration in order to determine the approximate service life for such textiles.
- It would be worth to investigate the application of other organic solvents.
- An additional effort should be given for developing methods, which can improve heavy metals extraction yield from oil sludge phase to the aqueous phase.
- Larger scale experiments should be conducted to verify the results and to optimize the performance.
- More work is required to quantify and evaluate the result from an economical point of view.

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Appendices

Appendix A:

Glossary

A

- **Absorption Spectroscopy**

The branch of spectroscopy treating the theory, interpretation, and application of spectra originating in the absorption of electromagnetic radiation by atoms, ions, radicals, and molecules.

- **Atomization**

The subdivision of a compound into individual atoms using heat or chemical reactions. This is a necessary step in atomic spectroscopy.

- **Attrition**

The reduction of ion exchange resin size during its operation.

B

- **Biomass**

Biomass, also known as bio-fuels or bio-energy, is obtained from organic matter either directly from plants or indirectly from industrial, commercial, domestic or agricultural products. The use of biomass is classed as a 'carbon neutral' process because the carbon

dioxide released during the generation of energy from biomass is balanced by that absorbed by plants during their growth.

C

• **Chelate**

A coordination compound in which a heterocyclic ring is formed by a metal bound to two atoms of the associated ligand.

• **Chelating agents**

1) An organic compound in which atoms form more than one coordinate bond with metals in solution. 2) A substance used in metal finishing to control or eliminate certain metallic ions present in undesirable quantities.

• **Chelation**

A chemical process involving formation of a heterocyclic ring compound that contains at least one metal cation or hydrogen ion in the ring.

• **Complex ion**

A complex ion has a metal ion at its centre with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by co-ordinate (dative covalent) bonds. (In some cases, the bonding is actually more complicated than that.)

- **Complexation**

The formation of complex chemical species by the coordination of groups of atoms termed ligands to central ion, commonly a metal ion. Generally, the ligand coordinates by providing a pair of electrons that forms an ionic or covalent bond to the central ion.

- **Coordination compound**

A compound with a central atom or ion bound to a group of ions or molecules surrounding it. Also known as coordination complex.

- **Crude Oil**

A naturally occurring mixture of hydrocarbons trapped in underground rock formations. Crude oil can be refined into many products such as transportation fuels (gasoline and diesel), heating oil, asphalt, petrochemicals and plastics.

D

- **Disposal**

The final placement of toxic or other wastes. Disposal may be accomplished through the use of approved secure landfills, surface impoundment, land farming, deep well injection, ocean dumping.

E

- **EDDS**

S, S'-ethylediaminedisuccinic acid, a structural isomer of EDTA, has been used as a biodegradable substitute. EDDS is a good complexing agent and is broken down during wastewater treatment processes.

- **Electrode potential**

The electrical potential difference between an electrode and a reference electrode. We cannot measure the "absolute" potential of an electrode; therefore, the electrode potential must always be referred to an "arbitrary zero point," defined by the potential of the reference electrode. Consequently, it is very important always to note the type of reference electrode used in the measurement of the electrode potential.

- **Electron volt (eV)**

electron-volt (eV), unit of energy used in atomic and nuclear physics; 1 electron-volt is the energy transferred in moving a unit charge, positive or negative and equal to that charge on the electron, through a potential difference of 1 volt. The maximum energy of a particle accelerator is usually expressed in multiples of the electron volt, such as million electron volts (MeV) or billion electron volts (GeV). Because mass is a form of energy (see relativity), the masses of elementary particles are sometimes expressed in electron-volts; e.g., the mass of the electron, the lightest particle with measurable rest mass, is $0.51 \text{ MeV}/c^2$, where c is the speed of light.

$$\text{KeV} = 1.602\,176\,53\,(14) \times 10^{-21} \text{ J.}$$

- **Energy**

The capacity for doing work as measured by the capability of doing work (potential energy) or the conversion of this capability to motion (kinetic energy). Energy has several forms, some of which are easily convertible and can be changed to another form useful for work. Most of the world's convertible energy comes from fossil fuels that are burned to produce heat that is then used as a transfer medium to mechanical or other means in order to accomplish tasks. Electrical energy is usually measured in kilowatt-hours, while heat energy is usually measured in British thermal units.

F

- **Fly Ash**

Particle matter from coal ash in which the particle diameter is less than 1×10^{-4} meter. This is removed from the flue gas using flue gas particulate collectors such as fabric filters and electrostatic precipitators.

- **Fossil Fuels**

Coal, Oil and Gas are called "fossil fuels" because they have been formed from the fossilized remains of prehistoric plants and animals. They provide around 66% of the world's electrical power, and 95% of the world's total energy demands (including heating, transport, electricity generation and other uses).

- **Fuel**

Any substance that can be burned to produce heat; also, materials that can be fissioned in a chain reaction to produce heat.

G

- **Gasification**

Breakdown of hydrocarbons into a syngas by carefully controlling the amount of oxygen present

- **Global warming**

A rise in global temperatures threatening wildlife and its habitat, often attributed to the burning of fossil fuels

H

- **Hazardous waste**

Defined by federal and state law as exhibiting either of the following characteristics: ignitability, corrosivity, reactivity, or toxicity

- **Heavy metal**

A reference to a group of metals including arsenic, chromium, copper, lead, mercury, silver, and zinc.

- **Hydrocarbon**

An organic compound containing only hydrogen and carbon, often occurring in petroleum, natural gas, and coal.

I

- **Incineration**

A treatment technology that involves the burning of certain types of solid, liquid, or gaseous materials under controlled conditions to destroy hazardous waste.

- **Innovative technology**

A process that has been tested and used as a treatment for hazardous waste or other contaminated materials, but lacks a long history of full-scale use and information about its cost and how well it works sufficient to support prediction of its performance under a variety of operating conditions.

- **Ion**

An ion is an atom or group of atoms (molecule) that carries a net positive (cation) or net negative (anion) electrical charge.

- **Ion Exchange**

Ion exchange is a remediation process that removes dissolved metals from liquids. Liquids are passed over a resin bed where ions (i.e., cations and anions) in the resins and in contaminated materials are exchanged. The resins attract the metallic ions. After the resin capacity has been exhausted, resins can be regenerated for re-use.

- **Ion-Exchange resin**

Any of a wide variety of synthetic polymers containing positively or negatively charged sites that can interact with or bind to an ion of opposite charge from a surrounding solution. Light, porous solids in granules, beads, or sheets, they absorb the solution and swell as they attract the target ions; when exhausted, they are removed from use and regenerated by an inexpensive brine or carbonate solution. A solid support of styrene-divinylbenzene copolymer to which are attached sulfonic or carboxylic acid groups is often used to attract and exchange cations (e.g., ions of hydrogen or metals). Quaternary ammonium groups on the solid matrix are used to attract anions (e.g., ions of chlorine). Industrially, the resins are used to soften hard water, purify sugar, and concentrate valuable elements (gold, silver, uranium) from their ores. In the laboratory they are used to separate and concentrate substances and sometimes as catalysts. Zeolites are minerals with ion exchange properties.

- **IET**

Ion exchange textiles are made of non woven textiles grafted with ion exchange materials.

L

- **Landfill Sites**

A landfill is a carefully designed structure built into or on top of the ground in which rubbish is isolated from the surrounding environment (groundwater, air, soil). Landfills are not designed to break down waste, merely to bury it. The modern landfill offers much more protection for the environment and for local people than traditional dumps did. Problems with odors, litter, vermin, etc., are greatly reduced by the careful management of the site.

- **Ligand**

The molecule, ion, or group bound to the central atom in a chelate or coordination compound.

- **Light Fuel Oil (LFO)**

Fuel suitable for use in liquid-fuel burning equipment without preheating, primarily domestic-type burners (includes Type 0, 1 and 2). Virtually all petroleum used in internal combustion and gas turbine engines is light oil.

M

- **Metal Fever**

Excessive inhalation of fumes from many metals can produce an acute reaction known as "metal fever" similar to influenza like syndrome. Symptoms consist of chills and fever

(very similar to and easily confused with flu symptoms) which become manifest 4-12 hours after exposure. Long-term effects have not been noted.

- **MSW (Municipal Solid Waste)**

The EPA (1998c) defined municipal solid waste as "a subset of solid waste and as durable goods (e.g., appliances, tires, and batteries), non-durable goods (e.g., newspapers, books, and magazines), containers and packaging, food wastes, yard trimmings, and miscellaneous organic wastes from residential, commercial and industrial non-process sources (p. II-2)

N

- **NO_x**

Nitrogen oxides (NO_x) act as indirect greenhouse gases by producing the tropospheric greenhouse gas 'ozone' during their breakdown in the atmosphere.

O

- **Off-gas**

Vapors that are emitted from extraction and treatment systems. These vapors can either be discharged directly to the atmosphere or captured or destroyed.

- **Organic chemical or compound**

A substance produced by animals or plants that contains mainly carbon, hydrogen, and oxygen.

P

- **Particulate Matter (PM)**

Microscopic material in the air. Particulate matter has been classified according to size.

PM10 are those particles which have a diameter equal to or smaller than, 10 microns.

PM2.5 is those particles which have a diameter equal to or smaller than, 2.5 microns.

- **Parts per million (ppm)**

A measure of concentration, or how much substance is in a given sample.

- **Petroleum**

A mixture of hydrocarbons existing in the liquid state found in natural underground reservoirs often associated with gas. Petroleum includes fuel oil No. 2, No. 4, No. 5, No. 6; topped crude; kerosene; and jet fuel.

- **Pyrolysis**

Thermal degradation of waste in the absence of air to produce char, pyrolysis oil and syngas.

R

• RECOFLO

Recoflo® ion exchange technology utilizes fine mesh resin beads, a fully packed resin bed, and counter-current regeneration. These unique features help to improve exchange kinetics, reduce regenerant consumption, and increase the concentration of strip solutions. Commercially, Recoflo technology has been extensively used in the following areas: the separation of strong mineral acids from dissolved metal salts, the purification, removal and recycle of dissolved metals in the surface finishing industries, and the production of high purity water.

• Residual Fuel Oil

The topped crude of refinery operation, includes No. 5 and No. 6 fuel oils as defined in ASTM Specification D396 and Federal Specification VV-F-815C; Navy Special fuel oil as defined in Military Specification MIL-F-859E including Amendment 2 (NATO Symbol F-77); and Bunker C fuel oil. Residual fuel oil is used for the production of electric power, space heating, vessel bunkering, and various industrial purposes. Imports of residual fuel oil include imported crude oil burned as fuel.

S

• Syngas

A mixture of light, combustible gases produced by the advanced conversion technology (gasification or pyrolysis)

T

- **Textile**

Any filament, fibre, or yarn that can be made into fabric or cloth, and the resulting material itself.

The word originally referred only to woven fabrics but now includes knitted, bonded, felted, and tufted fabrics as well. The basic raw materials used in textile production are fibers, either obtained from natural sources (e.g., wool) or produced from chemical substances (e.g., nylon and polyester). Textiles are used for wearing apparel, household linens and bedding, upholstery, draperies and curtains, wall coverings, rugs and carpets, and bookbindings, in addition to being used widely in industry.

Appendix B

Calculations equations

B.1 Calculation of a 1000mg/L standard solution Preparation from its metal salt of (M_mS_n) chemical formula

$$W_s = (m/n) * (M_{wtS} / M_{wtM}) * (V_{std} / 1000) / \text{Assay}$$

Where, W_s: is the salt weight (mg)

M: represents the metal

S: represent the metal salt

m,n: mole ratio of the M to S (mmole/mmole)

M_{wM}, M_{wS}: molecular weights of the sought metal and its salt respectively. (mg/mmole)

V_{std}: volume of standard solution (L)

Assay: purity of the salt (%)

B.2 Calculation of metals Concentration in oil sludge

B.2.1 Hexanes Calculations

$$C_{I.E.T} = C_A * V_A / V_o$$

Where:

$C_{I.E.T}$: Metals Conc. In original oil sludge after I.E.T, and after Hexanes evaporation

$V_{I.E.T}$: volume of the original oil sample after Hexanes evaporation

C_A : average conc. In sample tested in AAs

V_A : volume of tested sample

B.2.2 Mass Balance Calculations

$C_o = \frac{[(\text{Conc. In Original sample} * \text{wt of original sample}) - (\text{Average Conc. in oil resid.} * \text{Wt of oil resid.}) - (\text{Metals Conc. In original oil sludge after I.E.T} * \text{Oil in hexanes wt.})]}{\text{Oil in hexanes wt}}$

Or

$C_o = \frac{[\text{Metals wt in original oil sample} - \text{Metals wt. in Oil residue} - \text{Metals wt. in oil sludge after I.E.T}]}{\text{liquid Oil sludge sample wt.}}$

Where;

C_o is metals concentration in oil-Hexane liquid before I.E.T application.

B.2.3 Removal percentage calculations

Metal removal efficiency = $\frac{[(\text{metal wt in original oil sludge sample} - \text{metal wt in the sample after treatment})]}{\text{metal wt in original oil sludge sample}}$

*100%

B.2.4 Process efficiency

Σ metals removal Efficiencies /no. of metals

B.2.5. Extraction Efficiency of metals (Solvent Extraction)

%Extraction= [(Metals wt in oil sludge sample before extraction –Metals
Wt. in aqueous phase before I.E.T)/ Metals wt in oil sludge sample before
extraction]*100%