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REMEDIATION OF SOIL AND WATER CONTAMINATED BY HEAVY METALS AND HYDROCARBONS USING SILICA ENCAPSULATION

A dissertation submitted to the Faculty of Science, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science.

by

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University of the Witwatersrand, Johannesburg 2007

Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Masters of Science (Chemistry) in the University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

……

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……..day of…… 2007.

This dissertation is submitted after examination and approval by the supervisors.

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Abstract

Heavy metals and hydrocarbons are persistent pollutants in the environment. Problems associated with the cleanup of sites contaminated by metals and hydrocarbons have demonstrated the need to develop remediation technologies that are feasible, quick, and effective in a wide range of physical settings. Experiments were conducted to investigate the efficiency of silica encapsulation and the factors that influence its performance. Analysis was done by ICP-OES and GC-FID for metals and hydrocarbons respectively. This technology was tested using sodium silicate and Chemcap™.

Soils and water contaminated with hydrocarbons and heavy metals were successfully remediated by silica encapsulation. The silica coating was stable under both acidic and alkaline conditions. A new product that is based on sodium silicate formulation was developed and was more effective at encapsulating hydrocarbons and heavy metals. Laboratory tests indicated that it is more effective in an acidic medium and it continues to strengthen with time. Metal encapsulation was affected by the sizes of metal ions and the presence of hydrocarbons.

Dedication

To my parents

Mr Masikane Mbhele and Mrs Joyinile Mbhele

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Abbreviations

AEC - Anion exchange capacity

CCA - chromated copper arsenate

CEC - Cation exchange capacity

DCM – dichloromethane

DNAPLs - dense non-aqueous phase liquids

GC-FID - Gas Chromatography Flame Ionisation Detector

ICP-OES - Inductively coupled plasma optical spectroscopy

Kocs - soil organic carbon sorption coefficients

LNAPLs - light non-aqueous phase liquids

NAPL - non-aqueous phase liquids

NOM - natural organic matter

PAHs - polyaromatic hydrocarbons

PCBs - polychlorinated biphenyls

SAFIC - South African Fine Industrial Chemicals

SVE - Soil vapour extraction

SVOCs - semi-volatile organic compounds

TPH - total petroleum hydrocarbons

USEPA - U.S. Environmental Protection Agency

UST - underground storage tank

UV - Ultraviolet

VOC - volatile organic compound

CHAPTER 1

Introduction

Mining and the environment

The mining industry has been the mainstay of the South African economy for over a century. Since late in the last century, mining and beneficiation of a variety of minerals, in particular gold, have been the driving force behind economic development, particularly in the Witwatersrand area. However mining operations give rise to a number of serious environmental effects. In most cases impact of mining on the environment is both regional and local (Bell et al., 2001, Klukanová et al., 1999).

The extractive nature of mining operations creates a variety of impacts on the environment before, during and after mining operations. The extent and nature of impacts can range from minimal to significant depending on a range of factors associated with each mine (Bell et al., 2001). These factors include: the characteristics of the ore body, the type of technology and extraction methods used in mining, the on-site processing of minerals as well as the sensitivity of the local environment.

During mining operations heavy metals that occur naturally in many ores, are often released in the mineral extraction process. Metals contained in an excavated or exposed rock are leached out and carried downstream by flowing water (Salomons et al. 1995). In the mines hydrocarbons are also released to the environment from spillages of crude oil,

gasoline, diesel and petroleum products that are used in the combustion engines of locomotives underground. Owing to the persistence of heavy metals and hydrocarbons in soil and water and their toxic, mutagenic, and carcinogenic effects, the remediation of sites contaminated with these pollutants is an important environmental issue.

The contamination of surface and ground waters with highly mineralized mine waters or with compounds leached from mine dumps or tailings pose a very persistent environmental problem. Harmful contaminants, derived from such sources, enter the surface streams, settle in sediments, dissolve gradually and enter the environment as hazardous substances over long periods of time (Roychoudhury et al., 2006). These substances can be identified in soil and water. Underground mining often involves surface stockpiling with possible high levels of radionuclides which are potentially hazardous to the environment (Klukanová et al., 1999).

Within an active mining operation, acid mine drainage can be generated from a number of sources including waste rock dumps, ore stock piles, tailings deposits and the mine pit itself. The prerequisite for acid mine drainage is the generation of acid at a faster rate than it can be neutralized by any alkaline materials in the waste; access of oxygen and water and a rate of precipitation higher than evaporation. The most common mineral causing acid mine drainage is pyrite, but other metal sulphides will also contribute (Salomons et al., 1995, Roychoudhury et al., 2006).

Mining of ore deposits that contain large amounts of sulphide minerals and heavy metals is an important source of heavy metals in the environment. The main pathways include airborne distribution of polluted dust from mine tailings or waste rock piles and discharge of acid mine drainage waters. As a result of oxidation of pyrite (FeS_2) or pyrrhotite (FeS), pH in the affected soil and water body may drop below pH 4 , leading to the solubilization of heavy metals including Pb, Cd, Zn, Cu, Cr, Ni, and Fe (Chulin et al., 2005).

The principal impact of petroleum products on the environment is in the mobilisation and maintenance areas of a mine. These products leak or drop onto the soil, they then accumulate in the soil, and if in large enough concentrations, create a toxic environment.

Traditionally, conventional end-of-pipe technologies that aim to remediate problems with waste after it has been released had been used to combat the pollution problems in the industry. At present, cleaner technologies and strategies, including highly efficient environmental equipment, heavily retrofitted end-of-pipe designs, and comprehensive environmental management plans, are being used at many mine sites throughout the world. The ineffectiveness of these end-of-pipe systems has made it necessary to implement more effective remediation technologies and strategies (Hilson et al., 2000, Roychoudhury et al., 2006).

Problems associated with the cleanup of metals and hydrocarbons contaminated sites have demonstrated that there is a need to develop remediation technologies that are feasible, quick, and deployable in a wide range of physical settings. Government, industry, and the public now recognize the potential dangers that complex chemical

mixtures such as total petroleum hydrocarbons (TPH), polychloro biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and heavy metals, pose to human health and the environment. These contaminants have the potential to cause both acute and chronic impacts on human and ecosystem health (Urum et al., 2004). As a result a number of them have been classified as priority pollutants and are subject to legislation. Legislation aimed at safeguarding the environment against these pollutants has been instituted by governments (Mitchell et al., 1998). In response to these environmental laws more research is being done to find the most efficient and cost effective remediation technology.

With the growing interest in environmental remediation, various approaches have been proposed for treating heavy metals and hydrocarbon contaminated sites. Among these methods, silica encapsulation has been proposed as an innovative remediation technology due to its potential for treating not only heavy metals contaminated soils but also those contaminated by hydrocarbons. Silica encapsulation is less time consuming compared with bioremediation and phytoremediation, which are largely affected by climatic factors (Urum et al., 2004).

CHAPTER 2

Literature review

2.1 Heavy metals

Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems (Evanko et al. 1997). They are introduced into the environment during mining, refining of ores, combustion of fossil fuels and industrial processes. They cannot be degraded or destroyed (Davydova et al.,2005). To a small extent they enter our bodies via food, drinking water 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.

2.1.1 Toxicity of metals

The presence of metals in water and soils can pose a significant threat to human health and ecological systems. Heavy metal toxicity represents an uncommon, yet clinically significant, medical condition. If unrecognized or inappropriately treated, heavy metal toxicity can result in significant morbidity and mortality. Many metals are essential to biochemical processes in correct concentrations but at higher doses, heavy metals can cause negative health effects such as irreversible brain damage. Some metals such as lead and mercury easily cross the placenta and damage the brain (Levine et al., 2006).

Some effects of metals are summarised in table 1.

Table 2.1 Effects of metals (Levine et al., 2006)

Metal	**Effects**
Lead	Hypertension and chronic kidney disease
Cadmium	Human carcinogen
Aluminium	Liver dysfunction, Asthmatic conditions
Copper	Brain and Liver damage
Zinc	Hemolytic anaemia
Iron	Hemochromatosis, Conjunctivitis
Chromium	Cr VI carcinogenic
Mercury	Kidney disease, kidney failure
Arsenic	Brain damage, lung cancer
Thallium	Congenital disorders
Manganese	Nerve damage, lung embolism, bronchitis

2.1.2 Mobility and Speciation of metals in water and soil

Understanding the environmental behaviour of a metal by determining its speciation, mobility and occurrence is of paramount importance. The term speciation is related to the distribution of an element among chemical forms or species. Heavy metals can occur in several forms in water and soil (Catherine et al., 2001). Based on this information the most appropriate method for soil and water remediation can be determined (Gerber et al., 1991).

Soils are significant sinks for metals, while water represents an important pathway for the dispersion of metals over extremely large areas (Gibler et al., 1997, Gerber et al., 1991). The mobility of a metal in soil and water depends significantly on the chemical form and speciation of the metal. The mobility of metals in ground-water systems is hindered by reactions that cause metals to adsorb or precipitate, or chemistry that tends to keep metals associated with the solid phase and prevents them from dissolving. These mechanisms can retard the movement of metals and also provide a long-term source of metal contaminants. While various metals undergo similar reactions in a number of aspects, the extent and nature of these reactions varies under particular conditions (Gerber et al., 1991, Levine et al., 2006).

Studies on the mobility of heavy metals in soils have shown that the mobility is strongly influenced by several factors, e.g. pH redox potential, clay mineral content, organic matter content and water content. Various processes, e.g., adsorption-desorption, complex and ion-pair formation or activities of micro organisms are also involved (Gibler et al., 1997).

Simple and complex cations are the most mobile, exchangeable cations in organic and inorganic complexes are of medium mobility and, chelated cations are slightly mobile (Catherine et al., 2001, Gibler et al., 1997). Metals in organic particles are only mobile after decomposition or weathering. Precipitated metals are mobile under dissolution conditions (e.g. change in pH) (Catherine et al., 2001).

Influence of soil properties on mobility

Chemical and physical properties of the contaminated matrix influence the mobility of metals in soils and groundwater (Catherine et al., 2001, Gerber et al. 1991). Contamination exists in three forms in the soil matrix: solubilized contaminants in the soil moisture, adsorbed contaminants on soil surfaces, and contaminants fixed chemically as solid compounds. The chemical and physical properties of the soil influence the form of the metal contaminant, its mobility, and the technology selected for remediation (Gerber et al. 1991).

Chemical properties

The presence of inorganic anions (carbonate, phosphate, sulphide) in the soil water can influence the soil's ability to fix metals chemically (Levine et al., 2006). These anions can form relatively insoluble complexes with metal ions and cause metals to desorb and precipitate in their presence. Soil pH values generally range between 4.0 and 8.5 with buffering by Al at low pH and by $CaCO_3$ at high pH. Metal cations are most mobile under acidic conditions while anions tend to sorb to oxide minerals in this pH range. At high pH, cations precipitate or adsorb to mineral surfaces and metal anions are mobilized.

The presence of hydrous metal oxides of Fe, Al, Mn can strongly influence metal concentrations because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation (Gerber et al. 1991).

Sorption of metal cations onto hydrous oxides generally increases sharply with pH and is most significant at pH values above the neutral range, while sorption of metal anions is greatest at low pH and decreases as pH is increased. Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of soils for uptake of cations such as metals. Anion exchange capacity (AEC) indicates the affinity of soils for uptake of anions, and is usually significantly lower than the CEC of the soil. In addition to hydrous oxides, clays are also important ion exchange materials for metals. The presence of natural organic matter (NOM) has been shown to influence the sorption of metal ions to mineral surfaces. NOM has been observed to enhance sorption of Cu^{2+} at low pH, and suppress Cu^{2+} sorption at high pH (Gerber et al. 1991).

Physical properties

Particle size distribution can influence the level of metal contamination in a soil. Fine particles (<100µm) are more reactive and have a higher surface area than coarser material. As a result, the fine fraction of a soil often contains the majority of contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of a number of metal remediation technologies, for example, soil washing (Levine et al., 2006, Gerber et al. 1991).

Moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depend on the soil moisture content. Soil structure describes the size, shape, arrangement and degree of development of soils into structural units. Soil structure can influence contaminant mobility by limiting the degree of contact between groundwater and contaminants.

It has been demonstrated that the speciation of trace metals in natural soils depends on the physical and chemical characteristics of the soil. Soil pH, redox, organic, carbonate, clay and oxide contents all influence metal speciation and mobility. A study by Kabata (et al., 1992) showed that zinc and cadmium in soil are mostly associated with exchangeable, water soluble and organic fractions. Copper is mainly organically bound and exchangeable, whereas, lead is slightly mobile and bound to the residual fraction (Catherine et al., 2001, Kabata et al., 1992).

After discharge to an aquatic environment, metals are partitioned between solid and liquid phases. Within each phase, further partitioning occurs among ligands as determined by ligand concentrations and metal-ligand bond strengths. In solid phases, soil, sediment, and surface water particulates, metals may be partitioned into six fractions: (a) dissolved, (b) exchangeable, (c) carbonate, (d) iron-manganese oxide, (e) organic, and (f) crystalline (Elder et al., 1989). Partitioning is affected strongly by variations in pH, redox state, organic content, and other environmental factors. The dissolved fraction consists of carbonate complexes, whose abundance increases with pH, and metals in solution, including metal cation and anion complexes and hydrated ions whose solubilities are affected strongly by pH and tend to increase with decreasing pH.

Exchangeable fractions consist of metals bound to colloidal or particulate material (Elder et al.,1989, Gerber et al. 1991).

Metals associated with carbonate minerals in soil constitute the carbonate fraction, which can be newly precipitated in soil (Salomons et al., 1995). The iron-manganese oxide fraction consists of metals adsorbed to iron-manganese oxide particles or coatings. The organic fraction consists of metals bound to various forms of organic matter. The crystalline fraction consists of metals contained within the crystal structure of minerals and normally not available to biota. Hydrogen ion activity (pH) is probably the most important factor governing metal speciation, solubility from mineral surfaces, transport, and eventual bioavailability of metals in aqueous solutions. pH affects both solubility of metal hydroxide minerals and adsorption-desorption processes. Most metal hydroxide minerals have very low solubilities under pH conditions in natural water (Salomons et al., 1995, Elder et al., 1989).

Adsorption, which occurs when dissolved metals are attached to surfaces of particulate matter (notably iron, manganese, and aluminium oxide minerals, clay, and organic matter), is also strongly dependent on pH and, of course, the availability of particulate surfaces and total dissolved metal content. Metals tend to be adsorbed at different pH values, and sorption capacity of oxide surfaces generally varies from near 0 percent to near 100 percent over a range of about 2 pH units (Bourg et al., 1988, Elder et al., 1989). The adsorption edge, the pH range over which the rapid change in sorption capacity occurs, varies among metals, which results in precipitation of different metals over a large range of pH units. Consequently, mixing metal-rich acidic water with higher pH

metal-poor water may result in dispersion and separation of metals as different metals are adsorbed onto various media over a range of pH values. Cadmium and zinc tend to have adsorption edges at higher pH than iron and copper, and consequently they are likely to be more mobile and more widely dispersed. Adsorption edges also vary with concentration of the complexing agent thus, increasing concentrations of complexing agent increases pH of the adsorption edge (Bourg et al., 1988).

Major cations such as Mg^{2+} and Ca^{2+} also compete for adsorption sites with metals and can reduce the amount of metal adsorption. Particulate size and resulting total surface area available for adsorption are both important factors in adsorption processes and can affect metal bioavailability (Luoma et al., 1989). Small particles with large surface-area-to-mass ratios allow more adsorption than an equivalent mass of large particles with small surface-area-to-mass ratios. Reduced adsorption can increase metal bioavailability by increasing concentrations of dissolved metals in associated water. The size of particles released during mining depends on mining and beneficiation methods. Finely milled ore may release much smaller particles that can both be more widely dispersed by water and wind, and which can also serve as sites of enhanced adsorption. Consequently, mine tailings released into fine-grained sediment such as silty clays found in many places can have much lower environmental impact than those released into sand or coarse-grained sediment with lower surface area and adsorption (Elder et al., 1989).

Temperature exerts an important effect on metal speciation, because most chemical reaction rates are highly sensitive to temperature changes (Luoma et al., 1983). An increase of 10 ºC can double biochemical reaction rates, which are often the driving force

in earth surface conditions for reactions that are kinetically slow, and enhance the tendency of a system to reach equilibrium. Temperature may also affect quantities of metal uptake by an organism, because biological process rates (as noted above) typically double with every10 ºC temperature increment (Luoma et al., 1983). Because increased temperature may affect both influx and efflux rates of metals, net bioaccumulation may or may not increase (Luoma et al., 1983).

The chemical form and speciation of some of the more important metals are discussed below. The influence of chemical form on fate and mobility of these metals is also discussed.

Lead

Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead metal oxyanion complexes. Most lead that is released to the environment is retained in the soil. The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organolead compound tetramethyl lead may form in anaerobic sediments as a result of alkyllation by micro organisms (Gerber et al., 1991, Bourg et al., 1988).

The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground-water systems, a significant fraction of lead is undissolved and occurs

as precipitates ($PbCO_3$, PbO_2, $Pb(OH)_2$, $PbSO_4$), sorbed ions or surface coatings on minerals, or as suspended organic matter (Gerber et al., 1991, Bourg et al., 1988).

Chromium

Chromium (Cr) is one of the common element in South Africa. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$ (Gerber et al., 1991, Luoma et al., 1989).

Chromate and dichromate also adsorb on soil surfaces containing iron and aluminium oxides. Cr (III) is the dominant form of chromium at low pH (<4). Cr^{3+} forms solution complexes with NH_3, OH^-, Cl^-, F^-, CN^-, SO_4^{2-}, and soluble organic ligands. Cr (VI) is the more toxic form of chromium and is also more mobile. Cr(III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $Cr(OH)_3(s)$ (Luoma et al., 1989).

Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and unadsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr (VI) increases as soil pH increases. Most of chromium released into natural waters is particle associated, however, and is ultimately deposited into the sediment (Luoma et al., 1989, Bourg et al., 1988).

Zinc

Zinc (Zn) does not occur naturally in elemental form. It is usually extracted from mineral ores to form zinc oxide (ZnO). The primary industrial use for Zinc is as a corrosion-resistant coating for iron or steel. (Smith et al). Zinc usually occurs in the +2 oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zinc may precipitate as $Zn(OH)_2(s)$, $ZnCO_3(s)$, ZnS(s), or $Zn(CN)_2(s)$ (Gerber et al., 1991, Luoma et al., 1989, Bourg et al., 1988).

Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control zinc solubility. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may co precipitate with hydrous oxides of iron or manganese. Sorption to sediments or suspended solids, including hydrous iron and manganese oxides, clay minerals, and organic matter, is the primary fate of zinc in aquatic environments. Sorption of zinc increases as pH increases and salinity decreases (Gerber et al., 1991).

Copper

Copper (Cu) is mined as a primary ore product from copper sulphide and oxide ores. Mining activities are the major source of copper contamination in groundwater and surface waters. Other sources of copper include algicides, chromated copper arsenate (CCA), pressure treated lumber and copper pipes. Solution and soil chemistry strongly

influence the speciation of copper in ground-water systems. In aerobic conditions, sufficiently alkaline systems, $CuCO_3$ is the dominant soluble copper species (Luoma et al., 1989; Bourg et al., 1988). The cupric ion, Cu^{2+}, and hydroxide complexes, $CuOH^+$ and $Cu(OH)_2$, are also commonly present. Copper forms strong solution complexes with humic acids (Dzombak et al., 1990). The affinity of Cu for humates increases as pH increases and ionic strength decreases. In anaerobic environments, when sulphur is present CuS(s) will form. Copper mobility is decreased by sorption to mineral surfaces. Cu^{2+} sorbs strongly to mineral surfaces over a wide range of pH values (Dzombak et al., 1990).The cupric ion (Cu^{2+}) is the most toxic species of copper. Copper toxicity has also been demonstrated for $CuOH^+$ and $Cu_2(OH)_2^{2+}$ (LaGrega et al., 1994).

Mercury

The primary source of mercury is the sulfide ore cinnabar. Mercury (Hg) is usually recovered as a by-product of ore processing. Release of mercury from coal combustion is a major source of mercury contamination. Releases from manometers at pressure measuring stations along gas/oil pipelines also contribute to mercury contamination. After release to the environment, mercury usually exists in mercuric (Hg^{2+}), mercurous (Hg_2^{2+}), elemental (Hg^o), or alkyllated form (methyl/ethyl mercury). The redox potential and pH of the system determine the stable forms of mercury that will be present. Mercurous and mercuric mercury are more stable under oxidizing conditions. When mildly reducing conditions exist, organic or inorganic mercury may be reduced to elemental mercury, which may then be converted to alkyllated forms by biotic or abiotic

processes. Mercury is most toxic in its alkyllated forms which are soluble in water and volatile in air (Luoma et al., 1989, Bourg et al., 1988).

Hg(II) forms strong complexes with a variety of both inorganic and organic ligands, making it very soluble in oxidized aquatic systems. Sorption to soils, sediments, and humic materials is an important mechanism for removal of mercury from solution. Sorption is pH-dependent and increases as pH increases. Mercury may also be removed from solution by co-precipitation with sulfides. Under anaerobic conditions, both organic and inorganic forms of mercury may be converted to alkyllated forms by microbial activity, such as by sulfur-reducing bacteria. Elemental mercury may also be formed under anaerobic conditions by demethylation of methyl mercury, or by reduction of Hg(II). Acidic conditions (pH<4) also favor the formation of methyl mercury, whereas higher pH values favor precipitation of HgS(s) (Luoma et al., 1989).

Cadmium

Cadmium (Cd) occurs naturally in the form of CdS or $CdCO_3$. Cadmium is recovered as a by-product from the mining of sulfide ores of lead, zinc and copper. Sources of cadmium contamination include plating operations and the disposal of cadmium-containing wastes (LaGrega et al., 1994)

The form of cadmium encountered depends on solution and soil chemistry as well as treatment of the waste prior to disposal The most common forms of cadmium include Cd^{2+},cadmium-cyanide complexes, or $Cd(OH)_2$ solid sludge (LaGrega et al., 1994, Luoma et al., 1989, Bourg et al., 1988). Hydroxide ($Cd(OH)_2$) and carbonate ($CdCO_3$)

solids dominate at high pH whereas Cd^{2+} and aqueous sulfate species are the dominant forms of cadmium at lower pH (<8). Under reducing conditions when sulfur is present, the stable solid CdS(s) is formed. Cadmium will also precipitate in the presence of phosphate, arsenate, chromate and other anions, although solubility will vary with pH and other chemical factors (Bourg et al., 1988).

Cadmium is relatively mobile in surface water and ground-water systems and exists primarilyas hydrated ions or as complexes with humic acids and other organic ligands. Under acidic conditions, cadmium may also form complexes with chloride and sulfate. Cadmium is removed from natural waters by precipitation and sorption to mineral surfaces, especially oxide minerals, at higher pH values (>pH 6). Removal by these mechanisms increases as pH increases. Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals, and organic matter present in soils and sediments. Under reducing conditions, precipitation as CdS controls the mobility of cadmium (Luoma et al., 1989, Bourg et al., 1988).

Arsenic

Arsenic (As) is a semi metallic element that occurs in a wide variety of minerals, mainly as As_2O_3, and can be recovered from processing of ores containing mostly copper, lead, zinc, silver and gold. It is also present in ashes from coal combustion. Arsenic exhibits fairly complex chemistry and can be present in several oxidation states (-III, 0, III, V) (Luoma et al., 1989, Bourg et al., 1988).

In aerobic environments, As(V) is dominant, usually in the form of arsenate (AsO_4^{3-}) in various protonation states: H_3AsO_4, H_2AsO^{4-}, $HAsO_4^{2-}$, AsO_4^{3-}. Arsenate and other anionic forms of arsenic behave as chelates and can precipitate when metal cations are present. Metal arsenate complexes are stable only under certain conditions. As(V) can also co-precipitate with or adsorb onto iron oxyhydroxides under acidic and moderately reducing conditions (Dzombak et al., 1990). Coprecipitates are immobile under these conditions but arsenic mobility increases as pH increases. Under reducing conditions As(III) dominates, existing as arsenite (AsO_3^{3-}) and its protonated forms: H_3AsO_3, H_2AsO^{3-}, $HAsO_3^{2-}$.

Arsenite can adsorb or co-precipitate with metal sulfides and has a high affinity for other sulfur compounds. Elemental arsenic and arsine, AsH_3, may be present under extreme reducing conditions. Biotransformation (via methylation) of arsenic creates methylated derivatives of arsine, such as dimethyl arsine $HAs(CH_3)_2$ and trimethylarsine $As(CH_3)_3$ which are highly volatile. Since arsenic is often present in anionic form, it does not form complexes with simple anions such as Cl^- and SO_4^{2-}. Arsenic speciation also includes organometallic forms such as methylarsinic acid $(CH_3)AsO_2H_2$ and dimethylarsinic acid $(CH_3)_2AsO_2H$ (Dzombak et al., 1990, Bourg et al., 1988). Many arsenic compounds sorb strongly to soils and are therefore transported only over short distances in groundwater and surface water. Sorption and co-precipitation with hydrous iron oxides are the most important removal mechanisms under most environmental conditions. Arsenates can be leached easily if the amount of reactive metal in the soil is low. As(V) can also be mobilized under reducing conditions that encourage the formation of As(III), under alkaline and saline conditions, in the presence of other ions that compete for sorption

sites, and in the presence of organic compounds that form complexes with arsenic (Luoma et al., 1989, Bourg et al., 1988).

2.2 Hydrocarbons

Hydrocarbons are heterogeneous group of organic substances that are primarily composed of carbon and hydrogen molecules (Reeves et al., 2000). They are quite abundant in modern society; their use includes fuels, gasoline, petroleum, paints, paint, lubricants, and solvents. Hydrocarbons can be classified as being aliphatic, in which the carbon moieties are arranged in a linear or branched chain, or aromatic, in which the carbon moieties are arranged in a ring. Halogenated hydrocarbons are a subgroup of aromatic hydrocarbons, in which one of the hydrogen molecules is substituted by a halogen group (Minnich et al., 1993).

2.2.1 Toxicity of hydrocarbons

Toxicity from hydrocarbon ingestion can affect many body organs, but the lungs are the most commonly affected organs. The chemical properties of the individual hydrocarbon determine the specific toxicity, while the dose and route of ingestion affect organs that are exposed to the toxicity (Levin et al., 2006, Reeves et al., 2000).

Contamination of groundwater by gasoline, diesel fuels and oil spills is a widespread environmental problem. Hydrocarbons from these petroleum products are known to be carcinogenic and mutagenic when present in high concentration. High exposure to hydrocarbons can harm the reproductive systems, interfere with normal development of a fetus or child and may interfere with or block hormones.

Poly aromatic hydrocarbons (PAH) are a large group of organic compounds which are formed mainly as a result of the incomplete combustion of organic materials. There are many PAH's, however the best known is benzo(a)pyrene (BaP). Long term exposure is suspected to lead to some lung cancers.

Benzene is a volatile organic compound (VOC) and is a major constituent of petrol. Benzene is a known human carcinogen and long term exposure can lead to cancer.

Polychlorinated biphenyls are known to cause a variety of types of cancer in humans. Studies of PCBs in humans have found increased rates of melanomas, liver cancer, gall bladder cancer, biliary tract cancer, gastrointestinal tract cancer, and brain cancer (Levin et al., 2006, Reeves et al., 2000).

2.2.2 Transport and fate of hydrocarbons

The transport of organic pollutants is a function of various factors. In the mobile phase, i.e. water or gas phases, transport is governed by advective and dispersive processes, whereas in the immobile phase, such as soil or natural organic matter, the dominant transport mechanism is diffusion. The latter is thought to control the overall rate of mass transfer between mobile and immobile phases. This is particularly of importance regarding processes like sorption, desorption or microbial degradation, which can greatly influence the fate of contaminants by reducing transport velocity compared to groundwater flow, a phenomenon known as retardation (Silvers et al., 2003, Luthy et al, 1997)

Once a liquid petroleum product is released into the ground it partitions into three separate phases: dissolved, liquid and gas. A small fraction of the petroleum hydrocarbon dissolves in the soil moisture or groundwater, a portion of the product remains in soil pore space in its pure liquid form as residual saturation and some of it evaporates into the air of soil pores (Luthy et al, 1997, Nadim et al., 2000). Residual liquid is held in soil pores either by capillary forces or as small pools of liquids over clay and silt lenses. If not removed, residual petroleum hydrocarbon acts as a permanent source of contamination in the ground (Nadim et al., 2000).

Pure phase liquids that do not readily dissolve in water are called non-aqueous phase liquids (NAPL). In general NAPLs are subdivided into two classes: those that are lighter than water LNAPLs and those with a density greater than water DNAPLs. Hydrocarbon fuels such as gasoline, heating fuel, kerosene, jet fuel and aviation fuel are LNAPLs. Benzene, toluene, ethylbenzene, and xylene (BTEX) are light aromatic hydrocarbons that have relative high water solubility (Nadim et al., 2000, Silvers et al., 2003).

Low density immiscible liquids, or light non-aqueous phase liquids (LNAPLs), will float on the surface of the higher density groundwater and surface water. High density liquids, or dense non-aqueous phase liquids (DNAPLs), sink through water until they reach the aquifer or surface water bottom. While these liquids do not go completely into solution in groundwater, they do contain compounds with limited solubilities in water.

The possible fates of PAHs in the environment include volatilization, photooxidation, chemical oxidation, bioaccumulation, adsorption to soil particles or sediments, and leaching and microbial degradation. PAHs are highly persistent in the environment. This is a consequence of the resistance of PAHs to decomposition processes, their high affinity for organic matter and their low water solubility. PAHs are hydrophobic compounds and rapidly become associated with soil particles or sediments, where they may become buried and persist for long periods. Halogenated organic compounds are also soluble in water and can migrate in a dissolved phase in the direction of groundwater flow (Ou et al., 2000, Kögel-Knabner et. al., 1998).

Most PAHs, because of their low volatility, are classified as semivolatile organic compounds. In general, PAHs do not easily dissolve in water and are more likely to partition into sediments and soils rather than into ground water because of their low solubilities and high soil organic carbon sorption coefficients (Kocs). As a result, transport of PAHs tends to be associated primarily with erosion of contaminated soils and sediments. PAHs sorbed to sediments may potentially affect aquatic communities downstream of contaminated sites. Some PAHs such as naphthalenes are more volatile and more water soluble than most PAHs and can pose a threat to ground-water resources (Williams et al.; 2003, Goerlitz et al., 1985).

Crude oil weathering processes include adsorption of hydrocarbons to soil particles, volatilization of hydrocarbons, and dissolution of hydrocarbons in water. Alkanes and alkenes tend to be more volatile than aromatics. If volatilization is the most dominant weathering process, then the loss of lower molecular weight aliphatics will be the most

substantial change in the crude oil, and aliphatics may be the principal air contaminants at spill sites (Williams et al., 2003; Potter and Simmons, 1998).

Aromatic hydrocarbons, especially BTEX, tend to be the most water-soluble fraction of crude oil and other petroleum compounds. Benzene (10 times more soluble than ethylbenzene or xylenes) is the most water soluble of the BTEX compounds. BTEX compounds also are the most volatile of the aromatic compounds and are considered to be volatile organic compounds (Williams et al., 2003). BTEX compounds have the lowest soil organic carbon sorption coefficients (Koc) of the most common aromatic hydrocarbons. Koc is the ratio of the amount of a compound sorbed to the organic matter component of soil or sediment to the amount of the compound in the aqueous phase at equilibrium, and has been used as one variable in predicting the mobility of a compound from soil to ground water. Benzene (Koc of 59) is considered to be highly mobile in soil, toluene (Koc of 182) is considered to be moderate to highly mobile in soil, and xylenes (Koc of 363 to 407) are considered to be moderately mobile in soil (Williams et al., 2003; U.S. Environmental Protection Agency, 1995).

2.3 Remediation technologies

Several technologies exist for the remediation of metals-contaminated soil and water. These technologies are contained within five categories of general approaches to remediation: bioremediation, isolation, immobilization, toxicity reduction, physical separation and extraction.

2.3.1 Bioremediation

Bioremediation or biodegradation is a process in which naturally occurring micro organisms (i.e. yeast, fungi, or bacteria) break down or degrade hazardous substances into less toxic or non-toxic substances. Many organic contaminants such as petroleum can be biodegraded by micro organisms in the underground environment. Natural bacteria in soil and ground water will use petroleum compounds as their primary source of energy, thus biodegrading the compounds during the process. There are three processes by which micro organisms aid in the breakdown of hydrocarbons: fermentation, aerobic respiration, and anaerobic respiration. During fermentation, carbon, the energy source, is broken down by a series of enzyme-mediated reactions that do not involve an electron transport chain. In fermentation, organic compounds can act as both electron donors and acceptors (Khan et. al., 2004; Mulligan et al., 2001; Moutsatsou et al., 2006).

During aerobic respiration, microorganisms use available oxygen in order to function. In aerobic respiration, carbon, the energy source, is broken down by a series of enzyme-mediated reactions, in which oxygen serves as an external electron acceptor. Anaerobic conditions support microbial activity without oxygen present, so the microorganisms

break down chemical compounds in the soil to release the energy it needs. In anaerobic respiration, carbon, the energy source, is broken down by a series of enzyme-mediated reactions in which nitrates, sulphates, carbon dioxide, and other oxidized compounds(excluding oxygen) serve as electron acceptors (Moutsatsou et al., 2006).

In situ bioremediation technologies are potentially effective in degrading or transforming a large number of organic compounds to environmentally acceptable or less mobile compounds. The classes of compounds considered to be amenable to biodegradation include petroleum hydrocarbons (for example, gasoline and diesel fuel), non-chlorinated solvents, wood treating wastes, some chlorinated aromatic compounds, and some chlorinated aliphatic compounds. U.S. Environmental Protection Agency (USEPA) recognizes natural attenuation as a viable method of remediation for soil and groundwater, and its selection is often based on its ability to achieve remediation goals in a reasonable time frame and to be protective of human health and the environment. In addition to USEPA acceptance, many state underground storage tank (UST) programs now accept natural attenuation as a valid approach to remediating petroleum-contaminated sites. Natural attenuation processes can effectively clean soil and groundwater of hydrocarbon fuels, such as gasoline and BTEX compounds (U.S. Environmental Protection Agency, 1990, Khan et. al., 2004).

Important observations related to the performance of natural attenuation technology are:

- It is a relatively simple technology compared to other remediation technologies.
- It can be carried out with little or no site disruption.

- It often requires more time to achieve cleanup goals than other conventional remediation methods.
- It requires a long-term monitoring program; program duration affects the cost.
- If natural attenuation rates are too slow, the plume could migrate.
- It is difficult to predict with high reliability the performance of natural attenuation.

Sites must meet one or more of the following criteria:

- It must be located in an area with little risk to human health or to the environment.
- The contaminated soil or groundwater must be located an adequate distance from potential receptors.
- There must be evidence that natural attenuation is actually occurring at the site.
- High permeability speeds contaminant spread, low permeability slows the breakdown.

Ideally, natural attenuation works best in soils whose permeability ranks somewhere between high and low (Khan et. al., 2004; Algarra et al., 2004).

2.3.2 Soil washing

Soil washing uses liquids (usually water, occasionally combined with solvents) and mechanical processes to scrub soils. Solvents are selected on the basis of their ability to solubilize specific contaminants, and on their environmental and health effects. The soil washing process separates fine soil (clay and silt) from coarse soil (sand and gravel). Since hydrocarbon contaminants tend to bind and sorb to smaller soil particles (primarily

clay and silt), separating the smaller soil particles from the larger ones reduces the volume of contaminated soil. The smaller volume of soil, which contains the majority of clay and silt particles, can be further treated by other methods (such as incineration or bioremediation) or disposed in accordance with federal regulations. The clean, larger volume of soil is considered to be non-toxic and can be used as backfill. Soil washing is often combined with other technologies (Zoumis et al., 2001; Moutsatsou et al., 2006).

The target contaminant groups for soil washing include semi-volatile organic compounds (SVOCs), petroleum and fuel residuals, heavy metals, PCBs, PAHs, and pesticides. This technology permits the recovery of metals and it can clean a wide range of organic and inorganic contaminants from coarse-grained soils.

Important observations related to soil washing performance are:

- Complex waste mixtures require a combination of solvents.
- Pre-treatment is required for soils containing humic acids.
- Organics adsorbed onto clay particles are difficult to remove.
- Since soil washing does not destroy or immobilize the contaminants, the resulting soil must be disposed of carefully.
- Wash water needs to be treated before its final disposal.
- Soil washing is only effective for soil that does not contain a large amount of silt and clay (Zoumis et al., 2001; Moutsatsou et al., 2006).

2.3.3 Soil vapour extraction

Soil vapour extraction (SVE), also known as soil venting or vacuum extraction, is an accepted, recognized, and cost effective technology for remediating unsaturated soils contaminated with VOCs and SVOCs. SVE involves the installation of vertical and horizontal wells in the area of soil contamination. Air blowers are often used to aid the evaporation process. Vacuums are applied through the wells near the source of contamination to evaporate the volatile constituents of the contaminated mass which are subsequently withdrawn through an extraction well. Extracted vapours are then treated (commonly with carbon adsorption) before being released into the atmosphere. The increased airflow through the subsurface provided by SVE also stimulates the biodegradation of contaminants, especially those that are less volatile. This procedure is also used with groundwater pumping and air stripping for treating contaminated groundwater (Mulligan et al., 2001; Moutsatsou et al., 2006).

SVE is typically more applicable in cases where the contaminated unsaturated zone is relatively permeable and homogeneous. Ideally the site should be covered with an impermeable surface layer to minimize the short-circuiting of airflow and infiltration. SVE is generally most successful when it is applied to lighter, more volatile petroleum products such as gasoline. Heavier fuels, such as diesel fuel, heating oils, and kerosene, are not readily removed by SVE. The injection of heated air enhances the volatility of these heavier petroleum products, but the large energy requirements make it economically prohibitive. Benzene, toluene, xylene, naphthalene, biphenyl, perchloroethylene, trichloroethylene, trichloroethane, and gasoline are all effectively

removed from contaminated soils by SVE systems (Mulligan et al., 2001; Moutsatsou et al., 2006).

Important observations related to the performance of SVE technology are:

- As SVE is an in situ technology, the site disturbance is minimal, SVE can treat large volumes of soil at reasonable costs.
- It is effective at reducing VOCs in the vadozone, thereby reducing the potential for further migration
- It has a short treatment time (usually a few months to 2 years under optimal conditions). Its applicability is limited to cases involving volatile compounds and sites with a low groundwater table.
- It is difficult, if not impossible to develop models that permit an accurate prediction of SVE cleanup times from the data collected in short-term pilot studies has discussed in detail the method to estimate SVE operation time.
- Concentration reductions greater than 90% are difficult to achieve.
- The permeability of the soil affects the rate of air and vapour movement through the soil. Therefore, the higher the permeability of the soil, the more effective will be the SVE system at removing contaminants from the soil.
- Coarse-textured soils are best suited for SVE.
- High moisture levels in the soil can reduce its permeability, and thus reduce the effectiveness of SVE by restricting the air flow through the soil pores.
- SVE is generally not appropriate for sites with a groundwater table located less than 0.9 m below the land surface (Mulligan et al., 2001; Moutsatsou et al., 2006).

2.3.4 Solidification/stabilization

Solidification/stabilization, also referred to as waste fixation, reduces the mobility of hazardous substances and contaminants in the environment through both physical and chemical means. Stabilization generally refers to the process that reduces the risk posed by a waste by converting the contaminant into a less soluble, immobile, and less toxic form. Solidification refers to the process that encapsulates the waste materials in a monolithic solid of high structural integrity. In situ stabilization and solidification involves three main components: (1) a means of mixing the contaminated soil in place; (2) a reagent storage, preparation, and feed system; and (3) a means to deliver the reagents to the soil mixing zone. In situ and ex situ stabilization/solidification is usually applied to soils contaminated by heavy metals and other inorganic compounds. However, stabilization of soils that contain low levels of organic constituents is feasible, even for volatile organics. Most stabilization/solidification technologies have limited effectiveness against organics and pesticides, except for asphalt batching and vitrification which destroys most organic contaminants (Khan et. al., 2004; Mulligan et al., 2001).

2.3.5 Asphalt batching

Asphalt batching, a stabilization/solidification method for treating hydrocarbon-contaminated soils, incorporates petroleum-laden soils into hot asphalt mixtures as a partial substitute for stone aggregate. This mixture can then be utilized for paving. This process involves excavation of the contaminated soils, which then undergo an initial thermal treatment, followed by incorporation of the treated soil into an aggregate for asphalt. During the incorporation process, heating of the mixture results in the

volatilization of the more volatile hydrocarbon constituents. The remaining compounds are incorporated into an asphalt matrix during cooling, thereby limiting constituent migration. After it is given sufficient time to set and cure, the resulting solid now has the waste uniformly distributed throughout it and is impermeable to water (Mulligan et al., 2001; Moutsatsou et al., 2006).

Important observations related to the performance of asphalt solidification/stabilization technology are:

- The depth of the contaminants may limit these processes.
- Long-term monitoring is often necessary to ensure that the contaminants are actually immobilized.
- Organic constituents are generally not immobilized, and unless very high temperatures are used to destroy them, they will most likely migrate.
- If not completed properly, these processes may result in a significant increase in contaminant volume.
- Certain wastes are incompatible with these processes (Khan et. al., 2004, Mulligan et al., 2001)

2.3.6 Electrokinetics

Electrolytic processes for metal removal include the use of AC or DC fields. Electrokinetic processes involve passing a low intensity electric current between a cathode and an anode imbedded in the contaminated sediments. Ions and small charged particles, in addition to water, are transported between the electrodes. Anions move

towards the positive electrode and cations towards the negative. An electric gradient initiates movement by electromigration (charged chemicals movement), electro-osmosis (movement of fluid), electrophoresis (charged particle movement) and electrolysis (chemical reactions due to electric field) (Maturi et al., 2006, Rose et al., 2001).

Control of the pH and electrolyte conditions within the electrode casings is essential in the optimization of the process efficiency. Drying near the anode is a problem so recirculating processing fluids are necessary. The process can be used to recover ions from soils, muds, dredgings, and other materials. Dredged material is treated in lagoons between 2 and 7400 m^3 with batch time of 8 h to 5 days, depending on current loading and electrode spacing. Spacing can be up to 3m as long as the potential gradient of 1 V/cm is maintained. Metals as soluble ions and bound to soils as oxides, hydroxides and carbonates are removed by this method. Other non-ionic components can also be transported due to the flow. Unlike soil washing, this process is effective with clay soils (Maturi et al., 2006, Rose et al., 2001).

This technology is currently used for copper, zinc, lead, arsenic, cadmium, chromium and nickel. Other ions, such as cyanide and nitrate and radionuclides, such as uranium and strontium can also be treated by electrokinetics. Heterogeneities, large amounts of oxides, large rocks, large metal objects, gravel submerged foundations, moisture content, temperature and other contaminants can interfere with the process. Recently, new developments at the pilot stage have been made in using electrokinetics for high-level metal containing sediments. Metal recovery will improve the process economics to achieve partial cost-effectiveness (Maturi et al., 2006, Rose et al., 2001).

2.3.7 Phytoremediation

Phytoremediation uses plants to clean up contaminated soils and groundwater. This process takes advantage of the ability of plants to take up, accumulate and degrade constituents that are present in soil and water environments. All plants extract necessary components, including nutrients and heavy metals, from these environments. Some plants are referred to as hyperaccumulators as they have the ability to store large amounts of these metals that do not appear to be used in their function. Plants have also been known to take up various organics and either degrade or process them for use in physiological processes (Khan et. al., 2004, Mulligan et al., 2001).

There are five basic types of phytoremediation: (1) rhizofiltration, a water remediation technique in which contaminants are taken up by the plant's roots; (2) phytoextraction, which involves the uptake of contaminant from the soil; (3) phytotransformation, which is applicable to both soil and water and involves the degradation of contaminants through plant metabolism; (4) phytostimulation or plant-assisted bioremediation, which involves the stimulation of microbial degradation through the activities of plants in the root zone; and (5) phytostabilization, which uses plants to reduce the migration of contaminants through the soil medium. Small-scale experiments indicate that phytoremediation can clean up a number of different contaminants (Moutsatsou et al., 2006).

Phytoremediation has been applied to a number of contaminants in small-scale field and laboratory studies. These contaminants include heavy metals, radionuclides, chlorinated solvents, petroleum hydrocarbons, PCBs, PAHs, organophosphate insecticides, explosives, and surfactants (Khan et. al., 2004, Mulligan et al., 2001.

Important observations related to the performance of phytoremediation technology are:

- Remediation is accomplished with minimal environmental disturbance.
- It is an aesthetically pleasing and passive, solar energy driven technology.
- It can be used on a large range of contaminants.
- The generation of secondary wastes is minimal.
- Organic pollutants may be converted to CO_2 and H_2O instead of transferring toxicity.
- It is cost-effective for large contaminated sites (with a low concentration of contaminants.
- The topsoil is left in a usable condition and may be used in agriculture.
- The soil can remain at a site after the removal of the contaminant rather than being disposed of or isolated.
- The uptake of contaminated groundwater can prevent the migration of contaminants.
- Remediation usually requires more than one growing season.
- Treatment is limited to soils less than one meter from the surface and groundwater less than 3 m from the surface.
- Climate and hydrologic conditions such as flooding and drought may restrict plant growth and the type of plants that can be utilized (Khan et. al., 2004, Mulligan et al., 2001).

2.3.8 Aeration

This technology evaporates the volatile components of petroleum from the soil into the air. It is a well-developed process in which the area of contact between the water and the air is increased. The contaminated soil is spread thinly and tilled or turned to increase the rate of evaporation. The disadvantage of this method is that it should not be employed in urban areas or other locations where organic vapours could cause health, fire, or nuisance hazards. The collected vapours also require further treatment. Aeration is often placed lower on the hierarchy of treatment technologies than those that destroy the contaminants. In the groundwater, aeration brings about contact between the air and the water to promote biological degradation. It may be employed in activated sludge, rotating biological contactors, trickling filters and biological lagoons. Many configurations may promote aeration including jets to blow air into the water or mechanical aeration devices that propel water droplets through the air (Mulligan et al., 2001).

- The group of contaminants targeted by aeration includes SVOCs, pesticides, and fuels. VOCs may also be treated by aeration, followed by some off-gas treatments.
- Aeration may also be used for the reduction of odours.

There are several limitations associated with the use of aeration:

- It cannot be used with contaminants with a high VOC content without some off-gas treatment.
- Vapours may cause health, fire, and nuisance hazards.

2.3.9 Air sparging

In situ air sparging has been used for the past 15 years for the remediation of VOCs dissolved in groundwater, sorbed to the saturated zone soils, and trapped in the pores of the saturated zone. It involves injecting atmospheric air, under pressure, into the saturated zone to volatilize groundwater contaminants and to promote biodegradation by increasing subsurface oxygen concentrations. The injected air forms channels through the contaminated plume as it flows upwards through the saturated zone and into the vadose zone. The injected air volatilizes the contaminants in the flow channels and transports them to the vadose zone where they are either biodegraded or removed by a SVE system. Three contaminant removal mechanisms that occur during air sparging include: (1) in situ stripping of dissolved VOCs, (2) volatilization of trapped and sorbed contaminants present below the water table in the capillary fringe, and (3) aerobic biodegradation. Air sparging offers a means of remediating contaminated soils and groundwater without the need for active groundwater pumping. This technology addresses a broad range of volatile and semi-volatile soil and groundwater contaminants including gasoline and other fuel components and chlorinated solvents (Mulligan et al., 2001; Moutsatsou et al., 2006).

Those sites with relatively permeable, homogeneous soil conditions due to greater effective contact between the injected air and the media being treated and the effective migration/extraction of volatilized vapours favour the use of air sparging. Other site factors that influence the applicability of air sparging include the thickness of the saturated zone and the depth of the groundwater. For example, if the thickness of the

saturated zone is small and the depth of groundwater is shallow, the number of wells required for adequate coverage could become expensive for such a remediation project (Mulligan et al., 2001; Moutsatsou et al., 2006).

Important observations related to the performance of air sparging technology are:

- Silt and clay sediments are not appropriate for this technology.
- Heterogeneous geologic conditions, reduces the effectiveness of the system.
- This technology is ineffective in the case of non strippable and non-biodegradable contaminants.
- This technology is inefficient if the vertical passage of air becomes hampered while the lateral movement is being increased.

2.3.10 Ultraviolet-oxidation treatment

Ultraviolet (UV)-oxidation treatment methods represent one of the most important technologies emerging as a viable treatment for groundwater remediation. These systems generally use an oxygen-based oxidant (e.g. ozone or hydrogen peroxide) in conjunction with UV light. In this process UV bulbs are placed in a reactor where the oxidant comes in contact with the contaminants in the groundwater (Mulligan et al., 2001; Moutsatsou et al., 2006).

UV-oxidation has two basic forms:

- UV–peroxide systems: High intensity UV lights catalyze the formation of hydroxyl radicals from hydrogen peroxide. Under controlled conditions, the hydroxyl

radicals react with the contaminants and oxidize the chemicals into less harmful compounds. This reaction maybe aided by the ability of UV light to loosen some of the bonds in the organic contaminants and make them easier to destroy. With sufficient exposure to light and oxidation, the final product will be water, carbon dioxide, and the appropriate inorganic salt.

- UV–ozone systems utilize the strong oxidizing properties of UV light and ozone. UV light and ozone act synergistically to oxidize the contaminants.

This technology is applicable to all types of petroleum products. It also works on VOCs, SVOCs, aromatics, alcohols, ketones, aldehydes, phenols, ethers, pthalates and various other forms of organic carbons.

There are two advantages to use this technology:

- The chemicals used do not add to the system's pollutant load
- It is successful with substances such as ferricyanides on which other methods have failed.

Limitations to this technology include:

- When using H_2O_2, the process is only efficient at low wavelengths.
- Low turbidity and suspended solids are necessary for good light transmission.
- The presence of free radical scavengers may interfere with the reactions.
- The water may have to be treated for heavy metals, insoluble oil and grease, high alkalinity and carbonates to reduce fouling of the UV quartz sleeves.
- Ongoing treatment may be necessary to reduce future cleaning of the sleeves.

- The storage and handling of oxidizers may require special precautions.
- There may be potential air emission problems associated with the use of ozone.

2.4 Encapsulation

Encapsulation involves the mixing of the contaminated soils with other products such as lime, concrete, or asphalt (Christensen et al., 2005). The contaminated soil becomes part of the product mix and the contamination is thereby prevented from migrating to surrounding strata. The types of contamination treated vary with the desired end product mix.

Encapsulation by lime and concrete has been used concurrently in the effective treatment of heavy metals and waste oil contaminated soil. Asphalt encapsulation has been used effectively on hydrocarbon contaminated soils. The major drawback to these methods is that there needs to be an immediate market for the end product, otherwise the end result is random patches of concrete and asphalt (Mulligan et. al., 2001). It is because of these limitations that the research on this method has led to the development of a silica based encapsulation remediation technology.

2.4.1 Silica Encapsulation Remediation Technology

The remediation of sites contaminated with heavy metals and hydrocarbons by silica based encapsulation is an attractive potential remediation process. Different silica based reagents are used to encapsulate contaminants. The contaminants are controlled in a single step, without the need for pre-treatment with chemicals and post treatment of filtration. It has an advantage over the conventional treatment processes that typically

degrade over time in that the silica matrix continues to strengthen and tighten with time further isolating contaminants from the environment (Christensen et al., 2005).

This technique uses silica, one of the most inert natural substances, to minimize the concentration of the contaminants in the environment. It also controls and limits the inhaled and ingested particles by facilitating revegetation of the previously toxic soils. The encapsulating silica matrix completely isolates the metal species from the surrounding environment. The silica coating is resistant to degradation even under extreme environmental conditions (Christensen et. al., 2005).

Laboratory tests on silica encapsulation remediation technology using encapsulating reagents and lime indicates that lime increases the encapsulation of pollutants in the soil. Surfactants are essential for a satisfactory encapsulation of the pollutants in the soil. Studies done on silica encapsulation show that extractable hydrocarbons in soil polluted with diesel oil, after silica encapsulation were reduced by 70 to 100% (Christensen et. al., 2005). The structure silicate controls the type of cations that are encapsulated during silica encapsulation.

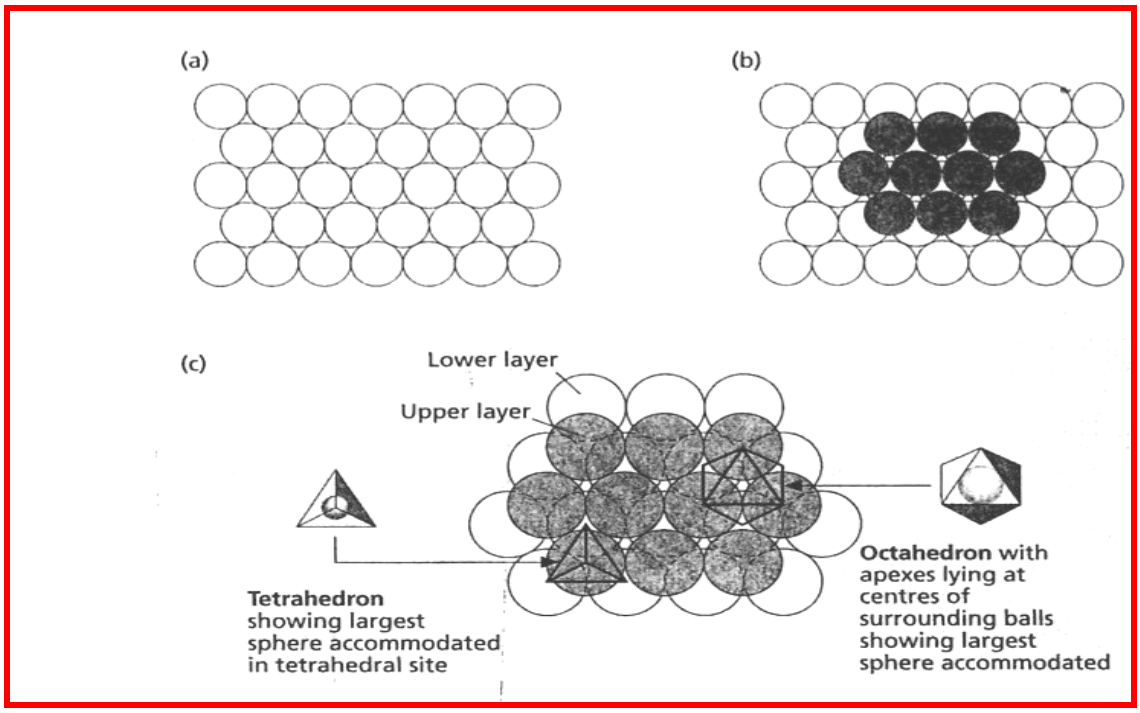


Figure 2.1 (a) Spheres in planar layers showing hexagonal symmetry. (b) An upper layer of spheres (shaded) is stacked on the layer in (a), such that each upper sphere fits into the depression between three spheres in the lower layer. (c) enlargement of (b), where heavy lines show coordination polyhedral, joining the centres of adjacent spheres, delineating two geometries, tetrahedral and octahedral.

Figure 2.1. shows the gaps between neighbouring spheres have one of two possible three dimensional geometries of silica. The first geometry is delineated by the surfaces of four adjacent spheres. A three dimensional shape constructed from the centre of adjacent spheres has the form of a tetrahedron, consequently these gaps are called tetrahedral sites. The second type of gap is bounded by six adjacent spheres and a three dimensional shape constructed from the centre of the spheres has the form of a regular octahedron. These are

called octahedral sites. Cations occupy some of these tetrahedral and octahedral sites. The type of site a cation occupies is determined by the radius ratio of the cation and anion, i.e.

Radius ratio = r_{cation} / r_{anion} where r = ionic radius

To fit exactly into octahedral site delineated by six spheres of radius r the radius ratio must be 0.414. Radius ratios are usually smaller or larger than this critical value of 0.414. If smaller, the optimum bond length is exceeded, and the structure collapses into a new stable configuration where the cation maintains optimum bond length with fewer, more closely packed anions.

It is believed that when the silica solution is added to hydrocarbons, the first step in this unique approach is to surround small quantities of the organic contaminant with an aqueous, silica-surfactant system to form a micelle with the silica additive (Figure 2.1). Within minutes, micro encapsulation is observed to occur in the form of precipitated agglomerates of wet silica containing the contaminant species in the micelle trapped inside the silica matrix. The pH of the micro encapsulated material is approximately neutral.

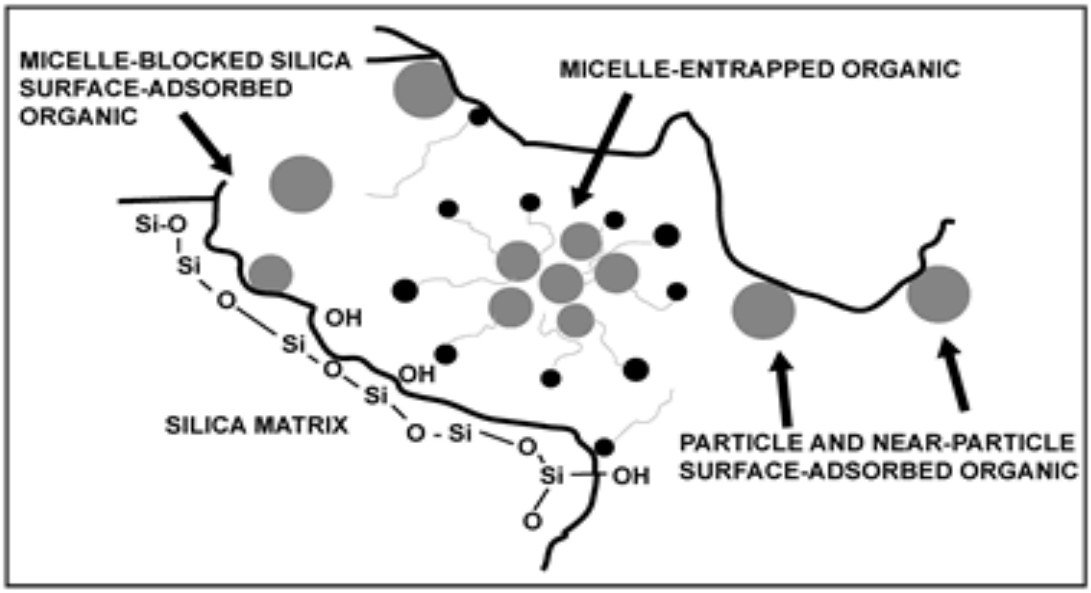


Figure 2.2 Schematic illustration of mechanism of silica encapsulation of micelles containing hydrocarbons (www.tepco.com).

2.4.2 Encapsulation with Sodium Silicate

Soluble silicates like sodium silicate have been shown to react with hazardous wastes to produce less hazardous substances. They do so by converting soluble metals into insoluble metal silicates and by encapsulating hazardous organic and inorganic components within an acid-resistant matrix. Sodium silicate is the basic component of most of products used for silica encapsulation. Treatment a waste with sodium silicate stream typically results in a strong, low-permeability, chemically stabilized solid that is easy to handle, transport, and landfill (Arocha et al., 1996, Christensen et. al., 2005).

Silicates react almost instantaneously with multivalent metal cations to form the corresponding insoluble metal silicate. Examples of common metal ions that are reactive with silicate include: Ca^{+2}, Mg^{+2}, Zn^{+2}, Cu^{+2}, Fe^{+3}, etc. If the material being agglomerated contains a significantly high amount of positive cations on its surface then the silicate can act as a chemical binder (Christensen et. al., 2005).

Sodium silicate is unique in that it can undergo four very distinct chemical reactions. These reactions have been defined as:

- hydration/dehydration
- gelation
- precipitation
- surface charge modification

These reactions allow silicate to act as a:

- film binder
- matrix binder
- chemical binder

Silicate can adhere an agglomerated material by one or more of its chemical reactions. Sometimes silicate-based formulations achieve their best performance by taking advantage of more than one of these adhesion mechanisms (U.S. patent 4105457, Christensen et. al., 2005).

Sodium silicate has also been used to encapsulate hydrocarbons in soil. A surfactant was initially applied before treatment with sodium silicate. A surfactant was added to facilitate wetting and to furnish an acidic medium for silica precipitation from the sodium silicate solution. Results from this work show that the concentration of hydrocarbons decreased after treatment of soil with sodium silicate. It was also found that the use of acetic acid prior to the treatment with silicate solution was enough to wet the surface such that it was unnecessary to add surfactant (Arocha et al., 1996)

Important observations related to the performance of silica encapsulation are:

- The amount of setting agent required for complete stabilization is reduced, thereby reducing raw material costs.
- The final volume of stabilized material requiring disposal is reduced, further reducing total treatment costs.
- Final physical properties of the stabilized waste are enhanced resulting in a stronger, less permeable matrix.
- A stable solid product that is resistant to the leaching effects of acid is produced.

2.5 Project motivation

The contamination of the environment by hydrocarbons and heavy metals is a concern to governments, environmental agencies and other stake holders. Legislation aimed at safeguarding the environment from these pollutants is instituted by governments worldwide. Like other countries, South Africa has legislation aimed at reducing hydrocarbon and heavy metal concentrations in the environment.

In response to the regulatory requirements, companies are in search of the best remediation technology they can use to clean the environment contaminated with hydrocarbons and heavy metals produced by their industrial processes. More research is being done to find the best remediation technology.

Mining companies have a problem of hydrocarbon contamination in their closed water systems which are under high pressure and on their concrete floors due to gasoline and oil spills. This creats a dangerous working environment. The environment is also contaminated as these pollutants are dumped with the mine waste. Heavy metals are also released to the environment during the mining activities.

The remediation methods that are currently used in the mines are encapsulating with cement and transporting waste to another place. These methods are costly and are not effective as long-term immobilization methods for toxic hydrocarbons and heavy metals. The limitations of these remediation methods present the need for an investigation of an efficient and cost-effective remediation technology.

The advantages of the silica encapsulation remediation technology which were discussed previously make it a better method when compared to others. This method involves the use of a silicate solution to encapsulate hydrocarbons and heavy metals in the environment. Silica encapsulation technology has been widely applied in Europe and very good results have been obtained. However, under South African conditions some problems are experienced when this technology is applied.

This project was initiated at the request of SAFIC and mining company in South Africa to test and evaluate this technology in the laboratory. The objective of this research is to investigate the effect of different environmental conditions on silica encapsulation and to provide means for a quick, permanent and economical way of remediating soil, water and concrete surfaces contaminated with hydrocarbons and heavy metals using silica encapsulation technology.

2.6 Objectives of the research

- To investigate silica encapsulation remediation technology on sites contaminated with hydrocarbons and heavy metals and its dependency on the environmental conditions.
- To test and compare the potential of sodium silicate and Chemcap^{TM} to encapsulate heavy metals and hydrocarbons in water and soil samples.
- To investigate the competition between hydrocarbons and heavy metals to see the efficiency of silica encapsulation in the removal of heavy metals in the presence of hydrocarbons and vise versa.
- To investigate potential additives to improve sodium silicate encapsulation and the optimal physiochemical conditions for the resulting product's use.

CHAPTER 3

Analytical techniques used in this project

3.1 Inductively coupled plasma optical spectroscopy (ICP-OES)

The question of determining what elements and in what concentrations a sample contains is a common and important one in many fields of study. Numerous techniques exist for determination of trace element concentrations, however because the matrix in which metals are to be measured is complex, the method of choice for analysis was inductively coupled plasma optical emission spectroscopy (ICP-OES) due to its sensitivity.

Inductively coupled plasma optical spectroscopy (ICP-OES) is a major technique for elemental analysis. The determination of trace concentrations of elements in a sample is commonly determined using atomic spectroscopy. Atomic spectroscopy is based on the measurement of the amount of electromagnetic radiation (usually in the UV/visible spectrum) that is absorbed or emitted by an analyte atom to determine its concentration in a sample. This can be performed in three ways: atomic absorption, emission and fluorescence. The most commonly used of these are atomic absorption and emission, however it was not until the development of ICP (inductively coupled plasma) that atomic emission has become an effective and efficient means of detection (Arcinas et al., 2000)

The sample to be analyzed, if solid, is normally first dissolved and then mixed with water before being fed into the plasma. The first step in the procedure is the conversion of the molecules in the sample to individual atoms and ions using a high temperature

radio frequency induced argon plasma. The sample is introduced into the plasma as a solution. Sample is pumped using a peristaltic pump to a nebulizer, where it is converted to a fine spray and mixed with argon in a spray chamber. The purpose of the spray chamber is to make sure that only droplets in a narrow size range make it through into the plasma. Most of the sample drains away from the chamber, the rest is carried into the plasma and instantly excited by the high temperatures (5000-10.000K). ICP-OES utilizes UV and visible spectrometry to image the plasma at the exact wavelength of ionic excitation of the element of interest.

Apparatus

The apparatus for the ICP-OES is composed of three main sections: the nebulizer, the torch and the detection system (Figure 3.1).

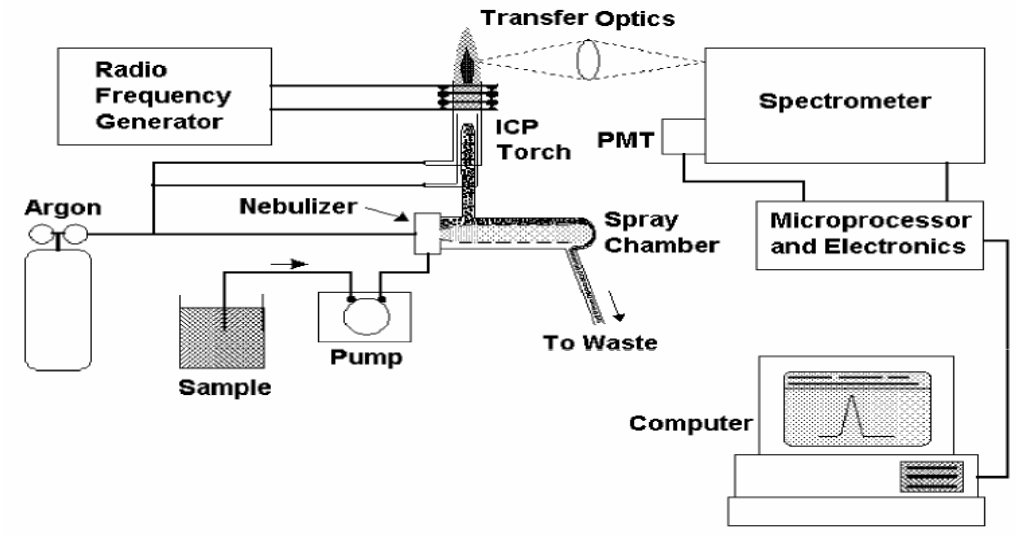


Figure 3.1 ICP-OES schematic diagram (Arcinas et al., 2000)

Nebulizer

The ICP-OES operates by introducing an aqueous sample into an energy source, which is plasma in this case. The sample is picked up by a peristaltic pump, and passed through a nebulizer, using inert argon gas as a carrier. This reduces the liquid sample to a fine aerosol, which is more effectively ionized by the plasma. Various types of nebulizers are available, including cross-flow, concentric, Babbington, and its variations. Although the resulting mists of these nebulizers generally contain small and consistent droplets, the nebulized samples are passed through a spray chamber, which filter out larger droplets to ensure consistency. The aerosol is then injected through the torch and into the plasma for ionization (Arcinas et al., 2000).

Detection

Upon contact with plasma, the analyte's electrons are excited and decay to ground levels. This causes the molecule to emit element specific spectra in the UV/visible region of 160 to 800 nm, which are detected and measured to determine concentration. Spectrometer mirrors then focus the emitted radiation to the entrance slit of wavelength dispersing device. These dispersing devices are usually comprised of diffraction gratings; however more recent systems use echelle gratings, as used in the Perkin Elmer Optima 100 ICP-OES (Arcinas et al., 2000).

3.2 Gas Chromatography (GC)

At present GC is still an important analytical method in the identification and quantification of organic pollutants in the environment (Richardson et al. 2001). It remains a healthy and growing measurement technique with expanding influence in innovative application. A schematic diagram of gas chromatograph is shown in figure 1.

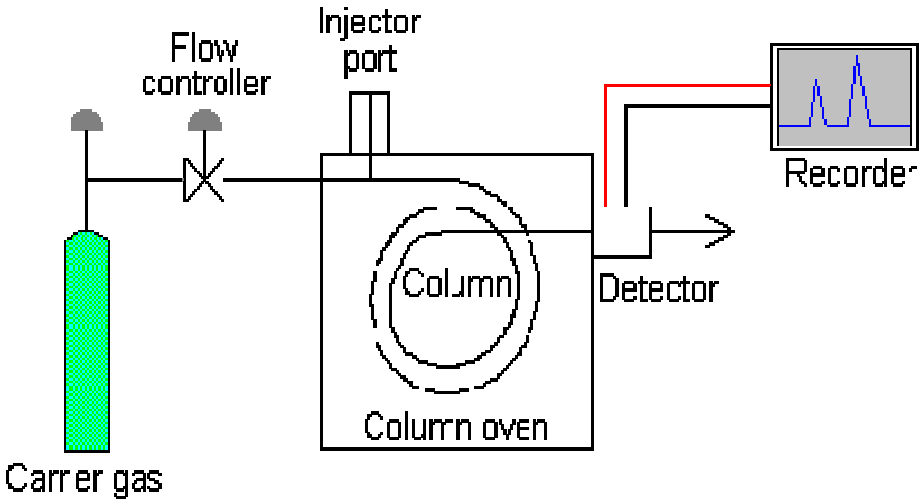


Figure 3.2 Gas Chromatography (Koester et al. 2003)

Carrier gas

The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependant upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities. In this project helium was used as a carrier gas.

Columns

There are two general types of column, packed and capillary (also known as open tubular). Packed columns contain a finely divided, inert, solid support material (commonly based on diatomaceous earth) coated with liquid stationary phase. Capillary columns have an internal diameter of a few tenths of a millimeter. A ZB1 capillary column was used to separate our compounds.

Column temperature

For precise work, column temperature must be controlled to within tenths of a degree. The optimum column temperature is dependant upon the boiling point of the sample. As a rule of thumb, a temperature slightly above the average boiling point of the sample results in an elution time of 2 - 30 minutes. Minimal temperatures give good resolution, but increase elution times. If a sample has a wide boiling range, then temperature programming can be useful. The column temperature is increased (either continuously or in steps) as separation proceeds.

Detectors

There are many detectors which can be used in gas chromatography. GC/FID is the method that is widely used for monitoring of hydrocarbons in environmental samples. The flame ionization detector is employed. It has an advantage over other detectors in that it does not respond to non-hydrocarbons such a H_2, N_2, CO etc, but it responds to most hydrocarbons.

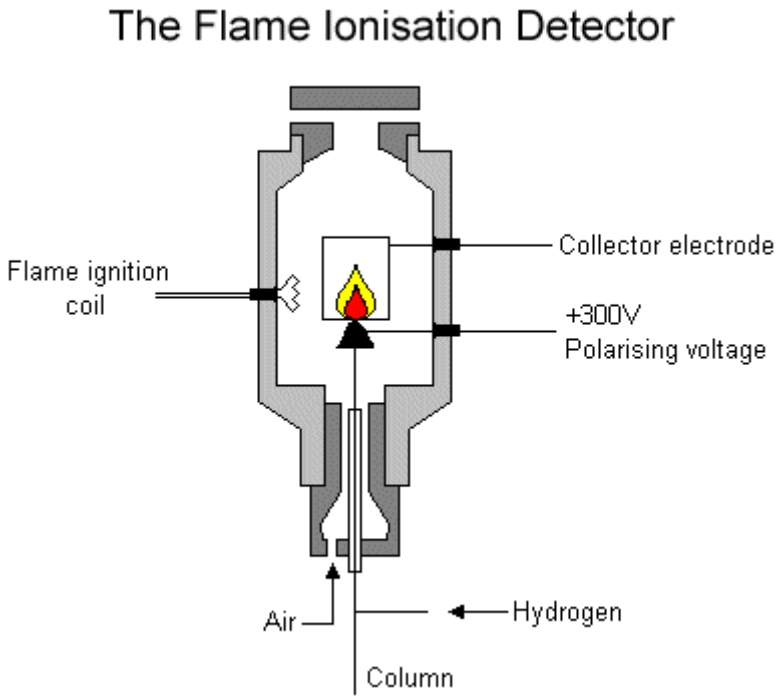


Figure 3.21 Flame Ionisation Detector (Koester et al. 2003)

The effluent from the column is mixed with hydrogen and air, and ignited. Organic compounds burning in the flame produce ions and electrons which can conduct electricity through the flame. A large electrical potential is applied at the burner tip, and a collector electrode is located above the flame. The current resulting from the pyrolysis of any organic compounds is measured. FIDs are mass sensitive rather than concentration sensitive; this gives the advantage that changes in mobile phase flow rate do not affect the detector's response. The FID is a useful general detector for the analysis of organic compounds; it has high sensitivity, a large linear response range, and low noise (Lee et al. 2003).

CHAPTER 4

Sample collection, preparation and analysis

Sample collection, preparation, and storage are critical in any analyses being carried out. These aspects should be undertaken in a way that will avoid the introduction of bias, systematic or non-systematic errors. The methods of collection and sample size should be chosen to ensure that the sample obtained is a representative of the environment from which it is taken. The value of laboratory data in soil and water studies largely depends on effective sampling. No amount of care in preparation and analysis can overcome the problems of careless or inappropriate sampling in the field (Kelly et al. 2003). This chapter outlines sample collection and preparation methods used in this project.

The basic objective of any sampling campaign is to collect a sample which is representative of the media under investigation. More specifically, the purpose of sampling at hazardous waste sites is to acquire information that will aid investigators in determining the presence and identity of onsite contaminants and the extent to which these compounds have become integrated into the surrounding environment (Barbizzi et al. 2004). This information can then be used as support for future litigations or as input to remedial investigations and risk assessments.

For storage of samples for metals analysis refrigeration is recommended and for organic analysis it is recommended that refrigeration temperatures be maintained at < 4°C. However it is recognized that many situations can occur where fluctuations to above this temperature are extremely difficult to avoid. Since temperatures slightly above 4 °C for

very short periods of time are unlikely to significantly affect sample quality, the maximum temperature is set at 10°C. Samples cannot be stored indefinitely for organic analysis (Buckland et al. 1999).

4.1 Soil samples

The simplest, most direct method of collecting soil samples for subsequent analysis is with the use of a spade and scoop. A normal lawn or garden spade can be utilized to remove the top cover of soil to the required depth and then a smaller stainless steel scoop can be used to collect the sample (Ford et al. 1994).

This method can be used in most soil types but is limited somewhat to sampling the near surface. Samples from depths greater than 50 cm become extremely labour intensive in most soil types. Very accurate, representative samples can be collected with this procedure depending on the care and precision demonstrated by the technician. A stainless steel scoop or lab spoon will suffice in most other applications. Care should be exercised to avoid the use of devices plated with chrome or other materials. Plating is particularly common with garden implements such as potting trowels (Ford et al. 1994).

Sampling of soil samples

All labware and sampling apparatus were pre-soaked in 5% nitric acid solution followed by distilled water for a day prior to sampling to remove trace concentrations of metals. Contaminated soil samples were collected from Gold Fields mining company to the west of Johannesburg. Underground areas of the mine are heavily contaminated with hydrocarbons and heavy metals from gasoline and hydrocarbons that are used in the

locomotives. Samples were collected at different points and along rail tracks underground using a stainless steel scoop. Two types of uncontaminated soil i.e. clay and sand soil were collected at two different locations. Clay soil was collected from the Braamfontein centre in Jorrisen Street. This soil was collected from a hole that was 1m deep and had been dug by roadworks workers. Clean sand soil was collected from the Contractor's soil at Wits University. All samples were collected into polyethylene sampling bottles. pH for the clay soil and sand soil collected from Braamfontein was adjusted using sulphuric acid and sodium hydroxide to acidic and basic conditions respectively. Soil pH was measured in deionised water.

4.2 Water samples

Most sampling requirements for surface water analysis can be fulfilled by manual sampling (i.e. grab sampling) using simple field equipment including: buckets, funnels, and suitable lengths of chain or dip poles. This equipment must conform to the same materials composition as the Teflon, stainless steel, glass, etc. The equipment must be suited to the sampling and analysis being performed (Ford et al. 1994).

All wettable surfaces that contact the water sample must be inert (i.e. must not contaminate, absorb nor desorb chemicals required to be analyzed in the water sample). This requirement can generally be met through consistent use of materials such as Teflon, glass, stainless steel and, where dictated by sampler design and function (i.e. peristaltic type pumps), short sections of surgical grade silicone rubber tubing. This type of tubing should be preferentially replaced by Teflon or other chemically inert materials as far as possible without impairing the performance of the sample device. Where surgical grade

silicone rubber tubing is used, the total length should be kept to an absolute minimum and it is generally accepted that this should be less than 2 meters. Particular care must be taken to ensure that this tubing and all other wettable parts are cleaned or replaced at the first indication of discolouration or fouling (Ford et al. 1994; Ščančar et al. 1999)

Sampling of water samples

The surface water samples were collected from Gold Fields in Kloof. Surface water samples were collected by immersion by hand of a polyethylene sampling bottles to well below the surface to avoid surface film. Tap water samples were collected from our laboratory.

4.3 Hydrocarbons extraction

Various methods for the extraction and analysis of hydrocarbons have been proposed. Extraction of hydrocarbons from soil has traditionally been performed using Soxhlet apparatus (Guerin et al 1998)**.** A disadvantage of the Soxhlet extraction is that it can take from 6 to 24 h to perform. Ultrasonic or sonication extraction is an alternative but has been recognized generally as less efficient than Soxhlet extraction. Sonication, however, provides a relatively low cost method, using small volumes of solvents, without the need for elaborate glassware. Depending on the contaminants and matrix, sonication can have the advantage of faster extraction (Guerin et al 1998). Other studies have also shown that hydrocarbons recoveries are higher with sonication extraction compared with Soxhlet, as a result commercial laboratories often employ sonication (Stephens et al. 1994). The study by Guerin emphasized the importance of establishing (and being consistent in the

application of a vigorous extraction, it indicates that vigorous sonication can achieve hydrocarbons recoveries similar to those obtained by Soxhlet extraction, particularly for commercial laboratories that handle samples of soil in batches (at different times) from a single site investigation or remediation process (Guerin et al 1998; Stephens et al. 1994).

4.4 Metals extraction

A widely used method for the identification and evaluation of the availability of heavy metals in soils is the leaching of soils by means of chemical extractants. In environmental analytical chemistry, acid leaching has become a common procedure as an alternative to total digestion (Maiz et al. 1997). The nitric acid extraction and Na_2CO_3 extraction used in this study was based on protocols found in the literature (Mielke et al. 2004). It is believed that nitric acid extraction leads to the maximum soluble acid amount of metals with recoveries from 89 to 100% for some metals in soils and sediments (Mielke et al. 2004). This simplified method has been shown to give results almost equivalent to EPA 3050 if the shaking time is over two hours (Mielke et al. 2004). Extraction with Na_2CO_3 has been successfully used to extract metals in soil especial chromium (Korolczuk et al. 2005).

4.5 Reagents and materials

Analytical grade reagents were employed High-purity, HPLC-grade. Nitric acid, sodium carbonate and dichloromethane (DCM) were purchased from Merck (SA). Milli-Q ultra pure water was used for preparation of extraction of solutions. Chemcap™ and sodium silicate solutions were provided by SAFIC. All reagents and standards were prepared or diluted in ultra-pure water supplied from a Millipore water filtration system. Diesel Range Organics standards in methylene chloride were purchased from ChemService.

4.6 Sample preparation

4.6.1 Homogenization of soil

To provide homogenized soil samples the soil was thoroughly mixed. The soil samples were dried for 24 hours, then finely ground and sieved through a 200 mesh sieve. Clean soil and water samples were contaminated with diesel bought from a Caltex garage. The contamination process was carried out by thorough mixing of diesel with soil and water.

4.6.2 Treatment of samples

Soil samples were accurately weighed (30g) and placed in polyethylene containers. These samples were divided in to two batches. One batch of samples was treated with Chemcap™ and the other was treated with sodium silicate solution at approximately 1 to 1 ratio. Samples were mixed well by stirring after application of a treatment solution. Immediately after stirring and mixing, samples were kept at room temperature until extraction and analysis. All experiments were done in triplicates.

4.6.3 Nitric acid extraction (Metals)

Metals from treated and untreated samples were extracted using a 5:1 ratio of 1M nitric acid to soil. They were extracted on a mechanical shaker for 2 h at room temperature, centrifuged (1000 × g for 15 min), and filtered. The supernatants from each extraction were separated by centrifuging and stored in polyethylene containers at 4ºC until analysis. Analyses were performed in triplicate. Metal ions in the extracts were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES).

4.6.4 Sodium carbonate extraction (Metals)

Metals were extracted using a 20:1 ratio of 0.1M Na_2CO_3 to soil. They were extracted on a mechanical shaker for 16 hours at room temperature, centrifuged (1000 × g for 15 min), and filtered. The supernatants from each extraction were separated by centrifuging and stored in polyethylene containers at 4ºC until analysis. Analyses were performed in triplicate. Metal ions in the extracts were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES).

4.6.5 Ultrasonic extraction (hydrocarbons)

An aliquot of the sample was accurately weighed (2g). Anhydrous granular sodium sulphate was added to wet samples and thoroughly mixed with the sample to dry the sample. The remaining sample was archived. The sample was serially extracted three times with 100 ml of dichloromethane (DCM) for10 min each time using sonication. The extracts were combined, dried and filtered by passing through a sodium sulphate layer.

The dried extracts were then concentrated to appropriate volume by rotary evaporation. A moderately polar solvent methylene chloride was used to extract hydrocarbons.

4.7 Instrumentation

4.7.1 Analysis of metals

Analysis for metals was performed using a GENESIS ICP optical emission spectrometer (SPECTRO Analytical Instruments, Kleve,Germany) The system was purged with pure Argon gas. The optimized instrument parameters were: plasma power of 1200W, coolant flow rate 12.0 L min^{-1}, auxiliary flow rate 1.0 $Lmin^{-1}$, nebulizer flow rate of 1.0 $Lmin^{-1}$.

4.7.2 Gas chromatograph

Chromatographic separations were performed on Hewlett-Packard gas chromatograph equipped with a flame ionization detector. Analysis was done using USEPA Method 3550 (USEPA Method 3550). The gas chromatograph was fitted with Phenomenex ZB-5 capillary column. The GC was operated under the following conditions: carrier gas (ultra-high-purity helium) flow rate, 2 ml/min; injection port, detector temperatures were kept at 200 and 280 ºC, respectively. Column temperature was programmed from 70ºC (1min) to 220ºC at 7.5 ºC /min and from 220 to 250ºC at 1ºC /min.

CHAPTER 5

Results and discussion

The efficiency of a remediation technology depends on several factors, pH, type of soil, time and competition between pollutants. Various experiments were designed to optimise silica encapsulation and to investigate the effect of these environmental factors on silica encapsulation remediation technology. The results of these experiments are presented and discussed in this chapter.

5.1 Effect of pH on encapsulation of metals with Chemcap^{TM} and silicate

The effect of pH on silica encapsulation was investigated by adjusting the pH of both sandy soil samples and clay soil samples to pH=2 and pH=8 using sulphuric acid and sodium hydroxide, respectively. Soil samples were then treated with either Chemcap^{TM} or sodium silicate solution at a ratio of approximately 1 to 1 as described in section 4.6.2 and were kept at room temperature until analysis. Soil samples were leached as described in section 4.6.3 and 4.6.4. After leaching, metal levels in the extracts were analyzed by inductively coupled plasma-optical emission spectrometry as described in section 4.7.1.

The concentrations of transition metals and lanthanides were determined. Results are presented in figures 5.1 – 5.9. The selection of these metals was based on their toxicity and importance to the environment. The levels of other metals were too low and as such are not included.

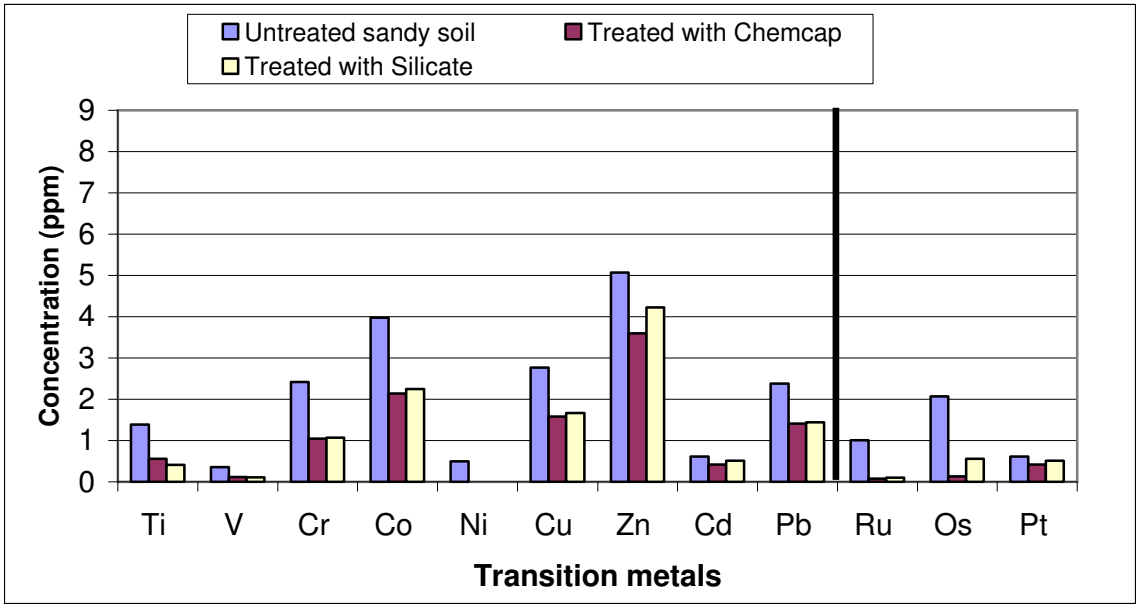
5.1.1 Effect of pH on silica encapsulation in sandy soil

Transition metals in figure 5.1 and 5.2 are arranged in order of the increasing atomic number and PGMs are separated by bold black line from other transition metals. Results in figure 5.1 and 5.2 show that silica encapsulation of transition metals such as Zinc, Cadmium, and Lead is affected by pH. These metals were effectively encapsulated in acidic sandy soil than in basic sandy soil. The percentages of encapsulation shown in table 5.1 indicate that the levels of Zinc, Cadmium, and Lead were reduced by high percentages in acidic sandy soil. Silica encapsulation of other extractable transition metals was effective in both acidic and basic sandy soil though there is consistently a larger percentage reduction at lower pH than at higher pH as shown in table 5.1.,

The reduction of all extractable transition metals in sandy soil at pH = 2 is greater than 50%. This suggests that both Chemcap^{TM} and Silicate were effective in removing metals in sandy soil. Metals such as Iron and Manganese which were present in high concentration were also reduced to very low levels (figure 5.2). The encapsulation of Iron is greater than 80% in both acidic and basic sandy soil.

These results also show that Platinum Group Metals (PGMs) were also encapsulated. However, silica encapsulation of platinum depends on pH as illustrated in the results (table 5.1). Platinum encapsulation is enhanced in acidic sandy soil. Platinum leachable concentration in acidic sandy soil is reduced by more than 70% whereas the reduction in basic sandy soil is less than 35% . The encapsulation of Ruthenium and Osmium is not strongly affected by pH (table 5.1). Levels of Ruthenium were reduced by more than 90% in acidic and basic sandy soil. Osmium was encapsulated by more than 70%.

(a)



(b)

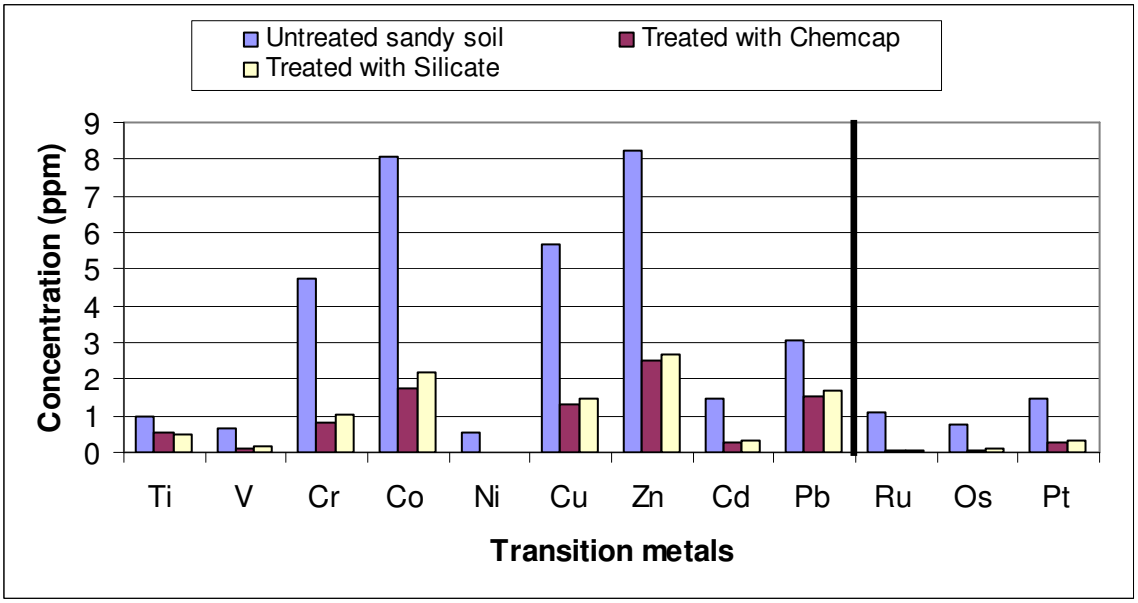
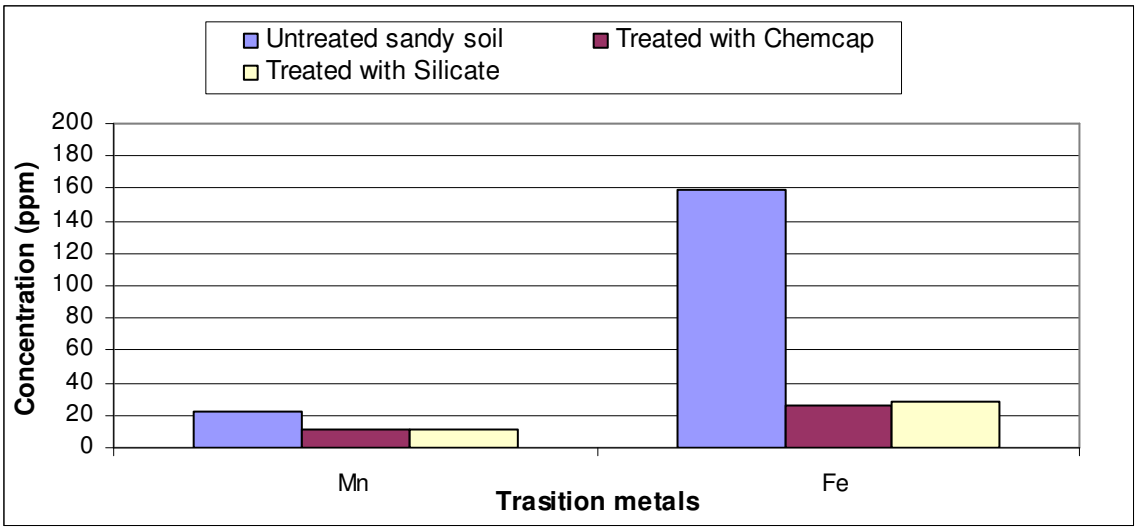


Figure 5.1 Leachable concentration of transition metals and PGMs in sandy soil at (a) pH=9.3 (b) pH= 2

(a)



(b)

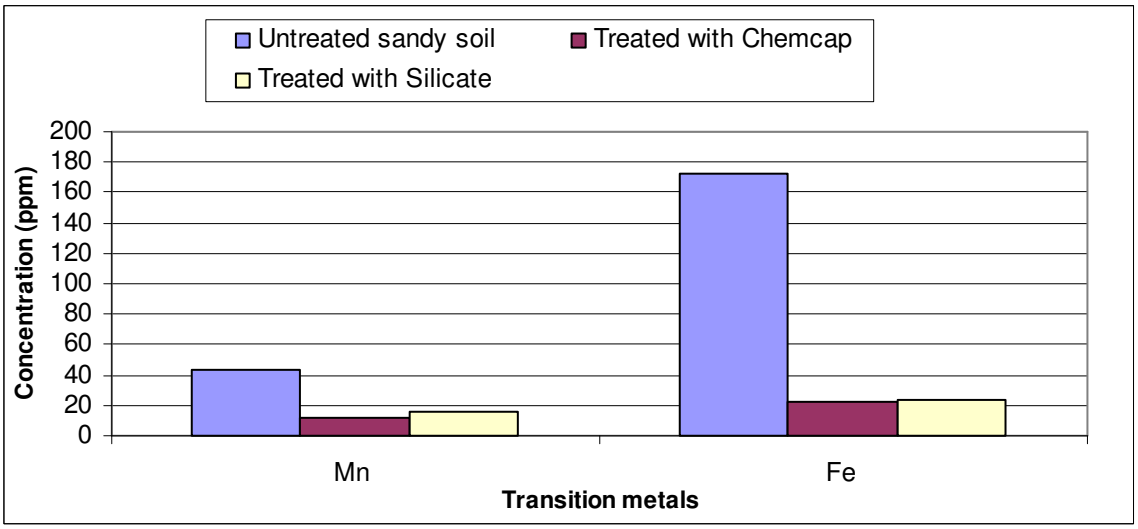


Figure 5.2 Leachable concentration of transition metals in sandy soil at (a) pH=9.3 (b) pH= 2

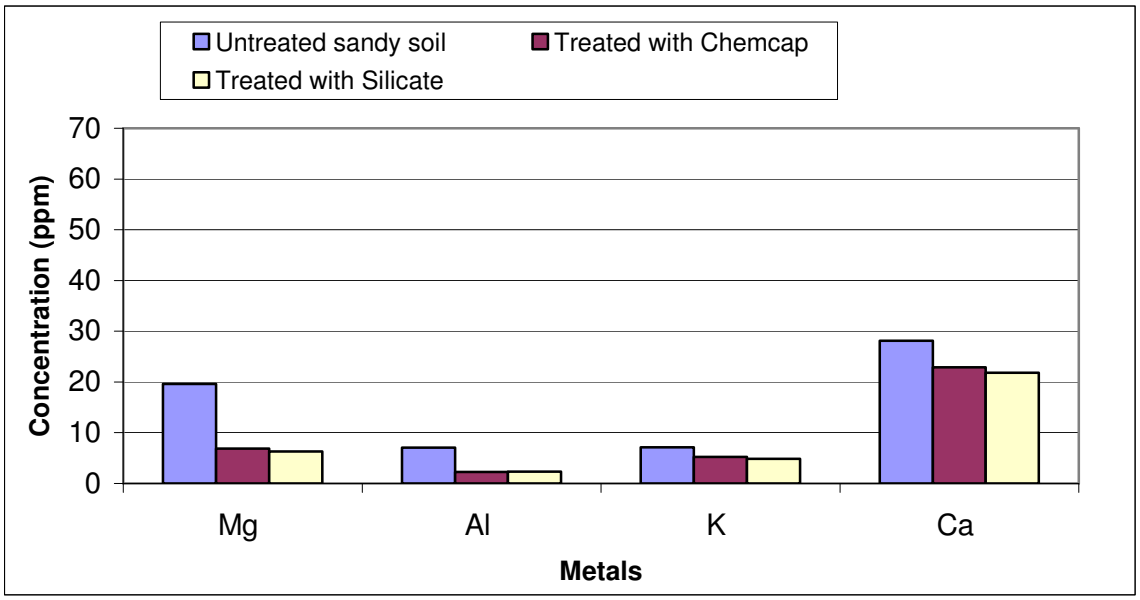
The initial leachable concentrations of metals such as Chromium, Cobalt, Copper and Zinc are high in the acidic soil compared to basic soil. The mobility of metals is known to

be enhanced at low pH, hence more metals are leached in the acidic environment. The final concentrations of metals after treatment are similar even though the initial concentrations are different. This may suggest that some equilibrium conditions are reached during treatment.

Table 5.1 Percentage reduction of leachable concentrations of transitions metals in sandy soil

Metal	% reduction of metals in sandy soil			
	Sandy soil (pH=2) treated with Chemcap™	Sandy soil (pH=9.3) treated with Chemcap™	Sandy soil (pH=2) treated with Silicate	Sandy soil (pH=9.3)treated with Silicate
Ti	70	46	60	48
V	82	66	77	69
Cr	82	56	78	55
Mn	72	52	65	54
Fe	87	84	87	82
Co	78	46	73	43
Cu	77	42	74	40
Zn	70	29	68	16
Cd	79	31	76	16
Pb	50	40	45	39
Ru	92	92	93	90
Os	89	94	87	73
Pt	79	31	76	16

(a)



(b)

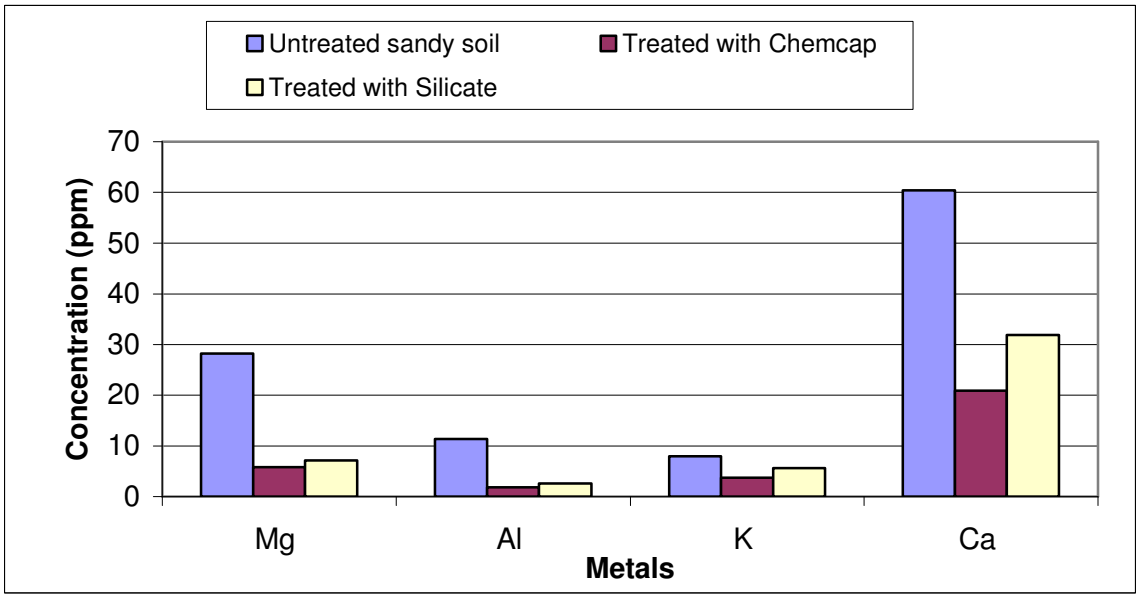


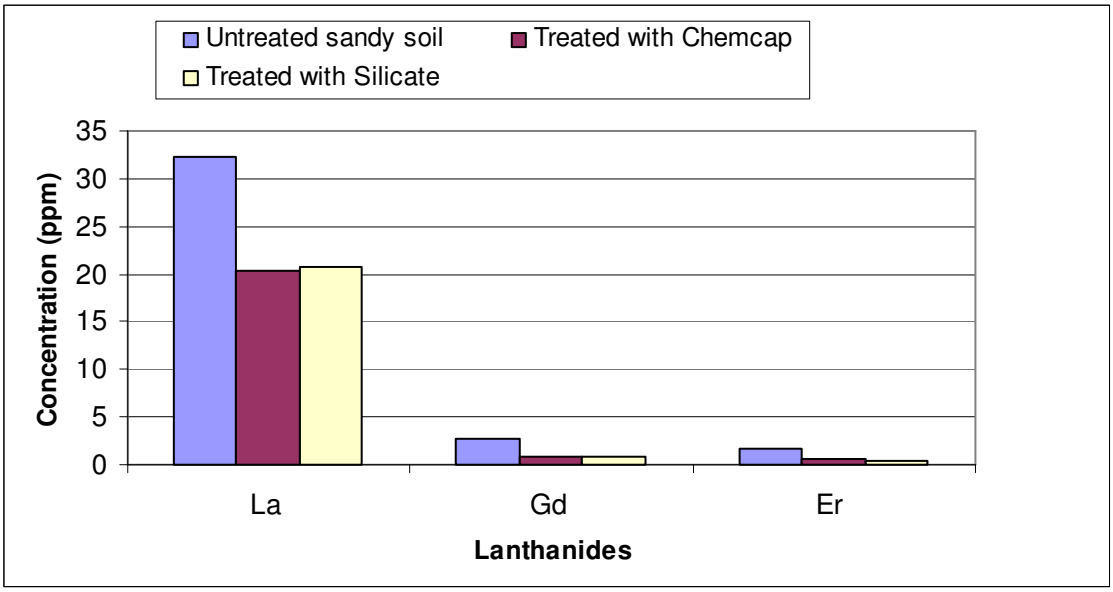
Figure 5.3 Leachable concentration of main groups elements in sandy soil at (a) pH= 9.3 (b) pH=2

The results obtained for metals (Mg, Al, K, Ca) indicate that the encapsulation of these metals in sandy soil is like that of transition metals not affected by pH significantly (figure 5.3). These metals were reduced by very high percentages in both acidic and basic sandy soil as shown in table 5.2. The percentages of encapsulation of these are metals are higher in acidic sandy soil than in basic sandy soil.

Table 5.2 Percentage reduction of leachable concentrations of main group metals in sandy soil

Metal	% reduction of metals in sandy soil			
	Sandy soil (pH=2) treated with Chemcap™	Sandy soil (pH=9.3) treated with Chemcap™	Sandy soil (pH=2) treated with Silicate	Sandy soil (pH=9.3)treated with Silicate
Mg	79	65	74	68
Al	83	68	77	67
K	53	26	29	32
Ca	65	18	47	22

(a)



(b)

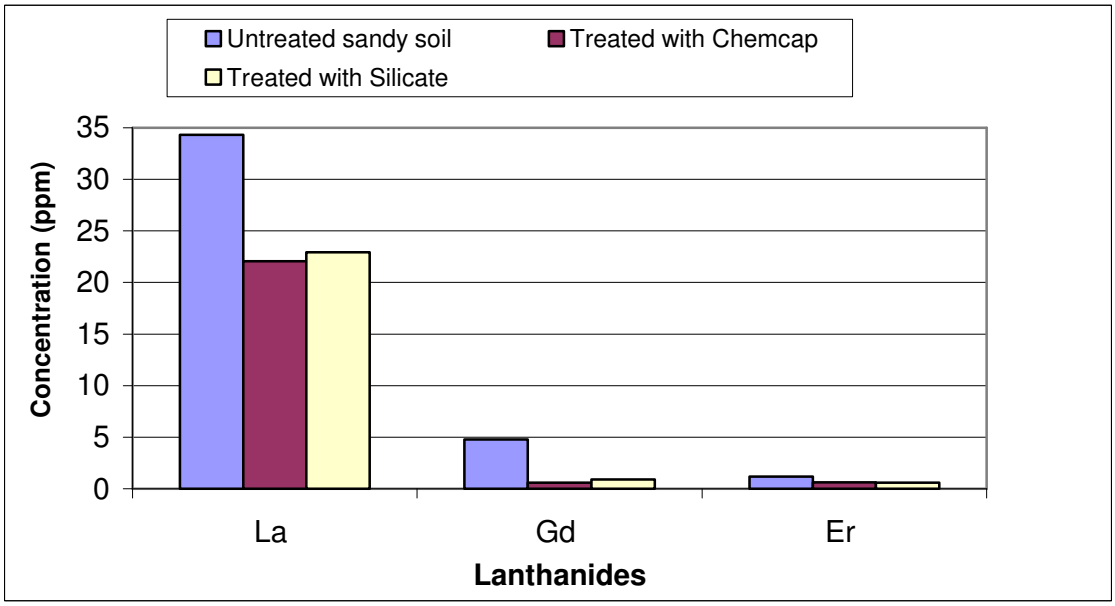


Figure 5.4 Leachable concentration of lanthanides in sandy soil at (a) pH= 9.3 (b) pH=2

Results of silica encapsulation of lanthanides show that Lanthanum was encapsulated by less than 40% in either acidic or basic sandy soil. The percentage reduction of Gadolinium and Erbium were high in both acidic and basic sandy soil. Gadolinium was reduced by more than 70% and Erbium by more than 40% (Table 5.3). These results indicate that silica encapsulation of Lanthanides is effective in either acidic or sandy soil (figure 5.4).

Table 5.3 Percentage reduction of leachable concentration of Lanthanides in sandy soil

Metal	% reduction of Lanthanides in sandy soil			
	Sandy soil (pH=2) treated with Chemcap™	Sandy soil (pH=9.3) treated with Chemcap™	Sandy soil (pH=2) treated with Silicate	Sandy soil (pH=9.3)treated with Silicate
La	36	37	33	35
Gd	88	70	81	70
Er	48	59	49	69

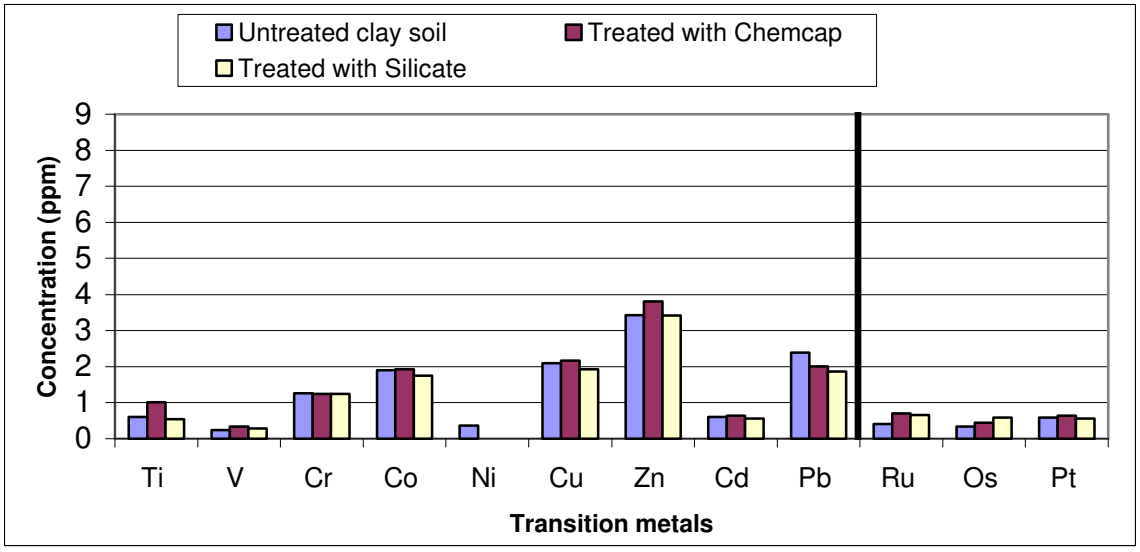
5.1.2 Effect of pH on silica encapsulation in clay soil

Transition metals in figure 5.5 and 5.6 are arranged in order of increasing atomic number. Results in figure 5.5 indicate that pH affects the efficiency of silica encapsulation in clay soil. These results show that more transition metals were removed in acidic clay soil than in basic clay soil. A small percentage of removal was obtained for metals such as Chromium, Manganese, Iron and Lead in basic clay soil treated with Chemcap™. Percentage of reduction of metals tabulated in table 5.4 shows that Titanium, Vanadium, Cobalt, Copper, Zinc, Cadmium, Ruthenium, Osmium and Platinum were not reduced at all in basic clay soil treated with Chemcap™, those that were reduced were removed by a very insignificant percentage. The leachable concentration of Titanium, Cobalt and Zinc increased even after treatment, this show that the efficiency of silica encapsulation in basic clay soil is decreased.

Vanadium, Ruthenium and Osmium were also not reduced in basic clay soil treated with sodium silicate. In clay soil pH affect the efficiency of both Chemcap™ and Silicate. These results further indicate that silica encapsulation is more effective in sandy soil than in clay soil and this agrees with the literature as most of the studies on silica encapsulation were done using sandy soil.

Levels of Iron and Manganese were also high in clay soil. Their encapsulation was much affected by pH in clay soil (figure 5.6). The percentage of removal of these metals in basic clay soil is very low compared to the high percentage of removal in acidic soil.

(a)



(b)

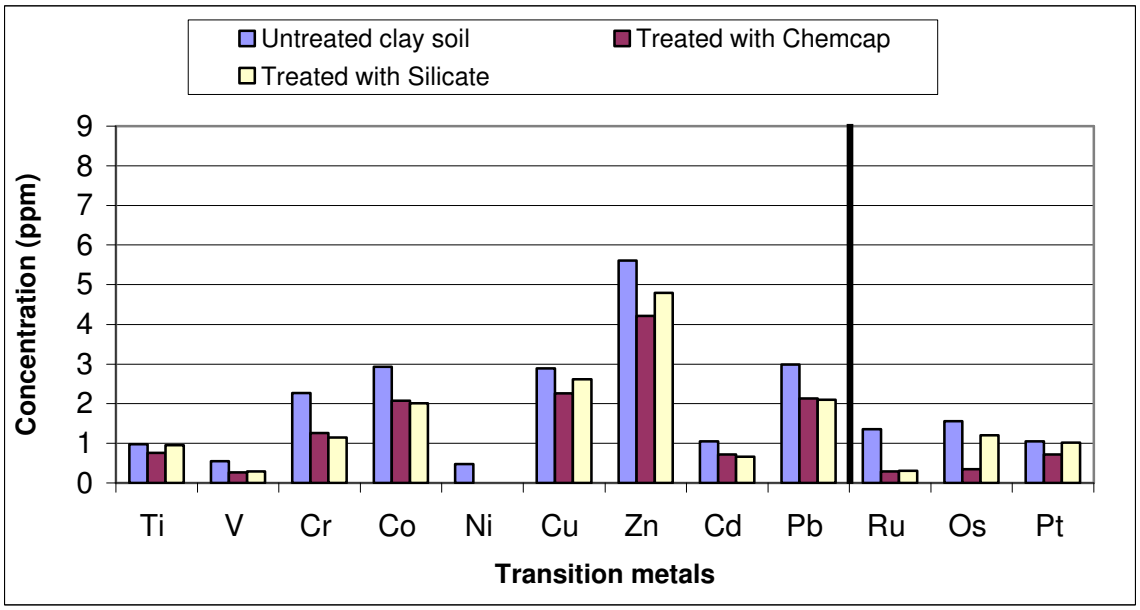
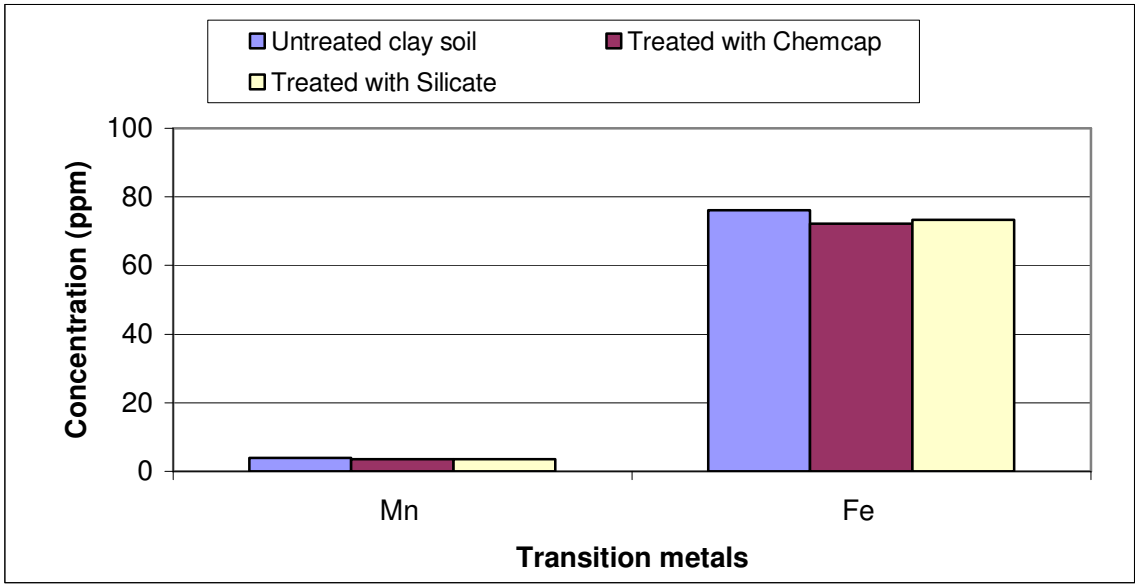


Figure 5.5 Leachable concentration of transition metals and PGMs in clay soil at (a) pH= 9.2 (b) pH=2

(a)



(b)

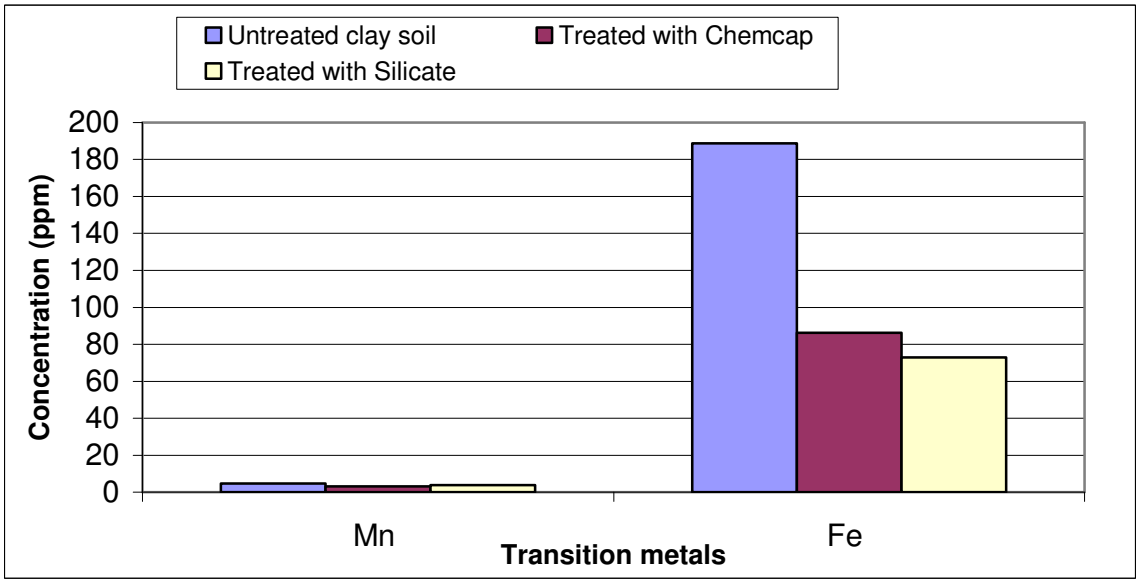


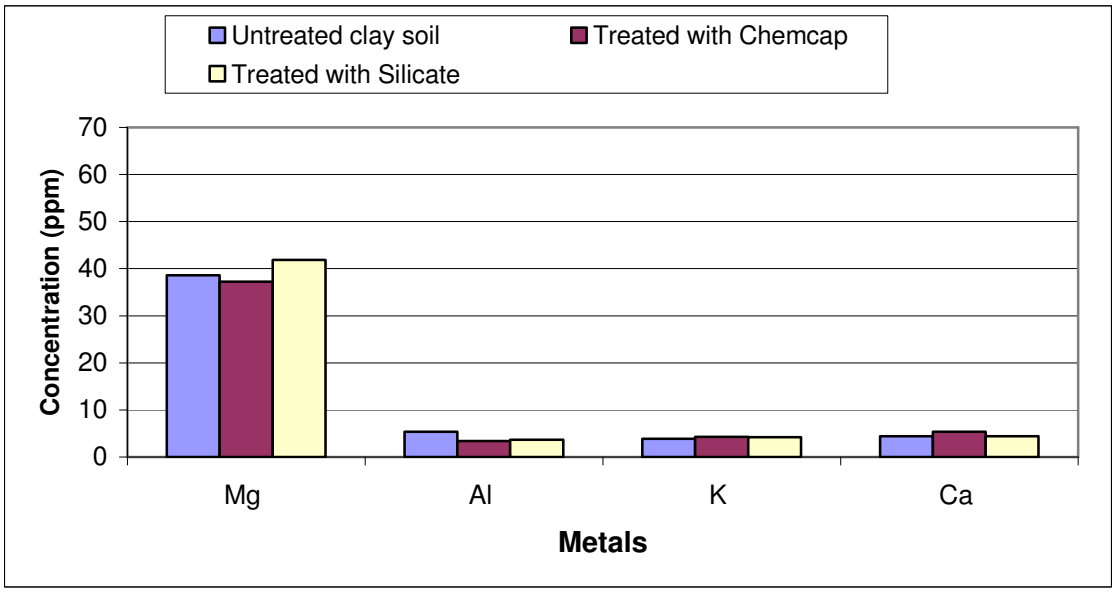
Figure 5.6 Leachable concentration of transition metals in clay soil at (a) pH= 9.2 (b) pH=2

Table 5.4 Percentage reduction of concentrations of transition metals in clay soil leachates

Metal	% reduction of metals in clay soil			
	Clay soil (pH=2) treated with Chemcap™	Clay soil (pH=9.2) treated with Chemcap™	Clay soil (pH=2) treated with Silicate	Clay soil (pH=9.2)treated with Silicate
Ti	22	-	3	10
V	51	-	47	-
Cr	44	1.6	49	1.6
Mn	33.8	9.3	19.78	11.58
Fe	54.2	5.16	61.3	3.8
Co	29	-	31	7.9
Cu	22	-	9.3	8.1
Zn	25	-	15	0.3
Cd	31	-	37	6.6
Pb	29	15.9	30	22
Ru	79	-	77	-
Os	77	-	23	-
Pt	46	-	2.8	5.1

- Leachable metal concentration in clay soil increased instead of decreasing as expected.

(a)



(b)

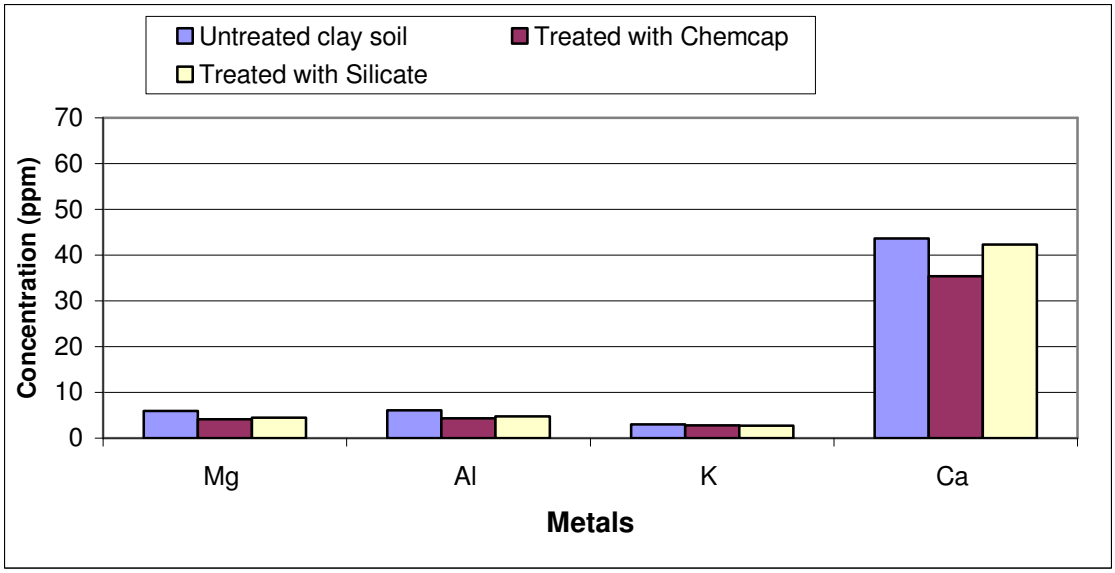


Figure 5.7 Leachable concentration of main groups elements in clay soil at (a) pH= 9.2 (b) pH=2

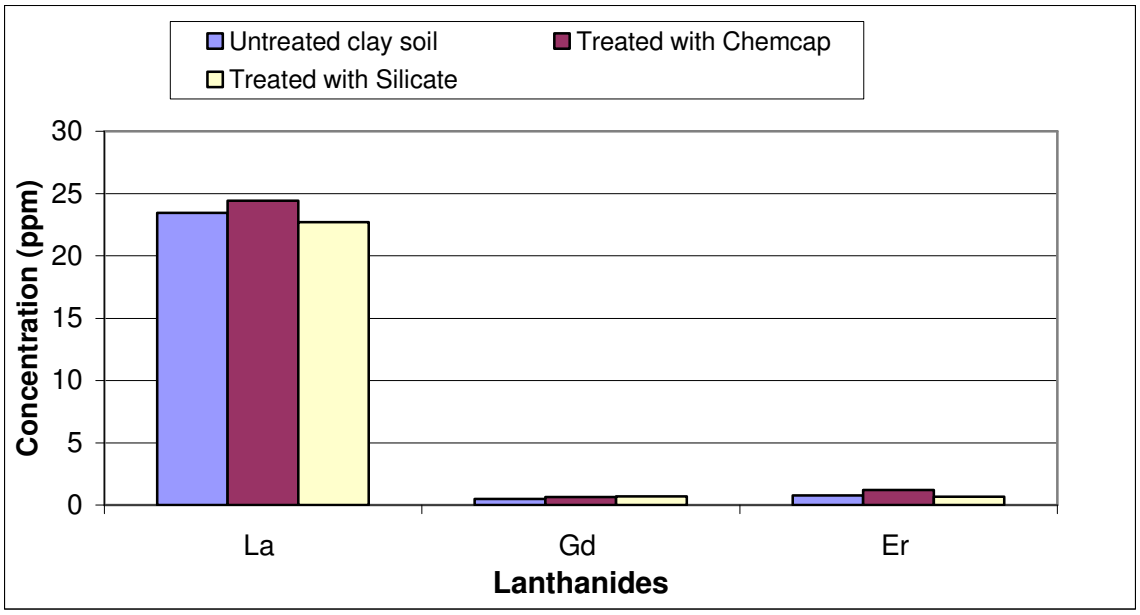
In clay soil the encapsulation of main groups metals was affected by pH as indicated by the results in figure 5.7. The percentage of reduction of these metals tabulated in table 5.5 shows that the efficiency of silica encapsulation of these metals in basic clay soil is reduced. Calcium and Potassium were not encapsulated in basic clay soil treated with Chemcap. Magnesium, Potassium and Calcium were also not encapsulated in basic clay soil treated with silicate.

Table 5.5 Percentage reduction of leachable concentration of main group metals in clay soil

Metal	% reduction of metals in clay soil			
	Clay soil (pH=2) treated with Chemcap™	Clay soil (pH=9.2) treated with Chemcap™	Clay soil (pH=2) treated with Silicate	Clay soil (pH=9.2)treated with Silicate
Mg	30	3.6	24.52	-
Al	28.4	37	21.96	32
K	7.6	-	8.9	-
Ca	18.8	-	3.0	0.02

- Leachable concentration of main groups metals in clay soil increased instead of decreasing as expected.

(a)



(b)

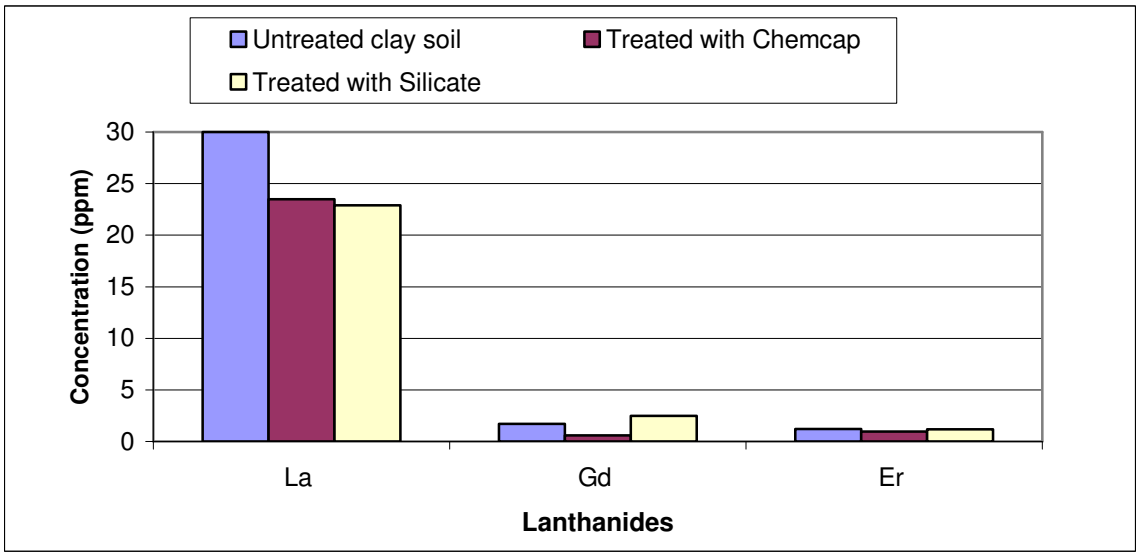


Figure 5.8 Leachable concentration of lanthanides in clay soil at (a) pH= 9.3 (b) pH=2

Results in figure 5.8 show that the encapsulation of lanthanides was affected by pH in clay soil. All extractable lanthanides were not encapsulated in basic clay soil treated with Chemcap™ and only a small amount was encapsulated in clay soil treated with silicate. Leached concentration of Lanthanum, Gadolinium, and Erbium increased by 4.2%, 31.2% and 60.5% respectively in basic clay soil treated with Chemcap™ (table 5.6). Encapsulation of Lanthanum and Erbium was enhanced in basic clay soil treated with sodium silicate as shown in table 5.6.

Table 5.6 Percentage reduction of concentration of Lanthanides in clay soil leachates

Metal	% reduction of Lanthanides in clay soil			
	Clay soil (pH=2) treated with Chemcap™	Clay soil (pH=9.2) treated with Chemcap™	Clay soil (pH=2) treated with Silicate	Clay soil (pH=9.2)treated with Silicate
La	22	-	24	31
Gd	34	-	-	-
Er	20	-	0.8	13.1

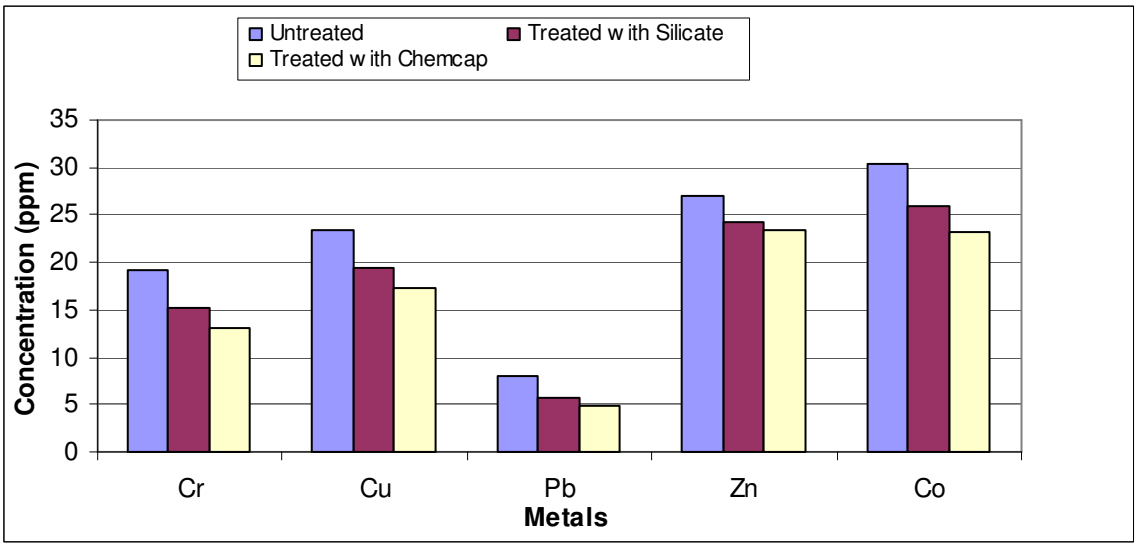
- Leachable metal concentration in clay soil increased by the percentage indicated instead of decreasing as expected.

5.1.3 Effect of pH on silica encapsulation in water

In order to investigate the effect of pH on silica encapsulation in water, samples that were contaminated with Cr, Cu, Pb, Zn and Co standards as described in section 4.6.1 were adjusted to pH=2 and pH=8 using sulphuric acid and sodium hydroxide respectively.

They were treated with either Chemcap™ or silicate and analyzed with ICP-OES as described in section 4.6.2. The results are presented in Figure 5.9.

(a)



(b)

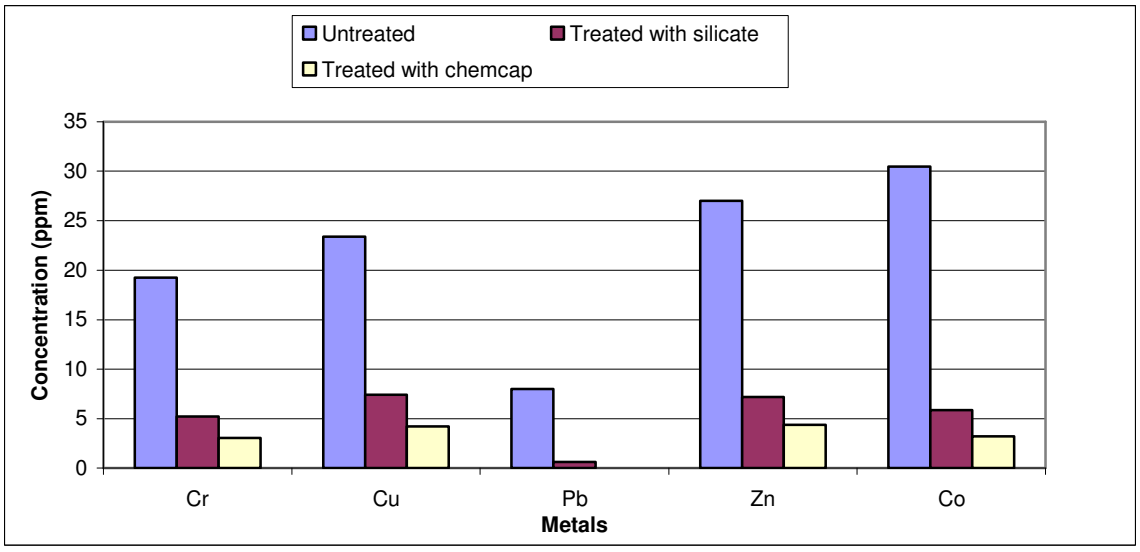


Figure 5.9 Concentration of transition metals in water at (a) pH= 9.2 (b) pH=2

Table 5.7 Percentage reduction of concentrations of transition metals in water

Metal	% reduction of metals in water			
	Water (pH=2) treated with Chemcap™	Water (pH=9.2) treated with Chemcap™	Water (pH=2) treated with Silicate	Water (pH=9.2) treated with Silicate
Cr	84	32	73	21
Co	89	24	81	15
Cu	81	26	68	17
Zn	84	13	73	10
Pd	100	39	92	30

Results obtained for water samples show that metals concentration were decreased after treatment and that silica encapsulation is more effective at low pH. Thus the efficiency of silica encapsulation in water is affected by pH as was found in soil samples. More metals were encapsulated in acidic water than in basic water. The percentage of reduction of metals was higher in acidic water than in basic water as shown in table 5.7. The encapsulation of metals in basic water was low, leachable concentration of metals such as Zinc were only reduced by 13% whereas in acidic water concentration was reduced by 84%. Water samples treated with either Chemcap™ or sodium silicate produced a dense sediment or sludge that can be separated from the water and disposed off.

It is evident from the results that silica encapsulation of metals is more effective in the acidic environment than in the basic environment. In an acidic environment silicate is protonated and can easily exchange with metals thus encapsulation of metals in the acidic environment is enhanced. In basic soil and basic water the reduction of metal concentration was very limited. This can be attributed to the polymerisation of the metal ions in a high pH region. Metals tend to form polymeric ions or metal hydroxides for example $Cu(OH)_2$ that cannot fit into a regular crystal lattice. These metal hydroxides are also known to block the pores of the silicate structure and decrease the retention capacity (Algarra et al. 2004).

Studies done by Ortego' reveal that silicate polymerization occurs when the samples are in the acidic media. The degree of cross-linking is directly proportional to the acidity of the soil (Ortego et al. 1991). This means that at high pH there will be no polymerization of silicate and the degree of cross linking will be low thus no significant encapsulation of metals will be observed.

Low pH accelerates cation leaching from soil and cation storage capacity decreases with decreasing pH. At low pH SiO_2 in soil is protonated and forms silanol. Protonation of silica leads to positively charged sites and poor adsorption of metals to soil surfaces. This causes metals to be available for encapsulation at low pH. However, pH dependent negative charge increases with increasing pH causing soil surfaces to become negatively charged at high pH and adsorbed more metal ions. For hydrous silica, the pH dependent negative charge arises from ionization of the weakly acidic surface silanol groups (Si-OH = Si-O- + H).

Silica accepts a hydrogen ion to become a $SiOH2^+$ site having a positive charge, or they release a hydrogen ion to become SiO^- site having a negative charge. The chemical reactions are written as:

$SiOH + H^+_{(Aq)} \rightarrow SiOH_2^+$

$SiOH \rightarrow SiO^- + H^+_{(Aq)}$

The concentration of the $SiOH_2^+$ and SiO^- species depends on the pH of the aqueous phase. The $SiOH_2^+$ species increases at pH<7, while the SiO^- species increases at pH>7.

It has been found that silica encapsulation reaction begins with pH adjustment that initiates the precipitation of heavy metals from water (including pore water in solid media) and conditions metal-bearing surfaces in solid phases. Once the metal species have been precipitated or conditioned, three-dimensional encapsulation by silica follows. The microscopic encapsulating silica matrix contains no fissures or fractures, completely isolating the metal species from the surrounding environment. The encapsulated metal is environmentally benign and resistant to degradation under even extreme environmental conditions (Mitchel et al. 2002).

5.1.4 Effect of metal charge and metal size on silica encapsulation

Results obtained in this study indicate that encapsulation of transition metals in sandy soil and clay soil does not depend significantly on the size of metals as all transition metals have similar ionic sizes.it is however highly affected by pH. However, encapsulation of alkali earth metals such as Magnesium, Aluminum, Potassium and Calcium is affected by

the metal charge and the size of the metal. The trend observed for the metal ion charge is that the efficiency of encapsulation increases with increasing metal charge.

Metal ions in figure 5.10 are arranged in the order of increasing metal charge and metal ionic size. These results in figure 5.10 show that cations with high charge (Al^{3+}) were encapsulated more efficiently than the metals with low charge (K^{+}). Based on these results the order of the efficiency of encapsulation of metal ions can be presented as $M^{3+} > M^{2+} > M^{+} > M^{0}$. This can be attributed to the difference in sizes of metal ions. As the charge increases on the cation the size of that particular metal ion get smaller and it is easily encapsulated. Metal cations with high charge are therefore small in size than those with low charge and are their encapsulation is enhanced by their small sizes. The effect of metal charge is more pronounced in metals such as magnesium, aluminium, potassium and calcium. The order of encapsulation of these metals is $Al^{3+} > Mg^{2+} > Ca^{2+} > K^{+}$.

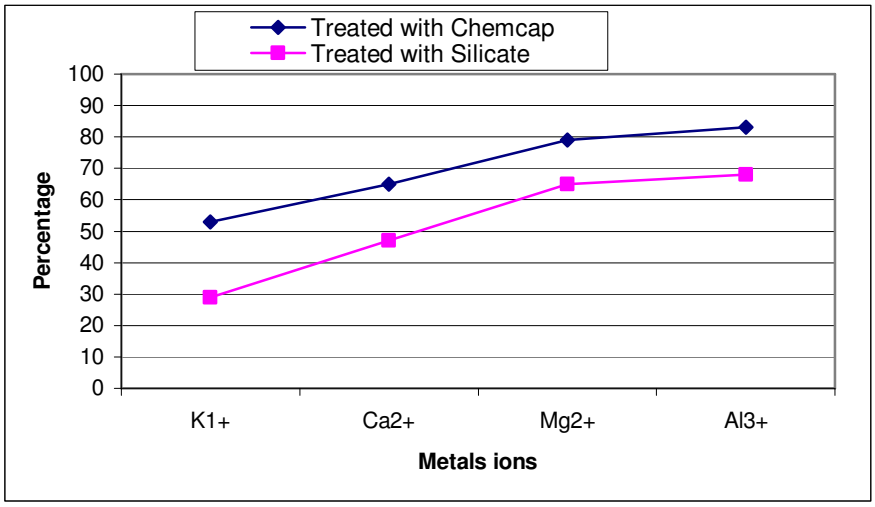
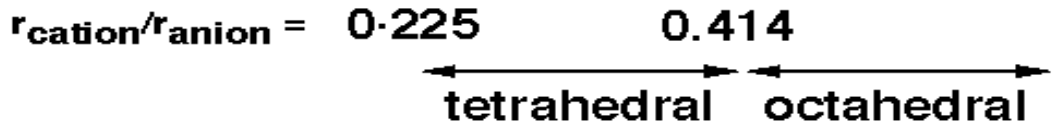


Figure 5.10 Percentage of reduction of major metals according to their metal charges (pH = 2)

The results also indicate that the size of metals atom influences silica encapsulation of metals. Generally, the trend for the ionic and atomic radius for metals is the same. Metals with small atomic radius were encapsulated more than the metals with bigger atomic radius. It decreases across a period from left to right and increases down a given group. Metals on the left of the period are encapsulated more than the metals on right of the period. The formation of the metal silicate can also be seen as the coagulation of positively charged metal colloids and negatively charged silicate colloids.

The silicate anions that are formed in the matrix are double tetragonal rings and octahedral rings of $(Si_6O_{15})^{-6}$, $(Si_8O_{20})^{-8}$, and $(Si_8O_{18}(OH)_2)^{-6}$. The size of these rings is too small for big metals to fit in them resulting in less encapsulation of these metals (US Patent 4853208). The way atoms are packed together or coordinated by larger anions, like oxygen depends on the radius ratio of the cation to the anion, Rx/Rz as discussed in section 2.4.1. For a perfect fit of a cation into the tetrahedral sites of silicate radius ratio r_{cation}/r_{anion} = 0.225. Similarly for a perfect fit of a cation into the octahedral sites r_{cation}/r_{anion} = 0.414.



If the radius ratios of cations are lager than 0.414 and these cations can not fit into octahedral sites as described in section 2.4.1. Transition metals cations have a radius ratio < 0.414 and the fit well in the tetrahedral and octahedral sites of silica, thus easily encapsulated. Metals with a radius ratio > 0.414 exist in eight-fold or 12-fold

coordination and usually require silicate to have an open often cubic structure, and as a result the efficiency of their encapsulation is decreased.

Metal size does not affect the silica encapsulation of transition metals as these metals have almost the same sizes. However silica encapsulation of alkali earth metals is affected by the size of the metal. Silica encapsulation of transition metals was mostly affected by environmental factors such as soil pH and soil type as indicated in table 5.1 and table 5.2.

5.1.5 Effect of soil type on silica encapsulation

Results in figure 5.11 show that silica encapsulation of transition metals is more effective in sandy soil than in clay soil. Transition metals in figure 5.11 are arranged in order of increasing atomic number. The percentages of reduction of metals are high in sandy soil compared to clay soil. This can be attributed to the fact that sandy soil is easily penetrated by silica solution and more surfaces are available for treatment. It can also be attributed to the relatively simple composition of sandy soil. Clay particles have a much greater surface area per unit volume than sand. However, clay soils often have few pores that are readily permeated by silica solution, so the usable surface area is quite small. Hence silica encapsulation is less efficient in clay soil than in sandy soil.

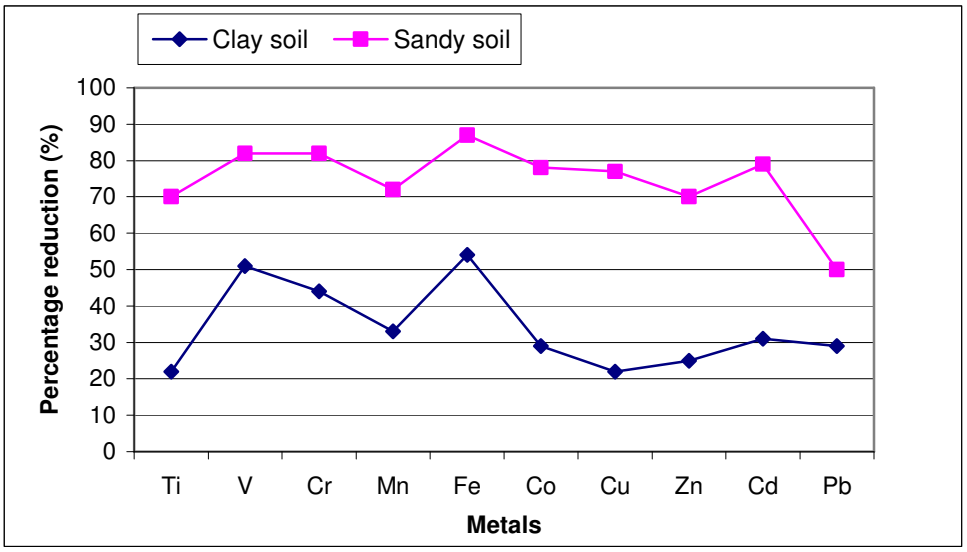


Figure 5.11 Percentage of reduction of transition metals in sandy and clay soil (pH = 2)

Soil surfaces play a role in silica encapsulation of contaminants when silica solution contacts them. Soil surfaces have to be positively charged for good encapsulation of metals since oxygen in the silicate structure is the major anion that coordinates the other cations. Silicate surfaces have some permanent negative charge. This charge is usually due to imperfections in the crystal structure. As a result of their negative charge, silicate can attract bond cations (positive ions) to their surfaces. This surface bonding is called adsorption.

Clay soils have high cationic exchange capacity (the sum total of exchangeable cations that a soil can absorb) than sandy soil. Generally ions with higher valency will exchange for those of lower valency, for example $Al^{3+} > Ca^{2+} > Mg^{2+} > K^{+}$. For ions of same charge, the cation with the smallest hydrated radius is strongly absorbed because it moves close to the site of charge. The rate of ion exchange in soils is affected by the type and

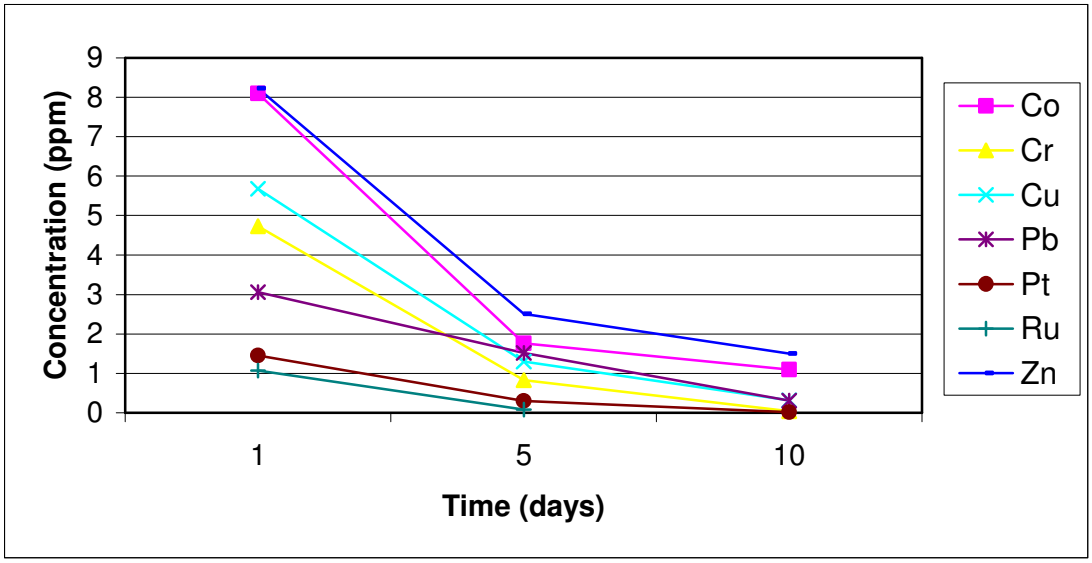
quantity of organic and inorganic colloids. Clay soil tend to have more rapid rate of exchange than sandy soil. However, if Al is occasionally substituted for Si in the tetrahedral sheet or if Ca or Mg is occasionally substituted for Al in the octahedral sheet, then there would be a net negative charge that must be compensated by adsorption of a cation on the surface. It is this mechanism that results in the large cation exchange capacity of clays. Metals adsorb on clay soil and are unavailable for encapsulation, they are then later released when the soil is subjected to harsh acidic or basic conditions.

In summary, results from this study suggest that factors such as pH, metal charge, metal ion size and soil type affect the efficiency of silica encapsulation of transition metals and lanthanides. Results indicated that silica encapsulation is more efficient at low pH than at high pH. Metals with high charge and hence small size were encapsulated more than the metals with low charge and bigger size. Results obtained further suggested that silica encapsulation is more effective in sandy soil than in clay soil.

5.2 Effect of time on encapsulation efficiency

To investigate the effect of time on silica encapsulation, soil samples and water samples were treated with either Chemcap^{TM} or sodium silicate as described in section 4.6.2. The leaching and analysis of samples was done after 5 days of treatment and after 10 days as described in section 4.6.3, 4.6.4 and 4.7.1. Results are presented in figure 5.12-5.16.

(a)



(b)

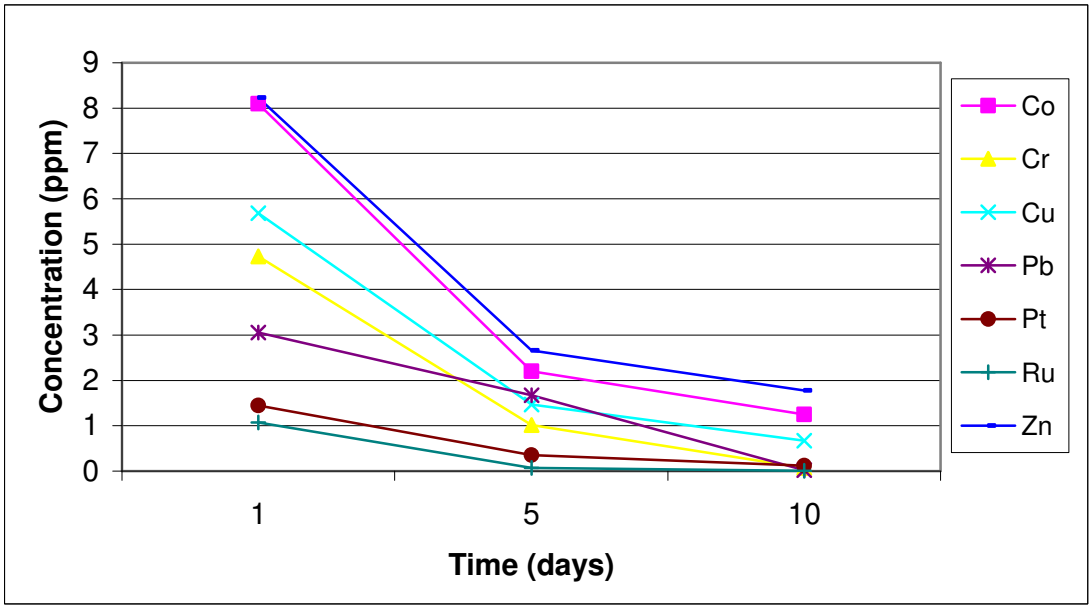
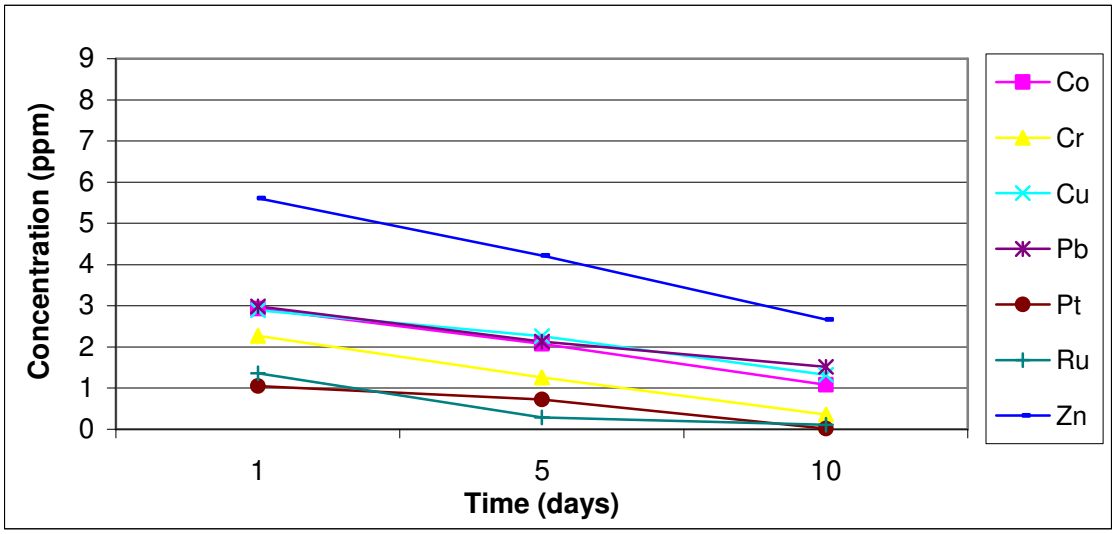


Figure 5.12 Effect of time on leachable concentration of PGMs and transition metals in sandy soil treated with (a) Chemcap^{TM} (b) sodium silicate (pH = 2)

(a)



(b)

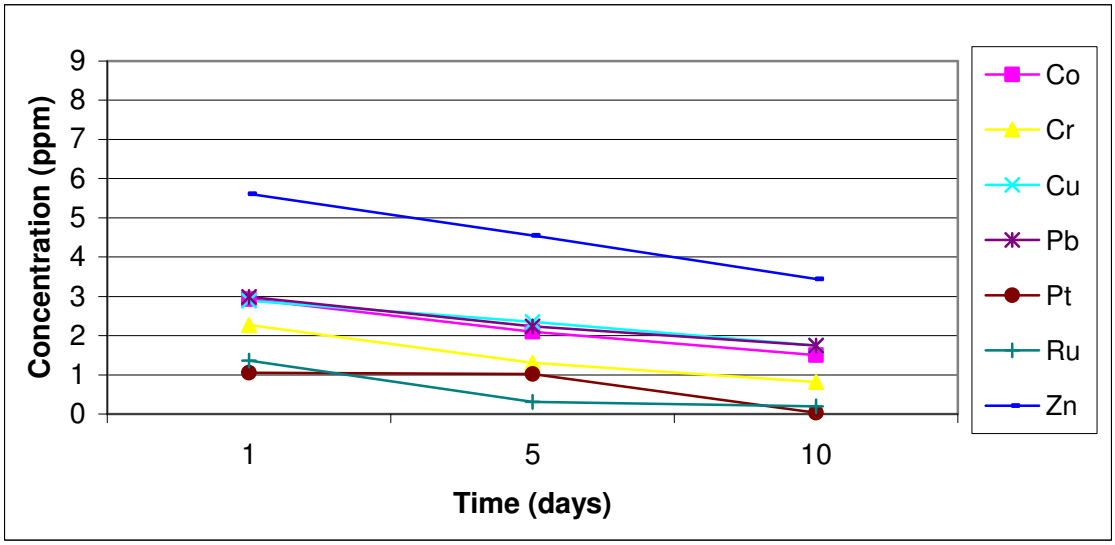


Figure 5.13 Effect of time on leachable concentration of PGMs and transition metals in clay soil treated with (a) Chemcap™ (b) sodium silicate (pH = 2)

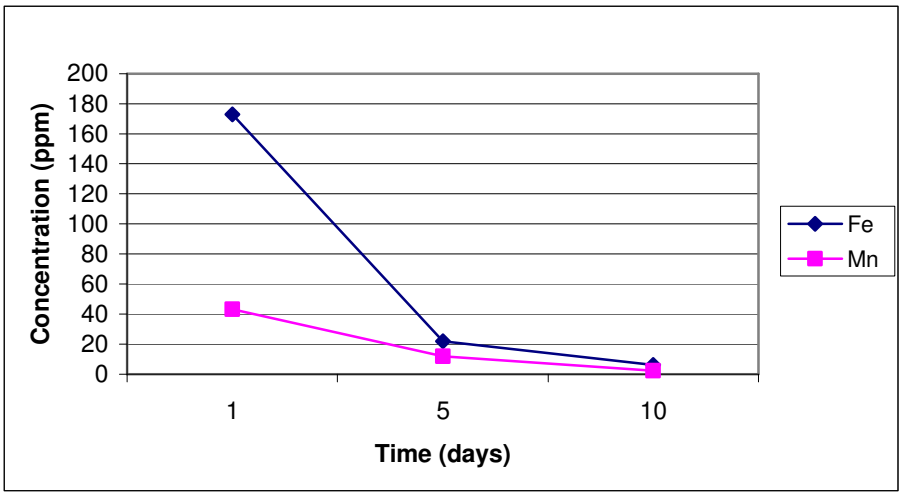


Figure 5.14 Effect of time on leachable concentration of metals in sandy soil (pH = 2)

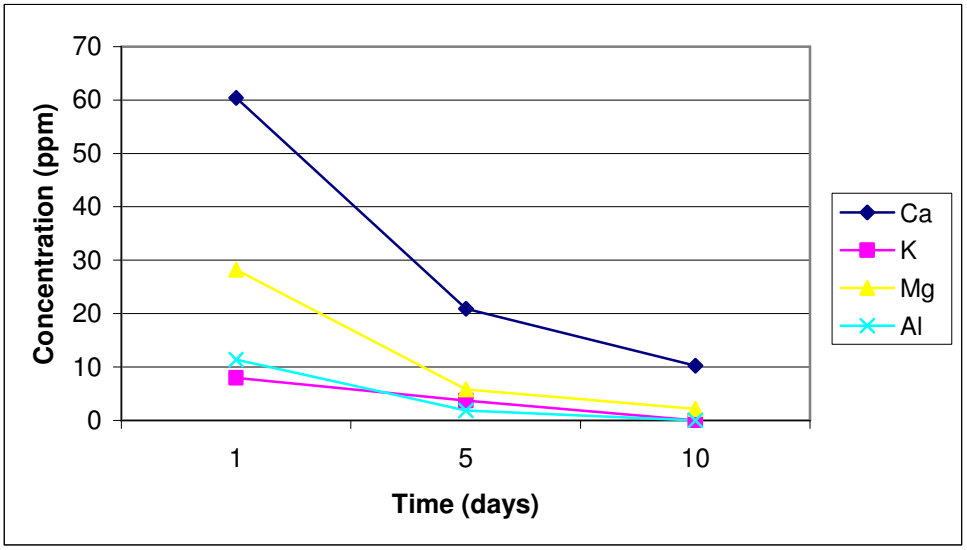
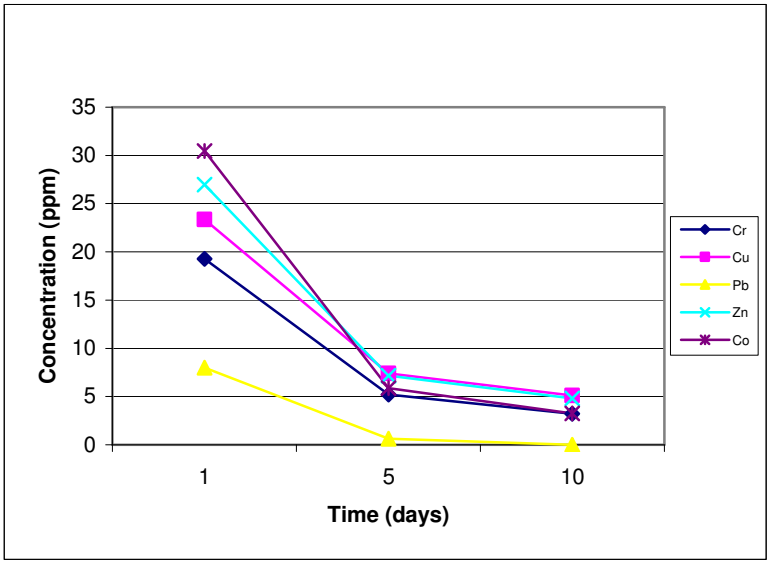


Figure 5.15 Effect of time on concentration of main groups elements in sandy soil (pH = 2)

(a)



(b)

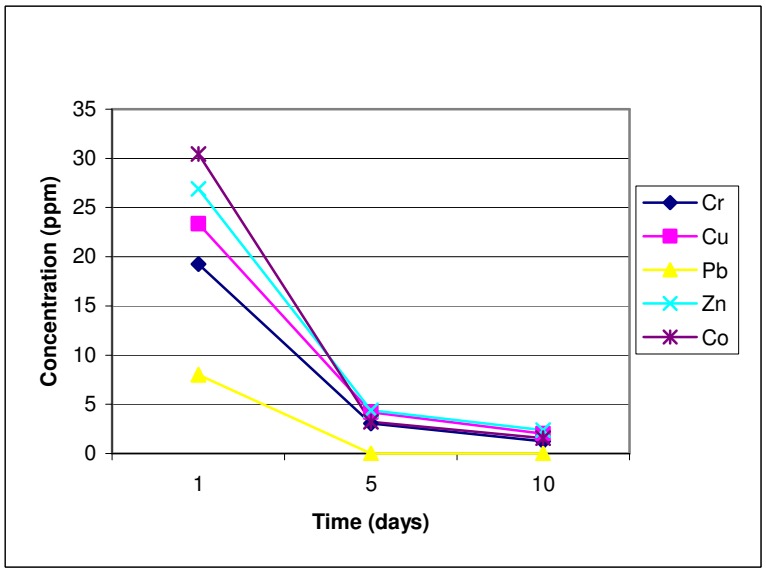


Figure 5.16 Effect of time on concentration of transition metals in water treated with (a) Chemcap^{TM} (b) sodium silicate (pH = 2)

In figure 5.12-5.16 it is observed that the leachable concentration of metals decreased with time in sandy soil, clay soil and water and this suggests that the silica coating

continues to strengthen with time. Contrary to conventional treatment processes where sludge typically degrade over time, in silica encapsulation, the silica matrix appears to continue to strengthen and tighten, providing for long-term isolation of contaminants from the environment.

The long-term stability associated with silica encapsulation indicates applicability for large in situ applications where treated materials will remain on site, exposed to the environment. In the study done by Mitchel et al. 2002, it was found that silica coating is very stable and it strengthens with time thereby further encapsulating metals from the environment.

5.2.1 Kinetics of silica encapsulation

The rate of a reaction is the speed at which a reaction happens. Chemical reactions require varying lengths of time for completion, depending upon the characteristics of the reactants and products and the conditions under which the reaction is taking place. Chemical Kinetics is the study of reaction rates, how reaction rates change under varying conditions and by which mechanism the reaction proceeds. In this study the kinetics of silica encapsulation were investigated and the results are presented in figure 5.17-5.20.

Results in figure 5.12, 5.14 and 5.15 in the above section suggest that silica encapsulation reaction is of first order in sandy soil and zero order in clay soil (figure 5.13). In water, results in figure 5.16 suggest that the reaction is a first order reaction as the concentration of metals decreases by ½ in each of a series of regularly spaced time intervals. This suggests that in silica encapsulation the concentration of metals can be expected to decrease by half after each time interval.

Rate constants, correspond to the slope of lines for the first order reactions tabulated in table 5.8 and 5.9 suggest that the rate of silica encapsulation reaction is faster in water than in soil.

Table 5.8 Rate constants (k) of silica encapsulation reaction in sandy soil

Metal in sandy soil	k ($mgl^{-1}day^{-1}$) Chemcap™	k ($mgl^{-1}day^{-1}$) Silicate
Co	0.2533	0.2354
Cr	0.4901	0.4375
Cu	0.3238	0.2605
Pb	0.3072	0.3209
Pt	0.5497	0.4015
Ru	0.5497	0.5563
Zn	0.2154	0.1993

Table 5.9 Rate constants of silica encapsulation reaction in water (pH = 2)

Metal in water	k ($mgl^{-1}day^{-1}$) Chemcap™	k ($mgl^{-1}day^{-1}$) Silicate
Co	0.3611	0.3542
Cr	0.5486	0.5324
Cu	0.2995	0.1856
Pb	0.4560	0.3956
Zn	0.2992	02815

Table 5.10 Rate constants of silica encapsulation reaction in sandy soil (pH = 2)

Metal	k($mgl^{-1}day^{-1}$) Chemcap™
Ca	0.3611
K	0.5486
Mg	0.2995
Al	0.4560

Results in table 5.10 indicate that Aluminium encapsulation is faster than that of other main group elements. This suggests that silica encapsulation of smaller metals is faster than that of bigger metals.

The rate constants for Iron and Manganese are 0.3842 and 0.3241 respectively. These metals were present in high concentration and their encapsulation was faster than other metals. This agrees with the rate law which states that the higher the concentration the faster the reaction. To test if silica encapsulation is first order in sandy soil and water, graphs of ln C vs. time were plotted (figure 5.17 – 5.19). These results suggest the process is first order, however more experiments would need to be done to confirm this.

where $\ln C = -kt$

C – final concentration of metals, C_o – initial concentration of metals

These plots are straight lines as expected and this proves that silica encapsulation is a first order reaction in sandy soil and water.

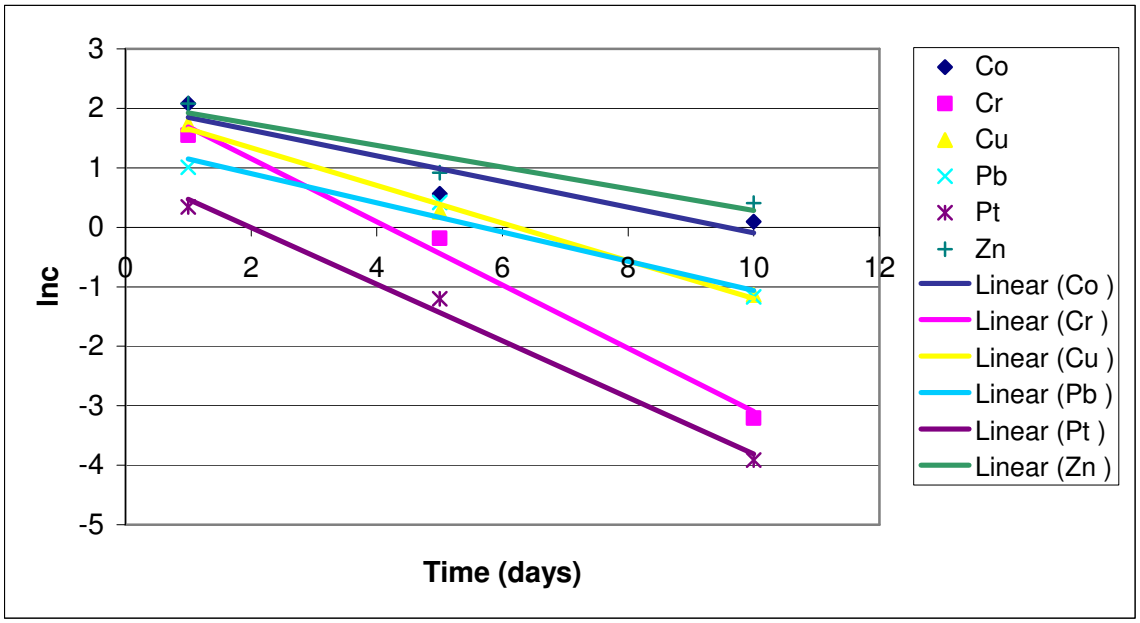


Figure 5.17 Reaction rate of silica encapsulation of transition metals in sandy soil treated with Chemcap™

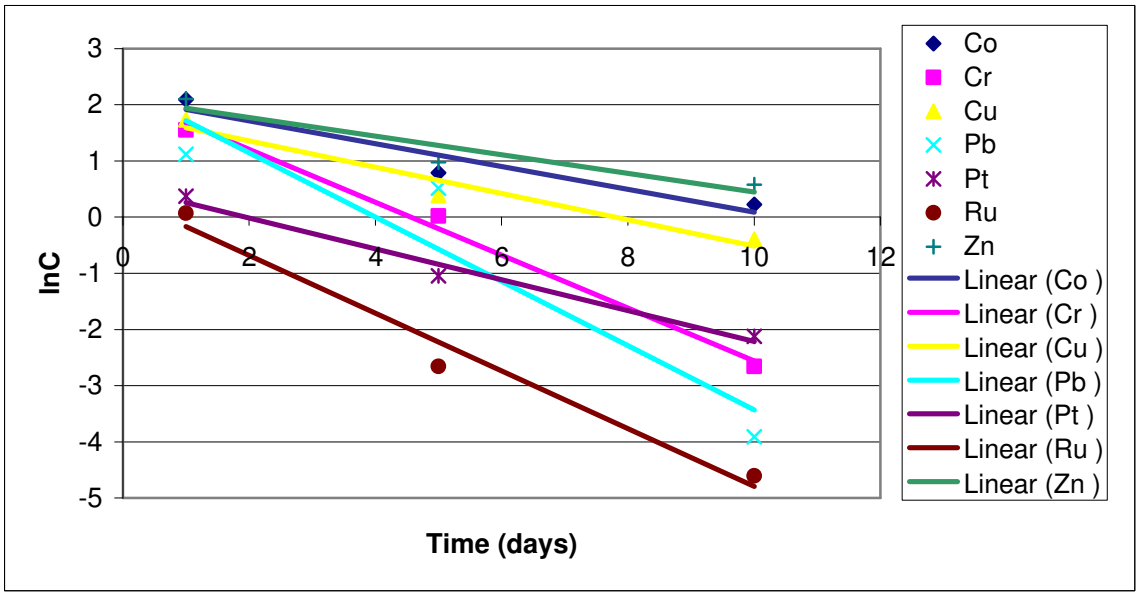


Figure 5.18 Reaction rate of silica encapsulation of transition metals in sandy soil treated with sodium silicate

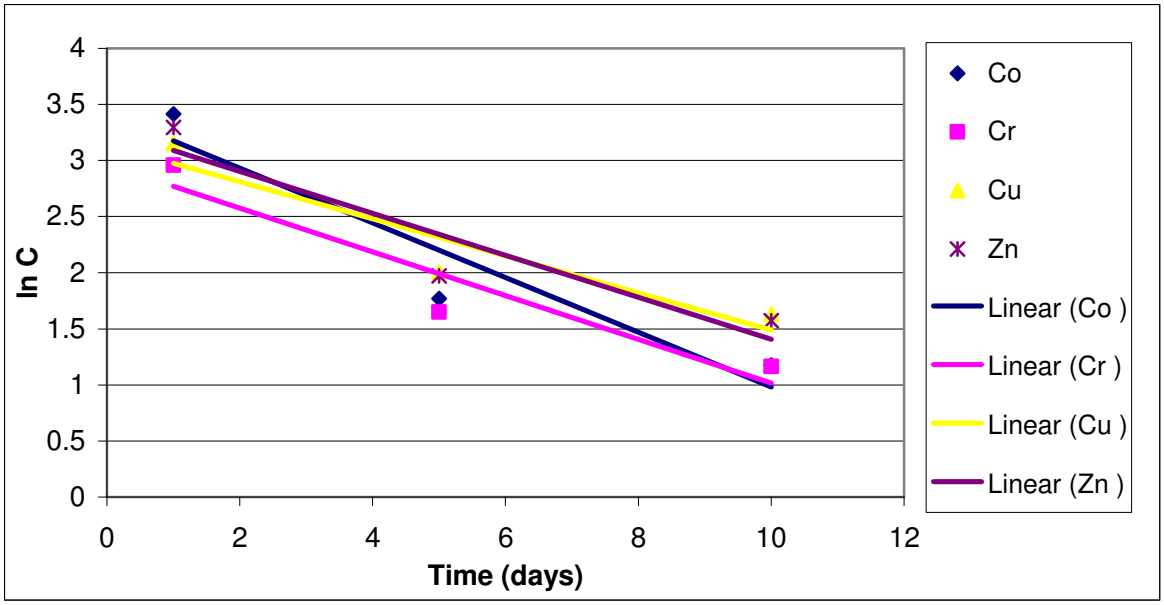


Figure 5.19 Reaction rate of silica encapsulation reaction of transition metals in water treated with sodium silicate

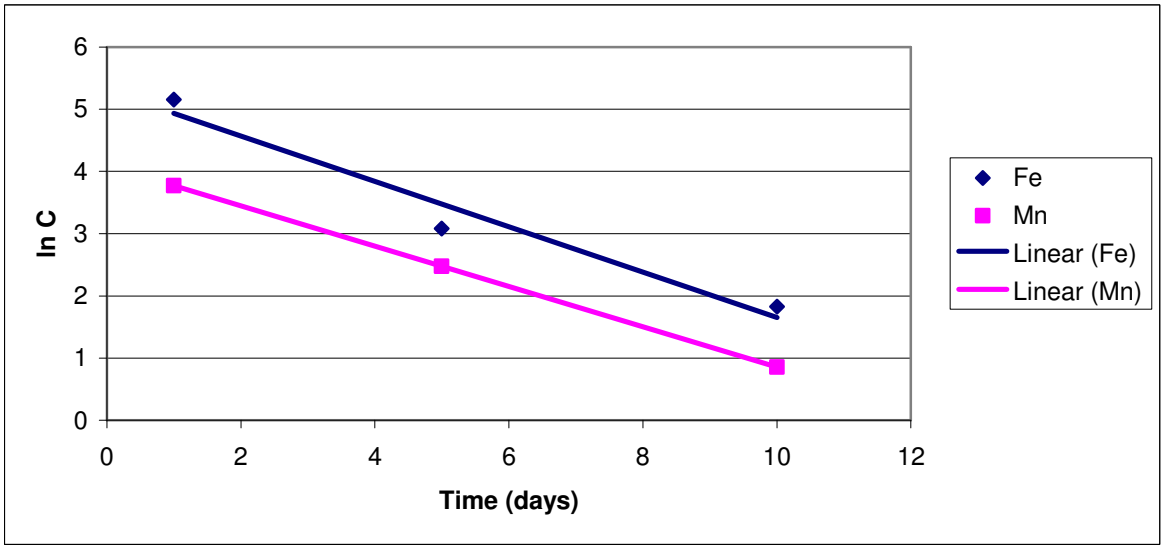


Figure 5.20 Reaction rate of silica encapsulation of main groups elemets in sandy soil treated with Chemcap™

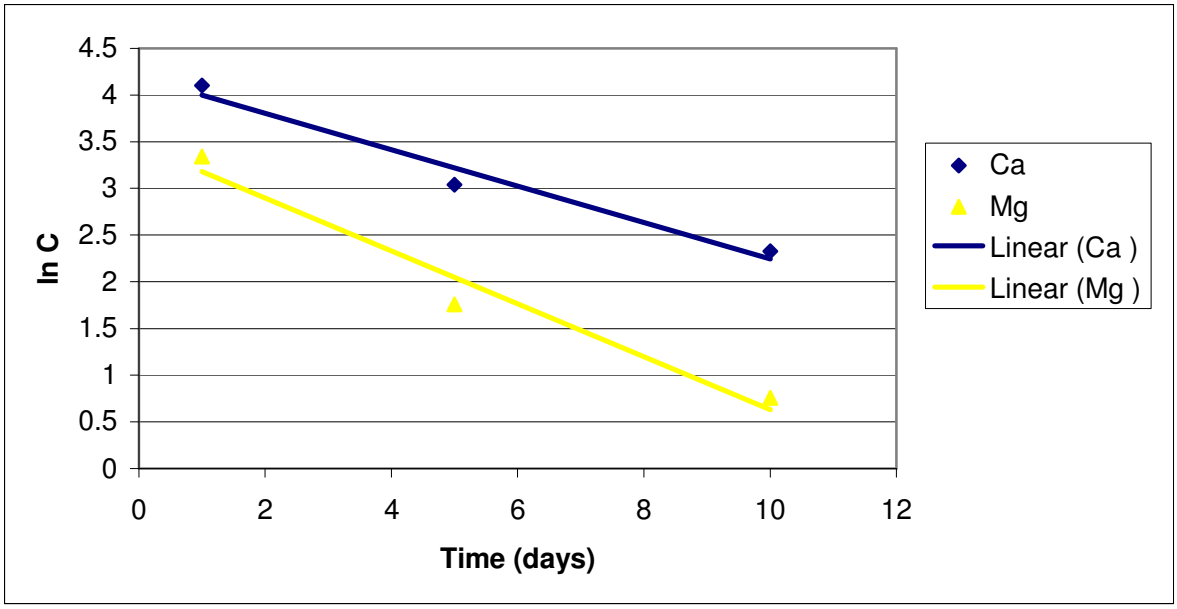


Figure 5.21 Reaction rate of silica encapsulation of main groups elemets in sandy soil treated with Chemcap™

Silica encapsulation of Iron, Manganese and main groups elements in sandy soil was also of first order as shown in figure 5.20 -5.21. A first-order reaction depends on the concentration of only one reactant (a unimolecular reaction). Other reactants can be present, but each will be zero-order. The rate law for a first-order reaction is

$$r = k\,[C]$$

k is the first order rate constant.

The integrated first-order rate law is

$$\ln [C] = -kt + \ln [C]_o$$

A plot of –lnC vs. time t gives a straight line with a slope equal to the reaction rate constant.

The encapsulation of metals in clay soil is a zero order reaction. This typically occurs if other effects such as mass transfer are limiting. A zero-order reaction has a rate which is independent of the concentration of the reactant(s). Increasing the concentration of the reacting species does not speed up the rate of the reaction. Zero-order reactions are typically found when a material required for the reaction to proceed, such as a surface or a catalyst, is saturated by the reactants. The rate law for a zero-order reaction is r = k, where r is the reaction rate and k is the reaction rate coefficient (table 5.11).

Therefore $C = C_o$ – contant time

Table 5.11 Rate constants of silica encapsulation reaction in clay soil (pH = 2)

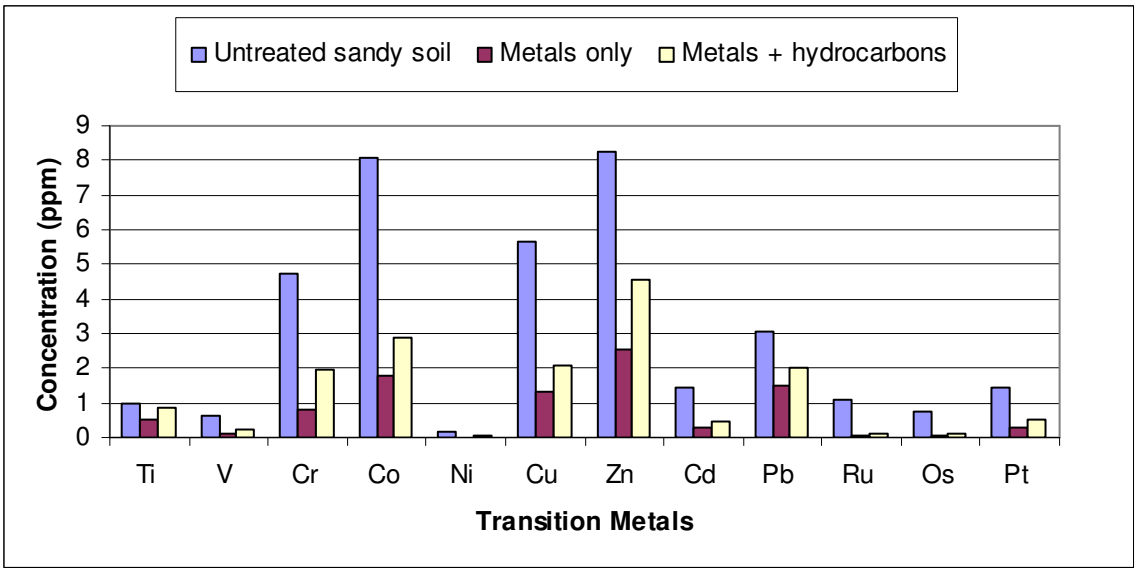
Metal in clay soil	k($mgl^{-1}day^{-1}$) Chemcap™	k ($mgl^{-1}day^{-1}$) Silicate
Co	0.925	0.715
Cr	0.955	0.725
Cu	0.925	0.57
Pb	0.735	0.62
Pt	0.519	0.51
Zn	1.47	1.08

5.3 Competition between contaminants

Competition between hydrocarbons and heavy metals was evaluated by analysing soil samples contaminated with heavy metals only and heavy metals and hydrocarbons. Soil samples contaminated with heavy metals only were treated with either Chemcap™ or sodium silicate as described in section 4.6.2. Samples contaminated with hydrocarbons and heavy metals were subjected to the same treatment method described in section 4.6.2.

All samples were leached using nitric acid extraction method described in section 4.6.3. and were analysed by ICP-OES as prescribed in section 4.7.1. The results are presented in Figure 5.22-5.25.The results in figure 5.22 show that hydrocarbons influence the efficiency of silica encapsulation in sandy soil. The efficiency of silica encapsulation is decreased by the presence of hydrocarbons as less metals are encapsulated in the presence of hydrocarbons. Concentration of metals in soil leachates increased after treatment with either Chemcap™ or sodium silicate and this can be attributed to the presence of hydrocarbons. The effect of hydrocarbons on PGM'S in sandy soil treated with sodium silicate is very small whereas in sandy soil treated with Chemcap™ it is significant.

(a)



(b)

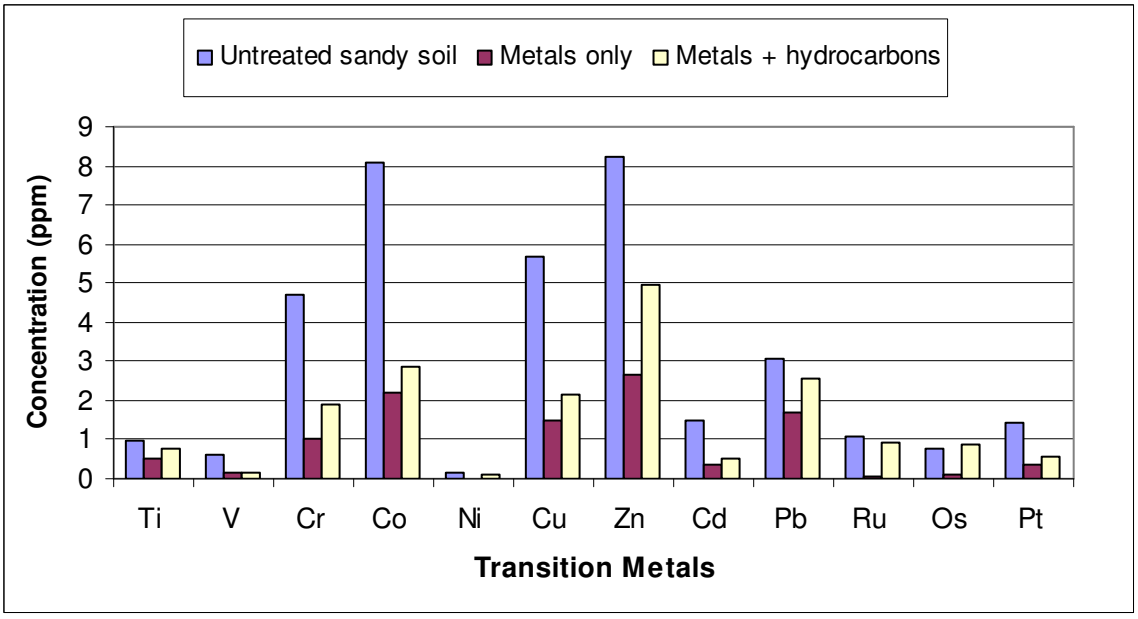
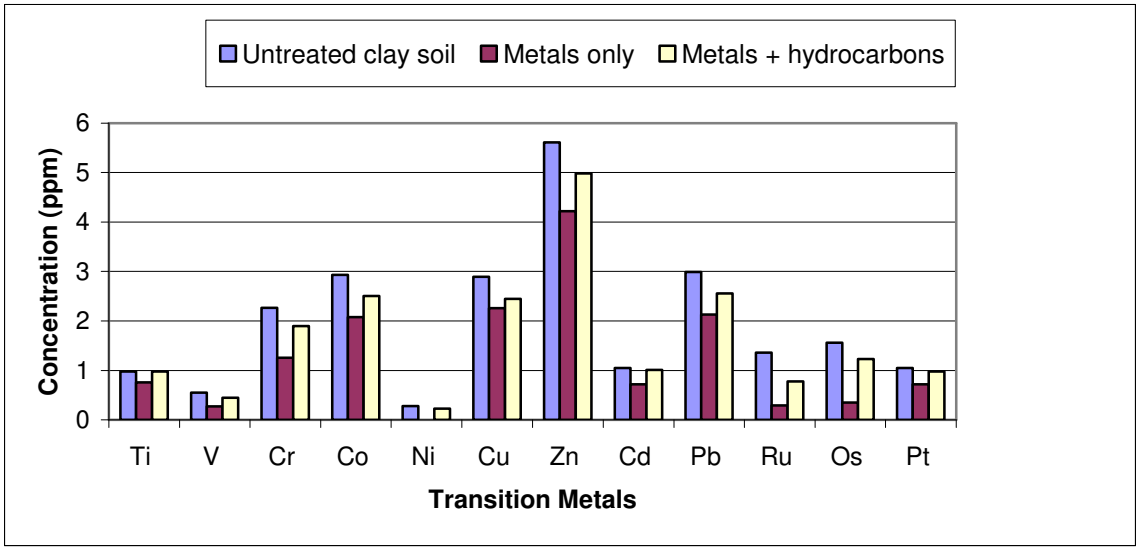


Figure 5.22 Effect of hydrocarbons on leachable concentration of transition metals in sandy soil treated with (a) sodium silicate (b) Chemcap^{TM} (pH = 2)

(a)



(b)

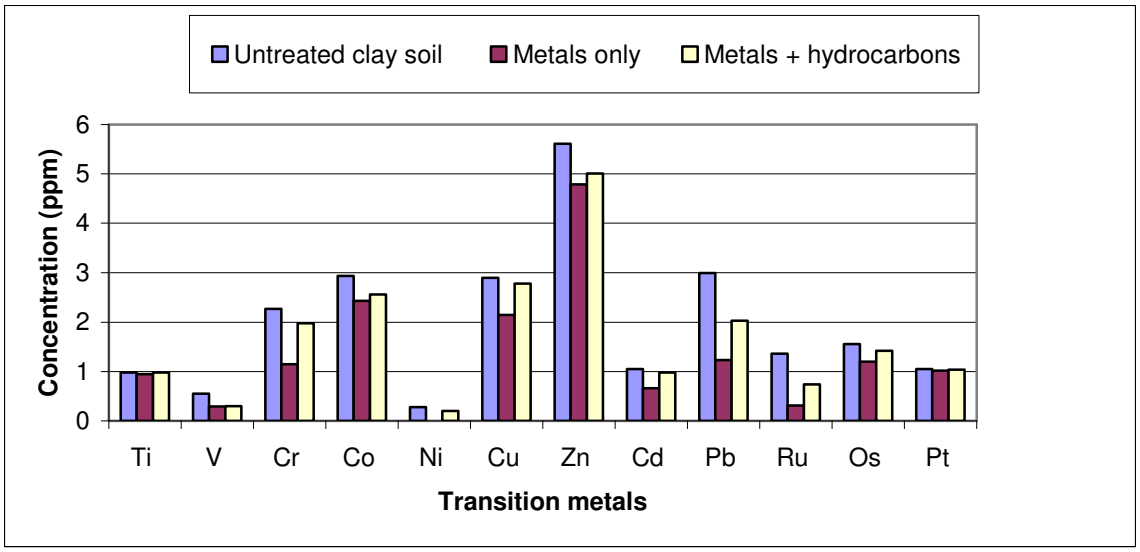
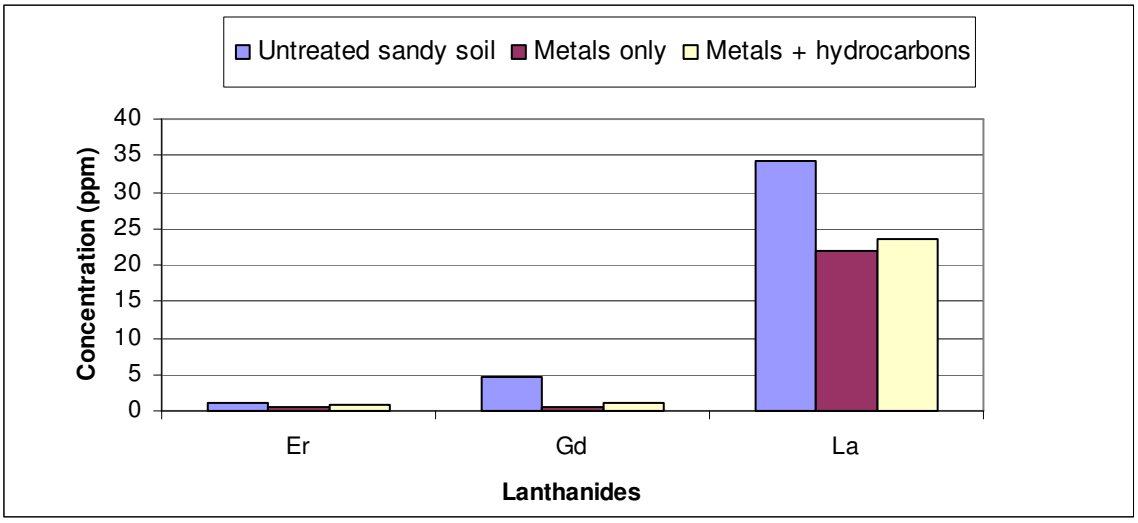


Figure 5.23 Effect of hydrocarbons on leachable concentration of transition metals in clay soil treated with (a) sodium silicate (b) Chemcap^{TM} (pH = 2)

In clay soil the effect of hydrocarbons is the same as in sandy soil. Results in figure 5.23 show that in the presence of hydrocarbons the encapsulation of metals is not enhanced.

The concentration of extractable metals increased after treatment when hydrocarbons were present.

(a)



(b)

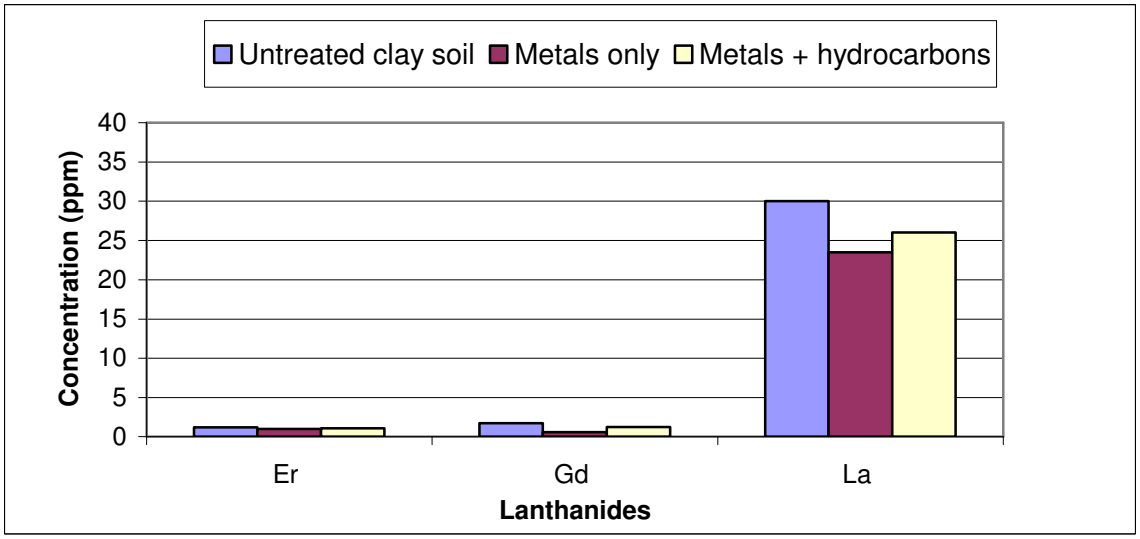
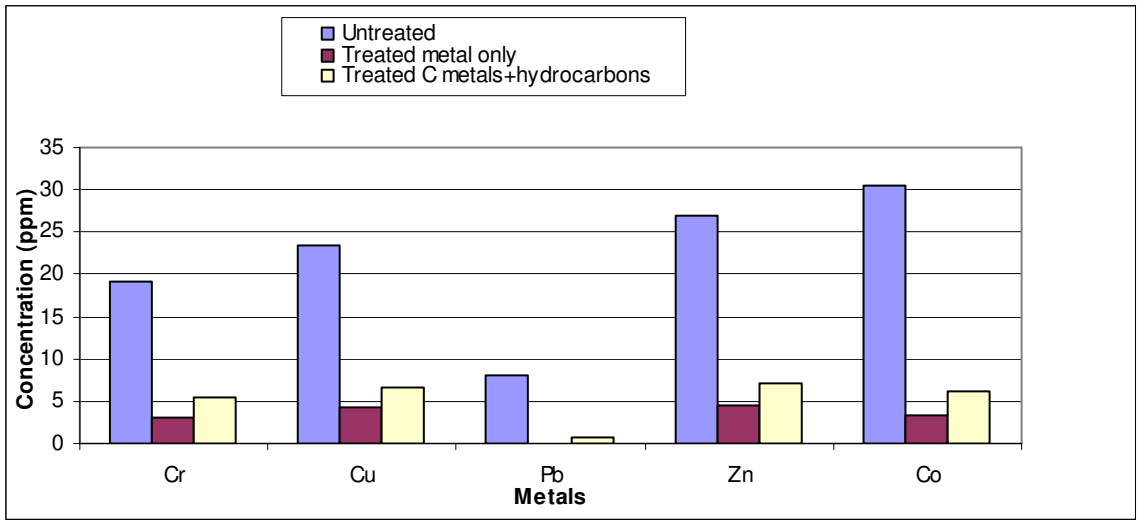


Figure 5.24 Effect of hydrocarbons on leachable concentration of lanthanides in (a) sandy soil (b) clay soil (pH = 2)

Results in figure 5.24 indicate that encapsulation of lanthanides in the presence of hydrocarbons is less effective. The effect of hydrocarbons on encapsulation of lanthanides is not as significant as in the case of metals.

(a)



(b)

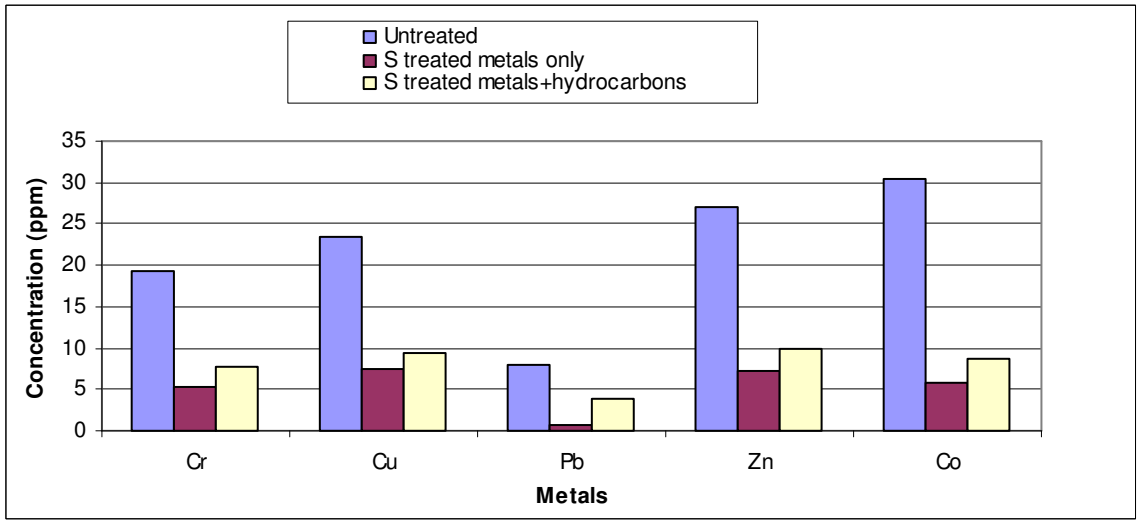


Figure 5.25 Effect of hydrocarbons on concentration of transition metals in water treated with (a) Chemcap^{TM} (b) sodium silicate (pH = 2)

Results presented in figure 5.25 also indicate that less metals were encapsulated in water in the presence of hydrocarbons. There is an increase in the concentration of metals after treatment of water in the presence of hydrocarbons. However, this increase is not significant.

Hydrocarbons have a negative effect on the encapsulation of metals. Fewer metals were encapsulated in the presence of hydrocarbons. In the presence of hydrocarbons metal complexes may be formed through complexation and chelation. The size of theses metal complexes is bigger than the size of uncomplexed metal and therefore can not fit in the rings of silicate as discussed above. The encapsulation of metals in the presence of hydrocarbons is therefore less efficient than in absence of hydrocarbons.

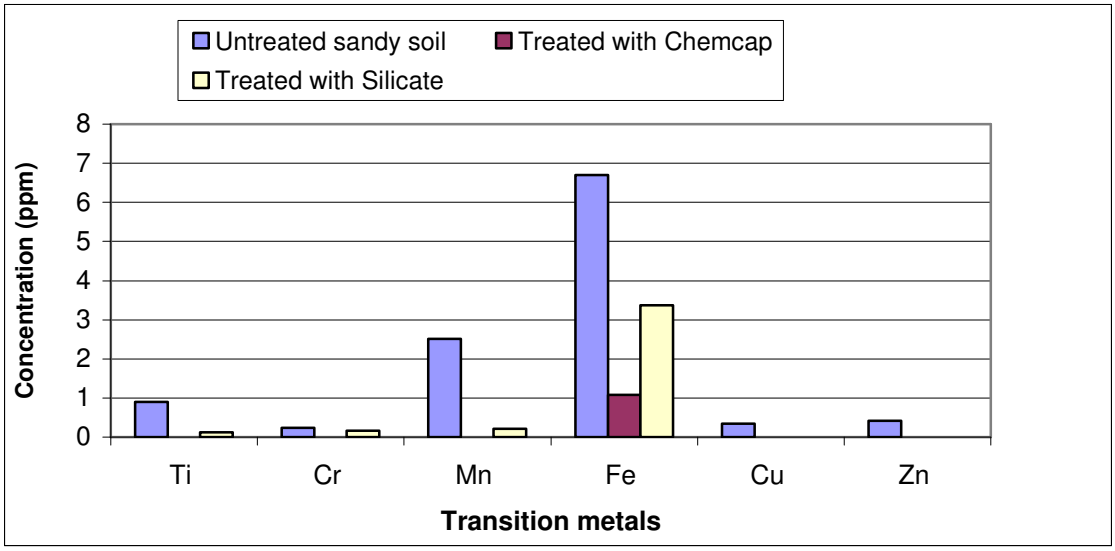
Organic ligands are suggested to chelate and mobilize heavy metals, and enhance the precipitation of metals in soil. Wide variety of organic compounds in soil and water can act as complexing agents for metal ions. Dissolved organic compounds are suspected of interacting with a wide variety of inorganic solutes in water (Manahan et al. 1999). These results suggest that the removal of metals by silica encapsulation in the environment where there is also high concentration of hydrocarbons remediation is not as effective.

5.4 Extraction with sodium carbonate

To investigate the stability of silica coating when subjected to basic conditions, samples were leached using 0.1 M sodium carbonate solution in a ratio of 20:1 as described in section 4.6.4. Metals levels in extracts were analyzed by inductively coupled plasma-

optical emission spectrometry as described in section 4.7.1. Results are presented in Figure 5.26.

(a)



(b)

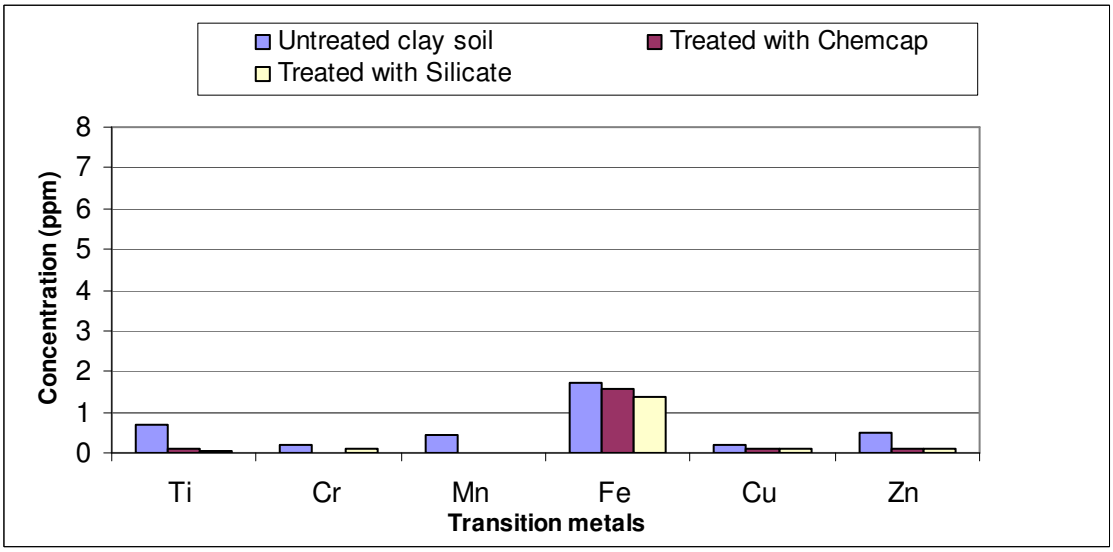


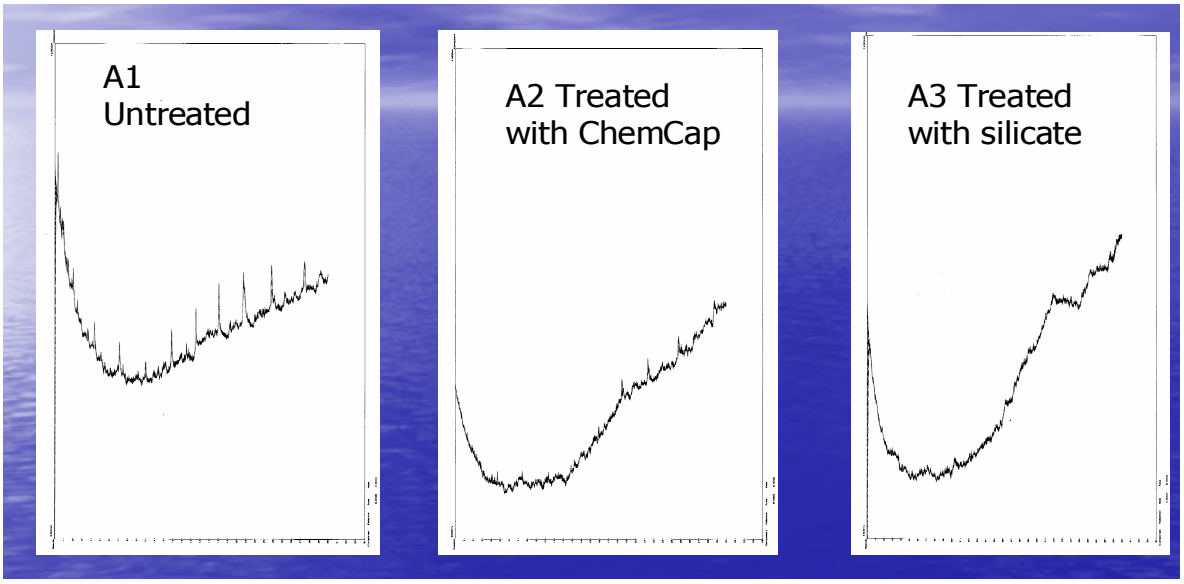
Figure 5.26 Leachable concentration of transition metals extracted with sodium carbonate in (a) sandy soil (b) clay soil

Silicate coating was found to be stable in both acidic (Figure 5.1-5.9) and basic medium (Figure 5.26). This was confirmed by extraction of metals using nitric acid and sodium carbonate. Results indicate that the leachability of metals was reduced even when samples were subjected to both acidic and basic environment. Previous research shows that sodium silicates react with polyvalent metal ions to produce metal silicate precipitates which are less soluble across a broader pH range than the metal hydroxides produced by non-silicate processes (Mitchel et al. 2002). These precipitates reduce the solubility and leachability of heavy metals to produce a more chemically stable non-toxic material.

5.5 Hydrocarbons encapsulation

Soil samples were contaminated with diesel and adjusted to a pH=2, pH=8.2, pH=13.1 and pH=3.4. They were treated with either Chemcap^{TM} or sodium silicate in a ratio of. They were extracted by ultrasonic extraction and analysed by GC-FID using the USEPA Method 3550 as prescribed in section 4.6.5 and 4.7.2. Results are presented in figure 5.27 – 5.28.

(a)



(b)

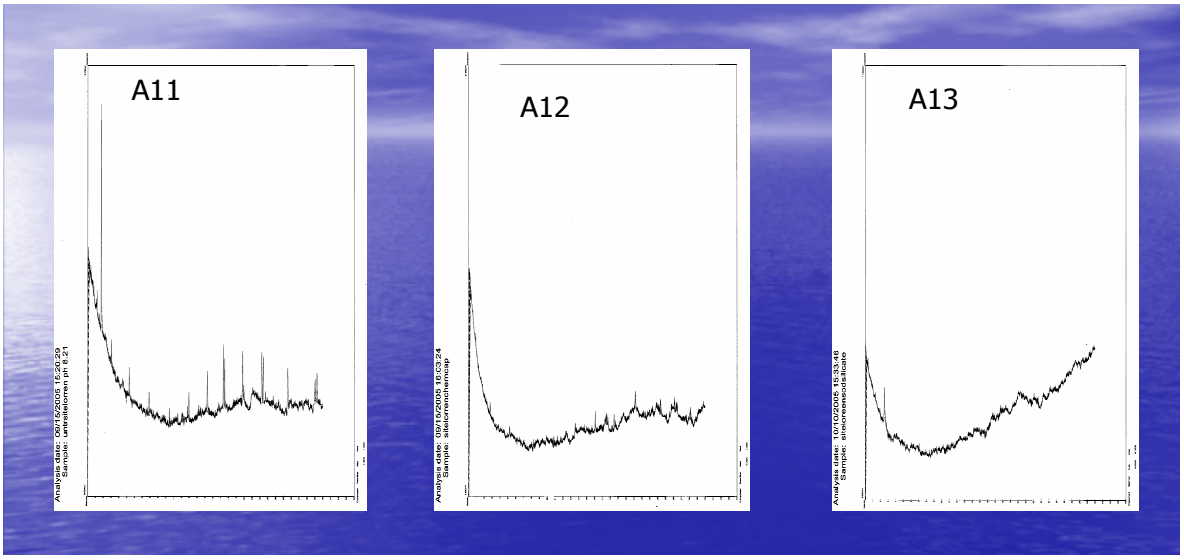
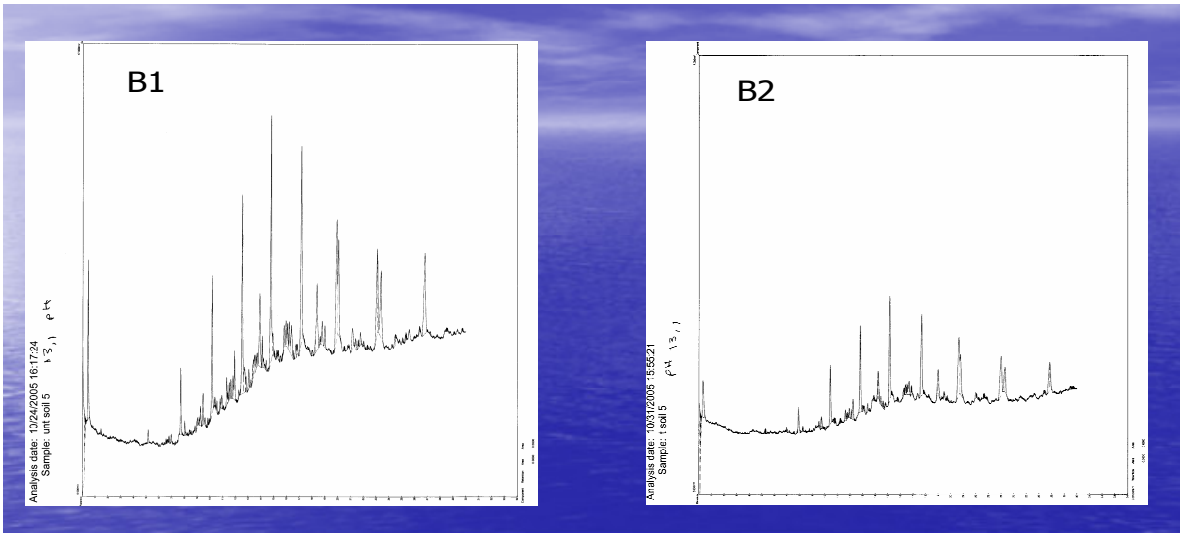


Figure 5.27 (a) Qualitative analysis of hydrocarbons before and after treatment at pH = 8.2 (b) Qualitative analysis of hydrocarbons before and after treatment at pH = 2 A11-Untreated, A12-Treated with Chemcap^{TM}, A13-Treated with sodium silicate

(a)



(b)

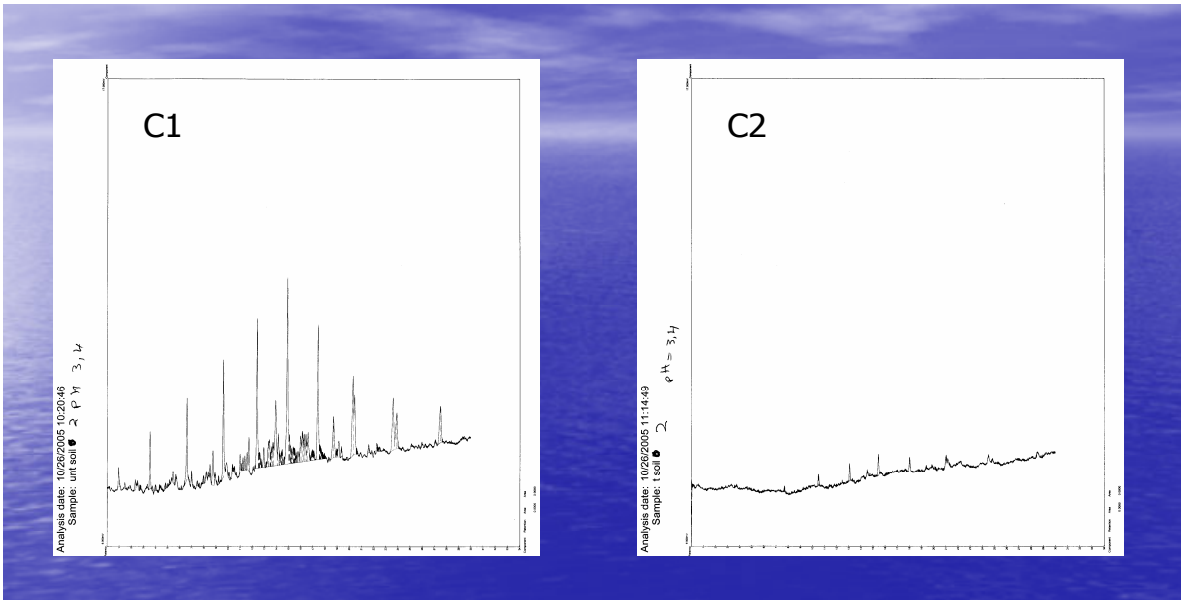


Figure 5.28 (a) Qualitative analysis of hydrocarbons before and after treatment at pH = 13.1 B1- Untreated, B2-Treated (b) Qualitative analysis of hydrocarbons before and after treatment at pH = 3.4 C1-Untreated, C2-Treated

Results show that hydrocarbons were removed by silica encapsulation process. Hydrocarbons encapsulation was more effective in the acidic soil than in the basic soil. The results above indicate that sodium silicate (Fig. 5.27 A3) was as good as Chemcap^{TM} (Fig. 5.27 A2) in encapsulating hydrocarbons. Some traces of hydrocarbons are still visible in A2. This is because this soil had a pH of 8.2 and silica encapsulation is so effective in basic soil.

The effect of pH was evaluated by adjusting the pH of soil to 13.1 and 3.4 using sodium hydroxide and sulphuric acid respectively. Results obtained suggest that hydrocarbons were effectively encapsulated in the acidic soil (fig 5.28). Chromatograms in figure 5.28 show that less amount of hydrocarbons was removed at pH 13.1 whereas at pH 3.4 a significant amount of hydrocarbons was removed. This means that before treatment is done the environment to be treated has to be made acidic for better results to be obtained. This was similarly observed in the encapsulation of heavy metals.

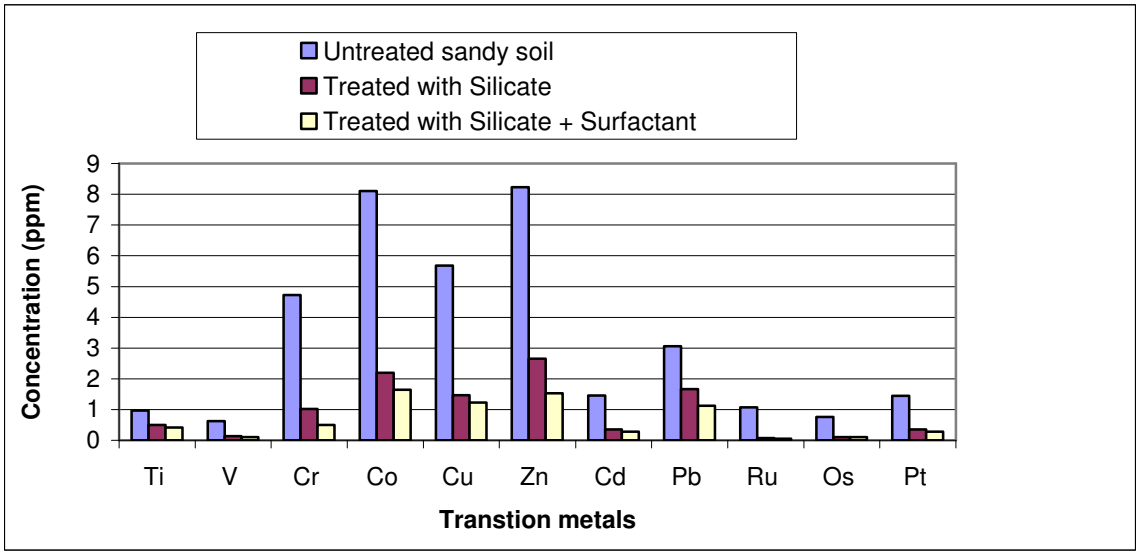
Although the precise mechanism by which the silica encapsulates hydrocarbons or chemicals is not fully understood, the proposed mechanism is as discussed in section 2.4.1.The surfactant orients itself with the hydrophobic portion toward the hydrocarbon and the hydrophilic portion toward the polar sites of the hydrophilic silica (Figure 2.2). Within minutes, micro encapsulation is observed to occur in the form of precipitated agglomerates of wet silica containing the contaminant species in the micelle trapped inside the silica matrix. The pH of the micro encapsulated material is approximately neutral.

5.6 Development of silica encapsulating product

Development of an encapsulation product was done using sodium silicate as a basic component. Literature reviewed suggests that surfactants can be used to enhance silica encapsulation. The effects of surfactants on silica encapsulation of metals on contaminated soils have been reported (Arocha et al. 1996). The choice of surfactants, sodium dodecylsulfate, was based on literature survey (Arocha et al. 1996, US Patent 4853208). Surfactant was mixed with sodium silicate at 2 to 1 ratio. Soil samples were treated with this solution at approximately 1 to 1 ratio as described in section 4.6.2. Leaching and analysis of samples were done according to the method prescribed in section 4.6.3 and 4.7.1. Results are presented in figure 5.29-5.30.

Results shown in Figure 5.29-5.30 illustrate that surfactant enhanced the encapsulation of metals by sodium silicate in soil as more metals were encapsulated after the addition of surfactant to sodium silicate. Surfactants are known to improve wettability of the solution on the substrate, thereby improving the efficiency of silica encapsulation process. However, care should be taken not to use excess surfactant as inclusion of an excessive amount of surfactant may reduce the adhesion properties of the coating. Generally, the surfactant can be used in amounts of up to about 0.5 weight percent of the solution. The combination of anionic and non-ionic surfactants has been found to be very effective in enhancing silica encapsulation of metals and hydrocarbons (US Patent 6602181).

(a)



(b)

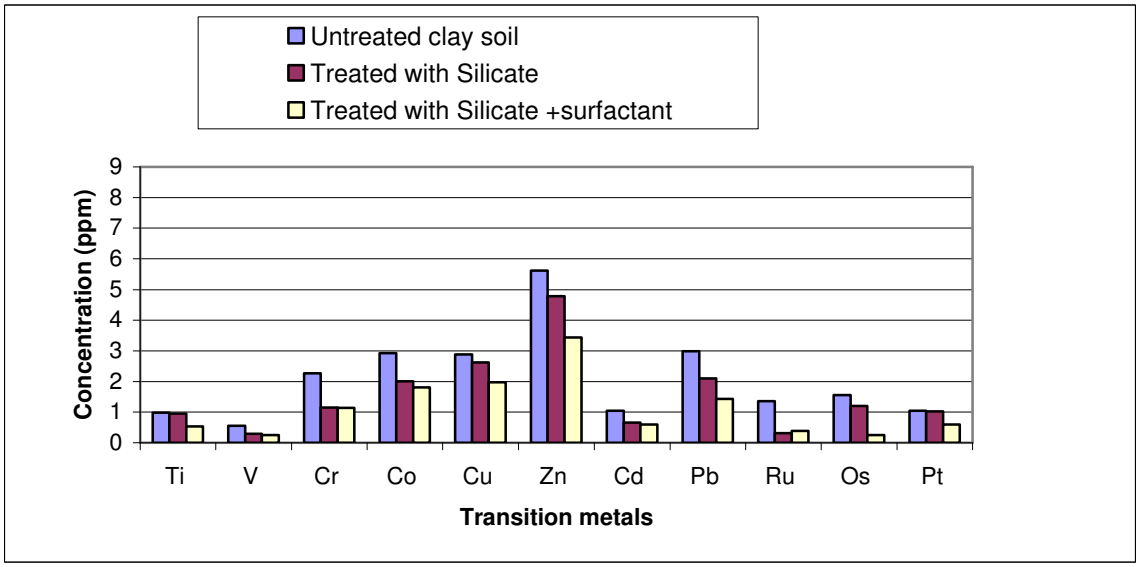


Figure 5.29 Concentration of transition metals after treatment with sodium silicate and surfactant (a) Sandy soil (b) Clay soil (pH = 2)

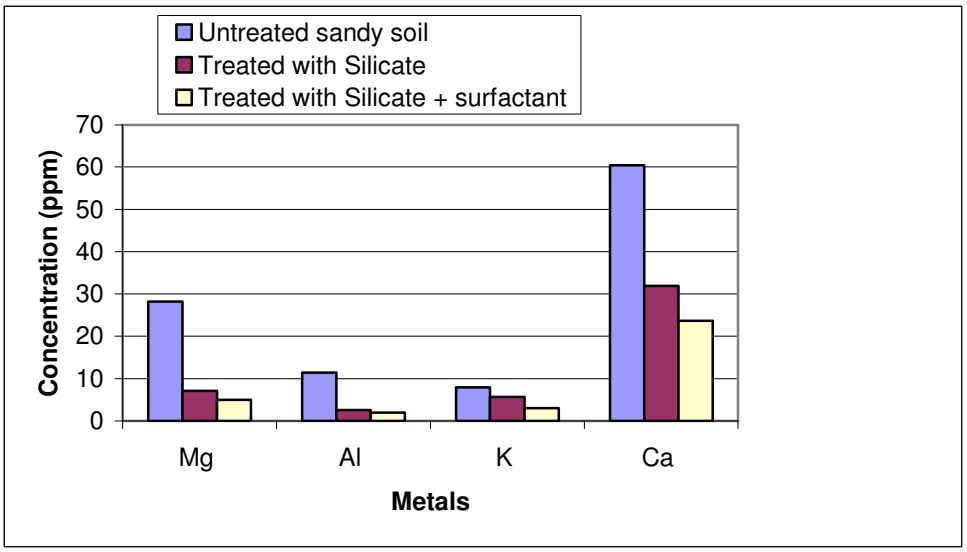


Figure 5.30 Concentration of main group elements after treatment with sodium silicate and surfactant (pH = 2)

Surfactants improve silica encapsulation because of their amphiphilic structure, meaning that it has ahead with a strong affinity for water and a tail with an aversion to water. It furnishes the acidic medium for silica precipitation from the sodium silicate solution

However, since both the silica solution and the surfactant solution are aqueous, either or both solutions may be diluted with water to a concentration which is optimum for use with the particular metals or chemicals being treated and so that measurement of amounts of each solution will be convenient at the site where treatment will be occurring. Mixing immediately produce an amorphous silica material within which the hydrocarbons or chemicals are micro encapsulated.

CHAPTER 6

Conclusions

The tests carried out in the laboratory have demonstrated that the levels of extractable transition metals, alkali earth metals and hydrocarbons in soil and water can be reduced by silica encapsulation. The leaching of metals and hydrocarbons to the environment is reduced by encapsulating these contaminants in a highly stable silica coating. This study has revealed that various factors such pH, type of soil, size of metal ions and the presence of hydrocarbons when removing heavy metals can affect the efficiency of silica encapsulation remediation.

Silica encapsulation was found to be more effective in acidic environment than in the basic environment. This suggested that the environment to be treated with silica encapsulation must be slightly acidic before treatment. The environment must also not be too acidic as H^+ would compete with contaminants for silicate sites.

Silica encapsulation technology is effective in encapsulating metals with small ionic sizes than those with large ionic sizess and radius ratio < 0.414. This technology was very efficient in encapsulating metal cations with high charges. This can be attributed to the fact that larger metals can not fit in the silica octahedral and tetragonal geometries. The efficiency of this technology is enhanced in sandy soil as opposed to clay soil. This is due to the relatively simple composition of sandy soil whereas clay soil has high cationic exchange capacity compared to sandy soil.

Results suggested that sodium silicate was as good in encapsulation of metals as Chemcap™. In the encapsulation of hydrocarbons, sodium silicate was found to be very effective compared to Chemcap™. Based on this, experiments were done to develop a silica encapsulation product that would be based on sodium silicate. Treatment of soil with sodium silicate mixed with anionic surfactant demonstrated to have a very positive effect on the encapsulation of metals. More metals were encapsulated after the addition of anionic surfactant to sodium silicate. Silica coating was stable under basic and acidic environment as leaching of contaminants was reduced in both acidic and basic environment.

Experimental results indicated that silica encapsulation continues to strengthen and does not degrade with time. The reaction of this technology was found to be of first order in sandy soil and water. It was of zero order in clay soil. The results demonstrate the potential applicability of this technology for the remediation of sites contaminated by both metals and hydrocarbons. However, the concentration of hydrocarbons must not be very high as this reduces the efficiency of the encapsulation of metals. This study has shown that silica encapsulation technology is unique in its permanent encapsulation of metal contaminants, which greatly reduces or eliminates the need for costly hazardous waste disposal and the environmental liabilities associated with future remobilisation of metals.

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APPENDIX 1 Analysis of soil samples

Table 1A.1 Leachable concentration of transition metals and PGMs in sandy soil at pH = 2 and pH = 9.3

Sample name	**Metals**										
	Ti **mg/l**	V **mg/l**	Cr **mg/l**	Co **mg/l**	Cu **mg/l**	Zn **mg/l**	Cd **mg/l**	Pb **mg/l**	Ru **mg/l**	Os **mg/l**	Pt **mg/l**
S1U	1.39	0.36	2.42	3.98	2.77	5.07	0.61	2.38	1.01	2.07	0.61
S1S	0.41	0.11	1.07	2.25	1.67	4.83	0.51	1.44	0.1	0.56	0.51
S1C	0.56	0.12	1.05	2.14	-	1.58	3.6	0.42	1.41	0.08	0.13
S2U	0.97	0.63	4.73	8.1	5.68	8.23	1.46	3.06	1.07	0.76	1.45
S2S	0.5	0.14	1.02	2.2	1.47	2.66	0.35	1.67	0.07	0.1	0.35
S2C	0.52	0.11	0.83	1.76	_-	1.3	2.51	0.3	1.52	0.08	0.08

Table 1A.2 Leachable concentration of transition metals in sandy soil at pH = 2 and pH = 9.3

Sample name	**Metals**	
	Mn **mg/l**	Fe **mg/l**
S1U	22.8	159.02
S1C	10.84	25.34
S1S	10.73	28.27
S2U	43.29	173.01
S2C	11.92	21.82
S2S	15.22	23.08

Table 1A.3 Leachable concentration of main group elements in sandy soil at pH = 2 and pH = 9.3

Sample name	**Main group elements**			
	Mg **mg/l**	Al **mg/l**	K **mg/l**	Ca **mg/l**
S1U	19.63	7.084	7.14	28.1
S1C	6.89	2.28	5.24	22.87
S1S	6.3	2.33	4.83	21.81
S2U	28.23	11.391	7.97	60.41
S2C	5.82	1.854	3.71	20.89
S2S	7.14	2.585	5.64	31.89

Table 1A.4 Leachable concentration of Lanthanides in sandy soil at pH = 2 and pH = 9.3

Sample name	**Lanthanides**		
	La **mg/l**	Gd **mg/l**	Er **mg/l**
S1U	32.332	2.81	1.62
S1C	20.265	0.85	0.66
S1S	20.845	0.84	0.5
S2U	34.321	4.77	1.19
S2C	22.052	0.59	0.62
S2S	22.931	0.89	0.6

Table 1A.5 Leachable concentration of transition metals and PGMs in clay soil at pH = 2 and pH = 9.2

Sample name	Metals											
	Ti **mg/l**	V **mg/l**	Cr **mg/l**	Co **mg/l**	Ni **mg/l**	Cu **mg/l**	Zn **mg/l**	Cd **mg/l**	Pb **mg/l**	Ru **mg/l**	Os **mg/l**	Pt **mg/l**
C2U	0.98	0.55	2.27	2.93	0.48	2.89	5.61	1.05	2.99	1.36	1.56	1.05
C2C	0.76	0.27	1.26	2.08	-	2.26	4.22	0.72	2.13	0.29	0.35	0.72
C2S	0.95	0.29	1.15	2.01	-	2.62	4.79	0.66	2.1	0.31	1.2	1.02
C5U	0.6	0.24	1.26	1.9	0.36	2.1	3.43	0.6	2.39	0.41	0.34	0.59
C5C	1.01	0.34	1.24	1.93	-	2.17	3.81	0.64	2.01	0.7	0.44	0.64
C5S	0.54	0.28	1.24	1.75	-	1.93	3.42	0.56	1.87	0.66	0.59	0.56

Table 1A.6 Leachable concentration of transition metals in clay soil at pH = 2 and pH = 9.2

Sample name	Metals	
	Mn **mg/l**	Fe **mg/l**
C2U	4.7	188.79
C2C	3.11	86.39
C2S	3.77	72.9
C5U	3.97	76.14
C5C	3.6	72.21
C5S	3.51	73.28

Table 1A.7 Leachable concentration of main group elements in clay soil at pH = 2 and pH = 9.2

Sample name	**Main group elements**			
	Mg **mg/l**	Al **mg/l**	K **mg/l**	Ca **mg/l**
C2U	5.94	6.101	3.03	43.61
C2C	4.16	4.366	2.8	35.41
C2S	4.48	4.761	2.76	42.3
C5U	38.56	5.37	3.88	4.44
C5C	37.18	3.37	4.26	5.356
C5S	41.85	3.66	4.21	4.439

Table 1A.8 Leachable concentration of Lanthanides in clay soil at pH = 2 and pH = 9.2

Sample name	**Lanthanides**		
	La **mg/l**	Gd **mg/l**	Er **mg/l**
C2U	29.992	1.71	1.2
C2C	23.484	0.59	0.96
C2S	22.878	2.49	1.19
C5U	23.432	0.48	0.76
C5C	24.416	0.63	1.22
C5S	22.707	0.69	0.66

APPENDIX 2 Analysis results for water sample

Table 2A.1 Concentration of metals in water at pH = 9.2 and pH = 2

Metals					
Sample name	Cr	Cu	Pb	Zn	Co
WU	19.272	23.361	7.999	26.988	30.461
W1S	5.211	7.404	0.629	7.175	5.868
W1C	3.047	4.207	-	4.379	3.205
W2S	15.211	19.404	4.9	24.175	25.868
W2C	13.047	17.207	5.69	23.379	23.205

APPENDIX 3 Effect of time on silica encapsulation

Table 3A.1 Effect of time on concentration of metals in soil samples treated with Chemcap™ and sodium silicate

Sample name	Transition metals							
	Cd **mg/l**	Co **mg/l**	Cr **mg/l**	Cu **mg/l**	Pb **mg/l**	Pt **mg/l**	Ru **mg/l**	Zn **mg/l**
S2U	1.46	8.1	4.73	5.68	3.06	1.45	1.07	8.23
S2C	0.3	1.76	0.83	1.3	1.52	0.3	0.08	2.51
S22C	0.1	1.1	0.04	0.32	0.31	0.02	-	1.5
S2U	1.46	8.1	4.73	5.68	3.06	1.45	1.07	8.23
S2S	0.35	2.2	1.02	1.47	1.67	0.35	0.07	2.66
S22S	0.1	1.25	0.07	0.67	0.02	0.12	0.01	1.78
C2U	1.05	2.93	2.27	2.89	2.99	1.05	1.36	5.61
C2C	0.72	2.08	1.26	2.26	2.13	0.72	0.29	4.22
C22C	0.12	1.08	0.36	1.32	1.52	0.012	0.11	2.67
C2U	1.05	2.93	2.27	2.89	2.99	1.05	1.36	5.61
C2S	0.95	2.1	1.31	2.35	2.24	1.02	0.31	4.55
C22S	0.1	1.5	0.82	1.75	1.75	0.03	0.2	3.45

Table 3A.2 Effect of time on concentration of main group elements in soil samples treated with Chemcap™ and sodium silicate

Sample name	Main group elements			
	Ca **mg/l**	K **mg/l**	Mg **mg/l**	Al **mg/l**
S2U	60.41	7.97	28.23	11.391
S2C	20.89	3.71	5.82	1.854
S22C	10.23	0	2.132	0
S2U	60.41	7.97	28.23	11.391
S2S	31.89	5.64	7.14	2.585
S22S	23.67	3.06	5.21	0.853
C2U	43.61	3.03	5.94	6.101
C2C	35.41	3.12	4.16	4.366
C22C	28.32	1.52	2.85	2.15
C2U	43.61	3.03	5.94	6.101
C2S	34.35	2.63	4.48	4.761
C22S	20.98	1.56	2.05	2.89

Table 3A.2 Effect of time on concentration of metals in water samples treated with Chemcap™ and sodium silicate

Sample name	Metals				
	Co	Cr	Cu	Pb	Zn
W1U	30.461	19.272	23.361	7.999	26.988
W1S	3.205	3.047	4.207	-	4.379
W12S	1.56	1.23	2.01	-	2.36
WIC	5.866	5.211	7.404	0.629	7.175
WI2C	3.24	3.21	5.11	-	4.82

Table 3A.3 Reaction rate of silica encapsulation of transition metals in sandy soil

Sample name	**Metals**						
	Co	Cr	Cu	Pb	Pt	Ru	Zn
S2U	2.0794	1.545	1.728	1.012	0.3436	0	2.079
S2C	0.5653	-	0.262	0.419	-	-	0.9203
S22C	0.0953	-	-	-	-	-	0.4054
S2U	2.0918	1.554	1.7369	1.118	0.3715	0.0676	2.107
S2S	0.7884	0.0198	0.3853	0.5128	-	-	0.978
S22S	0.2231	-	-	-3.912	-	-	0.5766

Table 3A.4 Reaction rate of silica encapsulation of transition metals in water

Sample name	Metals				
	Co **mg/l**	Cr **mg/l**	Cu **mg/l**	Pb **mg/l**	Zn **mg/l**
WIC	3.416	2.958	3.151	2.079	3.295
W2S	1.7692	1.6507	2.002	-0.464	1.97
W3S	1.175	1.166	1.6311	-	1.573

Table 3A.3 Reaction rate of silica encapsulation of main group elements in sandy soil

Sample name	Metals			
	Ca	K	Mg	Al
S2U	4.101	2.076	3.34	2.433
S2C	3.039	1.311	1.761	0.6173
S22C	2.325	-	0.757	-

Table 3A.4 Effect of hydrocarbons on leachable concentration of transition metals in sandy soil and clay soil

Sample name	Transition metals											
	Ti **mg/l**	V **mg/l**	Cr **mg/l**	Co **mg/l**	Ni **mg/l**	Cu **mg/l**	Zn **mg/l**	Cd **mg/l**	Pb **mg/l**	Ru **mg/l**	Os **mg/l**	Pt **mg/l**
S2U	0.97	0.63	4.73	8.1	0.17	5.68	8.23	1.46	3.06	1.07	0.76	1.45
SHC	0.52	0.11	0.83	1.76		1.3	2.51	0.3	1.52	0.08	0.08	0.3
SHHC	0.86	0.23	1.99	2.89	0.04	2.1	4.56	0.45	2.01	0.12	0.13	0.51
S2U	0.97	0.63	4.73	8.1	0.17	5.68	8.23	1.46	3.06	1.07	0.76	1.45
SHS	0.5	0.14	1.02	2.2		1.47	2.66	0.35	1.67	0.07	0.1	0.35
SHHS	0.78	0.15	1.89	2.86	0.09	2.14	4.96	0.49	2.563	0.92	0.89	0.55
C2U	0.98	0.55	2.27	2.93	0.28	2.89	5.61	1.05	2.99	1.36	1.56	1.05
CHC	0.76	0.27	1.26	2.08		2.26	4.22	0.72	2.13	0.29	0.35	0.72
CHHC	0.98	0.45	1.9	2.51	0.23	2.45	4.98	1.01	2.56	0.78	1.23	0.98
C2U	0.98	0.55	2.27	2.93	0.28	2.89	5.61	1.05	2.99	1.36	1.56	1.05
CHS	0.95	0.29	1.15	2.43		2.15	4.79	0.66	1.23	0.31	1.2	1.02
CHHS	0.98	0.3	1.98	2.56	0.2	2.78	5.01	0.98	2.031	0.74	1.42	1.04

Table 3A.5 Effect of hydrocarbons on leachable concentration of transition metals in water

Sample name	Metals				
	Cr	Cu	Pb	Zn	Co
WU	19.272	23.361	7.999	26.988	30.461
HC2	3.047	4.207	-	4.379	3.205
HHC	5.371	6.642	0.756	7.1	6.077
SH	5.211	7.404	0.629	7.175	5.868
SHH	7.609	9.318	3.907	10.01	8.762

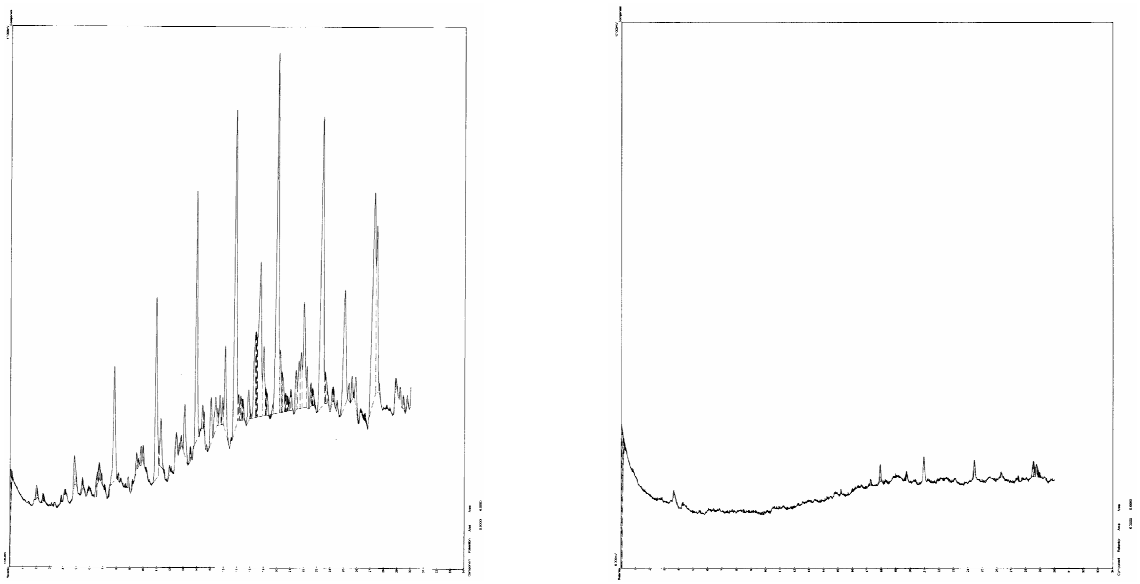
Table 3A.6 Leachable concentration of transition metals extracted with sodium carbonate in sandy soil and clay soil

Sample name	Transition metals					
	Ti mg/l	Cr mg/l	Mn mg/l	Fe mg/l	Cu mg/l	Zn mg/l
S2U	0.9	0.24	2.51	6.7	0.34	0.42
S2C	-	-	-	1.08	-	-
S2S	0.12	0.16	0.21	3.37	-	-
C2U	0.7	0.18	0.42	1.7	0.2	0.5
C2C	0.1	-	-	1.57	0.12	0.11
C2S	0.06	0.1	-	1.37	0.12	0.09

Table 3A.7 Leachable concentration of transition metals after treatment with sodium silicate and surfactant

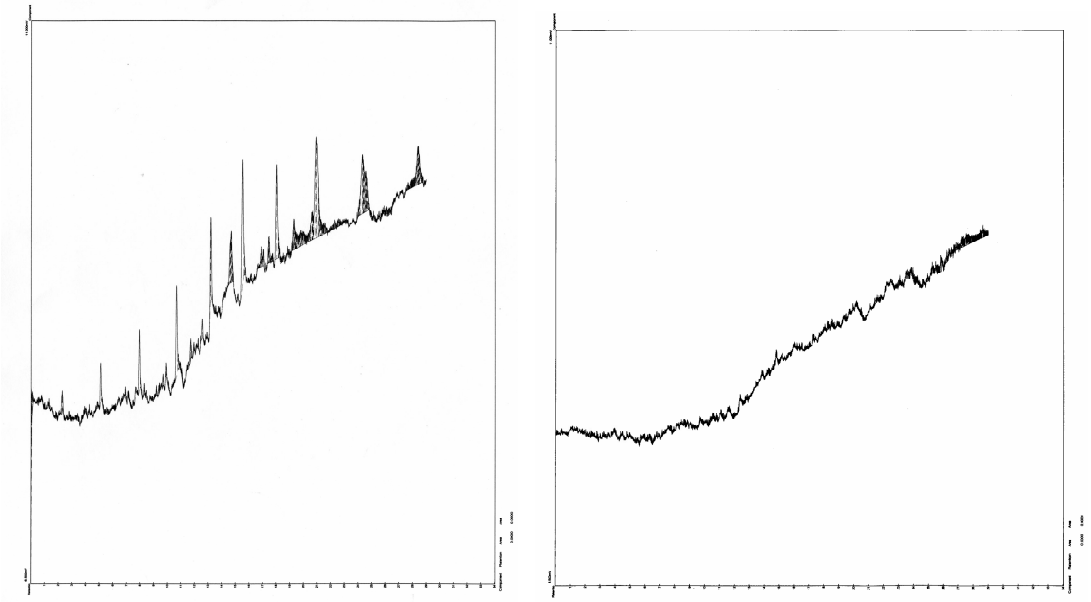
Sample name	Transition metals										
	Ti **mg/l**	V **mg/l**	Cr **mg/l**	Co **mg/l**	Cu **mg/l**	Zn **mg/l**	Cd **mg/l**	Pb **mg/l**	Ru **mg/l**	Os **mg/l**	Pt **mg/l**
S1U	1.39	0.36	2.42	3.98	2.77	5.07	0.61	2.38	1.01	2.07	0.61
S1S	0.41	0.11	1.07	2.25	1.67	4.83	0.51	1.44	0.1	0.56	0.51
S1F	0.3	0.1	1.06	2.02	1.12	4.54	0.5	1.13	0.27	0.21	0.58
S2U	0.97	0.63	4.73	8.1	5.68	8.23	1.46	3.06	1.07	0.76	1.45
S2S	0.5	0.14	1.02	2.2	1.47	2.66	0.35	1.67	0.07	0.1	0.35
S2F	0.42	0.1	0.5	1.65	1.23	1.53	0.28	1.12	0.05	0.1	0.28
C2U	0.98	0.55	2.27	2.93	2.89	5.61	1.05	2.99	1.36	1.56	1.05
C2S	0.95	0.29	1.15	2.01	2.62	4.79	0.66	2.1	0.31	1.2	1.02
C2F	0.53	0.25	1.14	1.81	1.98	3.44	0.6	1.43	0.39	0.25	0.6
C5U	0.6	0.24	1.26	1.9	2.1	3.43	0.6	2.39	0.41	0.34	0.59
C5S	0.54	0.28	1.24	1.75	1.93	3.42	0.56	1.87	0.66	0.59	0.56
C5F	0.59	0.29	1.08	1.65	1.84	3.8	0.55	1.54	0.71	0.75	0.55

APPENDIX 4 Results of hydrocarbons analysis in soil samples



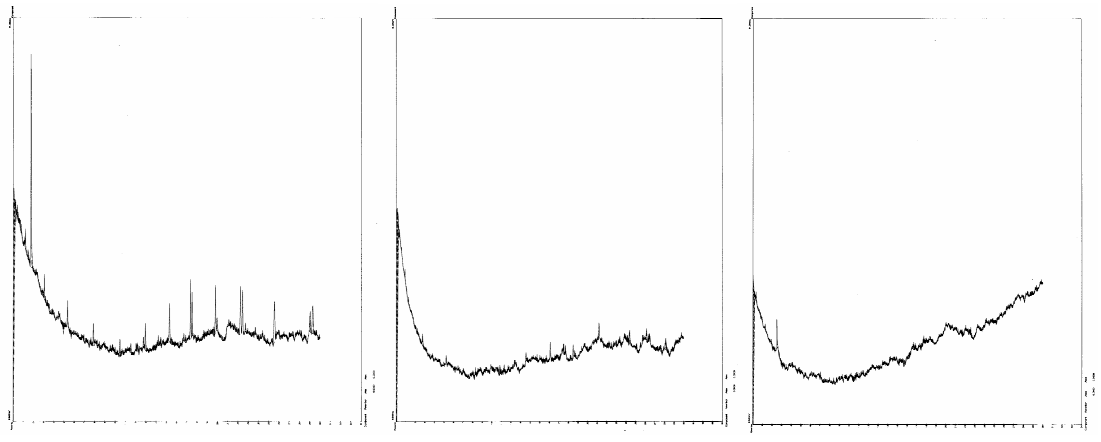
(a) (b)

Figure 4A.1 Qualitative analysis of hydrocarbons at pH 8.2 (a) before treatment (b) after treatment



(a) (b)

Figure 4A.2 Qualitative analysis of hydrocarbons at pH=3.4 (a) before treatment (b) after treatment



(a) (b) (c)

Figure 4A.3 Qualitative analysis of hydrocarbons at 8.4 (a) before treatment (b) treated with Chemcap (c) treated with sodium silicate

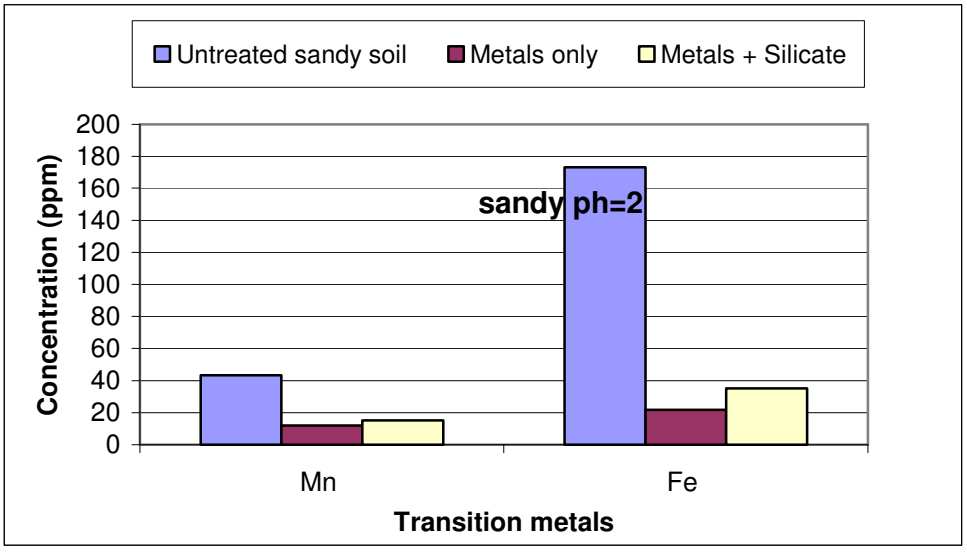
Sample name	Lanthanides		
	Er **mg/l**	Gd **mg/l**	La **mg/l**
S2U	1.19	4.77	34.321
SHC	0.62	0.59	22.052
SHHC	0.78	1.2	23.65
S2U	1.19	4.77	34.321
SHS	0.6	0.89	22.931
SHHS	0.85	1.56	24.65
C2U	1.2	1.71	29.992
CHC	0.96	0.59	23.484
CHHC	1.05	1.21	25.98
C2U	1.2	1.71	29.992
CHS	1.19	1.49	22.878
CHHS	1.2	1.69	24.36

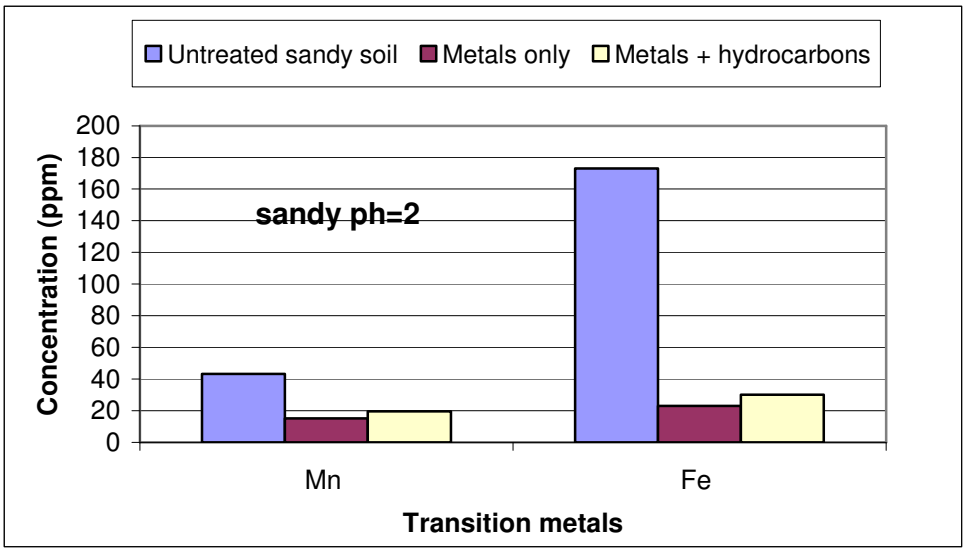
The silica encapsulation technology represents an opportunity to meet the ever-increasing demand for better treatment of metal and hydrocarbons contaminated wastes. It represents a substantive stepping-stone for industry to use in the course of strengthening its commitment to more environmentally responsible mining and related waste management.

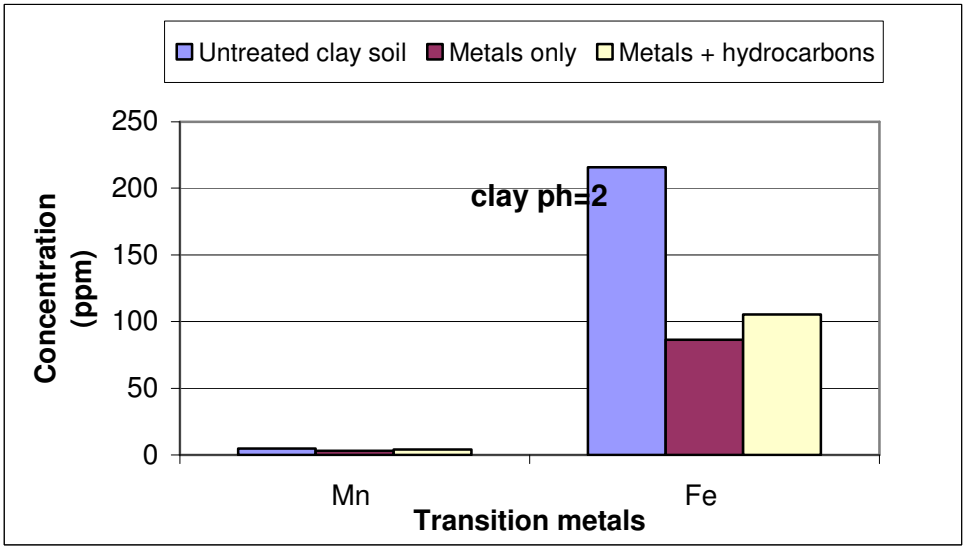
Important observations related to the performance of silica encapsulation technology are:

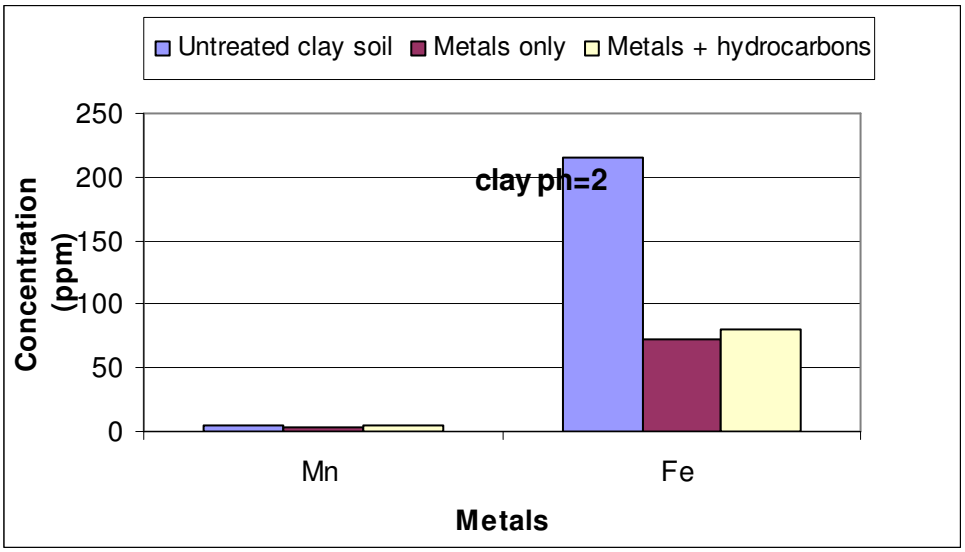
- Encapsulation is by silica, an economic and environmentally safe material whose physical and chemical characteristics resemble soil, provides a metal and hydrocarbons impermeable coating of the soil-sorbent mixture.

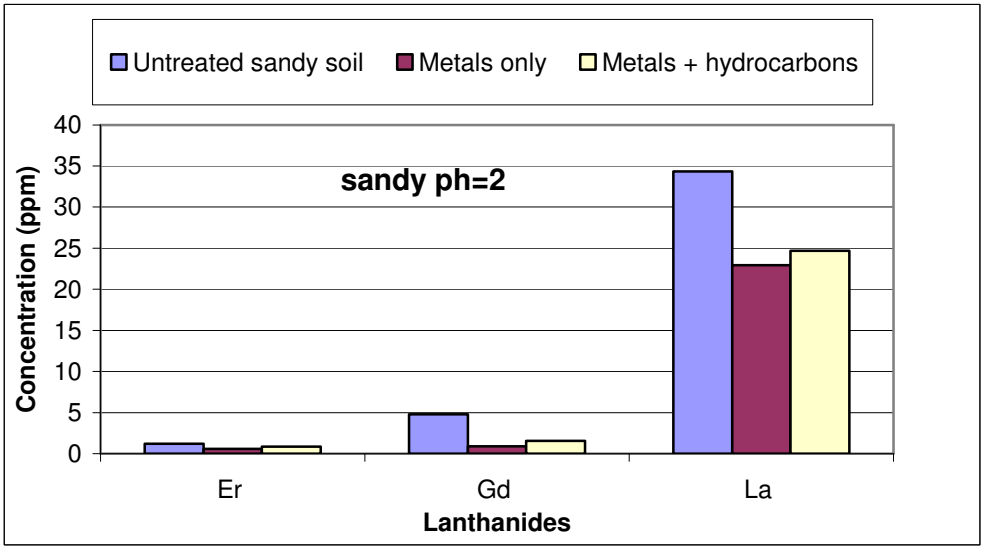
- Remediation is accomplished within a short period of time and with minimal environmental disturbance.
- It is effective in the acidic environment.
- It can be used to remediate the environment contaminated by both hydrocarbons and metals
- The silica coating is stable over a broad pH range, contaminants can not be released even when the environment is subjected to harsh acidic and basic conditions.
- Metals are not as effectively encapsulated in the presence of hydrocarbons as large organometallic complexes are formed and because of their big sizes they can not fit in the silicate anions.

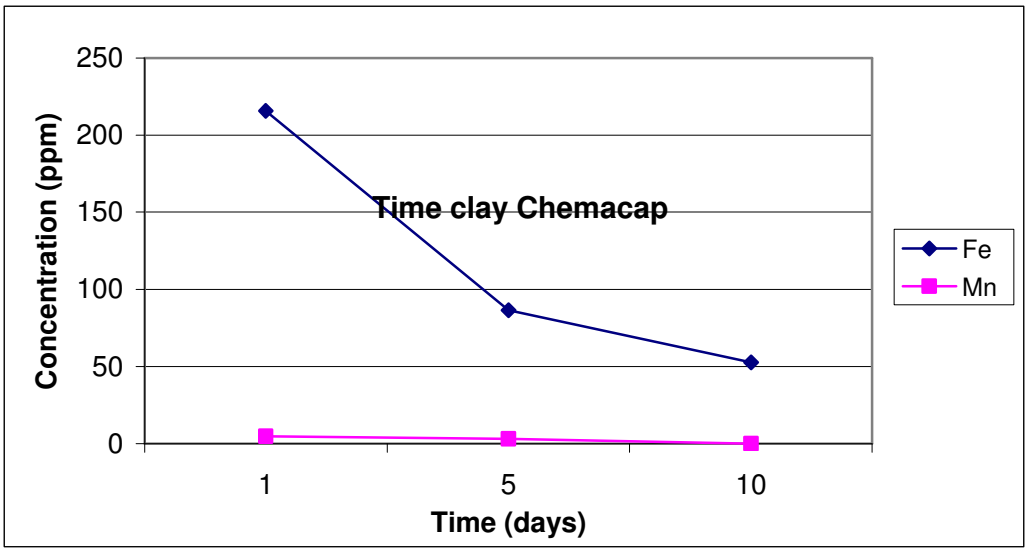


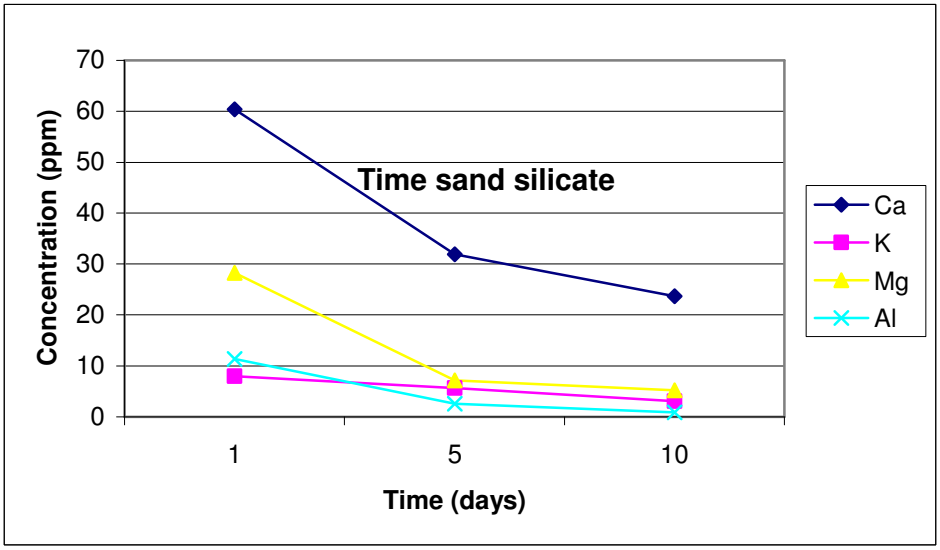

Untreated sandy soil
Metals only
Metals + hydrocarbons
Concentration (ppm)
200
180
160
140
120
100
80
60
40
20
0
sandy ph=2
Mn
Fe
Transition metals


Untreated clay soil
Metals only
Metals + hydrocarbons
Concentration (ppm)
250
200
150
100
50
0
clay ph=2
Mn
Fe
Transition metals

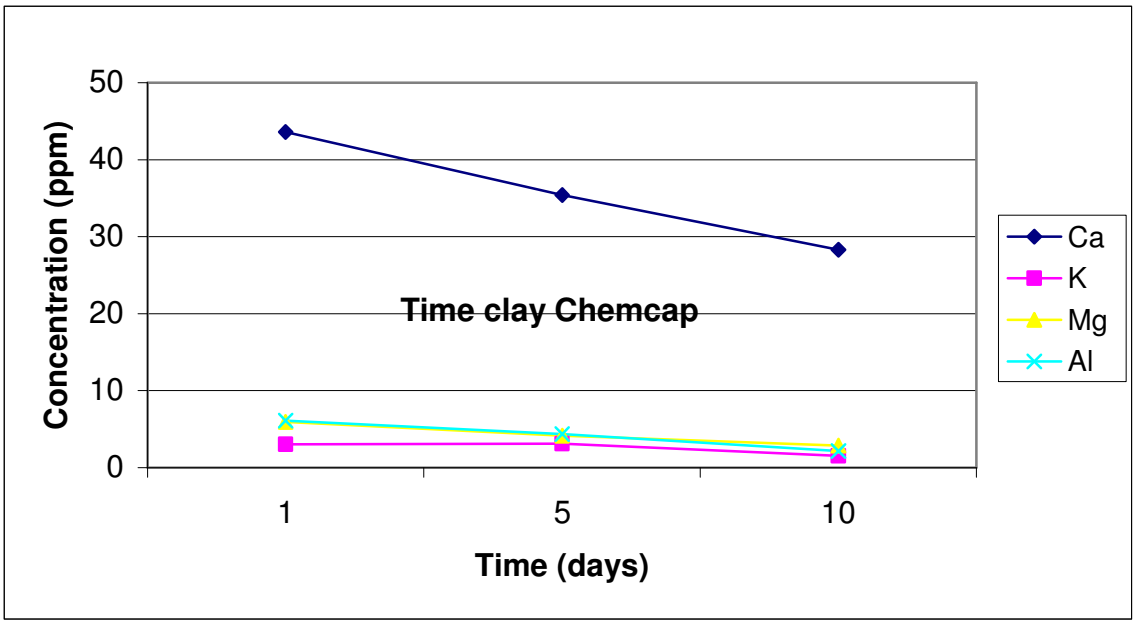

Untreated clay soil
Metals only
Metals + hydrocarbons
clay ph=2
Concentration (ppm)
250
200
150
100
50
0
Mn
Fe
Metals


Untreated sandy soil
Metals only
Metals + hydrocarbons
sandy ph=2
Concentration (ppm)
40
35
30
25
20
15
10
5
0
Er
Gd
La
Lanthanides

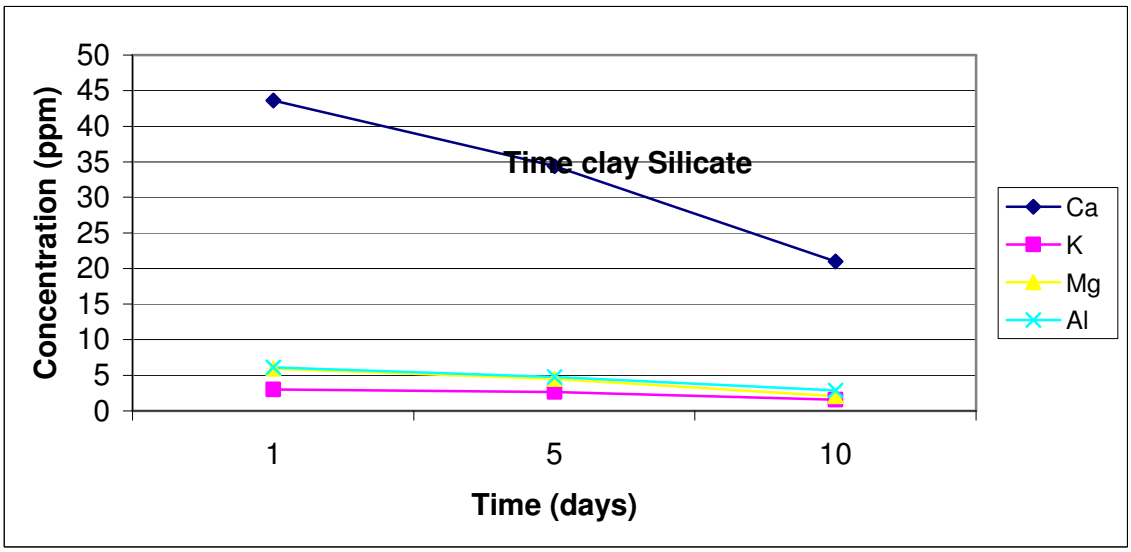

Time clay Chemacap
Concentration (ppm)
250
200
150
100
50
0
1
5
10
Time (days)
Fe
Mn


Time sand silicate
Concentration (ppm)
70
60
50
40
30
20
10
0
1
5
10
Time (days)
Ca
K
Mg
Al

(b)

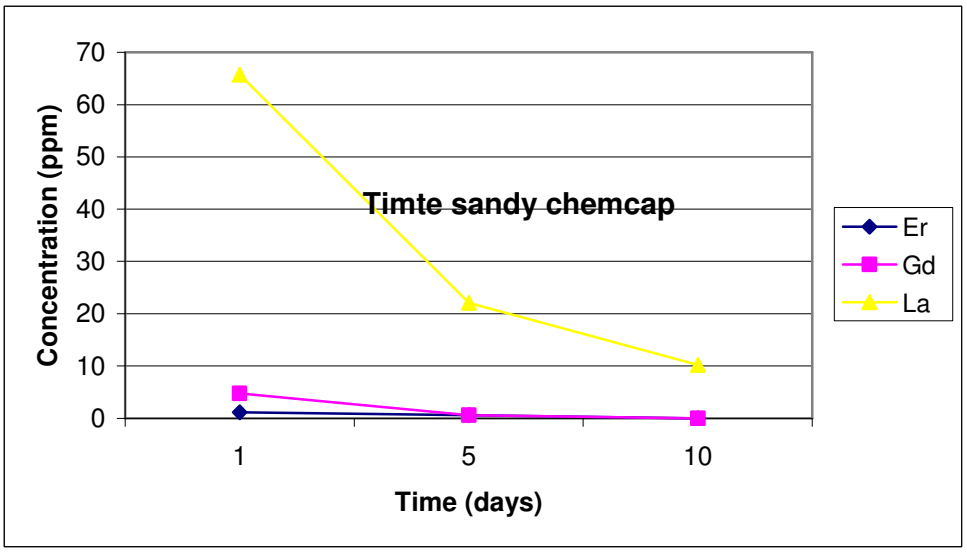


(a)

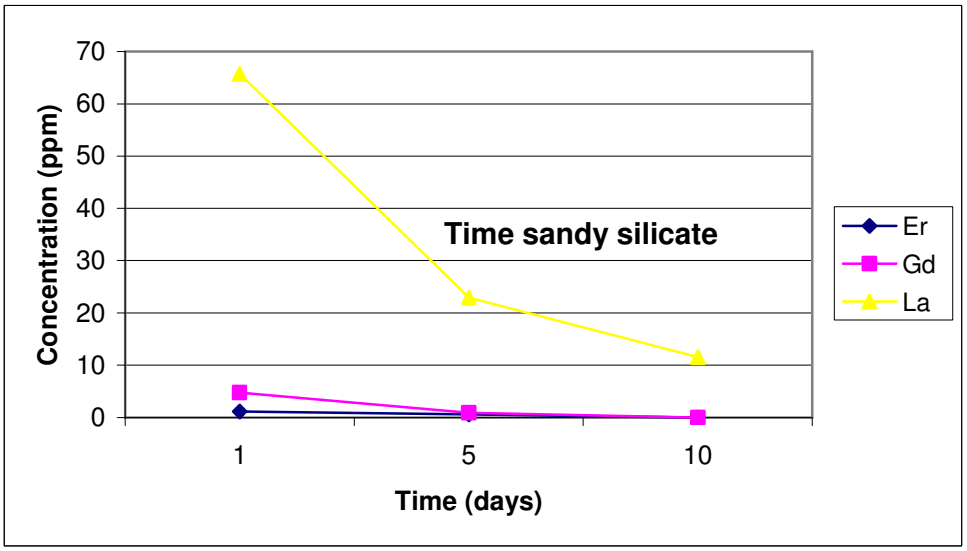


(b)

Figure 5.25 Time effect on concentration of metals in (a) Clay soil treated with Chemcap (b) Clay soil treated with sodium silicate

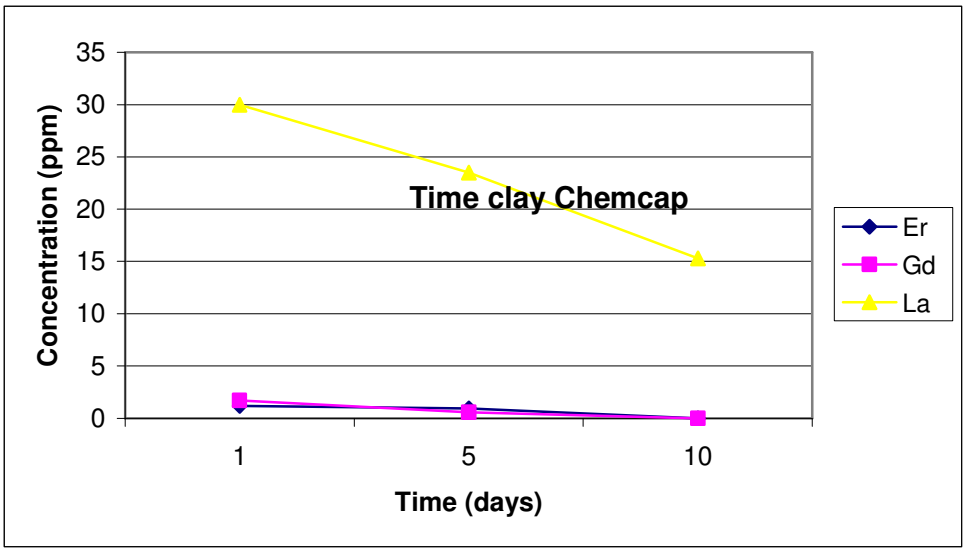


(a)

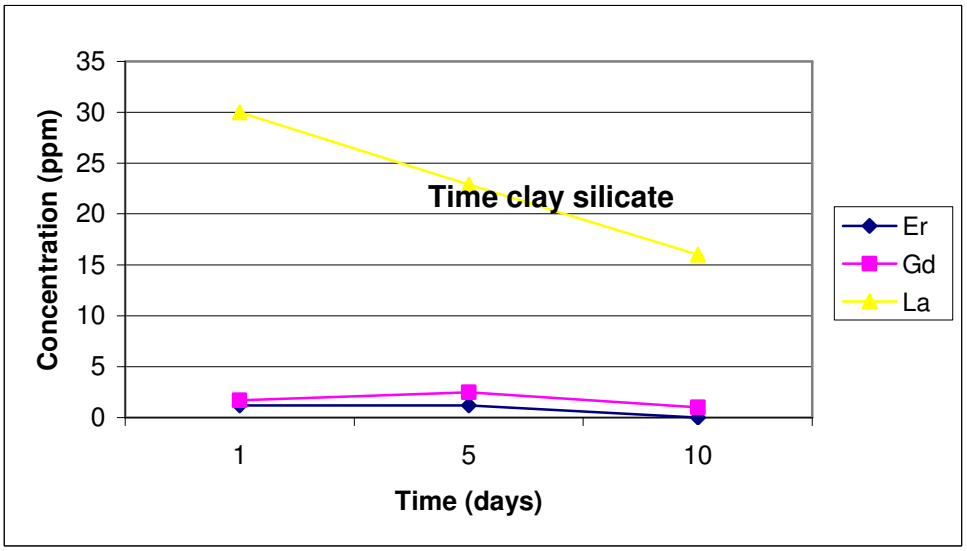


(b)

Figure 5.26 Time effect on concentration of Lanthanides in (a) Sandy soil treated with Chemcap (b) Sandy soil treated with sodium silicate

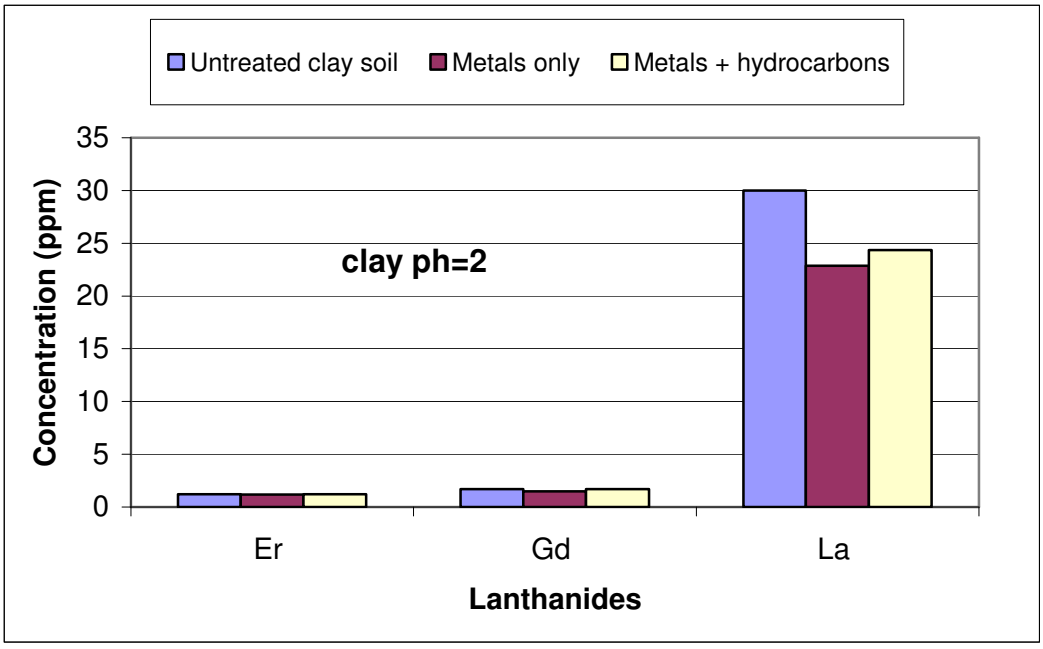


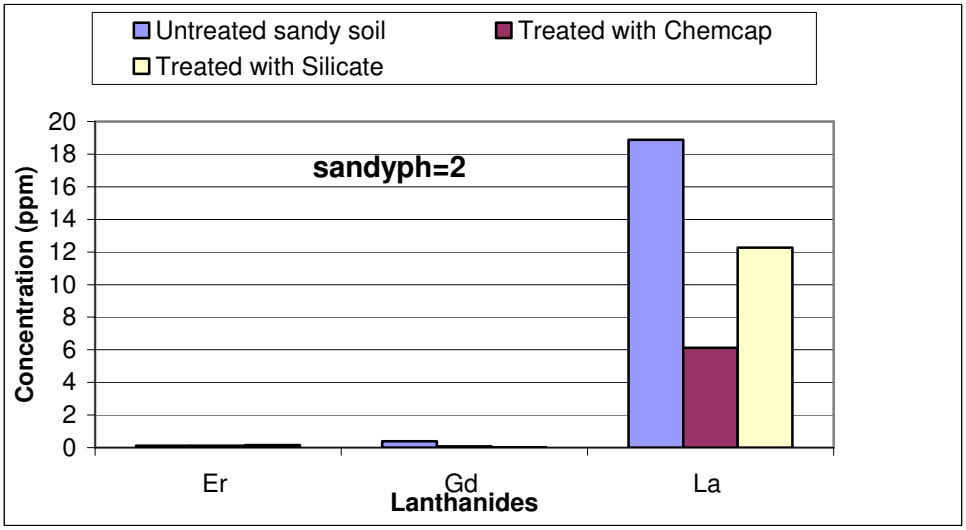
(a)

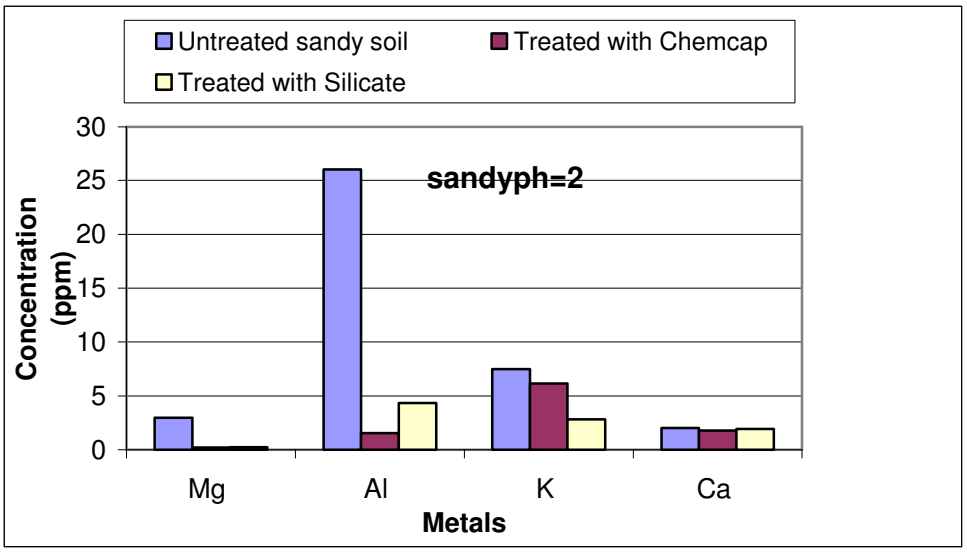


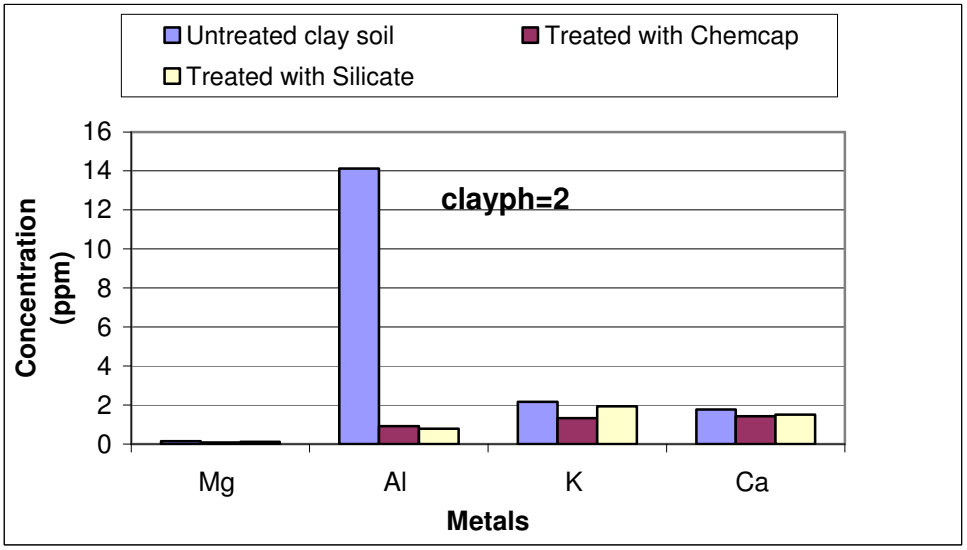
(b)

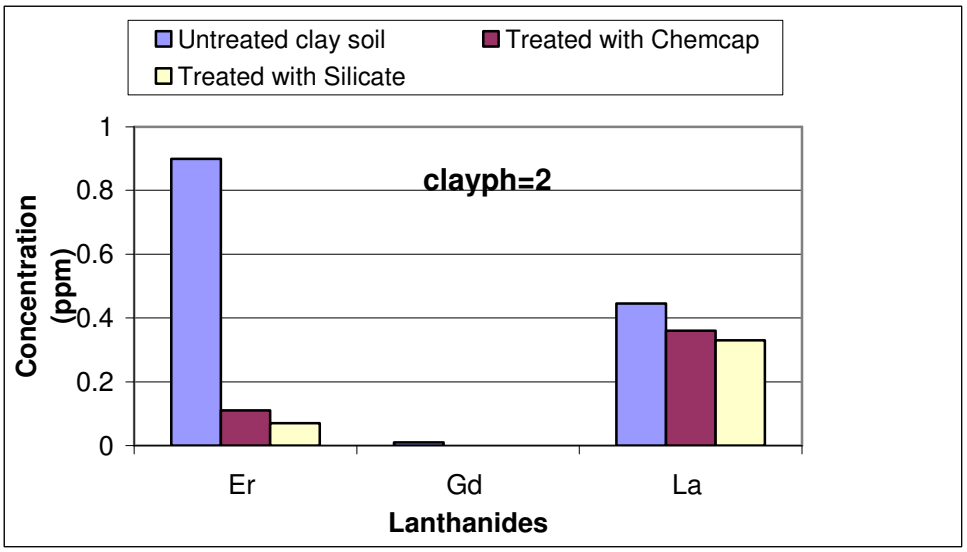
Figure 5.27 Time effect on concentration of Lanthanides in (a) Clay soil treated with Chemcap (b) Clay soil treated with sodium silicate

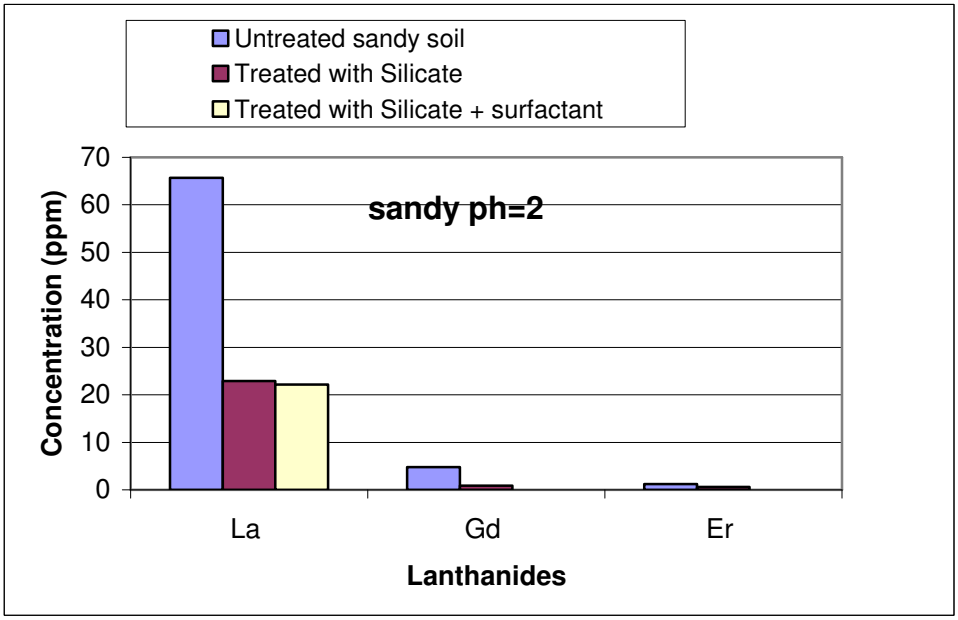

Untreated clay soil
Metals only
Metals + hydrocarbons
clay ph=2
Concentration (ppm)
35
30
25
20
15
10
5
0
Er
Gd
La
Lanthanides

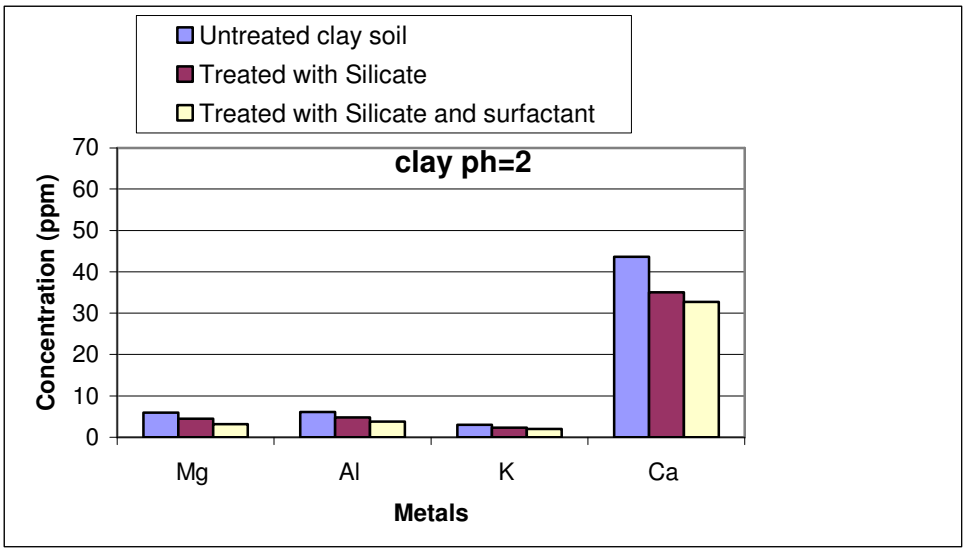

Untreated sandy soil
Treated with Chemcap
Treated with Silicate
sandyph=2
Concentration (ppm)
20
18
16
14
12
10
8
6
4
2
0
Er
Gd
La
Lanthanides

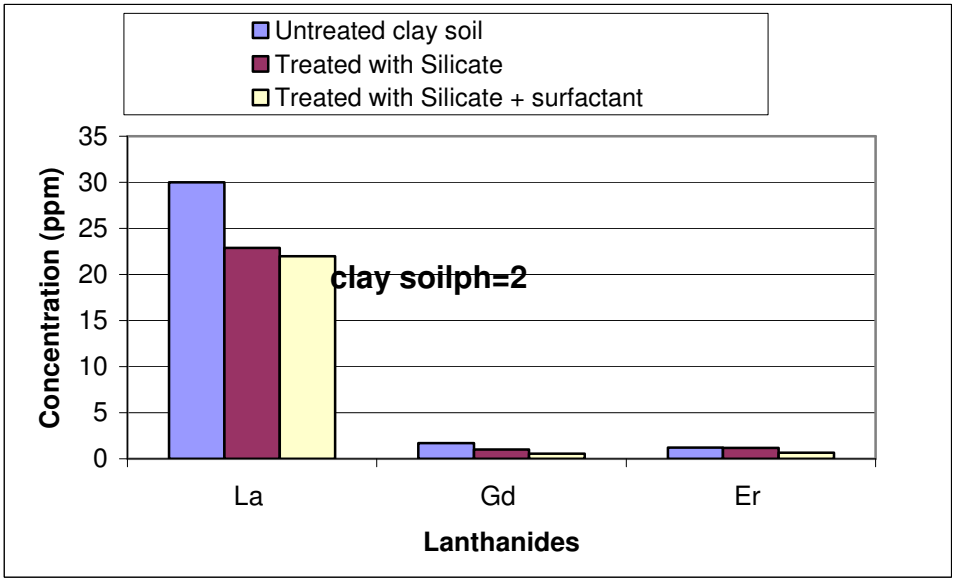

Untreated sandy soil
Treated with Chemcap
Treated with Silicate
sandyph=2
Concentration (ppm)
30
25
20
15
10
5
0
Mg
Al
K
Ca
Metals

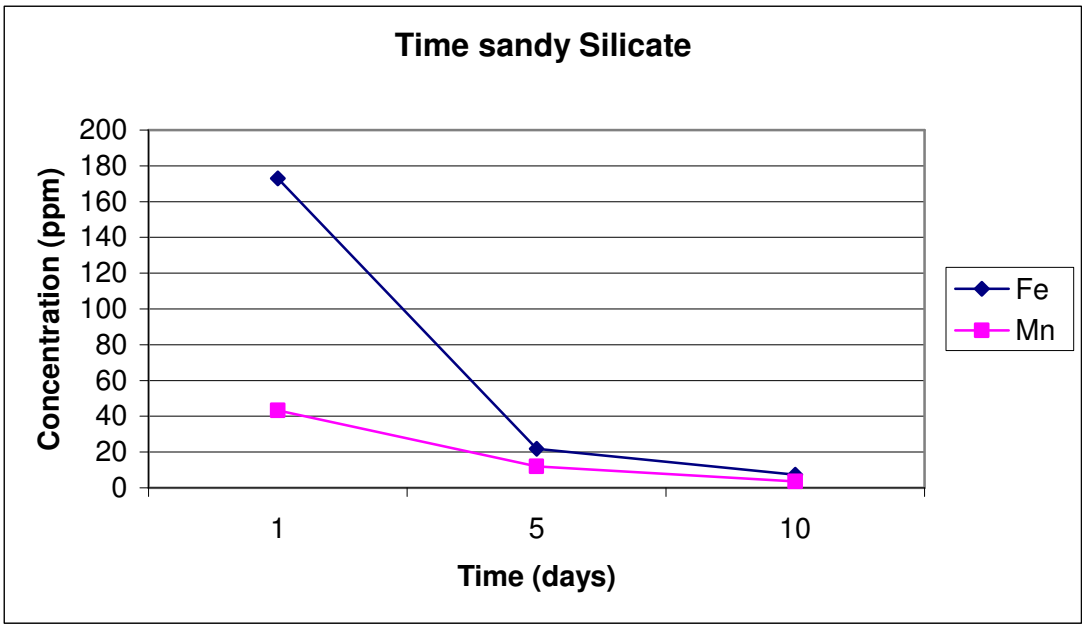

Untreated clay soil
Treated with Chemcap
Treated with Silicate
clayph=2
Concentration (ppm)
16
14
12
10
8
6
4
2
0
Mg
Al
K
Ca
Metals


Untreated clay soil
Treated with Chemcap
Treated with Silicate
clayph=2
Concentration (ppm)
1
0.8
0.6
0.4
0.2
0
Er
Gd
La
Lanthanides


Untreated sandy soil
Treated with Silicate
Treated with Silicate + surfactant
sandy ph=2
Concentration (ppm)
70
60
50
40
30
20
10
0
La
Gd
Er
Lanthanides


Untreated clay soil
Treated with Silicate
Treated with Silicate and surfactant
clay ph=2
Concentration (ppm)
70
60
50
40
30
20
10
0
Mg
Al
K
Ca
Metals


Untreated clay soil
Treated with Silicate
Treated with Silicate + surfactant
clay soilph=2
Concentration (ppm)
35
30
25
20
15
10
5
0
La
Gd
Er
Lanthanides


Time sandy Silicate
Concentration (ppm)
200
180
160
140
120
100
80
60
40
20
0
1
5
10
Time (days)
Fe
Mn

APPENDIX 2 ICP-OES RESULTS

Table 2A.1 ICP-OES results for the time effect on encapsulation

Metal	Sample name								
	S2U	S2S	S2S	C2U	C2S	C2S	S1U	S1S	S1S
Cd	0.61	0.42	0	0.61	0.51	0.1	1.05	0.95	0.1
Co	3.98	2.14	1.1	3.98	2.25	1.25	2.93	2.1	1.5
Cr	2.42	1.05	0.04	2.42	1.07	0.07	2.27	1.31	0.82
Cu	2.77	1.58	0.32	2.77	1.67	0.67	2.89	2.35	1.75
Pb	2.69	1.41	0.31	2.69	1.44	0.43	2.8	2.24	1.75
Zn	5.07	4.17	2.8	5.07	2.83	1.78	5.61	4.55	3.45

Table 2A.2 ICP-OES results for the effect of surfactant on encapsulation

Metal	Sample name								
	S1U	S1S	S1C	S1F	S2U	S2C	S2S	S2F	C2U
Cd	0.061	0.051	0.042	0.058	0.146	0.03	0.035	0.028	0.105

Co	0.398	0.225	0.214	0.302	0.81	0.176	0.22	0.165	0.293
Cr	0.242	0.107	0.105	0.179	0.473	0.083	0.102	0.097	0.227
Cu	0.277	0.167	0.158	0.212	0.568	0.13	0.147	0.123	0.289
Pb	0.269	0.144	0.141	0.113	0.306	0.152	0.167	0.112	0.28
Zn	0.507	0.283	0.417	0.454	0.823	0.251	0.266	0.263	0.561

Table 2A.3 ICP-OES results for the competition of contaminants in water

Metal	Sample name					
	WU	HC2	HHC	WU	SH	HC2
Cr	19.272	3.047	5.371	19.272	5.211	3.047
Cu	23.361	4.207	6.642	23.361	7.404	4.207
Pb	7.999	0	0.756	7.999	0.629	0
Zn	26.988	4.379	7.1	26.988	7.175	4.379
Co	30.461	3.205	6.077	30.461	5.868	3.205

Table 2A.4 ICP-OES results for the samples extracted with sodium carbonate

Metal	Sample name								
	S1U	S1S	S1C	SS2U	S2S	S2C	C5U	C5S	C5C
Cr	0.26	0.16	0.11	0.24	0.16	0.07	0.12	0.06	0.09
Cu	0.09	0.04	0.04	0.34	0.04	0.02	0.19	0.11	0.13
Mn	0.19	0.1	0.13	0.51	0.21	0.09	0.02	0.01	0.02

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