

Master Thesis in Geosciences

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Geochemical modelling

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UNIVERSITY OF OSLO

FACULTY OF MATHEMATICS AND NATURAL SCIENCES

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Discipline: Environmental Geology

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ABSTRACT

Simulation of heavy metal leaching from cement-stabilized polluted sediments

A lot of concern has been raised by individuals and organizations regarding the menace associated with heavy metal contamination of marine sediments in Norway. This has necessitated the remediation of heavy metal contaminated areas. Stabilization and solidification is one of the techniques used to immobilize heavy metals in marine sediments. Laboratory leaching tests are generally used to assess the effectiveness of stabilization and solidification. Results of laboratory leaching tests are, however, used only on short term basis. Geochemical models have evolved into invaluable tools that can be used as a substitute for laboratory leaching experiments. Results from geochemical modelling can be used for future predictions and also help in management options. Previous studies have revealed that several leaching experiments have been successfully simulated with geochemical models. This study, which is in connection with a larger project being carried out by NGI, has been designed with the intent of using geochemical modelling code, PHREEQC to simulate the binding and release of Pb and Cu and their long-term behaviour in cement-stabilized polluted sediments from three Norwegian harbours namely: Hammerfest, Grenland and Bergen.

The Freundlich empirical adsorption isotherm was utilized in this study to describe the behaviour of the heavy metals in the three stabilized sediments. Results showed that the Freundlich empirical isotherm could be used to describe the adsorption characteristics of the stabilized sediments for Cu and Pb as the isotherm fitted rather well to experimental data from the three sediments. The sorption capacities of the stabilized sediments for the heavy metals were determined using the nonlinear Freundlich equation. Stabilized sediments from Hammerfest demonstrated the least sorption capacity for both metals with stabilized sediments from Bergen showing the highest capacity to sorb the two heavy metals. The sorption capacity of the stabilized sediment from Grenland was between that of Bergen and Hammerfest. In general, results indicated that the sorption capacities of the sediments were higher for Pb than for Cu.

A 1-dimensional transport based on PHREEQC using diffusion and a non-linear sorption was employed to simulate heavy metal releases from the cement-stabilized sediment into sea water and to predict their long-term behaviour using time spans of 2, 10 and 20 years. It followed thus from the results of the fluxes calculated that stabilized sediment from Bergen was effective in retaining the heavy metals and consequently reduced their

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diffusive transport for all the time spans studied. The fluxes of both metals from Hammerfest stabilized sediment for all the time spans were relatively high due to the inability of the sediment to retain the metals. Fluxes of both metals from Grenland sediments were between those of Bergen and Hammerfest sediments.

DEDICATION

This piece of work is dedicated to my lovely family.

ACKNOWLEDGEMENT

Firstly, I give thanks to God Almighty, Jesus Christ my redeemer and the Holy Spirit my comforter for the life, wisdom and the strength that I was graced with to carry out this research successfully.

In this life, I have met people who have greatly imparted my life. Two are my supervisors, Professor Per Aagaard and Professor Gijs Breedsveld, all of the University of Oslo. The role they have played throughout the entire period of this research is very enormous. I therefore give many thanks to them for their guidance, constructive supervision and immense support without which the success of this work would have remained a delusion.

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LIST OF ABBREVIATIONS

<i>As</i>	Arsenic
<i>Cd</i>	Cadmium
<i>Cr</i>	Chromium
<i>Cu</i>	Copper
<i>Eh</i>	Redox potential
<i>EPA</i>	Environmental Protection Agency
<i>Pb</i>	Lead
<i>Hg</i>	Mercury
<i>NGI</i>	Norwegian Geotechnical Institute
<i>Ni</i>	Nickel
<i>OM</i>	Organic matter
<i>PAH</i>	Polycyclic aromatic hydrocarbon
<i>PCB</i>	Polychlorinated biphenyl
<i>S/S</i>	Stabilization and solidification
<i>TBT</i>	Tributyltin
<i>TOC</i>	Total organic carbon
<i>Zn</i>	Zinc

CHAPTER ONE

1.0 INTRODUCTION

In many parts of the world, especially in the more technologically advanced countries, sediments have often been exposed to a broad spectrum of organic and inorganic chemicals, both of natural and anthropogenic origins. The range of chemicals found in polluted sediments is often enormous. These include heavy metals such as lead and copper; polycyclic aromatic hydrocarbons (PAH's); and polychlorinated biphenyls (PCB's). Compared to other media such as water and air, sediments have high capacity to retain contaminants. Sediments generally act as sinks that accumulate pollutants (Theofanis et al., 2001), which upon any disturbance can release them to cause pollution even long after the source of pollution has been removed (Forstner, 1989; Salomons and Stigliani, 1995; Lee *et al.*, 2001).

1.1 BACKGROUND

The sediments used in this study were collected from fjords and harbours in Bergen, Grenland, and Hammerfest, which are areas along the Norwegian coastline where serious contamination of sediments has been identified by the Norwegian authorities. Contamination of sediments by metals and non-metals primarily via anthropogenic activities at fjords and harbours in Norway is widespread and well documented (Sparrevik et al., 2009). Biocides and other additives used in making antifouling paints for ships, boats and buildings; mine tailing wastes; fertilizers; sewage sludge etcetera, represent some of the main sources of sediment pollution in these areas (SFT, 1997; Herngren, 2005; Laugesen, 2007). Generally, it is not so much of a threat if pollutants are contained at their source of pollution (Michael, 1989). The danger of these pollutants arises, however, when their bioavailability potential increases and there is a high possibility for them to be leached and transported to other areas, which is often the situation encountered in reality. Investigations done by the Norwegian authorities have revealed an enormous need for such areas to be remediated to prevent further transport of the identified pollutants to other areas. In response to this, several attempts have been made by researchers and various concerned organizations by designing methods to remediate the polluted areas.

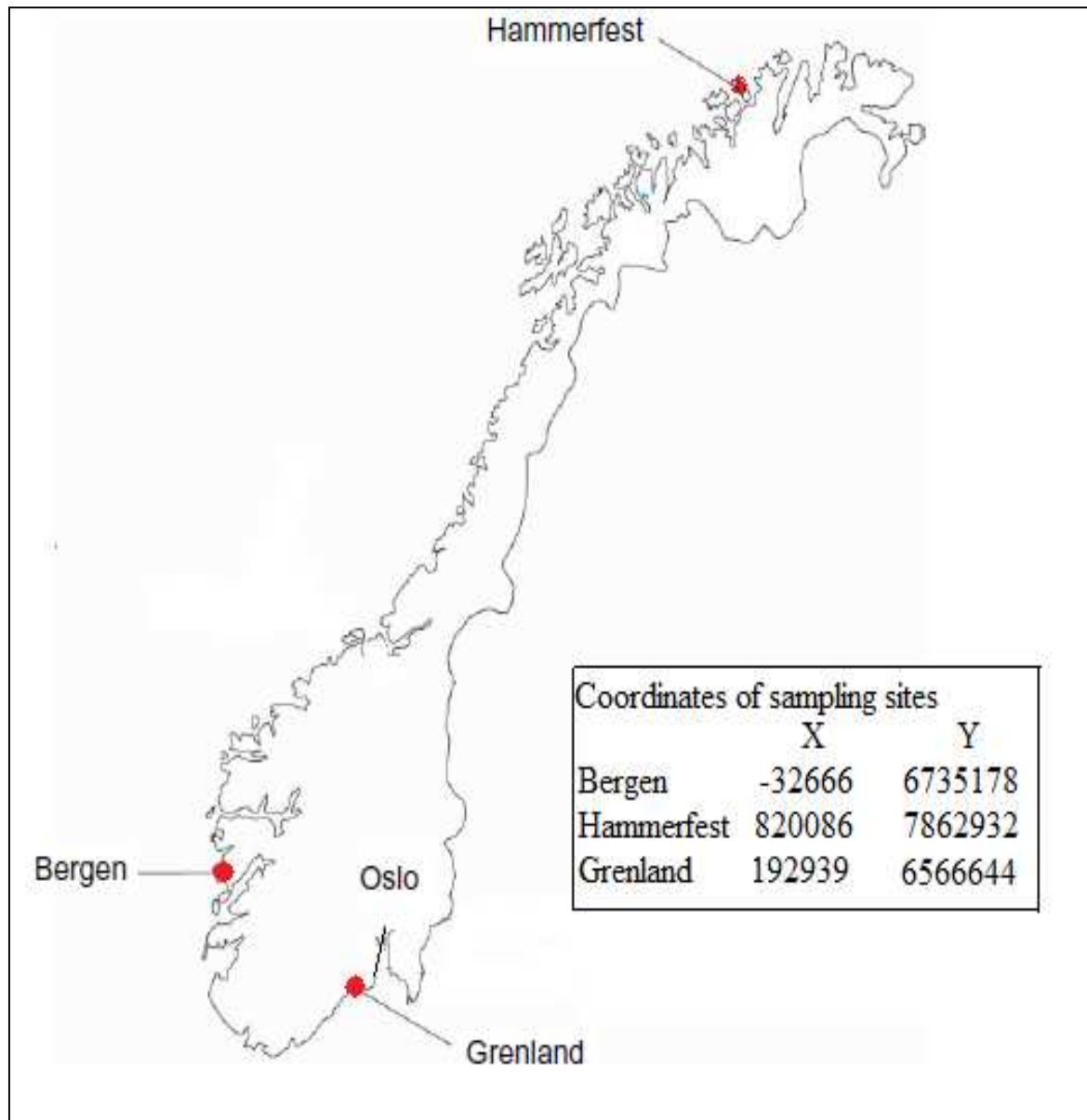


Figure 1.1 Map of Norway showing areas from where sediments were sampled

1.2 STUDY DONE BY THE NORWEGIAN GEOTECHNICAL INSTITUTE

The Norwegian Geotechnical Institute (NGI) is one of the organizations which have been actively involved in designing projects that deal with the pollution menace in Norway. This thesis is in connection with a larger project that is being carried out by the Norwegian Geotechnical Institute (NGI). The project has been designed to investigate effective methods of treating contaminated sediments at harbours and fjords in order to curtail their transport to other areas. Past and recent studies have shown that several physicochemical methods have and are being used for the removal of heavy metals from polluted sediments.

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Some of the techniques include sedimentation, precipitation, chemical and electrochemical oxidation, filtration, coagulation etc. (Chingombe et al., 2005; Thinakaran et al., 2008). Though each of them has its own merits and demerits, the objective of using an effective and efficient (in terms of cost and effectiveness in contaminant remediation); and environmentally amiable remediation method in many scientific investigations in recent times does not favour their wide application. As such, techniques that achieve such milestones have been on a high demand in recent times.

The technology employed by the NGI and studied herein is referred to as stabilization and solidification (S/S) of contaminated sediments. It involves using a binding agent usually cement to contain the hazardous chemicals in place. This method of treating hazardous waste has been utilized for quite a long time (Corner, 1990; Alunno and Medici, 1995; Conner and Hoeffner, 1998; and Malviya and Chaudhary, 2006), but compared with other techniques, S/S is gaining tremendous interest in the research community in recent times. The reason for this stems from its ability to transform pliable polluted materials to that with a high structural integrity which can be used for construction works or makes it easier to handle (Batchelor, 2006; Sparrevik et al., 2009). In addition, the physico-chemical properties of the polluted sediments are generally altered to reduce the transport of contaminants to other areas. Stabilization and solidification of contaminated sediments is also environmentally friendly and cost effective (Sparrevik et al., 2009).

1.3 JUSTIFICATION

Several studies have endorsed the S/S technology as effective for contaminant remediation (Shi and Spence, 2004). Generally, the effectiveness of S/S-treated waste materials is assessed by performing chemical and physical tests after the waste material has been solidified and cured (Islam et al., 2004). The most common chemical test that is used to investigate this is leaching test (Malviya and Chaudhary, 2006). Leaching tests give the possibility to determine the parameters that control the release of the elements of concern and the amounts that are released. Many of these tests are, however, studied on short term scales which make them unable to predict the long-term behaviour of many of the compounds being investigated. NGI has undertaken series of leaching tests to investigate the performance of the heavy metal-polluted stabilized sediments of which the results have

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briefly been discussed in the ensuing chapters. Geochemical models have evolved into invaluable tools that can be used as a substitute for laboratory experiments and for future predictions. As the assessment of the S/S technology is largely based on leaching tests and the fact that the method is being widely applied in recent times, being able to perform geochemical simulations of the leaching of the heavy metals in S/S materials can greatly help in understanding the mechanisms of leaching. It will also help in predicting the long-term leachability of pollutants. Results of such simulations can also be used to supplement or buttress results obtained from laboratory experiments. Many of the leaching tests have however been modelled but most of them are also based on approaches which are unable to give a direct indication of the chemical processes controlling their release (Halim et. al, 2005). PHREEQC (Parkhurst, 1995) is geochemical modelling tool that is capable of simulating several geochemical processes including chemical reactions and transport processes in natural or polluted water.

1.4 OBJECTIVE

The results of the investigations of NGI showed a great difference in the behaviour of lead and copper in terms of their solubility. The focus of this study was therefore on the two heavy metals (Cu and Pb). The objective of the study was to use geochemical modelling code PHREEQC to:

- Simulate the binding and release of Pb and Cu and their long-term behaviour in cement-stabilized polluted sediments from three Norwegian harbours namely: Hammerfest, Grenland and Bergen.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 HEAVY METALS

2.1.1 BRIEF OVERVIEW OF HEAVY METALS

Heavy metal is a generic term used for metals and semimetals (metalloids) that are associated with contamination. Their atomic densities are usually greater than 6 g/cm^3 (Alloway, 1995; Wild, 1993; Van der Perk, 2006). Examples of such metals include copper, lead, mercury, zinc, chromium, nickel, arsenic, tin, silver, and cadmium. Heavy metals are also referred to as trace metals due to their relatively low natural concentrations in soils, sediments, water, and organisms. In most environments, heavy metals occur in their cationic forms, though some occur as oxyanions for example, arsenate (AsO_4^{3-}) (Van der Perk, 2006). Whereas some heavy metals such as Cd and Zn are less strongly sorbed to soils and sediments others such as Pb and Cu have been found to sorb strongly and are released into solution slowly when the ambient conditions are favourable. Unlike other compounds, heavy metals are not biodegradable and many of them are toxic, mutagenic, and carcinogenic. As a consequence, they accumulate in sediments and pose a great threat to the environment especially when they encounter conditions that increase their solubility and, when their concentrations in soils, sediments, water and organisms exceed their acceptance levels (MacCarthy et al. 1991; Volesky, 1994; Clement et al. 1995; Volesky and Holan, 1995; Bozkurt et al., 2000). While present in sediments, heavy metals could be occluded in amorphous materials; adsorbed on clay surfaces or iron/manganese oxyhydroxides; precipitated as sulphides or oxides; or complexed with organic matter (OM) (Tessier et al., 1979).

The releases of heavy metals to the environment started increasing tremendously from the mid 19th century when industrialization began. From this period, enormous amount of heavy metals of deleterious effects have constantly been released to the environment. These releases have occurred via several pathways such as air, water and soil. Emissions via air are of enormous concern due to the large quantities involved, the widespread dispersion, and the potential for extensive human exposure (Järup, 2003). During the late 1970s, Norway encountered problems related to atmospheric long-range transport of heavy metals from other European countries. However, with the adoption of stringent

environmental policies among some European countries, these inputs have greatly reduced (SFT, 1997).

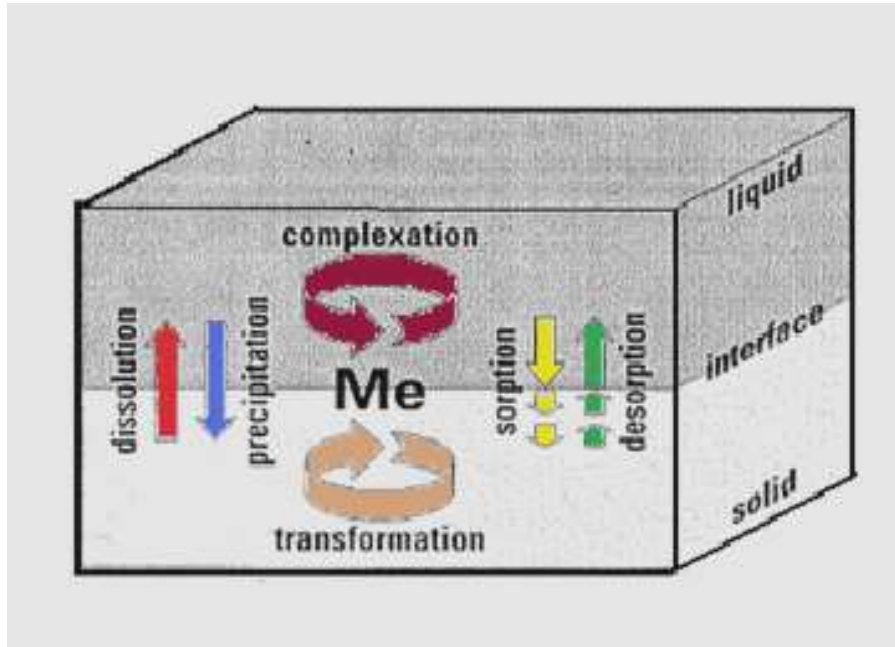


Figure 2.1 Schematic representation of the various processes of heavy metals undergo in sediments (Adapted and modified from Ziegler, 2000)

2.2 SOURCES OF HEAVY METAL POLLUTION

Pollution of sediments with heavy metals can occur in several ways. However, these sources have been put into two main categories- natural and anthropogenic sources. Anthropogenic inputs of heavy metals to the environment by far, exceed the natural inputs.

2.2.1 Natural sources

Naturally, pollution of sediments with heavy metals occurs through weathering of rocks. Weathering of rocks can occur through processes such as hydrolysis and hydration reactions; oxidation and reduction reaction; dissolution and dissociation of minerals; immobilization by precipitation; loss of mineral components via leaching and volatilization; and chemical exchange processes such as cation exchange. Heavy metals occur naturally in rocks as constituents. Through natural geological weathering by any of the processes aforementioned, heavy metals can be released into the environment. The concentrations of heavy metals due to natural geological weathering are often referred to as background concentrations. Background concentrations are not necessarily a threat to the

environment but are considered so only when their amounts exceed the acceptable limits in the environment. They could serve as point source pollution or they may be transported to other places via surface runoff or erosion, causing diffused pollution (Van der Perk, 2006).

2.2.2 Anthropogenic sources

It is no longer a matter of argument in many scientific debates that anthropogenic activities are the main reasons for the observed increases of heavy metal concentrations in sediments worldwide. Potential anthropogenic sources of heavy metals worldwide include sewage sludge, application of fertilizers both of organic and inorganic origins, leaching from building materials, industrial discharges and disposals and atmospheric fallout (from smelting or from burning coal and gasoline). Heavy metals released from anthropogenic activities are usually unstable and more soluble and available than their natural forms (Dudley et al., 1991; Alloway, 1995; Andersen et al, 1996; Van der Perk, 2006).

Anthropogenic releases of heavy metals to the environment increased greatly in the 19th century. This raised enormous concern worldwide for the adoption of measures that would reduce their concentrations in the environment. With the implementation of environmental regulations and improvement in technology, there has been substantial reduction in the releases of heavy metals to the environment for the past three decades (Van der Perk, 2006). Currently in Norway, efforts are being made to reduce the levels of heavy metals released into the ecosystem to background levels for naturally occurring heavy metals and close to zero for those released via anthropogenic activities (SFT, 1997).

2.3 HEAVY METALS INVESTIGATED IN THIS THESIS

2.3.1 Copper (Cu)

Naturally, copper occurs in the Earth's crust as free metal or in the +1 or +2 oxidation states. In oxidized environments (e.g. oxygenated seawater) copper may occur as either Cu²⁺ or Cu¹⁺ (cuprous) nevertheless, Cu¹⁺ has a high tendency of undergoing disproportionate reactions (equ. 2.1) which may result in Cu²⁺ (cupric) predominating in oxic solution.



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The Cu^{2+} formed, however, can be reduced again to Cu^0 and Cu^{1+} when reduced conditions begin to prevail (Jacob and Emerson, 1982). When present in sediments, Cu can be adsorbed on surface of metal oxides, clay minerals, humic substances or organo-mineral complexes; or be occluded in structures of secondary minerals or in amorphous iron and manganese oxides. They could also be associated with authigenic sulphides (Hang, 1993). Copper ions are susceptible to complexation, especially with hydroxide and carbonate ligands. In aerated natural waters containing dissolved carbonates, Cu^{2+} can react with the carbonates to form a strong CuCO_3 (aq), which is usually the main form of inorganic dissolved Cu though CuOH^+ and $\text{Cu}(\text{CO}_3)_2$ can also be present based on thermodynamic calculations (Stumm and Morgan, 1981). However, when the pH under such conditions is above neutral, $\text{Cu}(\text{OH})_3^-$ complexes are formed. These complexes are slightly soluble and can reduce the copper concentrations in water to below $10\mu\text{g/l}$. In the case where there is adsorption of Cu to sediments and soil minerals or coprecipitated with ferric oxyhydroxide, the Cu concentration can even decrease further. In the presence of sulphates under reduced conditions, Cu can react to form strong insoluble sulphides (Jacob and Emerson, 1982; Van der Perk, 2006).

2.3.2 Lead (Pb)

Some decades after the World War II, lead became ubiquitous in sediments. This was due to the high usage of Pb-alkyls as gasoline for automobiles. However, with the switch from using leaded to unleaded automobile gasoline in the past few decades, studies have revealed that there has been a substantial decline in the concentrations of lead in sediments (Bruland et al., 1974; Barbeau et al., 1981; Gobeil and Silverberg, 1989). Lead usually occurs in moderate amounts in the Earth's crust in the form of lead sulphide. In natural solutions, lead reacts to form lead hydroxide, carbonate, and phosphate. These compounds are less soluble reducing the mobility of lead greatly in natural waters. In oxygenated seawater, dissolved inorganic lead carbonate is predominant whereas in anoxic conditions, the sulphides of lead predominate (Stumm and Morgan, 1981; Emerson et al., 1983; Van der Perk, 2006). The concentrations of lead in natural waters is often low because lead sorbs strongly to mineral and organic materials and it is also able to form complexes with manganese oxide which can be precipitated in solution. Lead is an amphoteric metal in that its hydroxides can be soluble in natural waters at high or low pH (Van der Perk, 2006).

2.4 SOLIDIFICATION AND STABILIZATION

Solidification and stabilization (S/S) is a technology whereby waste materials are treated in a manner that alters the physico-chemical properties of the contaminants. This reduces their spread via leaching thereby minimizing the threat they pose to the environment. The process may involve chemical bonding or physical entrapment of the hazardous compounds. Most applications of S/S either utilize Ordinary Portland Cement as the sole binder or may be combined with other materials such as lime, fly ash, blast furnace slag etc (Batchelor, 2006). Solidification/stabilization of contaminants may be done in-situ or ex-situ. The in-situ methods are usually accomplished by injecting the binding agent into the contaminated site without excavating the waste material. This method does not expose the waste material to environment, thus pollution of other areas is greatly reduced. The ex-situ method on the hand involves excavation of the contaminated material and mixing it with the cement-based agent. The mixed material may then be returned to the ground at the site of excavation or placed in a landfill. The area may thereafter be covered with clean soil or pavement. Without proper handling, the ex-situ method of treating the waste material can lead to contamination of other areas. However, compared to the in-situ method, the ex-situ method can result in proper mixing of the binder with the waste material that can greatly reduce leaching of pollutants, which is the main objective of contaminant stabilization and solidification (Barth and Wiles, 1989). Corner (1990) investigated the chemical fixation and solidification of hazardous waste and identified high-unconfined compressive strength, low permeability, and less interconnected pores in the stabilized material as very important parameters for the success of the S/S. Batchelor (2006) later supported this when he did a general review on stabilization and solidification of waste materials.

2.4.1 Solidification

Solidification as defined by the Environmental Protection Agency (EPA) is a technique that is employed to encapsulate the waste into a monolithic solid of high structural integrity without any necessary chemical interactions between the hazardous chemicals and the solidifying reagent (Conner, 1990; Glasser, 1997; Poon et al., 2004). Solidification prevents the hazardous chemical from spreading in the environment in that, it results in

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reduced surface area and low permeability of the monolith. Advective flow through the waste material is greatly reduced (Cullinane and Jones, 1986; Batchelor, 2006) thereby reducing contact between the hazardous waste and other external substances that would otherwise enhance contaminant mobility. Generally, permeabilities in the range of 10^{-5} to 10^{-9} cm/sec for cement-based matrices and 10^{-6} - 10^{-7} cm/sec for pozzolanic-based waste forms have been documented (Arniella and Blythe, 1990). Malviya and Chaudhary (2006) have also proposed a minimum unconfined compressive strength of 50 psi.

2.4.2 Stabilization

Stabilization is a process that leads to a reduction of the hazard potential of a waste by converting the contaminants into their least soluble, mobile or toxic forms by changing the chemical nature of the contaminants. The components of the binding material react with the contaminants, culminating in changes in the chemical reactivity of the contaminants. The changes in the chemical properties of the hazardous substance is however dependent on the binding agent used and the result of the chemical interaction between the binder and the waste form (Conner, 1990; Glasser, 1997; Poon et al., 2004).

2.5 BINDER (CEMENT)

Apart from physical and chemical parameters such as pH of the waste form, presence of complexing agents, redox potential etcetera that influence the immobilization of contaminants, the type of cement used also has a great effect in retaining heavy metals in s/s waste forms. The cement does not only provide physical solidity, but also chemical stability of the hazardous metals as mentioned above. The interaction between the binder and the waste material is most often very complex such that there is no cement formulation that can be ideal for all the different waste forms (Chen et al., 2008). Thus, in many of the cases, binders that are specific for the site and the compounds to be dealt with have been formulated and used.

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Table 2.1 Composition of Portland cement

Constituent	Percent by weight	Constituent	Percent by weight
CaO	64.5	Na ₂ O	0.64
SiO ₂	21.8	SrO	0.31
Al ₂ O ₃	3.7	P ₂ O ₅	0.24
Fe ₂ O ₃	4.20	Mn ₂ O ₃	0.04
SO ₃	2.2	F	0.08
MgO	1.0	ZnO	0.01
K ₂ O	0.17	Cr ₂ O ₃	0.01
TiO ₂	0.24	Ign. loss	0.7
Total	100.06		

National Bureau of Standards (SRM 633)

Most of the constituents of the cement have usually been represented by abbreviations. The following are some of the abbreviations commonly used (Taylor, 1997).

C = CaO; S = SiO₂; A = Al₂O₃; F = Fe₂O₃; M = MgO; K = K₂O;

S = SO₃; N = Na₂O; T = TiO₂; P = P₂O₅; Č = CO₂; H = H₂O

In this case, Alite, which has the formula 3CaO.SiO₂, is usually represented as C₃S.

2.5.1 Minerals available for binding in the cement matrix

Several binders are available for the stabilization of contaminated sediments. For this study, hydrated Portland cement, which is a product of Portland cement, was used. Portland cement is by far the most important cement produced in terms of quantity. It contains four main phases namely: (1) Alite- tricalcium silicate (C₃S); (2) Belite- β-dicalcium silicate (β -C₂S), (3) tricalcium aluminate (C₃A), and (4) ferrite solid solution. Each of these phases reacts with water during the hydration of Portland cement. This results in a complete breakdown of their structure leading to the formation of a cement matrix which contains calcium silicate hydrate (C-S-H, 50%), Portlandite (Ca(OH)₂, 20 wt %) and Ca aluminates. According to Taylor (1997), the most important Ca aluminates in Portland cement, perhaps for binding and hardness of the material, are ettringite (3CaO.Al₂O₃.3CaSO₄.32H₂O, 4wt %), monosulphate (3CaO.Al₂O₃.3CaSO₄.12H₂O; 7wt %) and Ca carboaluminate (3CaO.Al₂O₃.3CaSO₄.32H₂O; 7wt %). Among the three main constituents found in the hydrated Portland cement, Portlandite has been shown to play an inconspicuous role in the binding process whereas C-S-H, ettringite, and mono sulphate

have been identified as the main constituents that are involved in heavy metal binding. This is owes to their structure and abundance in the cement (Johnson, 2004).

2.5.1.1 Calcium silicate hydrate gels (C-S-H)

Calcium silicate hydrate is a generic term that encompasses over 30 crystalline calcium silicate hydrates, which have structures that range from semi crystalline to nearly amorphous. C-S-H is the main product formed during the hydration of tricalcium silicate (C_3S) or β -dicalcium silicate ($\beta-C_2S$), which altogether constitutes about 70% by weight of a Portland cement. C-S-H gel is used in order to distinguish it from other forms of C-S-Hs which are not by-products of cement hydration. Figure 2.2 below shows a proposed structure of the C-S-H gel in cement. It shows a distorted Ca-O sheet in the middle with a row of SiO_4 chains that repeat at intervals of three silicate tetrahedrals on both sides in the form of a bridge. The C-S-H gel is found to have a large surface area and a lot of nanopores that have unbalanced charges which arises from the substitution of some atoms in the mineral. This promotes sorption of both anions and cations as well as physical and chemical incorporation. Owing to these characteristics and coupled with their abundance in the cement, C-S-H gels play an enormous role in the immobilization of heavy metals in cement-stabilized materials (Johnson, 2004).

2.5.1.2 AFt phases (Ettringite)

After C-S-H, ettringite is the next in terms of biding capabilities in cement. Ettringite is the most important AFt phases and most stable among the other constituents that are formed during the initial stages of cement hydration. It is made up of columns composed of Al octahedral sheets that alternate with triangular groups of edge sharing CaO_8 polyhedra in a hexagonal arrangement. The crystal structure of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) is shown in figure 2.3. Initially, it is dominantly made up of Al_2O_3 and Ca. However, as the cement matures with time, Fe substitutes much of the Al such that it is often referred to in terms of cement nomenclature as an AFt phase (A= Al_2O_3 , substituted by F (Fe_2O_3); t is trisulphate. It has columns which are composed of (Al,Fe)(OH)₆ octahedra alternating with triangular groups of edge sharing CaO_8 polyhedra, with which they share OH ions. The channels are occupied by water molecules and SO_4^{2-} ions which balance unsatisfied charges. The main process of heavy metal binding in ettringite is ion exchange. Binding of

Simulation of heavy metal leaching from cement-stabilized polluted sediments

cationic heavy metals occurs when bivalent cations are exchanged for Ca^{2+} , trivalent cations and $\text{Si}(\text{OH})_4$ for Al^{3+} . The presence of SO_4^{2-} ions also makes binding of anions possible through ion exchange (Taylor, 1997).

2.5.1.3 AFm phases (Monosulphates)

The role this class of minerals plays in heavy metal binding is almost similar to that of ettringite. Monosulphates with chemical formulae $(3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 12\text{H}_2\text{O})$ and $(3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaCO}_3 \cdot 12\text{H}_2\text{O})$ are common phases in cement paste. They are referred to as AFm (m = monosulphate) phases in cement nomenclature. The atoms in the minerals have been arrayed in a manner that forms a hexagonal platelet. The structure is such that it has a main layer of $\text{Ca}(\text{OH})_2$ and an interlayer which is made up of either SO_4^{2-} and/or CO_3^{2-} . Unlike ettringite where the exchange is between Al and Fe, in the monosulphates, the exchange is between Ca and Al or Fe such that one in three of the Ca^{2+} cations in the main layer is replaced by Al^{3+} or Fe^{3+} ions. The excess charge is balanced by anions in the interlayer. The anions may however, be exchanged for other anions.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

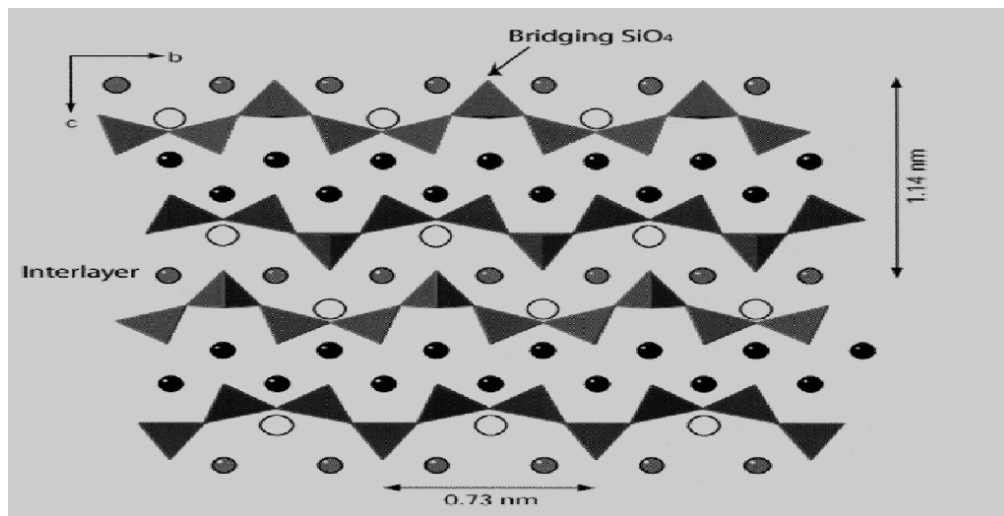


Figure 2.2 Structure of calcium hydrated silicate (C-S-H) (Taylor, 1997)

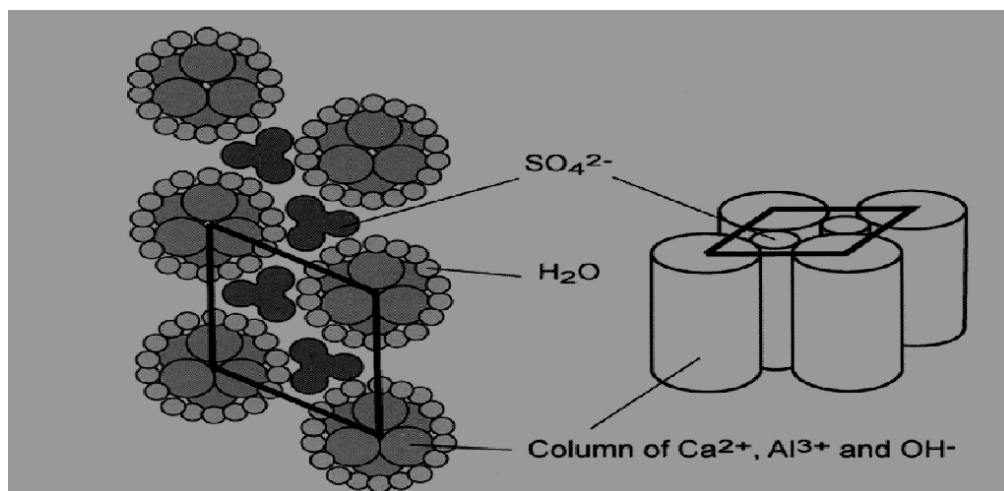


Figure 2.3 Structure of Ettringite (Taylor, 1997)

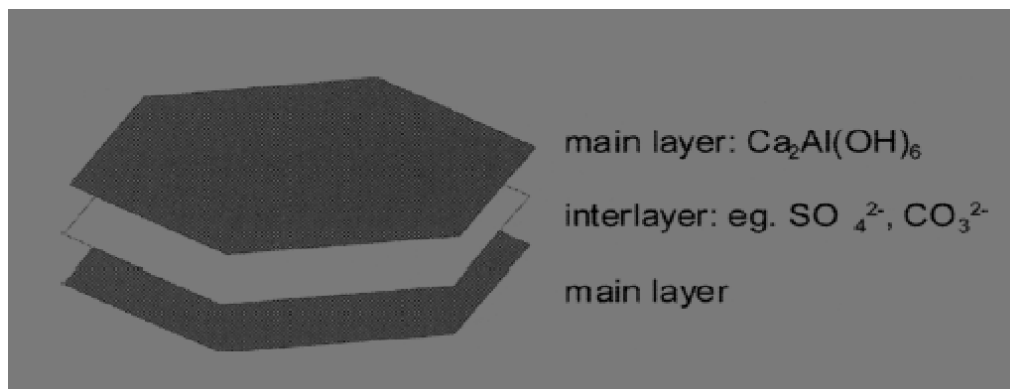


Figure 2.4 Structure of AFm (Johnson, 2004)

2.6 MECHANISMS OF HEAVY METAL BINDING IN CEMENT

The interaction between cement and heavy metals in cement-based s/s waste forms is usually complex in nature and there appears to be insufficient knowledge about the binding mechanisms of heavy metals in cement matrix. Possible mechanisms of heavy metals immobilisation include sorption, ion exchange, precipitation, or complexation (Trussel and Spence, 1994; Glasser, 1997; Glasser et al., 2006; Engelsen et al., 2006; Macherzynski et al., 2008). None of these mechanisms, however, can singly account for the immobilization of heavy metals in cement-stabilized sediments.

2.6.1 Adsorption

Sorption is a general process whereby chemicals become associated with solid phases by either being taken up from the liquid or air phases onto or into organic or mineral matter. The phenomenon whereby adsorbates are held onto a two-dimensional surface of an adsorbent by Van der Waal's forces is referred to as adsorption. It is absorption on the other hand if there is penetration of the adsorbate into a three-dimensional matrix of an adsorbent. Sorption is an extremely important phenomenon because it considerably affects the fate and impacts of contaminants in the environments (Cheng and Bishop, 1992; Schwarzenbach, 2002).

2.6.1.1 Adsorption isotherms

Equations that describe the capacity of the adsorbent, the equilibrium concentration of a substance that is sorbed and the concentration that is in solution at constant temperature are referred to as sorption isotherms (Igwe and Abia, 2007). These values are usually determined experimentally, but there are also models to predict them, both for single metal adsorption and multi component adsorption. Sorption of contaminants can be linear or non-linear.

2.6.1.1.1 Linear sorption isotherm

Linear sorption is described by equation 2.2. In this case, the affinity of the sorbate for the sorbent remains the same over the entire adsorption period. Thus, increasing the concentration of the chemical in solution will result in a proportionate increase in the

amount that is sorbed. Generally, linear sorption is found to be unrealistic although it is often used in contaminant transport modelling.

$$C_{is} = K_{id}C_{iw} \quad [2.2]$$

K_{id} (L/kg solid) is the partitioning coefficient that describes the relationship between the amount that is sorbed and the amount of the compound in the liquid phase. C_{is} is the amount sorbed (mass/kg) and C_{iw} (kg/L) represents the concentration in the liquid phase.

2.6.1.1.2 Non-linear sorption

Non-linear sorption is the case whereby the affinity of the sorbate for the sorbent diminishes at higher adsorbate concentrations. This, however, depends on the adsorbate, adsorbent and the prevailing environmental conditions. Freundlich (equation 2.3) and Langmuir (equation 2.4) sorption isotherms can be used to illustrate non-linear sorption. Freundlich isotherm describes sorption in which adsorption is non-linear and there is non-limited sorption capacity whereas the Langmuir isotherm is used when sorption capacity is limited and adsorption is non-linear (Igwe and Abia, 2007).

$$C_{is} = K_{iF}C_{iw}^{ni} \quad [2.3]$$

$$C_{is} = \frac{\Gamma_{max} \cdot K_{iL} \cdot C_{iw}}{1 + K_{iL} \cdot C_{iw}} \quad [2.4]$$

Where K_{iF} is the Freundlich constant or capacity factor; and ni is the Freundlich exponent which, ranges between 0 and 1. The steepness and curvature of the Freundlich isotherm, respectively, are determined by the K_{iF} and ni , (Akgerman and Zardkoohi, 1996). Γ_{max} is the maximum achievable surface concentration of a given compound i . K_{iL} is the Langmuir constant, C_{iw} (kg/L) represents the concentration in the liquid phase and C_{is} is the amount sorbed (mass/kg). There are also cases where the relationship between the adsorbate and adsorbent cannot be exclusively described by one isotherm. In such cases, a combination of both linear and non-linear sorption isotherms is employed. Equation 2.5 shows a combination of linear and Freundlich isotherms and equation 2.6 is a combination of linear and Langmuir sorption isotherms (Schwarzenbach, 2002).

$$C_{is} = K_{iF}C_{iw} + K_{iF}C_{iw}^{ni} \quad [2.5]$$

$$C_{is} = K_{iF}C_{iw} + \frac{\Gamma_{max} \cdot K_{iL} \cdot C_{iw}}{1 + K_{iL} \cdot C_{iw}} \quad [2.6]$$

The first part, $K_{iF}C_{iw}$ in equations 2.5 and 2.6 represents the linear sorption isotherm and the second terms, $K_{iF}C_{iw}^{ni}$ and $(\Gamma_{max} \cdot K_{iL} \cdot C_{iw}) / (1 + K_{iL} \cdot C_{iw})$ represent the Freundlich and Langmuir sorption isotherms respectively. K_{iF} is the Freundlich constant or capacity factor; ni is the Freundlich exponent. Γ_{max} is the maximum achievable surface concentration of a given compound i . K_{iL} is the Langmuir constant; K_{iF} is the partitioning coefficient of the linear isotherm; C_{iw} is the concentration of the compound in the liquid phase and C_{is} is the amount of the compound that is sorbed.

Sorption of heavy metals is often non-linear (Selim and Sparks, 2001). The Langmuir and Freundlich isotherms have been used a lot to describe the behaviour of heavy metals in sediments. The Freundlich isotherm does not have a sound theoretical background, in that it was developed on laboratory research basis. However, it gives adequate description of adsorption data over a range of concentrations. In addition, the Freundlich isotherm is suitable for both homogeneous and heterogeneous surfaces whereas the Langmuir isotherm only gives a good fit for homogeneous surfaces (Juang et al., 1996; Calace et al., 2002). Several studies have documented sorption as the main process that results in the retention of large amounts of heavy metals in sediments (McLaren and Crawford, 1973; Stevenson and Fitch, 1981; Bruemmer et al., 1983; Tiller et al., 1984; Bolton and Evans, 1996).

2.6.2 Non-Specific adsorption (Ion exchange)

Ion exchange is a chemical process in which an ion in solution is exchanged for another ion of similar valence (charge) attached to an immobile solid particle. The immobile solid particles (i.e. sediment mineral particles such as clay or other solid materials) usually carry either positive or negative charges. These charges are usually balanced by oppositely charged ions in solution. Major cations and anions that balance the charges on the surfaces of the immobile solid particles include H^+ , Na^+ , Mg^{2+} , K^+ , Ca^{2+} , NH_4^+ and SO_4^{2-} , Cl^- , PO_4^{3-} , NO_3^- (Bhattacharyya and Gupta, 2008). These ions are also exchangeable with heavy metals such as Pb^{2+} , Cd^{2+} , Cs^+ , Cu^{2+} , Co^{2+} , Cr^{3+} , Zn^{2+} , Ni^{2+} , Hg^{2+} in an ion exchange

Simulation of heavy metal leaching from cement-stabilized polluted sediments

process (Breck, 1964; Barer, 1987; Erdem, 2004). Sometimes, the exchange can be between the heavy metals. Factors that generally affect the extent of ion exchange include the size and valence (charge) of the ions entering into the exchange, the concentration of ions in the water or solution, the nature (both physical and chemical) of the ion exchange substance, and the temperature. Alloway and Ayres (1993) observed that the degree of exchange is usually higher for metals with higher valencies. However, for metals of the same valence, preference is given to those with smaller ionic radii. Ion exchange processes are reversible and stoichiometric in that, the total number of ions that are removed from solution is in balance with the number that enters the solution (Al-Enezi et al., 2005). The ions phased out of sediment surfaces into solution could remain soluble or form compounds or complexes with other substances which can affect their solubility.

2.6.3 Complexation

Heavy metals show high ability to form a wide variety of organic and inorganic complexes in sediments, particularly when the environment for such mechanisms is conducive. Complexes are formed when a central atom or ion covalently bonds to a number of other atoms, ions or molecules known as ligands. Stability of the complexes depends on the charge density of the central atoms or ions that are involved in the complexation. Positive ions with high charge density tend to form stable complexes. Thus, Li or K will show a lower tendency to form complexes compared with Pb and Cu (Toon et al., 1968). Potential inorganic ligands in sediments include H_2O , NH_3 , Cl^- , OH^- , and $(\text{SO}_4)^{2-}$. Heavy metals also have a great affinity to form complexes with dissolved organic carbon which in turn affects their mobility. Whereas some complexes enhance the mobility of heavy metals, others result in their immobilization. Castilho et al. (1993) conducted a study on the influence of cattle manure slurry application on the solubility of cadmium, copper and zinc in acidic manure, loamy-sandy soil. Their study revealed that the concentration of metals in the soil solution increased with an increase in the concentration of dissolved organic carbon (DOC). The authors also concluded that copper mobility is highly associated with DOC. The potential for heavy metals to form organic and inorganic complexes depends on a number of factors. For instance, chloride is able to form complexes with many heavy metals. However, this process is only very effective in saline environments where the concentrations of the Cl^- are high. Generally, factors such as the nature and concentration

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of the ligands present, the concentration of the hardness cations (Ca, Mg) and other metals (Fe, Mn), the pH of the system and the degree to which equilibrium is attained affect the mechanism of complexation (Doner, 1978).

2.6.4 Precipitation

Heavy metals are generally characterized by high saturation indices, and high nucleation and aggregation rate. This makes precipitation one of the dominant processes, if not the main, that immobilize heavy metals in s/s materials particularly those of low solubility (Cannell et al., 2000; Salhan et al., 2003), and when heavy metals are present in large amounts (Naidu et al., 1997). Precipitation of heavy metals in s/s materials occurs when they are absorbed into the lattice of the cement-base material to form a solid solution. Heavy metals are usually precipitated as hydroxides, carbonates, phosphates and sulphates (Hills et al., 1994; James, 1996; Conner and Hoeffner, 1999, Chen et al., 2009) with each form being dominant at specific conditions for specific metals. For instance, precipitation of heavy metals as hydroxides occurs when the pH of the s/s system is raised to some optimum level which may differ for each metal. Figure 2.5 is a schematic diagramme showing various mechanisms of heavy metal immobilization in cement.

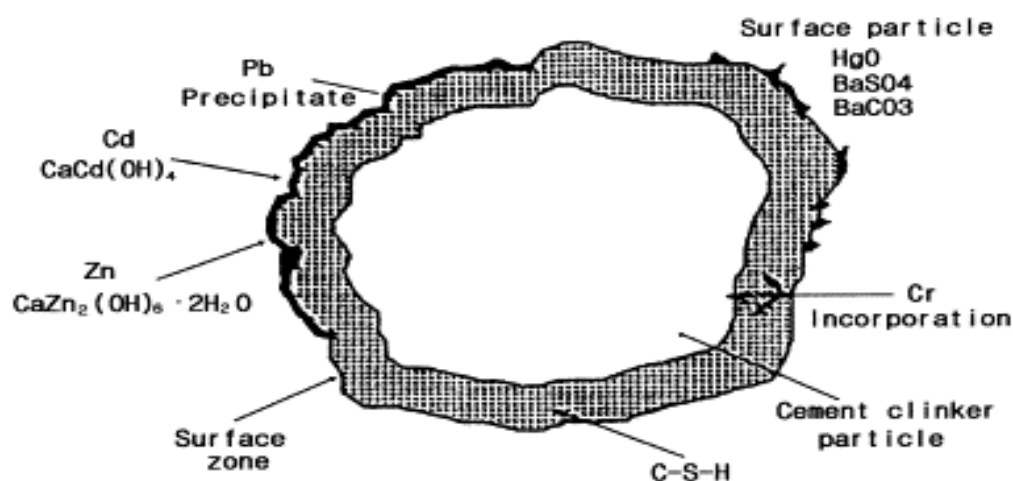


Figure 2.5 Schematic diagramme showing various mechanisms of heavy metal immobilization in cement (Conner, 1990)

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Cadmium, Zn and Pb are usually precipitated on the surface of hydrates whereas Cr is incorporated in hydrates, especially C-S-H. Cadmium forms a double compound $\text{CdCa}(\text{OH})_4$ due to its participation and incorporation into Portlandite, $\text{Ca}(\text{OH})_2$ and a subsequent substitution for Ca. For Zn and Pb, studies have shown that it is usually their anionic species that are precipitated on the surfaces of the cement hydrates. This usually occurs at high pH when their anionic species are available. The effects of S/S of heavy metals are, however, dependent on the amounts of hydrates created.

2.7 FACTORS AFFECTING HEAVY METALS IMMOBILIZATION

The principal geochemical parameters that govern the mechanisms of heavy metals immobilization in sediments include redox potential, pH and the presence of complexing agents. These parameters affect the chemical forms of the metals. Although several studies have shown the effects of pH to be enormous in immobilization/solubilization of heavy metals (Brown et al., 1997), the effects of the other factors cannot be overemphasised.

2.7.1 pH

2.7.1.1 Effect of pH on mineral surface charge development

Surface chemistry of minerals greatly affects the solubility and hence the mobility of contaminants in the environment in that, reactions between solutions and solids often involve the interface between these phases. Hydroxyl groups as a result of the interaction of sediments with and the subsequent dissociation of water molecules usually occupy the surfaces of sediments and soils in water. At high or low pH, negative or positive charges, respectively, can be developed on the mineral surfaces. This dictates the type of ionic compounds that can be sorbed onto mineral surfaces. Generally, the surfaces of C-S-H in basic solutions are deprotonated. This potentially attracts positively charged metals in solution, thereby affecting their mobility. Thus, adsorption of cationic metals is greatly enhanced in basic media.



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On the other hand, lowering the pH would lead to the development of positive charges on the surfaces of the minerals. This favours the adsorption of negatively charged metals or compounds. This explains why most cationic heavy metals are found in acidic solutions.

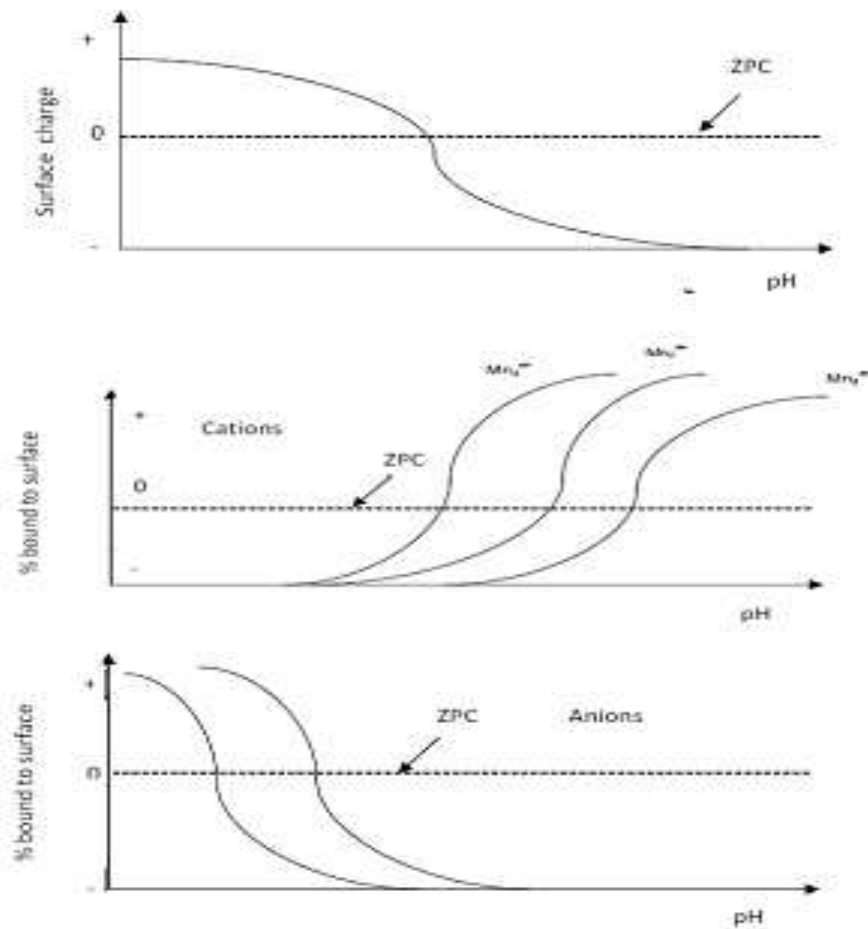


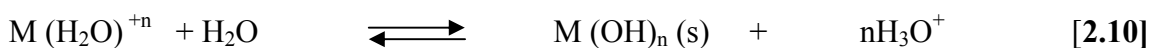
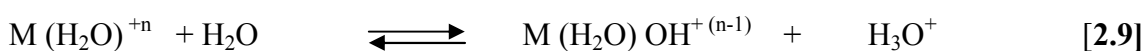
Figure 2.6 Effect of pH on cations and anion adsorption to hydrated oxides surfaces

Figure 2.6 shows the pH response of cations and anion adsorption on hydrated oxides surfaces. The pH value at which the surface charge is zero, is called the point of zero charge (ZPC). Different materials have different ZPCs. As can be seen from the graph, anion adsorption increases with decreasing pH whereas cation adsorption increases with increasing pH. The figure shows that as the pH increases, the percentage of cationic heavy

metals bound to the surface increases and for anionic metals, their percentage adsorption increases with decreasing pH

2.7.1.2 Effect of pH on immobilization/leaching of heavy metals

As stated above, pH plays an enormous role in mineral surface charge development which in turn, controls the adsorption of charged species. The dissolution and mobility of heavy metals in soils and sediments can also be influenced by pH. Metals in solution usually exist in hydrated forms due to their interaction with water molecules.



It follows from the equilibria reactions above that adding more acid, H_3O^+ shifts the reaction to the left producing more dissolved species. On the other hand, if the pH is increased by increasing the OH^- concentrations, the reaction shifts to the right precipitating more insoluble metal hydroxides. Increasing the pH further will result in the metal hydroxide forming complexes with OH^- with negative charges. This negatively charged polyhydroxide metal can, however, be engaged in a strong interaction with water molecules which eventually can result in their dissolution.



In cement stabilized sediments, the pH of fluid that fills the pore structures is usually alkaline in nature. This aids in the precipitation of insoluble species, particularly metal hydroxides. It is therefore imperative for the pore fluid to be maintained at high pH to ensure long term retention of contaminants. This, however, is independent of the amount of hydrated phases in the cement which have the potential of raising the pH but rather, by keeping the quasi-equilibrium between solid and aqueous phases constant (Bone et al. 2004). However, studies have shown that over time, the equilibrium between the solid and the liquid phases can be disrupted due to changes in the conditions of the waste form. In some cases, however, high pH favours the mobility of certain cations.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

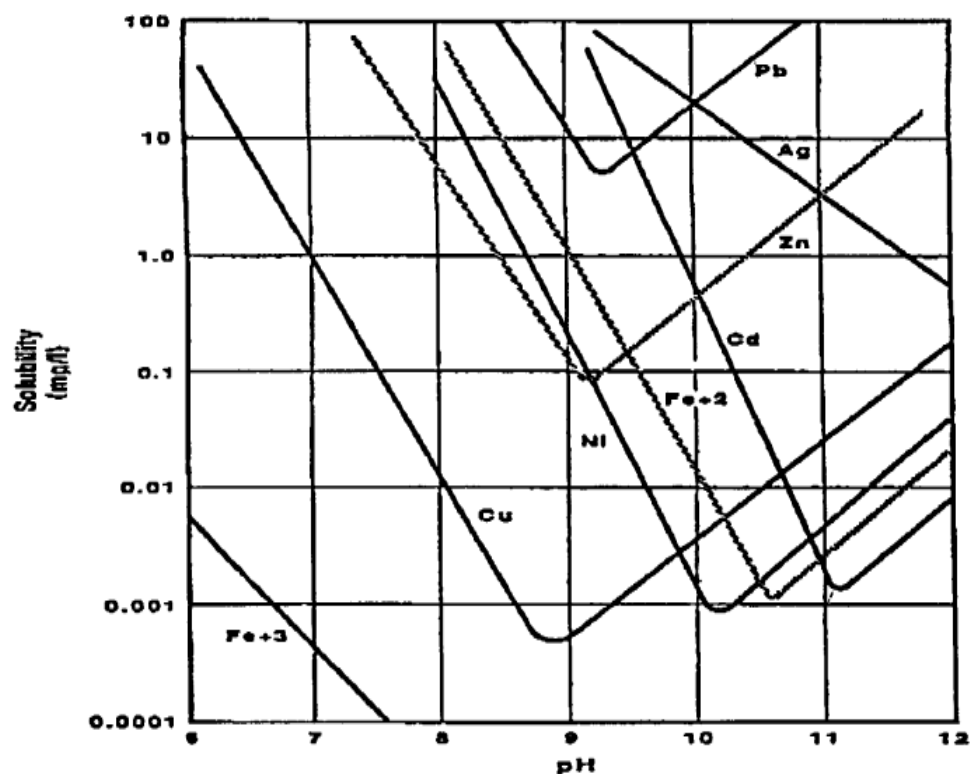


Figure 2.7 Solubility of metal hydroxide as a function of pH (Corner, 1990)

Figure 2.7 shows the solubility of metal hydroxide as a function of pH. The two metals under investigation -Pb and Cu- are referred to as amphoteric metals i.e. their hydroxide forms can dissolve when the solution pH is very low or high (Corner, 1990; Li, 2001 and Huang, 1993). It can be seen from the figure that the pH at which metals begin to redissolve defers for each metal. For instance, Cu begins to solubilise again from pH 9 and above whereas that of lead begins from 9.4 and above. The effect of pH on leaching of heavy metals for the different sediments was investigated by NGI. Results are shown below. Figure 2.8 shows the effect of stabilization on pH of the sediments. The results show that the pH of all the sediments increased after stabilization. Specimens stabilized with 150g of cement recorded the highest pH with those stabilized with 50g cement recording the lowest pH. This may be attributed to the dissolution of calcium, sodium and potassium hydroxides in the cement. Figure 2.9a and b are showing the leaching behaviour of Cu and Pb, respectively from stabilized sediments, unstabilized sediments and cement.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

It can be seen that with the exception of the sediment from Bergen, leaching of Cu increased significantly after stabilization. On the contrary, leaching of lead was lower after stabilization with the exception of samples from Hammerfest, for which leaching of Pb was either lower or higher after stabilization for the different rates of cement.

In studying the relationship between pH and leaching of heavy metals (figure 2.10a and b), it was observed that leaching of Pb does not correlate with pH. However, a different observation was made for Cu. With the exception of sediments from Bergen, stabilized sediments with pH above 9 gave higher leaching of Cu than for the unstabilized sediments. Thus, whereas leaching of Cu is shown to be somewhat dependent on pH, the pH effect on the leaching of lead could not be substantiated in this study. From this, it is therefore inferred that leaching of heavy metals from cement-stabilized materials is not exclusively controlled by pH. Other factors such as physical conditions and chemical composition of the sediment, and their interaction with the stabilizing agents also contribute immensely to the leaching of heavy metals (Sparrevik, 2009)

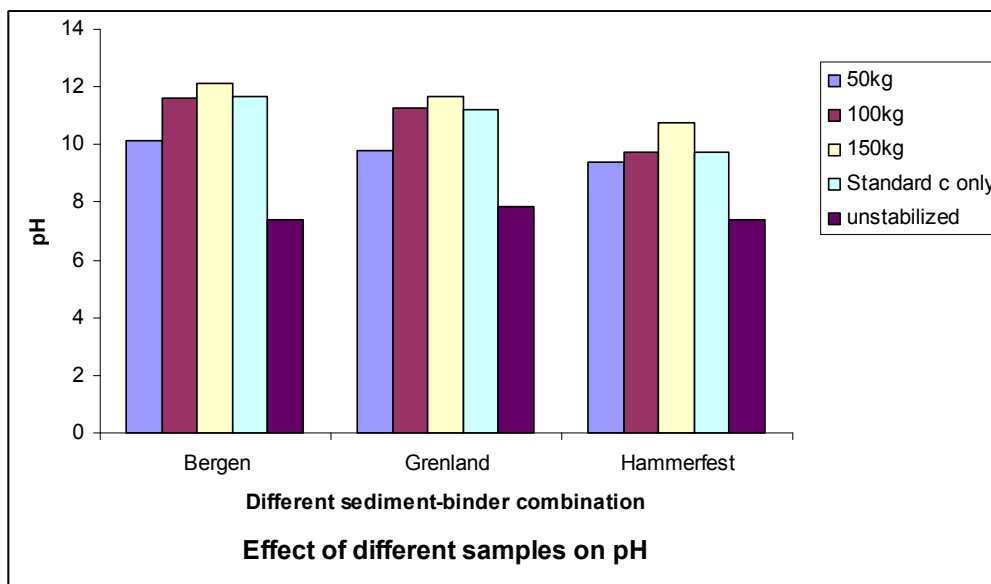
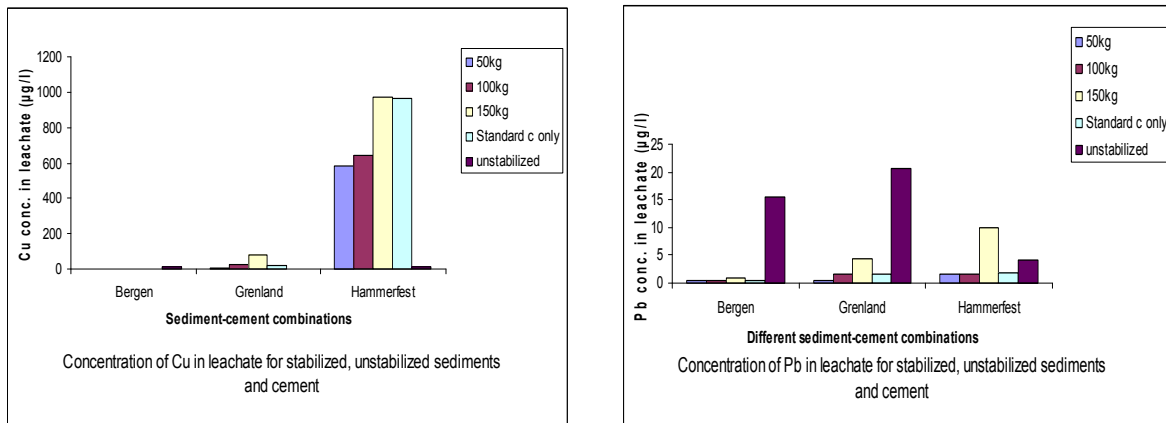


Figure 2.8 Effect of stabilization on pH

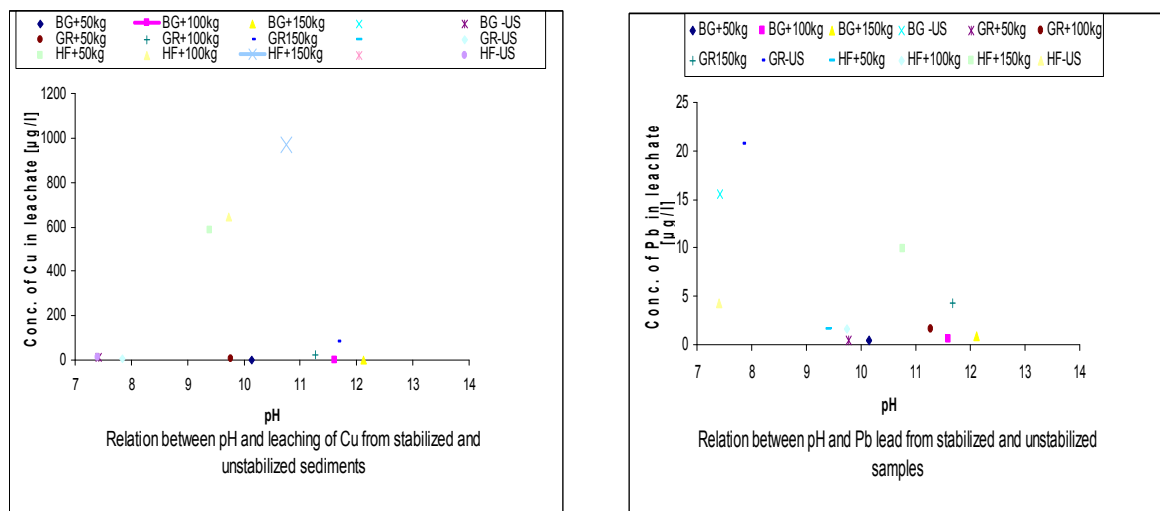
Simulation of heavy metal leaching from cement-stabilized polluted sediments



a)

b)

Figure 2.9 Leaching of a) Cu and b) Pb from stabilized sediment and unstabilized sediments and cement



a)

b)

Figure 2.10 Effect of pH on a) leaching of Cu and b) Pb from stabilized sediments, unstabilized sediments and cement

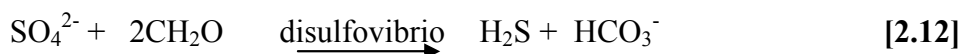
2.7.2 Redox potential

The influence of redox potential on the immobilization/solubilisation of heavy metals is enormous as it affects the electron structure of metals and consequently, their ability to react with other substances. Oxidation occurs if there is loss of electrons or addition of oxygen to a compound while the phenomenon in which there is acceptance of electrons or

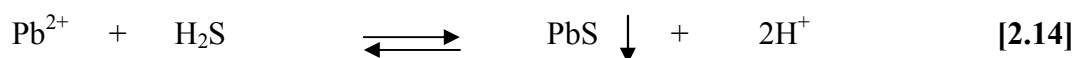
Simulation of heavy metal leaching from cement-stabilized polluted sediments

the removal of oxygen or addition of hydrogen to a compound or an element is termed reduction. Metals are oxidized when they donate electrons while the recipient of the electrons is in turn reduced. Under oxic conditions, oxygen is the main recipient of electrons. However, under anoxic conditions, other oxidizing agents such as Fe^{2+} , SO_4^{2-} , H_2S and CH_4 dominate. Under this condition, different chemical phases with different solubilities can be observed.

In marine environments, for instance, there is abundance of H_2S which are formed due to the anaerobic conversion of large amounts of SO_4^{2-} by obligate anaerobes. This results in the accumulation of large amounts of H_2S in marine sediments.



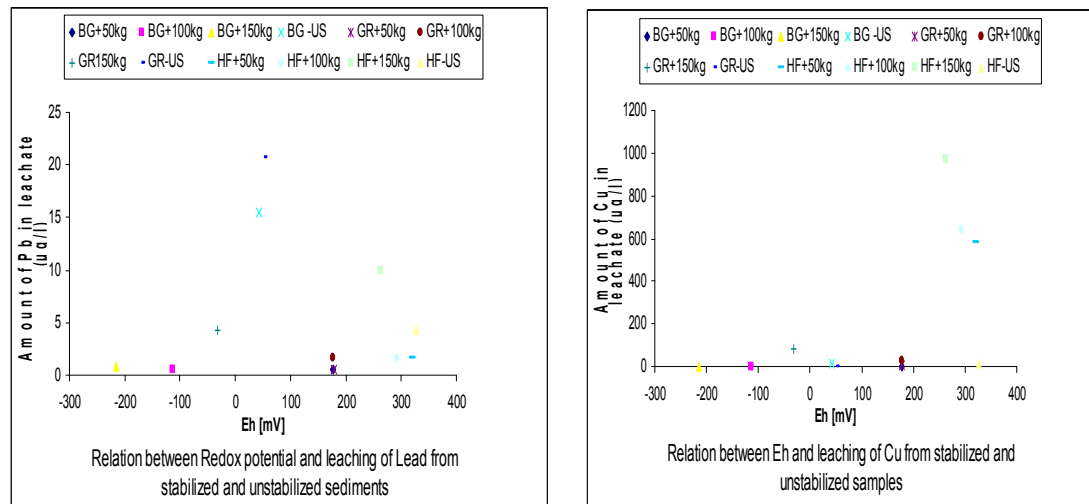
Initially, a large amount of the H_2S formed in sediments is bound to iron as solid iron mono sulphide (FeS) which is readily converted to pyrite, crystalline mackinawite (FeS), pyrrhotite (FeS), greigite (Fe_3S_4), or exists as free sulphides. The sulphide, however, has high preference for heavy metals such that in the presence of heavy metals, iron is displaced and the H_2S reacts with the heavy metals to form precipitated metal sulphides with low solubility (Hansen et al., 1996).



It is, however possible for the precipitated metal sulphides to redissolve if the environmental conditions that favour their dissolution is enhanced. For instance, if organic matter is present and the sediments are exposed to high redox potential conditions, there will be oxidation of metal sulphides and decomposition of organic matter concurrently. Both processes favour the release/dissolution of adsorbed/precipitated or complexed heavy metals (Calmano, 1993; Peng et al., 2009). It is a generally accepted phenomenon that at high redox potentials, heavy metal leaching is increased. The studies done by NGI showed

Simulation of heavy metal leaching from cement-stabilized polluted sediments

parallel results. The Norwegian Geotechnical Unit investigated the effect of cement stabilization on redox potential and its relationship with the release of heavy metals. The results are shown in Figure 2.11



a) b)

Figure 2.11 Effect of Redox potential on heavy metal leaching

Figure 2.11a and 2.11b are showing the relationship between redox potential and leaching of Cu and Pb, respectively. Results indicate that there is high leaching of Cu and Pb under high oxidic conditions and low for anoxic conditions. High oxidic conditions were found for Hammerfest sediments. This gave high leaching of both Cu, Pb. Anoxic conditions prevailed in the Bergen sediments, and that contributed to low leaching of both Cu and Pb.

2.7.3 Effect of complexing agents

The dissolution and mobility of heavy metals is also controlled by the prevailing ambient conditions. Under certain environmental conditions, some heavy metals are found to be more soluble while insoluble in other conditions. However, it has been observed that the low solubility of some heavy metals under conditions that do not favour their dissolution can be changed if some specific compounds that they are able to form soluble complexes with are present. For instance, at somewhat high pH cationic Cu is not soluble. However, studies have shown that if organic matter at such pH conditions is present, the mobility of Cu can be enhanced. The organic matter complexes with Cu and prevents its adsorption onto suspended particles which inhibit Cu mobility (Sholkovitz and Copland 1981;

Zomeren and Comans, 2004). This is however, impossible with insoluble organic compounds (Amina et al., 1999). In a study on the coagulation, solubility and adsorption properties of some heavy metals and humic acids in river water with alkaline pH, Sholkovitz and Capland (1981) observed that Cu solubilisation by organic substances could be the main process determining speciation and bioavailability of Cu.

2.8 GEOCHEMICAL MODELLING (PHREEQC-2)

Over the years, modelling has evolved to be an important tool that helps in expanding our knowledge of real life environmental conditions. PHREEQC (VERSION 2) is an invaluable geochemical modelling tool developed by Parkhurst and Appelo in 1995. It has been used to simulate several geochemical processes including chemical reactions and transport processes in natural or polluted water. This program is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces. It is capable of modelling kinetic reactions with rate equations that are completely user-specified in the form of Basic statements. It has different databases with different master species to choose from depending on the kind of simulation to be performed.

PHREEQC is based on the Fortran program PHREEQE (Parkhurst et al., 1995). PHREEQE was capable of simulating a variety of geochemical reactions for a system. These include:

- Mixing of waters
- Addition of net irreversible reactions to solution
- Dissolving and precipitating phases to achieve equilibrium with the aqueous phase
- Effects of changing temperatures

In 1995, Parkhurst developed a completely new program; PHREEQC version 1, written in the C programming language. PHREEQC version 1 was capable of performing all the functions of PHREEQE in addition to newly developed ones. Among the improvements are:

- Ion-exchange equilibria

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- Surface-complexation equilibria
- Fixed-pressure gas-phase equilibria
- Advective transport

PHREEQC version 2 is a modification of PHREEQC version 1. Most of the code and all of the capabilities for version-1 have been retained. In addition, it is able to perform newly added functions which include:

- Kinetically controlled reactions
- Solid-solution equilibria
- Fixed-volume gas-phase equilibria
- Variation of the number of exchange or surface sites in proportion to a mineral or kinetic reactant
- Diffusion or dispersion in 1D transport
- 1D transport coupled with diffusion into stagnant zones
- Isotope mole balance in inverse modelling

Whilst this geochemical modelling tool can be of invaluable help in performing several geochemical simulations, an understanding of its operation is very important if accurate results are to be obtained. In addition, as the results of the model are only as good as the parameters on which they depend, any shortcomings with respect to the input data will have enormous consequence that can produce misleading results.

CHAPTER THREE

3.0 MATERIALS AND METHODS

The study was carried out between February and May 2010 at the University of Oslo. It is presented in this chapter a brief description of the materials and procedures used in both the previous and current studies. However, for details of the experimental procedures and materials used for the stabilization of the sediments and the leaching test, the reader is referred to the project entitled “Development of binder and additions, final report from phase 1, 2, and 3 (2008).” Emphasis is however placed on the geochemical simulations since that has been the main aim of this study.

3.1 Materials used

The main materials used for the previous and current studies include heavy metal polluted sediments from Bergen, Hammerfest, and Grenland; Portland cement; seawater from NIVA and computer-based geochemical modelling tool.

3.1.1 Sediments and cement

The sediments were sampled from three different locations along the Norwegian coast. They are Bergen, Grenland, and Hammerfest. The sediments were sampled from the upper seabed (0-10 cm) using the Van Veen grab, after which they were dewatered by gravity and stored in airtight containers in a cooling room at 10⁰C. The physical and mechanical properties of the sediments and cement are shown in Table 4.1. Their chemical properties have also been presented in Table 4.2. The chemical analysis was done to characterize the sediments by determining the various contaminants present. Table 4.2 also shows the level of sediment contamination and their classification based on the Norwegian Classification System.

3.1.2 Seawater

Seawater was collected from NIVA research station in Solbergstrand and was used for the preparation of the specimen and as leachant in the leaching experiment. This was done since the contaminants were obtained from marine environments and to ensure that

experimental conditions are somewhat similar to the prevailing conditions at the polluted sites. Results of the characterization of the seawater can be found in Table 4.3.

3.2 XRD analysis

Before the modelling was done, it was necessary for the mineralogical composition of the sediments to be established. This was made possible by performing an X-ray diffraction (XRD) analysis. XRD is a non-destructive qualitative (or at best, semi-quantitative) technique for characterising minerals. It provides information on structures, phases, and other structural parameters such as average grain size, crystallinity etcetera. XRD generates peaks that are as a result of constructive interference of monochromatic beam that are dispersed from each set of lattice planes at specific angles. The intensities of the peak are determined by the atomic decolouration within the lattice planes. Consequently, the X-ray diffraction pattern is the fingerprint of periodic atomic arrangement in a given material.

Specimens of the three sediments to be used for the XRD were ground to powdered form. The metal plate used in making the square slab was thoroughly cleaned with soapy water and dried with ethanol before being used to avoid contamination. About 2-3g of the dry powdered sample was used to prepare the square slabs and thereafter analysed for their mineralogical composition.

3.3 Combinations of test specimens, sample preparation and leaching test

Specimens were prepared by combining the sediments with different rates of cement. In the experiment, 50g, 100g and 150g of cement were combined with 1 litre of sediment. The sediments were then stabilized and solidified. Mechanical strength and permeability tests were performed after the samples were cured for 28 days. Leaching tests were then performed, after which the eluates were analysed for Cu and Pb; Eh, pH, temperature and conductivity.

3.4 GEOCHEMICAL MODELLING

As was mentioned in the introduction, the focus of this thesis was on the simulation of the results obtained from the leaching studies done by NGI. Geochemical simulations were

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performed to ascertain the possibility of simulating the leaching of pollutants from the three cement-stabilized sediments with geochemical model and also to unveil the mechanisms leading to the retention and release of the heavy metals. The geochemical modelling tool, PHREEQC version 2 was used for the simulations. Two main processes were considered:

- Geochemical equilibrium modelling of the behaviour of heavy metals in stabilized sediments by utilizing the Freundlich Isotherm
- Contaminant transport (1-Dimensional transport by diffusion) modelling

For both simulations, the thermodynamic data used were obtained from the PHREEQC database. Below is a scheme showing the procedure used in calibrating the model by a trial and error approach for the simulations.

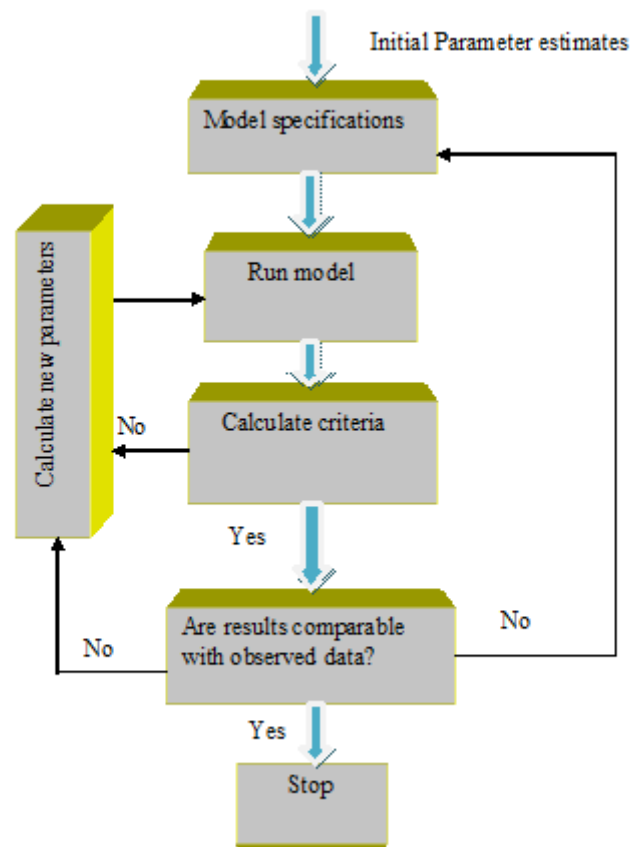


Figure 3.1 Procedure for model calibration using a trial and error approach

3.4.1 Adsorption capacity and adsorption isotherms

The adsorbed concentrations for the experimental data were obtained using the formula below:

$$C_s - (C_{iw} * V_L) / W$$

Where C_s is the initial concentration in sediment (mg/kg); C_{iw} is the concentration in the leachate (mg/L); V_L is the volume of leachant (L); and W is the mass of sediment (kg).

The Freundlich isotherm was used to estimate the adsorption capacity of the sediment towards the heavy metals and to compare results with the observed data. Due to time constraints, different adsorption isotherms were not tried to ascertain which isotherm best models the leaching of heavy metals from the three cement stabilized sediments. The Freundlich isotherm was chosen for this study for two principal reasons. Firstly, it is one of the most extensively used isotherms in modeling leaching of heavy metals from waste forms (Juang et al., 1996). Secondly, the Freundlich isotherm is non-linear and it describes sorption in which there is unlimited sorption capacity. Thus, for a first time approach, it was preferable to use an isotherm which assumes multi-sorption sites to gain a general view about the behaviour of the metals in the sediments. The empirical equation that is used to describe the Freundlich isotherm is given as:

$$C_{is} = K_{iF} C_{iw}^{ni}$$

Where K_{iF} is the Freundlich constant or capacity factor (distribution coefficient); and ni is the Freundlich exponent which, ranges between 0 and 1. The steepness and curvature of the isotherm are determined by the K_{iF} and ni , respectively. The Freundlich isotherm is linear if $n = 1$ and, as n decreases, the isotherm becomes more nonlinear. C_{iw} (kg/l) represents the equilibrium concentration in the liquid phase and C_{is} is the equilibrium amount sorbed (mass/kg).

The Freundlich equation above can be transformed into a logarithmic form to obtain linear equation as:

$$\log C_{is} = \log K_{iF} + ni \log C_{iw}$$

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Fitting $\log C_{is}$ against $\log C_{iw}$, the intercept $\log K_{iF}$ (the antilog of which equals K_{iF}) and the inclination n_i by regression can be generated.

The PHREEQC commands for the simulation of Pb and Cu sorption using the Freundlich adsorption isotherm are shown in appendices 1 to 12. The major data blocks under which specific commands are specified are represented with the bold upper cases. The `surface_master_species` data block defines the surface sites for sorption. The association reaction and thermodynamic data for the surface species have been described under the `surface species` data block. In PHREEQC, it is imperative for the mass-action equation to be defined. This can be derived from the chemical reaction equation that defines a species. The surface complexation reaction from which the correct mass-action equation for the Freundlich equation is generated is shown in the second line of the `surface species` data block. The `solution` data block defines the temperature and the composition of the solution. The data blocks `solution 1` and `surface 1` describe the moles of the heavy metals in solution and moles of surface sites available for the adsorption. Results of the simulations are shown and discussed in chapter four below.

3.4.2. Simulation of 1D-Transport of heavy metals by diffusion

The dispersal of contaminants by the intermolecular nature of gas, pore water, and surface water is known as molecular diffusion. Diffusion is one of the processes that control the release of elements from cement-based materials. Diffusion results in concentration gradient which is due to the progressive reduction of species as they migrate through the medium. Transport by diffusion has been used herein because many studies have indicated that when the permeability of the material under investigation is lower than 10^{-7} m/s, the principal mechanism governing the transport of contaminants is diffusion (Cheung et al, 1986). PHREEQC was used to simulate a 1-dimensional transport by diffusion that incorporates non-linear sorption isotherm from the cementitious sediment. The default PHREEQC values for transport processes in one-dimension were used. Transport calculations for 1 dimension were added to the input data from non-linear isotherm simulations to include the effects of sorption on transport of contaminants. Conditions for the TRANSPORT calculations were established next. The cells were divided into 20 segments with each being 0.0025 m in length. The number of shifts (which defines the

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number of diffusion periods) was 10. The effective diffusion coefficient (D_{eff}) was $3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and the experiment was assumed to be conducted for 2, 10 and 20 years i.e. $6.3 \times 10^7 \text{ s}$, $3.15 \times 10^8 \text{ s}$ and $6.3 \times 10^8 \text{ s}$, respectively. The PHREEQC commands for the simulation of Pb and Cu 1-D transport by diffusion incorporating non-linear sorption are shown in appendices 1 to 12.

3.4.2.1 Assumptions

In order to carry out the simulations, certain assumptions in modelling the transport of the heavy metals in the cementitious sediments were made. The assumptions include:

- The porous medium of the cementitious waste is homogeneous and isotropic.
- Metal migration occurs only through the aqueous phase so that there is no transport via other phases.
- The adsorption and desorption of metals in solid particles are reversible.
- Diffusion of pollutants is 1-dimensional and there is no advective flow
- The boundary condition is a constant flux

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Laboratory investigations by NGI

The project which lasted for two years, aimed at developing new techniques for stabilization and solidification of contaminated sediments using a stepwise approach. The following were studied to assess the effectiveness of the technique:

- Mechanical strength
- Permeability
- Leaching of heavy metals from stabilized material
- Leaching of tin organic constituents
- Leaching of organic compounds

This thesis uses the results obtained from the experiment on leaching of heavy metals from the stabilized material. Part of the results of the project has been used to throw more light on the factors affecting contaminant mobility in cement-stabilized sediments in chapter two of this study. However, for a detailed report, the reader is referred to the project entitled “Development of binder and additions, final report from phase 1, 2, and 3 (2006-2008)” (Sparrevik et al., 2006)

This section presents general results obtained from both the geochemical modelling and some part of the laboratory experiments. A general discussion of the results of the physical and mechanical characterisations of the sediments has been made here. However, discussions on the results of the chemical characterization of the sediments have been limited to only the two metals- lead and copper-, which are the principal focus of this study.

4.1.1 Characterization of sediments, cement and seawater

The physical and mechanical characterisations of the sediments and the cement used for the study are shown in Table 4.1. From the results, it can be observed that the bulk densities of the sediments ranged between 1.28 and 1.53 kg/l. The highest bulk density was measured for Hammerfest and the lowest for Bergen. Sediments from Bergen and Grenland had the same one-axial uncompressive strength of 0.1 KPa. It was impossible to determine the one axial uncompressive strength for Hammerfest due to the sandy nature of the sediments. The permeabilities of the sediments varied from $3.4 \cdot 10^{-9}$ to $4.5 \cdot 10^{-9}$ m/s. A relatively high water content of 196.4% was measured for Bergen with relatively very low water content of 21.7% for Hammerfest. The percentage of clay, sand, silt, and gravel, respectively, ranged between 0.6% and 17.3%; 15% and 68%; 15.4% and 67.4%; and 0 and 16%. Bergen recorded the highest percentage of clay and silt and the lowest percentage of sand and gravel. Hammerfest on the other hand was highest in terms of sand and gravel amounts and lowest in clay and silt. Measurements of the relative proportions of the different sediment separates for Grenland were between that of Bergen and Hammerfest. The total organic carbon ranged between 5.7% and 11%. The only physical parameter that was determined for the cement was TOC which was 0.6%. The others were not determined. The overall results of the particle size analysis for the different sediments according to the USDA (1999) indicated that sediments from Bergen and Grenland were silty loam whereas Hammerfest sediment was sandy loam. The low bulk density and high porosity of the Bergen sediment could be attributed to the high TOC and clay content. The high bulk density and low porosity of Hammerfest sediment may have also resulted from its high sand and gravel content and low clay and organic matter content. It is also observed that, even though the TOC determined for Grenland was the lowest, it gave a higher bulk density and porosity compared to Hammerfest and lower compared to Bergen. This may be attributed to its clay and silt fractions. These explanations are in agreement with the explanations given by Tan (2000).

Table 4.2 below is the result of the chemical characterization of the sediments and cement. The concentrations of lead measured in the sediments ranged from 210 mg/kg to 650 mg/kg, and 34 mg/kg for the cement. The highest was measured for Bergen and the lowest for Hammerfest. The concentration of copper was also between 51 mg/kg and 410 for the

Simulation of heavy metal leaching from cement-stabilized polluted sediments

sediments and 170 mg/kg for the cement. Bergen recorded the highest concentration and the lowest was measured for the specimen from Grenland. According to the Norwegian classification system for contaminated sediments, all the three sediments have been heavily contaminated with lead. The contamination of Bergen with Cu is very heavy, whereas it is heavy and significant contamination for Hammerfest and Grenland, respectively. The cement used also shows a very heavy contamination with Cu (Sparrevik et al., 2006).

Table 4.3 is the result of the physical and chemical characterization of the seawater. The concentrations of Pb and Cu were 1.53 μ g/l and 1.36 μ g/l, respectively. It can be observed that the amounts of Cu and Pb present in the seawater are several magnitudes lower compared to their concentrations in the sediments. It is therefore assumed that the input from seawater in terms of Cu and Pb are negligible and are therefore not included in the calculations.

Table 4.1 Physical and mechanical characterisation of the sediments and cement

Parameter	Unit	sediments			Cement
		Bergen	Grenland	Hammerfest	
Bulk density	(kg/l)	1.28	1.38	1.53	-
One axial strength	(KPa)	0.1	0.1	-	-
Permeability	(m/s)	3.4*10 ⁻⁹	4.5*10 ⁻⁹	4.4*10 ⁻⁹	-
Water content	(%)	196.4	113.5	21.7	-
TOC	(%)	11	5.7	6.8	0.64
Clay	(%)	17.3	8.4	0.6	-
Silt	(%)	67.7	58.6	15.4	-
Sand	(%)	15	31	68	-
Gravel	(%)	0	2	16	-
Porosity	(%)	52	48	42	-

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Table 4.2 Chemical characterisation of the sediments and cement

Parameter	Sediments (mg/kg)			Cement (mg/kg)
	Bergen	Grenland	Hammerfest	
Arsenic	21	14	6, 5	13
Lead	650	270	210	31
Cadmium	3, 2	6, 3	0, 52	<0, 2
Chromium	70	27	20	82
Copper	410	51	67	170
Mercury	13	1, 9	0, 8	<0, 05
Nickel	23	14	15	24
Zinc	1200	890	270	120
TBT (µg/kg)	790	170	93	<1
Chlorobenzene	<0, 01	0, 08	0,021	<0, 01
PAH benzo (a) pyrene	4, 6	1, 5	1, 3	<0, 1*
Sum 16 PAH	37	16	19	<0, 8*
PCB Sum 7 PCB	0, 24	0, 25	0, 11	<0,025
Oil Fraction > C5-C8	<10	<10	<10	<10
Fraction > C8-C10	<10	<10	<10	<10
Fraction > C10-C12	7, 2	<2, 0	<2, 0	<2, 0
Fraction > C12-C16	280	19	28	6.4
Fraction > C16-C358	5000	730	760	70

Legend:

Bold/ italic

below

detection limit. Half of detection limit is used for classification

* *no classification performed in case of elevated detection limit

Class i
Class ii
Class iii
Class iv
Class v

Low contamination

Moderate contamination

Significant contamination

Heavy contamination

Very heavy contamination

-No class definitions/too high detection limit to classify

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Table 4.3 Physical and Chemical characterisation of the Seawater

Chemical	Parameters	Units	Amount
Metals	Arsenic	µg/l	<0.5
	Lead	µg/l	1.53
	Cadmium	µg/l	<0.05
	Chromium	µg/l	2.24
	Copper	µg/l	1.36
	Mercury	µg/l	<0.002
	Nickel	µg/l	<0.05
	Zinc	µg/l	4.39
	TBT	ng/l	<1
	Chlorobenzene	µg/l	<0.1
PAH	benzo (a) pyrene	µg/l	<0.02
	Sum 16 PAH	µg/l	<0.19
PCB	sum 7 PCB	µg/l	<0.02
Oil	fraction > C5-C8	µg/l	<10
	Fraction > C8-C10	µg/l	<10
	Fraction > C10-C12	µg/l	<5
	Fraction > C12-C16	µg/l	<5
	Fraction > C16-C358	µg/l	<30
Physical	TOC	mg/l	1.3
	Density	kg/l	1.023

4.2 Results of the XRD analysis

The results of the XRD analysis have been presented in the Tables 4.4, 4.5, and 4.6 below. There were significant differences in the mineral content of the different sediments. The analysis showed that the Hammerfest sediment contains quartz, albite, halite, calcite, gypsum and muscovite as the dominant minerals. Sediment from Bergen was found to be composed dominantly of quartz, pyrite, albite, halite, calcite, amphibole, biotite, K-feldspar and chlorite. Sediment from Grenland mainly consisted of quartz, K-feldspar, albite, halite, illite, amphibole and kaolinite. The percentage compositions of the different minerals in the sediments have been shown in the same tables.

Quartz, albite and halite were common to all the sediments. Halite is common to all of them probably because the sediments are marine sediments. Quartz is also common to the three sediments because it is the second most abundant mineral in the earth's continental crust, after feldspar. Feldspars or plagioclase feldspar (albite) are also common to all the minerals because of their abundance in the earth's continental crust. The other minerals are probably due to the differences in the geology of the area.

The particle size analysis of Hammerfest sediments indicated that the percentage of particles which fall within the clay fraction is 0.6%. The XRD analysis however, did not show the presence of any clay mineral in the Hammerfest sediment, which probably means the particles are only clay-sized particles and not necessarily clay minerals.

Sediments from Bergen and Grenland on the other hand contained clay minerals such as illite, kaolinite and chlorite. Bhattacharyya and Gupta (2008) demonstrated that sediments with such characteristic clay minerals have been good adsorbents because of the existence of several types of active sites on the surface- and ion-exchange sites. Though their percentage amounts in the sediments are relatively small, their presence in the sediments could influence the adsorption of the heavy metals. Sediment from Bergen contained additional mineral, pyrite which has also been shown to demonstrate a strong affinity for metals due to the presence of sulphide.

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Table 4.4 XRD analysis results for sediments from Hammerfest

Minerals	Empirical formula	Percentage composition
Quartz	SiO ₂	64
Albite	NaAlSi ₃ O ₈	24
Halite	NaCl	2
Calcite	CaCO ₃	7
Gypsum	CaSO ₄ ·2 H ₂ O	1
Muscovite	KAl ₂ Si ₃ AlO ₁₀ (OH) ₂	2

Table 4.5 XRD analysis results for sediments from Bergen

Mineral	Empirical formula	Percentage composition
Quartz	SiO ₂	28
Pyrite	FeS ₂	3
Albite	NaAlSi ₃ O ₈	33
Chlorite	(Ni,Mg,Al) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	1
Dolomite	Ca(Mg,Fe)(CO ₃) ₂	1
K-feldspar	KAlSi ₃ O ₈	18
Halite	NaCl	8
Calcite	CaCO ₃	7
Amphibole	(Na _{2(0,02)} Ca _{0,85} K _{0,1})(Mg _{4,63} Ti _{0,16} Cr _{0,08} Al _{0,07} Fe _{0,05})Si ₈ O ₂₂ F	1
Biotite	K(Mg,Fe ⁺²) ₃ (Al,Fe ⁺³)Si ₃ O ₁₀ (OH,F) ₂	3

Table 4.6 XRD analysis results for sediments from Grenland

Mineral	Empirical formula	Percentage composition
Quartz	SiO ₂	64
K-feldspar	KAlSi ₃ O ₈	7
Albite	NaAlSi ₃ O ₈	18
Halite	NaCl	3
Illite	K _{0,5} (Al,Fe,Mg) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂	5
Amphibole	Na ₂ Fe ₃ Fe ₂ Si ₈ O ₂₂ (OH) ₂	2
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	1

4.3 RESULTS FROM GEOCHEMICAL SIMULATION

This part of the thesis was carried out to investigate the possibility of using geochemical modelling code, PHREEQC to simulate the behaviour of the heavy metals in the three stabilized sediments. Issues which have been investigated in connection with this study include:

- Investigating the possibility of fitting a simplified adsorption isotherm to the experimental data to describe the behaviour of the two heavy metals in the stabilized sediments.
- Comparing the different sediments in terms of their adsorption capacities, diffusive transport and their long-term behaviour in the stabilized sediments. This aspect of the study is of prime importance and worth investigation because the information generated from the leaching tests could be used on short time scale and it is not certain whether or not the heavy metals will behave similarly in the long term. In addition, information obtained from this study will help in assessing management options.

Results of the simulations have been presented on the same graphs as the experimental data for easy comparison and discussed below. The equations for all the curves were obtained by using the non-linear Freundlich model.

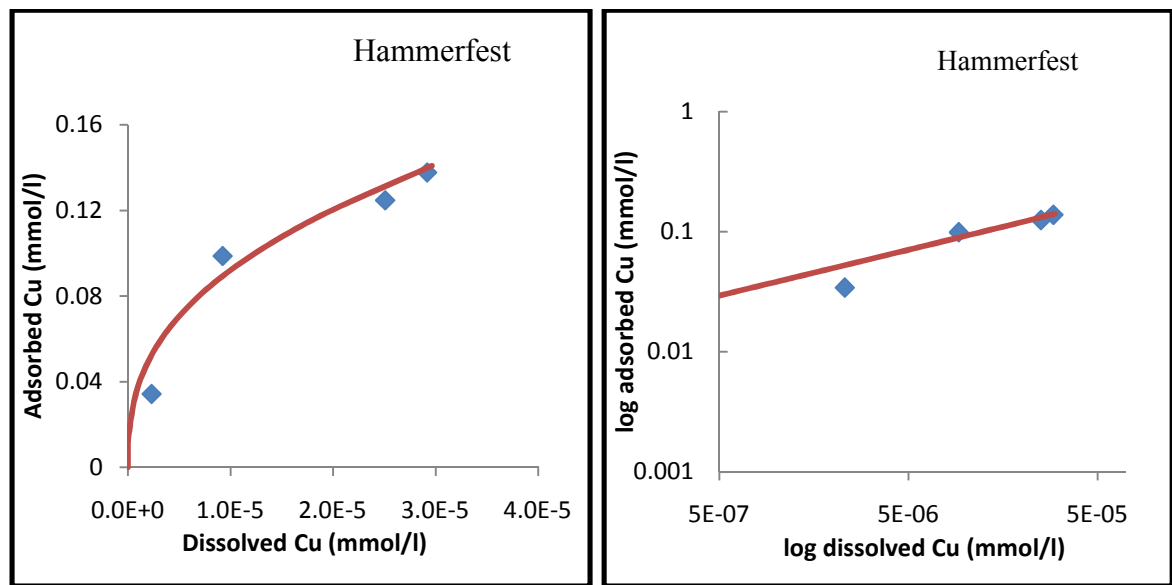
4.3.1 Adsorption isotherms of Cu and Pb for the different stabilized sediments

The simulated Freundlich isotherms and experimental data plots for Cu and Pb for the different stabilized sediments using the linear and non-linear Freundlich equations are shown in figures 4.1 to 4.6 below, as the amount of Cu or Pb adsorbed to the stabilized sediments as a function of the equilibrium aqueous concentration. The results show different adsorption characteristics for the different stabilized sediments. The study has, however, revealed that it is possible to use a simplified Freundlich adsorption equation to describe the behaviour of the contaminants in the sediments as the model fitted rather well to the experimental data as shown in Figures 4.1 to 4.6.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

The deviations of the experimental data from the Freundlich isotherm, however, may be attributed to the availability of exposed particle surfaces or other compounds that could result in rapid immobilization of the contaminants, which may not have been accounted for by the model. Furthermore, results generated from the model were the equilibrium concentrations for both the adsorbed and dissolved phases since the model has only been designed to operate on equilibrium basis for such reactions. However, in the experiment, it is uncertain that reactions were allowed to attain equilibrium before measurements were taken. Further explanations given by Appelo and Postma (2005) indicate that some chemical phenomena of equilibrium chemistry are insufficiently explained, and that many of the minerals that are involved in sorption processes are thermodynamically unstable. Factors such as variations in grain sizes, preferred fluid flow paths, primary and secondary mineral coatings that can decrease the porosities of the material and affect experimental results which are usually not accounted for by geochemical models (Palandri and Kharaka, 2004) could also explain the differences between the results from the experiment and the model. To address such limitations, Phanikumar and McGuire (2004) suggested that a combination of equilibrium and kinetics should be used. However, geochemical models that have been designed with such capabilities are limited (Aagaard et al., 2001).

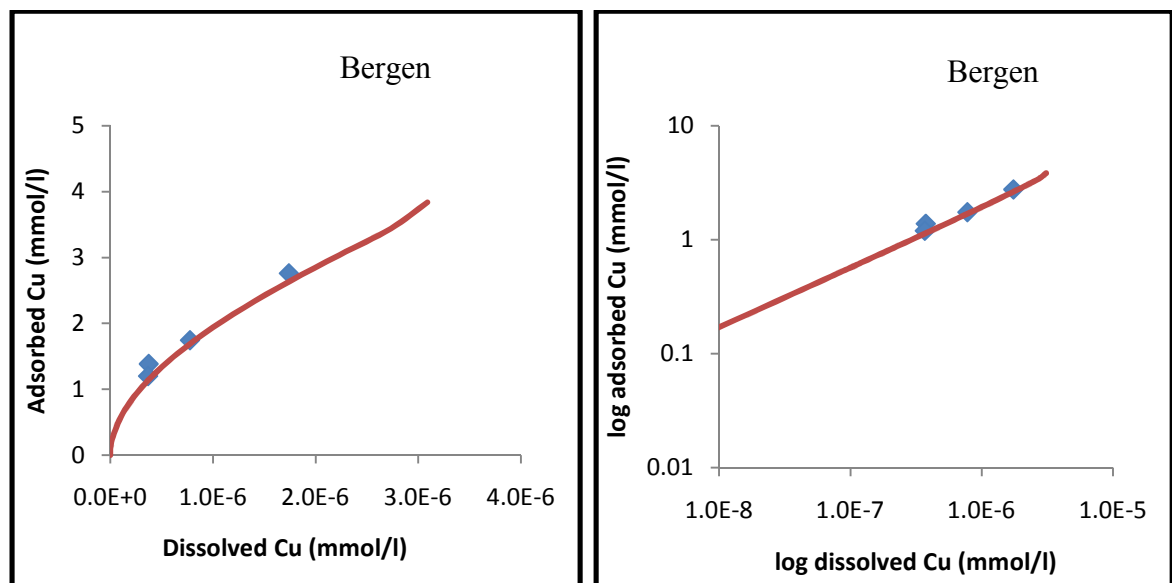
Simulation of heavy metal leaching from cement-stabilized polluted sediments



a)

b)

Figure 4.1 Equilibrium adsorption isotherms for Cu for stabilized sediment from Hammerfest. The symbols are the experimental data points and the solid line represents a) Freundlich isotherm obtained by non-linear regression analysis of the experimental data and b) linearized Freundlich isotherm obtained by transforming the non-linear Freundlich equation to a logarithmic form.

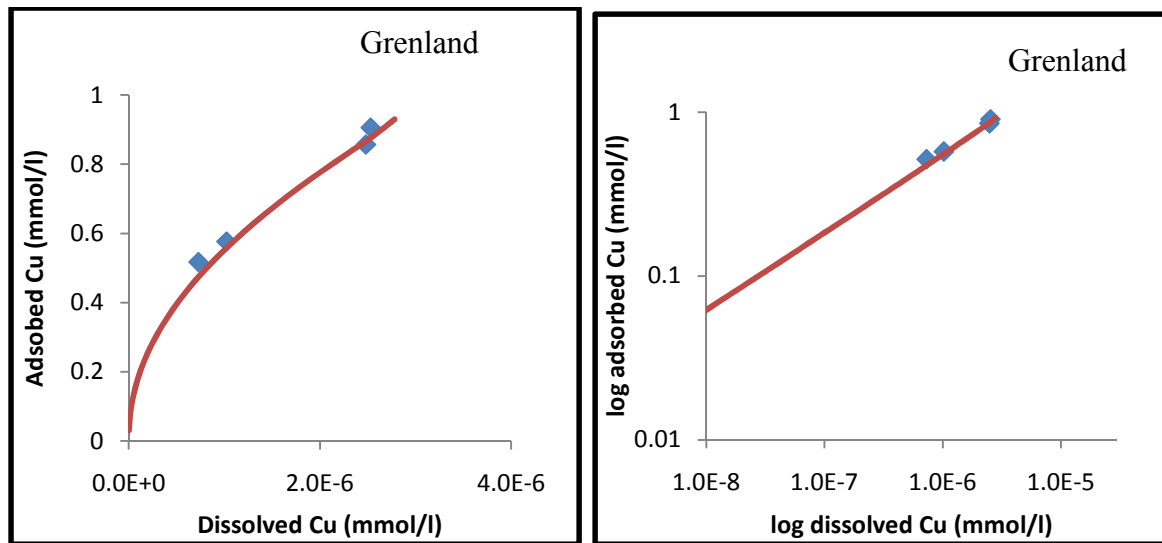


a)

b)

Figure 4.2 Equilibrium adsorption isotherms for Cu for stabilized sediment from Bergen. The symbols are the experimental data points and the solid line represents a) Freundlich isotherm obtained by non-linear regression analysis of the experimental data and b) linearized Freundlich isotherm obtained by transforming the non-linear Freundlich equation to a logarithmic form.

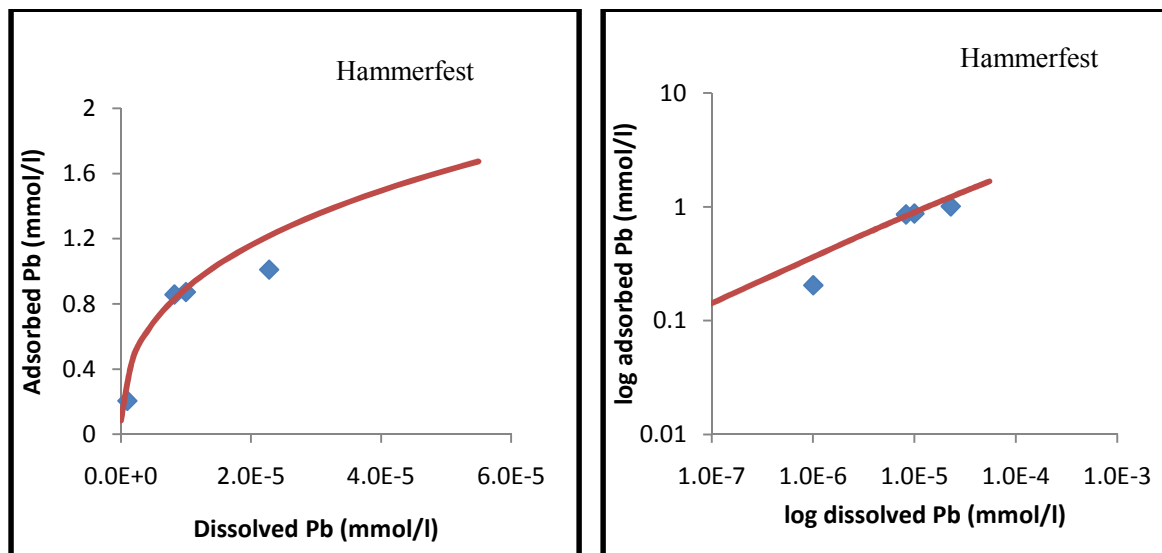
Simulation of heavy metal leaching from cement-stabilized polluted sediments



a)

b)

Figure 4.3 Equilibrium adsorption isotherm of Cu for stabilized sediment from Grenland. The symbols are the experimental data points and the solid line represents a) Freundlich isotherm obtained by non-linear regression analysis of the experimental data and b) linearized Freundlich isotherm obtained by transforming the non-linear Freundlich equation to a logarithmic form.



a)

b)

Figure 4.4 Equilibrium adsorption isotherm of Pb for stabilized sediment from Hammerfest. The symbols are the experimental data points and the solid line represents a) Freundlich isotherm obtained by non-linear regression analysis of the experimental data and b) linearized Freundlich isotherm obtained by transforming the non-linear Freundlich equation to a logarithmic form.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

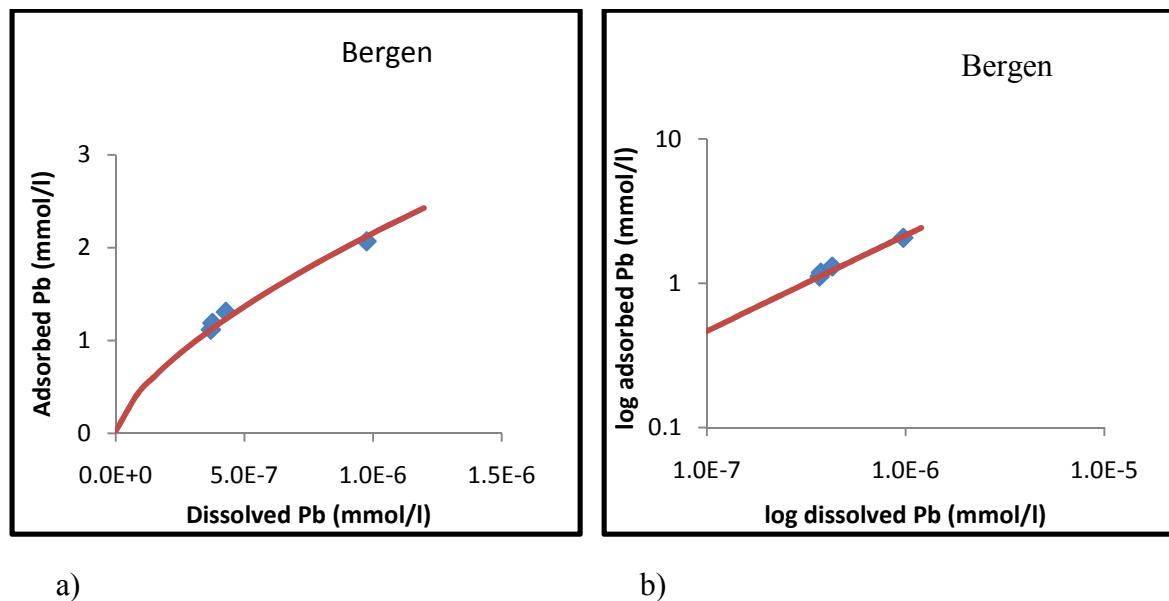


Figure 4.5 Equilibrium adsorption isotherm of Pb for stabilized sediment from Bergen. The symbols are the experimental data points and the solid line represents a) Freundlich isotherm obtained by non-linear regression analysis of the experimental data and b) linearized Freundlich isotherm obtained by transforming the non-linear Freundlich equation to a logarithmic form.

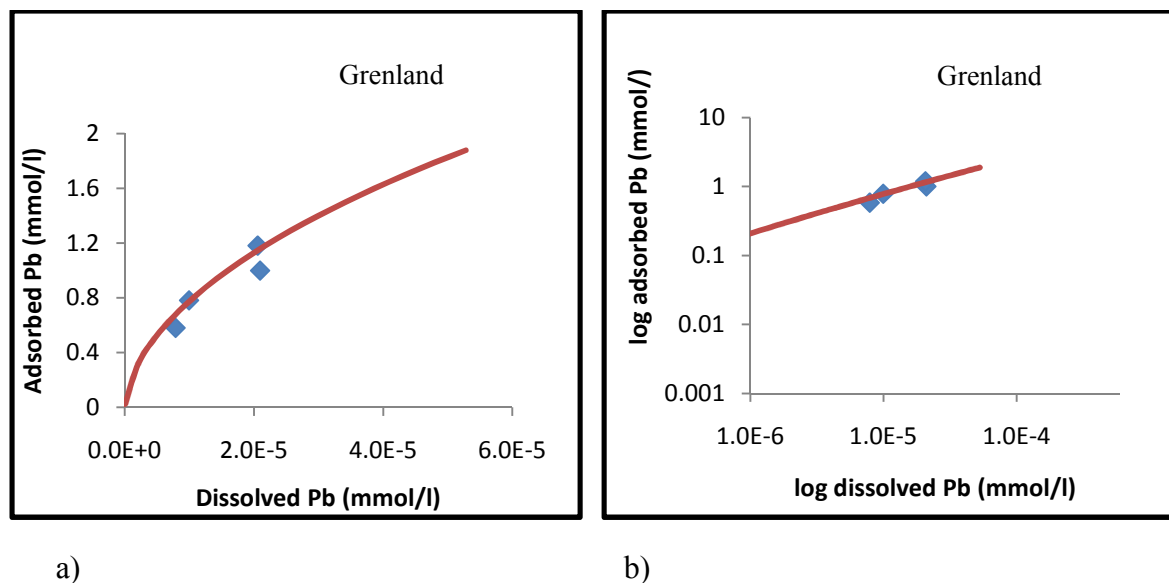


Figure 4.6 Equilibrium adsorption isotherm of Pb for stabilized sediment from Grenland. The symbols are the experimental data points and the solid line represents a) Freundlich isotherm obtained by non-linear regression analysis of the experimental data and b) linearized Freundlich isotherm obtained by transforming the non-linear Freundlich equation to a logarithmic form.

4.3.2 Adsorption capacities of the different sediments for Cu and Pb

As mentioned in the preceding chapters, adsorption is one of the key processes that can stabilize heavy metals in cement-stabilized sediments. In this study, a non-linear Freundlich isotherm was used to obtain the adsorption capacity, K_{iF} and the adsorption intensity, n_i of the Freundlich isotherm for Cu and Pb for the different sediments. Results are presented in Table 4.7 below and in Figures 4.7 and 4.8, plots of the isotherms for the different sediments have been made on the same graph to show the differences in adsorption capacities of the different stabilized sediments for Cu and Pb, respectively. The results revealed that the adsorption capacities of the different sediments for Cu and Pb ranged from 37 to 2781(L/L) and 431 to 9615 (L/L), respectively. The degree of deviation from non-linearity, n_i for the different stabilized sediments was also found to be between 0.38 and 0.52 for Cu, and 0.54 and 0.61 for Pb. Results show that stabilized sediment from Bergen has relatively high K_{iF} and n_i for both metals indicating relatively high adsorption capacities and intensities for both metals. On the other hand, the K_{iF} and n_i calculated for the stabilized sediment from Hammerfest were relatively low which suggests a low adsorption capacity and intensity of the sediment for the two heavy metals. The adsorption capacities of the sediment from Grenland towards the two heavy metals were between those obtained for Hammerfest and Bergen. The isotherms for the Bergen stabilized sediments were steeper than those of Grenland and Hammerfest due to the relatively high n_i values. Generally, all the sediments showed a consistent preference in adsorbing Pb than Cu as demonstrated by the sediments adsorption capacities and intensities for the Pb and Cu. This result is similar to what Saeedi et al. (2010) observed in their study on competitive heavy metals adsorption on natural bed sediments of Jajrood River.

There are a number of physico-chemical factors, as discussed in chapter two of this study that control the interaction between contaminants and sediments. Some of these factors may have influenced the results obtained. Factors such as pH control and redox potential of the waste have been documented as some of the principal parameters that greatly influence the adsorption of metals in the cement stabilized sediments (Buchter et al., 1989; Connor and Hoeffner, 1998). In the previous study done by NGI, an attempt was made using the pH and redox potential of the stabilized sediments to explain the behaviour of the heavy metals. In chapter two of this study, the results have briefly been discussed. Particularly for

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redox potential, results showed some correlation between this parameter and the behaviour of the metals. However, these two controlling factors alone could not be used to explain the results found in the experiment. In this study, however, an attempt has been made using the mineralogical composition and other physical parameters such as grain size and TOC to elucidate the behaviour of the metals. From the XRD analysis, the mineralogical composition of the sediments indicated the presence of pyrite (FeS_2) in the sediment from Bergen. Sulphides generally have high preference for heavy metals such that in the presence of heavy metals, iron is displaced in the pyrite and the resulting H_2S reacts with the heavy metals to form precipitated metal sulphides with low solubility (Hansen et al., 1996). This could explain the low leaching concentrations of both lead and Cu from the stabilized sediment from Bergen. Jain and Ram (1997) and Jain et al. (2004) have reported that the extent of adsorption of metal ions on sediments generally decreases with large adsorbent particle size. Fine particles result in increased surface area and hence, increased interaction between the heavy metals and the sediments. According to the XRD analysis, however, quartz is the dominant mineral in Hammerfest and Grenland sediments. Quartz has been documented to have low sorption capacity for metals (Crannell et al., 2004) and the sizes are generally larger than clay particles. Bergen on the other hand was relatively high in clay-sized particles. This may have also contributed to the low adsorption of the heavy metals in the Grenland and Hammerfest sediments and high heavy metal adsorption in the Bergen sediment.

It has also been documented in many studies that clay-rich sediments generally have higher retention capacities than sediments with little or no clay (Harvey and Murray, 2006; Bhattacharyya and Gupta 2008). No clay mineral was found in the Hammerfest sediments according to the XRD analysis whereas some clay minerals were found in Bergen and Grenland sediments. This probably may have also contributed to the higher adsorption capacities of the sediments from Bergen and Grenland in comparison with the Hammerfest sediment. The role of organic carbon in heavy metal adsorption is also worth mentioning. A wealth of information in the literature has indicated that organic matter is the most important sorbent that controls the activity of Cu^{2+} and Pb^{2+} in sandy materials (Weng et al., 2001). The physical characterization of the sediments revealed that quartz-dominated

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Hammerfest and Grenland sediments were low in TOC whereas Bergen was high in organic matter which possibly favoured the adsorption of the heavy metals. All these differences in the physical and chemical properties of the sediments may have contributed to the observed behaviour of the metals in the stabilized sediments. It can therefore be said that not a single parameter is controlling the observed behaviour of the heavy metals in the sediments, but a multiple of factors. This buttresses the conclusion of Sparrevik et al. (2009) who indicated that adsorption/leaching of heavy metals from stabilized materials is dependent on the physical conditions and the chemical composition of the sediment, and the interaction with the stabilizing agents

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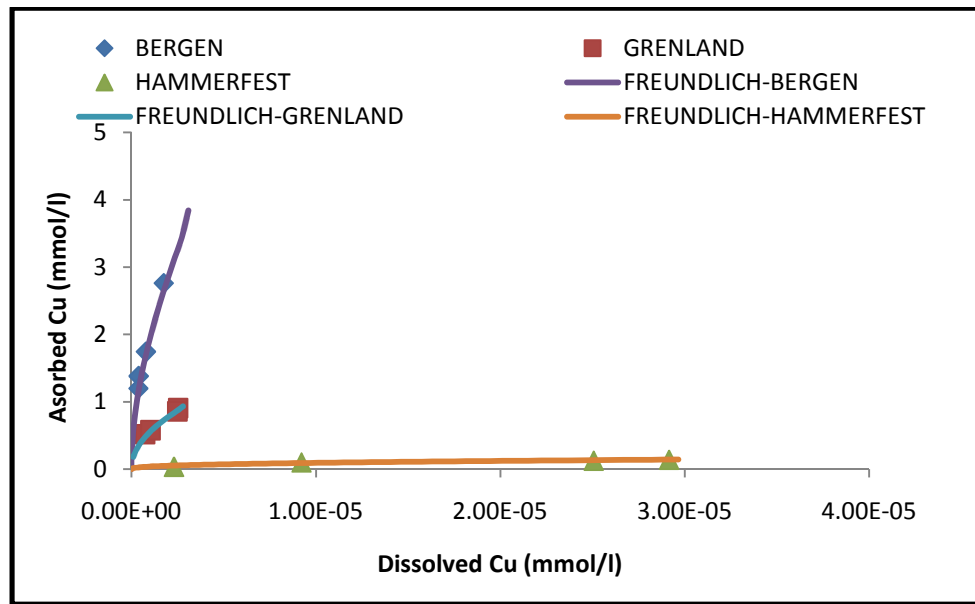


Figure 4.7 Comparing sorption isotherms of Cu for the three stabilized sediments. The symbols are the experimental data points and the solid line represents Freundlich isotherm obtained by non-linear regression analysis of the experimental data

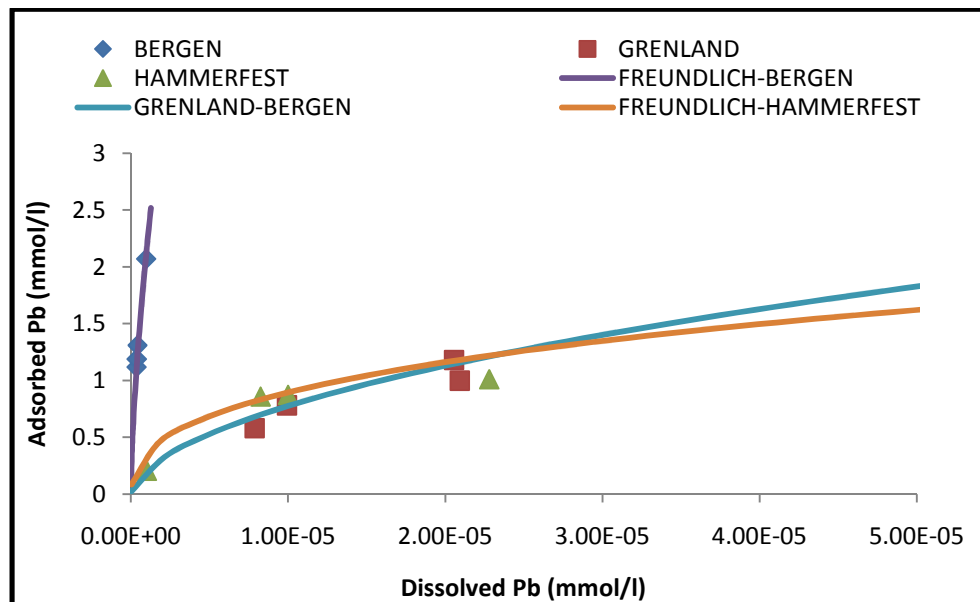


Figure 4.8 Comparison of sorption isotherms of Pb for the three stabilized sediments. The symbols are the experimental data points and the solid line represents Freundlich isotherm obtained by non-linear regression analysis of the experimental data

Table 4.7 Coefficient of determination and Freundlich constants for the adsorption of Cu and Pb in the three sediments

Heavy metal	Sediment	K_F (L/L)	n_i	R^2
Cu	Bergen	2781	0.52	0.971
	Hammerfest	37	0.38	0.944
	Grenland	443	0.48	0.992
Pb	Bergen	9615	0.61	0.988
	Hammerfest	431	0.54	0.943
	Grenland	591	0.58	0.898

4.3.3 1-D diffusional transport of heavy metals and their long term stabilities

Diffusive transport of the heavy metals that incorporates a non-linear sorption of the contaminant was used to study the release and the long-term behaviour of the heavy metals in the stabilized sediments. As is illustrated by the conceptual model below, the fluxes of contaminants were estimated after certain periods of time. It was assumed here that the stabilized material is 5cm long and it is submerged in seawater. The fluxes (the concentration of the contaminants that will diffuse out of the stabilized material from the reservoir through the cells into the sea water) after 2, 10 and 20 years were then estimated to study the release rate of contaminants and the long-term effects of stabilization on the release of heavy metals from the stabilized material. Fick's first law which relates the flux of a chemical to the concentration gradient was the governing equation used. The equation is given as:

$$F = - D_e \delta c / \delta x$$

D_e is the effective diffusion coefficient (m^2/s). It integrates the porosity of the material and the diffusion coefficient. The D_e has been applied here because in porous media, diffusion cannot proceed as fast as it can in water due to the fact that ions must follow longer pathways as they travel around mineral grains. The concentration in mol/m^3 is represented

Simulation of heavy metal leaching from cement-stabilized polluted sediments

by c and x is the distance in m. The negative sign indicates that the movement is from greater to lesser concentrations.

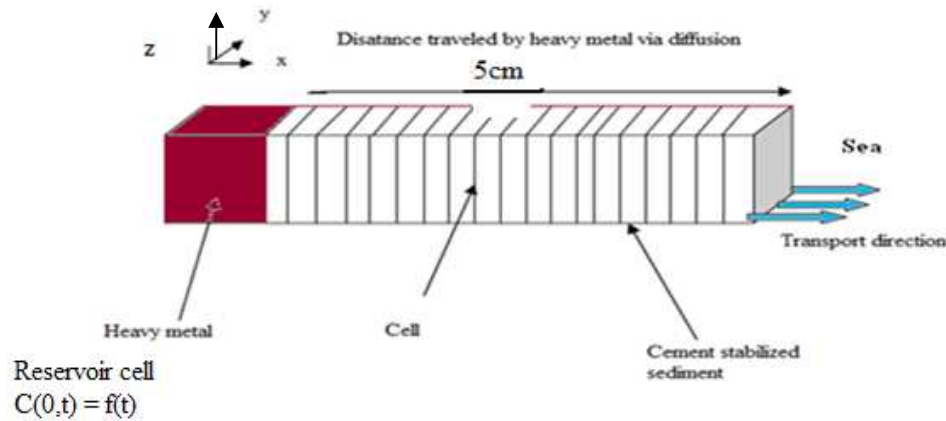


Figure 4.9 A conceptual model showing a 1-D transport of heavy metals by diffusion from stabilized polluted sediments in seawater. The cells are filled with seawater. According to the Cartesian co-ordinate system, diffusion happens from left to right. The figure is not drawn to scale.

Figures 4.10 to 4.14 below show the diffusive transport of heavy metals from three stabilized sediments at three time spans (2, 10 and 20 years) after stabilization.

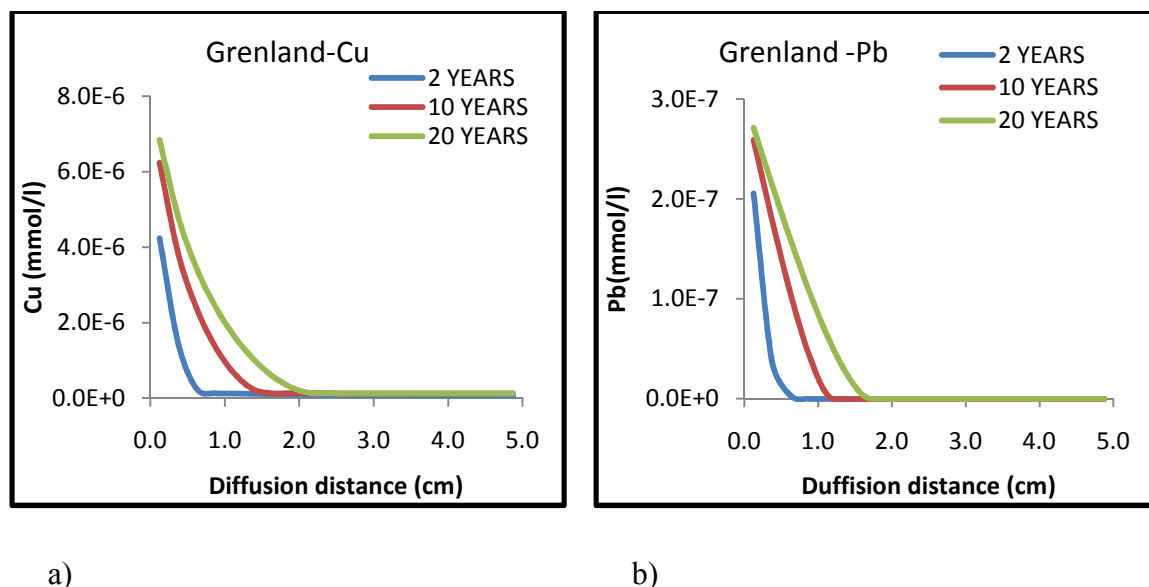
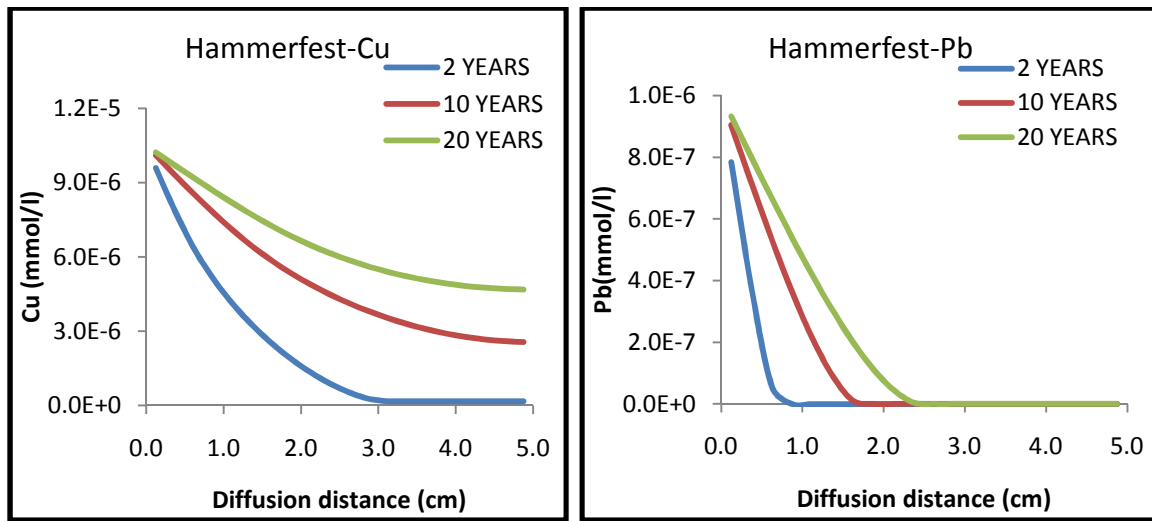


Figure 4.10 1-D transport of a) Cu and b) Pb by diffusion from a 5cm stabilized sediment from Grenland to sea water after 2, 10 and 20 years of stabilization

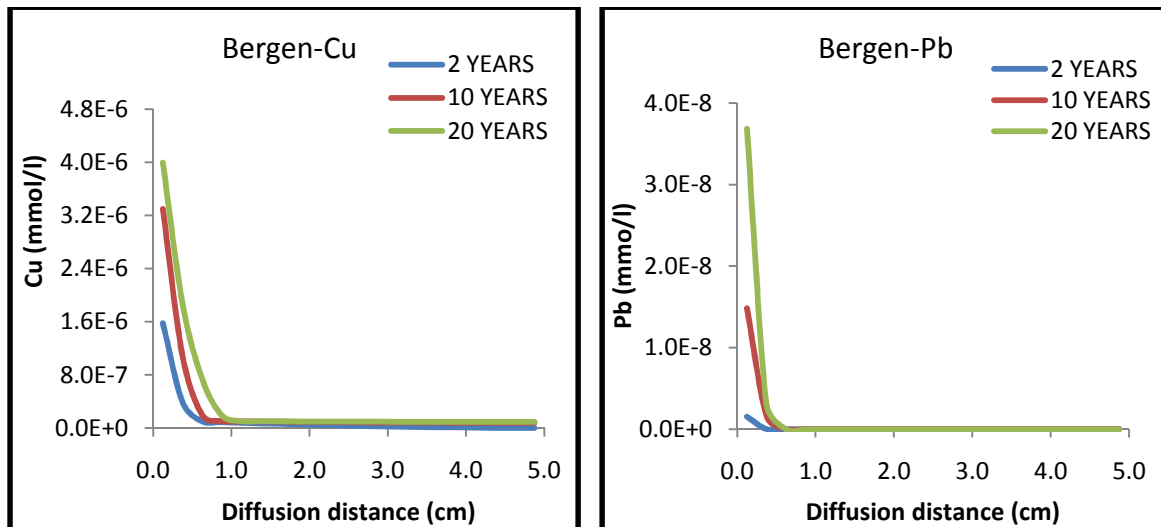
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a)

b)

Figure 4.11 1-D transport of a) Cu and b) Pb by diffusion from a 5cm stabilized sediment from Hammerfest to sea water after 2, 10 and 20 years of stabilization



a)

b)

Figure 4.12 1-D transport of a) Cu and b) Pb by diffusion from a 5cm stabilized sediment from Bergen to sea water after 2, 10 and 20 years of stabilization

From figures 4.10 to 4.12, it can be observed that irrespective of the sediment type and the various processes prevailing in them, the diffusive distance increases with year in all the stabilized sediments as the concentrations of the heavy metals reach very low or non-detectable levels at shorter distances for shorter time scales and further for longer time scales.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Figures 4.13 to 4.14 below show a comparison of the fluxes of Cu and Pb, respectively for the three stabilized sediments. The calculated fluxes have also been presented in Tables 4.8 and 4.9 below for Cu and Pb, respectively.

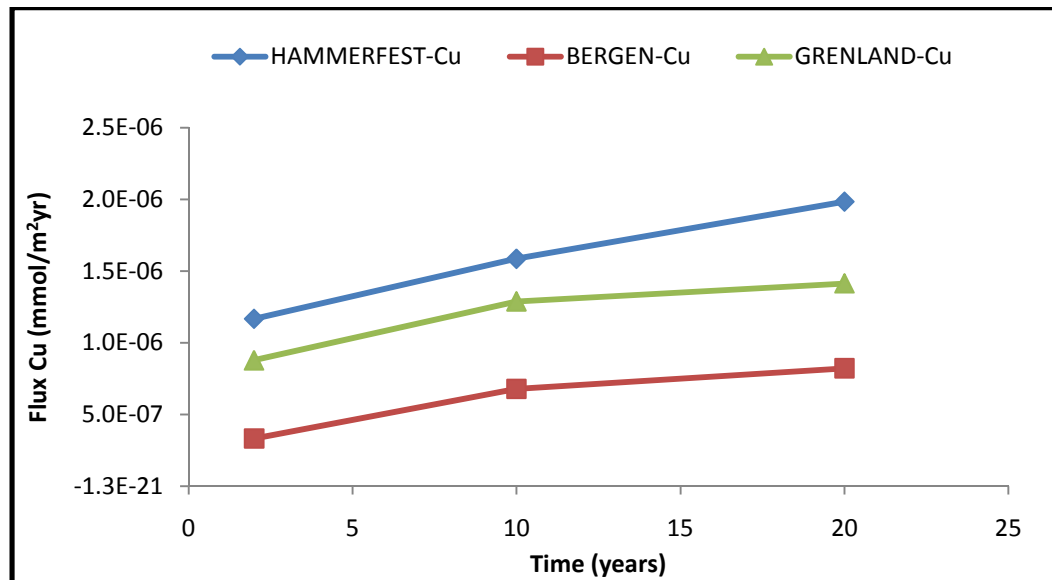


Figure 4.13 Comparing sorption isotherms of Cu after 2, 10 and 20 years of stabilization for the three stabilized sediments.

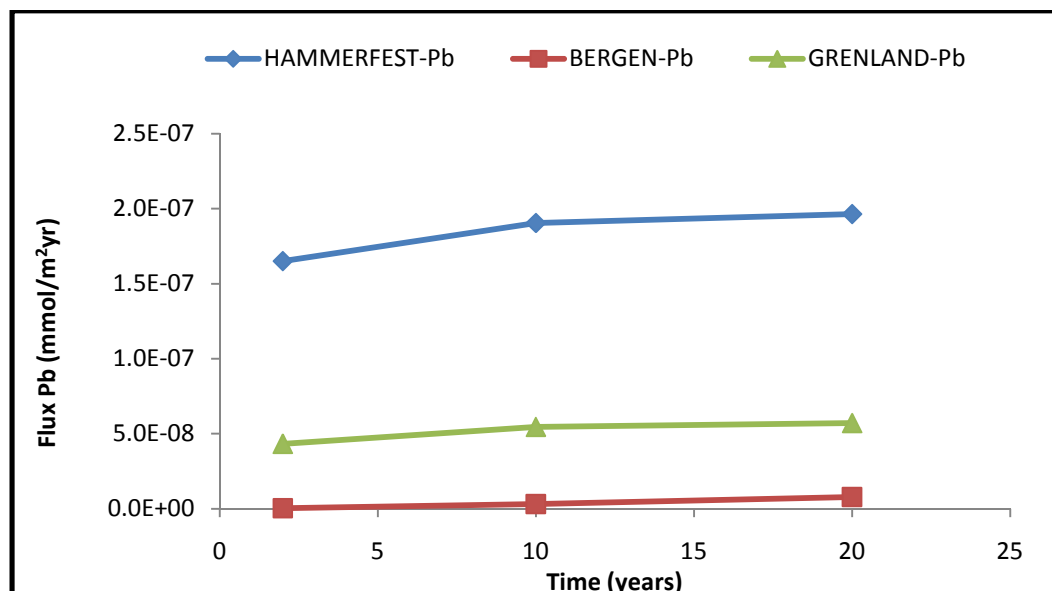


Figure 4.14 Comparison of Pb fluxes after 2, 10 and 20 years of stabilization for the three stabilized sediments.

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Table 4.8 Fluxes of Cu ($\mu\text{mol}/\text{m}^2\text{yr}$) in the three sediments after 2, 10 and 20 years of stabilization

Time (years)	Bergen	Grenland	Hammerfest
2	3.32E-04	8.78E-04	1.17E-03
10	6.78E-04	1.29E-03	1.59E-03
20	8.22E-04	1.41E-03	1.98E-03

Table 4.9 Fluxes of Pb ($\mu\text{mol}/\text{m}^2\text{yr}$) in the three sediments after 2, 10, and 20 years of stabilization

Time (years)	Bergen	Grenland	Hammerfest
2	3.20E-7	4.33E-05	1.65E-04
10	3.13E-06	5.46E-05	1.90E-04
20	7.77E-06	5.71E-05	1.96E-04

The intent of this part of the study was to:

- Investigate the effect of stabilization on the release of heavy metals and their long term behaviour in the stabilized sediments.

It is to be noted that the effectiveness of stabilization with cement cannot be expected to last longer than a few decades (Baccini and Brunner, 1985). This has been supported by Bone et al. (2004) who indicated that the service conditions of cement deteriorate over long periods, leading to the release of heavy metals. This happens due to the disruption of equilibrium between the solid and aqueous phases by internal or external factors which create an imbalance in some of the processes that control the retention/adsorption phenomena in the cement and eventually result in the release of contaminants. Usually, for there to be a continued retention of heavy metals in the cement stabilized sediments, it is of

Simulation of heavy metal leaching from cement-stabilized polluted sediments

necessity that a quasi-equilibrium be maintained between the solid and aqueous phases (Bone et al. 2004). For instance, the aqueous phase present in the pore structure of cement-based waste forms is alkaline. This usually promotes the precipitation/retention of insoluble species, particularly metal hydroxides. Thus, if metals are to be retained over long term periods, the alkalinity of the pore fluid has to be maintained. However, with continuous interaction of the components within and without the cement stabilized waste form over time, the alkalinity of the pore fluid can be expected to reduce. This then results in mobilization of some of the contaminants.

The results have shown a steady increase in the fluxes of Cu and Pb for each time span in all the three stabilized sediments which, generally agree with the hypothesis that the service conditions of the cement deteriorates over time culminating in mobilization of contaminants. The increase is however higher for Cu than for Pb. Stabilized sediment from Bergen recorded the lowest fluxes for both Cu and Pb. On the other hand, the release rates of Cu and Pb were relatively high for each time span for the Hammerfest sediment, with stabilized sediment from Grenland showing an intermediate release rate. The results of the calculated fluxes show that both metals releases from all the stabilized sediments are influenced by their adsorption to the stabilized sediments. For instance, relatively low fluxes were calculated for stabilized sediment from Bergen whose adsorption capacity for the two metals was relatively high whilst relatively high fluxes were calculated for Hammerfest sediment whose adsorption capacity was relatively low.

The main purpose of stabilization is to keep contaminants out of the aqueous phase thereby minimizing their mobility and toxicity effects. From the fluxes calculated, it is clear how much of the contaminants will be released into solution after each time span. The results have also made it evident that after 20 years of stabilization there are still considerable amounts of the heavy metals retained. On the other hand, comparing the fluxes after 20 years with the concentrations of the heavy metals in the sediments (Table 4.2), it can be said that it will take several years for all the heavy metals to be released from the stabilized sediments. In uncontaminated seawater, the accepted range for total copper is 0.07-10 $\mu\text{g/l}$ (Spencer et al., 1970; Alexander and Corcoran, 1967) and that of lead is 0.03 $\mu\text{g/l}$ (Turekian, 1968). Comparing the fluxes of the heavy metals to the background concentrations in the seawater in Table 4.3, and the accepted concentrations in seawater,

Simulation of heavy metal leaching from cement-stabilized polluted sediments

the concentrations of heavy metals released from all the three sediments were very low which can even be reduced further in the sea due to dilution and precipitation or complexation with other compounds. As a result, it can be said that the releases of Cu and Pb from the stabilized sediments may not represent a great threat to marine life or to the environment as a whole for the time periods and under the conditions studied. However in future, if any of the metals is to be given attention with respect to posing any threat to the environment, it should be copper due to its low retention and relatively high release rates from the three sediments.

On the whole, the fluxes for the different time spans have given an indication of the effectiveness of cement stabilization in the different sediments on a long term basis. Comparing all the three sediments in terms of effectiveness in stabilizing the two heavy metals studied on long term basis, the following observation was made:

Bergen > Grenland > Hammerfest



Effectiveness in stabilizing contaminants in a decreasing order

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

This study was conducted with an objective of using geochemical modelling to simulate the binding and release mechanisms of two heavy metals, Cu and Pb in cement-stabilized polluted sediments. Sorption isotherms for the heavy metals were first studied using the Freundlich sorption isotherm. Experimental data from the leaching experiments done by NGI were used in this study. A 1-dimensional transport based on PHREEQC using diffusion and a non-linear sorption was used to predict the long-term behaviour of the heavy metals by simulating heavy metal releases from the cement-stabilized sediments into seawater after 2, 10 and 20 years. Generally, this study demonstrated the possibility of using a simplified non-linear sorption isotherm and diffusion model to describe the behaviour of the metals in terms of their adsorption to and release from the stabilized sediments. Below are the main conclusions drawn from the study.

Adsorption of Cu and Pb obeyed the Freundlich empirical adsorption isotherm as the isotherm fitted rather well to the experimental data for all the sediments. Adsorption capacities of the different sediments were determined using the non-linear Freundlich adsorption equation. All the three sediments used exhibited a higher sorption affinity for Pb compared to Cu. Among the three stabilized sediments investigated, however, quartz-dominated stabilized sediment from Hammerfest demonstrated a significantly lower sorption capacity for the heavy metals with stabilized sediment from Bergen showing the highest potential to sorb the two heavy metals. Stabilized sediment from Grenland showed intermediate adsorption behaviour. These were explained as due to the influence of physical properties of the sediments such as sediment mineralogy, grain size and TOC. The sorption studies showed that sorption isotherms for heavy metals are site and compound specific.

It also followed from the results of the fluxes calculated that stabilized sediment from Bergen was relatively effective in retaining the heavy metals and consequently reduced their diffusive transport. The fluxes of both metals from Hammerfest stabilized sediment for all the time spans studied were relatively high due to their poor retention in the sediments. The study has also revealed that the sediment from Bergen can stabilize the

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heavy metals on a long-term basis than Grenland followed by Hammerfest. Compared to the background concentrations of the heavy metals in the sediments and the seawater, the amount of heavy metals released from all the sediments is very low to represent any threat to marine life or the environment as a whole for the time period studied.

It should be mentioned that the many reasons adduced herein for the observed behaviour of the metals in the cement stabilized sediments are inexhaustive due to the complex nature of the cement-sediment-interaction. They can however be used as a basis for future studies. The following recommendations have thus been made:

- Further studies should be carried out using different sorption isotherms to envisage which isotherm will best describe the behaviour of the heavy metals in the three sediments.
- Further studies should look into the diffusive transport of the metals in a three dimensional manner as this can well describe what happens in reality.

REFERENCES

- Aagaard, P., Zheng, Z.P., Breedveld, G. (2001). Modelling natural attenuation of aromatic contaminants in sandy aquifers: comparison with laboratory experiments and field observations (Manuscript).
- Akgerman, A. and Zardkoohi, M. (1996). Adsorption of phenolic compounds on fly Ash. *Journal of Chemical and Engineering Data*, March, 41:185-187.
- Al-Enezi, M., Hamoda, F. and Fawzlon, N. (2005). Exchange Extraction of Heavy Metals from Wastewater Sludges. *Journal of environmental science Part A*, 39:455-464
- Alexander, J. E., and Corcoran, E. F. (1967). The distribution of copper in tropical seawater. *Limnol. Oceanogr.* 12 : 236-243.
- Alloway, B.J. (1990). *Heavy metals in soils*. John Wiley and Sons, Inc. New York.
- Alloway, B.J. and D.C. Ayres. (1993). *Chemical Principles of Environmental Pollution*.
- Alloway, B.J. (1995). *Soil Processes and the behaviour of Metals*. In: *Heavy Metals in Soil*. Edited by: B.J. Alloway, Blackie Academic & Professional, London
- Alunno, R.V. and Medici, F. (1995) Immobilisation of toxic metals in cement matrices, *Cement and Concrete Research* 25: 1147–1152.
- Amina, L.R.S., Mandal, R., Nouri, M.H., Murimboh, J., Chakrabart, C.L., Back, M.H., Grégoire, D.C. and Schroeder, W.H. (1999). Effect of metal/fulvic acid mole ratios on the binding of Ni(II), Pb(II), Cu(II), Cd(II), and Al(III) by two well-characterized fulvic acids in aqueous model solutions, *Anal. Chem. Acta* 402: 211–221.
- Anderson, S., Rasmussen, G., Snilsberg, P., Amundsen, C.E., and Westby, T. (1996). Assessing Toxicity and Mobilization of Impregnation Salts at a Contaminated Site. *Fresenius J. Anal. Chem.* 354:676-680.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Appelo, C. A.J, Postma, D. (2005) *Geochemistry, groundwater and pollution*, 2nd edition, A.A. Balkema Publishers.

Arniella, E. and Blythe, L. (1990). "Solidifying Traps Hazardous Wastes". *Chemical engineering*. 97:92-102.

Barbeau, C., Bougie, R., and Côté, J.E. (1981). Temporal and spatial variations of mercury, lead, zinc, and copper in the sediments of the Saguenay fjord. *Can J. Earth Sei.* 18: 1065-1074.

Barer, R.M (1987) *Zeolites and Clay Minerals as Sorbent and Molecular Sieves*, Academic Press, New York, 1987.

Barth, E.F. and Wiles, C.C. (1989). *Technical and Regulatory Status of Stabilization/Solidification in the United States, Solidification and Stabilization of Hazardous Waste*, Noyes Corporation, Park Ridge, NJ, USA

Bar-Yosef B, Barrow NJ, Goldschmidt J (eds) (1989) *Inorganic Contaminants in the Vadose Zone*. Springer, Berlin Heidelberg New York.

Batchelor, B. (2006). Overview of waste stabilization with cement. *Waste management* 26: 689-698

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Bhattacharyya, K.G, Gupta, S.S. (2008). Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Adv Colloid Interface Sci* 140:114–131

Bolton, K.A. and Evans, L.I. (1996). Cadmium adsorption capacity of selected Ontario soils. *Canadian J. Soil Sci.* 76: 183-189.

Bone, B.D., Barnard, L.H., Boardman, D.I., Carey, P.J., Hills, C.D., Jones, H.M., MacLeod, C.L. and Tyrer, M. (2004). Review of Scientific Literature on the Use of Stabilisation/Solidification for the Treatment of Contaminated Soil, Solid Waste and Sludges. Environment Agency - United Kingdom 343 pp.

Bozkurt, S., Moreno, L. and Neretnieks, I. (2000). Long term processes in waste deposits. *The science of total environment* 250:101-121

Brown, S., Chaney, R., and Angle, J.S. (1997). Surface Liming and Metal Movement in Soil Amended with Lime-Stabilized Bio solids. *J. Environ. Qual.* 26:724-732.

Bruiland, K.W., Bertine, K., Koide, M., and Goldberg, E.D. (1974). History of metal pollution in the southern California coastal zone. *Environ. Sci. Technol.* 8:425-432.

Bruemmer, G.W., Tiller, K.G., herms, U. and Clayton, PM. (1983). Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils. *GeodDma* 31: 337-354.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

- Buther, B., Davidoff, B., Amacher, M.C., Hinz, C., Iskander, I.K. and Selim, H.M., (1989). Correlation of freundlich K_d and n retention parameters with soils and elements. *Soil Sci.* 148: 370–379
- Calace, N., Muro, D.A., Nardi, E., Petronio, B.M. and Pietroletti M. (2002). Adsorption Isotherms for Describing Heavy-Metal Retention in Paper Mill Sludges *Ind. Eng. Chem. Res.* 41:5491–5497
- Calmano, W., Hong, J.F. and Forstner, U. (1993). Binding and mobilization of heavy metal in contaminated sediment affected by the pH and redox potential, *Water Sci. Technol.* 28:223–235.
- Cannell, B.S., Eghmy, T.T. and Krzow, J.E. (2000). Heavy metal stabilisation in municipal solid waste combustion bottom ash using soluble phosphate, *Waste Management* 20:135–148.
- Castilho, P., W.J. Chardon, and W. Salomons. (1993). Influence of cattle-manure slurry application on the solubility of cadmium, copper, and zinc in a manured acidic, loamy sand soil. *J. Environ. Agric. Press, Beijing.Qual.* 22:689–697
- Chen, Q.Y., Tyrer, M., Hills, C.D., Yang, X.M. and Carey, P. (2009). Immobilisation of heavy metal in cement-based solidification/stabilisation: A review. *Waste management* , 29: 1390-403
- Cheng, K.Y and Bishop, P.L. (1992). Sorption, important in stabilised/solidified waste forms, *Hazardous Waste and Hazardous Materials* 9:289–296.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Cheung, S.C.H., Oscarson, D.W. and Gray, M.N. (1986). Diffusion of Cs^+ and Γ^- in compacted bentonite-based materials. In: Proc. Can. Nucl. Soc., 2nd Int. Conf. on Radioactive Waste Management, pp. 217–220.

Chester, R. (1990) Marine Geochemistry. Unwin Hyman, London, 698 pp.

Chingombe, P., Saha, B., and Wakeman, R.J. (2005). Surface modification and characterization of a coal-based activated carbon, Carbon 43: 3132–3143.

Clement RE, Eiceman GA, Koester CJ (1995) Environmental analysis. Anal Chem 67:221R–225R D.W.

Conner J.R. and Hoeffner, S.L. (1998). The history of stabilisation/solidification technology, Critical reviews in Environmental Science and Technology 28: 325–396

Baccini, P., Brunner, PH., 1985: Behandlung und Endlagerung von Reststoffen aus Kehricht-verbrennungsanlagen. GWASA 65, 403-409.

Breck, J. (1964) Chem. Edu. 41: 678. Glasgow, UK: Blackie Academic & Professional.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Conner, J.R. (1990) *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, NY, USA.

Conner, J.R. and Hoeffner, S.L. (1998). The history of stabilisation/solidification technology, *Critical reviews in Environmental Science and Technology* 28: 325–396.

Crannell, B.S., Eighmy, T., Willson, C., Reible, D., Yin, M., (2004) “Pilot-Scale Reactive Barrier Technologies for Containment of Metal-Contaminated Sediments and Dredge Materials,” A Final Report Submitted to the NOAA/UNH Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET).

Cullinane, M.J. and Jones, L.W. (1986) *Stabilization/Solidification of Hazardous Waste*. Cincinnati: U.S. Environmental Protection Agency (US. EPA) Hazardous Waste Engineering Laboratory (HWERL), EPA/600/D-86/028.

Doner, H. E. (1978). *Soil Sci. Soc. Am. J.*, 42: 882-885.

Dudley, L.M., McLean, J.E., Furst, T.H. and Jurinak, J.J (1991). Sorption of Cadmium and Copper from an Acid Mine Waste Extract by two Calcareous Soils: Column Study. *Soil Sci.*, 151:121-135.

Erdem, A.N. Karapinar B, and Donat. R. (2004) The removal of heavy metal cations by natural zeolites *E-Journal of Colloid and Interface Science* 280: 309–314

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Engelsen, C.J., van der Sloot, H.A., Petkovic, G. Stoltenberg-Hansson, E. Wibetoe, G. Lund, W. In WASCON (2006), 6th International Conference on the Environmental and Technical Implications of Construction with Alternative Materials; M. Ilic, J.J.J.M. Goumans, S. Miletic, J.J.M. Heynen, J. Senden, Eds.: Belgrade, 2006.

Emerson, S., Jacobs, L., and Lebo, B. (1983). The behaviour of heavy metals in marine anoxic water: Solubilities at the oxygenhydrogen sulfide interface. In C. S. Wong, E. Boyle, K. W. Bruland, J. D. Eurton & E. D. Goldberg (eds), Trace Metals in Sea Water, Plenum Press, New York, 579–608.

Forstner, U. (1989). Contaminated Sediments: Lectures on Environmental Aspects of Particle-Associated Chemicals in Aquatic Systems, Berlin.

Glasser, F.P, Johnson, A. Lothenbach, B. Winnefeld, F Wieland, E.. Wallisch, A. (2006). Mechanisms and modeling of waste/cement interactions - International Workshop, May 8 to 12, 2005, Meiringen, Switzerland, Waste Management 26: 687-688.

Glasser, F.P.(1997). Fundamental aspect of cement solidification and stabilisation, Journal of Hazardous Material, 52:151–170

Gobeil, C., and Silverberg, N. (1989). Early diagenesis of lead in Laurentian Trough sediments. Geochim. Cosmochim. Acta 53: 1889-1895.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

- Halim, C.E., Short, S.A., Scott, J.A., Amal, R. and Low, G. (2005). Modelling the leaching of Pb, Cd, As, and Cr from cementitious waste using PHREEQC. *Hazardous metals* : 45-61
- Hansen, D.J., Berry, W.J., Mahony, J.D., Boothman, W.S., Di, T.D.M, Robson, D.L., Ankley, G.T., Ma, D., and Pesch, C.E. (1996). Predicting the toxicity of metal-contaminated field sediments using interstitial concentrations of metals and acid-volatile sulfide normalizations, *Environ. Toxicol. Chem.* 15: 2080–2094
- Harvey, C.C. and Murray, H.H. (2006) Clays - An Overview, in *Industrial Minerals and Rocks*, 7th edition, J.E. Kogel, et al., editors, SME, pp. 335-342.
- Herngren, L. Goonetilleke A. and Ayoko, G.A. (2005), Understanding heavy metal and suspended solids relationships in urban stormwater using simulated rainfall, *J Environ Manag* 76:149–158.
- Hills, C.D., Sollars, C.J. and Perry, R. (1994). A calorimetric and micro-structural study of solidified toxic wastes – part 2: a model for poisoning of OPC hydration, *Waste Management* 14:601–612.
- Huang, P.M. (1993). An Overview of Dynamics and Bio toxicity of Metals in the Freshwater Environment. *Water Poll. Res. J. Canada.* 28:1-5.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Huang, W. J. (2003). A study on the cement-like properties of municipal waste incineration ashes. *Cement and Concrete Research*, 33: 1795–1799

Islam, M.Z., Catalan, L.J.J., and Yanful, E. K. (2004). A Two-Front Leach Model for Cement-Stabilized Heavy Metal Waste Environ. Sci. Technol. 38:1522–1528

Jacobs, L., and Emerson, S. (1982). Trace metals in an anoxic Fjord. *Earth Planet. Sci. Lett.* 60: 237-252.

James, B.R. (1996). The challenge of remediating chromium-contaminated soil, *Environmental Science and Technology* 30:248A–251A.

Järup, L. (2003). Hazards of Heavy Metal Contamination. *Brit Med Bull* 68: 167-182.

Johnson, C.A. (2004). Cement stabilization of heavy-metal-containing wastes Geological Society, London, Special Publications, 236:595-606 *Journal of Hazardous Materials* 125:45-61

Juang, R.S., WU, F.C. and Tseng, R.L. (1996). Adsorption isotherms of phenolic compounds from aqueous solutions onto activated carbon fibers. *Journal of Chemical and Engineering Data*, 41:487-492.

Igwe, J.C. and Abia, A.A (2007) Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk, *Electronic Journal of Biotechnology* ISSN: 10:

- Lee, K.T., Tanabe, S. and Koh C.H. (2001) Contamination of Polychlorinated Biphenyls (PCBs) in Sediments from Kyeonggi Bay and Nearby Areas, Korea. *Marine pollution Bulletin*. 42:273-279
- Li, X. D. (2001). Heavy metal speciation and leaching behaviours in cement based solidified/stabilized waste materials. *Journal of Hazardous Materials*, A82: 215–230
- Laugesen, J. (2007). Behaviour of solidified/stabilised contaminated sediments in confined disposal facilities (CDFs). Doctoral Thesis, Faculty of Engineering Science and Technology - Department of Civil and Transport Engineering, Norwegian University of Science and Technology, Trondheim. 113.
- MacCarthy P, Klusman RW, Cowling SW et al (1991) Water analysis. *Anal Chem* 63:301–342
- Macherzynski, M., Reczyński, W., Parker. A., Górecki, J., and Gołaś, J., (2008). Distribution of Cr, Pb, Cu, Cd And Zn in sediments of the Dobczyce Dam Reservoir (Southern Poland). *Proceedings of ECOpole*. 2: 281-289
- Malviya, R. and Chaudhary, R. (2006). Factors affecting hazardous waste solidification/stabilization: a review, *Journal of Hazardous Materials* 137: 267–276.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

McLaren, R.G. and Crawford, D.V. (1973). Studies on soil copper: The specific adsorption of copper by soils. *J. Soil Sci.* 24: 443-452.

Michael, F. and Isenbeck, M.S. (1989). Batch Studies for the Investigation of the Mobility of the Heavy Metals Cd, Cr, Cu and Zn. *Journal of Contaminant Hydrology*. Vol. 4, pp. 69-78.

Naidu, R., Kookana, R.S., Summer, M.E., Butler, R.D. and Tiller, K.G. (1997). Cadmium sorption and transport in variable charge soils: A review. *J. Environ. Qual* 26:602-617.

National Bureau of Standards Certificate of Analysis, SRM 633, Portland Cement, Washington, DC. (1983)

Norway State of Environment. (2007). Polluted marine sediments, October, 2006 [Accessed: 2009].

Palandri, J., Kharaka, Y.K., (2004). A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. *US Geol. Surv. Open File Report 2004-1068*, 64 pp.

Parkhurst, D. L. (1995). Users guide to PHREEQC - A Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations', *U.S. Geological Survey Open-File Report*, pp. 1-43.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Peng, J.F., Song, Y.H., Peng, Y., Cui X.Y., and Qiu G.L. (2009). The remediation of heavy metals contaminated sediment. *Journal of Hazardous materials* 161:633-640

Phanikumar, M.S.and. McGuire, J.T.(2004). A 3D Partial Equilibrium Model to Simulate Coupled Hydrogeological, Microbiological and Geochemical Processes in Subsurface Systems, *Geophysical Research Letters*, 31:11, L11503, doi: 10.1029 / 2004GL019468.

Poon, C.S., Qiao, X.C., and Lin, Z.S. (2004). Effects of flue gas desulphurization sludge (FGD) on the pozzolanic reaction of rejected fly ash blended cement paste. *Cement and concrete research* 34: 1907-1918.

Saeedi, M., Hosseinzadeh, M., and Rajabzadeh, M. (2010). Competitive heavy metals adsorption on natural bed sediments of Jajrood River, Iran. *Environ Earth Sci*

Salhan, A. Billingham J. and King, A.C. (2003). The effect of a retarder on the early stages of the hydration of tricalcium silicate, *Journal of Engineering Mathematics* 45:367–377.

Salomons, W. and Stigliani, W.M. (1995). Bio geodynamics of Pollutants in Soils and Sediments: Risk Assessment of Delayed and Non-linear Responses. *Environmental Science*, Springer-Verlag. 331–343.

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. 2002. *Environmental organic chemistry*. 2 ed, Hoboken, N.J.: Wiley-Interscience. 1313 pp.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Selim, H.M. and Sparks, D.L. (2001). Editors, Heavy Metals Release in Soils, Lewis Publishers, Boca Raton, FL

Shi, C. and R. Spence, R. (2004). Designing of cement-based formula for solidification/stabilization of hazardous, radioactive and mixed wastes, *Critical Reviews in Environmental Science and Technology* 34: 391–417.

Sholkovitz, E.R., and Copland, D. (1981). The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Geochem. Cosmochim. Acta* 45: 181-189.

Sparrevik, M., Hernandez Martinez, F., Eggen, A. and Eek, E. (2006). Stabilization and Solidification of Contaminated Sediments - State of the Art Report (Draft report). Norwegian Geotechnical Institute (NGI), Rambøll A/S, NOAH A/S.

Sparrevik, M., Eek, E, Grini, R.S. (2009). The importance of sulphide binding for leaching of heavy metals from contaminated Norwegian marine sediments treated by stabilization/solidification *Environmental Technology* 30: 831 – 840

Spencer, D. W., D. E. Robertson, K. K. Turekian, and T. R. Folsom. (1970). Trace element calibrations and profiles at the Geosces test station in the northeast Pacific Ocean. *J. Geophys. Res.* 75: 7688-7696.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

- Stevenson, F.J. and Fitch, A. (1981). Reactions with Organic Matter. In: COPpeT in Soils and Plants. (Eds. Lonegran, J.F., Robson, AD. and Grahams, G.H.). pp. 60-95. Academic Press, New York.
- Stumm, W., and Morgan, J. (1981). Aquatic Chemistry 2nd Ed. Wiley Interscience, New-York. 780 pp.
- Tan, K.H. (2000). Environmental Soil Science. Second ed., Revised and expanded. Marcel Dekker, Inc. Pp 452.
- Taylor, H. F. W. (1997). Cement Chemistry, 2nd ed. Thomas Telford, London, 459.
- Tessier, A., Campbell, P.G.C., and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51: 844–850.
- Theofanis, Z.U., Astrid, S., Lidia, G. and Calmano, W.G. (2001). Contaminants in sediments: remobilisation and demobilization, *Sci. Total Environ.* 266: 195–202.
- Thinakaran, N., Baskaralingam, P., Thiruengada Ravi S.V., Panneerselvam, P., and Sivanesan, S. (2008). Adsorptive Removal of Acid Blue 15: Equilibrium and Kinetic Study *CLEAN-Soil, Air, Water* 36: 798-804

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Tiller, K.G., Gerth, I. and Bruemmer, G. (1984). The sorption of Cd, Zn, and Ni by a soil clay fraction: Procedures for partition of bound forms and their interpretation. *Geoderma* 34: 1-16.

Trussel, S.S. and Spence, R.D. (1994). A review of stabilisation/solidification processes, *Waste Management* 14:507–519.

Turekian, K. K. (1968): *Oceans*. Prentice-Hall

USDA (1999). Soil taxonomy; a basic system of soil classification for making and interpreting soil surveys, (Washington DC: United States department of agriculture, natural resources conservation service), agriculture handbook No. 436.

Van der Perk, M. (2006). Soil and water contamination from molecular to catchment scale. Taylor and Francis/Balkema Pp 389

Volesky, B. and Holan, Z.R. (1995). Biosorption of heavy metals. *Biotechnology Progress*, 11:235-250.

Volesky, B. (1994). Advances in biosorption of metals: selection of biomass types. *FEMS Microbiology Reviews*, 14: 291-302.

Weng, L., Temminghoff, E.J., and Riemsdijk, W.H.V., (2001) Contribution of Individual Sorbents to the Control of Heavy Metal Activity in Sandy Soil, *Environ. Sci. Technol.*, 35: 4436-4443

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Wild, A. (1993). *Soils and the Environment: An introduction*. Cambridge University Press. 189-210.

Ziegler, F. 2000. *Heavy Metal Binding in Cement-Based Waste Materials: An Investigation of the Mechanism of Zn Sorption to Calcium Silicate Hydrate*. Diss. ETH No. 13 569, ETH Ziirich, Switzerland.

Zomeren, A.V., and Comans, R.N.J. (2004). Contribution of natural organic matter to copper leaching from municipal solid waste incinerator bottom ash, *Environmental Science and Technology* 38:3927–3932.

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 1 # Hammerfest

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor = Sor; log_k 0.0

Sor + 0.54Pb+2 = SorPb+2 # Freundlich. SorPb+2 = Kf * Pb+2^0.54

-no_check

-mole_balance SorPb+2

log_k -97.37 # log_k= log ((Kf = 431) / m_Sor)

END**SOLUTION** 1 units mmol/kgw

Pb 1.5e-5 # All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

-equil 1

-no_edl true

REACTION 1

Pb 0.001

10 in 15

SELECTED_OUTPUT

-file freundlich.prn

-reset false

USER_PUNCH

-heading __c_Pb__ __q_Pb+2__ ____Kf__

10 punch tot ("Pb"), mol ("SorPb+2")

20 punch mol ("SorPb+2")/tot ("Pb") ^0.54

USER_GRAPH

-heading __c_Pb__ __q_Pb__

-axis_scale x_axis 0 2e-5 5e-6

-axis_scale y_axis 0 2.0 0.5

-axis_titles "Lead solution conc ($\mu\text{mol/l}$)" "Lead adsorbed (mmol/l)"

Simulation of heavy metal leaching from cement-stabilized polluted sediments

```
-chart_title "Lead adsorption - Freundlich isotherm"  
-start  
10 graph_x mol ("Pb+2")*1e3  
20 graph_y mol ("SorPb+2")*1e3  
-end
```

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 2 #HAMMERFEST CU FREUNDLICH

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor = Sor; log_k 0.0

Sor + 0.38Cu+2 = SorCu+2 # Freundlich. SorCu+2 = Kf * Cu+2^0.38

-no_check

-mole_balance SorCu+2

log_k -98.4

log_k= log ((Kf = 37) / m_Sor)

END**SOLUTION** 1 units mmol/kgw

Cu 2e-5

All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

-equil 1

-no_edl true

REACTION 1

Cu 0.0005

10 in 20

SELECTED_OUTPUT

-file freundlich.prn

-reset false

USER_PUNCH

-heading __c_Cu__ q_Cu+2__ Kf__

10 punch tot("Cu"), mol("SorCu+2")

20 punch mol("SorCu+2")/tot("Cu")^0.38

USER_GRAPH

-heading __c_Cu__ q_Cu__

-axis_scale x_axis 0 3.2e-5 0.5e-5

-axis_scale y_axis 0 2.5 0.5

-axis_titles "Copper solution conc (mmol/l)" "Copper adsorbed (mmol/l)"

-chart_title "Copper adsorption - Freundlich isotherm"

-start

10 graph_x mol("Cu+2")*1e3

20 graph_y mol("SorCu+2")*1e3

-end

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 3 #Hammerfest TRANSPORT

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor = Sor; log k 0.0

Sor + 0.54Pb+2 = SorPb+2 # Freundlich. SorPb+2 = Kf * Pb+2^0.54

-no_check

-mole_balance SorPb+2

log_k -97.37 # log_k= log ((Kf = 431) / m_Sor)

END**SOLUTION 0** units mmol/kgw

Pb 1e-2

SOLUTION 1 units mmol/kgw

Pb 1.5e-5

All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

END**TRANSPORT**

-cells 20

-length 0.0025

-flow_direction diffusion_only

-shifts 10

-diffc 3.0e-10 # diffusion coefficient = 3.0e-10 m²/s

-bcon constant flux

-timest 6.3e6 #2 years

USER_GRAPH

-heading Distance/cm Pb

-axis_scale x_axis 0 0.5

-axis_scale y_axis 0 0.001

-axis_titles Distance/cm mmol/l

-chart_title

-initial_solutions false

-start

10 graph_x Dist *100

20 graph_y tot("Pb")*1e3

-end

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

```

APPENDIX 4      # HAMMERFEST

SURFACE_MASTER_SPECIES
  Sor Sor
SURFACE_SPECIES
  Sor = Sor; log_k 0.0
  Sor + 0.38Cu+2 = SorCu+2      # Freundlich. SorCu+2 = Kf * Cu+2^0.38
  -no_check
  -mole_balance SorCu+2
  log_k -98.4                    # log_k= log ((Kf = 37) / m_Sor)
END
SOLUTION 0 units mmol/kgw
  Cu 1.6e-3
SOLUTION 1 units mmol/kgw
  Cu 2e-5                        # All concentrations 1 mol/l
SURFACE 1 units mol
  Sor 1e100 1.0 1e100
END
TRANSPORT
  -cells 20
  -length 0.0025
  -flow_direction diffusion_only
  -shifts 10
  -diffc 3.0e-10                 # diffusion coefficient = 3.0e-10 m2/s
  -bcon constant flux
  -timest 3.15e7 #10 years
USER_GRAPH
  -heading Distance/cm Cu
  -axis_scale x_axis 0 0.5
  -axis_scale y_axis 0 0.001
  -axis_titles Distance/cm mmol/l
  -chart_title
  -initial_solutions false
  -start
  10 graph_x Dist *100
  20 graph_y tot("Cu")*1e3
  -end
END

```

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 5 # FREUNDLICH ISOTHERM BERGEN

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor = Sor; log_k 0.0

Sor + 0.61Pb+2 = SorPb+2 # Freundlich. SorPb+2 = Kf * Pb+2^0.61

-no_check

-mole_balance SorPb+2

log_k -96.01 # log_k= log ((Kf= 9615) / m_Sor)

END**SOLUTION** 1 units mmol/kgw

Pb 5.32e-7 # All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

-equil 1

-no_edl true

REACTION 1

Pb 0.001

10 in 15

SELECTED_OUTPUT

-file freundlich.prn

-reset false

USER_PUNCH

-heading __c_Pb_ __q_Pb+2_ ____Kf__

10 punch tot ("Pb"), mol ("SorPb+2")

20 punch mol ("SorPb+2")/tot ("Pb") ^0.61

USER_GRAPH

-heading __c_Pb_ __q_Pb_

-axis_scale x_axis 0 2e-5 5e-6

-axis_scale y_axis 0 2.0 0.5

-axis_titles "Lead solution conc (µmol/l)" "Lead adsorbed (mmol/l)"

-chart title "Lead adsorption - Freundlich isotherm"

Simulation of heavy metal leaching from cement-stabilized polluted sediments

```
-start  
10 graph_x mol ("Pb+2")*1e3  
20 graph_y mol ("SorPb+2")*1e3  
-end
```

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 6 # BERGEN CU FREUNDLICH

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor - Sor; log_k 0.0

Sor + 0.56Cu+2 = SorCu+2 # Freundlich. SorCu+2 = Kf * Cu+2^0.56

-no_check

-mole_balance SorCu+2

log_k -96.56 # log_k= log ((Kf= 2781) / m_Sor)

END**SOLUTION** 1 units mmol/kgw

Cu 8.2e-7

All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

-equil 1

-no_edl true

REACTION 1

Cu 0.0005

10 in 20

SELECTED_OUTPUT

-file freundlich.prn

-reset false

USER_PUNCH

-heading __c_Cu__ q_Cu+2__ Kf__

10 punch tot("Cu"), mol("SorCu+2")

20 punch mol("SorCu+2")/tot("Cu")^0.56

USER_GRAPH

-heading __c_Cu__ q_Cu__

-axis_scale x_axis 0 3.2e-5 0.5e-5

-axis_scale y_axis 0 2.5 0.5

-axis_titles "Copper solution conc (mmol/l)" "Copper adsorbed (mmol/l)"

-chart_title "Copper adsorption - Freundlich isotherm"

-start

10 graph_x mol("Cu+2")*1e3

20 graph_y mol("SorCu+2")*1e3

-end

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 7 #BERGEN TRANSPORT

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor = Sor; log_k 0.0

Sor + 0.61Pb+2 = SorPb+2 # Freundlich. SorPb+2 = Kf * Pb+2^0.61

-no_check

-mole_balance SorPb+2

log_k -96.01 # log_k= log ((Kf= 9615) / m_Sor)

END

SOLUTION 0 units mmol/kgw

Pb 1e-2

SOLUTION 1 units mmol/kgw

Pb 5.32e-7

All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

END

TRANSPORT

-cells 20

-length 0.0025

-flow_direction diffusion_only

-shifts 10

-diffc 3.0e-10 # diffusion coefficient = 3.0e-10 m²/s

-bcon constant flux

-timest 6.3e6 #2 years

USER_GRAPH

-heading Distance/cm Pb

-axis_scale x_axis 0 0.5

-axis_scale y_axis 0 0.001

-axis_titles Distance/cm mmol/l

-chart_title

-initial solutions false

-start

10 graph_x Dist *100

20 graph_y tot("Pb")*1e3

-end

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 8 # BERGEN

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor = Sor; log_k 0.0

Sor + 0.56Cu+2 = SorCu+2

Freundlich. SorCu+2 = Kf * Cu+2^{0.56}

-no_check

-mole_balance SorCu+2

log_k -96.56

log_k = log ((Kf = 2781) / m_Sor)

END**SOLUTION 0** units mmol/kgw

Cu 1.6e-3

SOLUTION 1 units mmol/kgw

Cu 8.2e-7

All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

END**TRANSPORT**

-cells 20

-length 0.0025

-flow direction diffusion only

-shifts 10

-diffc 3.0e-10

diffusion coefficient = 3.0e-10 m²/s

-beon constant flux

-timest 3.15e7 #10 years

USER_GRAPH

-heading Distance/cm Cu

-axis_scale x_axis 0 0.5

-axis_scale y_axis 0 0.001

-axis_titles Distance/cm mmol/l

-chart_title

-initial_solutions false

-start

10 graph_x Dist *100

20 graph_y tot("Cu")*1e3

-end

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 9 # FREUNDLICH ISOTHERM GRENLAND

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor = Sor; log_k 0.0

Sor + 0.58Pb+2 = SorPb+2 # Freundlich. SorPb+2 = Kf * Pb+2^0.58

-no_check

-mole_balance SorPb+2

log_k -97.23 # log_k= log ((Kf = 591) / m_Sor)

END**SOLUTION** 1 units mmol/kgw

Pb 1.3e-5 # All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

-equil 1

-no_edl true

REACTION 1

Pb 0.001

10 in 15

SELECTED_OUTPUT

-file freundlich.prm

-reset false

USER_PUNCH

-heading __c_Pb__q_Pb+2__Kf__

10 punch tot ("Pb"), mol ("SorPb+2")

20 punch mol ("SorPb+2")/tot ("Pb") ^0.58

USER_GRAPH

-heading __c_Pb__q_Pb__

-axis_scale x_axis 0 2e-5 5e-6

-axis_scale y_axis 0 2.0 0.5

-axis_titles "Lead solution conc (µmol/l)" "Lead adsorbed (mmol/l)"

-chart title "Lead adsorption - Freundlich isotherm"

Simulation of heavy metal leaching from cement-stabilized polluted sediments

```
-start  
10 graph_x mol ("Pb+2")*1e3  
20 graph_y mol ("SorPb+2")*1e3  
-end
```

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 10 # GRENLAND CU FREUNDLICH

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor = Sor; log_k 0.0

Sor + 0.48Cu+2 = SorCu+2 # Freundlich. SorCu+2 = Kf * Cu+2^0.48

-no_check

-mole_balance SorCu+2

log_k -97.35 # log_k - log ((Kf - 443) / m_Sor)

END**SOLUTION** 1 units mmol/kgw

Cu 1.7 e-6

All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

-equil 1

-no_edl true

REACTION 1

Cu 0.0005

10 in 20

SELECTED_OUTPUT

-file freundlich.prn

-reset false

USER_PUNCH

-heading c_Cu q_Cu+2 Kf

10 punch tot("Cu"), mol("SorCu+2")

20 punch mol("SorCu+2")/tot("Cu")^0.48

USER_GRAPH

-heading c_Cu q_Cu

-axis_scale x_axis 0 3.2e-5 0.5e-5

-axis_scale y_axis 0 2.5 0.5

-axis_titles "Copper solution conc (mmol/l)" "Copper adsorbed (mmol/l)"

-chart_title "Copper adsorption - Freundlich isotherm"

-start

10 graph_x mol("Cu+2")*1e3

20 graph_y mol("SorCu+2")*1e3

-end

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 11

#GRENLAND TRANSPORT

SURFACE_MASTER_SPECIES

Sor Sor

SURFACE_SPECIES

Sor = Sor; log_k 0.0

Sor + 0.58Pb+2 = SorPb+2 # Freundlich. SorPb+2 = Kf * Pb+2^0.58

-no_check

-mole_balance SorPb+2

log_k -97.23 # log_k= log ((Kf = 591) / m_Sor)

END**SOLUTION 0** units mmol/kgw

Pb 1e-2

SOLUTION 1 units mmol/kgw

Pb 1.3e-6 # All concentrations 1 mol/l

SURFACE 1 units mol

Sor 1e100 1.0 1e100

END**TRANSPORT**

-cells 20

-length 0.0025

-flow_direction diffusion_only

-shifts 10

-diffc 3.0e-10 # diffusion coefficient = 3.0e-10 m²/s

-bcou constant flux

-timest 6.3e6 #2 years

USER_GRAPH

-heading Distance/cm Pb

-axis_scale x_axis 0 0.5

-axis_scale y_axis 0 0.001

-axis_titles Distance/cm mmol/l

-chart title

-initial_solutions false

-start

10 graph x Dist *100

20 graph_y tot("Pb")*1e3

-end

END

Simulation of heavy metal leaching from cement-stabilized polluted sediments

```

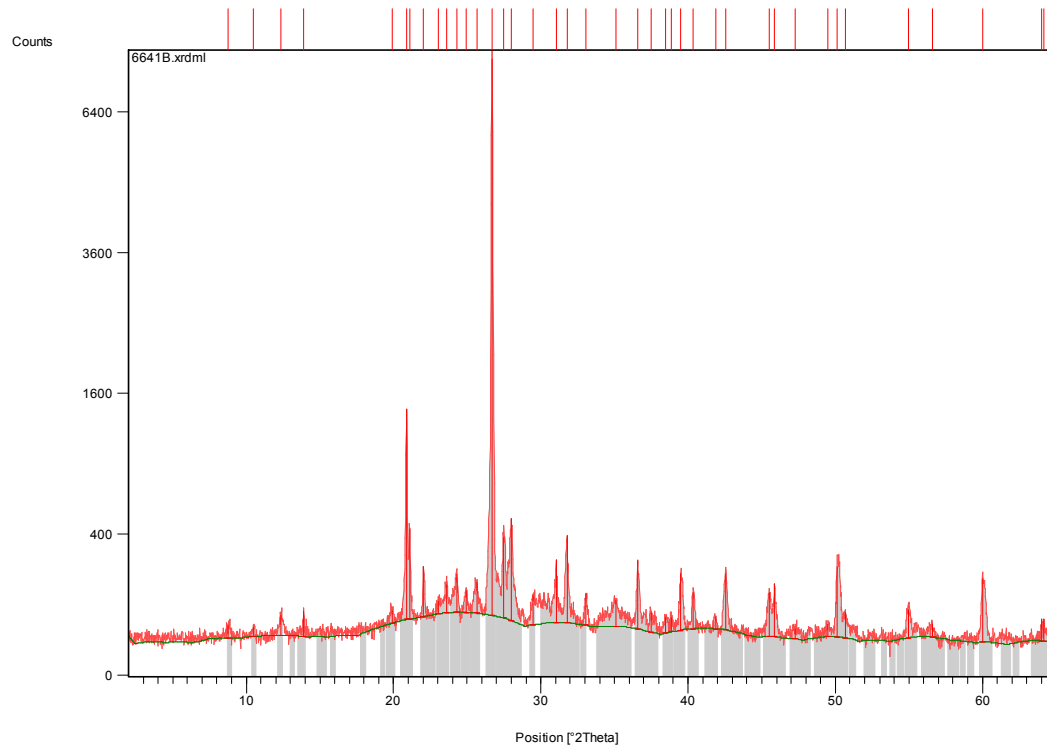
APPENDIX 12          # GRENLAND

SURFACE_MASTER_SPECIES
  Sor Sor
SURFACE_SPECIES
  Sor = Sor; log_k 0.0
  Sor + 0.48Cu+2 - SorCu+2          # Freundlich. SorCu+2 - Kf * Cu+2^0.48
  -no_check
  -mole_balance SorCu+2
  log_k -97.35                      # log_k= log ((Kf= 443) / m_Sor)
END
SOLUTION 0 units mmol/kgw
  Cu 1.6e-3
SOLUTION 1 units mmol/kgw
  Cu 1.7e-6                          # All concentrations 1 mol/l
SURFACE 1 units mol
  Sor 1e100 1.0 1e100
END
TRANSPORT
  -cells 20
  -length 0.0025
  -flow_direction diffusion_only
  -shifts 10
  -diffc 3.0e-10                      # diffusion coefficient = 3.0e-10 m2/s
  -bcou constant flux
  -timest 3.15e7 #10 years
USER_GRAPH
  -heading Distance/cm Cu
  -axis_scale x_axis 0 0.5
  -axis_scale y_axis 0 0.001
  -axis_titles Distance/cm mmol/l
  -chart_title
  -initial_solutions false
  -start
  10 graph_x Dist *100
  20 graph_y tot("Cu")*1e3
  -end
END

```

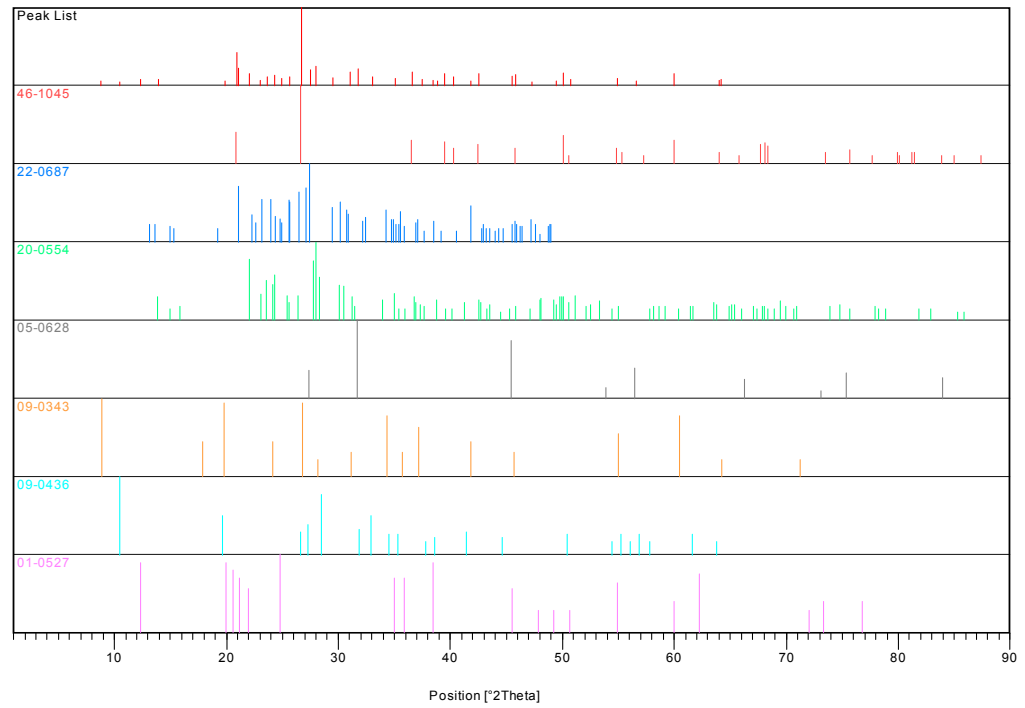
Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 13: Results from XRD analysis

Main Graphics, Analyze View: Grenland**Pattern List: Grenland**

Compound Name	Ref. Code	Empirical Formula	Score
Quartz	46-1045	Si O ₂	46
K-feldspar	22-0687	K Al Si ₃ O ₈	44
Albite	20-0554	Na Al Si ₃ O ₈	43
Halite	05-0628	Na Cl	38
Illite	09-0343	K _{0.5} (Al , Fe , Mg) ₃ (Si , Al) ₄ O ₁₀ (O H) ₂	12
Amphibole	09-0436	Na ₂ Fe ₃ Fe ₂ Si ₈ O ₂₂ (O H) ₂	21
Kaolinite	01-0527	Al ₂ Si ₂ O ₅ (O H) ₄	34

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Pattern View: Grenland

Simulation of heavy metal leaching from cement-stabilized polluted sediments

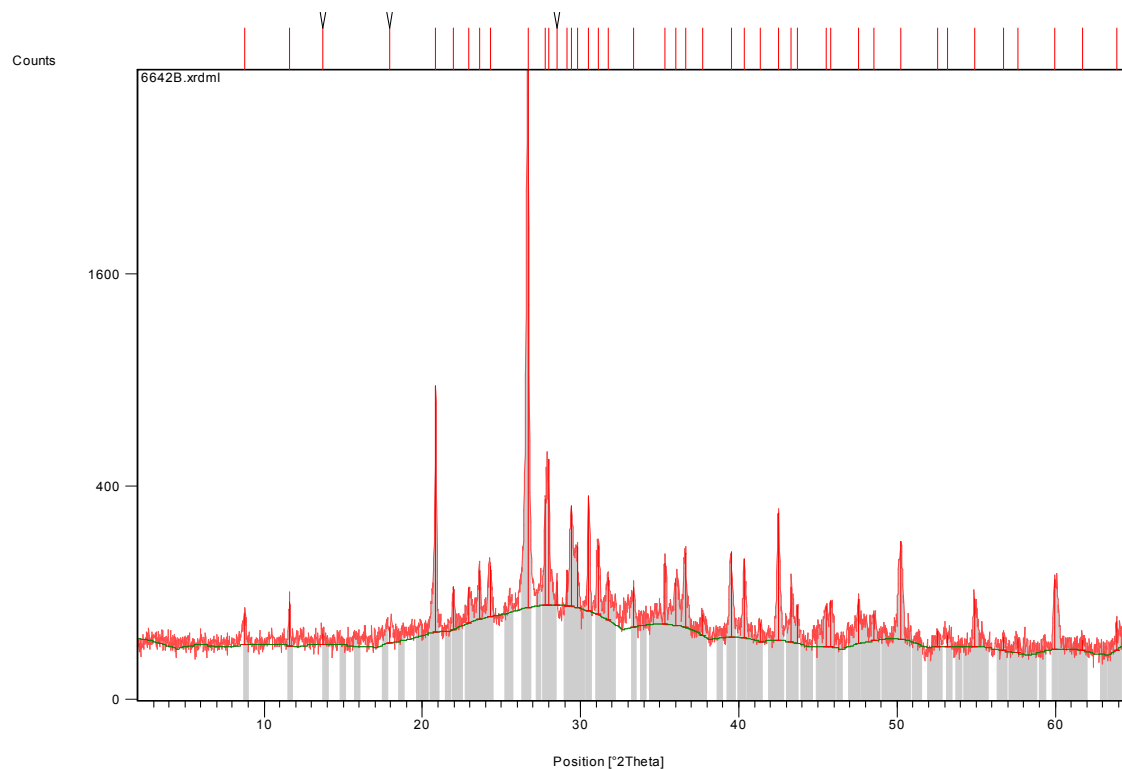
Peak List: Grenland

Pos. [°2Th.]	d-spacing [Å]	Matched by	Height [cts]	FWHM [°2Th.]
8.7962	10.05315	09-0343	21.47	0.2362
10.4605	8.45716	09-0436	15.82	0.2362
12.3549	7.16428	01-0527	40.57	0.1968
13.9051	6.36889	20-0554	51.63	0.0787
19.8919	4.46353	09-0343; 01-0527	27.44	0.2362
20.8944	4.25159	46-1045	1363.35	0.0984
21.0862	4.21334	22-0687; 01-0527	369.30	0.0787
22.0371	4.03365	20-0554; 01-0527	167.53	0.0787
23.0466	3.85919	22-0687; 20-0554	33.24	0.2362
23.6176	3.76717	20-0554	84.52	0.0984
24.2742	3.66674	22-0687; 20-0554	126.25	0.1574
24.9173	3.57354	22-0687; 01-0527	62.91	0.1968
25.6406	3.47435	22-0687; 20-0554	95.51	0.2755
26.6802	3.34129	46-1045; 09-0343; 09-0436	7572.96	0.1378
27.4738	3.24654	22-0687; 05-0628	318.07	0.0984
27.9944	3.18734	20-0554; 09-0343	433.52	0.1574
29.4890	3.02912	22-0687	76.65	0.1968
31.0461	2.88065	22-0687; 09-0343	210.00	0.0787
31.7840	2.81544	05-0628; 09-0436	334.56	0.1574
33.0735	2.70855	09-0436	83.54	0.1378
35.1043	2.55638	22-0687; 20-0554; 01-0527	64.81	0.2362
36.5823	2.45439	46-1045	221.63	0.0720

Simulation of heavy metal leaching from cement-stabilized polluted sediments

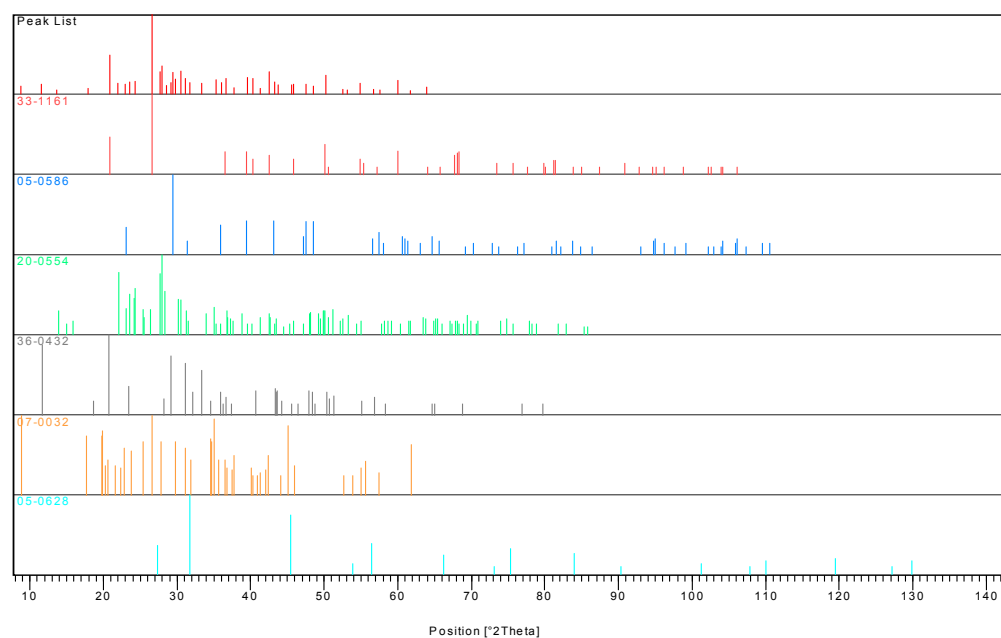
37.4703	2.40022	22-0687; 20-0554	40.13	0.1181
38.4761	2.33976	22-0687; 09-0436; 01-0527	30.60	0.2362
38.8856	2.31606	20-0554	28.60	0.1181
39.4961	2.28166	46-1045; 20-0554	167.06	0.0984
40.3310	2.23633	46-1045; 20-0554	93.37	0.1378
41.8474	2.15873	22-0687; 09-0343	26.22	0.1968
42.5481	2.12479	46-1045; 20-0554	166.00	0.0984
45.4909	1.99395	22-0687; 05-0628; 09-0343; 01- 0527	106.46	0.0984
45.8673	1.97682	46-1045; 22-0687; 20-0554	138.56	0.0720
47.2861	1.92236	22-0687; 20-0554	17.11	0.4723
49.4977	1.84152	20-0554	22.66	0.2362
50.1354	1.81808	46-1045; 20-0554	207.48	0.0720
50.7100	1.80031	46-1045; 20-0554; 01-0527	51.00	0.1500
54.9342	1.67145	46-1045; 20-0554; 09-0343; 01- 0527	59.19	0.2755
56.6009	1.62612	05-0628	22.82	0.4723
59.9935	1.54075	46-1045; 01-0527	164.03	0.0960
64.0200	1.45441	46-1045	39.00	0.1500
64.2000	1.45077	46-1045; 09-0343	40.00	0.1500

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Main Graphics, Analyze View: Hammerfest**Pattern List: Hammerfest**

Compound Name	Ref. Code	Empirical Formula	Score
Quartz	33-1161	Si O ₂	57
Calcite	05-0586	Ca C O ₃	40
Albite	20-0554	Na Al Si ₃ O ₈	39
Gypsum	36-0432	Ca S O ₄ !2 H ₂ O	42
Muscovite	07-0032	K Al ₂ Si ₃ Al O ₁₀ (O H) ₂	25
Halite	05-0628	Na Cl	31

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Pattern View: Hammerfest***Peak List: : Hammerfest***

Pos. [°2Th.]	d-spacing [Å]	Matched by	Height [cts]	FWHM [°2Th.]
8.7943	10.05539	07-0032	38.24	0.1574
11.6259	7.61184	36-0432	57.68	0.0787
13.6963	6.46551		11.69	0.4723
17.9008	4.95525		17.41	0.4723
20.8560	4.25933	33-1161; 36-0432	828.77	0.0984
21.9800	4.04400	20-0554	68.29	0.1181
22.9348	3.87775	05-0586; 20-0554; 07-0032	57.69	0.2362
23.6056	3.76905	20-0554	88.33	0.0984

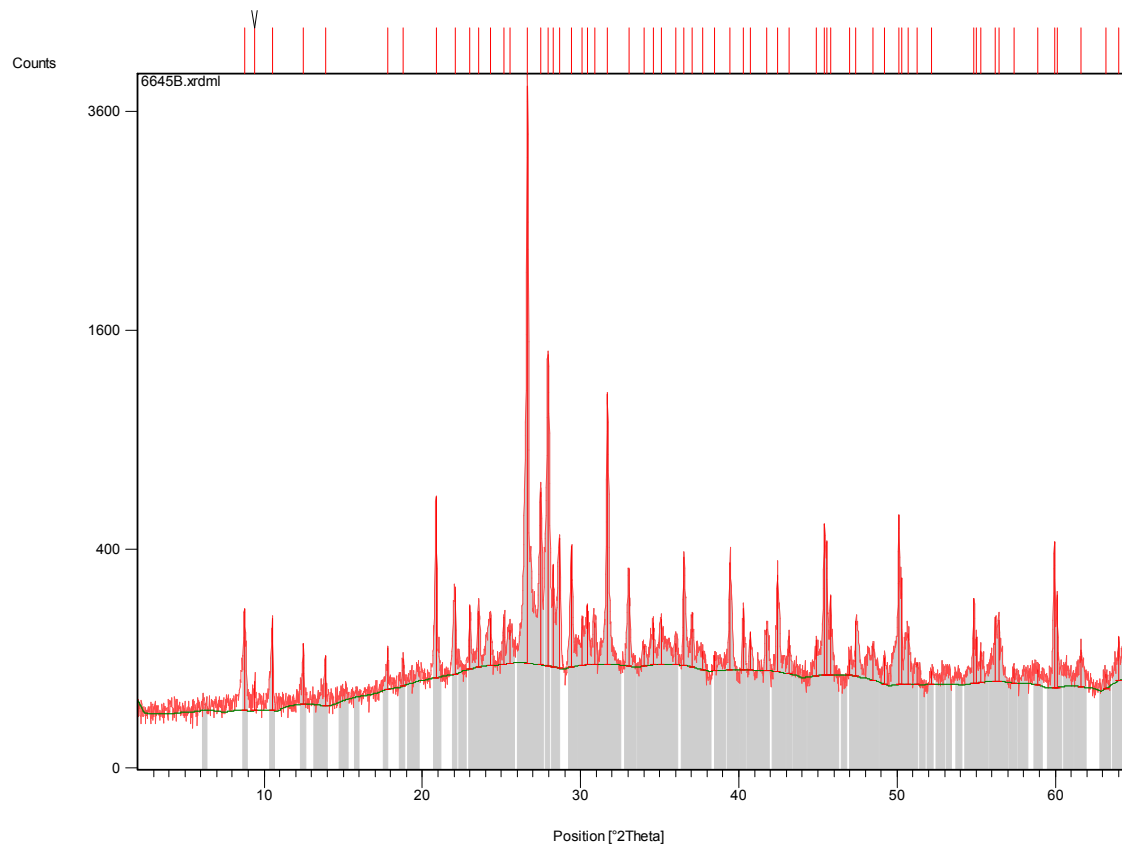
Simulation of heavy metal leaching from cement-stabilized polluted sediments

24.2774	3.66626	20-0554	96.37	0.2362
26.6688	3.34269	33-1161; 07-0032	3423.36	0.1378
27.7620	3.21350	20-0554; 07-0032	275.79	0.0590
27.9802	3.18893	20-0554; 36-0432	430.27	0.0984
28.5133	3.13051		42.64	0.1181
29.1468	3.06389	36-0432	70.65	0.0590
29.4054	3.03754	05-0586	250.35	0.1181
29.8023	2.99798	07-0032	132.78	0.1574
30.4996	2.93101	20-0554	295.48	0.0787
31.1043	2.87539	20-0554; 36-0432; 07-0032	145.65	0.1574
31.7458	2.81873	07-0032; 05-0628	75.34	0.1968
33.3653	2.68554	36-0432	65.35	0.1181
35.3167	2.53939	20-0554	111.84	0.0720
36.0298	2.49281	05-0586; 20-0554; 36-0432	78.62	0.1968
36.6301	2.45129	33-1161; 20-0554; 36-0432; 07- 0032	142.88	0.0720
37.7313	2.38422	20-0554; 07-0032	26.84	0.2362
39.5467	2.27885	33-1161; 05-0586; 20-0554	156.30	0.0787
40.3401	2.23585	33-1161; 07-0032	138.00	0.0787
41.3386	2.18412	20-0554; 07-0032	20.95	0.1968
42.4768	2.12820	33-1161; 20-0554; 07-0032	276.72	0.0984
43.2977	2.08800	05-0586; 20-0554; 36-0432	81.68	0.0720
43.7064	2.07113	20-0554; 36-0432	49.26	0.1181
45.5335	1.99219	36-0432; 05-0628	52.14	0.1574
45.8284	1.98005	33-1161; 20-0554; 07-0032	59.93	0.1181

Simulation of heavy metal leaching from cement-stabilized polluted sediments

47.5899	1.91079	05-0586	60.79	0.0984
48.5080	1.87675	05-0586; 36-0432	33.87	0.2362
50.2492	1.81573	33-1161; 20-0554; 36-0432	187.15	0.0984
52.5627	1.74113	20-0554; 07-0032	15.93	0.3149
53.1972	1.72185	20-0554	11.87	0.3149
54.8833	1.67149	33-1161; 20-0554; 07-0032	65.06	0.0960
56.7309	1.62270	05-0586; 36-0432	13.17	0.2362
57.6115	1.59998	20-0554; 07-0032	12.28	0.2362
59.9741	1.54248	33-1161	103.51	0.2755
61.7400	1.50253	20-0554; 07-0032	9.14	0.4723
63.8674	1.45631	33-1161; 20-0554	32.48	0.1440

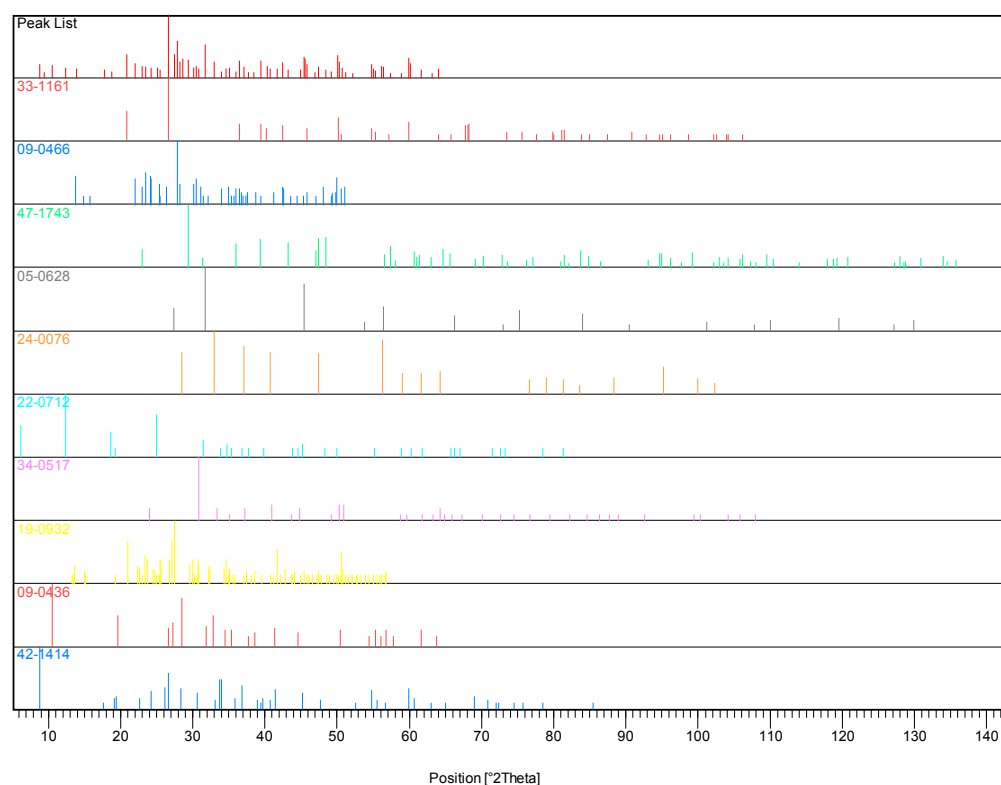
Simulation of heavy metal leaching from cement-stabilized polluted sediments

Main Graphics, Analyze View: Bergen***Pattern List: Bergen***

Compound Name	Ref. Code	Empirical Formula	Score
Quartz	33-1161	Si O ₂	61
Albite	09-0466	Na Al Si ₃ O ₈	52
Calcite	47-1743	Ca C O ₃	50
Halite	05-0628	Na Cl	46
Pyrite	24-0076	Fe S ₂	45
Chlorite	22-0712	(Ni , Mg , Al) ₆ (Si , Al) ₄ O ₁₀ (O H) ₈	24
Dolomite	34-0517	Ca (Mg , Fe) (C O ₃) ₂	21
K-Feldspar	19-0932	K Al Si ₃ O ₈	35

Simulation of heavy metal leaching from cement-stabilized polluted sediments

Amphibole	09-0436	Na ₂ Fe ₃ Fe ₂ Si ₈ O ₂₂ (O H) ₂	29
Biotite	42-1414	K (Mg , Fe +2) ₃ (Al , Fe +3) Si ₃ O ₁₀ (O H , F) ₂	30

Pattern View: Bergen**Peak List: Bergen**

Pos. [°2Th.]	d-spacing [Å]	Matched by	Height [cts]	FWHM [°2Th.]
8.7612	10.09320	42-1414	182.68	0.0787
9.4136	9.39518		33.97	0.1181
10.5184	8.41072	09-0436	158.52	0.1181
12.4762	7.09493	22-0712	94.95	0.0787

Simulation of heavy metal leaching from cement-stabilized polluted sediments

13.8612	6.38895	09-0466	72.68	0.0590
17.8167	4.97845	42-1414	69.07	0.0590
18.7845	4.72410	22-0712	43.18	0.1181
20.8575	4.25902	33-1161	544.12	0.0787
22.0564	4.03016	09-0466	201.11	0.0984
23.0123	3.86487	09-0466; 47-1743; 19-0932	138.53	0.0984
23.5354	3.78013	09-0466; 19-0932	119.36	0.0984
24.2925	3.66402	09-0466; 42-1414	98.35	0.1181
25.1663	3.53874	22-0712	98.14	0.0984
25.5447	3.48717	09-0466; 19-0932	66.47	0.2362
26.6384	3.34643	33-1161; 19-0932; 09-0436; 42-1414	3794.80	0.0984
27.4805	3.24577	05-0628; 19-0932	543.05	0.1181
27.9323	3.19429	09-0466	1336.97	0.0787
28.2693	3.15697	09-0466; 42-1414	259.05	0.0787
28.6647	3.11432	24-0076	357.41	0.1378
29.4125	3.03682	47-1743	325.04	0.1181
30.1204	2.96704	09-0466; 19-0932	104.27	0.0590
30.4455	2.93609	09-0466; 19-0932	132.91	0.0590
30.8982	2.89410	34-0517; 19-0932	84.46	0.2362
31.6945	2.82318	05-0628; 09-0436	1087.80	0.0984
33.0314	2.71191	24-0076; 09-0436; 42-1414	248.48	0.0984
34.0025	2.63665	09-0466; 22-0712; 42-1414	37.37	0.2362
34.5966	2.59272	22-0712; 19-0932; 09-0436	87.03	0.1574
35.0790	2.55817	09-0466; 34-0517; 19-0932	94.70	0.1574
36.0356	2.49242	09-0466; 47-1743	39.39	0.1968

Simulation of heavy metal leaching from cement-stabilized polluted sediments

36.5385	2.45927	33-1161; 09-0466	283.70	0.0787
37.0657	2.42548	09-0466; 24-0076; 19-0932	116.40	0.1574
37.7417	2.38358	09-0466; 22-0712; 09-0436	33.05	0.3936
38.4851	2.33923	09-0436	27.88	0.1181
39.4538	2.28400	33-1161; 09-0466; 47-1743; 19-0932; 42-1414	272.51	0.1181
40.2917	2.23842	33-1161	131.86	0.1181
40.7133	2.21621	24-0076; 19-0932; 42-1414	74.60	0.0787
41.7411	2.16399	19-0932	81.58	0.2755
42.4358	2.12839	33-1161; 09-0466	233.35	0.0720
43.1855	2.09490	47-1743	70.31	0.1181
44.9129	2.01826	34-0517; 19-0932	65.79	0.1181
45.4235	1.99510	09-0466; 05-0628; 19-0932	424.17	0.0960
45.5511	1.99475		355.71	0.0720
45.7951	1.97977	33-1161; 09-0466; 19-0932	175.59	0.0720
47.0035	1.93165	09-0466; 47-1743	27.03	0.2400
47.4113	1.91599	47-1743; 24-0076; 19-0932	108.59	0.0960
48.4990	1.87553	47-1743; 19-0932	65.33	0.1440
49.1976	1.85052	09-0466; 34-0517	41.70	0.2400
50.1259	1.81840	33-1161; 09-0466; 19-0932	476.60	0.0720
50.2661	1.81816		244.03	0.0480
50.7155	1.79863	33-1161; 09-0466; 19-0932	92.60	0.4320
51.2352	1.78160	09-0466; 19-0932	33.40	0.3840
52.1934	1.75113	19-0932	19.90	0.2880
54.8702	1.67186	33-1161; 42-1414	179.27	0.0960
55.0297	1.67154		82.73	0.0720

Simulation of heavy metal leaching from cement-stabilized polluted sediments

55.3132	1.65952	33-1161; 22-0712; 09-0436	53.63	0.2880
56.2146	1.63502	24-0076; 19-0932; 09-0436	126.14	0.0960
56.4438	1.62893	47-1743; 05-0628	118.96	0.1200
57.4278	1.60333	47-1743	21.43	0.2880
58.9112	1.56645	24-0076; 22-0712; 34-0517	23.28	0.5760
59.9444	1.54189	33-1161; 42-1414	371.80	0.1200
60.1113	1.54183		196.26	0.0720
61.6066	1.50422	24-0076; 22-0712; 34-0517; 09-0436	60.82	0.1920
63.1881	1.47032	47-1743; 34-0517; 42-1414	20.56	0.3840
64.0175	1.45326	33-1161	80.17	0.0720

Simulation of heavy metal leaching from cement-stabilized polluted sediments

APPENDIX 14 RESULTS OF THE LABORATORY ANALYSIS

Sediment	Adsorbed Cu(mmol/l)	Adsorbed Pb(mmol/l)	Dissolved Cu(mmol/l)	Dissolved Pb(mmol/l)
Bergen	2.75	1.11	1.74E-06	3.7E-07
Bergen	1.74	1.18	7.78E-07	3.76E-07
Bergen	1.38	1.30	3.76E-07	4.28E-07
Bergen	1.20	2.06	3.7E-07	9.74E-07
Grenland	5.18E-01	0.58	7.3E-07	7.87E-06
Grenland	5.77E-01	0.68	1.02E-06	9.93E-06
Grenland	9.06E-01	0.99	2.53E-06	2.09E-05
Grenland	8.57E-01	0.78	2.48E-06	2.06E-05
Hammerfest	0.13	0.87	1.92E-05	1E-05
Hammerfest	0.12	1.00	2.51E-05	2.28E-05
Hammerfest	0.098	0.85	9.22E-06	8.25E-06
Hammerfest	0.034	0.60	2.31E-05	1.01E-05