Master Thesis in Geosciences

Leaching tests comparison for solidified and stabilized contaminated sediments

Assessment of selected inorganic contaminants

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Discipline: Environmental Geology and Geohazards

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Abstract

Contaminated sediments in Norway represent a significant problem for the public's health as well as the environment, especially in urban coastal regions where former harbour areas are converted to residential zones requiring more strict environmental standards. As a result, environmentally motivated remediation efforts led by the Norwegian authorities and supported by the public and independent institutions have become increasingly important to solve the problem. The method of Solidification and Stabilization (S/S) of contaminated sediments is one of the alternatives proposed for mitigation in such situations. This thesis is part of a larger research project with respect to S/S of contaminated sediments, where the following participants are involved: Norcem, The Norwegian Geotechnical Institute (NGI), Det Norske Veritas (DNV), Rambøll, Skanska Norway, and NOAH. The larger project is financed by the Research Council of Norway (NRC) and this thesis is worked under the supervision of the Norwegian Geotechnical Institute (NGI).

Leaching test is one important aspect in the environmental assessment of the remedial measures of solidified and stabilized (S/S) contaminated sediments. Selection of an appropriate test or combination of tests is of vital importance for the proper judgment of results, as well as for predicting the long term release of S/S contaminants into the environment. The experimental program reported here consists of six different leaching tests carried out on the S/S Trondheim contaminated sediments to assess the leaching of four inorganic pollutants Cr, Cu, Ni and Zn. The main objectives of this investigation were to study how the performance of different leaching tests affects the release of inorganic contaminants and to find the most suitable leaching test(s) for predicting contaminants release from the S/S materials. These leaching tests performed are as follows:

- Static diffusion test (tank test),
- Dynamic diffusion test (modified tank test),
- Batch leaching test for crushed material,
- Up-flow percolation test (column test),
- Batch leaching test for monolithic samples, and
- .Leaching test of monoliths with magnetic agitation,

The diffusion tests (static and dynamic) were performed in accordance with the norm EA NEN 7375:2004 protocol, for leaching of inorganic components. The difference between the two diffusion tests lied in the way the S/S samples are exposed to the leachant. In the dynamic diffusion test the leachant was constantly circulated in the cell throughout the course of the experiment using a peristaltic pump whereas in the static test, the leachant was kept stationary. In both tests the leachant was intermittently renewed at specific intervals determined by the norm

designed to maintain a significant diffusive driving force. The batch leaching test for crushed material was performed in accordance to the European Standard EN 12457-2, 2002 at liquid solid (L/S) ratio of 10. The up-flow percolation test was performed in accordance to the European committee for standardization CEN/TS 14405, 2004. However, some modifications were made to the test setup given the low permeability and monolithic nature of the sample.

The batch leaching test for monolithic samples was an experimental test designed specifically for the purpose of this thesis. It is a hybrid test made from the batch and diffusion tests. The objective was to assess the possibility of finding an alternative type of test that is more suitable for testing S/S materials than the batch test while is not as demanding as the diffusion test with respect to the test duration. An L/S ratio of 10 and test duration of 24 hours were used to perform this hybrid leaching test for monolithic samples. The experiments for this type of test were not successful since much of the monoliths were largely damaged during agitation in the end-over-end shaker. In such circumstance, interpretation of the data is a rather futile exercise since the tests were deemed not reproducible. As such, a new leaching test was designed with the same objective with the consideration that the monolithic structure is preserved (i.e. not disintegrated). This test was called leaching test of monoliths with magnetic agitation. The magnetic agitation test was performed at three different times: 24hrs, 48 hrs and 96 hrs.

Sea water was used as the leachant in all of the tests performed. This selection was made based on the fact that S/S contaminated sediments under study are considered to be exposed to this type of leachant in field conditions.

The results indicated that the total composition of the studied metals (Cu, Cr, Ni and Zn) in the S/S contaminated sediments is mostly irrelevant for their leaching prediction. Further, different types of tests give different contaminants release estimations. Amongst the leaching tests performed, the diffusion test was considered to be the most suitable test for determining the long-term leaching behaviour of the S/S contaminated sediments.

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1.0 INTRODUCTION

The Norwegian authorities have identified contaminated sediments in various localities along the Norwegian coast line. The sediments represent a significant problem for the public's health as well as for the environment especially in urban costal regions where former harbour areas are converted to residential zones requiring more strict environmental standards. As such, environmentally motivated remediation efforts have become increasingly relevant to solve the problem. The option of Solidification and Stabilization (S/S) of contaminated sediments was one of the alternatives proposed to solve this situation.

The stabilization and solidification (S/S) of contaminated sediments is a commonly applied environmental technique with a goal to reduce the leaching potential of the contaminants in both physical and chemical means. An environmentally acceptable S/S waste can also be used for construction purposes (e.g. foundation material). The effectiveness of the remedial measures of this type of treatment for environmental purposes is normally determined via leaching test. However, a good understanding of leaching processes is essential for the selection of a reliable set of experiments and at the same time for the proper judgment of the results. To that extent, the project for this thesis was designed with the main objective of determining how the performance of different leaching tests will affect the release of selected inorganic contaminants from the stabilized and solidified contaminated sediment.

This thesis is part of a larger research project with respect to S/S of contaminated sediments, where the following participants are involved: Norcem, The Norwegian Geotechnical Institute (NGI), Det Norske Veritas (DNV), Rambøll, Skanska Norway, and NOAH. The larger project is financed by the research council of Norway and this thesis is worked under the supervision of the Norwegian Geotechnical Institute.

The S/S specimens produced for the work of this thesis project were made from contaminated sediments from the Trondheim fjord and fly Ash (FA) standard cement produce at Norcem. The appropriate mix design and material characteristics were taken form the previous investigations carried out by NGI. A total of six different leaching tests were carried out for the S/S sample using seawater as a common leachant. An additional objective of the thesis project is the determination of the most suitable leaching test, among the six tests studied for leaching behaviour prediction of the S/S contaminated sediments under natural field conditions.

2.0 BACKGROUND INFORMATION

2.1 A brief overview of contaminated sediments in the Norwegian fjords

In many estuaries and fjords surrounded by large populations and/or harbours, the top layer of marine sediments usually becomes contaminated due to a variety of potentially polluting anthropogenic activities. Norwegian coastlines have a unique characteristics where the shallow sills within the fjords restrict water exchange between the fjords and open sea. As a consequence, the dispersion of the pollution from the fjords into the sea is largely reduced and therefore, the contaminants mainly remain near the source(s). This phenomenon is schematically shown in Figure 1. With time, the contaminated sediments act as a reservoir of pollutants, even long after the source(s) of pollution is removed. The pollutants may be mobilized by natural processes and/or man-induced changes in external parameters (e.g. pH changes due to acid rain, complexing agents or just ships traffic).

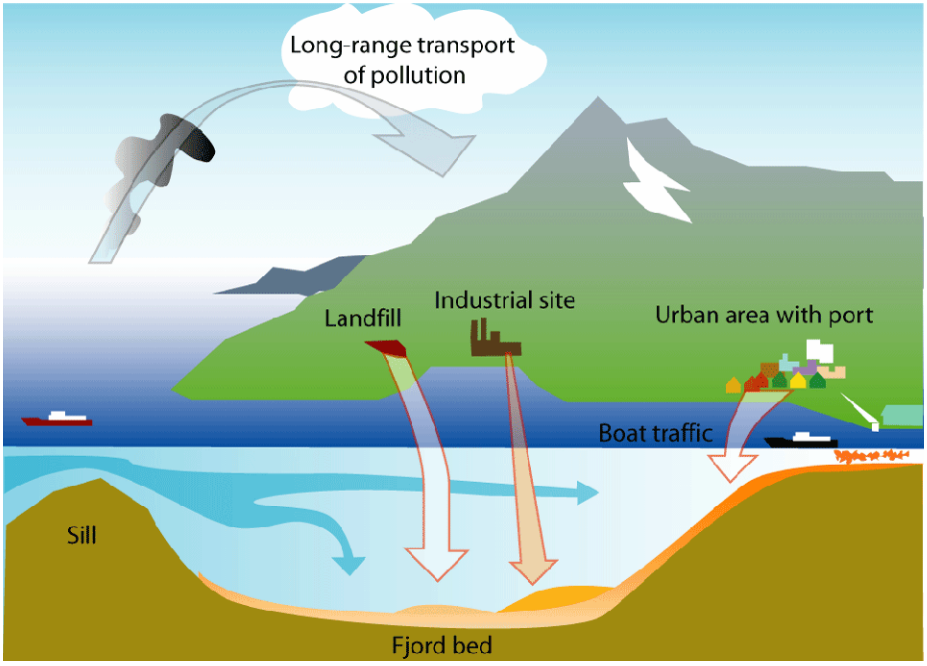


Figure 1 Fjord system and sources of sediments' contamination modified from MD (2002)

In Norway, as in many other countries, contaminated sediments represent a significant problem for the public's health as well as the environment. Larger cities such as Oslo, Bergen and Trondheim face more severe problems. More than 120 polluted localities along the Norwegian coastline were investigated between 1993 and 1996 of which, about 90 were found to be heavily polluted by mainly one or more pollutants such as PCBs, PAHs, organic tin compounds, mercury, lead and cadmium (Norway State of Environment 2006). A major portion of the sediments contamination in the fjords has taken place within the past 50 - 100 years. The health authorities have restricted commercial exploitation of marine species (fish and shellfish) in about 30 affected areas (Laugesen 2007). As such, environmentally motivated remediation efforts have become increasingly relevant to solve the problem. Currently, the government has developed policies to cope with the problem. These policies are described in the white paper titled, ‘Protecting the Riches of the Seas (Report No. 12 (2001-2002) to the Storting)’.

2.2 Investigations by the Norwegian Geotechnical Institute (NGI)

The research council of Norway is financing a large project for the assessment and research on remediation measures of contaminated sediments of the Norwegian fjords. S/S of contaminated sediments is one of the alternatives proposed for solving the problem, where the following institutions are involved: Norcem, The Norwegian Geotechnical Institute (NGI), Det Norske Veritas (DNV), Rambøll, Skanska Norway, and NOAH.

The Norwegian Geotechnical Institute (NGI) has carried out various investigations related to contaminated sediments in Norwegian fjords. Various remedial measures have been proposed one of which is Stabilization and Solidification (S/S) of the contaminated sediments. In this respect, NGI has initiated a major Research and development project titled, “Stabilization and Solidification of Contaminated Sediments”. The objective is to develop methods to stabilize and solidify contaminated fjord sediments for construction areas with minimal contaminant migration. Most of NGI’s work is still under progress at present. However, a portion of the early investigations consists of the S/S mix design and chemical characterization of the contaminated sediments and cement, the results of which are presented in an internal report titled, “Development of Binders - Data report from characterization and initial experiments”. In this study, different contaminated sediment samples taken from various contaminated Norwegian fjords, were mixed with various cement types in different proportions to find out the most efficient combination. The efficiency of the S/S material was defined in terms of the geotechnical strength, economics and workmanship while being environmentally acceptable to the regulators.

Among the various sites and possible binders, contaminated sediments from the Trondheim fjord and FA standard cement produced at Norcem were selected and used to make the S/S specimens for the work of this thesis project.

3.0 MOTIVATION AND OBJECTIVES

The effect of remedial measures such as S/S of contaminated sediments is determined using leaching test(s). NGI has carried out a series of batch leaching tests for different Stabilized and Solidified (S/S) contaminated sediments. Given the large number of samples, the batch leaching test was selected for three reasons; it is simple to set up, easy to perform, and has the shortest duration. As such, the batch leaching test was considered suitable for a quick first screening when selecting the appropriate S/S mix design. However, the batch leaching test is inherently qualitative and does not accurately simulate leaching of the contaminants from the S/S waste material in a natural setting. Further, the S/S samples have to be crushed for the batch leaching tests which in turn, results in over estimation of the contaminants release.

The selection of an appropriate test or combination of tests is of vital importance for the proper judgment of results of contaminants release from an S/S treated waste. There are many other leaching tests that are suggested for the assessment of the leaching characteristics of S/S sediments of which, the diffusion test is highly recommended for solid monolithic material. However, the diffusion test requires a very long duration and in some cases the results may be difficult to interpret, especially if the waste type is not heavily polluted and leachate concentrations are low or if the test might not be a good representation of the site conditions.

Given the above, an experimental program was designed for this thesis project and conducted at NGI. The experimental program consisted of performing six different leaching tests on S/S Trondheim sediments to assess the leaching of inorganic pollutants. The objectives of the experimental program were as follows:

- Study how the performance of different leaching tests affects the release of the inorganic contaminants under study from the S/S contaminated sediments,

- Explore the possibility for developing a new type of test(s) with a duration shorter than the diffusion tests and reliable results for assessment of contaminants release from S/S contaminated sediments materials, and

- Find the most suitable leaching test or a combination of tests for prediction of release of inorganic components in the S/S material placed in natural conditions.

The details of the six leaching tests designed for the experimental program are given in Section 5.2.

4.0 LITERATURE REVIEW

4.1 Stabilization and Solidification (S/S) as a remediation technology for treatment of contaminated sediments

In the case of marine sediments, the most widely use and traditional procedure for reducing contamination effects has been dredging and disposal of materials in controlled landfills. Lately in a lot of cases this method is becoming impractical because is increasingly difficult to find adequate space (Cangialosi et al. 2006). Therefore, S/S technology has become a promising alternative to solve this problems because it provides an economically viable means of treating contaminated sites close to the areas where the problem exist by reducing the need of landfills.

The process and techniques of Stabilization/Solidification (S/S) have matured into an important and accepted part of environmental technology. As a result many S/S methods are being promoted and offered for treatment of hazardous and other waste types from industry, municipalities and government sources. This technology, which involves mixing cement into contaminated material, protects the environment by immobilizing hazardous contaminants within the treated material. The cement reacts chemically with the water in the material being treated, creating changes in its physical and chemical properties that stabilize these hazardous constituents and prevent their release into the environment.

Stabilization refers, to techniques that reduce the hazard potential of a waste by converting the contaminants in less soluble, mobile or toxic forms (chemical changes). These changes will be mainly a result of the high pH induced by the addition of the most common binders, such as lime and Portland cement, that result in the precipitation of many contaminant species. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization (Conner and Hoeffner 1998).

Solidification, refers to a technique through which the waste is encapsulated in a monolithic solid of high structural integrity. It will increase its compressive strength that enables it to support more weight. Solidification does not necessarily involve chemical interaction between the waste and the reagents used for solidification, but the waste will be mechanically bound into a monolith. Contaminant migration will be restricted by vastly reducing the surface area exposed to leaching and/or by isolating the waste within an impervious capsule, as an effect it will be seen that the large decrease in its permeability will reduce water infiltration and therefore contaminant transport.

Although S/S technology was originally developed for treatment of nuclear waste in 1950s and later on different types of hazardous wastes. From around 1980s the technology also was applied for treatment of contaminated soil and sediments (Laugesen 2007). Interesting examples have been found in the case of treatment of contaminated sediments in Norway using Stabilization/Solidification technologies as is the case for Trondheim sediments.

Trondheim harbour dates back to early 10th century and is in part formed by a natural river and receives 1.3 million tones of goods through approximately 5 000 ships frequenting the harbour yearly. The main sediment pollutants found in Trondheim harbour are tributyltin (TBT), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCB), and heavy metals (Laugesen 2007). The Norwegian environmental authorities have started a program for testing technologies to solve the contaminated sediments problem. One of the field scale pilot projects is in the Trondheim harbour with the following objectives.

- Removal of contaminated sediments in areas where there is a high risk of contaminant dispersion due to traffic or natural currents.
- Safe deposition of polluted sediments in a confined disposal facility (CDF)
- Reduction of possible leakage of environmental pollutants from the CDF by mixing it with stabilizing components
- Achievement of geotechnical stability of the stabilized material to allow the utilization of the area for commercial purposes.

4.2 Common binders used for the S/S treatment technology

As mentioned earlier the main advantages of using a binder when treating a waste product is their capacity of provide chemical stability and physical solidity. Appropriate binders are selected for a specific site and contaminants based on a set of design criteria. The design criteria, have usually been depended on the properties of the end products, and required taking into account the nature of the material and contaminants that are being treated.

Binders can in general be dived in two main groups (Bone et al. 2004). Primary stabilizing agents and secondary stabilizing agents.

4.2.1 Primary stabilizing agents

Primary stabilizing agents are widely applied in the remediation of contaminant soils worldwide. They are characterized as the ones that can be used alone to bring on the stabilizing action required. When a cementitious binder is used the waste or sediment particle is encapsulate chemically and physically. The interaction of binders and waste material is complex and is shortly described in the next section of this thesis. The most common binders used in S/S technology are: Portland cement, lime and thermoplastic materials that include bitumen and sulfur polymer cement.

Cement and lime can be blended with some secondary stabilizing agents for example, Pulverized fuel ash (PFA, named fly ash in Europe and the USA) or ground granulated blast-furnace slag (ggbs) to modify physical and chemical properties of the solidified and stabilized waste forms. This allows optimization of the binder to a contaminated medium.

For more information refer to (Bone et al. 2004) and (Al-Tabbaa and Perera 2005) who treated this topic in detail.

4.2.2 Secondary stabilizing agents

Secondary stabilizing agents include materials that are not very effective on their own but can be usefully used in conjunction with lime or cement (Bone et al. 2004). Sometimes, only a small proportion of cement or lime is needed as an activator and the secondary agent may comprise the major proportion of the binder. Secondary materials may be added an S/S system for particular contaminants, in quantities that provide an economic binder system, without compromising technical properties.

Some of the most common secondary stabilizing agents are: Ground granulated blastfurnace slag (ggbs), used mainly to enhance lower diffusion rates in the mixture, additionally it lowers redox potential of pore solutions, and improves durability of S/S waste performance in comparison with conventional cements.

Another widely used secondary stabilizing agent is; Pulverized fuel ash (PFA), which is a synthetic pozzolana created by the combustion of coal. Some of the characteristics take into consideration when PFA is used are: The content of unburned carbon, because carbon surfaces can sorb some of the contaminants including organics; the ability to decrease water demand on the binder; the pozolanic activity of the PFA, that is important in the development of strength and reduce permeability of the S/S material in stages of setting and hardening; and the ability to influence the redox environment.

Other secondary stabilizing agents include e.g. natural pozzolands, polymers, silica fume, rice husk ash (that contain pozzolanic material), organoclays (Bone et al. 2004). For more information refer to (Bone et al. 2004) and (Al-Tabbaa and Perera 2005) who treated this topic in detail.

4.3 Stabilization/solidification and their effect in inorganic contaminants

As explained before stabilization and solidification processes can be used together to encapsulate the contaminants in the treated product. The contaminants are chemically immobilized in the matrix of the treated waste form by adsorption, hydrolysis and precipitation reactions.

The effective use of S/S has been demonstrated with a range of inorganic contaminants groups, (Bone et al. 2004) including:

- Volatile metals;
- Non-volatile metals
- Radioactive materials
- Asbestos
- Inorganic corrosives
- Inorganic cyanides

The physical and chemical processes by which anions and cations interact with cementitious binders, allow useful predictions to be made regarding the treatment of waste. There are several processes that are combined to facilitate chemical stabilization of inorganic contaminants in soils. These will have a large effect on S/S and are dominated by the clay fraction of a soil or sediment. The reaction of clay soil/sediment particles and binders provides a long-term stabilizing process that encourages adsorption and metal precipitation.

The aqueous phase present in the pore structure of cement-based waste forms is alkaline and promotes the precipitation of insoluble species, particularly metal hydroxides. However, the high pH of pore fluids is not dependent on the amount of hydrated phases but on the maintenance of a quasi-equilibrium between solid and aqueous phases (Bone et al. 2004) and this results in continued retention of metallic contaminants in a waste form.

The disruption of equilibrium by internal or external effects will eventually result in the release of contaminants. This important observation tell us that over time and in response to changing conditions of service, a reduction in pore fluid pH will occur resulting in the mobilization of some contaminants.

4.3.1 Inorganic contaminant – binder interactions

Interaction of contaminants with sediments and/or binder involves a number of fixation mechanisms (Bone et al. 2004) such as:

Adsorption to binder-sediment matrices

Adsorption in binder-soil matrices is achieved at high pH in order to bring better surface adsorption at the mineral edge sites. The effectiveness of sorption processes will depend on both soil/sediment mineralogy and preservation of a high pH environment.

It has been reported in several documents, that there is a process of cation exchange that results in the displacement of the host cations from a clay soil. As an example, reports show that high levels of leachable Ca recorded were attribute to exchange of Ca by metals on the ion exchanger. Surface sorption of metals is one of the important factors in metal immobilization mechanisms of lime-stabilized soils. Different types of soils/sediments with different types of chargeable surfaces will present distinct adsorption selectivity of metals.

pH dependent precipitation

An increase in the concentration of OH^- ions in solution can result in the formation of metal-hydroxide complexes and precipitation of metals salts can occur.

Redox controlled precipitation of insoluble compounds

Generally cements are produced under typical oxidizing conditions with high E_h values. However, considering that binder addition rates are generally low during S/S, the potential for an specific contaminated material to influence the redox environment in a treated waste form, should not be underestimated. The most favorable environment for immobilization of contaminants would appear to involve maintenance of reducing environment so that multivalent anionic metals can be reduced to less soluble cationic species.

Adsorption/encapsulation into and onto nanoporous C-S-H gels

Calcium silicate hydrate (C-S-H) gels are known to be persistent under geological conditions thousands of years and thus, are very important where retention of metals in S/S waste forms are concerned. C-S-H gels have a nanoporous structure, which gives a high specific surface area (between 10 and 50 m^2/g) to which both anions and cations may be sorbed.

Preferential binding for either anions or cations can be accomplished by altering the calcium:silicon ratio (c/s), of the C-S-H gel and this can be done by cautiously choosing the binder system. Calciumrich C-S-H gel possesses a positive surface charge to which preferential sorption of anions may occur, whereas silicon-rich C-S-H gel favours the sorption of cations (Bone et al. 2004).

The abundant C-S-H produced during hydration of Portland cement has a dominant influence on the retention of metals in solidified waste forms. Evidence shows that immobilization is through both sorption processes and by substitution for Ca or Si in the gel phase. Additionally, physical encapsulation of contaminants by C-S-H gel also provides another simple mechanism for the effective retention of pollutants.

Incorporation into crystalline components of the cement matrix

Chemical immobilization of contaminants by S/S is successful due to the fact that contaminants can become incorporated into the solid, crystalline phases of the cementitious matrix. The various phases of cementitious binders (portandite, ettringite and monosulfate and tetracalcium aluminate) play and important roll in the interaction with contaminants.

4.3.2 Interaction with specific groups of inorganic contaminants

A very detail description of the list of the more important groups of inorganic contaminants and their interaction with S/S material is given by Bone and co-workers (2004). These groups include: transition metals including heavy metals, oxyanions, Organo-metallic complexes, amphoteric metals, other inorganic compounds and waste streams. This is summarized in Table 1

A summary of the models describing the interaction of priority metal pollutants with cement is presented on Figure 2 (Spence 1992). Zinc, Cadmium, and lead are preferentially deposited on the surface of the cement grains according to Spence (1992). The surface compounds of Cd and Zn have been identified as mixed hydroxides. These species apparently result from the Ca adsorption of the normally anionic Cd and Zn species at high pH. Although The Pb surfaces species have yet to be identified it is likely to be negative species in solution at high pH. Hg has been proven to be present as surface particulate, HgO. Ba has been found to be present as sulphate and carbonate. Cr is incorporated into the C-S-H matrix although the process remains unclear.

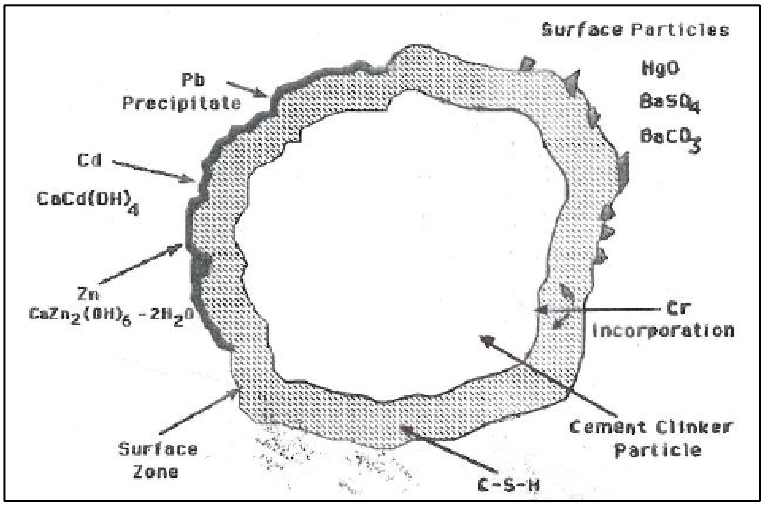


Figure 2 Summary of models for the interaction of priority metal pollutants with cement after Spence (1992)

Table 1 Stabilization experience for selected metals modified from (Bone et al. 2004)

Metal	Common Compound include	Comments
Antimony	Forms inorganic and organic compounds	Easy to treat by S/S no problem encountered
Arsenic	Metal arsenates, metal arsenites, e.g. $Ca_3(AsO_4)_4$, sodium arsenite ($NaAsO_2$), and arsenic sulfides and oxides.	Normally chemical methods are suitable for immobilizing As. Some species e.g. As_2S_3 need alkaline oxidation to produce insoluble species e.g calcium arsenate. As may respeciate under influence of carbonation
Barium	Present in many wastes	Addition of gypsum will precipitate insoluble barium sulphate
Beryllium	Limited data	Spiked soils treated by cement effectively. Building blocks produces from some wastes
Cadmium	Cadmium arsenates, borates, carbonates, halides, hydroxides and oxides	Compounds generally have low solubility in alkali and can be treated with lime and cement. Cd may require additional treatment step. Cd may be physically encapsulated in some binders.
Chromium	Pigments with chromium, chromium sulphate, chromium arsenate, chromic acid, nitrate, sodium or potassium dichromate, and ammonium dichromate	Cr is amphoteric and may form basic or acid compounds. Reduction of $Cr^{(6+)}$ salts produces $Cr(OH)_3$ of low solubility. Soils contaminated with $Cr^{(6+)}$ may require a two-step treatment regime. $Cr^{(6+)}$ may remain mobile if Portland cement (PC) binder used.
Lead	Lead halides, oxides, sulphates, nitrates, carbonates and silicates	Pb is amphoteric and forms soluble anionic compounds. Control of pH is important, additives such as carbonate e.g. $Pb_3(CO_3)_2(OH)_2$ insoluble precipitates in treated soils. Lead may be sorbed onto C-S-H and treated with lime and PC.
Mercury	Mercury chloride, oxide, nitrate, sulphate and sulphides	Most of S/S binders effective. Elemental sulphur or organic sulphides additives can be used. Organo mercury compounds may prove difficult. Sorbents may be used.
Nickel	Nickel oxide, sulphate, nitrate, halides, carbonates, hydroxides, cyanide and sulphide.	Good pH control, generally effective for Nickel. Under some circumstances Organo-sulphure compounds are required. Ni may be chemically encapsulated by sulfoaluminate binders
Thallium	Limited data	Spiked soils treated by cement effectively
Vanadium	Limited data	Spiked soils treated by cement effectively
Zinc	Commonly encountered	Control of pH effective. Cynide complexes may prove difficult

4.4 General principles for leaching

A simple definition of leaching is the transfer of a substance or compound from a solid to a liquid phase when the two are in contact (Bone et al. 2004). It is a complex phenomenon and occurs in nature as a result of physical and chemical weathering processes involving the interaction between a soil or rock and water. There is a large number of factors that can influence the rate of dissolution of constituents and they are divided into three categories: Physical, Chemical and Biological. (Sloot et al. 1997).

4.4.1 Physical factors influencing leaching

In general, physical factors influence the way the liquid and solid materials come into contact, and the condition in which the materials are subjected to leaching in nature or laboratory. Some typical physical influencing factors are described below.

Particle properties

- *Average particle size* : Leaching is in part related to the surface exposed to leaching. The surface area increases exponentially with a reduction in particle size.

- *Internal pore structures in the material:* Materials with low values of internal porosity and low permeability will hardly transport water. Consequently, the flow velocity will be quite low.

- *Particle surface area to volume ratio:* Larger surfaces per mass or volume can allow more rapid dissolution at the surface.

- *Homogeneity or heterogeneity of the solid matrix:* In terms of mineral phases, in a bulk sample consisting of a wide range of heterogeneous particles the leachability observed in the field or laboratory reflects the sum of all interactions.

- *Chemical and mineralogical properties of particles:* Some major and minor minerals are more soluble than others and the leacheate, pH and oxidation/reduction potential are governed largely by the major elements (more soluble major minerals).

Hydrogeological conditions

The rate of dissolution of constituents largely depends on the way that water flow passes the particles, also known as the hydrogeological condition. For a slow fluid flow and a highly soluble solid phase, the dissolution rate can be faster than the velocity at which the dissolved constituents are transported.

Therefore, equilibrium conditions between solid and liquid can be achieved. On the other hand, when the flow is fast and solid phases are relatively insoluble, the rate of transport is greater than the rate of dissolution. Therefore, equilibrium will not be reached and, kinetics in a physical sense will come into play. The mass transfer from the particle to the bulk solution is critical in such cases.

Degree of saturation

Laboratory leaching tests are generally carried out under saturated conditions. However, the liquid/solid ratio in the field is often much lower than those conducted under laboratory conditions since the in-situ soil is usually unsaturated. When the soil is unsaturated, it is exposed to oxidation by O_2 and neutralization by CO_2 Partially filled pores lead to a faster carbonation due to the 10,000 times higher diffusion of carbon dioxide in air than in water (Sloot et al. 1997). As such, the concentrations in pore water of in-situ soils are much higher than the ones obtained in most leaching tests. The unsaturated conditions in the field, can lead to a much lower pH and higher redox potential than the ones found in laboratory tests

Ageing, weathering and mineralization

In time scales considerably larger than those used in the laboratory, physical changes in surface mineralogy of a material may occur. This comprises processes such as carbonation and oxidation. In such cases, the leachate composition may change with time.

For example, in cement-stabilized materials that are exposed to seawater, precipitation of new mineral phases leads to surface sealing. This will result in a significant reduction in the uptake of sea salts in the matrix and therefore the release of mobile contaminants from the S/S matrix will be reduced. The precipitation largely consist of calcite and brucite formed by the reaction of lime from the cementitious product that is combined with the magnesium and sulphate present in high concentrations in seawater (Sloot et al. 1997).

Temperature

Temperature affects both the solubility of chemical species and rate of reactions. In the case of laboratory experiments, temperature will affect results of both the equilibrium and kinetic tests.

4.4.2 Chemical and biological factors Influencing leaching

The main chemical factors influencing leaching are: pH, redox potential, complexation and sorption (Sloot et al. 1997)

Influence of pH

- *pH with respect to liquid solid ratio (L/S):* The pH in leaching experiments designed at (semi-)equilibrium is usually governed by the dissolution of the major mineral phases in the solid or by atmospheric CO_2. The initial and the equilibrium pH of a leachant may differ widely. Particularly, if the liquid solid ratio (L/S) is low and the solid phase dominates the system. On the other hand, at high L/S ratios the solution may become more important.

- *pH with respect to some important groups of constituents:* The pH will influence the dissolution of some important constituents in a material being leached, as is the case of many metals that are species whose solubility varies according to pH variations (refer to Figure 17). However, there are some species that also show independence in their solubility with pH variations such as in the case of the halogens (with exception of fluorine). These species are generally not controlled by solubility limitations. Therefore, the complete fraction that is available for leaching will be leached out readily. Alkali elements such as lithium, sodium and potassium that are very similar with respect to their leaching behaviour; have not presented relationship between pH variations and their leaching characteristics (Sloot et al. 1997).

- *pH with respect to open or closed system from the atmosphere:* In open systems, the pH can be strongly affected by uptake of CO_2 from the air. This is particularly important in percolates collected from laboratory column experiments, lysimeter test and field collected percolates (Sloot et al. 1997). The effect is largest in the latter case as the exposure time to the atmosphere is generally longest. Therefore, the evaluation of long term conditions of alkaline materials must always take neutralization by carbonation into account. The degree of wetting is also important for the rate of carbonation as illustrated in Figure 3, the porous matrix is presenting the highest rate of carbonation under partial saturation. Partially filled pores lead to a faster carbonation due to the 10,000 times higher diffusion of carbon dioxide in air than in water. In this respect, the acid neutralization capacity of the material is a crucial parameter since it dictates how long a material can maintain alkaline properties.

- *pH influenced by biological factors:* The formation of CO_2 through biological degradation of organic matter may affect the pH. Biologically generated CO_2 must be considered with respect to the neutralizing effects on the alkaline materials brought in or in contact with the soil. Other biologically mediated process is the oxidation of sulphide to sulphate generating acid solutions (such as in acid mine drainage).

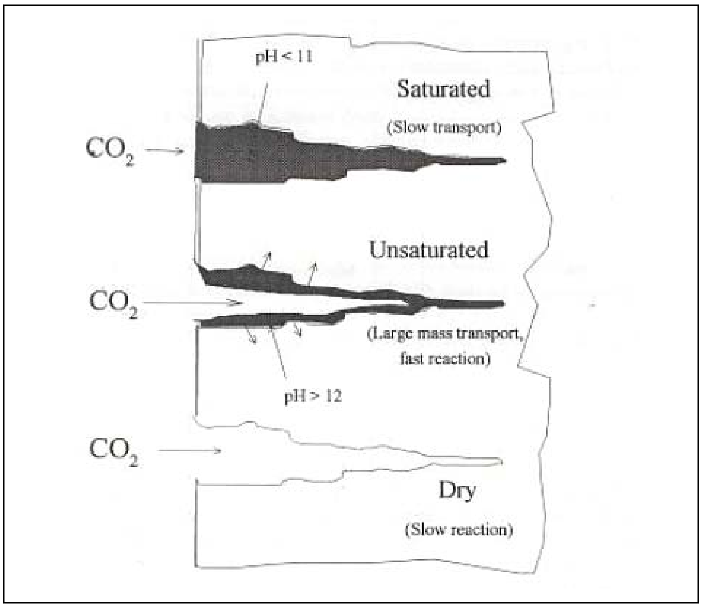


Figure 3 Rate of carbonation in relation to the wetting degree (Sloot et al. 1997)

Influence of oxidation-reduction potential

Under anoxic environmental conditions, the redox potential has an important role in the leaching process. The absence of oxygen leads to formation of different chemical phases with significantly different solubilities when compared to oxidized conditions. The formation of very insoluble metal sulphides is a clear example of such reactions. The reducing conditions can be a property of the material studied (e.g. industrial slags and sediments). In leaching tests the role of redox changes is often neglected. However is important to be aware of such conditions, since the leaching of components may present changes of orders of magnitude with this respect.

Influence of complexation

The presence of specific complexing agents, may affect the mobilization of some constituents than otherwise would not be soluble under this specific conditions. As such, they may reach concentrations far exceeding the equilibrium concentration of mineral phases present in the system. Stability of the complexed state ensures that the bounded solute is not accessible to participate in solid phase dissolution/precipitation equilibrium as in the absence of the complexant.

In the case of soluble complexants, the hydrology of the system under consideration is also important. The soluble complexes can percolate from the surroundings into a material and mobilize constituents. Soluble complexants can also be washed out of the matrix and therefore loose its mobilizing potential. Some examples of complexation are: Inorganic complexation of cadmium chloride and organic complexation.

In systems with presence of organic matter, complexation of metals with dissolved organic carbon (DOC) is a well known process in several matrices. Figure 4 shows the leachability of Cu from municipal solid waste incinerator bottom ash controlled by the formation of Cu-DOC complexes. In the figure the top solid line reflects the total composition of Cu in bottom ash, the broken line represents the potential leachability, the drawn line with the black squares reflects the actual Cu release. The dotted line reflects the leaching behaviour of inorganic copper (Sloot et al. 1997).

The formation of DOC can occur through biological or chemical degradation. An example of chemical degradation is the release of DOC form material containing organic matter exposed to an alkaline environment.

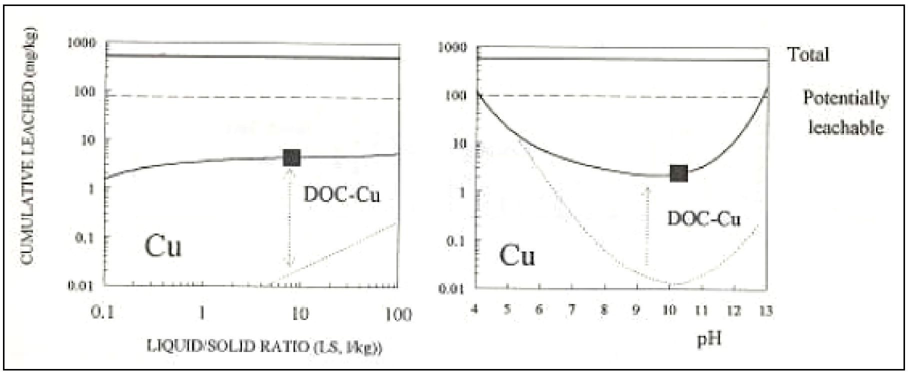


Figure 4 Cu-DOC complexes formation with respect to L/S ratio and pH (Sloot et al. 1997)

Influence of sorption

The sorption property of solid minerals is defined as the capacity of binding dissolved constituents on the surface. Sorption reactions can involve the formation of bonds that are relatively weak to those that are quite strong. Strong bindings imply that the adsorbed species will hardly become desorbed again unless the conditions of the leachate or extractant change significantly. This conditions may be: pH, redox or complexation (Sloot et al. 1997).

Many sorption processes are strongly pH dependent. The surface charge of the sorption sites is important and determines whether anions or cations are retained. Mostly the surface charge is a function of pH. The zero point of charge determines a specific pH if a surface may form an adsorption/desorption edge. Figure 5 shows a typical example of vanadium sorption onto ferrchydroxide. Above pH 9 the role of sorption of ferrichydroxide is limited.

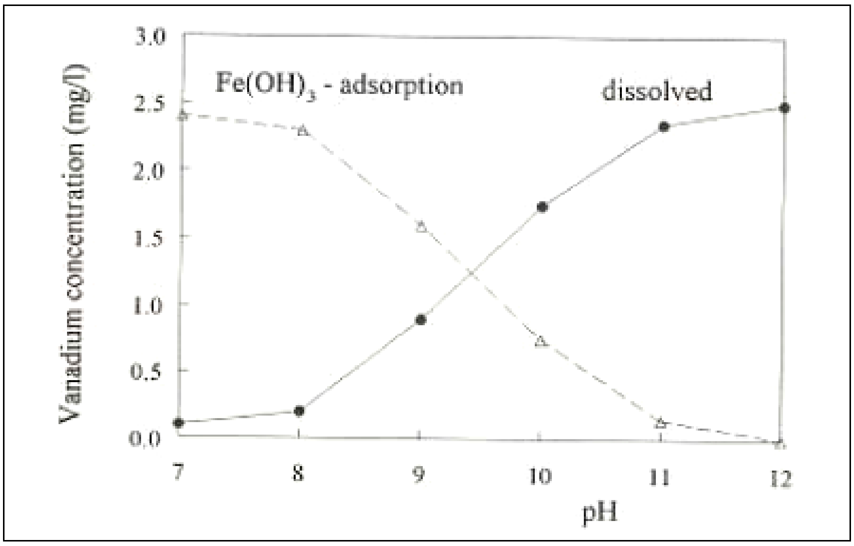


Figure 5 **Sorption characteristic of V on ferrichydroxide as a function of pH (Sloot et al. 1997)**

4.5 Laboratory leaching tests

Leaching tests are commonly used worldwide to determine the concentration of contaminant(s) that are present in the S/S waste form and their likely mobility. The conditions of these tests can be modified to assess significant parameters that will affect leaching behaviour in the environment of deposition of the waste-form and at the same time evaluate performance of the S/S waste form if environmental conditions vary through time. It is the ultimate goal of any testing to be able to evaluate if the remediation option selected complies with the regulatory requirements. In addition, Leaching tests should mimic the field conditions as close as possible. Further, they should be easy to control and model.

It is important to mention that under natural conditions there are a large number of factors influencing leaching behavior of materials, as it has been described in section 4.4 . However, It has to be considered that in laboratory conditions it may not be possible to entirely reflect natural conditions with a particular leaching test. A range of tests may be required to predict the leaching behaviour of the waste form in the environment of deposition (Bone et al. 2004, Schuwirth and Hofmann 2006)..

4.5.1 Parameters controlling leaching tests under laboratory conditions

The main parameters controlling leaching of a substance in laboratory conditions are sample heterogeneity, sample curing and preparation, presence of organics, leachant composition, liquid solid ratios, contact time, contact method, test environmental conditions, solid and leachant separation methods, sample storage, pH (Bone et al. 2004). A brief summary of the most important controlling parameters when performing a laboratory leaching test is presented below..

Sample heterogeneity

It is important to assure the test samples are representative of the field materials to have a better approximation of the leaching phenomena under natural conditions.

Sample curing and preparation

The curing time of the S/S material may have a large influence on their leaching behaviour. Because physical properties such as strength may vary with time, specially the first months after the mixture preparation. Some authors have recommended a 90 days of curing time to determine, longer-term strengths and leachibility of the material.

Leaching tests generally require a specific preparation technique (e.g. drying, screening and/or crushing) prior to testing. As such, the test shall be selected in accordance with the field conditions or objectives of testing. Sometimes the objective of a test is to analyze the worst case scenario as supposed to field conditions. In such cases, the test is carried out by reducing the maximum particle size as much as possible to obtain the highest leaching rate. The potential impact of sample preparation must then be considered, in particular with regard to the objectives of the test.

It should also be noted that the way samples are collected and stored can have a significant impact on the test results. Specially in the case of materials that present reducing conditions, such as sediments. Therefore, recommended procedures for sample storage should be followed.

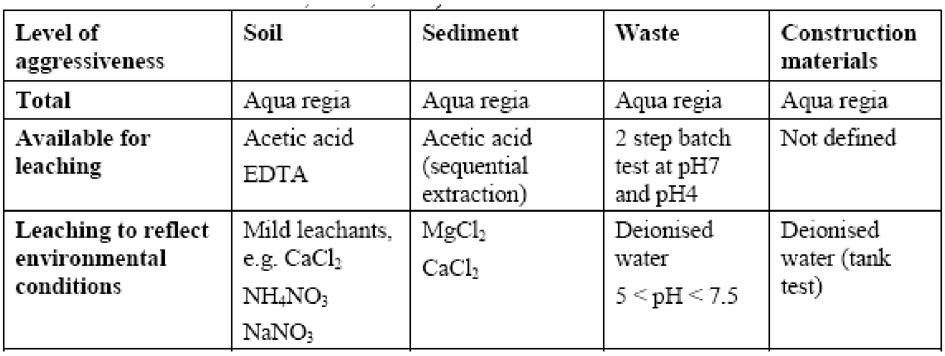
Presence and composition of organics

The dissolution of organic compounds present in a sample may have an influence on the leachant pH, solubility of inorganic contaminants (i.e. heavy metals) due to complexation, and the solubility of organic contaminants. This point has been addressed in more detail in section 4.4.2 (influence of complexation)

Leachant composition

Although demineralised water is the most common leachant agent used in soil studies, in some cases some mild salt solutions (e.g. $CaCl_2$) may also be used instead, to assess mobilization of labile bound species. More aggressive leachants such as EDTA and acetic acid may also be applied. In specific situations special leachants may be used. For example, seawater may be used to assess the release under marine exposure conditions. A large number of leachants have been used to suit specific objectives including the level of aggressiveness required (i.e. total, available and actual leaching under specified conditions), the nature of the material being leached, and the receptor (i.e groundwater, plant uptake). Table 2 provides examples of leachants that are used to assess different leaching scenarios (Sloot et al. 1997)

Table 2 Typical leachants and level of aggressiveness used to assess different leaching scenarios (Sloot et al. 1997)



Level of aggressiveness	Soil	Sediment	Waste	Construction materials
Total	Aqua regia	Aqua regia	Aqua regia	Aqua regia
Available for leaching	Acetic acid EDTA	Acetic acid (sequential extraction)	2 step batch test at pH7 and pH4	Not defined
Leaching to reflect environmental conditions	Mild leachants, e.g. $CaCl_2$ NH_4NO_3 $NaNO_3$	$MgCl_2$ $CaCl_2$	Deionised water $5 < pH < 7.5$	Deionised water (tank test)

Liquid solid ratios

The ratio of liquid to solid (L/S) in a leaching test is usually significantly greater than that in soil pores in-situ and consequently, chemical equilibrium is significantly different. This will affect the quantities of soluble contaminants detected and does not represent the true in-situ leaching characteristics.

The most common L/S is 10. This selection is more based on practical considerations than on the actual situation being evaluated, as was explained above. The reason is that liquid can be separated more easily from the solid at higher L/S and it will also provide a sufficient amount of liquid for analysis. However, if the intention is simulation of systems at higher concentration (such as pore water), the L/S ratio should be as low as possible. In some cases renewal of solids is an alternative (Bone et al. 2004). This leads to sequential lower and lower cumulative L/S.

However, it is necessary to consider how the L/S used in the leaching tests represents the in-situ condition and how the differences in L/S ratio may affect the results and prediction of long-term performance.

Contact time

The contact time will influence the concentration of leached substances at fixed L/S, until equilibrium conditions are reached, when a maximum concentration will occur. Equilibrium is a unique thermodynamic state of a system depending only on temperature. As such, this state provides a framework within which comparisons to other systems may be made. The true equilibrium, or even steady state conditions are unlikely to be reached in natural systems. Equilibrium conditions will exist in a test when the total dissolved solids have reached steady state conditions. This can be measured indirectly by monitoring conductivity and/or pH.

The leaching period is also important when the contaminated material is continually or sequentially subjected to fresh leachant over a time period, dependent on pore volume and permeability. Therefore the driving force for desorption is constant, resulting in time dependent desorption curves. Such methods may be useful where a material will be exposed to rainfall, particularly in a wet climate(Bone et al. 2004).

Contact method

The contact method is directly linked to the leaching period in the sense that the two together affect particle abrasion and subsequent breakdown. The level to which a container is filled is also relevant because this governs the amount of air and also CO_2 present, and the degree to which the solid and liquid can be agitated within the confined space.

The contact method is of importance in flow-through tests because the shape and orientation of the confined material, as well as the pressure at which the leachant is passed though the sample, governs the sample structural breakdown. Sample shape (height to diameter ratio) can have a large influence on end effects that result in non-uniform flow through the sample. This can directly affect the quantities of contaminant removed from a sample.

Test environmental conditions - Temperature

The most important environmental condition is temperature, which affects the results of both equilibrium and kinetics tests. Temperature affects both the solubility of the test species and the rate of reactions. Therefore, changes in the temperature of a system may change also the reaction mechanisms.

Generally most leaching tests are performed at room temperature without any temperature control. It is important to consider that temperature under field conditions may be lower than during test conditions. Therefore, since solubility and in particular diffusion are temperature sensitive variables, this factor needs to be taken into account for the translation of test results to practice.

Solid and leachate separation methods

This is generally not a significant factor for samples where solids settled within a few minutes and the solution can be decanted through filter papers. However, in some other cases centrifugation is used for separation of solid and liquid components. The action of centrifugation can cause particle abrasion and, if not refrigerated, significant heat is produced which may affect the leachate chemical composition. In this circumstances the separation technique is particularly aggressive and may produce a leachate that does not reflect the true quantitative properties of the original material-solution mixture.

Sample storage, preservation and sample analysis method

It may also influence the leachate composition specially if the original condition of the sample is changed. This is an important point for example in the case of sediments.

pH

In the majority of the cases pH is not controlled therefore it is dictated by the material being tested. However, pH may be largely affected when the system is exposed to the atmosphere, due to uptake of CO_2. pH may also change during a leaching experiment, these changes are seldom reproducible and the most sensitive systems are the ones that have a limited buffering capacity. That is why testing in closed vessels without headspace is generally more reproducible.

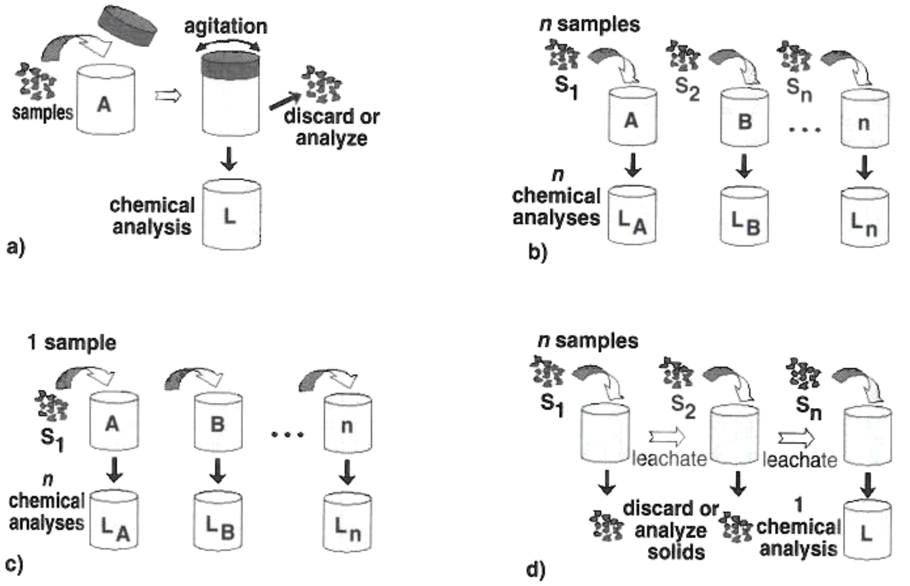
4.5.2 Classification of test methods

Worldwide there is large number of available leaching tests. However, many tests are a variation on the same basic principle with small modifications in specific testing conditions. Generally, leaching tests fall into two categories, based on whether or not equilibrium or steady-state is established during the test duration,. These categories are: extraction tests (also called equilibrium tests) and dynamic tests, (Spence and Shi 2005). The categories and the most important groups within each category are schematically presented on Figure 8

Extraction tests

Extraction tests are usually designed to reach a steady-state release, termed “equilibrium test”. Equilibrium-based leaching protocols typically require particle size reduction of the material under study, in order to reduce the time required to obtain steady-state release via increased surface area and minimized kinetic transport (Spence and Shi 2005). In agitated extraction, shaking or stirring further accelerates the extraction rate and ensures continuous solid/liquid contact.

Common equilibrium tests are: single batch extraction, parallel batch extractions, sequential-batch extractions and concentration build-up extraction (Spence and Shi 2005). The common equilibrium tests are schematically represented in Figure 6.



a) agitated batch extraction test, b) parallel batch test, c) sequential chemical extraction test, and d) concentration build-up test

Figure 6 Schematic representation of extraction test after Spence and Shi (2005)

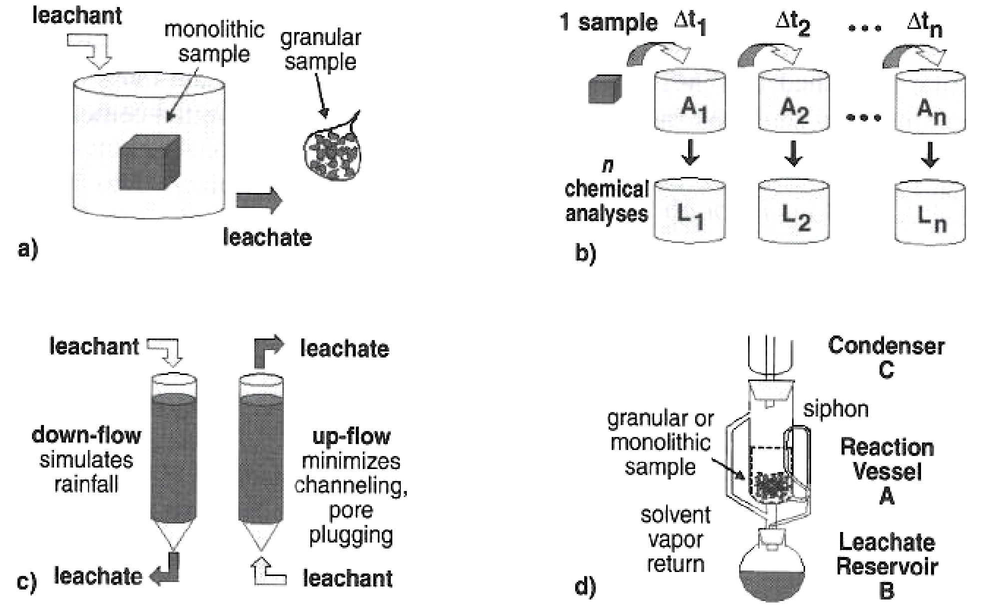
From the common equilibrium tests the single batch test is the one that is mainly used in diverse laboratory analysis and at the same time it is important for this thesis project. The goal of single-batch extraction tests is to characterize solubility or release of constituents at a single set of release conditions. Single-batch tests include standardized protocols (e.g TCLP, SPLP, ASTM 3987, DIN 38 414 S4, and EN 12457 parts 1, 2 or 4).

Dynamic tests

Dynamic tests involve continuous or intermittent restitution of the leachant to retain a high concentration difference between the solid and liquid phase. Although these tests are more complex, expensive and time consuming than the simple batch tests, they provide data relating to the kinetics of contaminant mobilization prior to steady-state conditions (e.g., release flux, cumulative mass release with time, controlling mass-transport mechanisms). and the complex mechanisms related to leaching.

The frequency of leachant renewal may be continuous or may follow a predetermined schedule of intermittent leachant renewals. The ratio of leachant to solid material is much larger than that of the equilibrium leaching test and often is based on the surface area of the subject material exposed to leaching. The physical state of the solid material may be monolithic or granular, depending on the specifics of the testing protocol.

Within this category four groups may be identified based on procedural differences, they are: flow around test, tank leaching test (diffusion test), flow through test (column test), and soxhlet type test (Spence and Shi 2005). These for groups are schematically represented in Figure 7.



a)flow-around test, b) tank leaching test, c)flow-through column test, and d) soxhlet testing apparatus

Figure 7 Schematic representation of mass-transport rate tests, after Spence and Shi (2005)

From the four groups presented as above two of those tests are the most common ones when representation of a dynamic test is required and they are ; the tank leaching test and the column test. These two tests are also considered relevant for this thesis project. A short description of each one of them is presented below.

Tank leaching tests are “semi-dynamic” mass transport rate tests that essentially are serial-batch extractions using large volumes of leachant. The leachant is intermittently renewed at intervals designed to maintain a significant diffusive driving force. In comparison to the dynamic flow-around tests, one advantage of tank leaching testing is that release concentrations tend to be more consistent with analytical capabilities. In addition, procedural simplicity is increase, as no pumps are required.

Standardize examples of tank leaching tests are the protocols such as the Netherlands Monolithic Leach Test (NEN 7345) and ANSI/ANS-16.1-2003.

The flow-through test most commonly know as column test, usually involve passing the leaching solution through a solid material and collecting the leachate after contact. The resulting leachate concentration may be used to determine the rates of constituent release during advective mass transport and to infer primary release mechanisms at low L/S ratios. Usually this type of test is performed on columns in granular material as is shown in Figure 7c. Modifications in the flow direction (changing down flow to up-flow) are normally done to avoid problems such as preferential flow pathways (channeling and pore plugging),.(Spence and Shi 2005). Examples of flow through test for granular materials include ASTM 4874, the Netherlands regulatory "up-flow" column test (NEN 7343), CEN/TS 14405.

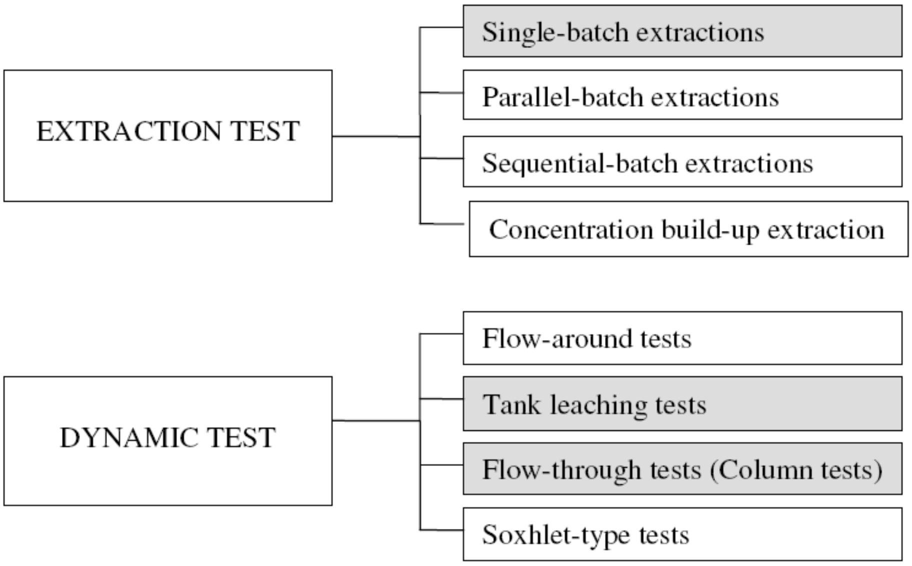


Figure 8 Leaching test Categories and most important groups

As addressed before from the most important groups presented in Figure 8 three of those test are considered the most common ones and they are single batch extraction test, tank leaching test and column test (highlighted in grey in figure 8). The main advantages and disadvantages have been classified by (Bone et al. 2004), and are presented in Table 3.

From Table 3 it can be concluded that using a single leaching test it may not be possible to simulate the leaching mechanism under natural conditions, due to the limitations that each test present. However, knowing the advantages and disadvantages and the specific goals that the investigation requires, one or various test may be selected to fulfill specific requirements of the study.

Table 3 Advantages and disadvantages of the principal types of leaching tests (Bone et al. 2004)

TEST CATEGORY/ OPERATING PARAMETER	ADVANTAGES	DISADVANTAGES
Agitated extraction tests (Batch tests)	• Tests are simple to set up and perform. • Tests can be of short duration (hours) in controlled conditions and if performed at various times can highlight the mechanisms of contaminant retention. • Disturbed samples can be tested easily. • Drying material makes it easier to crush samples if desired and achieve required solid to liquid ratios. • Deionised water is an easily controllable substance that does not affect the stabilization and solidification contaminant retention mechanism in the same way as an acid. • Once equilibrium is achieved leachate can be removed and replaced with ‘fresh’ leachant as many times as required. • Synthetic or real leachants, representing leachants *in-situ* can provide a more representative leaching model.	• Does not represent environmental leaching conditions and is therefore inherently qualitative. • Drying can affect the species of contaminants present and remove volatile organics. • Neither drying nor crushing represent environmental conditions. • Distilled water does not necessarily represent site-leaching conditions. • Synthetic or *in-situ* leachants require characterization to obtain leaching results by subtraction. • There is no account of time dependent changes in leachant composition. Some minerals do not separate easily from the liquid fraction. • Filter medium can affect chemical determination by element release or attenuation from or onto filter membranes respectively. • Centrifugation can affect results.
Flow-around tests (Diffusion tests)	• Easy to control leachant, solution temperature. • Contaminated samples can be tested as monoliths without pretreatment. • Diffusion mechanisms are investigated, which are important in low leachate flow conditions. • Solid and liquid separation is not necessarily required.	• Difficult to interpret the results and may not represent the diffusion conditions of a particular disposal site. Results are therefore qualitative, similar to the extraction tests.
Flow-through tests (Column leach tests)	• Can represent environmental leaching conditions. • Conditions can be controlled and changed throughout the test. • Unlike the other tests the sample can be subjected to varying physical stress conditions to represent individual sites. • Monolithic samples can be tested without pre-treatment. • Leachate can be passed through samples under pressure to accelerate leaching.	• The tests are not considered suitable for regulatory purposes due to the poor reproducibility and long duration. • Tests can last a number of months depending on material permeability and are difficult to set up and perform. • It is difficult to obtain representative undisturbed *in-situ* samples. • Data from this process are inherently qualitative.

5.0 PROCEDURES AND MATERIALS

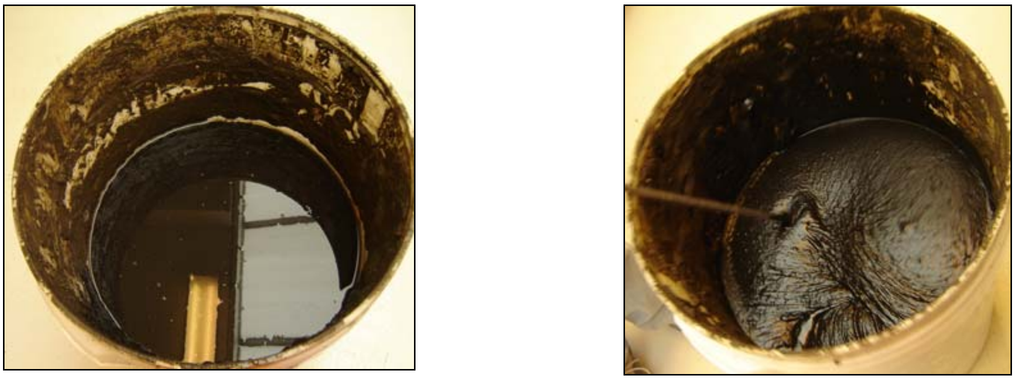
The experimental procedures consisted of first preparing the Stabilized and Solidified (S/S) contaminated sediment samples and then conducting the leaching tests. The experimental procedures and material properties are described in the following sections.

5.1 Stabilization and solidification of contaminated sediments

5.1.1 Materials

Contaminated Sediments

The sediment samples used for the thesis project are coming from the Trondheim harbour. The sediment samples were collected in September of 2006 using a Van Veen grab (Sparrevik and Kvalvaag 2007). The samples were dewatered by first compacting the sediments manually in a 100 liter container and then removing the excess water. In terms of water content, the dewatered sediment sample was similar to that of a dredged sample. After dewatering, the sediment sample was stored in a cooling room at 10ºC to prevent decomposition of the organic material. The anoxic characteristic of the sediments was preserved by a layer of water formed on top while the sediments settled at the bottom of the container as is shown on Figure 9a.



a) Trondheim sediments before stirring b) Stirred Trondheim sediments

Figure 9 Trondheim sediments

Table 4 summarizes the chemical characteristics of the contaminated Trondheim sediment and the cement used for the S/S process used in this thesis project. The concentrations represent the total content of components expressed in mg/kg of dry weight. Analysis were carried out by ALS laboratories.

The main objective of the chemical analysis was to characterize the sediments under study by determining the water content, total organic carbon (TOC) and main pollutants. The classification of contamination in sediments is based on the Norwegian classification system. Each one of the colors in the table represent a certain degree of contamination as is described in the legend of the Table 4.

Table 4 Chemical Characterization results of Trondheim sediments and cement, in mg/kg dw (Sparrevik et al. 2006)

Group	Parameter	Trondheim sediments	FA cement
Physical	water content (%) **	44.9	0
	TOC	2.3	0.61
Metals	Arsenic	5.4	12
	Lead	45	31
	Cadmium	0.34	0.27
	Chromium	45	93
	Copper	64	11
	Mercury	0.52	0.1
	Nickel	24	28
	Zinc	250	130
	TBT (µg/kg)	580	***<1***
Chlorobenzene	HCB	0.01	***<0.01***
PAH	benzo(a)pyrene	1.1	***<1****
	sum 16 PAH	11	***<8****
PCB	sum 7 PCB	0.073	***<0.025***
Oil	Fraction >C5-C8	***<10***	***<10***
	Fraction >C8-C10	***<10***	***<10***
	Fraction >C10-C12	4.8	<2
	Fraction >C12-C16	68	<3
	Fraction >C16-C35	1000	270

** Expressed as the mass percentage of the dry sediment sample.

Legend:

Bold / italic	Below detection limit. 1/2 of detection limit is used for classification
*	No classification performed in case of elevated detection limit
🟦	Low contamination
🟩	Moderate contamination
🟨	Significant contamination
🟧	Heavy contamination
🟥	Very heavy contamination

As mentioned previously, the scope of this thesis only encompasses the leaching behaviour of inorganic components (i.e. metals). From all the metal concentration presented in Trondheim sediments, five elements are considered of concern and highlighted as a elements that represent moderate contamination when compare with the Norwegian classification system for contaminated sediments (refer to Table 4 metals highlighted in green). These five components are; Pb, Cd, Cu, Hg and Zn.

Cement

Several types of binders and additives can be used for contaminated sediment and soil stabilization. Binders used for S/S of contaminated sediments are normally cement based. Several types of cement are available in the market.

For this thesis project, standard Fly Ash (FA) cement was used. This type of cement is one of the main types produced at Norcem AS for ordinary construction and is readily available. The formulation has an addition of 16-20% fly ash compared to standard Portland cement. This type of cement is characterized by the producers as "environmentally friendly" due to the reduced CO_2 emission when it is produced. The chemical and physical properties of standard FA cement are shown in Table 4 and Table 5, respectively.

Table 5 Physical properties of Norcem Standard FA cement modified from Sparrevik et al. (2006)

Physical properties	Setting time (min.)	Compressive strength, 1d (MPa)	Compressive strength, 2d (MPa)	Compressive strength, 7d (MPa)	Compressive strength, 28d (MPa)	Fineness (m^2/kg)	Specific weight (kg/dm^3)
FA Cement	130	22	31	41	52	450	2.95
Comments	High fineness → rapid hardening	Early strength			Final strength	High fineness → rapid hardening and rapid heat generation	

As indicated in Table 4, three of the metals found in the FA cement (i.e. Pb, Cd and Cr) are also of concern. These three metals are categorized as components that present moderate contamination according to the Norwegian classification system for contaminated sediments. Pb and Cd concentrations in mg/kg dw in FA cement present lower values of contamination with respect to the Trondheim sediment sample. However, concentration of Cr appears as a metal of moderate contamination just in the case of cement but it is a background concentration in the Trondheim sediment sample.

5.1.2 Preparation and physical properties of the S/S specimens

Stabilization and solidification of the Trondheim contaminated sediments was the first step of the experimental plan. A total of 66 samples were prepared in three separate batches (S/S 1, S/S 2 and S/S 3) each containing 22 samples. The physical properties of the samples are summarized in Table 6. The groups of specimens were prepared at different times to allow a comfortable working window for setting up of the different leaching tests. The mixture proportions and preparation methods were carefully repeated in each batch. The mix design consisted of 100 grams of the standard FA cement to 1 litre of the Trondheim contaminated sediments.

Table 6 Physical properties of Sediments and S/S material

	Sediment			S/S material before curing			
Stages and dates	density	water content	dry sediment	density	water content	dry sediment	Cement
	(kg/l)	(%)	(%)	kg/l	(%)	(%)	(%)
S/S 1 (16/07/07)	1.796	30.59	69.41	1.90	28.97	65.73	5.30
S/S 2 (23/07/07)	1.811	30.84	69.17	1.91	29.22	65.55	5.23
S/S 3 (30/07/07)	1.779	30.68	69.32	1.88	29.05	65.63	5.32
average	1.795	30.702	69.298	1.896	29.080	65.637	5.283
St dev	0.013	0.101	0.101	0.013	0.105	0.074	0.039
%St dev	0.728	0.330	0.146	0.688	0.362	0.112	0.730

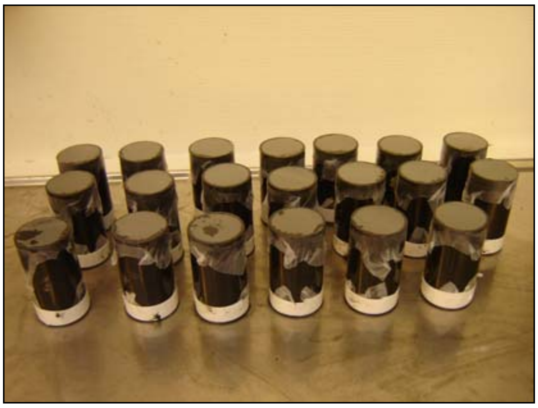
Notes:

1) The water content is expressed as the mass percentage of the total wet sediment or wet S/S material. The water density was taken as 1kg/l.
2) The calculations have been performed the same day as the sample preparation.

The sample preparation procedures were as follows:

The sediments were stirred and remix using a manual mixer (refer to Figure 9), after of which the determination of the physical parameters (density and water content) of the sediment were carried out. The mixture of sediment and cement is done in accordance with the NS-EN 196-1 protocol titled, “Methods of testing cement – Part 1: Determination of strength” (STANDARD 2002b). Once the mixture process was finished the mixture was placed in plastic cylindrical containers while manually de-airing the mixture to avoid formation of bubbles in the sample matrix. The plastic containers were 50 mm in diameter and 100 mm in height. Parafilm was used to seal the top and bottom of the containers (see Figure 10). To allow the samples to be cured they were placed in a moist air environment for 28 days ± 8hrs. The moist air environment was created by placing each sample in a sealed plastic bag with a wet sponge inside to ensure 100% humidity.

It should be noted that the placement of the mixture in the selected moulds and the curing method slightly deviate from the NS-EN 196-1 protocol in terms of the sample container dimensions and curing environment. The protocol calls for a 160 mm high sample container with a cross sectional dimensions of 40 mm x 40 mm and curing of the samples in water.


S/S contaminated sediments


Samples storage

Figure 10 S/S sediment samples

A hydraulic conductivity test was carried out to determine the permeability of the S/S specimen. The specimen used in the hydraulic conductivity test was 50 mm in diameter and 99 mm in height. The test set up is shown on Figure 6. A constant water head equal to 2 m was applied in the test. The hydraulic conductivity constant or permeability coefficient is defined as the rate of flow under laminar flow conditions through a unit cross sectional area of a porous medium under unit hydraulic gradient. The Darcy's law (Equation 1) was used to calculate the hydraulic conductivity. The calculated hydraulic conductivity value (*k*) for the S/S contaminated sediment was 5.95×10^{-09} m/s.

Equation 1 Hydraulic conductivity constant

$$k = \frac{q \times L}{A \times h}, \text{ where}$$

k= hydraulic conductivity constant (m/s)
q=Discharge (m^3/s)
L=Length of the sample (m)
A=Cross-sectional area of the S/S specimen in (m^2)
h=Constant water head causing flow in (m)

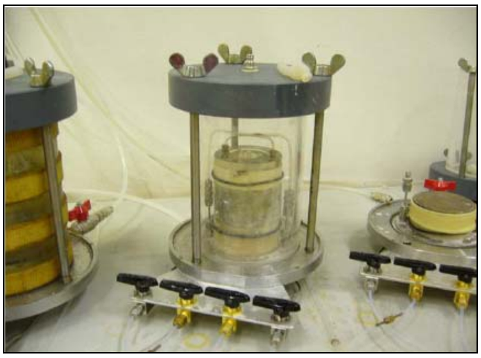


Figure 11 Set up of the permeability test

5.2 Leaching tests

Six different leaching tests were carried out for the same S/S contaminated sediment sample using the same leachant. The selected leachant was seawater. The six different leaching tests carried out in this thesis project are:

- Diffusion leaching test (Static and dynamic),
- Batch leaching test,
- Column leaching test,
- Modified batch leaching test using a monolithic sample, and
- Leaching test of monolith samples with magnetic agitation (spinning leaching test).

The S/S 1 specimens were used for diffusion tests (dynamic and static); S/S 2 specimens for the batch and spinning magnet tests and S/S 3 specimens for column test. It is also important to mention that each one of the different leaching tests performed has been duplicated for quality control purposes.

5.2.1 Leachant used in leaching tests

Although the available literature and protocols recommend the use of demineralized water as the preferable leachant in performing leaching tests, seawater was used as the leachant in this thesis project. The selections of seawater as leachant was based on the fact that S/S contaminated sediments under study will be exposed to this type of leachant under field conditions. That is, the use of seawater in the laboratory leaching test was believed to better mimic the exposure conditions.

The seawater was obtained from the NIVA research station in Solbergstrand. The seawater was kept in a polyethylene cylinder at room temperature during the complete experimental program. For quality control purposes, chemical analyses of inorganic components in the seawater were also carried out at three stages throughout the project, the beginning, middle and at the end, during the three months course of the experimental program. The results of the seawater chemical analyses are summarized in Table 7.

It should be noted that where the concentration of a component in the analyses was determined to be below the detection limit, its average value was calculated using the detection limit itself.

Table 7 Chemical analysis of seawater samples (Solbergstrand NIVA research station)

Chemical Element	Units	Sample 1 (14/08/07)	Sample 2 (28/08/07)	Sample 3 (16/10/07)	Average
Ca	mg/l	434	428	410	424
Fe	mg/l	0.0168	<0,004	<0.004	0.010
K	mg/l	388	374	404	388.7
Mg	mg/l	1290	1300	1250	1280
Na	mg/l	11100	11400	10900	11133.3
S	mg/l	1060	1010	1010	1026.7
Al	µg/l	2.00	2.67	2.83	2.50
Ba	µg/l	14.90	7.66	7.29	9.95
Cd	µg/l	0.0738	0.0735	0.196	0.114
Co	µg/l	<0.05	<0,05	<0.05	0.050
Cr	µg/l	0.521	<0,1	0.888	0.705
Cu	µg/l	2.44	1.15	1.06	1.55
Hg	µg/l	<0.002	<0,002	<0.002	0.002
Mn	µg/l	10.9	<0,1	2.76	6.830
Ni	µg/l	1.67	<0,5	<0.5	1.085
Pb	µg/l	0.941	<0,3	0.51	0.726
Zn	µg/l	6.45	5.43	7.37	6.417
Measured Parameters	**Units**				
T	°C	21.3	20.7	20.1	20.7
pH		7.88	7.75	7.85	7.83
E.C.	mS/cm	52.1	52.3	52.3	52.23

5.2.2 Diffusion test - tank leaching test (Static and dynamic)

The diffusion test was the first test that was set-up since it takes the longest time to complete (64 days). Two different types of diffusion tests were conducted: static and dynamic. The difference between the two diffusion tests is that in the dynamic test the leachant is circulated constantly throughout the course of the experiment whereas in the static test, the leachant is still. However, in both cases the leachant is intermittently renewed at intervals established for the protocol. Including the duplicates, a total of four diffusion tests were set up and performed. All test were run simultaneously.

The tests were performed in accordance with the protocol “Netherlands Monolithic Leaching test” (Environmental Agency 2005), except that seawater was used as the leachant. The total volumes of the specimens and the required seawater used in each test were approximately 589 cm^3, and 2.5 l, respectively.

The experiments setup is shown on Figure 12. Three specimens, each approximately 10 cm in height and 5 cm in diameter, were used in each test. The specimens were stacked on top of each other, fasted using a fishing string and then suspended in the tank. Coarse plastic grid nets were placed at the interfaces of the specimens to prevent them from sliding while allowing the leachant water to reach all surfaces. Hence, the presence of the fishing string and plastic grids did not influence the test results. The total height of the S/S specimens used in each diffusion test was approximately 30 cm, which is similar to that required for the column test.

a) Set up of the three pieces of S/S material b) Diffusion test (Tanks D1, D2, D3 and D4 respectively)

Figure 12 Set up of the diffusion test (Tank test) – Static and dynamic

Static Diffusion Test

The static diffusion test (tanks labeled as D1 and D3) consists of placing the monolith (S/S specimen) in a column of seawater with no circulation.

According to the protocol, the water in each tank is to be replaced eight times. In successive steps of specified durations: 0.6, 1.0, 2.25, 4.0, 9.0, 16.0, 32.0 and 64.0 days. After each replenishment, approximately 125 ml and 100 ml eluate samples were collected in plastic and glass containers, respectively, and sent to the laboratory for metal and mercury contents measurement. The chemical analyses were performed for 17 components, all listed in Appendix 1. The metals of environmental concern found in the sediment sample (refer to Table 4) are included in the list. The samples collected for chemical analysis where not preserved after collection, instead they were sent to the laboratory in the shortest possible time. Parameters such as pH, Electrical conductivity and temperature were measured immediately after the eluate samples collection according to the norm.

The presentation of the results, the concentration values were converted from ‘mg/l’ to ‘mg of component per square meter of the sample surface (mg/m^2)’. The measured leaching of a component per fraction was calculated using the Equation 2 in accordance with the norm.

Equation 2 Measured leaching of a component per fraction – Diffusion test

$$E_i^* = \frac{C_i \times V}{f \times A}, \textit{ where}$$

E_i^*= is the measured leaching of a component in fraction i, in mg/m^2
C_i= is the concentration of the component in fraction i in µg/l
V= is the volume of the eluate in l
A= is the surface area of the test piece in m^2
f= is aconversion factor: 1000µg/mg

To find out the measured cumulative leaching of an specific component all the leaching fractions should be added. The same formulas were used for the dynamic diffusion test.

Dynamic Diffusion test

The dynamic diffusion test (tanks labeled as D2 and D4) was set up in a similar way as the static diffusion test, the only difference with respect to the static test was that the seawater was constantly circulated using a Peristaltic pump P-1, at an approximate rate of 55 ml/hr (Figure 12b). The flow rates in tanks D2 and D4 (i.e. Tank D2 and its duplicate tank D4) were checked a number of times throughout the tests. The measurement of parameters and eluate sampling were exactly the same as the static test. As such, the water in each tank was replaced eight times. In successive steps of specified durations: 0.6, 1.0, 2.25, 4.0, 9.0, 16.0, 32.0 and 64.0 days.

The dynamic test is a modification of the static diffusion test normalized by the Netherlands Monolithic Leaching test (EA- NEN 7375:2004). This test was performed to see if there is any significant difference between a diffusion test performed with still seawater and a diffusion test performed with a circulating leachant. The latter is more representative of the field conditions for the S/S contaminated sediments studied.

5.2.3 Batch Leaching test for crushed material

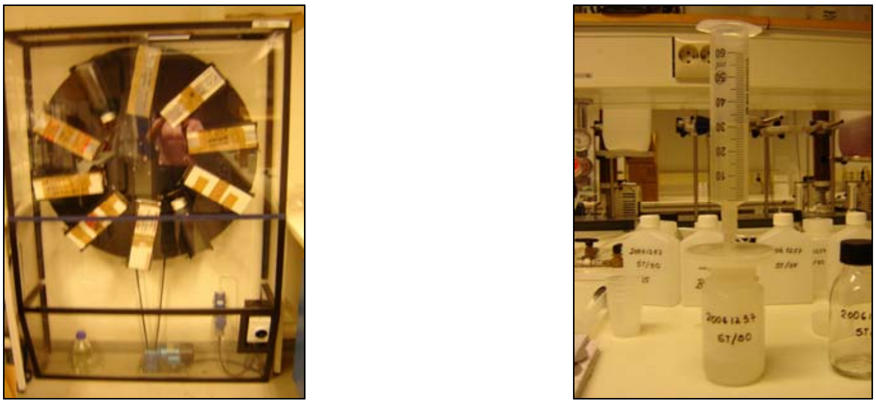
The batch leaching test of crushed material was performed according to the (STANDARD 2002a) EN 12457-2, at liquid solid (L/S) ratio of 10. S/S contaminated sediments cured for 28 days were manually crushed using appropriate devices to avoid sample contamination. Water content of the sample was measured and then 248 g of wet sediment was placed in a bottle and leachant was added (1.75 l) to complete an L/S of 10. Once the set up was completed, the samples were left for agitation on an end-over-end shaker with rotation speed of approximate 40 rpm for a period of 24 hours according to the standard. Once agitation was ended, the samples were allowed to rest for 15 minutes for the solids to settle out from the liquid phase, after which, the eluate was filtered and then collected. The filter paper was a 0.45 µm membrane filter. The filtration procedure is shown on Figure 13b, which did not require any vacuum or pressure devices.

Part of the eluate samples were placed in approximately 125 ml and 100 ml containers and sent to the laboratory for metal and mercury contents measurement, respectively. Laboratory analyses were performed for 17 components and are shown in Appendix 1. According to the norm, parameters such as pH, Electrical conductivity and temperature were measured immediately after the eluate samples collection. The laboratory results are expressed in terms of concentrations. In order to express the final results in the amount of constituent leached relative to the total mass of the sample (mg/kg of dry matter -mg/kg dw) Equation 3 was used.

Equation 3 Calculation of the release of constituent in mg/kg dw for batch test

$$A = C \times \left[\left(\frac{L}{M_D} \right) + \left(\frac{MC}{100} \right) \right], \textit{ where:}$$

A= is the release of a constituent at a L/S=10 (in mg/kg of dry matter)
C= is the concentration of a particular constituent in the eluate (in mg/l) – laboratory results
L= is the volume of leachant used (in l)
MC= is the moisture content ratio expressed as a percentage of the dry mass(in %)
MD= is the dry mass of the test portion (in kg)



a) Agitation device for batch leaching test b) Filtration of eluates

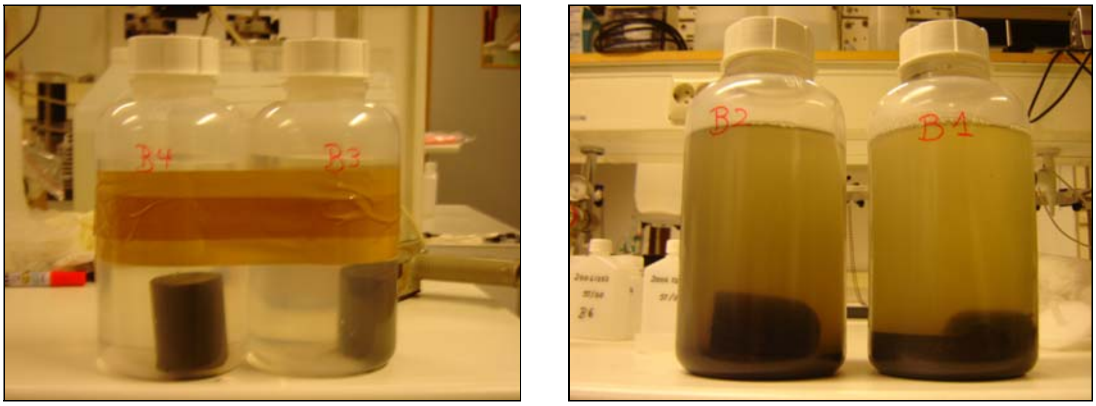
Figure 13 Batch leaching test

5.2.4 Batch leaching test for monoliths

The batch leaching test of crushed material gives a large contact area between water and sediments. By crushing the S/S sample the porous structure itself in the S/S sample is destroyed and therefore, the release control of metals is more dependent on the solubility at equilibrium conditions inside the test chamber. This method has been severely questioned by many researchers, especially when used for S/S materials (Sloot et al. 1997). Batch test is manly used to assess the leaching potential of the S/S contaminated sediments rather than predicting the natural release of contaminants. On the other hand, diffusion test is the one that is mainly recommended for assessing the lechability of S/S material (Sloot et al. 1997; Bone et al. 2004). However, the disadvantage of the diffusion test lies in its long duration.

To that extent, an experimental work was carried out with similar conditions as the batch leaching test with L/S ratios of 10, but using the monolith samples instead of granular/crushed material. The objective was to assess the possibility of finding an alternative and intermediate type of test that gives more realistic values and does not demand a large time to perform.

In the batch leaching test for monoliths, four tests were run at the same time. The samples were set up as is shown on the Figure 14a and then placed in a horizontal position in an end-over-end shaker. The positioning of samples was carefully arranged in a way that the monoliths will gently roll on contact with the container wall. It was assumed that in this condition the monoliths will not get destroyed. It was expected that using this method lower and more realistic concentrations of contaminants in the eluate would be found in comparison with batch test. However, the experiments were not successful since much of the monoliths were damaged during agitation (Figure 14b). As such, it would have been difficult to interpret the findings and besides, accomplish one of the major requirements of laboratory experiments that is the capacity of re-produce the experiment under similar conditions. Therefore, none of the eluates of the four batch leaching tests for monolith samples were sent to the laboratory for chemical analysis.



a) Batch leaching test of monolith samples before agitation

b) Batch leaching test after 24h agitation

Figure 14 Batch leaching test for monolith samples

5.2.5 Leaching test of monolith samples with magnetic agitation

Due to the failure of the batch leaching test for monoliths presented in the section 5.2.4 another set up of the S/S sample without crushing was carried out. This time, the leachant was circulated gently around the monolith, so that the S/S material would not disintegrate. The water was agitated in the container using a spinning magnet. This test was also designed similarly to the batch leaching test, such as the L/S ratio of 10 and also with similarities to the diffusion test because the test piece was placed in a leachant as a monolith sample. The details about sample weigh, dimensions and leachant volume are given in Table 8.

Table 8 Magnetic agitation test - sample dimensions and leachant volume

Test duration (hrs)	Sample label	wet weight of S/S mat	dry weight of S/S mat	volume of water	volume of S/S sample
96	A	239.74	173.48	1735.4	136.9
96 (dup)	B	241.93	175.06	1751.6	136.2
24	C	238.38	172.42	1725	132.5
24 (dup)	D	239.74	173.48	1735.3	135.3
48	E	236.62	171.22	1712.4	134.4
48 (dup)	F	238.95	172.9	1729.3	135.7

The main differences reside in the monolithic nature of the samples for batch test, in the more gentle way of agitation and in the duration of the test. The monolith was completely submerged in the liquid, suspended by a fishing strings and then fixed to the neck of the bottle as is shown in Figure 15. Three duplicates were run in parallel, the first duplicate was stopped 24 hrs after the agitation, the second after 48 hrs and the third 96 hours later. The intention of the experiment using different time frames was to evaluate changes in the eluates through time. It was difficult to determine and make a uniform agitation for all the six leaching tests due to the fact that each magnet had a different spinning velocity, that with the equipment used was difficult to control. However, the monolith sample was not destroyed in any of the tests, which so far was considered a success for this new experimental test.

The collection of eluates and measurement of parameters were performed in a similar way as in the other leaching tests. Laboratory results and measured parameters are shown in the Appendix 1.

The laboratory analysis of the eluates produced by the leaching test provides the concentrations of the constituents in the eluates, expressed in ‘mg/l’. This test was considered to behave more similar to a diffusion test than a batch test. Therefore, in order to express the final results in the amount of constituent leached relative to the area of the monolith expose to contact with the leachant. The same equations used for diffusion test have been used.

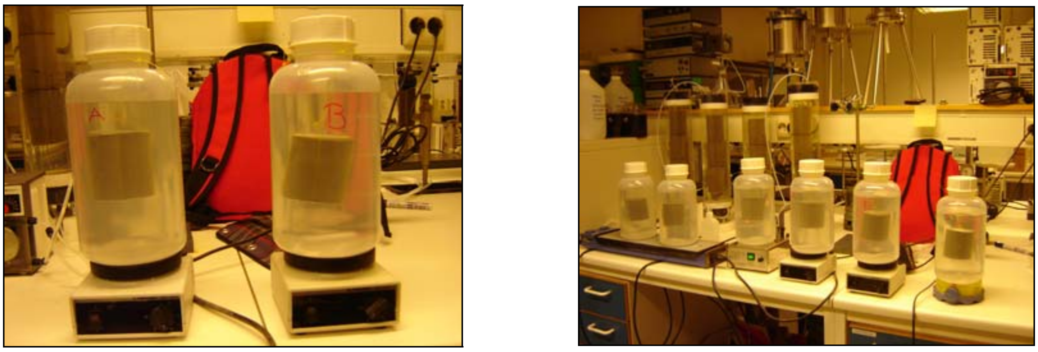


Figure 15 Leaching test of monolith samples with magnetic agitation

5.2.6 Up-flow percolation test (column test)

Two column tests (labeled C1 and its duplicate C2) were performed using the technical specifications, (STANDARD 2004), norm CEN/TS 14405. The protocol specifies that only materials with a saturated hydraulic conductivity between (10^{-7}m/s to 10^{-8}m/s) can be subjected to this test. The application of this test on materials with lower hydraulic conductivities is not recommended. The S/S contaminated sediments had a much lower hydraulic conductivity (5.95×10^{-9}m/s) than the range specified by the protocol for testing. Regardless, the tests were performed on a column built of three specimens, total of 30 cm lenght. Therefore, the modification made was with respect to the test set up and the use of sea water as leachant.

The column test usually simulates field conditions such as fluid flow, mass transfer and dissolution mechanism in a more realistic manner (Sloot et al. 1997). However, the column test is normally used to evaluate the leaching characteristics of granular material, where percolation of water is an important factor influencing leaching. Percolation is an extremely rare phenomenon for S/S waste given the low permeability (often below 10^{-9} m/s). Washing or diffusion (phenomena which only take into account contact between the liquid and the external surface of the solid) and immersion, (the solid, saturated with water is in continuous contact with the liquid) are more likely scenarios presented for the S/S waste (Sloot et al. 1997). Nevertheless, this test was carried out since it was expected that results may complement the traditional diffusion test suggested by the literature for S/S samples.

The set up of the up flow-column test was performed as follows: three monoliths were put on top of each other building a 30cm high column. Then, the column of about 30 cm was completely covered by two overlapped elastic impermeable membranes, each one of about 20 cm. The membranes were used to avoid any water go in or out from it. To secure the joins between membranes "O" rings were placed around the match points of the membranes as is shown on Figure 16a. A peristaltic pump P-1 with flow rates which can be regulated between 0.6ml/h-500 ml/h was used to force water through the sample at a rate that is around 12.3 ml/hr ± 0.82ml/hr, this value was obtained from the suggestion of linear velocity of the norm that is in the range of (15cm/day ± 2cm/day). As mention by the norm, it was expected that the specified flow rate will allowed to perform the complete test in about a month. The test performance lasted 23 and 26 days for column C1 and C2, respectively.

Before starting the test, the column was saturated with water to allow pre-equilibration for about 2 hours and then the pumps were started to force the water go through the sample (up-flow test). In order to ensure that the water goes through the sample and not around it, the surrounding environment of the column was filled with pressurized water. The pressure was initially set to at about 1 bar and then increased to 1.5 bars in the 6th day of the performance of the test. The pressure was increased due to the fact that the lower part of the membrane (first 15cm approximately) in the column one (C1) started to swell as water was starting to go around the column. After the increase of the pressure, the swelling effect was apparently controlled. Although, it was not easy to maintain a very stable flow rate for the case of the column one (C1) few days after the pressure increment. The presence of the membrane, did not allow the surrounding water (pressurized water) to have contact with the testing sample and the leachant. The set up of the experiments is as shown on Figure 16b. Water leaking was not observe at any time while performing the tests.

As specified by the standard, the eluates should be collected seven times; with each one corresponding to a specific Liquid solid ratio (L/S) of (0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 respectively). The collection of eluates and measurement of parameters were performed as specified by the standard and in a similar way that in the other leaching tests. Laboratory results and measured parameters are shown in Appendix 1.

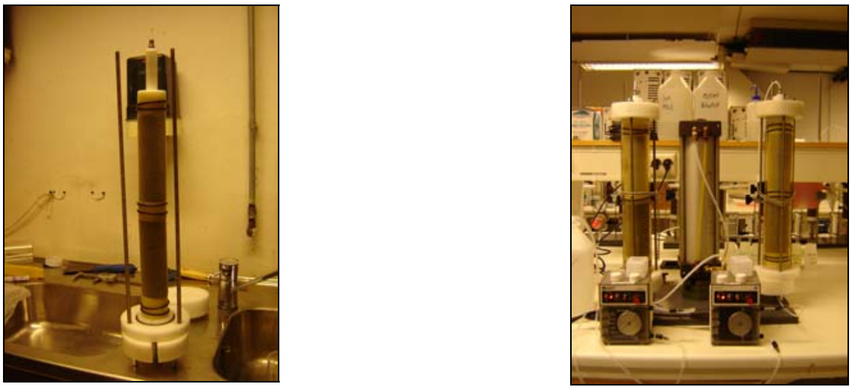

a) Membrane placed around the column b) Column test set up

Figure 16 Up – flow percolation test (column test)

Table 9 Summarized table of the main characteristics of the different leaching tests performed

	Test name (reference)	Sample dry weight (mg)	Sample Dimension (cm^3)	L/S ratio	Total added water (l)	Refresh interval	Contact time (hrs or days)	Output information
1)	Batch test EN 12457-2	≈ 175	Granular NA	10:1 (m/m)	≈ 1.75	NA	24 hrs	Concentration (mg/l)
2)	Column test CEN/TS 14405 (Modified)	≈ 760	Monolith ≈ 590	10:1 (v/m)	≈ 7.6	26 days total	26 days	Concentration (mg/l) Cumulative release (mg/kg) with L/S
3)	Static diff test EA NEN 7375:2004	≈ 760	Monolith ≈ 590	4.3:1 (v/v)	≈20.4	6hr, 1, 2.25, 4, 9, 16, 36, 64d	64 days	Concentration (mg/l) Cumulative release (mg/m^2)
4)	Dynamic diff test EA NEN 7375:2004 (modified)	≈ 760	Monolith ≈ 590	4.3:1 (v/v)	≈20.4	6hr, 1, 2.25, 4, 9, 16, 36, 64d	64 days	Concentration (mg/l) Cumulative release (mg/m^2)
5a)	Magnetic agitation 24	≈ 173	Monolith ≈ 126	10:1 (m/m)	≈1.73	NA	24 hrs	Concentration (mg/l) Cumulative release (mg/m^2)
5b)	Magnetic agitation 48	≈172	Monolith ≈ 126	10:1 (m/m)	≈1.72	NA	48 hrs	Concentration (mg/l) Cumulative release (mg/m^2)
5c)	Magnetic agitation 96	≈174	Monolith ≈ 126	10:1 (m/m)	≈1.74	NA	96hrs	Concentration (mg/l) Cumulative release (mg/m^2)

Note:

1) In the column L/S ratio the symbols (m/m) = (mass/mass), (v/m)= (volume/mass), (v/v) = (volume/volume)
2) NA = non applicable
3) The leachant was see water for all the cases. The water density was taken as 1kg/l.

6.0 RESULTS AND DISCUSION

6.1 Selection of elements for analysis

The laboratory analyses of the eluates collected from the six different leaching tests were carried out for inorganic components in the sediment sample, seventeen elements were analyzed. Details of the laboratory analysis results are presented in Appendix 1. Table 10 summarizes the percentages of element concentrations above the detection limits obtained from the laboratory analyses. The main elements of concern in Trondheim sediments are Pb, Cd, Cu, Hg and Zn (see Table 4, Section 5.1.1). These elements were present in the sediment sample at concentrations categorized as the moderately contaminated according to the Norwegian classification system. The elements of concern have been highlighted in Table 10. Given that the number of observations above the respective detection limit for Cd, Hg and Pb are significantly low, accurate analyses and comparisons of these elements amongst the different leaching tests is not meaningful. As such, no further analysis for Cd, Hg and Pb were carried out. For the purpose of this study, analyses were carried out only on the following four elements: Cu, Zn, Cr and Ni.

Table 10 Percentage of observations of element concentration in eluate analyses of the different leaching tests above the detection limit (average of duplicate analysis)

ELEMENT	Detection limit	Static Diff test	Dynamic Diff test	Sp magnet 24 hrs	Sp magnet 48 hrs	Sp magnet 96 hrs	Batch test	Column test	Average
Units		%	%	%	%	%	%	%	%
Ca		100	100	100	100	100	100	100	100
Fe	0.004 (mg/l)	75	100	100	100	100	100	57	90
K		100	100	100	100	100	100	100	100
Mg	0.5 (mg/l)	100	100	100	100	100	100	86	98
Na		100	100	100	100	100	100	100	100
S		100	100	100	100	100	100	100	100
Al	0.70 (µg/l)	100	100	100	100	100	100	100	100
Ba		100	100	100	100	100	100	100	100
Cd	0.05 (µg/l)	31	44	0	0	100	0	14	27
Co	0.05 (µg/l)	100	100	100	100	100	100	100	100
Cr	0.10 (µg/l)	88	88	100	100	100	100	100	96
Cu	0.50 (µg/l)	100	100	100	100	100	100	36	91
Hg	0.002 (µg/l)	25	6	0	0	0	50	86	24
Mn	0.10 (µg/l)	88	75	100	100	100	100	86	93
Ni	0.50 (µg/l)	100	100	100	100	100	100	100	100
Pb	0.30 (µg/l)	88	81	0	0	0	50	25	35
Zn	2.00 (µg/l)	100	100	50	50	50	50	64	66

Legend

🟩	Elements that represent moderate contamination of sediments (from Table 5)
Red font	Selected elements for further analysis in the thesis project

It should be noted that Cu and Zn are considered elements categorized as the moderately contaminated according to the Norwegian classification system, for Trondheim sediments having average percentages of concentrations above the detection limits of 91% and 66%, respectively. Cr and Ni, with 96% and 100% concentrations above detection limits are elements only found at low levels in the sediment, nonetheless they were selected for the analyses since their concentrations are high and provide a good basis for comparison of the leaching tests. Further, Cr concentration in the binder (FA standard cement) represents moderate contamination according to the Norwegian classification system for contaminated sediments (refer to Table 4).

Where the concentration values are below detection limits, the actual detection limit value was used in the analyses. This criterion is conservative representing the worst case scenario conditions.

6.2 Total mass of Cu, Zn, Cr and Ni in the S/S materials

The total mass of Cu, Zn, Cr and Ni in milligrams of dry weight (mg dw) in the S/S specimens used in the leaching tests are based on the results presented in Table 4 and Table 6. These values are summarized in Table 11. It was assumed that the total metal content is directly related to the sum of metal content in dry sediment and metal content in the cement type used for the formulation of S/S material. The leachant (seawater) metal content was not taken into consideration for this calculations due to its very low metal concentration(in the order of µg/l) and therefore low contribution to the total amount, see Table 7.

Table 11 Total amount of elements of interest in each of the leaching test performed

S/S sediment sample			**Diff test**			**Batch test**			**Magnetic agitation**			**Column test**		
Units	**mg/kg dw**			**mg dw**			**mg dw**			**mg dw**			**mg dw**	
Metal	Sed	Cement	Sed	cement	**Total**	Sed.	cement	**Total**	Sed.	cement	**Total**	Sed.	cement	**Total**
Cr	45	93	33.03	5.50	**38.53**	7.13	1.18	**8.31**	7.05	1.16	**8.22**	32.98	5.53	**38.51**
Cu	64	11	46.98	0.65	**47.63**	10.14	0.14	**10.28**	10.03	0.14	**10.17**	46.91	0.65	**47.56**
Ni	24	28	17.62	1.66	**19.27**	3.80	0.35	**4.16**	3.76	0.35	**4.11**	17.59	1.66	**19.25**
Zn	250	130	183.51	7.69	**191.21**	39.63	1.64	**41.27**	39.19	1.63	**40.82**	183.23	7.72	**190.96**

Table 6 shows that the physical properties measured for sediments and S/S material are very similar in the three stages of S/S contaminated sediments fabrication. Standard deviation of the values presented in Table 6 are smaller than 0.8% for all the measured properties. This indicates that the formulation of S/S material is very similar in all three stages.

The most abundant metal found in the S/S contaminated sediments summarized in Table 11 is Zinc followed by Copper and Chromium, leaving Nickel as the less abundant metal of all four.

The values presented in Table 11 are first converted to the corresponding units of each leaching test to find out the percentage depletion of the metal due to leaching using the following formula.

Equation 4 Percentage depletion in relation to total content of specific component

$$\%D_t = \frac{A_{leaching,t}}{T} \times 100$$

For batch and column test, $\%D_t$ is the percentage leached component in time 't' in relation with the total component content in the sample. $A_{leaching,\ t}$ is the leached quantity of the component in time '*t*' in mg, and *T* is the total quantity of the component obtained from Table 11 in mg.

For diffusion and magnetic agitation tests, $\%D_t$ is the percentage leached component in time 't' in relation with the total component content in the sample. $A_{leaching,\ t}$ is the leached quantity of the component in time '*t*' in mg/m^2, and *T* is the total quantity of the component obtained from Table 11 expressed in mg/m^2. For this, 'T' should be used in units of mg/m^2. The total amount of the component was divided by the total volume of leachant used for the specific test, then concentration values were obtained. This result was placed in Equation 2, with the assumption that the total amount of component is available for leaching through diffusion.

6.3 Leaching tests results

6.3.1 Diffusion test results (Static and dynamic)

As part of the test procedure, pH, temperature, and Electrical Conductivity (E.C.) were measured (refer to Table 12). These parameters are of vital importance in the leaching behavior of the matrix since they can strongly influence the leaching process.

pH is one of the most important chemical parameters influencing leaching since the pH of soil, or specified material has a major influence on the solubility of contaminants by influencing the degree of ionization and their subsequent overall charge (Bone et al. 2004). The pH values in the diffusion tests (static and dynamic), in Table 12 were calculated from the average pH values of the respective eluate samples collected and the duplicates. The standard deviation values showed that there is not a considerable difference between the duplicates in any of the measured parameters, including pH. The pH average and error bars are presented in Figure 18a

The pH values in the diffusion test (static and dynamic) did not show significant variation from the initiation to the end of the tests. It is known that at the concrete surface, a pH value close to the leachant pH will be maintained, since the supply of alkalinity from the S/S matrix by diffusion is not sufficient to build up a high pH environment near the S/S surface (Sloot et al. 1997). This is the case for the diffusion tests carried out in this project. This effect may be explained as the released hydroxide is either dispersed or neutralized by the buffering in natural water, in this case the used seawater has a high buffer capacity (alkalinity pH ≈ 7.8). In general terms, it can be said that pH values during the performance of the diffusion test tend to decrease little with time. Further, each time that the leachant is replaced in the diffusion test the alkalinity of the S/S sample at the surface is reduced due to the washing effect. It should be noted that the leachant was changed 8 times in the diffusion tests.

The average pH values measured in the static and dynamic diffusion tests are 8.6 and 8.3, respectively. It was observed that the dynamic diffusion test yields relatively lower pH values than the static diffusion test and also a more systematic reduction of pH with time than the static diffusion test (see Figure 18a). The explanation may be in the carbon dioxide uptake from the atmosphere enhanced by the stirring or agitation in the dynamic diffusion test. Materials with a limited buffering capacity are most sensitive to changes like carbon dioxide uptake. This is why testing in closed vessels are generally more reproducible.

Table 12 Diffusion test measured parameters

Sample collection number	Static Diffusion Test						Dynamic Diffusion Test					
	pH average	% st.dev	Temp. (°C) average	% st.dev	E.C (mS/cm) average	% st.dev	pH average	% st.dev	Temp. (°C) average	% st.dev	E.C (mS/cm) average	% st.dev
1	8.57	0.29	21.93	0.67	51.90	0.19	8.59	0.00	21.85	0.83	51.85	0.10
2	8.77	0.11	21.43	0.69	51.85	0.10	8.76	0.23	21.53	0.20	51.90	0.00
3	8.63	0.35	21.20	0.33	52.15	0.10	8.59	0.00	21.30	0.33	51.95	0.10
4	8.57	0.35	21.28	0.39	52.10	0.19	8.37	0.90	21.33	0.39	52.15	0.10
5	8.69	0.29	22.65	0.22	52.05	0.10	8.24	0.49	22.68	0.19	52.00	0.00
6	8.55	0.23	20.70	0.59	52.30	0.19	8.16	0.25	20.83	0.71	52.50	0.38
7	8.61	0.52	20.70	0.76	52.70	0.19	7.96	0.44	20.60	2.25	53.03	1.18
8	8.44	1.42	21.30	1.15	52.90	0.38	8.09	0.12	21.13	1.55	53.05	0.28

The temperature and the electrical conductivity of the eluates are also almost constant along the performance of both diffusion tests. The test temperature is controlled by the room temperature. The electrical conductivity does not present a major variation since leachant (seawater) ions are dominant in the test over those of the S/S matrix.

Normally pH is the most important factor to asses solubility of inorganic compounds (metals) in S/S contaminated sediments. The most common metal species in S/S soil or sediments are hydroxides (Laugesen 2007); (Malviya and Chaudhary 2006); (Spence 1992); (Sloot et al. 1997). The "chemical sensitivity" of each component, that is the variation in solubility in relation to the pH in pore water, may be determined experimentally. Most metal hydroxides have a minimum solubility in the alkaline region and the solubility increase if the pH moves up or down (Figure 17). In the case of eluates from S/S material, pH may increase due to the high alkalinity of the binder and it may result in higher solubility of several metals.

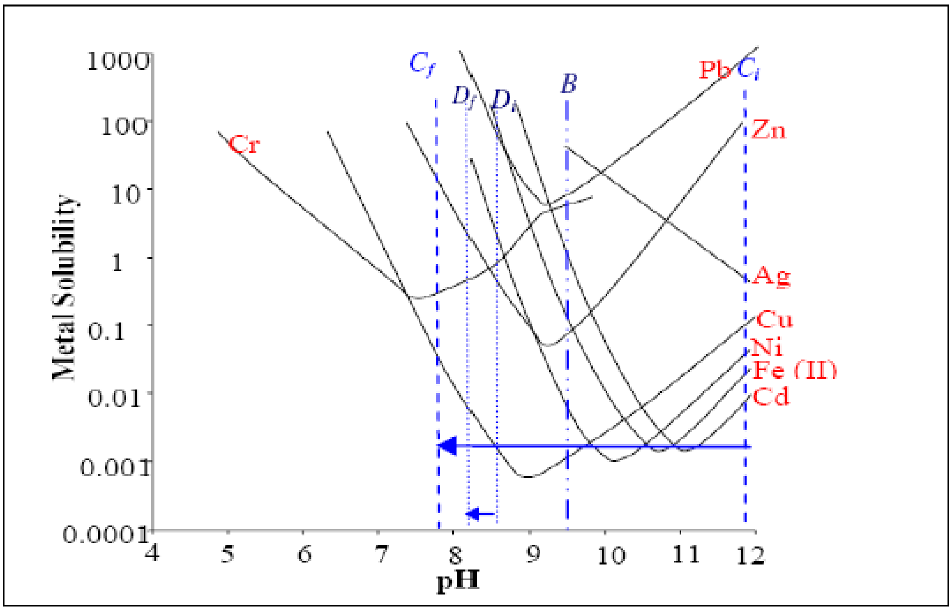


Figure 17 Initial and final pH for performed leaching tests versus theoretical solubilities (mg/l) of metal hydroxides as a function of pH modified from Bone et al. (2004)

However, solubility of metals may also be affected by other factors such as metal complexation as is the case of copper and nickel that are sensitive to complexation to dissolve organic carbon DOC (Sloot et al. 1997). In the case of Zinc the leachability of this metal is similar to that of lead, as it also has amphoteric properties. However, the leachability at high pH is not as pronounced as in the case of lead (Sloot et al. 1997).

With respect to the leaching characteristics of the metals under study (Cr, Cu, Ni and Zn), the following results were found:

Chromium (Cr)

The leaching characteristics of Cr in the static and dynamic diffusion tests are very similar in terms of the metal release versus time and the cumulative release versus time (Figure 18). In reference to

Table 11, Cr is the third component in terms of abundance after Zn and Cu from the four elements. However, it is the one that presents the lowest leaching under diffusion test conditions in comparison with the other three elements (less than 7µg/l). Additionally, it is the only element from the four that has some concentration values below the detection limit in both the static and dynamic diffusion tests (refer to Table 10 and/or Appendix 1). The leachant presents also traces of chromium concentration as it is represented in Figure 18a and Table 7. The chromium concentrations after the third eluate collection in both diffusion tests drop to levels that are even below the leachant chromium concentrations. This indicates that the available chromium for leaching in the S/S sample suffers a drastic wash off in the initial stage of the diffusion test. Furthermore, the fact that the concentrations of Cr in the eluate samples are even lower than the average seawater Cr concentration indicates that part of the Cr that is in the seawater is possibly absorbed by the S/S material.

Cr is an amphoteric metal and chromium hydroxides is least soluble when the pH values are in range of 7.5-8. The pH values of the performed diffusion tests were very close to this range (see Figure 17). Further, theory states that chromium may become incorporated and encapsulated into the nanoporous of the C-S-H gel (refer to Figure 2). Also it may be integrated into the crystalline components of the cement matrix (ettringirite) by substitution of calcium or the sulphate ions for oxyanions (Sloot et al. 1997). Therefore, it may be assumed that under these conditions Cr will present extremely limited availability for leaching as it has been observed during the diffusion tests here.

Copper (Cu)

Cu is the second component in terms of abundance in the S/S samples (Table 11) and is also considered a metal of concern in the contaminated sediments. However, Cu presents the second less abundant concentration values in the leachant after Cr (Figure 18a). Characteristics of Cu leaching in the dynamic and static diffusion tests are also very close. However, the small differences that exist between the concentrations in these two tests may be due to their different pH values. Lower pH values presented by the dynamic diffusion test (pH≈8.3) will promote a slightly higher solubility for Cu compared to the static diffusion test (pH≈8.6). The leaching differences between the two tests are in the order of ≈1 mg/m^2 for cumulative leaching after 64 days. These results are in agreement with what is referred to in the literature, where the lower solubility of copper hydroxide is presented around pH 9 (refer to Figure 17).

Nickel (Ni)

For the case of Ni which is the least abundant metal in the S/S materials (Table 11), larger leaching values were found compared to the other three metals. Such a phenomenon is explained by the theoretical solubility of nickel hydroxide which is higher at pH values between 8.3 and 8.6 compared to the other three metals (see the blue doted lines $D_{f,} D_i$ in Figure 17).

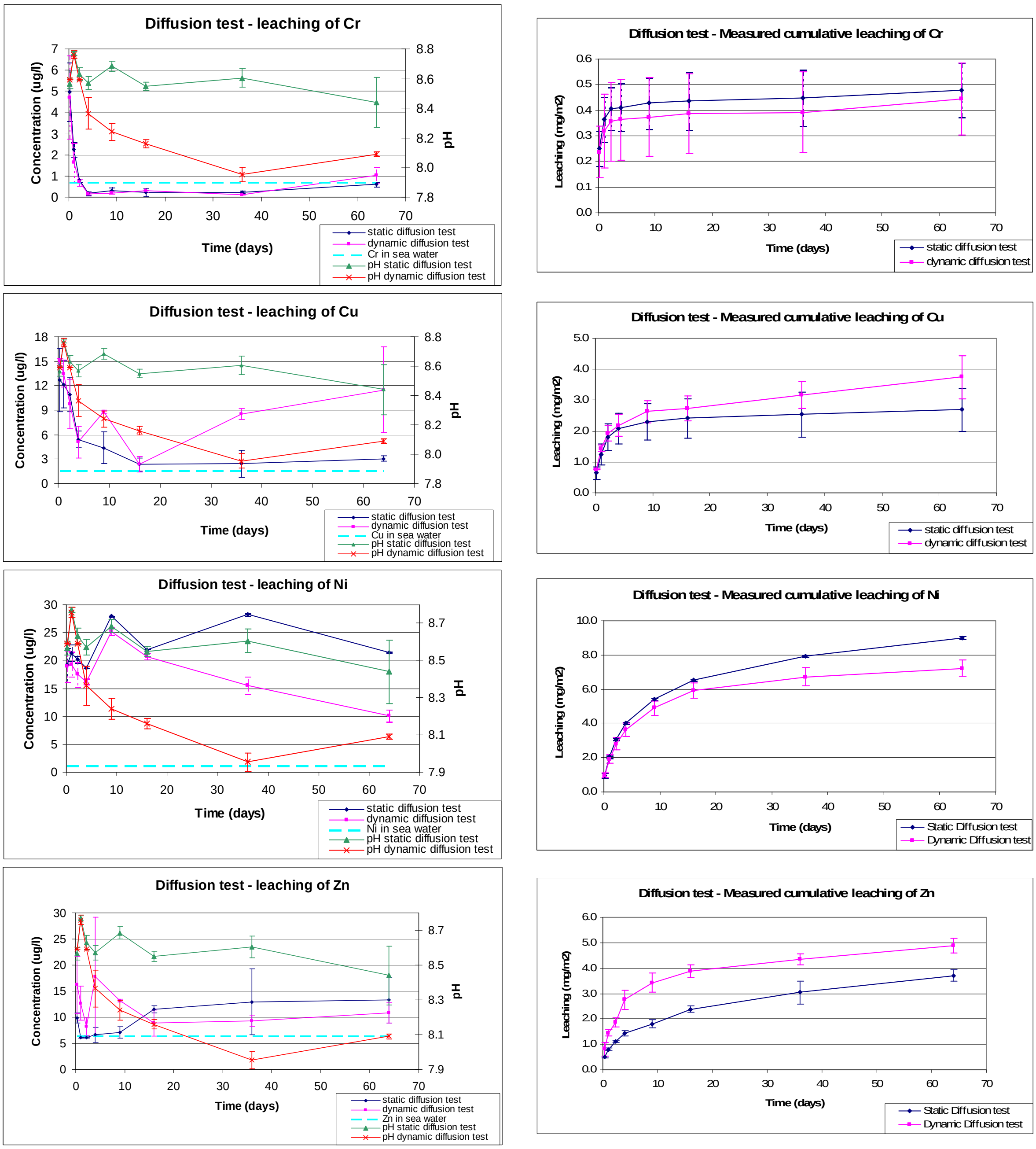
When comparing the static and dynamic diffusion test results for Ni, there is no major difference between the two. Slightly higher solubility of Ni was found in the static diffusion test than the dynamic test (in the order of ≈ 2 mg/m^2 for cumulative values after 64 days). It is not clear why the slightly higher pH in the static diffusion test endorses higher solubility of this component. However, beside the pH, there is another parameter that could affect the leaching behaviour. That is the contact method (see Section 4.5.1, Contact Method). Therefore, the agitation of water could potentially withdraw higher amounts of Ni from the sample as is the case in the dynamic test. Nonetheless, this difference in the cumulative leaching value is so small that is difficult to pin point the reason.

Zinc (Zn)

Zn is the most abundant of the four metals (refer to Table 11). At the same time Zn is also considered a metal of concern in the contaminated Trondheim sediments. However, under the diffusion leaching conditions, Zn presents less cumulative leaching values than Ni and very close solubility values to Cu that is considered the other metal of concern and the second most abundant from the 4 metals under study.

Zn presents its theoretical lowest solubility at pH around 9. However, at the beginning of the test Zn presents higher solubility, although the pH values are higher than at the end of the test. It may be explained by the washing effect of metals at the beginning of the diffusion test. However, the solubility goes down with time.

When comparing static and dynamic diffusion tests for the case of Zn leaching, the results show that there is a slightly higher solubility of the metal in the dynamic diffusion test (in the order of ≈ 1 mg/m^2 for the cumulative leaching after 64 days). This result is in agreement with what is affirmed by the literature and is shown on Figure 17, where lower pH values generates higher leaching of zinc hydroxides.



a)Leaching values in ug/l versus pH values b)Measured cumulative leaching in mg/m^2

Figure 18 Diffusion test results for Cr, Cu, Ni and Zn

Total metal content versus cumulative leaching

According to the literature, the leachable fraction of the selected metals from the S/S contaminated sediment sample is less than and not directly related to the total contaminant concentration. The test results also confirm this theory. Figure 19 shows the cumulative leaching of the selected four metals for analysis (given in mg/m^2) versus the total amount of each one of those metals in the S/S contaminated sediment samples. Equation 4 (Section 6.2) was used to compare the test results. As the figures show the diffusion test leaching mechanisms of the selected metals is largely reduced by the S/S process in the case of the four metals under study. Furthermore, on these figures it is also evident that Ni is the component that is more available for leaching with respect to the others although it is the less abundant in the S/S sample.

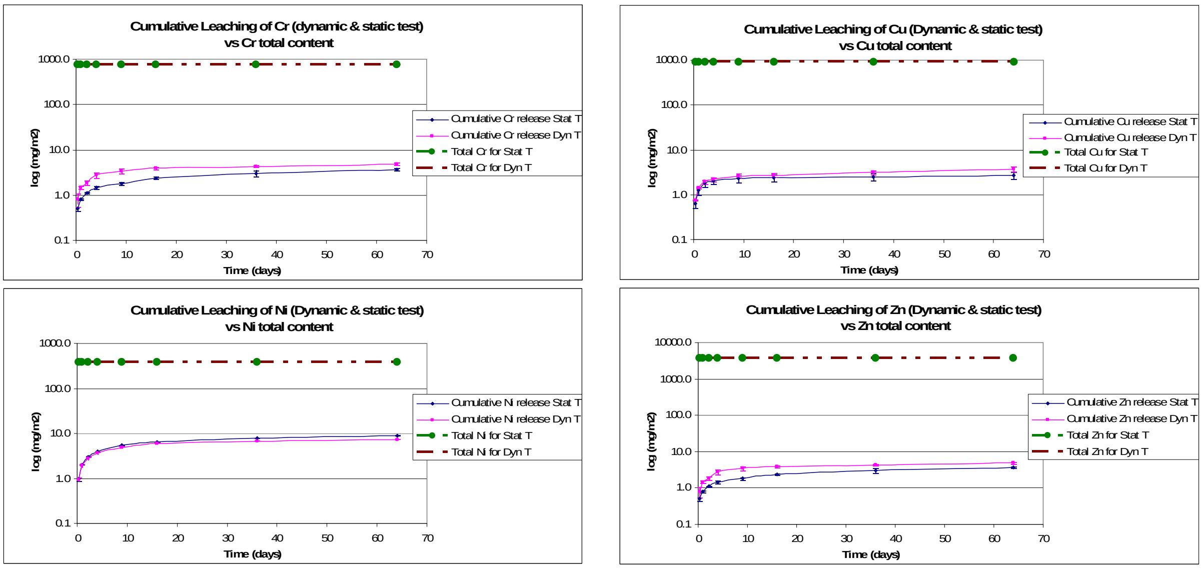


Figure 19 Diffusion test – Cumulative leaching vs Total metal content in logarithmic scale

6.3.2 Up-flow - column test

Depending on the flow rate and the length of the column, column tests can be performed under equilibrium or non-equilibrium conditions. The flow rates used in column tests are usually much faster than natural seepage water velocities due to technical requirements. In the column tests performed, the average flow rate was 1.74×10^{-6}m/s. This is at least three orders of magnitude larger than the natural flow rate of the S/S material. Given the high flow rate and the length of the column designed for the test (which is much shorter than the thickness of the S/S waste in the field), it is more likely that non-equilibrium conditions existed throughout the test. Subsequently, leaching processes in the column test were most likely kinetically controlled. In such a case, the mass transfer from the particle to the bulk solution may be critical (Sloot et al. 1997).

For the interpretation of the test results it is important to take into account that the initial concentration of a column test strongly depends on the experimental design. If the column is saturated before the start for pre-equilibration, then higher concentrations will occur and the initial concentrations will possibly reflect field concentration. However, if the column test is started immediately without pre-equilibration, initial concentrations will be lower and will depend on the flow velocity and column length (Schuwirth and Hofmann 2006). For the experiments performed here, the columns were saturated for about 2 hours. It can not be proven if the first eluate samples collected represent the field concentration of the pore water of S/S material. However, it can be said that these values may be very close (especially the first and second eluate samples).

Table 13 summarizes the measured parameters determined as average value between the column test and its duplicate (C1 and C2 respectively) for the respective eluate fractions. In the same table it is also shown the standard deviation between the respective parameter and its duplicate. The standard deviation indicates that there are not major differences between the test and its duplicate with respect to the measured parameters.

Table 13 Summary of the column test measured parameters

Eluate fraction number	pH average (C1&C2)	% st.dev	Temp. (°C) Average (C1&C2)	% st.dev.	E.C. (mS/cm) average (C1&C2)	% st.dev.
1	11.85	0.46	20.67	0.62	48.30	0.41
2	11.66	1.07	20.55	1.46	50.05	0.10
3	11.35	0.00	20.29	1.42	51.10	0.00
4	10.59	0.00	20.73	0.91	51.30	0.00
5	9.37	0.00	19.77	0.86	52.50	0.00
6	7.73	0.06	20.18	1.23	52.85	0.09
7	7.79	0.96	19.80	1.56	53.40	0.00

Table 13 also shows that there is a considerable reduction in pH during the column test. This variation may be explained by the kinetics governing the performance of the test. The higher pH values appearing during the initial stages of the tests are due to influence of the pore water of the matrix (highly alkaline). That is the matrix is exposed to a very low liquid solid ratios goes through the material in the early stages. However, later in the test the pH values drop drastically as the liquid solid ratios increase with time. Hence, at the later stages the leachant starts to show a more significant effect on the pH variation in the successive collected eluates. These pH variations have a great influence on the metal concentrations. As such, the metal concentrations in the eluates decrease with time. If the leaching process would have been developed under equilibrium conditions the metal concentrations would have been limited only by the solubility or another distribution equilibrium. Therefore, the pH variation and/or eluates concentration would not have been a function of the L/S ratios.

The pH variation with respect to the selected metals concentrations are graphically shown on Figure 20. Interpretation of the results for Cu and Zn should be elaborated with caution. Table 10 shows that in the column test the percentage of concentrations values of Cu and Zn above the detection limits are

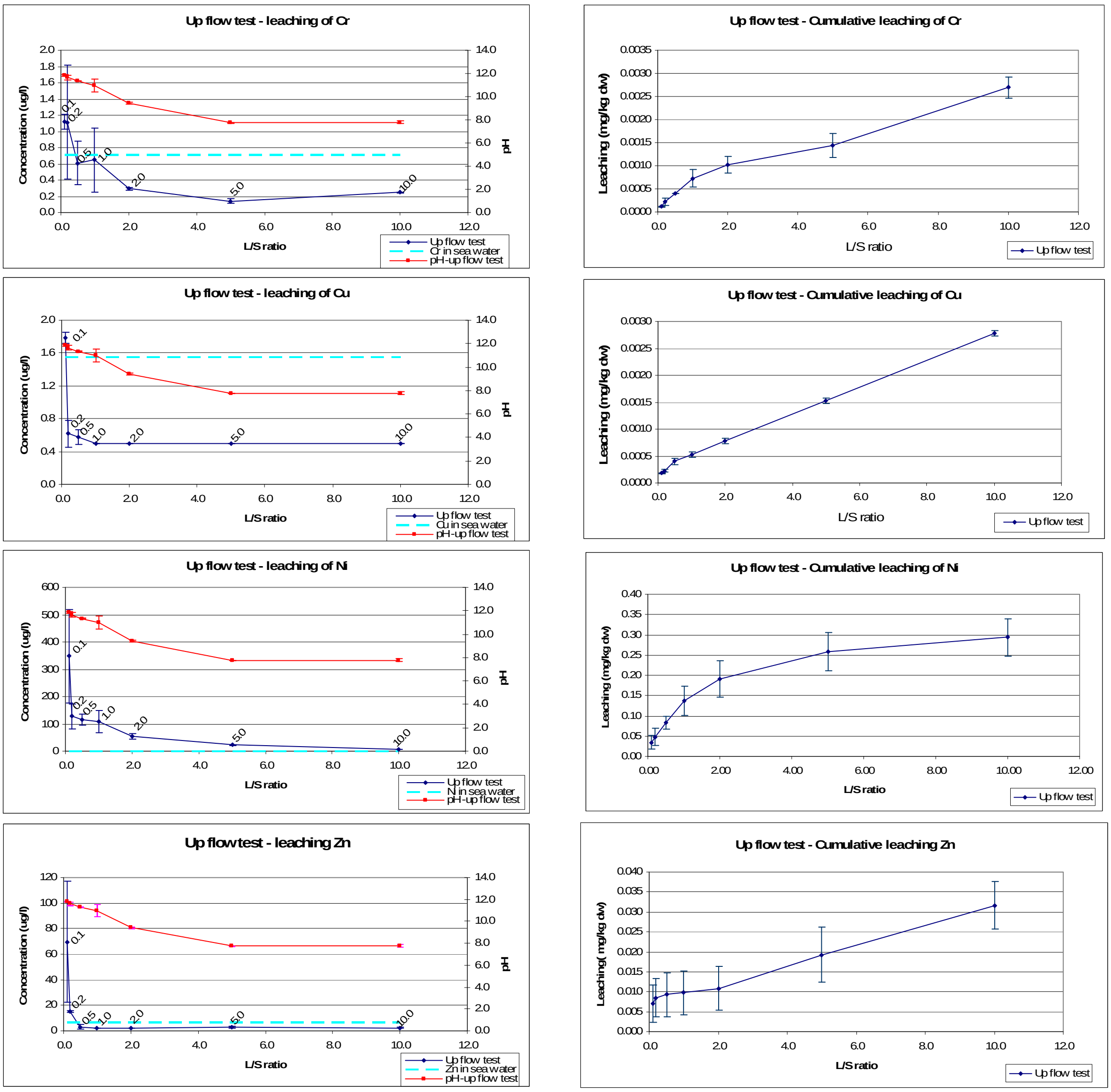
35% and 69%, respectively. This situation limits the quality of the interpretation for both metals, particularly for Cu.

In general terms it may be said that the available Cr, Cu and Zn for leaching show a very fast wash off effect at the early stages where small liquid solid ratios are used (L/S smaller than 0.5 for the case of Cr and Zn and 0.2 for the case of Cu). The decrease in Cr, Cu and Zn concentrations in the later stages of the test is explained by the effect of pH in metal hydroxides solubility (see dashed blue lines C_i C_f and the arrow showing decrease on pH versus hydroxides solubility on Figure 17). Higher pH values close to 12 present higher solubilities for the three mentioned components.

An interesting phenomenon is the Cr, Cu and Zn concentrations traced in the eluates dropping below the concentrations measured in the seawater before coming in contact with the S/S material (Figure 20). This suggests that the S/S material is apparently capable of absorbing some of Cr, Cu and Zn from the leachant at increased L/S ratios.

Nickel (Ni)

Ni is the only metal that presents different behaviour than the other three. Apparently Ni is more available for leaching in this leaching method than the other three components. Although Ni has the least quantity in the S/S sample compared to the others (Refer to Table 11), this metal presents the higher concentrations in the eluate samples. According to the test results, nearly 80% of the Ni measured in eluates was released in the early stages of the test before the pH reached a value of 10 when Ni is least soluble.



a)Leaching values in ug/l vs pH values b)Measured cumulative leaching in mg/kg dw

Figure 20 Up flow column test results for Cr Cu Ni and Zn

It should be noted that a problem was found in the performance of the test which may have significantly affected the test results causing the concentrations in the eluates to be very low. The problem was that part of the leachant may have flow around the sample which was not observed visually. However, simple calculations as explained below demonstrated the probability that this phenomenon has occurred.

The experimental set up was designed on the basis of the assumption that the leachant will completely flow through the S/S medium and not around it (Section 5.2.6). To that extent, the sample covered by an elastic membrane was placed inside of a cell filled with water with a confining pressure of 1 bar, which later was increased to 1½ bars. Equation 1 was used to calculated pressure gradients obtained during the performance of the column test, using an average flow of 12ml/hr (3.33E-09 m^3/s), hydraulic conductivity equal to 5.95E-09 m/s, with a cross sectional area equal to 1.96E-03 m^2, and a column length of 0.3 m. The pressure gradient is given by the pressure difference between the initial pressure at which the water is going through using the peristaltic pump P-1 and the pressure at which the eluate is collected at the top of the column. Using the above data, the estimated pressure gradient value under which the tests were conducted would have been equal to 85.6 m of water column (approximately 8.6 bars). This is a significant pressure. It is beyond the pump capacity and much larger than the confining pressure.

This situation indicates that the measured Cr, Cu, Ni and Zn concentrations may be incorrect. It was not possible to correct the problem and repeat the test due to time constrains. Therefore, for this study analysis and data interpretation should be done with caution.

It should be noted that the correct performance of the test is crucial if the data are intended to be used for leaching predictions in specific physical and hydraulic disposal or utilization scenario. Nonetheless, if one want to use the concentrations presented here to predict leaching of S/S material placed above the ground water level, the L/S ratios can be converted to a time scale using the Equation 5 (Sloot et al. 1997).

Equation 5 Conversion of L/S ratios to time scale for column test results

$$t - t_0 = (L/S) \times d \times H / I \text{, } where$$

L= the total volume of leachate produced at time t(t=0 at start of disposal/application)(l)
S= the total amount of waste deposited/applied (dry bulk weight)(kg)
t_0= the time elapsed until the appearance of the first leachate (days)
d= the average dry buld density of the deposited waste (l/kg)
H= average height of disposal site/application (m)
I= net rate of infiltration of precipitation (m/day)

Total metal content versus cumulative leaching

Figure 21 shows the actual cumulative release of Cr, Cu, Ni, and Zn versus the total amount of components in the S/S sample and compared with part of the batch test results for the correspondent L/S ratio of 10. As is shown in the figure the release of components from the batch test are always higher than the release of components in column test. However, the comparison of both tests are not completely valid due to the fact of the probable failure in the performance of the column test.

Additionally, as suggested in the literature (Schuwirth and Hofmann 2006), if there are two different principles governing both tests the comparison is not possible. The different principle between the batch and column tests is that in the batch test the equilibrium conditions are more likely reached, which is not the case in the column test where the kinetics govern the release.

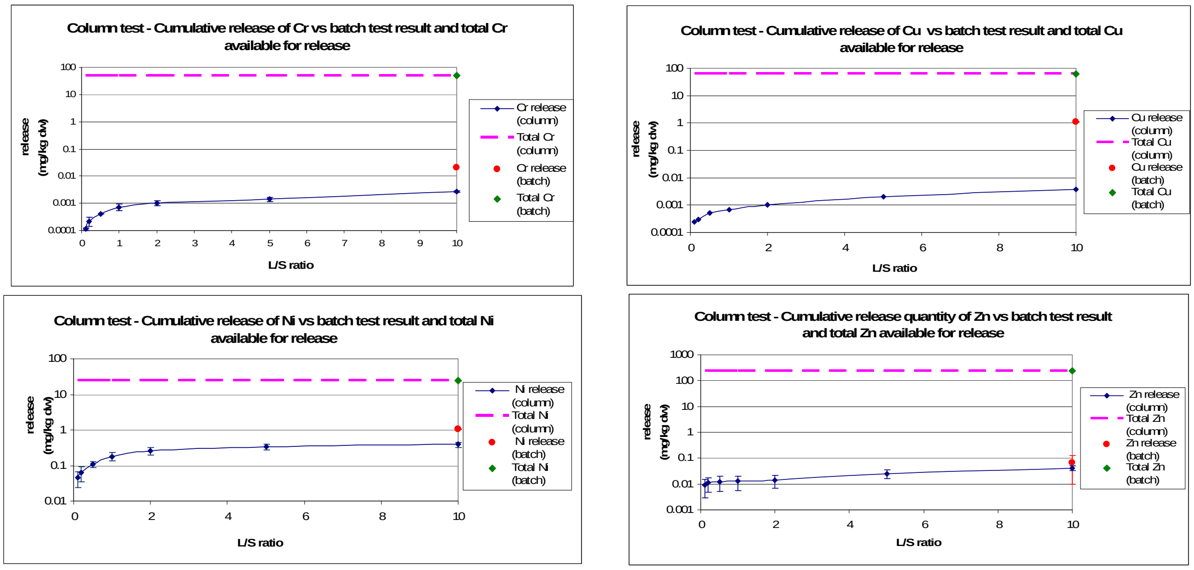


Figure 21 Column test – cumulative release of components vs batch test results and total metal content in the test samples

6.3.3 Batch test

Table 14 shows the average values of the parameters (pH, temperature and electrical conductivity); as well as the percentage of standard deviation. Standard deviation values show the both tests (the original and duplicate) produced very similar results.

Table 14 Summary of the Batch test measured parameters

pH average	% st.dev	Temp (°C) average	% st.dev.	E.C. (mS/cm) average	% st.dev.
9.53	0.005	22.03	0.34	52.3	0.19

The average pH value is shown by a blue dashed line on Figure 17 (line *B*). Temperature and electrical conductivity parameters are similar among all the tests.

The interpretation of the results for the case of Zn should be elaborated with caution. Table 10 shows that just 50% of Zn concentrations are above the detection limit. This situation will limit the quality of the interpretation of results for this specific component.

Table 11 shows that among the four metals, Zn is the most abundant element, followed by Cu, then Cr and finally Ni.

Figure 22 shows that Cu is the element that presents a major amount of release compared to the other three, followed very closely by Ni. Zn and Cr are the components that present minor release.

Copper (Cu)

Cu is the element that presents the highest concentration in the eluate sample compared to the other three (refer to Figure 22). This can not be easily explained using pH as the main controlling factor. According to Figure 17 Cu solubilities are smaller than Zn at pH of 9.5, which is the one reached in the batch test. However, this was not the case here. The literature states that besides pH there are other parameters such as organic complexants (dissolved organic carbon-DOC) may influence the release of metals. Complexation of Cu with dissolved organic carbon (DOC) has been registered as an important factor in the literature. In addition, the literature also states that at higher pH values complexation with dissolved organic matter becomes more important because of the increased DOC concentrations in solution (Schuwirth and Hofmann 2006). Although DOC measurements were not carried out during the experiments, it is believed that this parameter has largely influenced the Cu release at the registered pH values.

Nickel (Ni)

Ni presents the second largest release amount after Cu (refer to Figure 22). According to Figure 17, the solubility of Ni at pH value 9.5 should be smaller than the solubility of Cr and Zn. However, this situation was not observed here. The reason is that Ni suffers the same complexation effect with DOC as Cu does. This is also supported by the literature (Sloot et al. 1997). The important effect of DOC in the batch test may be justified by the pH of 9.5 reached during the tests and because the crushed materials present a smaller physical barrier than monolithic samples.

Zinc (Zn)

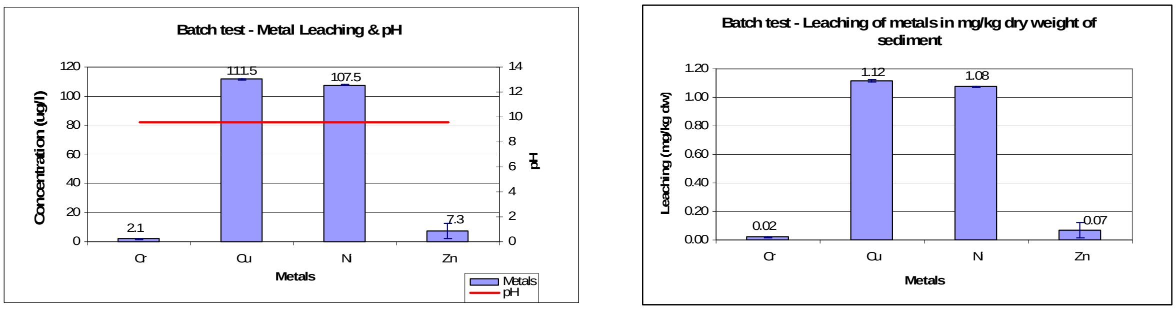
Zn is the most abundant of the four metals (refer to Table 11). However, under the batch test conditions, Zn presents considerable less leaching values than Cu and Ni (refer to Figure 22). The higher concentrations of Cu and Ni found in the eluates may be explained by their organic complexation with DOC. The complexation of these metals with the DOC has an apparently larger effect in the metals release when comparing with the effect of pH . As such, it is not possible to affirm that the metals concentrations in the eluates samples during the batch test are mainly governed by the pH.

Chromium (Cr)

Cr is the third component in terms of abundance in the S/S sediment sample after Zn and Cu from the four elements (Table 11). However, it is the one that presents the lowest leaching under batch test conditions in comparison with the other three elements (refer to Figure 22). This can not be easily explained using pH as the main controlling factor. According to Figure 17, the Cr solubility at pH of 9.5 is the highest compared to that of the other three components at the same pH. However, it is assumed that other parameters than pH are governing the release pattern of the metals during the batch test performance.

Figure 21 shows the batch leaching results versus total amount of component in the S/S material. It is easy to observe the difference between the higher release of Cu and Ni in comparison with the case of Cr and Zn.

Batch tests present the following characteristics: 1) are designed to approach equilibrium between the solid and the liquid phase; hence, the leaching behaviour of metals is mainly limited by the solubility or another distribution equilibrium, 2) a L/S equal to 10 is widely applied in batch test; in many cases, the high L/S ratio of 10 leads to a significant dilution compared to real soil solutions 3) crushing of the S/S samples is necessary, and 4) mechanical stress (shaking) is applied during the test performance. These characteristics have been the topic of significant criticism of the batch leaching test in among various authors in the literature. As such, this method is found to be particularly insufficient for the prediction of metal mobility of the S/S material under natural conditions.



Leaching values in mg of metal per litre of leachant

Leaching values in mg of metal per kilogram of S/S sediments (dry weight)

Figure 22 Batch test results for Cr, Cu Ni and Zn

Total metal content versus cumulative leaching

Figure 21 shows the release of Cr, Cu, Ni, and Zn for the batch and column test versus the total amount of components in the S/S sample used for each tests (batch and column). The figures show that although the batch test is one of the most aggressive ones in comparison with the other test, the leaching of the four selected components is largely reduced by the S/S process. However as in previous cases Zn and Cr present lower release amounts. Furthermore, on these figures it is also evident that Ni is the component that is more available for leaching with respect to the others, although it is the less abundant in the S/S sample.

6.3.4 Leaching test of monolith samples with magnetic agitation

The magnetic agitation test was designed to combine the principles of the batch and diffusion tests. The objective was to assess the possibility of finding an alternative and intermediate type of test that better suites S/S materials providing more realistic values than the batch test for metals release while requiring shorter duration than the diffusion test. Here the monolith sample is not crushed and is tested under a L/S ratio of 10.

A total of three different magnetic agitation tests were run. The difference among them are the test duration: 24hrs, 48hrs and 96 hrs. Each test was run with its respective duplicate and the parameters (pH, temperature and electrical conductivity) were measured for all of them. The average values of these parameters are summarizes in Table 15. The calculated standard deviations indicate that the originals and duplicates were producible and quite similar.

It should be noted that there was no means to control the velocity of the spinning magnets. Further, in numerous occasions the magnets were stuck in the concaved base of the bottles. Finding a way to control this conditions will give more reliable results when comparing release amounts versus leachant/matrix contact time. It is recommended that the above issues be addressed when performing this type of test in the future.

Table 15 Summary of the magnetic agitation test parameters

Label (original and duplicate)	Time of performance	pH average	% st.dev	Temp (°C) average	% st.dev.	E.C. (mS/cm) average	% st.dev.
B-C, B-D	24 hrs	8.84	0.11	20.80	0.34	52.15	0.29
B-E, B-F	48hrs	8.65	0.87	22.30	2.03	52.00	0.19
B-A, B-B	96hrs	8.26	0.79	22.28	0.80	52.40	0.38

The pH values (Table 15) for the three magnetic agitation tests are very similar to the pH values measured in the diffusion tests. It was noted that longer agitation times tends to reduce the pH of the eluates. The reason is explained in the same manner as for the dynamic diffusion tests. More agitated systems take up higher amounts of carbon hydroxides from the atmosphere.

If leaching results of the same metals are compared for magnetic agitation and batch test, it may be seen that there is a large difference between them. However, leaching results of the magnetic agitation tests have more similarities with the diffusion tests. Therefore, as assumed beforehand, it is most likely that the physical process controlling the type of release is diffusion. For further analysis, concentrations values of magnetic agitation tests were compared with the concentration values found in the diffusion tests at equivalent times. It was noted that the diffusion tests present slightly lower values than the magnetic agitation except for zinc. This results are quite interesting since the relation of the volume of the leachant and the volume of the test piece is larger for the magnetic agitation test (volume relation approximate 12:1, refer to Table 8), while in the case of the diffusion test this relation is ≈4:1. This results lead us to the conclusion that the violence of the agitation also plays an important roll in the release of components from the matrix under diffusion conditions. This may be explain as follows; the leachant stirring reduces the diffuse boundary layer (DBL) thickness and increases wash of at the surface of the sample.

Two main parameters controlling leaching in the magnetic agitation tests can be easily visualized and their influence over the release of contaminants may be compared. These parameters are pH and contact time of leachant and S/S material. The interpretation of the metal release with respect to those two in the magnetic agitation test can be explained as follows:

Larger release of Ni and Cu are observed in comparison with Cr and Zn (Figure 23). Although Zn is the most abundant metal in terms of total mass in the S/S sample (Table 11), the concentration values on the eluates are below the average concentration value of the seawater. Therefore, as observed for the diffusion test and batch test performed, the magnetic agitation tests present the same pattern of release of the selected components under study.

Nickel (Ni)

Although Ni is the least component in the S/S material (Table 11). Ni presents the highest concentration, with respect to the other three metals under study. The increasing release of Ni with the decrease of the pH can be observed on Figure 17. As such, higher Ni concentrations are found for the 96 hrs test when comparing with the 24 and 48 hrs. Apparently, the contact time also contributes to the Ni release amounts. Therefore, consistent higher concentrations were found between the tests of 24, 48 and 96 hrs of agitation. However it is difficult to identify which one of the two parameters play a more important roll in Ni release from the S/S sample.

As explained in previous cases leaching also depends on many other different factors such as complexation. Although, it was not part of the thesis to investigate this effect, it is possible that complexation of Ni and Cu with DOC plays a fundamental role on their release amounts.

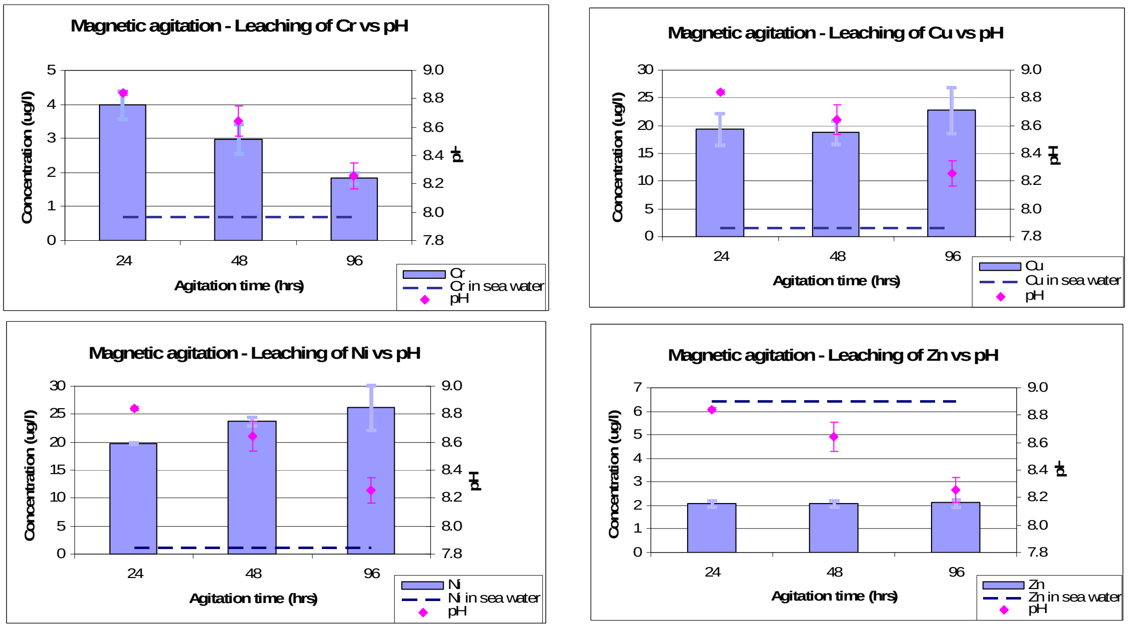


Figure 23 Leaching of selected metals - Magnetic agitation test results

Copper (Cu)

The minimum solubility of Cu lies around pH=9, higher release of this metal is obtained with a reduction of pH. The 96 hours test show the highest release of Cu when comparing with the 24 and 48 hrs tests, due to its lowesr pH value (Figure 23). This condition may have been increased by the contact time between the leachant and the S/S sample. Therefore, higher concentrations have been found in the 96 hrs test. However, there is an important finding when comparing the Cu release with the other tests. If the release of all the component would have only been governed by pH, Cu should have been the less soluble metal from the four elements studied. As mentioned earlier it is believed that DOC complexation with Cu plays and important role on this respect.

Chromium (Cr)

With respect to Cr the pattern of release (decreasing with time of agitation), may be explained by the effect of pH. Cr shows its lowest solubility a pH values close to neutral and increase of solubility with increase of pH. In this case it is possible to observe that the pH parameter has a strong influence on the released amount than the contact time. Therefore lower concentrations have been found in the test run for 96 hours when comparing with 24 and 48 hrs test.

Zinc (Zn)

Careful interpretation of the release of Zn should be done, because 50% of the results are found below detection limits for the three magnetic agitation tests run for different times (Table 10). This situation limits the quality of the interpretation of results for this specific component. However, the available results indicate that some of the Zn may be absorbed by the S/S matrix. Therefore Zn concentration in the collected eluates were lower than the Zn concentrations in the seawater (Figure 23). It may be possible that some of Zn is being integrate to the C-S-H gel of the cement if it is still hardening and hydrating.

Total metal content versus cumulative leaching

The results of leaching of the four different elements under study with respect to their total content in the S/S contaminated sediments are summarized on Figure 24. To make the calculations it was assumed that the leaching of the selected components in the magnetic agitation tests is governed by the same principles as the diffusion test. Therefore, the same units and formulas were used to express the comparison.

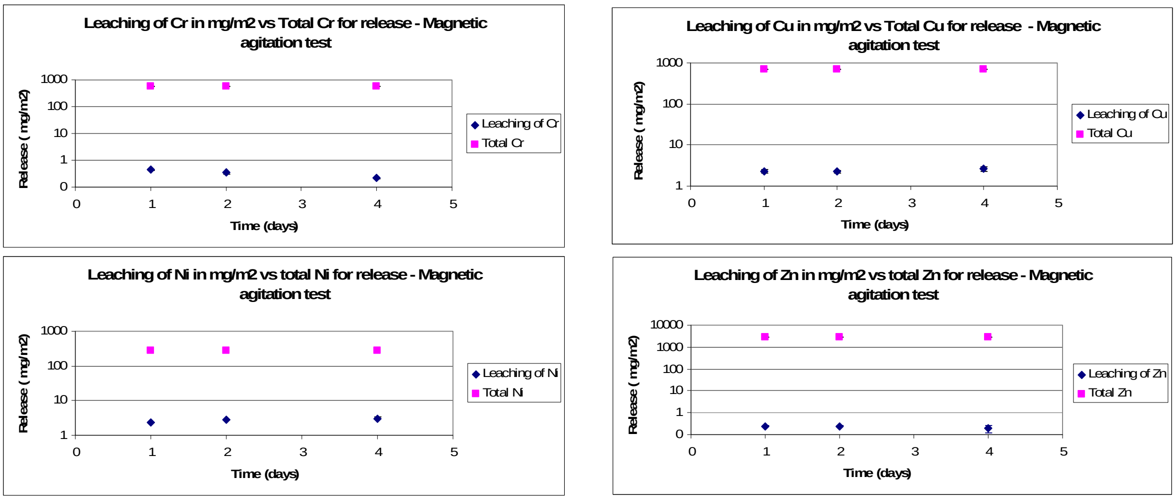


Figure 24 Actual release of selected metals vs Total metal content -Magnetic agitation test

6.4 Leaching tests comparison

This section presents an indirect comparison of the different leaching tests performed. The comparison was carried out between the cumulative release of the four metals under study (Cr, Cu, Ni, Zn) versus the total content of each one of them in the specific test. Figure 25 shows the leaching tests comparison results, given as the percentage of the cumulative leached amount of the selected metals compared with the total amount of the selected metals in the S/S contaminated sediment.

When comparing metal release among the different tests performed, Figure 25 shows that Ni is the component that present the highest release with respect to its total amount in the S/S contaminated sediments. This result has been found in all the different leaching tests performed. Cu is also a metal that present considerable release among the tests, with exception of the column test. Zn is the element that shows the least release of all. The low leaching results of Zn in comparison with the other metals under study may be explained by the high retention of Zn in the C-S-H gel produced during hydration of cement. Zn is a metal that may be substituted for Calcium in C-S-H. This substitution has a particular influence on the C-S-H for many metals, but this effect has been particularly observed in the case of Zn (Bone et al. 2004). Cu and Ni higher amounts of leaching can be explained by the fact that this are components that may be mobilized by organic complexation with DOC.

Table 16 show the summarized results of the leaching tests comparison graphically presented in Figure 25.

Table 16 Summarized table of the results for leaching test comparison

	Test name	pH range (init –fin)	E.C. (mS/cm) T (°C)	Amount leached with respect to total content in the S/S sample (%)	Major parameters controlling release	Comments with respect to the leaching test comparison (numerical results are shown in the 5th column of this table)
1)	Batch test	≈ 9.5	≈ 52 ≈ 22	Ni = 4.42 Cu = 1.86 Cr = 0.04 Zn = 0.03	- Sample preparation - Contact method - Contact time - pH - DOC	- Batch test show the higher amounts of release for Ni and Cu. Complexation with DOC is supposed to play an important role in this case. - Batch test does not show an overestimation of release for the complete set of metals under study as it was supposed.
2)	Column test	≈ 11.8-7.8	≈ 48-53 ≈ 20	Ni = 1.60 Zn = 0.02 Cr = 0.01 Cu = 0.01	Unclear results	The results of column test can not be properly judged by a potential leakage along the column during the test performance.
3)	Static diff test	≈ 8.6 – 8.4	≈ 52-53 ≈ 22-21	Ni = 2.38 Cr = 0.49 Cu = 0.29 Zn = 0.10	- Contact time - pH - DOC	- The static diffusion test shows the second higher amounts of release for Cr and Zn, these results are possibly related to the contact time parameter. - The results of the static diffusion test for the 4 elements under study are very close to the ones found for the dynamic diffusion test
4)	Dynamic diff test	≈ 8.6 - 8.1	≈ 52-53 ≈ 22-21	Ni = 1.90 Cr = 0.64 Cu = 0.40 Zn = 0.13	- pH - DOC - Contact time - Contact method	- It is believed that Zn and Cr have a release that is time dependent, as such the largest observation of the release of those two metals correspond to the diffusion test (that has a duration of 64 days), while the release for the case of batch test and magnetic agitation test is at least one order of magnitude smaller.
5a)	Magnetic agitation 24	≈ 8.8	≈ 52 ≈ 21	Ni = 0.83 Cu = 0.33 Cr = 0.08 Zn = 0.01	- pH - DOC - Contact method	-All the magnetic agitation tests (24, 48 and 96hrs) present the same behaviour pattern with very small dissimilarities among them. - The release of the more leachable components (Cu and Ni) is very similar to the diffusion test . However, in the case of metals where time is more important to built up a considerable release (Cr, Ni), this test present lower concentrations than the diffusion test. - In general it may be said that the Magnetic agitation test of 96 hrs present the largest amount of release for the case of Ni and Cu, while the 24hrs test present the least amount of release for these two components. - Zn and Cr are components with very low availability (at least one order or magnitude lower than the other two components) this may be one of the reasons why is quite difficult to observe a meaningful release pattern among the different magnetic agitation tests. -dissimilarities in the spinning velocity of the magnets may have had an influence in the components release.
5b)	Magnetic agitation 48	≈ 8.6	≈ 52 ≈ 22	Ni = 1.00 Cu = 0.32 Cr = 0.06 Zn = 0.01	- pH - DOC - Contact method	
5c)	Magnetic agitation 96	≈ 8.2	≈ 52 ≈ 22	Ni = 1.10 Cu = 0.39 Zn = 0.04 Cr = 0.01	pH DOC Contact method	

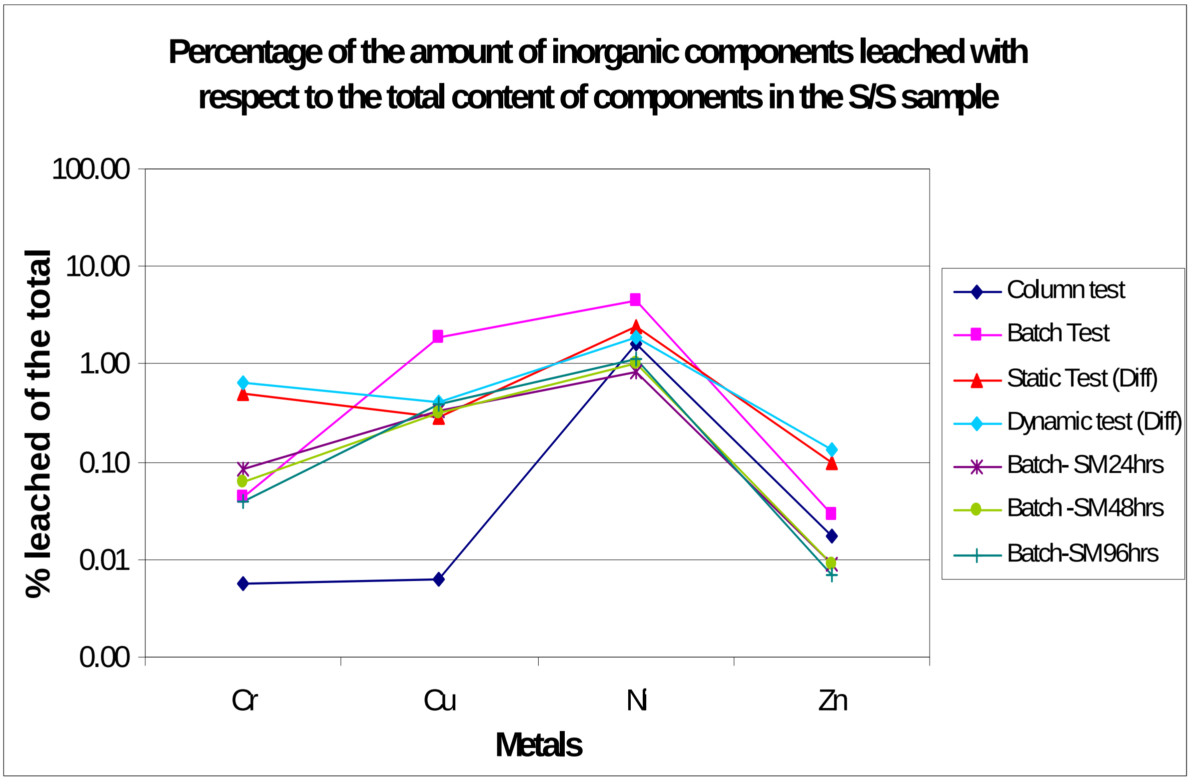


Figure 25 Leaching tests comparison

Literature states that the correlation between results obtained by different leaching tests methods, may not be significant (Schuwirth and Hofmann 2006). Therefore, comparison of different leaching tests carried out under different conditions and with different parameters controlling the release of components, should be made with caution. As such the results obtained in this section, should be interpreted cautiously. One can not be certain if the relations found among the tests in this thesis will be maintained when applying different test conditions. The different test conditions can be: changing the surface area of the S/S material for diffusion tests, changing leachant characteristics, changing L/S ratios for batch test, and/or changing the flow rates and dimensions of column test, etcetera. Therefore, the results of the comparison are only valid for the specific conditions, on which the leaching test were performed here.

It is important to take into account, that the results shown on Figure 25 may be affected by the concentration of the metals already existing in the leachant (seawater). The different leaching tests performed in this thesis project, have used different leachant amounts (i.e. diffusion test, static and dynamic ≈20.4 l, column test ≈7.6 l, batch test ≈1.75 l, and magnetic agitation ≈1.73 l of seawater). Specific amounts and L/S ratios for each one of the tests are presented in Table 9. The trace concentrations of Cu, Cr, Ni and Zn found in the leachant (seawater) act as a background level, and therefore precise determination of the amount of components coming out exclusively from the S/S matrix are difficult to determine.

One may be tempted to believe that the higher cumulative release amounts found for the diffusion tests (static and dynamic) may be largely influenced by the concentration of metals in the leachant and the larger amounts of leachant used for the performance of this test (≈20.4 l). Especially for the case of Zn that is the most abundant trace metal found in the sea water (refer to Table 7). However, it is not possible to withdraw a certain assumption to this respect because this situation does not present a uniform pattern for all the metals under study. In addition is difficult to quantify the exact effect of the trace metals in sea water with respect to the eluates concentration found for each test. Cases when the eluate sample has presented lower concentrations than the leachant have been found for Cr in the case of diffusion test. This condition makes it difficult to subtract the seawater concentrations of Cr, Cu, Ni and Zn from the collected eluates.

The results of column test can not be properly judged by a potential leakage along the column. However, it is expected that a perfect performance of the test would show very high values for leaching of Cu and Ni similar to the ones for the batch test. Also values similar to the diffusion test in the case of Cr and Zn would have been expected.

7.0 CONCLUSIONS

- The leaching test results indicate that the leaching of the four metals (Cu, Cr, Ni and Zn) varies according to the type of test. As such, selection of the appropriate(s) laboratory leaching test(s) and understanding of its limitations(s) is crucial for leaching prediction under natural conditions.

- The total composition of the studied metals (Cu, Cr, Ni and Zn) in the S/S contaminated sediments is mostly not related to the observed leaching. The level of release of the components is dependent on the physical-chemical leaching context that governs the solid/liquid interface. Ni was the least abundant metal when compared to other three elements in the S/S contaminated sediment. However, it shows the largest release amount in most of the leaching tests performed. On the other hand, Zn which is the most abundant metal in the S/S sample, presents the lowest release amounts in most of the different leaching tests performed.

- The pH tends to be the most important parameter controlling the leaching behaviour of the studied metals. Therefore, variations in the pH environment among the different leaching tests has a large influence on the leaching of Cu, Cr, Ni and Zn. However, it was observed that some other controlling parameters such as contact time, contact method, the L/S ratio and the DOC may also affect the leaching process.

- It is believed that the larger release amounts of Ni and Cu compared to Cr and Zn is promoted by the organic complexation with DOC from the contaminated sediments. Complexation with DOC has been documented by many researchers especially in highly alkaline environments.

- Due to the aggressiveness under which the batch test is performed, it was initially expected that the batch test would give the largest release amounts of all the four metals under study in comparison with the other tests performed. However, the batch leaching test shows the largest leaching amounts for Cu and Ni, but that was not the case for Cr and Zn. In the diffusion tests performed, Cr and Zn release amounts are the largest in comparison to the other tests. The results are not totally explained by the difference in pH between the two tests, especially in the case of Cr which should present higher solubility in pH conditions of the batch test (pH = 9.5) than in diffusion (pH = 8.3). Therefore, it is believed that the release amount of some metals such as Cr are time dependent. However, it is impossible to confirm this conclusion with total certainty due to the fact that the leachant used for the tests performance (seawater) was containing trace concentrations of Cr.

- With respect to the batch leaching test it was observed that not in all the cases batch test overestimates the release amounts of components in comparison with the other tests. At the same time batch test presents some limitation for long term leaching release predictions, because the release of some metals it is considered time dependent. However, this test type may still be suitable for a rapid estimation of leaching

- With respect to the column test, it was considered not suitable for leaching prediction of the S/S material under study, due to its low permeability. If S/S samples with higher permeabilities are tested, then the out put data of this test type may be considered important in combination with the diffusion test for long leaching prediction.

- The performance of the magnetic agitation tests was elaborated expecting that their results will provided a more realistic leaching behaviour than the batch test while requiring a shorter time than the diffusion test. However, it is concluded that the magnetic agitation tests can not simulate the leaching process appropriately for some of the metals such as Cr and Zn the release of which is apparently contact time dependent. The release mechanisms from the monolithic S/S contaminated sediments depend on the chemical context at the solid/liquid interface as well as the time. Therefore, the diffusion test is probably still the most suitable test for the S/S leaching simulation under field conditions.

- With respect to the diffusion tests performed, the dynamic tests present lower pH values than the static tests due to the uptake of CO_2 from the atmosphere (i.e. the air locked in the small recirculation bottle). As a result, the leaching amounts of Cr, Cu Ni and Zn present some differences when comparing the static and dynamic tests for S/S contaminated sediments.

- From all of the leaching tests performed, it is concluded that the dynamic diffusion test best represents the long-term leaching behavior of the S/S contaminated sediments.

- For the case of leaching behaviour modeling of S/S material , geochemical leaching models have been used and recommended for prediction of the leaching behavior of the S/S material under field conditions. The model input data should be provided by the most suitable leaching test(s) identified for the specific S/S material. In this case, the dynamic diffusion test is considered to better simulates long term prediction.

8.0 RECOMMENDATIONS AND FUTURE OUTLOOK

1) With respect to the selection of the most appropriate leaching test(s) for the S/S contaminated sediments, the following considerations should be taken into account; a) the boundary conditions and accuracy to which the results are required, b) the cost of the testing, analytical services, data handling, and interpretation, c) the objective(s) of candidate testing procedures, and d) the expected environment conditions where the S/S material is going to be placed. In the majority of the cases, more than one leaching test may be required to fully describe the contaminants release from S/S material under a particular scenario. However, the final decision of which tests should be carried out will depend on the four points addressed above.

2) The leaching characterization and long term release assessment should also consider changes in the chemical and physical properties of the material due to degradation processes via testing of aged and degraded materials. For example, as suggested by the literature (Spence and Shi 2005) samples may be aged in the laboratory using accelerated carbonation techniques prior to testing in parallel to un-aged materials. In addition, the same authors suggest that some important considerations should be taken into account when selecting leaching test for the evaluation of S/S material in a specific scenario. Those considerations are presented in Table 17.

Table 17 Important consideration for leaching test selection of an S/S material in different scenarios of deposition (Spence and Shi 2005)

For an S/S material to be disposed in a monofill scenario with leachate control	For a S/S material used near-surface placement without leachate control
The infiltration rate will be low due to leachate controls, thus a low L/S ratio prevails	The S/S material may be subjected to high volumes of water (infiltration or diffusion) on and intermittent wetting basis
The small amount of leachant that contacts the waste will be highly alkaline due to percolation through and/or contact with cementitious wastes above the subject material	The contact mode for liquid and solid phases may be either percolation (e.g. loose granulated fill) or flow around (e.g. compacted granular or monolithic material)
The concentration in the infiltrating leachant will tend to come to a steady state with the contaminants in the waste as a result of slow percolation rates	Release rates may be controlled by equilibrium or mass transport, depending on infiltration rates, leachant volume, and contact time.
	Degradation via chemical (e.g., carbonation, chloride penetration, sulphate attack) or physical (e.g., cyclic loading, freeze/thaw) mechanisms will change equilibrium and mass transport based release parameters.

In cases where S/S materials are placed near surface and without leachant control, the literature (Spence and Shi 2005) suggests that the most complete approach for testing would be to combine the results of an equilibrium-based test over a range of possible pH scenarios, with a mass-transport test for a monolithic test sample. Equilibrium testing will give information of the neutralization consumption from infiltrating acidic (if it is the case) or low pH components, while the mass-transport test would provide information on rates of constituent release from S/S monolithic material. Suggested protocols would include pH-dependent test (e.g. , prEN 14429, Acid Neutralization Capacity test) and diffusion test for monolithic materials (e.g., NEN 7345). However, as emphasized previously if the intention of the test is to mimic the leaching of the S/S material in its natural place of deposition, then the variations with respect to the protocols should be in strict accordance with the specific scenario conditions where the S/S material is going to be placed.

3) At the beginning of this experimental program, it was thought that the total leaching behaviour of the S/S contaminated sediments will be better represented by a combination of diffusion and column tests, a method designed in-house and referred to as the modified column test. However, as explained previously the possibility of having a significant amount of water flowing through the S/S material is very unlikely under the standard test conditions given the low permeability of the S/S contaminated sediment sample used in this thesis. However, the S/S material may undergo chemical and physical changes due to degradation - to observe those changes additional aging testing is suggested. This test type was not conducted in this thesis project. In the case that results of aging tests of S/S contaminated sediments in future investigations show an increase in the permeability of the matrix, which in turn, corresponds to larger amounts of water infiltration through the S/S waste, then it may be prudent to perform the column test. In such condition, some important considerations should be taken into account after the knowledge gained during the up-flow test (column test), performed as part of the experimental program. These considerations are as follows; the flow rate, column length and the pressure of the pump are key factors. Inducing a high water pressures to achieve the required flow rates is unrealistic and may result in development of preferential flow pathways (channelling) along the sample and not through it; large advection and unrealistic kinetic conditions all of which result in faulty data in terms of large quantities of components being released. Therefore, careful consideration should be given to adjust the test to the expected scenario, or to the environmental condition that one wants to represent.

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List of Appendices:

Appendix 1	Laboratory results of the performed leaching tests
Appendix 2	Figures of diffusion test laboratory results (concentration of components versus time)
Appendix3	Figures of the measured cumulative leaching of laboratory results for diffusion test
Appendix 4	Figures of column test laboratory results (concentration of components versus L/S ratio)
Appendix 5	Figures of the measured cumulative leaching of laboratory results for column test (Up-flow test)

Appendix 1 Laboratory results of the performed leaching tests and measured parameters (Selected metals for this thesis study are highlighted in grey)

Leaching test		Static diffusion test								Static diffusion test (Duplicate)							
Collection date		13/08/07	14/08/07	15/08/07	17/08/07	22/08/07	29/08/07	18/09/07	16/10/07	13/08/07	14/08/07	15/08/07	17/08/07	22/08/07	29/08/07	18/09/07	16/10/07
ELEMENT	**Units**	**D1-N1**	**D1-N2**	**D1-N3**	**D1-N4**	**D1-N5**	**D1-N6**	**D1-N7**	**D1-N8**	**D3-N1**	**D3-N2**	**D3-N3**	**D3-N4**	**D3-N5**	**D3-N6**	**D3-N7**	**D3-N8**
Ca	**mg/l**	533	623	631	699	866	921	1410	1310	552	621	641	691	869	920	1380	1330
Fe	**mg/l**	0.0067	<0.004	<0,004	0.005	0.0101	0.0287	0.0381	0.0438	0.0045	<0.004	<0,004	0.006	<0,004	0.0308	0.0414	0.0327
K	**mg/l**	432	424	465	462	404	385	388	422.00	434	430	446	470	390	382	379	421
Mg	**mg/l**	1170	1110	1070	1080	893	909	708	711	1180	1120	1070	1090	885	904	703	716
Na	**mg/l**	11000	11300	11300	10800	11100	11100	11400	10800	11300	11100	11400	11000	10900	11000	11200	10800
S	**mg/l**	1060	995	961	999	913	913	988	1020	1090	1080	902	998	924	910	942	1020
Al	**µg/l**	9.2	19.9	14.9	16.3	12.1	7.83	11	13.6	13.8	23.6	21.8	23.3	17.2	13.1	15.9	9.68
Ba	**µg/l**	142	168	163	153	267	275	423	348	158	181	136	145	267	273	444	367
Cd	**µg/l**	<0.05	<0.05	0.0618	0.0745	<0,05	<0,05	0.0516	<0.05	<0.05	<0.05	<0,05	0.098	<0,05	<0,05	0.0782	<0.05
Co	**µg/l**	0.447	0.831	0.526	0.573	1.03	0.669	0.552	0.352	0.734	0.831	0.583	0.599	1.03	0.7	0.664	0.331
Cr	**µg/l**	4	2.02	0.855	<0,1	0.192	<0,1	0.28	0.681	5.94	2.51	0.764	0.246	0.424	0.376	0.201	0.523
Cu	**µg/l**	9.93	10.1	9.43	4.75	3.03	1.74	1.27	3.28	15.4	14.2	12.4	6.12	5.76	2.91	3.61	2.85
Hg	**µg/l**	<0.002	<0.002	<0,002	<0,002	<0,002	0.0027	0.0041	<0.002	<0.002	<0.002	<0,002	<0,002	<0,002	0.0065	0.005	<0.002
Mn	**µg/l**	1.28	<0.1	3.24	4.63	7.65	17.2	23.4	24.2	<0.1	<0.1	4.61	5.51	3.74	24	26.9	23.6
Ni	**µg/l**	17.1	22.4	20.6	18.7	27.9	22	28.1	21.3	21.4	20.3	19.8	18.7	28	21.8	28.4	21.6
Pb	**µg/l**	0.779	0.319	0.583	0.432	0.895	0.621	<0,3	0.834	0.511	0.344	0.418	0.371	1.21	0.657	<0,3	0.767
Zn	**µg/l**	9.23	6.23	6.15	5.6	6.35	12	8.47	16.4	10.6	6	6.02	7.68	7.84	11	17.5	10.2
Parameters	**Units**																
pH		8.54	8.78	8.6	8.54	8.66	8.53	8.56	8.32	8.59	8.76	8.66	8.6	8.71	8.57	8.65	8.56
Temp.	**ºC**	22.05	21.55	21.25	21.2	22.7	20.65	20.75	21.4	21.8	21.3	21.15	21.35	22.6	20.75	20.65	21.2
E.C.	**mS/cm**	51.8	51.8	52.2	52	52	52.2	52.6	53.1	52	51.9	52.1	52.2	52.1	52.4	52.8	52.7

Appendix 1 (Continuation) Laboratory results of the performed leaching tests and measured parameters (Selected metals for this thesis study are highlighted in grey)

Leaching test		**Dynamic diffusion test**								**Dynamic diffusion test (duplicate)**							
Collection date		**13/08/07**	**14/08/07**	**15/08/07**	**17/08/07**	**22/08/07**	**29/08/07**	**18/09/07**	**16/10/07**	**13/08/07**	**14/08/07**	**15/08/07**	**17/08/07**	**22/08/07**	**29/08/07**	**18/09/07**	**16/10/07**
ELEMENT	**Units**	**D2-N1**	**D2-N2**	**D2-N3**	**D2-N4**	**D2-N5**	**D2-N6**	**D2-N7**	**D2-N8**	**D4-N1**	**D4-N2**	**D4-N3**	**D4-N4**	**D4-N5**	**D4-N6**	**D4-N7**	**D4-N8**
Ca	**mg/l**	536	624	631	738	879	944	1370	1310	539	619	624	702	867	933	1390	1330
Fe	**mg/l**	<0.004	<0.004	<0,004	0.0099	0.0099	0.0138	0.039	0.02	0.0191	0.0065	0.0068	0.0096	0.0092	0.0394	0.0725	0.0174
K	**mg/l**	436	426	462	481	397	386	378	418	431	429	464	465	383	384	382	419
Mg	**mg/l**	1170	1100	1060	1080	883	880	701	725	1160	1110	1070	1080	870	893	704	727
Na	**mg/l**	11100	11100	11300	11000	11200	11000	11100	10800	11100	11100	11400	10900	10800	11000	11200	10900
S	**mg/l**	1050	996	932	1020	888	894	930	1050	1000	1010	946	1000	923	904	948	1060
Al	**µg/l**	13.7	19.2	15.6	19.8	12.1	13	9.32	14.6	26.6	28.1	23.5	24	13.5	20.9	16.5	19.5
Ba	**µg/l**	143	160	169	151	269	277	377	327	147	167	167	159	271	275	391	334
Cd	**µg/l**	<0.05	0.0537	<0,05	0.0853	<0,05	<0,05	0.0598	0.634	<0.05	<0.05	0.0508	0.0671	<0,05	<0,05	<0,05	0.153
Co	**µg/l**	0.439	0.542	0.592	0.676	0.941	0.735	0.474	1.05	0.633	0.654	0.571	0.546	0.868	0.762	0.574	0.393
Cr	**µg/l**	3.32	0.978	0.598	0.115	0.251	0.257	<0,1	1.3	6.11	2.29	0.831	0.203	0.157	0.317	<0,1	0.788
Cu	**µg/l**	14.9	12.3	7.64	3.71	8.64	1.73	8.02	7.76	15.3	14.7	11.9	6.44	8.95	3.02	8.96	15.2
Hg	**µg/l**	<0.002	<0.002	<0,002	<0,002	<0,002	<0,002	<0,002	<0.002	<0.002	<0.002	<0,002	<0,002	<0,002	0.0024	<0,002	<0.002
Mn	**µg/l**	<0.1	<0.1	3.69	5.81	8.88	12.4	20.8	22.2	<0.1	<0.1	5.61	6.02	7.45	19.3	27	20
Ni	**µg/l**	17	17.7	15.9	15.8	24.8	20.4	14.5	10.8	21	20.9	19.1	16.6	25.7	21.1	16.7	9.26
Pb	**µg/l**	0.694	0.398	0.514	0.663	0.683	<0,3	<0,3	1.37	0.741	0.367	0.488	<0,3	0.642	0.603	0.404	0.752
Zn	**µg/l**	12.3	15	7.06	25.8	13.4	7.16	8.53	12.2	20.1	10.4	9.33	9.81	13	10.7	10.1	9.48
Parameters	**Units**																
pH		8.59	8.78	8.59	8.44	8.28	8.18	7.92	8.1	8.59	8.74	8.59	8.29	8.2	8.14	7.99	8.08
Temp.	**ºC**	22.0	21.6	21.4	21.3	22.7	20.9	20.3	21.0	21.8	21.5	21.3	21.4	22.7	20.8	20.9	21.3
E.C.	**mS/cm**	51.8	51.9	51.9	52.2	52	52.3	53.65	53.2	51.9	51.9	52	52.1	52	52.7	52.4	52.9

Appendix 1(Continuation) Laboratory results of the performed leaching tests and measured parameters(Selected metals for this thesis study are highlighted in grey)

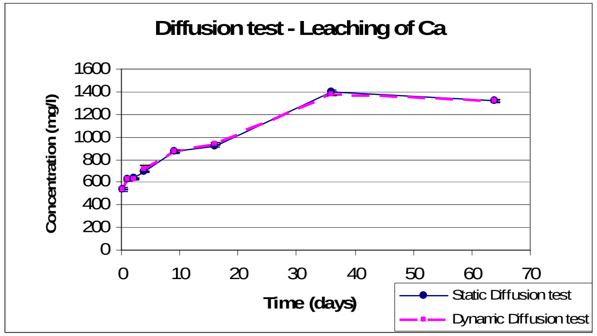
Leaching test		**Magnetic agitation test**						**Batch test**	
		24hrs	**24hrs(dup)**	**48hrs**	**48hrs(dup)**	**96hrs**	**96hrs(dup)**	**24 hrs**	**24hrs(dup)**
ELEMENT	**Units**	**B-C**	**B-D**	**B-E**	**B-F**	**B-A**	**B-B**	**B-5**	**B-6**
Ca	**mg/l**	553	551	639	641	749	741	1790	1840
Fe	**mg/l**	0.0075	0.0064	0.008	<0,004	0.019	0.0083	<0,004	0.233
K	**mg/l**	406	402	402	399	437	438	423	423
Mg	**mg/l**	1140	1150	1060	1060	970	988	389	394
Na	**mg/l**	11200	11100	10900	10900	10900	10900	10900	11100
S	**mg/l**	989	976	958	962	967	952	1860	1500
Al	**µg/l**	79.5	72	40.3	34.6	22.6	15	10.7	179
Ba	**µg/l**	155	145	196	208	236	245	945	866
Cd	**µg/l**	<0,05	<0,05	<0,05	<0,05	0.083	0.0883	<0,05	<0,05
Co	**µg/l**	1.27	1.05	1.23	1.13	1.53	1.19	14.1	13.6
Cr	**µg/l**	4.29	3.71	3.3	2.68	1.95	1.72	1.78	2.33
Cu	**µg/l**	21.4	17.4	17.4	20.3	25.7	19.8	111	112
Hg	**µg/l**	<0,002	<0,002	<0,002	<0,002	<0,002	<0,002	<0,002	0.0049
Mn	**µg/l**	3.98	3.35	3.18	2.81	6.21	5.82	<0,1	3.06
Ni	**µg/l**	19.7	19.9	23.2	24.3	29	23.4	108	107
Pb	**µg/l**	<0,3	<0,3	<0,3	<0,3	<0,3	<0,3	<0,3	1.86
Zn	**µg/l**	2.19	<2	2.18	<2	2.23	<2	<2	12.6
Parameters	**Units**								
pH	**pH**	8.83	8.85	8.57	8.72	8.32	8.19	9.52	9.53
Temp.	**ºC**	20.8	20.8	22.75	21.85	22.3	22.25	22	22.05
E.C.	**mS/cm**	52.3	52	51.9	52.1	52.2	52.6	52.4	52.2

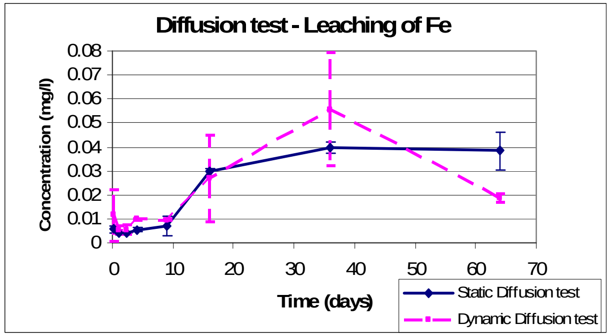
Appendix 1 (Continuation) Laboratory results of the performed leaching tests and measured parameters (Selected metals for this thesis study are highlighted in grey)

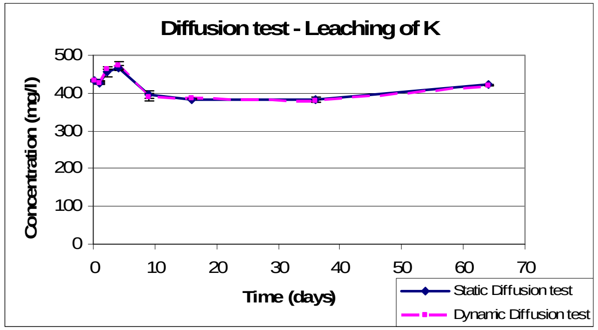
Leaching test		Column test – Up flow test							Column test – Up flow test (duplicate)						
Collection date		28/08/07	29/08/07	29/08/07	30/08/07	03/09/07	09/09/07	22/09/07	28/08/07	29/08/07	29/08/07	30/08/07	03/09/07	10/09/07	23/09/07
ELEMENT	**Units**	**C1-N1**	**C1-N2**	**C1-N3**	**C1-N4**	**C1-N5**	**C1-N6**	**C1-N7**	**C2-N1**	**C2-N2**	**C2-N3**	**C2-N4**	**C2-N5**	**C2-N6**	**C2-N7**
Ca	**mg/l**	717	1250	1450	1680	1910	1850	1500	706	1130	1460	1790	1680	1750	1380
Fe	**mg/l**	0.176	0.0643	0.0067	0.0153	<0,004	<0,004	<0,004	0.195	0.0961	0.0466	0.0098	<0,004	<0,004	<0,004
K	**mg/l**	1210	964	755	685	519	398	393	1170	949	772	624	504	405	392
Mg	**mg/l**	<0,5	5.26	5.46	2.09	85.7	419	665	<0,5	<0,5	0.658	19.8	246	423	708
Na	**mg/l**	9170	10100	11000	10900	11200	11200	10800	9700	10400	9950	11000	10900	11200	10900
S	**mg/l**	3920	2440	1710	975	774	945	1050	1660	1110	938	816	817	903	989
Al	**µg/l**	1680	334	21.7	8.15	2.19	2.02	5.69	2150	782	258	5.93	2.5	<0,7	1.06
Ba	**µg/l**	1330	1530	1340	1150	869	594	402	1250	1440	1220	1040	731	606	419
Cd	**µg/l**	<0,05	<0,05	<0,05	0.179	<0,05	<0,05	<0,05	<0,15	<0,05	<0,05	<0,05	<0,08	0.0763	<0,05
Co	**µg/l**	18.4	8.04	4.6	3.06	1.97	1.15	0.661	10.5	4.5	2.89	1.93	1.56	1.01	0.532
Cr	**µg/l**	1.18	1.61	0.42	0.37	0.304	0.122	0.254	1.05	0.615	0.798	0.927	0.283	0.159	0.246
Cu	**µg/l**	1.74	0.736	0.64	<0,5	<0,5	<0,5	<0,5	1.83	<0,5	0.516	<0,5	<0,5	<0,5	<0,5
Hg	**µg/l**	0.642	0.333	0.187	0.0814	0.0372	0.0025	<0,002	0.565	0.212	0.131	0.0472	0.0148	0.0022	<0,002
Mn	**µg/l**	0.485	0.568	<0,1	2.79	0.941	0.805	3.24	0.869	0.541	<0,1	1.04	0.658	0.802	4.54
Ni	**µg/l**	468	160	102	137	61.7	22.5	7.13	227	96	131	80.8	47.3	21.8	7.32
Pb	**µg/l**	1.02	0.556	<0,3	<0,3	<0,3	<0,3	<0,3	3.77	<0,3	0.321	<0,3	<0,3	<0,3	<0,3
Zn	**µg/l**	36.2	14.8	<2	<2	<2	2.48	2.62	103	15.7	4.43	<2	<2	3.15	2.36
Parameters	**Units**														
pH	**pH**	11.79	11.53	11.33	11.37	9.47	7.72	7.71	11.9	11.78	11.35	10.59	9.37	7.73	7.86
Temp.	**ºC**	20.7	20.3	20.7	20.6	19.6	20.0	19.9	20.7	20.8	20.1	20.8	19.9	20.4	19.7
E.C.	**mS/cm**	48.5	50.1	50.6	51.5	52.6	52.9	53.4	48.1	50	51.1	51.3	52.5	52.8	53.4

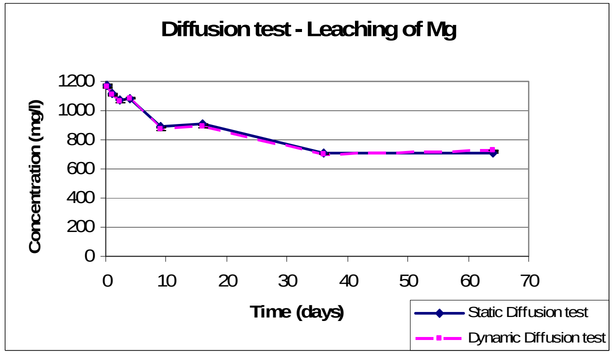
Appendix 2- Figures of diffusion Test laboratory results (concentration of components versus time in days)

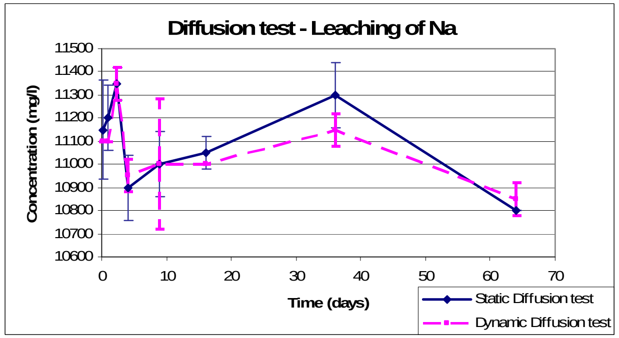
Diffusion test figures are shown as a concentration of component (mg/l and ug/l respectively) with respect to time (days).

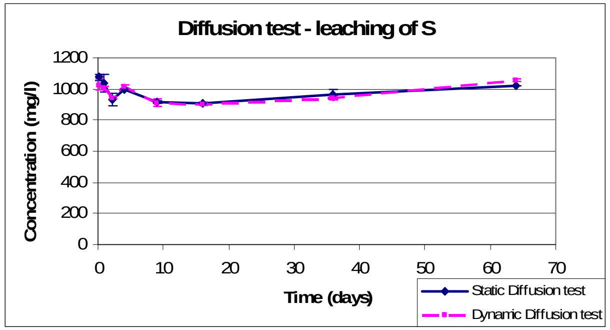




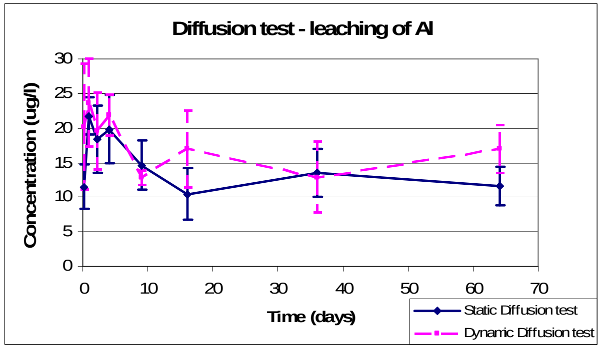


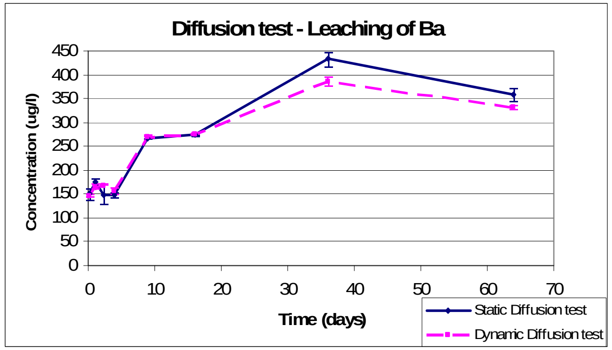


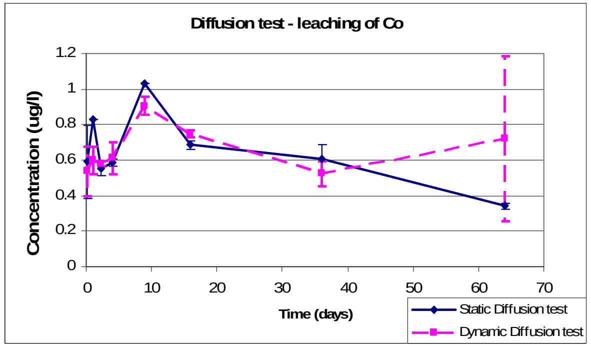


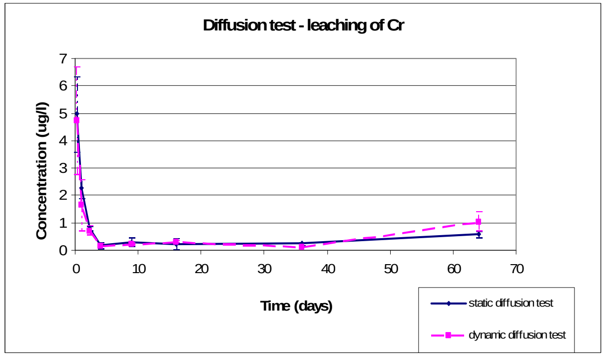


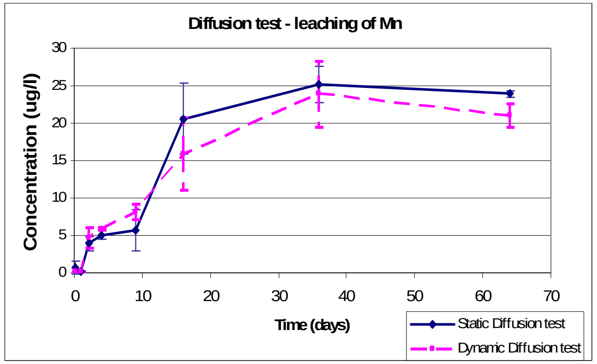
Appendix 2 (Continuation)- Figures of diffusion Test laboratory results (concentration of components versus time in days)

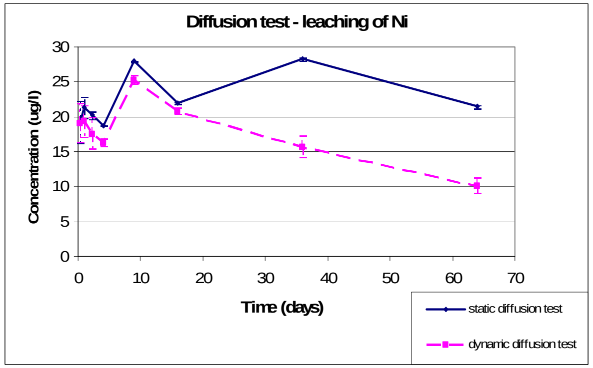




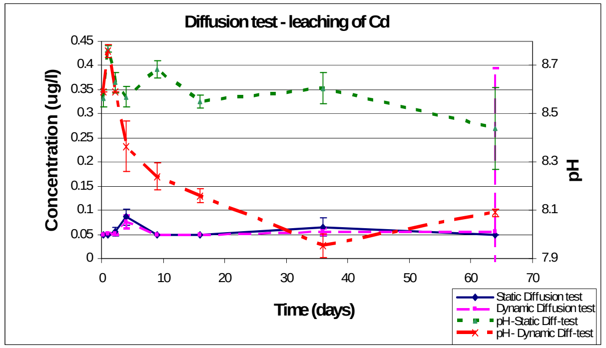


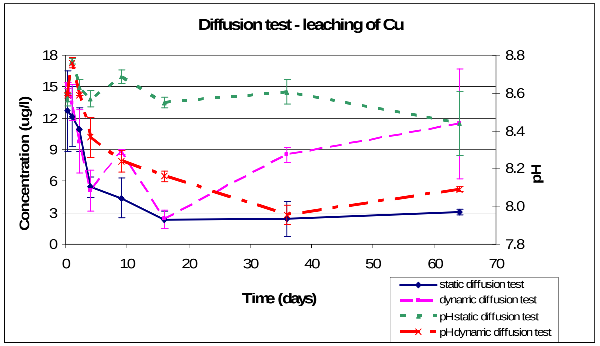


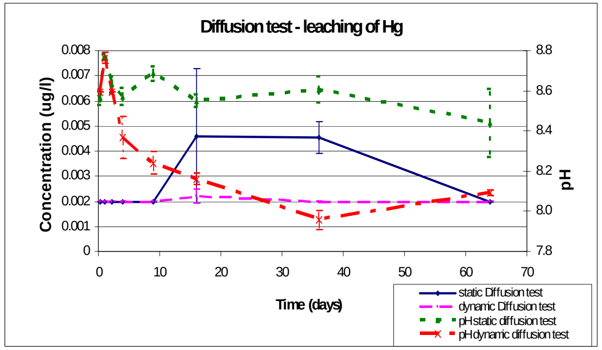


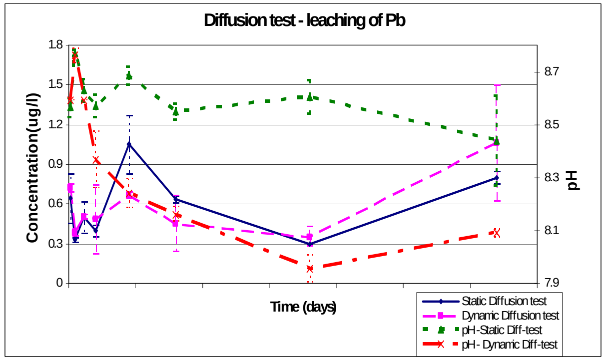


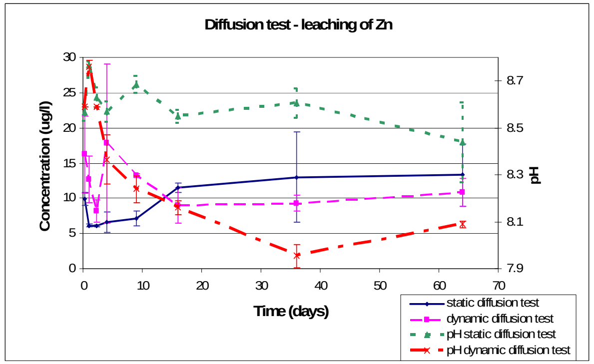
Appendix 2 (Continuation)- Figures of diffusion Test laboratory results (concentration of components versus time in days)





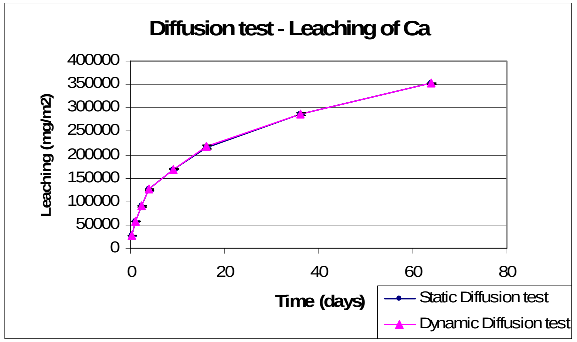


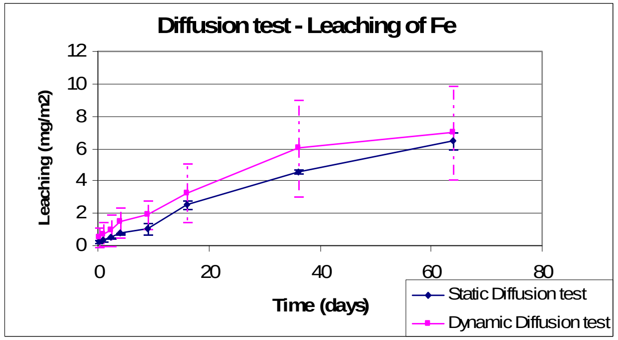


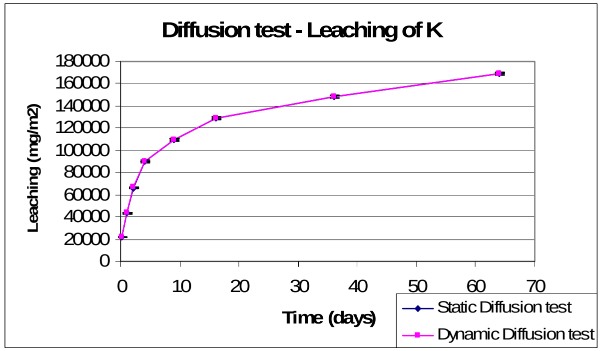


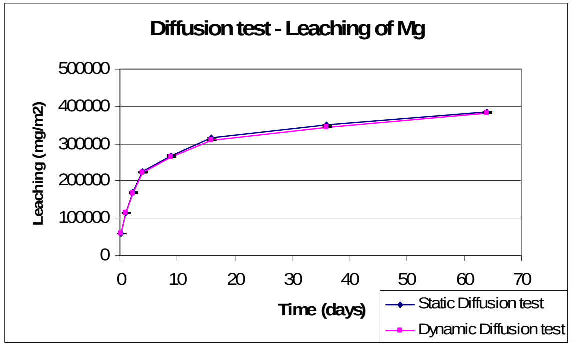
Appendix 3 Figures of measured cumulative leaching of laboratory results for diffusion Test (concentration of components versus time in days)

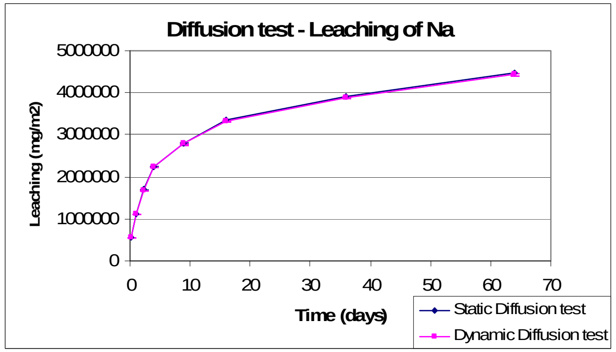
Measured Cumulative leaching of a component (mg/m2), considering that in the case where concentration where below detection limits and average of lower and upper limits have been done

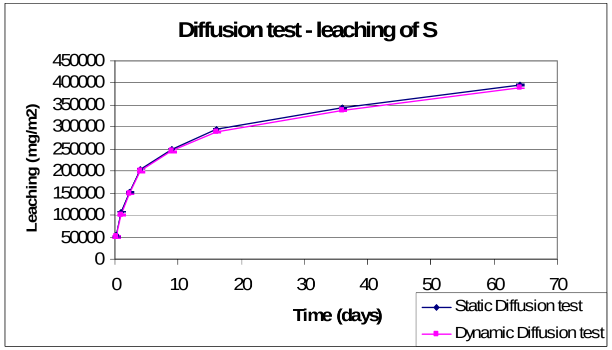




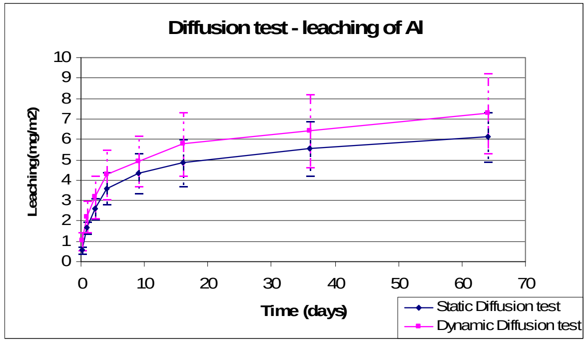


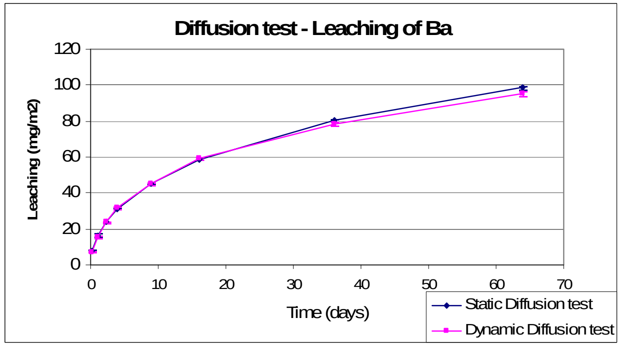


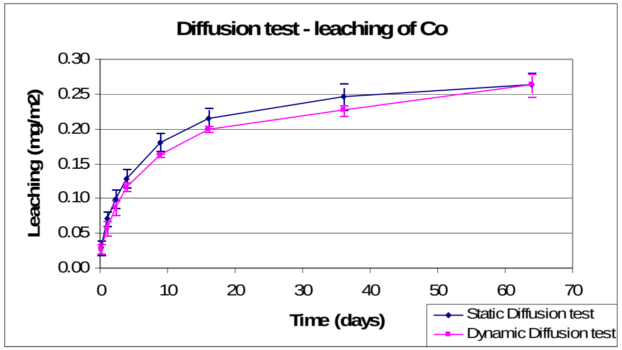


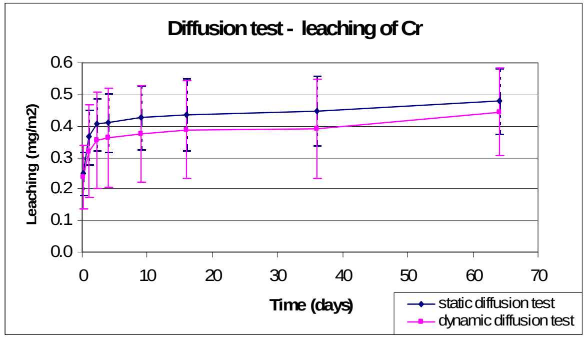


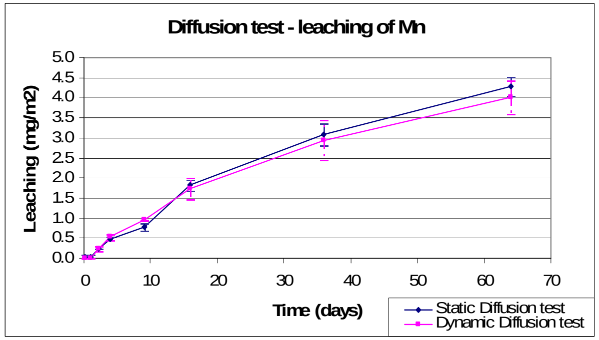
Appendix 3 (continuation) Figures of measured cumulative leaching of laboratory results for diffusion Test (concentration of components versus time in days)

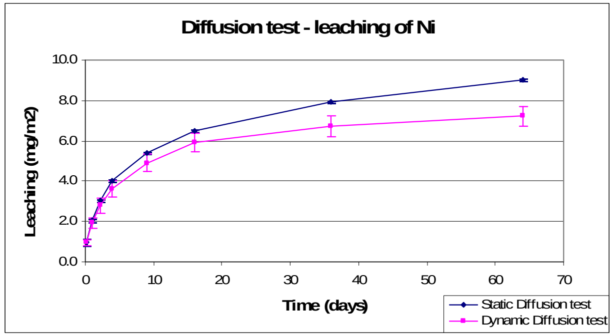




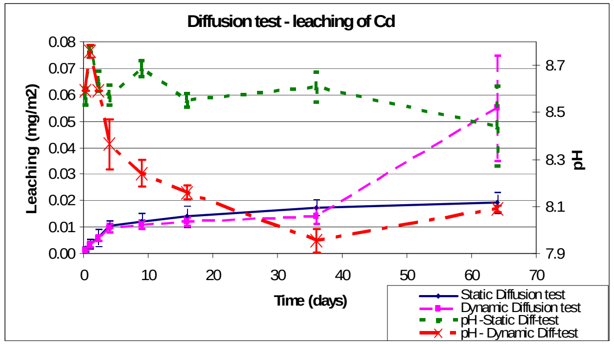


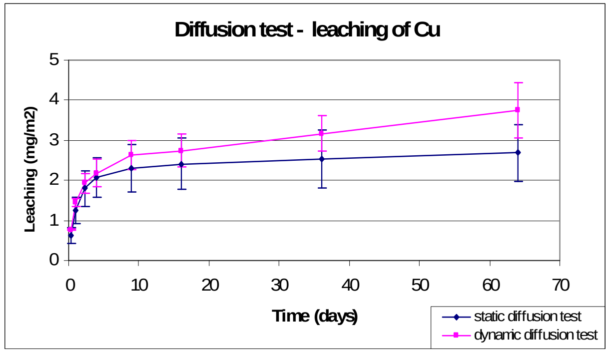


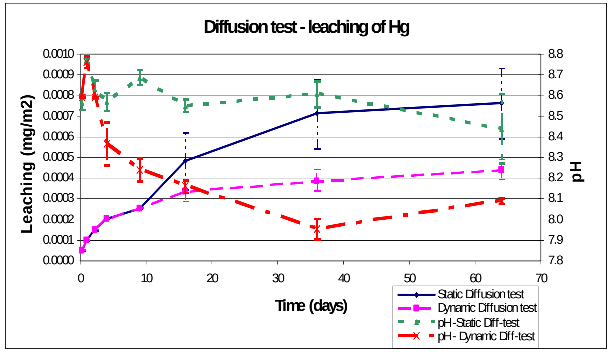


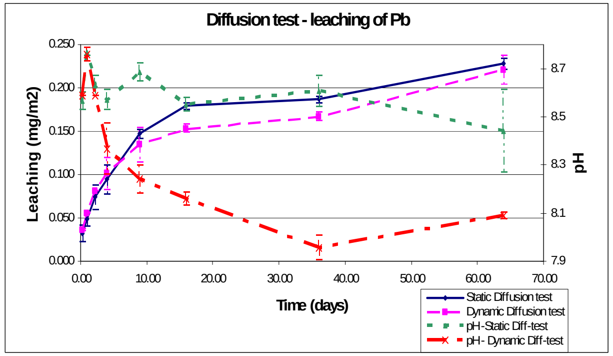


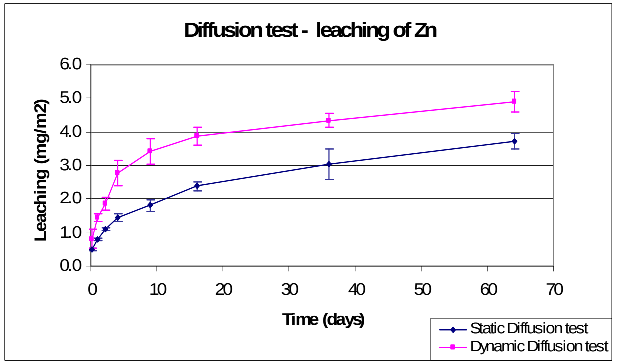
Appendix 3 (continuation) Figures of measured cumulative leaching of laboratory results for diffusion Test (concentration of components versus time in days)





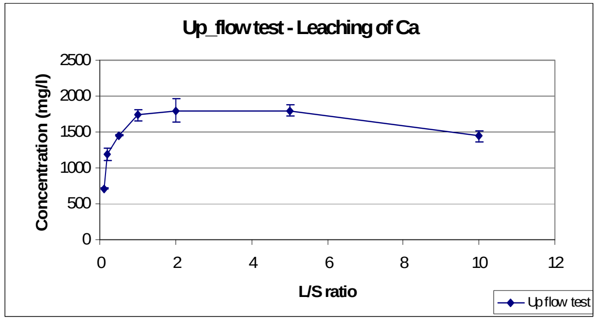


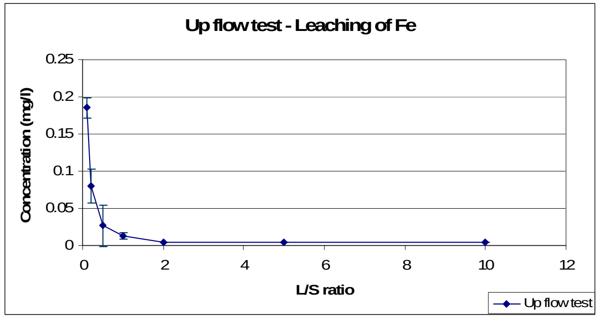


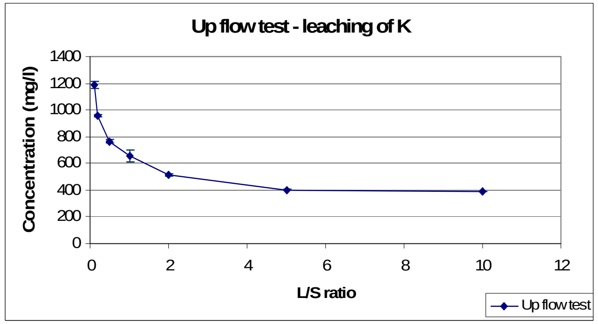


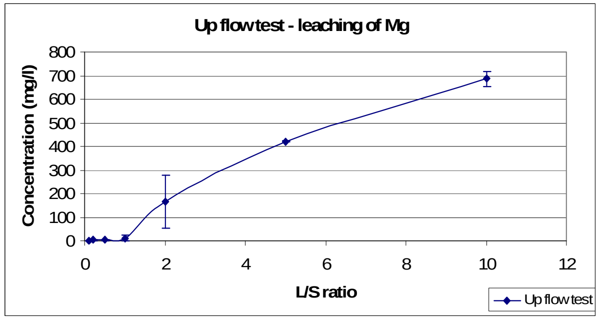
Appendix 4 Figures of Column test laboratory results (concentration of components versus L/S ratio)

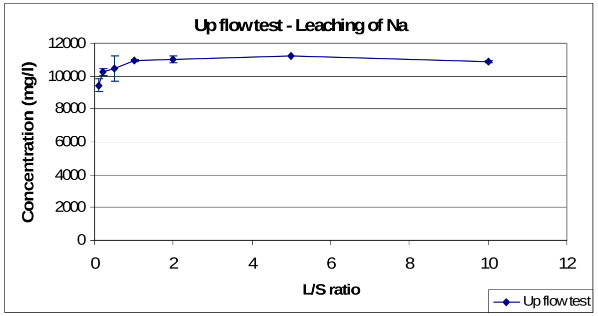
Up flow test (column test) figures are shown as a concentration of component (mg/l or µg/l respectively) versus L/S ratio

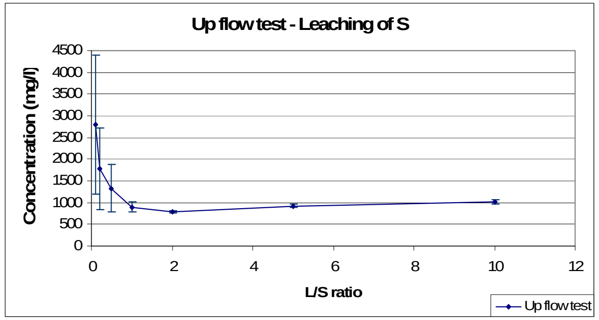




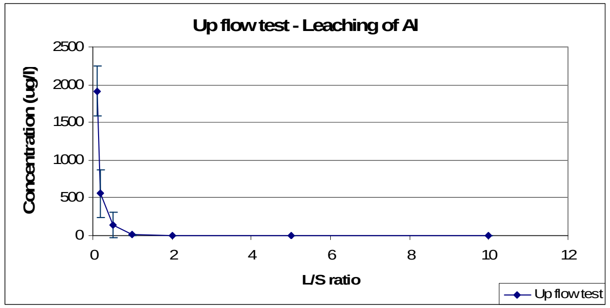


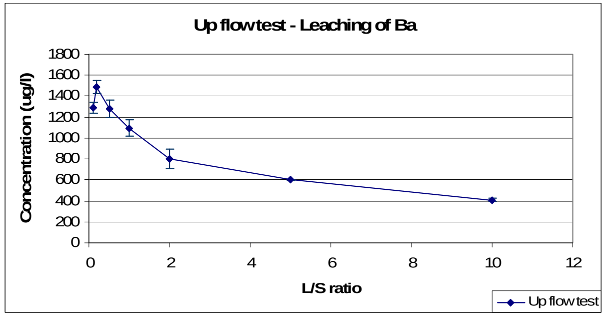


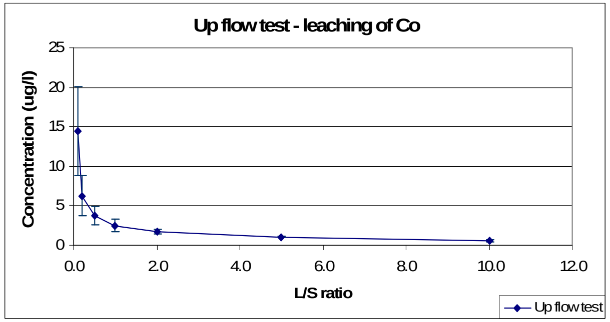


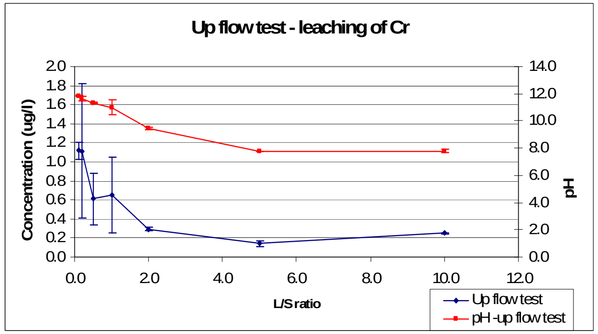


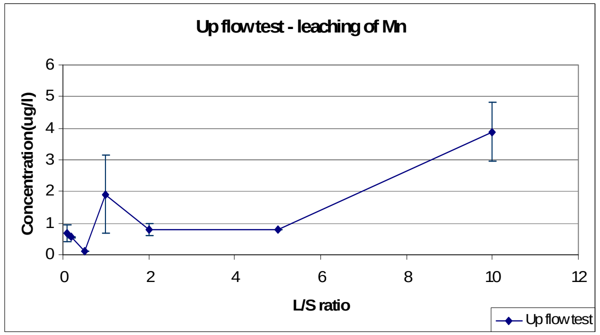
Appendix 4 (continuation) Figures of Column test laboratory results (concentration of components versus L/S ratio)

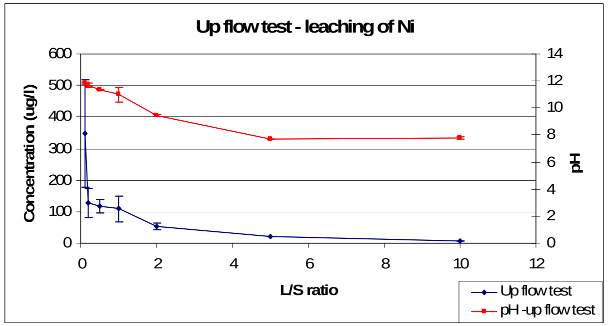




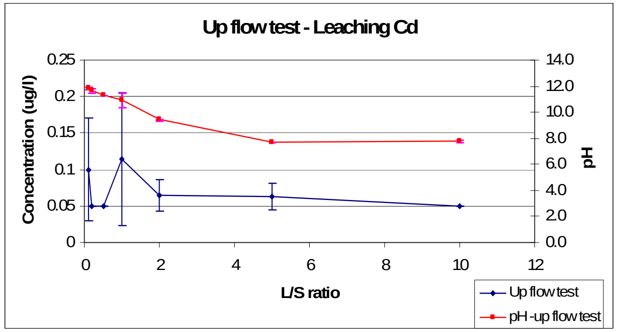


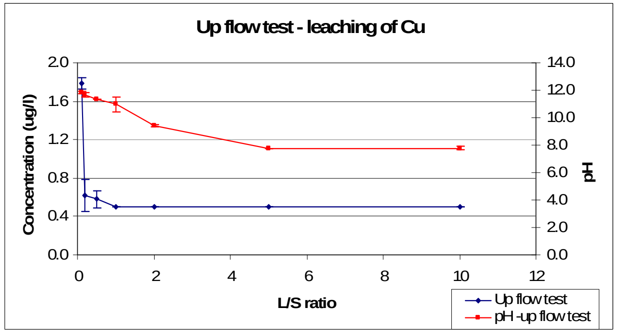


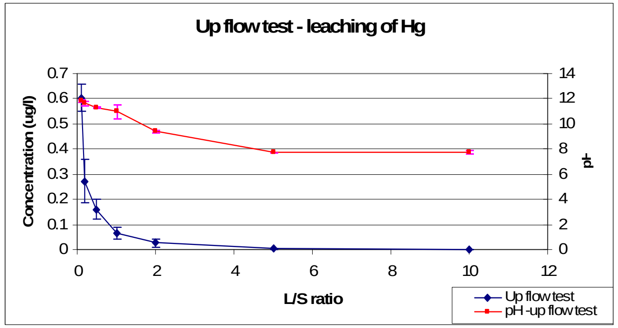


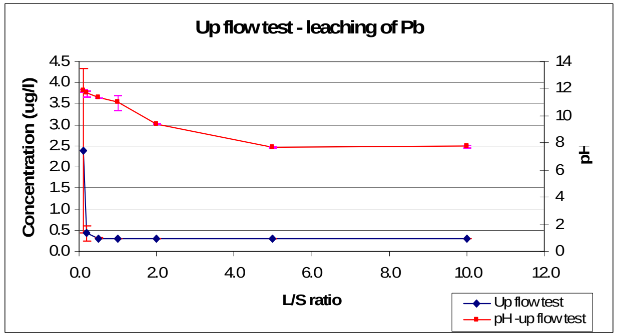


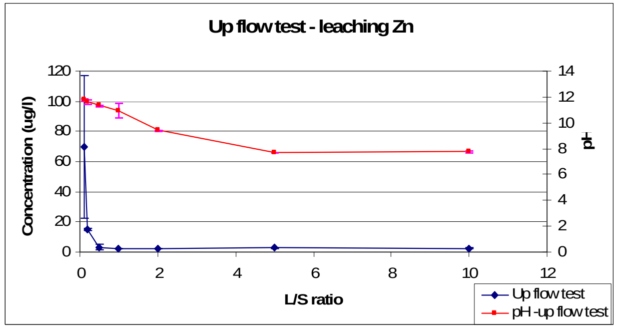
Appendix 4 (continuation) Figures of Column test laboratory results (concentration of components versus L/S ratio)





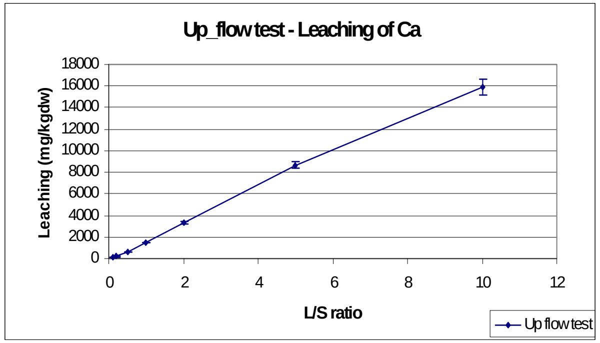


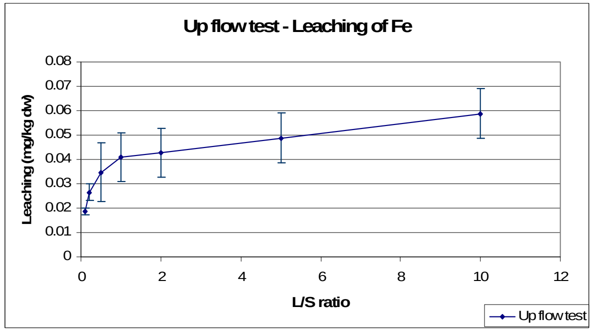


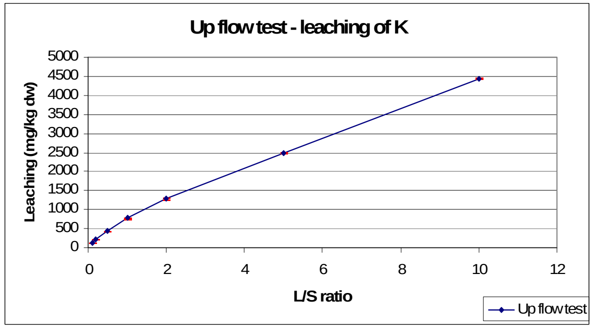


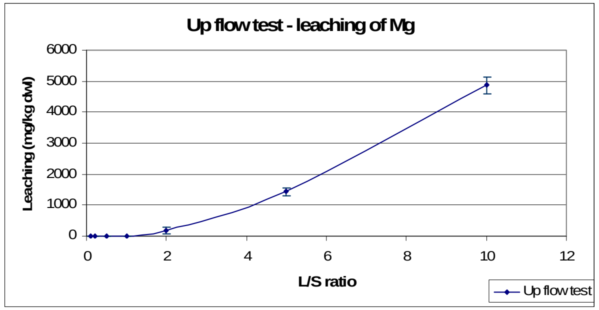
Appendix 5 Figures of the measured cumulative leaching of column test laboratory results (concentration of components versus L/S ratio)

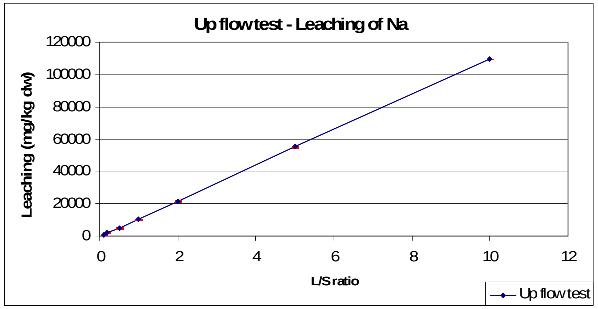
Cumulative released quantities calculated for each component in mg/kg dry mass (Considering that in the case where concentration where below detection limits and average of lower and upper limits have been done)

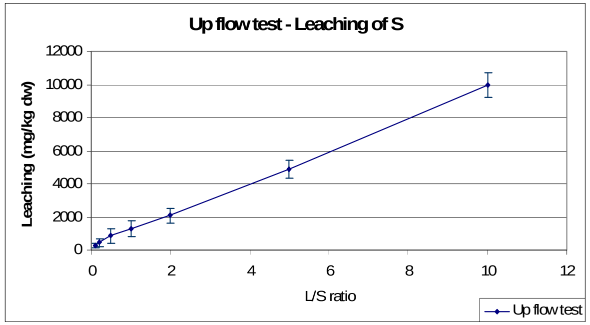




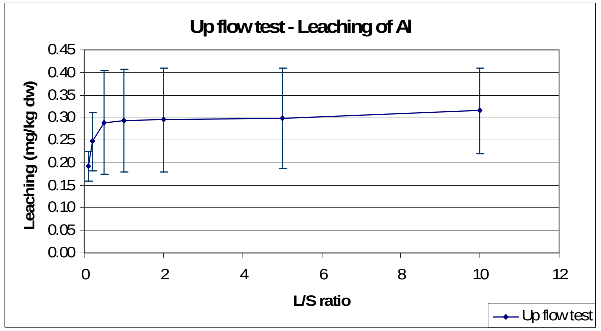


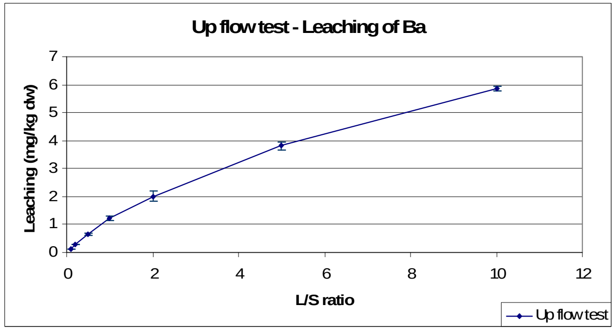


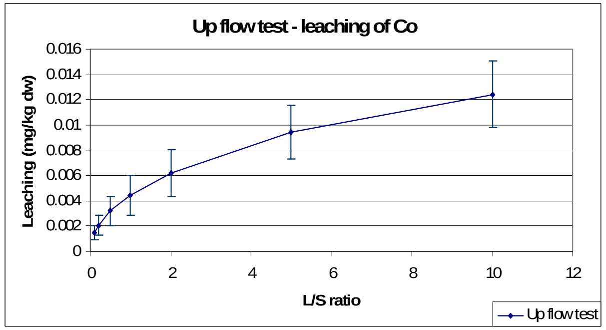


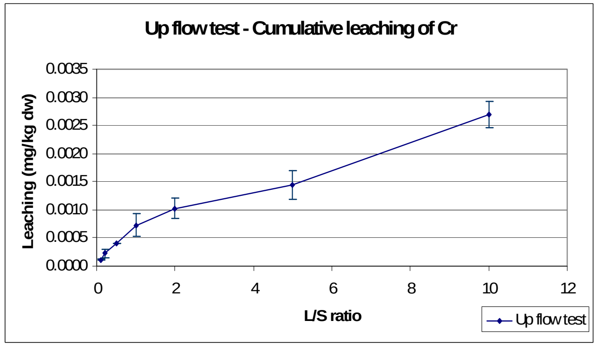


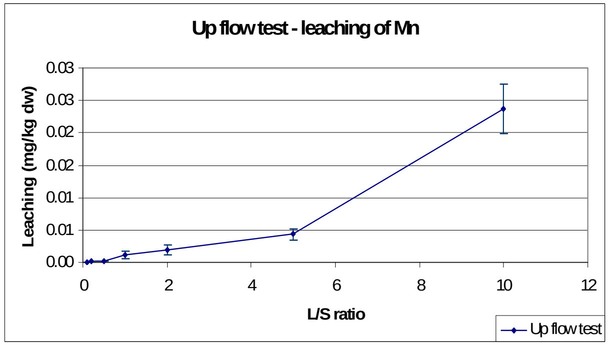
Appendix 5 (continuation) Figures of the measured cumulative leaching of column test laboratory results (concentration of components versus L/S ratio)

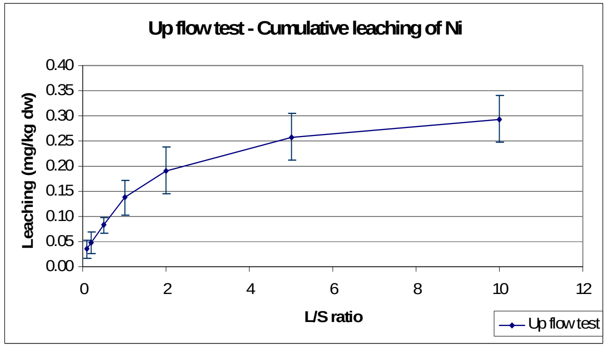












Appendix 5 (continuation) Figures of the measured cumulative leaching of column test laboratory results (concentration of components versus L/S ratio)