Leachate Treatment of Heavy Metals by Natural and Residual Product Materials

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Water Environment Transport
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg

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Abstract

This report presents a study of natural adsorbents ability to remove heavy metals from an industrial landfill leachate at the cable producing company, Nexans IKO Sweden AB. The results of the work will be used by the company as a base for design and construction of a filter-bed for leachate treatment.

A previous study of natural and rest-products materials sorption ability showed that peat moss, fiber ash from recycled paper and pine bark were the most efficient adsorbents for heavy metals, and these materials were chosen to study further in this project. Their performance was investigated in column experiments in order to simulate real flow conditions. Columns were installed at the landfill near the groundwater well and fresh leachates were used.

Field experiments were complemented with laboratory column experiments using artificial solutions of metals. The purpose of these experiments was to investigate factors influencing adsorption, such as extremely high concentrations and competition for adsorption sites.

Different grain sizes of adsorbent material, as well as mixtures of materials, were used in the column experiments. As fiber ash showed to be highly impermeable, also in mixtures with sand, it was not possible to use as a pure material in the column tests. Instead, part of the ash (10%) was added to a ground peat moss column in order to observe effects on adsorption by comparison of results from a column packed with pure peat moss. The other columns contained untreated peat moss and bark. Like in previous batch experiment, dried and ground peat moss showed higher sorption capacity than untreated peat moss. In general, dried and ground peat moss showed the highest efficiency and sorption capacity among the column materials studied. The lower performance of the peat and ash mixture compared to pure peat moss suggests use of these materials in separate treatment steps. Possible mechanism of adsorption inhibition by fiber ash is through competition for adsorption sites between \( \text{Ca}^{2+} \) ions, released from the ash, and heavy metals in the leachates.

Columns packed with the same adsorbent materials, but loaded with 10 times more concentrated artificial metal solutions, showed much higher sorption rates and sorption capacity. A possible explanation can be the absence of competitive ions in the artificial solution. From these results it is concluded that laboratory studies with artificial solutions can overestimate adsorbents performance and give unexpected results when applied in field. Thus specific studies with real leachates are recommended as a complement to laboratory tests for future sorption studies.

The leachate used in this study contained extremely high concentrations of iron, but it was effectively removed by sedimentation. Two equal columns with ground peat were run with different metal solutions, one containing iron and another iron-free. Result of the experiment showed that iron is substantially inhibiting sorption of other metals. As a conclusion, sedimentation is preferable as a pre-treatment of the leachate. Other metals also showed to be successfully removed by sedimentation. This procedure can prolong the service time of the adsorbent used for treatment.
Acknowledgements

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1. Introduction

It is estimated that there are more than 30 000 contaminated sites in Sweden (Swedish EPA, 2003), and the number of contaminated sites is expected to be much higher in developing countries. In most of the cases remediation of contaminated soil and groundwater is very expensive and leads to inactivity. In order to find affordable methods of remediation of contaminated leachates and groundwater, a study of low-cost adsorbent materials was carried out in this project.

Contaminated groundwater from the landfill at a cable-producing company, Nexans IKO Sweden AB, was used for the case study of sorption capacity of low-cost adsorbent materials. As adsorbents, peat moss, fiber ash from recycled paper and bark, were used which showed the best results in a previous study (Chauvet, 2003). Heavy metals were the object for the adsorption studies. Column technique was chosen to estimate the adsorbents performance under dynamic conditions. Columns were packed and installed near the landfill groundwater well, and fresh leachates was used to obtain true results. The study was continued with laboratory experiment in which influence of high load of pollutants and competition between ions in the solution for adsorption sites were studied.

This report presents the theoretical background of metals adsorption, conducted experiments, their results and discussion. The result of the work is summarized in conclusions and recommendations, with suggestions of further studies.

1.1. Background

Environmental impact of the landfill

This study was requested by Nexans IKO Sweden AB, situated in Grimsås, Tranemo, Sweden. The company is producing PVC-coated cables since 1948. At the territory of the company a landfill is situated used for both, community and company waste. The landfill was used for communal wastes by the municipality during 1948 - 1965. In addition, a nearby petrol station dumped car repair and oil rests. Finally, residues from the cable production were stored from 1948 until 2002 by Nexans. At one location of the landfill, PVC cables were burned and caused contamination of the soil with extreme concentrations of dioxins; 1000 times exceeding the Swedish EPA guideline value.

Nexans IKO Sweden AB has been concerned about the landfill environmental impact since 1999, and started to investigate the landfill environment at 2000. Hydrological studies were conducted first by the consultant company KM, and then continued with a pollution study carried out by EnviroVision HB. The studies gave a survey of the history of the landfill; types of wastes dumped and levels of pollution (Hargelius, 2002). These investigations showed extreme pollution of landfill soil and groundwater by heavy metals and organic compounds. The landfill is classified as a high-risk waste area and requires urgent remediation to protect surrounding groundwater from pollution.

A summary of the contamination of the landfill groundwater is partly presented in Table 1 and 2.
Table 1. Heavy metals concentrations in the landfill groundwater (from Hargelius, 2002).

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. conc. (µg/l)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Well point 202 (µg/l)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extremely serious* (µg/l)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Very serious*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Criteria for classification of the conditions for the groundwater, Swedish EPA report 5053.

Table 2. Organic pollutants concentrations in the landfill groundwater and soil (from Hargelius, 2002).

<table>
<thead>
<tr>
<th></th>
<th>Aromatic &gt;C8-C10 (µg/l)</th>
<th>Carcinogenic PAH (µg/l)</th>
<th>Oil (mg/kg of dry soil)</th>
<th>Dioxins (mg/kg of dry soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well point 202 and 216</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extremely Serious* (µg/l)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Criteria for classification of the conditions for the groundwater and soil, Swedish EPA report 5053.

Several objectives were proposed to protect nearby areas from groundwater contamination:

- Cover the landfill with an impermeable material.
- Collection of leachate and treatment ex-situ or in-situ in a filter bed
- Natural or rest-product material to be used as filter materials, to achieve a sustainable management and to reduce the costs.

These ideas initiated a master’s thesis project that was carried out in spring 2003 (Chauvet, 2003).

**Batch tests of adsorbents**

In order to find suitable adsorbents for the filter-bed, six adsorbent materials were studied (Chauvet, 2003). The adsorbents were chosen based on a literature study and should be effective, cheap, easy available and environmentally friendly. Saw dust, bark, peat moss, shrimps shells, seaweed and fiber ash were used in batch experiments. Only adsorption of metals was evaluated, but a study of organic contaminants sorption was initiated.

The results showed best sorption capacities for fiber ash and peat moss. Fiber ash was sorbing Cd, Co, Cu, Fe, Mg, Mn, Zn and Pb, and all these metals were removed by more then 80%. Peat moss sorbed Cu and Zn by more then 90%, but Cd was removed only by 40%. Several other findings were done, and the fiber ash was noticed to be leaching Al, Ba and Cr. Many of the metals were precipitated in the fiber ash solution as a result of the high pH at 12. Therefore, a possible use of the fiber ash as a precipitant and adsorbent in a contact tank was recommended.
1.2. Aims and objectives

The objective with this project was to carry out column experiments with different adsorbents in order to find the adsorbent material or mixture of materials, which satisfies the following requirements:

- Adsorb both metals and organic contaminants with a high capacity.
- Long service time.
- Easy to handle and cheap.
- Sustainable in a lifecycle perspective.

As evaluation of adsorbent performance, for both metals and organic contaminants require long time, this project was divided in two parts. In this report the study of heavy metal adsorption is described. The experiments and results for adsorption of organic pollutants are described in another report (Potrebko, 2004).

2. Sorption theory

In the first part of this section interaction of metals and soil solutions is discussed, where soil solution is a medium of soil and its pores water. All the mechanisms of such interaction are valid for adsorbent solution (Christensen, 2002). Precipitation, adsorption and solid formation are discussed. As this study focuses on adsorption of metals, factors influencing metal adsorption are described.

2.1. Behavior of metals in soil solution

Metals exist in soil solutions as free metal ions, in soluble complexes with inorganic and organic ligands or associated with inorganic or organic colloidal material (Shuman, 1991). Common inorganic ligands in soil are anions as SO$_4^{2-}$, Cl$^-$, OH$,\text{PO}_4^{3-}$, NO$_3^-$ and CO$_3^{2-}$. Organic ligands include low molecular weight aliphatic, aromatic, amino acids and soluble constituents of fulvic acids. Colloidal particles include iron and manganese oxides, clay minerals and organic matter.

There are several processes, which govern metal retention in soil. Among them are precipitation, inclusion, adsorption, solid formation which are distinguished by the type of association between metal and host mineral (Sposito, 1989). Metal can precipitate as pure solid: CdCO$_3$, Pb(OH)$_2$, ZnS$_2$, or co-precipitate producing mixed solids, e.g. (Fe$_x$Cr$_{1-x}$) (OH)$_3$. Solid formation occurs when metals are compatible with the host elements and can replace them throughout the mineral, e.g. substitution of Cd for Ca in calcium carbonate. Adsorption is defined as the accumulation of ions at the interface between a solid phase and an aqueous phase. Metals in soil can adsorb onto organic matter, clay minerals, iron and manganese oxides and hydroxides, carbonates and amorphous aluminosilicates. The organic matter consists of biochemicals and humic substances. They provide acid functional groups: carboxylic, phenolic, alcoholic and amino groups as adsorption sites.
Adsorption is related to three properties of the soil solution: permanent negative charge, pH-dependent charge of the surface, and adsorption of hydrophobic compounds. Permanent negative charge is usual for clay minerals and weakly soluble salt arising from “broken bonds” on the crystal surface and isomorphic substitutions. For example, Al\(^{3+}\) can substitute for Si\(^{4+}\) in a silica oxide, the ions Mg\(^{2+}\) and Fe\(^{2+}\) can substitute for Al\(^{3+}\) in aluminosilicate clays, resulting in permanent negative charge. pH-dependent charged surfaces are associated with the edges of clay minerals, surfaces of oxides, hydroxides and carbonates, and with organic matter. The charge arises from the association and dissociation of protons from surface functional groups. Due to dissociation at higher pH-values the negative charge arise, as for example -Fe-OH\(^0\) to –Fe-O\(^-\). At low pH values functional groups accept a proton, resulting in neutral or positive charged ions as -Fe-OH\(^0\) to –Fe-OH\(^2+\). For all pH-dependent surfaces as the pH decreases, the number of negatively charged sites also decreases. Under more alkaline conditions the majority of sites will be negatively charged. Adsorption of hydrophobic compounds is thought to be relevant for fulvic and humic acids. Their hydrophobic groups can bind to a particle surface while hydrophilic groups can serve as an adsorption sites.

A surface complexation model is often used to describe adsorption behavior and is presented in Figure 1. Several types of bonding can be involved between the surface and the metal ion. Metals in diffuse ion association or in outer sphere complex are surrounded by coordination water and are not directly bonded to the surface. These types of bonds represent “non-specific” sorption when bonding is general and is related to the electrostatic strength; the coulombic attraction due to the difference in charge, or to the polarization strength; the attraction between dipoles. These reactions are rapid and reversible with only a weak dependence on the electron configuration of the surface group and the adsorbed ion. They are also called exchange reactions as the introduction of other cations into the system in sufficient concentration, causes the replacement of the former cations. Thus exchangeable metals can be a significant reserve of the potentially mobile metals in the soil. With inner sphere complexation, the metal is bound directly to the surface, having ionic and/or covalent character of the binding that depends on the electron configuration of both the surface group and the metal. This type of adsorption is called specific adsorption. As energy of adsorption for cations is different they do not effectively compete for specific surface
sites. Thus specifically adsorbed metals are relatively immobile and unaffected by high concentrations of other cations due to large differences in their energies of adsorption. At low concentration metals are adsorbed by the specific adsorption sites. With increasing concentration of the metal, the specific sites become saturated and the exchange sites are filled.

2.2. Factors effecting adsorption in soil

Adsorption of metal cations is proven to be correlated with such properties of the matrix as pH, redox potential, clay, organic matter, Fe and Mn oxides, and calcium carbonate content (Sposito, 1989).

**pH**

Several studies of adsorption of metals by soils showed that the heavier textured soils with higher pHs were effective in retention of metals, while sandy soils and/or soils with low pH did not retain the metals effectively (Korte et al. 1976). Several studies also showed that cationic metals adsorption increases with pH (Harter, 1983; McBride, 1979). However, the retention of metals do not significantly increase until the pH is greater then 7. This effect is partly due to preferential adsorption of the hydrolyzed metal in comparison to the free metal ion. It was also shown that the proportion of hydrolyzed metals increases with pH. For example, hydrolysis of Cu occurs at pH 6, Cd at pH 8, Zn at pH 5.5. The other effect of pH is on adsorption sites which are pH dependent. As the pH diminishes, the number of negative sites decreases. Moreover, as the pH becomes more acidic, metal cations have to compete for available negatively charged sites with Al$^{3+}$ and H$^+$. Precipitation of metals is also strongly dependent on pH. All trace metals hydroxides, oxides, carbonates and phosphates precipitate only under alkaline conditions. The dissolution of these metals also depends on pH. Hydroxides of Fe and Mn, in particular, play an important role in the retention of metals in soil. Thus, solubility of these hydroxides, which is pH-dependent, is essential for metals speciation. Below pH 6, the hydroxides of Fe and Mn dissolve, releasing adsorbed metals into solution. Complexation of metals with organic ligands is also influenced by pH and affects the adsorption (see section Complex formation below). For example, concentration of Zn and Cu in solution is decreasing with higher pH but increase after pH 7.5, which is attributed to the solubilization of organic complexing ligands, which effectively compete with the soil surfaces for the metal cations (Sposito, 1989).

**Redox potential**

The redox potential of the system is the measure of the electrochemical potential or availability of electrons within a system (Sposito, 1989). A chemical reaction in which electron transfer takes place is called a reduction-oxidation process. Metals, which gain electrons and lose in valence, are called being reduced, while those losing electrons and gaining in valence are oxidized. As many of the metals have more, then one oxidation state they are directly effected by changes in redox potential of the matrix. Reduced conditions are observed in absence of oxygen (anaerobic) and oxidized - in presence of oxygen (aerobic). The redox potential is usually closely related to the microbial activity. Redox reactions can greatly affect contaminant transport, in slightly acidic to alkaline conditions. For example Fe(III) precipitates as a highly adsorbtive solid (ferric hydroxide), while Fe(II) is very soluble and does not
retain other metals. Thus, reduction of Fe(III) to Fe(II) will cause release of iron, and any metals which were adsorbed onto ferric hydroxide surface. In general, oxidizing conditions favor retention of metals, while reducing conditions accelerate migration.

**Competing cations**

For specific adsorption sites, trace cationic metals are preferentially adsorbed over the major cations (Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\)) and trace anionic metals over major anions (SO\(_4^{2-}\), NO\(_3^-\)). However, when the specific adsorption sites became saturated, exchange reactions dominate and competition for these sites with major ions becomes important. For example, Cu, Cd, Pb and Ni compete with Ca (Cavallaro and McBride, 1978; Harter, 1992). Moreover, trace metals also compete with each other for adsorption sites. For example, copper is showed to be interfering with the adsorption of Zn and Cd (Kuo and Baker, 1980).

**Complex formation**

Metal cations form complexes with inorganic and organic ligands. The resulting complexes has a lower positive charge than the free metal ion, and maybe uncharged or carry negative charge. This decrease in positive charge of the complexed metal reduces adsorption to a negatively charged surface. The exception is the preferential adsorption of hydrolyzed metals (MeOH\(^+\)) versus the free bivalent metal (James and Healy, 1972). For example, the presence of Cl\(^-\) and SO\(_4^{2-}\) inhibit adsorption of Cd and Ni, Cu, Zn to form complexes with Cl that decrease their adsorption (Hirsh et al., 1989). In addition, high levels of phosphate inhibit adsorption of Cu and Zn. Phosphate do not form strong complexes with these metals, but will actively adsorb to soil surfaces thus blocking the specific adsorption sites for Cu and Zn. On the other hand, low concentrations of phosphate enhance adsorption of Zn and Cd on oxide surfaces. The adsorption of phosphate onto oxide surfaces increases their negative charge, thus enhancing adsorption of the metal cations (Kuo and McNeal, 1984).

### 3. Natural and residual product adsorbent materials

#### 3.1. Literature review

In this section a short review of the literature concerning adsorption of metals on peat moss, ashes and bark is presented. Only the most recent studies are referred to.

Interest in the so-called “low cost” adsorbents started 1980 and a number of research projects was carried out; most of them concerning peat moss. Generally, adsorbent can be assumed as “low cost” if it requires little or no processing, is abundant in nature, or is a by-product or waste material from another industry (Bailey, 1999). At present, use of such adsorbents is recognized as a sustainable in long-run perspective management. Several reviews about low-cost adsorbents can be recommended (Brown, 2000; Bailey, 1999; Couillard 1994; Horacek, 1994).

**Peat moss**

Peat moss is the most investigated natural adsorbent, but many applications remain controversial and it is difficult to use the reported results because different conditions were used in the tests, which makes obtained data specific. The most investigated
subject is dealing with kinetics of adsorption and equilibrium studies of peat moss (Ringqvist, 2002; Ho and McKay, 1999; Allen et al., 1997; Fattahpour 1996, Ho et al., 1995). Most of the studies are conducted in batch experiment with single-component solution, and effects of changes in pH and concentration is investigated. The number of column studies conducted (Ko et al., 2003; Twardowska et al., 1999; Sharma and Forster, 1995) and only a few have been used multicomponent solution or real polluted water (Zhou et al., 2003; Ho et al., 1995). The results obtained could not be generalized as it was shown that adsorption depends heavily on peat origin, degree of decomposition, particle size, metal concentration, ligand concentration and competing ions. Several authors investigated adsorption characteristics of different types of peat, considering its botanical origin and degree of degradation (Ringqvist and Öborn, 2002, Fattahpour, 1996). The mechanism by which metal ions are sorbed onto peat is not clear and only a few investigations pursued (Gardea-Torresday et al., 1996; Crist et al., 1996; Sharma and Forster, 1993). An attempt of modeling of the sorption of metal ion onto peat has been carried out (Chen et al., 2001). Different physical and chemical methods were developed in order to enhance sorption of metals by peat (Morine et al., 1991).

**Fiber ash**

There are no studies available about sorption of metals onto fiber ash, but a number of studies was done with fly ashes, which are similar in chemical composition to fiber ash (see Table 3). Fly ashes are mostly used as construction material and their recognition as possible adsorption material began recently. A limited number of studies is available, in many of them sorption properties of different types of ashes are compared, as fly ashes vary substantially in composition (Bayat, 2002; Rio et al., 2002; Chien-Jung Lin and Juu-En Chang, 2001; Ricou-Hoeffer et al., 1999; Ayala et al., 1998). Most of the papers contains results of batch experiments for various contact times, pH, metal concentrations, metal/adsorbent mass ratio (Ricou-Hoeffer et al., 1999; Apak et al., 1998; Viraraghavan and Dronamaraju, 1993). Results for removal of copper, nickel, and zinc have been reported by several authors (Bayat, 2002; Viraraghavan and Dronamaraju, 1993). Adsorption of cadmium and lead has been investigated (Ricou-Hoeffer et al., 1999; Apak et al., 1998). Dynamic column experiments have been conducted and saturation capacities of adsorbents determined (Apak et al., 1998; Diamadopoulos et al., 1993). Fly ash was used in a case study at a wastewater treatment plan for reducing metals concentration (Gupta and Torres, 1998). The mechanism of the adsorption of metals onto fly ashes was not deeply investigated (see section Adsorption on fiber ash). Methods for production of zeolites from fly ash have been developed and zeolites adsorption properties investigated (Queraol et al., 1997; Lin et al., 1996).

**Bark**

Bark is widely used as adsorbent material for organic pollutants, and since 1980 investigated as a possible adsorbent for heavy metals. Studies covered all the heavy metals of concern and bark from different sorts of trees. Most of the papers describe batch experiments with one-metal solutions and changes in pH conditions. Pine bark is one of the most investigated materials and showed good adsorption properties for lead, copper, cadmium and nickel (Al-Ashen et al., 2000; Al-Ashen and Duvnjak, 1997; Vazques et al., 1994). Comparison of sorption properties of several coniferous barks has been done (Martin-Dupont et al., 2002; Seki et al., 1997). Eucaliptus and yohimbe bark were also showed to be efficient in adsorption of metal ions (Saliba et
al., 2002 and Villaescusa et al., 2000). Several studies were carried out with chemically pretreated pine bark, a few of these studies showed decreasing sorption capacity of pre-treated bark compared to crude bark (Palma et al., 2003; Montes et al., 2003, Gloaguen et al., 1997).

3.2. Mechanisms of adsorption

Adsorption on peat moss

Peat is formed due to incomplete degradation of organic matter. The quality of the peat formed depends on the degree of decomposition and the type of peat-forming plants. Both these factors showed to be influencing adsorption capacity of the peat (Fattanpour, 1996). Main constituents of the Sphagnum peat moss, which is used in this work, are humin (up to 85%), humic and fulvic acids (15%) (Gardea-Torresdey, 1996). They are called humic substances and are shown to be heterogeneous consisting of numerous oxygen-containing groups, including carboxyl, phenol, hydroxyl and carbonyl structures of various types. Humic substances are decomposed organic matter with destroyed cell walls and other tissues, and the functional groups are exposed to the surface of biomass. This is believed to account for the rapid adsorption of metals by peat. It was shown that adsorption of metal ions onto peat is due to both complexation and ion exchange (Chen et al., 1990). But when the solution concentration is high, complexation becomes about ten times as important as ion exchange. The main mechanism of complexation might be as follows (Dupuy, 2001):

$$\text{OH} \quad \text{OH} \quad + \quad M^{2+} \quad \leftrightarrow \quad \text{OH} \quad \text{OH} \quad \text{M} \quad + \quad 2H^+$$  \hspace{1cm} (1)

$$\text{O} \quad \text{O} \quad + \quad M^{2+} \quad \leftrightarrow \quad \text{C} \quad \text{C} \quad \text{M} \quad + \quad 2H^+$$  \hspace{1cm} (2)

$$\text{OH} \quad \text{OH} \quad \text{C} \quad \text{C} \quad + \quad M^{2+} \quad \leftrightarrow \quad \text{OH} \quad \text{OH} \quad \text{M} \quad + \quad 2H^+$$  \hspace{1cm} (3)

The amount of adsorption sites on the peat surface is pH dependent due to dissociation of hydrogen ions from carboxylic and phenolic groups. The isoelectric point of peat lies in the pH interval 2.5 - 3.0 (Ringquist et al., 2002). Below this point the surface is positively charged, and above negatively charged. The uronic acid content in the peat is another of the variables positively correlated to a high surface charge (Ringquist et al., 2002).
Table 3. Main components in fiber and fly ashes.

<table>
<thead>
<tr>
<th></th>
<th>Fiber ashes</th>
<th>Fly ashes*</th>
</tr>
</thead>
<tbody>
<tr>
<td>% TS</td>
<td>% TS</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>28.9</td>
<td>44.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>20.7</td>
<td>22.0</td>
</tr>
<tr>
<td>CaO</td>
<td>43.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>

*(Rio et al., 2002)

Adsorption on fiber ash

Several authors examined the suitability of fly ash as an adsorbent for heavy metal ions from aqueous solution (Bayat, 2002; Chien-Jung Lin and Juu-En Chang, 2001; Ayala et al., 1998, Ricou-Hoeffler et al., 1999). As fiber ash has the same composition as many of the fly ashes, it can be assumed that the same processes of adsorption occur. A comparison of fly ash and fiber ash composition is presented in Table 3. The fiber ash contains more CaO than most of the fly ashes. However, it was shown that fly ashes with a higher CaO content (44%) has better adsorption capacity, and the possible mechanism explaining this phenomena is presented in formulas 5 and 6 (Bayat, 2002; Mavros at al., 1993). Therefore, fiber ash can even be a better adsorbent than fly ash.

It was concluded, that metal ions might adsorb on ash because of its high content of silica and alumina. On the surface of the ash the functional oxidized groups are present as SiO$_2$, Al$_2$O$_3$. The surface of silica has a high affinity towards metal ions (Bayat, 2002). The central ion of silicates (Si$^{4+}$) has a very strong affinity for electrons. Therefore, the oxygen atoms that are bound to the silicon ions have a low basicity, making the silica surface acting as a weak acid. The oxygen atoms react with water, forming surface silanol (SiOH) groups. The acidity of these groups determines the dependence of the charge of silica surface on pH. At low pH, a positively charged silica surface prevails, and at high pH negatively charged surface dominates. Alumina and iron also show the same phenomenon of developing positive or negative charges depending on pH. In accordance with this theory, maximum adsorption of metals was observed at pH range 6-8, which can be contributed to the electrostatic interaction of the adsorbate with surface silica, aluminum and iron sites. Aminosilicates in ashes may also be involved in adsorption of metal ions through a SiO bond, as showed below (Ricou-Heffer et al., 1999):

In acid solutions

$$Si-OH…H-O-H[Me(OH)_{2}]^{2+} \leftrightarrow Si-OMe + H_2O^+$$  \hspace{1cm} (4)

The higher efficiency of ashes with high CaO content is thought to be due to the formation of Ca and Si complexes such as calcium silicates ($2\text{CaO*SiO}_2$).

In neutral solutions

$$m\text{CaSiO}_3\text{HSiO}_3^- + \text{MeOH}^+ \leftrightarrow m\text{CaSiO}_3\text{MeSiO}_3 + H_2O$$ \hspace{1cm} (5)

In alkaline conditions

$$m\text{CaSiO}_3\text{HSiO}_3^- + \text{Me(OH)}_2 \leftrightarrow m\text{CaSiO}_3\text{MeSiO}_3 + H_2O + OH^-$$ \hspace{1cm} (6)
Adsorption on pine bark

Sorption capacity of bark is attributed to its high tannins content. Tannins are a group of water-soluble phenolic compounds having molecular weigh between 500 and 300 giving usual phenolic reactions, and having special properties such as ability to precipitate alkaloids, gelatin and other proteins (Bate-Smith, 1962). Molecular weights as high as 20 000 have been reported (Haslam, 1998). Approximate empirical formula of tannic acid, or gallotannic acid which is most often referred as “tannin” is C_{76}H_{52}O_{46}. The chemical structure of one tannin is presented in Figure 2.

![Chemical structure of a tannin compound.](image)

The polyhydroxy polyphenol groups of tannins are thought to be the active species in the metal sorption process (Vazquez et al., 1994). Ion exchange takes place as metal cations displace phenolic hydroxyl groups, forming a chelate. This reaction is similar to reaction (1), presented above in section Adsorption on peat moss.

4. Experimental section

4.1. Sorption studies

Sorption studies can be done in order to evaluate the capability of adsorbents to retain metals. They can be used to generate adsorption coefficients or used for comparison of different adsorbents. The adsorption coefficient can be defined as the amount of sorbate (metal) adsorbed per unit weight of sorbent used. In a sorption study, the adsorbent interacts with metals in solutions, using batch or column techniques. The schematic view of batch and column experiments is presented in Figure 3. In batch technique, the adsorbent and the metal solution are placed into a vessel and mixed for a prescribed time period. The adsorbent and the solution are then separated by centrifugation or filtration and analyzed. This technique is the most widely used as it is ease in operation and data handling. However, it has several disadvantages. Results are sensitive to the adsorbent/solution ratio used, real adsorbent/solution ratio can not be used in batch experiment, scaling of results to real systems is uncertain, results are sensitive to the mixing rate, separation techniques can effect results and the coefficients generated are often not adequate to the behavior of metals in flow-through systems. Nevertheless, batch experiment is applicable as a first step of sorption studies and should then be followed by column experiments.
The column technique consists of packing column with adsorbent and pumping through solutions of metals. The effluents are collected and analyzed. In addition to adsorption coefficient, the breakthrough and number of bed volumes are normally used in the description of results. Breakthrough occurs when the effluent concentration equals the influent concentration. The number of bed volumes is defined as volume of treated solution divided by volume of adsorbent. In this work volume of treated solution, and mass of metal passed through column will be used for description of results. The advantages of the column technique are: real adsorbent/solution ratios can be used, separation of the adsorbent and effluent is not required, and column studies more closely simulate field conditions. The disadvantages are: results depend on flow rate used, columns are difficult to set-up and maintain and uniform packing of column is difficult and channeling often occur.

4.2. Selection of methodology

In this study peat moss, bark and fiber ash were selected as adsorbents. As the aim of this study is to determine the best adsorbent for the construction of the filter-bed in soil, the column technique has been chosen to simulate field conditions. Up flow was used to assure even distribution of water throughout adsorbent bed. Columns have been operated both with real leachates and with artificial solutions, which had the same ratios of metals as real leachate, but ten times higher concentrations.

4.3. Pre-study of column technique

First set of experiments was conducted in laboratory. It contained dynamic and adsorbent packing technique studies. Adsorbents checked were peat moss, fiber ash and bark.

*Column with fiber ash*

The fiber ash used in the study was the same as used in the previous batch experiment (Chauvet, 2003) showing promising results for adsorption of metals. Fiber ash was shown to be highly impermeable, which can be contributed to the high content of CaO...
(44 %) that gives a plastic features (Envipro Miljöteknik AB, 2001). Dynamic experiments are difficult to conduct as fiber ash becomes concrete in contact with water. Several experiments with mixtures of fiber ash and different size of sand were carried out in order to find a permeable bed for column experiment. The mixtures of fiber ash and sand, coarser than ash itself, were quickly separated by the water flow into an ash and a sand layers. The flowing water washed out more fine ash from the sand, and the sand appeared on the bottom of the column and a layer of ash on the top. Mixtures of fiber ash and sand of the same size can be homogeneous for several days. Different proportions of sand and ash were used: 30/70, 40/60, 50/50. The mixture of 50/50 worked for 4 days but than became impermeable. Increase in sand content seems not to be a solution, as the content of adsorbent is not high enough for effective adsorption. Thus, the adsorbent will be quickly used and have to be replaced often. In this case, problems with recycling of large quantities of contaminated sand will occur. Moreover, a time consuming and expensive preparation of adsorbent is needed; sieving of sand and mixing with ash.

Considering the physical properties of the fiber ash, adsorption studies with pure fiber ash in column were not done. Instead, a small fraction of fiber ash (10% by weight) was added to one of the peat moss columns. Then data from the pure peat moss column was compared with data from the mixture to see the effect of sorption by fiber ash.

**Column with mixture of peat and ash**
Fiber ash seems to be a good complementary material to peat moss for adsorption of heavy metals. From one side, fiber ash adsorbs in high degree Zn, Cd and Fe for which peat moss was shown to be less effective (Chauvet, 2003). In addition, peat moss solutions have a low pH of 4, which hinder adsorption of metals. On the other hand, fiber ash has a high pH of 12.6. These materials can then be mixed, to achieve preferable pH.

Different mixtures of peat and fiber ash were investigated in order to find the best solution for dynamic experiments. The pH was monitored to achieve the best pH of 7, for adsorption of metals. The parts of the mixtures were taken by weight. The final mixture was made from dried and ground peat moss with 10% of fiber ash added. The pH of the mixture was 7.

**Columns with peat moss**
Two types of peat moss, collected from the Grimsås area, were investigated in the dynamic experiments: fresh peat moss and dried and ground peat moss. Dried and ground peat moss has a granulated structure that makes good conditions for water flow. In contrary, fresh peat moss is difficult to investigate in columns. It showed a great adsorption of water and was expanding constantly, at least for a week. Expanding lower layer of peat moss was pushing upper layers, while they did not receive any water. As a result, the column bed was divided in two distinctive areas: a muddy saturated lower part and a dry upper layer. Some of the peat moss was taken out to ensure that the saturated part remained, and made water flow through the column possible, but water velocity could not be more than 0.7 ml/min. Another cause of hindered flow through the column could be the character of effluent. It became very humic and has a colloidal structure, which makes it difficult to percolate and filtrate through the layer of sand. On the other hand, if taking away the sand layer, a
big part of the adsorbent will escape with effluent and will cause difficulties to analyse samples.

As a result, two columns with peat moss were packed for the adsorption study: dried and ground peat moss and fresh peat moss. This allows a comparison of adsorption on differently prepared adsorbent.

**Column with bark**
The bark used in the experiments was a pine bark produced for adsorption of oil spills (Ecobark, Sydkraft Värme Syd AB, Värnamo, Sweden). This bark contains 90% of pine bark and 10% of wood fibre. It was additionally ground before use in the column experiments. Packed in the column, bark showed good kinetic characteristics.

### 4.4. Field experiment

As results of the study will be used for the pilot filter-bed construction, real leachate was chosen for the column experiments to assure true results. In order to avoid leachate changes during transportation and preservation, field column experiment was done. Four large columns were packed in field, and installed in a barak on the landfill. Adsorbents used were: row peat moss, dried and ground peat moss, mixture of fiber ash (10%) and dried and ground peat moss (90%) and bark. Design of the column tests is presented in Table 6, Appendix.

To assure constant concentration of the metals entering the columns, 3 000 liters of leachate were pumped from a groundwater well to the sedimentation tank. All experiments were supplied with this water. This pre-treatment of water caused unexpected result in reducing concentrations of all metals by a factor of 10. As a result, the columns were loaded with water that was ten times cleaner then fresh leachates. This caused substantial prolongation of the experiment, as breakthrough of the metals occurred much later then expected. On the other hand, this event suggested sedimentation as a pre-treatment technique, where large quantities of pollutants can be concentrated in the sediment and removed. Such pretreatment will also extend the service time of the adsorbent, as pollutants load will be lower.

Columns were working for one month in the field, and then moved to the laboratory as the weather became cold and leachate began to freeze in the tank. The leachate from the tank was then transported to the laboratory. Columns were run one more month at the laboratory.

### 4.5. Laboratory experiment

Along with the four large-scale columns, which were loaded with real leachate, smaller column with fresh peat moss and two columns with a mixture of ground peat moss and 10% of fiber ash were packed for the study with artificial solution of metals. The purposes of this experiment were to check influence of 10 times higher concentration on sorption, observe effects of competition between heavy metals and other compounds in leachate compared to artificial solution, assess influence of high iron content on sorption of other metals. All the columns were run with artificial solution which contained the same ratios of metals as in the leachate, but 10 times higher concentrations (Table 7, Appendix). Two equal columns with a mixture of peat
moss and ash were run with different solutions. One of the solutions contained iron and the other was iron-free.

**Columns parameters**
The flow rate was chosen to be the same, 2 ml/min, in all the columns except row peat column in order to assure the same conditions. Row peat could not support flow rate higher, then 1 ml/min. Still flow conditions can be assumed to be insignificant different in all columns. Upward flow was used in order to minimize channelling and assure even distribution of metals solution throughout the adsorbent. Design of the column tests is presented in Table 6, Appendix. Columns were run until breakthrough of several metals and partial breakthrough of others. The time scale of this experimental work was 3 month and did not allow time enough for breakthrough of all the metals. Moreover, as the results of this study are going to be used in a field filter-bed, precise data on those metals, which experience breakthrough first is most important. Once the filter-bed is saturated with one heavy metal and starts to leach, replacement of the adsorbent is needed. Thus critical metals, which will leach first, could be indicated by the column test.

**4.6. Chemical analysis**

Samples of influent and effluent were taken in 12 ml plastic sample tubes. Each was separated into 2 samples: one with total concentration of metals, dissolved and particulate fractions, and another with only dissolved fraction, filtrated through 0,45 µm cellulose acetate filter. Samples were preserved by 1% of concentrated, suprapure HNO₃ and stored in refrigerator (4°C) 1-2 weeks before analysis. Samples were microwave digested with 20% by volume concentrated, suprapure HNO₃ for 2 hours at 150°C. Then they were diluted 10 times and metals concentration was measured by inductive plasma source mass spectrometer (ICP-MS). In the ICP-MS the sample enters the plasma and get ionized. The ions are directed under vacuum to a mass spectrometer and sorted into the mass-to-charge ratio. Finally the ions are detected by an electron multiplier (Fisher and Adbon, 1997). The detection limit of the method is 0.1 ng ml⁻¹. Concentration of 7 metals was measured; Fe, Al, Ni, Cu, Zn, Cd, and Pb. The internal standard used was a 1 ppm Rhodium solution, as this metal is not naturally found in water. Two blank samples were run to zero the instrument. For all the measured metals, standard solutions were run for calibration (multi element standard Merck XI CertiPUR). Concentrations of the standard solutions are presented in Table 7 in Appendix.

**5. Results and discussion**

In this section results and discussion of the experimental work will be presented. As the aim of the project was to find adsorbents for industrial use, both sorption rates and adsorbents service time will be discussed.

In these column experiments adsorption, precipitation, complexation and other removal processes were not distinguished. Thus the term “sorption”, which shows the total removal of the metals by different processes in column will be used.

**5.1. Breakthrough curves**
First estimation of the adsorbents behaviour can be done by a visual comparison of the breakthrough curves. The mass of adsorbents used, their humidity and packing density (see Table 6) are approximately equal, and the same solution was used why the same conditions can be assumed.

The form of the breakthrough curves allows deriving such information as: time needed to reach maximum adsorption, materials service time, the time it can be used before replacement, and character of the breakthrough, rapid or smooth. It can be noticed that all materials adsorbed different metals with similar patterns (Figures 3-5). This feature is natural for ground peat and the mixture of ground peat and ash as they have almost the same material, except for 10% of ash. However, even peat and bark columns show similar patterns for most of the metals, which can imply similar mechanisms of adsorption.

The breakthrough curve of a metal can give important information for selection of adsorbent and an estimation of its service time. For the treatment of industrial leachate with many components, the pollutant that is the most toxic or for which breakthrough occurs first can be used as a criteria pollutant. Breakthrough of this pollutant will indicate the time of necessary replacement of the adsorbent. For example, as cadmium breakthrough occurs first (Figures 1-3) and it is one of the most toxic metals, cadmium can be chosen as an indicator metal. For this particular leachate from Nexans, Cd is not exceeding the reference value very much, but Pb concentration is exceeding the reference value by factor 300 (Swedish EPA, 2003). In addition, Pb is second after Cd to breakthrough. Thus Pb is also recommended as a criteria metal.

Depending on the pollutant concentration different strategies of remediation can be chosen. For example, if the pollutant concentration is not exceeding the guideline value very much, then the adsorbent, which adsorbs in lower degree but for longer time can be chosen. For the given leachate from Nexans the order of degree of pollution by metals follows: Pb > Zn > Cu > As > Ni > Cr > Cd > Al, where Pb is exceeding the reference value by the highest factor (Swedish EPA, 2003). Thus it is important to choose adsorbents that will remove the metals effectively enough to comply with guideline value.

For most of the metals of concern Pb, Zn, Cu and Ni, ground peat appeared to be the best adsorbent both in degree of sorption and service time (Figures 4-8). Bark was adsoring copper and cadmium in higher degree, but for shorter time (Figures 4 and 6).The column with a mixture of peat and ash showed similar results as the one with ground peat in degree of adsorption, except for Cd and Ni that were adsorbed less. The column with a mixture of peat and ash had a more rapid breakthrough (Figures 4-5).

Earlier studies showed significant release of Al, Ca and Cr ions from fiber ash during batch experiment (Chauvet, 2003). This can be correlated with the composition of the ashes (Table 3), which consists of high amount of CaO (44%) and Al₂O₃ (20%). Significant concentrations of Ca³⁺ in solution can compete with bivalent metals and could cause a diminished sorption of Cd, Cu, Ni and Pb in the ground peat and fiber ash mixture compared to pure ground peat.
Figure 4. Sorption of metal ions by bark.

Figure 5. Sorption of metal ions by dried and ground peat moss.

Figure 6. Sorption of metal ions by a mixture of peat and ash.
Figure 7. Sorption of $\text{Cd}^{2+}$ on different adsorbent materials.

Figure 8. Sorption of $\text{Ni}^{2+}$ on different adsorbent materials.

Figure 9. Sorption of $\text{Cu}^{2+}$ on different adsorbent materials.
One of the objectives of this study was to investigate the influence of high metal concentrations on adsorbents behaviour. For this purpose artificial solution of metals was prepared with concentrations 10 times higher than those in the original leachate (see Table 7 in Appendix for composition). This experiment also allowed to observe effects of competition between metals of concern and other components in the complex matrix of the real leachate. This became possible as the artificial solution contained only metals contrary to the complex matrix in the real leachate.

A comparison of two columns with a mixture of ground peat and ash, one field column run with leachate and a laboratory run with artificial solution, became possible and can be observed in Figures 9-12. For all compared metals Ni, Pb, Cu and Zn the adsorption rate was significantly higher when artificial solution was used, even though concentration were by one order higher. Service time was also approximately twice as long for Cu, Ni and Zn.
Figure 12. Comparison of Cu$^{2+}$ sorption from real leachate and artificial solution.

Figure 13. Comparison of Ni$^{2+}$ sorption from real leachate and artificial solution.

Figure 14. Comparison of Pb$^{2+}$ sorption from real leachate and artificial solution.
As at least two factors, higher by one order concentrations and limited competition, can cause such a difference in results, precise conclusion cannot be drawn. Generally, one would expect rapid saturation of the adsorbent when extremely high concentrations of metals are used. However, column with artificial solution was adsorbing metals for approximately ten times longer time. Thus, it can be assumed that higher by one order concentrations does not influence significantly adsorption. On the other hand, effects of competition are more obvious as column with the real leachate was adsorbing metals in lower degree and for shorter time. In addition, these results points out that laboratory tests can overestimate adsorbents performance, and further experiments should be more specific and using real leachates.

The other objective checked was the influence of iron on adsorption of other metals (Figures 13-15). It was done by duplicating small peat and ash columns, one was run with artificial solution with iron and another without iron. Presence of iron showed no result on sorption of Cd and Cu, but other metals e.g. Ni, Pb and Zn were sorbed for much more longer time in the absence of iron. This confirms the necessary to use sedimentation as a pre-treatment step for removal of a significant part of the iron from solution.

One of the positive effects of high iron concentration in the leachate can be reducing and immobilizing of Cr(VI) in the solution. The leachate was shown to have high concentrations of chromium (Hargelius, 2002). In general, chromium can be found in two oxidation forms: a trivalent form Cr(III) and a hexavalent form Cr(VI) (Brady, 2002). From the two forms, Cr(IV) is more soluble, mobile, and bio-available under a wide range of pH conditions and is highly toxic to humans. Fe(II) ions can reduce Cr(VI) to less toxic Cr(III) by following reaction:

\[
\text{Cr(VI)} + 3\text{Fe(II)} \rightarrow \text{Cr(III)} + 3\text{Fe(III)} \quad (7)
\]

Moreover, reduced chromium can precipitate as Cr(OH)₃ or co-precipitate in the form of CrₓFeₙ₋ₓ(OH)₃ as shown below (Seaman, 1999):

\[
\chi\text{Cr(III)} + (1-x)\text{Fe(III)} + 3\text{H₂O} \leftrightarrow (\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3(s) + 3\text{H}^+ 
\]
Figure 16. Sorption of metal ions from iron-containing solution by peat and ash mixture.

Figure 17. Sorption of metal ions from iron-free solution by peat and ash mixture.

Figure 18. Sorption of metal ions from artificial solution by row peat.
Table 4. Maximum sorption rates and sorption capacities of adsorbents used in field columns.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Bark</th>
<th>Peat and ash mixture</th>
<th>Ground peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max sorption (%)</td>
<td>Sorption capacity (μg/g)</td>
<td>Max sorption (%)</td>
</tr>
<tr>
<td>Cd</td>
<td>66</td>
<td>0.18</td>
<td>75</td>
</tr>
<tr>
<td>Ni</td>
<td>65</td>
<td>13.17</td>
<td>74</td>
</tr>
<tr>
<td>Pb</td>
<td>87</td>
<td>1.81</td>
<td>86</td>
</tr>
<tr>
<td>Cu</td>
<td>95</td>
<td>56.05</td>
<td>97</td>
</tr>
<tr>
<td>Zn</td>
<td>95</td>
<td>71.17</td>
<td>96</td>
</tr>
</tbody>
</table>

*- no breakthrough was observed, adsorbing at maximum rate

Table 5. Maximum sorption rates and sorption capacities of adsorbents used in laboratory columns.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Peat and ash (without Fe)</th>
<th>Peat and ash (with Fe)</th>
<th>Row peat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max sorption (%)</td>
<td>Sorption capacity (μg/g)</td>
<td>Max sorption (%)</td>
</tr>
<tr>
<td>Cd</td>
<td>100</td>
<td>269.23</td>
<td>100</td>
</tr>
<tr>
<td>Ni</td>
<td>99</td>
<td>*</td>
<td>95</td>
</tr>
<tr>
<td>Pb</td>
<td>99</td>
<td>134.62</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
<td>7307.69</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>100</td>
<td>*</td>
<td>100</td>
</tr>
</tbody>
</table>

*- no breakthrough was observed, adsorbing at maximum rate

5.2. Sorption capacities of different adsorbents

One of the characteristics of an adsorbent is its adsorption capacity. It is defined as maximum amount of pollutant that can be adsorbed by one unit (gram) of adsorbent. In this column experiments adsorption, precipitation, complexation and other removal processes were not distinguished. Thus term “sorption capacity”, which shows total removal of pollutant by different processes in column will be used and is calculated as mass of metal sorbed before 50% breakthrough/dry mass of adsorbent. Sorption capacities calculated for the adsorbents used are presented in Tables 4-5. It should be noticed that values derived are very specific, and only shows the sorption capacity for the conditions used in this study.

Dried and ground peat moss showed the best results for both, maximum sorption rates and sorption capacity for all the metals of concern. The mixture of ground peat moss and fiber ash has lower values, which can be explained by competition for adsorption sites between Ca$^{2+}$ ions released from the fiber ash and heavy metals in the solution. All the results showed compliance with conclusions drawn from the visual comparison of breakthrough curves. This confirms reliability of such a method for comparison.

In the laboratory experiment two equal columns with a mixture of peat moss and ash were run with different solutions. One of the solutions contained iron and another was free from it. This experiment was conducted to estimate influence of iron on sorption of other metals, as the landfill leachate contains high concentrations of iron. The
results showed a much higher sorption capacities for all the metals when the iron-free solution was run. Thus removal of iron by sedimentation seems to be a promising technique to increase sorption of other metals.

Row peat moss showed a lower sorption capacity. In addition, this column was run only for one week because breakthrough of many metals occured during the first week. The other two laboratory columns were run for 3 weeks.

6. Conclusions and recommendations

In this work four different adsorbent materials were investigated for sorption of heavy metals from industrial leachate. Main components of the adsorbents were peat moss, bark and fiber ash.

Different grain sizes of peat moss were used such as row peat moss and dried and ground peat moss. Fiber ash appeared not to be adequate to use in column experiment as it has a very low hydraulic conductivity. As a solution, mixture of ground peat moss and 10% fiber ash was used. Estimation of influence of fiber ash on sorption of metals onto peat moss became possible by comparison of performance of two columns, ground peat with addition of ash and without. The conclusion made is that fiber ash is negatively influencing sorption onto peat moss. Possible mechanism of this inhibiting can be based on competition for adsorption sites of \( \text{Ca}^{2+} \) released from ash with heavy metals ions. As a recommendation fiber ash should not be used in mixture with peat moss as adsorbent. The best results for sorption capacity and sorption rates were showed by dried and ground peat moss, which is recommended for use as material for the filter-bed. Row peat moss showed low sorption capacity. Possibility of pre-treatment of row peat moss before use in the infiltration filter-bed in soil should be investigated.

Columns, run with artificial solution of metals, compared to those with real leachate, showed much higher sorption rates and sorption capacities. The possible cause is competition between the metals for adsorption sites, complex formation and other inhibiting sorption processes in real leachate. These results indicate that laboratory tests can overestimate performance of adsorbent for use in field. Thus, specific studies for leachate should always be conducted.

Sedimentation showed to be a successful pre-treatment method in removing high quantities of metals from solution. Particularly useful is this method in removing iron. As the investigated leachate is very rich on iron, the study was made to assesse the influence on sorption of other metals. Results show much higher sorption capacities for all the metals when iron-free solution was used. Thus removal of iron by sedimentation seems to be a promising technique to increase sorption of other metals.

More studies are needed before the design and construction of the filter-bed. First of all, adsorption of organic pollutants by the same adsorbents should be investigated in order to find the adsorbents, which will remove both types of pollution. In addition, economical profitability and lifecycle assessments on the adsorbent materials should be done. As a final step parameters of the filter-bed in field can be calculated and the filter-bed designed.
7. References


Christensen T. H. (2002) Sorption of heavy metals, lecture notes of the course “Soil and groundwater pollution”, Technical University of Denmark


Envipro Miljötcknik AB (2001) Ask from förbränning av fiberslam


### Appendix

Table 6. Design of column tests.

<table>
<thead>
<tr>
<th></th>
<th>Large-scale columns (landfill leachate)</th>
<th>Small-scale columns (artificial metal solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Row peat moss</td>
<td>Peat moss/ash</td>
</tr>
<tr>
<td>Mass of adsorbent (g)</td>
<td>645</td>
<td>779</td>
</tr>
<tr>
<td>Dry mass of adsorbent (g)</td>
<td>116</td>
<td>235.8</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>82</td>
<td>70</td>
</tr>
<tr>
<td>Height (cm)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Internal diameter (cm)</td>
<td>6.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Volume of adsorbent (ml)</td>
<td>937</td>
<td>937</td>
</tr>
<tr>
<td>Packing density (g/ml)</td>
<td>0.12</td>
<td>0.25</td>
</tr>
<tr>
<td>Average flow (ml/min)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Time of experiment (days)</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>Frequency of sampling</td>
<td>Once a day</td>
<td>Once a day</td>
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</table>

Table 7. Composition of artificial metals solution.

<table>
<thead>
<tr>
<th></th>
<th>Concentration (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>60</td>
</tr>
<tr>
<td>Cr</td>
<td>33</td>
</tr>
<tr>
<td>Cu</td>
<td>2310</td>
</tr>
<tr>
<td>Ni</td>
<td>890</td>
</tr>
<tr>
<td>Pb</td>
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</tr>
<tr>
<td>Zn</td>
<td>6000</td>
</tr>
<tr>
<td>Al</td>
<td>533</td>
</tr>
<tr>
<td>Fe</td>
<td>1200000</td>
</tr>
</tbody>
</table>

Table 8. Concentration of standard solutions for ICP-MS

<table>
<thead>
<tr>
<th>Merck XI CertiPUR (mg/l)</th>
<th>Dilution (µg/l)</th>
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<tr>
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<tr>
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</tr>
<tr>
<td>Cu</td>
<td>847</td>
</tr>
<tr>
<td>Hg</td>
<td>9</td>
</tr>
<tr>
<td>Ni</td>
<td>204</td>
</tr>
<tr>
<td>Pb</td>
<td>902</td>
</tr>
<tr>
<td>Zn</td>
<td>2420</td>
</tr>
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<td>From ICP standards</td>
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</tr>
<tr>
<td>Fe</td>
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