

Assessment of Thermal Treatment of Trace Element Contaminated Soil

Désirée Nordmark

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LICENTIATE THESIS

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of Trace Element Contaminated Soil

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PREFACE

This licentiate thesis work was carried out at the Division of Waste Science and Technology, Department of Civil, Mining and Environmental Engineering at Luleå University of Technology.

In this thesis the effect of thermal treatment on trace element mobility in CCA (chromated copper arsenate) contaminated soil is assessed.

The origin of this work arises from the history of impregnation of wood in Sweden. The purpose of wood impregnation is to protect the wood from bacterial, fungal and insect attack. Due to less strict regulations in the past, the impregnation activities have caused environmental problems at many sites, i.e. the soil is contaminated with both organic and inorganic wood preserving chemicals. The remediation of soil contaminated with both organic and inorganic contaminants is usually carried out in several steps. Thermal treatment is considered to be an efficient method for the destruction of organic contaminants. However, inorganic contaminants cannot be destroyed. Instead, thermal treatment affects the mobility of inorganic contaminants by making them more or less mobile than before treatment. This has to be considered when choosing a thermal treatment technique and deciding about the aftercare and further use of the thermally treated soil.

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SUMMARY

Many contaminated sites in Sweden contain a complex mixture of organic and inorganic contaminants. Wood preservation with creosote, pentachlorophenol and chromated copper arsenate (CCA) in particular has generated a number of such co-contaminated sites. Generally, a stepwise remediation has to be carried out for remediation of these sites with separation and destruction of the organic contaminants and concentration, separation and stabilization of the inorganic contaminants during separate treatment steps. Thermal treatment methods are suitable for the destruction of organic contaminants but can increase the mobility of some inorganic contaminants due to phase transitions in the soil minerals. These changes have to be considered during further handling of the soil. In this work, the effects of thermal treatment on the mobility of CCA and critical factors affecting the mobility were studied. Also, different types of thermal treatment methods suitable for remediation of wood preservatives are discussed.

The study included laboratory tests and a literature study. A CCA-contaminated soil was separated in four particle size fractions and thermally treated at 800 °C. Batch leaching tests showed that the thermal treatment increased the leaching of As and Cr while the leaching of Cu decreased. A chemical sequential extraction test indicated that the enhanced As leaching was probably caused by the reduction of available adsorption sites for trace elements in the soil, due to crystallisation of Fe oxides. The enhanced leaching of Cr could be explained by a minor increase of easily soluble Cr(VI), an increase in pH, and competition for sorption sites with other oxyanions. However, the amount of highly stable Cr species increased during the thermal treatment. The reduced leaching of Cu could be explained by the formation of stable Cu species. The volatility of trace elements is positively correlated to treatment time and temperature. Arsenic is relatively volatile while Cr and Cu are not, although chlorides in the soil enhance Cu volatility. Thermal treatment in a reducing atmosphere enhances the volatility of As. Thermal treatment techniques are divided into extraction/desorption techniques (100-800 °C) and incineration techniques (800-1400 °C). Because of the high energy demand, incineration is most beneficial for smaller quantities of soil. Thermal desorption techniques imply an after treatment of the volatilized organic contaminants: they are combusted in an afterburner, condensed, or collected in a filter. An effective air pollution control (APC) system is necessary in order to control emissions to the air. In rotary dryer/kiln facilities particles < 0.075 mm are transferred to cyclones and bag filters causing pressure drops and problems of particle build-up. For the treatment of trace element contaminated soil this fact could be beneficial, because the highly contaminated fine fraction of the soil can subsequently be handled separately. Although a low temperature is beneficial to control the volatility of trace elements, it is not always the best choice in terms of contaminant leaching, because some trace elements have their leaching maxima after thermal treatment at 200-400 °C. The concentration and mobility of trace elements in the treated soil is controlled by factors such as chemical speciation of the trace elements, interactions between trace elements and soil constituents, and process parameters such as fuel, atmosphere, treatment temperature and time. Stabilizing amendments mixed in the soil before thermal treatment could probably reduce the mobility of trace elements and should be investigated further.

SAMMANFATTNING

Många förorenade områden i Sverige har en komplex föroreningsituation, med en blandning av organiska och oorganiska föroreningar. Impregnering av trä med kreosot, pentaklorfenol samt vattenlösliga krombaserade salter av typen CCA (krom, koppar, arsenik) är ett exempel på en verksamhet som orsakat sådana områden. Denna typ av förorenad jord kräver i regel en efterbehandling i flera steg, där de organiska föroreningarna separeras och destrueras, och de oorganiska föroreningarna koncentreras, separeras och stabiliseras i separata behandlingssteg. Termiska efterbehandlingsmetoder är lämpliga för destruktion av organiska föroreningar men kan öka mobiliteten av oorganiska föroreningar på grund av förändringar i mineralsammansättningen i jorden. Detta måste beaktas vid det fortsatta omhändertagandet av jorden. I det här arbetet har effekten av termisk behandling på mobiliteten av CCA i en förorenad jord undersökts, och de kritiska faktorer som förorsakar förändringarna har identifierats. Även egenskaper i termiska efterbehandlingsmetoder som påverkar det fortsatta omhändertagandet av jorden diskuteras.

Arbetet har utförts genom laboratorieförsök med termisk behandling vid 800°C av en CCA-förorenad jord, uppdelad i fyra partikelstorleksfraktioner, samt genom litteraturstudier. En-stegs lakttest visade att utlakningen av As och Cr ökade efter termisk behandling, medan utlakningen av Cu minskade. Sekventiella extraktionsanalyser visade att den ökade utlakningen av As troligen orsakades av en minskning av sorptionsplatser på grund av en ökad kristallisation av Fe-oxider. Den ökade utlakningen av Cr kan förklaras med en ökning av lättlöslig Cr(VI), en ökning av pH samt genom konkurrens om sorptionsplatser från andra oxyanjoner. Andelen mycket stabila Cr-föreningar ökade dock. Den minskade utlakningen av Cu kan kopplas till en ökad andel stabila Cu-föreningar. Flyktigheten av As, Cr och Cu är positivt korrelerad till temperatur och behandlingstid vid termisk behandling. As har den största flyktigheten följt av Cu och Cr. Kloridhaltiga föroreningar ökar flyktigheten av Cu och en reducerande atmosfär ökar flyktigheten av As. Termiska efterbehandlingsmetoder uppdelas i extraktions-/desorptions- (100-800°C) och förbränningsmetoder (800-1400°C). Förbränning är endast lämpligt för mindre mängder kraftigt förorenad jord på grund av den stora energiförbrukningen. I termiska desorptionsmetoder tas de förångade organiska föroreningarna om hand i en efterbrännkammare, kondenseras eller samlas upp i filter. Ett effektivt avgasreningssystem bör vara kopplat till anläggningen för att kontrollera luftemissioner. I anläggningar som består av en roterande ugn kan partiklar < 0,075 mm förorsaka tryckfall och problem med för stora mängder fint material i cykloner och filter. När jorden innehåller oorganiska föroreningar kan detta vara en fördel genom att den kraftigt förorenade finfraktionen kan separeras och behandlas separat fortsättningsvis. Även om en låg temperatur är att föredra för att kontrollera flyktigheten av As, Cr och Cu är det inte alltid det bästa valet för att begränsa deras utlakning eftersom utlakningen för t.ex. Cu har ett maximum efter termisk behandling vid 200-400°C. Koncentrationen och mobiliteten för CCA i den behandlade jorden bestäms av faktorer som den kemiska specieringen av föroreningen, interaktioner mellan föroreningar och andra jordkomponenter samt processparametrar som bränsle, atmosfär, temperatur och tid. En inblandning av stabiliserande tillsatsmedel i jorden före förbränning skulle kunna minska CCAs mobilitet och bör undersökas vidare.

LIST OF PAPERS

- Paper I Nordmark, D. Treatment techniques for contaminated soil from wood preservation sites – Literature review.
- Paper II Nordmark, D., Kumpiene, J., Lagerkvist, A. (in manuscript). Mobility and fractionation of arsenic, chromium and copper in thermally treated soil.
- Paper III Rönkkö, R., Nordmark, D., Kumpiene, J., Lagerkvist, A. (2007) Metal balance in thermal treatment of CCA-contaminated soils. *Tenth International Symposium on Environmental Issues and Waste Management in Energy and Mineral Production (SWEMP 2007)*, Bangkok, Thailand.

PUBLICATIONS BY THE AUTHOR NOT INCLUDED IN THE THESIS

Nordmark, D., Robinson, R. and Kumpiene, J. (2008) Landfilled organic carbon: is it all organic? *The Fifth Intercontinental Landfill Research Symposium*, Colorado, USA. (abstract and poster)

Kumpiene, J., Nordmark, D. and Robinson, R. (2008) Minskad mängs organiskt avfall på deponi. Effekt på redox-förhållanden, nedbrytning av organiskt material och utlakning av redox-känsliga ämnen. Rapport D2008:01, *Avfall Sverige*, Malmö.

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1 INTRODUCTION

The Swedish definition of a contaminated site is: "a landfill site or area of soil, groundwater or sediment which is so contaminated by a point source that concentrations significantly exceed local or regional background levels" (Swedish EPA, 2002). By 2007 more than 80,000 potentially contaminated sites had been identified in Sweden (Österlund, 2007). Many of these sites have a complex contamination situation, with a mixture of organic and inorganic (trace element) pollutants, so called co-contaminated sites. According to the US-EPA, about 40% of hazardous contaminated sites are co-contaminated (Sandrin and Maier, 2003).

Due to the complex remediation situation, a common way to remediate a co-contaminated site is to excavate and landfill the soil. This is possible as long as the soil fulfils the EU criteria for waste acceptance at landfills (EC, 2003). If the soil does not fulfil the criteria, the remediation options are to treat the soil before landfilling, or use other suitable remediation techniques.

Only a few methods can remediate soil contaminated with both organic and inorganic contaminants simultaneously. Usually, step wise remediation is required. In Paper I three main treatment sequences are identified for remediation of co-contaminated soil (Figure 1). Because inorganic contaminants can not be destroyed, the final treatment step for such species always has to be immobilization.

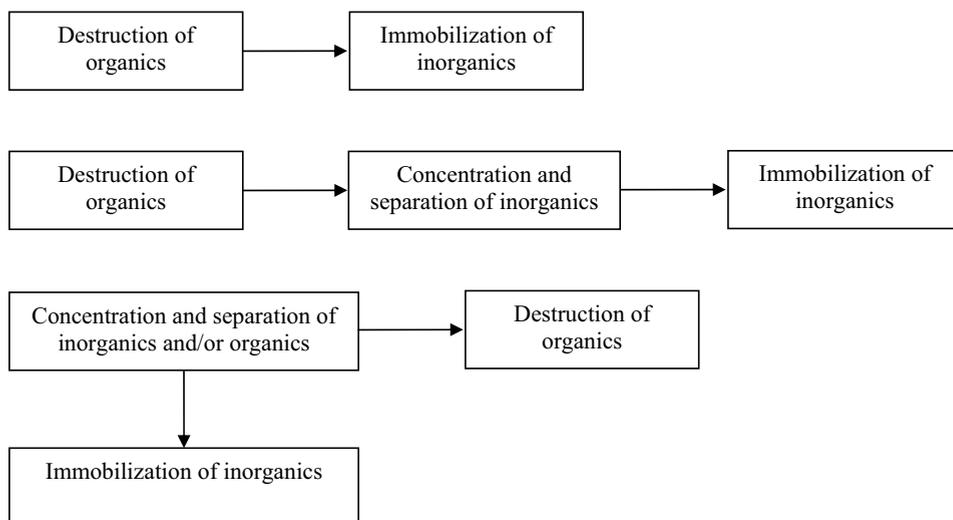


Figure 1 Treatment sequences for co-contaminated soil.

For the remediation of co-contaminated soil, potential interactions between organic and inorganic contaminants have to be considered. For instance, biodegradation (which is a destruction method) of organics can be inhibited by trace elements (Sandrin and Maier,

2003) and organic contaminants can also enhance trace element mobility and decrease trace element retention by the soil (Dube *et al.*, 2004).

Due to less strict regulations in the past, wood preservation activities using creosote, light organic solvent preservatives as PCP (pentachlorophenol) and water soluble preservatives as CCA (chromated copper arsenate) at the same industrial site have caused co-contamination of several sites (Paper I). According to the US-EPA guidelines for remediation of co-contaminated soil from wood preservation sites, the organic contaminants should be treated first using bioremediation, thermal desorption or incineration in the above priority order, while the inorganic contaminants should be treated subsequently with the aid of immobilization techniques (US-EPA, 1995).

Hence, thermal remediation is a recommended and useful technique for treatment of organic contaminants from wood preservation sites. In co-contaminated soil however the inorganic contaminants and their biogeochemical environment are affected by thermal treatment. These changes have to be considered when thermal treatment is used, because it affects the mobility of the inorganic contaminants and consequent decisions concerning the next concentration and/or immobilization step in the treatment sequence.

The questions dealt with in this thesis are:

- What thermal treatment methods are suitable for the remediation of soil contaminated with wood preservatives, and why?
- How does thermal treatment affect the volatility and leaching of As, Cr and Cu, and what are the critical factors affecting the volatility and leaching?

2 MATERIAL AND METHODS

To investigate the thermal treatment effect on the leaching of As, Cr and Cu a laboratory experiment was performed. Materials and methods used in the laboratory experiments are described briefly in the following chapter. Complete descriptions are given in Paper II.

2.1 Soil

The soil used in the laboratory experiments originated from a former wood treatment industrial site situated in Northern Sweden and was contaminated with chromium (Cr), copper (Cu) and arsenic (As) (a so-called CCA contaminated soil) (Table 1). Dried (25 °C) and homogenized soil was separated into four particle size fractions (< 0.125; 0.125-0.250; 0.250-0.500 and 0.500-1.0 mm) through dry sieving.

2.2 Thermal treatment

About 500 g of each fraction was thermally treated in stagnant air at 800 °C for 20 minutes in a Carbolite Furnaces CSF 1200.

Table 1 Principal characteristics of bulk soil < 10 mm (\pm SD, n=3).

Soil properties	Unit	Value
pH	-	6.9
Electrical conductivity (EC)	μ S cm ⁻¹	708
Redox potential (E _h)	mV	457
Total solids (TS)	g kg ⁻¹	994
Loss on ignition (LOI)	wt. %	2.3
Water holding capacity (WHC)	wt. %	26
Total element concentration	mg kg ⁻¹ dw	
As	"	266 \pm 39
Cr	"	123 \pm 30
Cu	"	66 \pm 5

2.3 Evaluation methods

2.3.1 Total element concentrations

Extracts for determination of pseudo-total element concentrations (hereafter called total concentrations) in untreated and thermally treated soil fractions were prepared by digestion of 1 g of soil in 10 mL *aqua regia* (HCl:HNO₃=3:1) using a microwave digester (CEM Microwave Sample Preparation System, Model Mars 5).

2.3.2 Batch leaching test

One step batch leaching tests were performed on untreated and thermally treated soil fractions at a liquid-to-solid ratio of 10 L/kg dry matter (L/S 10) according to EN 12457-2 (CEN, 2002).

2.3.3 Arsenic speciation

Arsenic speciation in soil pore water was determined on the finest (< 0.125 mm) treated and untreated soil fraction. Deionised water was added to the soil to a soil moisture content of 23%. After five days, soil pore water was extracted from the soil using Rhizon soil moisture samplers (Eijkelkamp). Analysis of As(III) and As(V) was carried out using ion chromatography followed by inductively coupled plasma mass spectrometry (IC-ICP-MS).

2.3.4 Sequential extraction

A sequential chemical extraction procedure according to Tessier *et al.* (1979) was performed to operationally define four elemental fractions in both treated and untreated soil. A fifth residual fraction was determined through digestion of the residue from the fourth extraction step in *aqua regia* using a microwave digester (CEM Microwave Sample Preparation System, Model Mars 5). The five fractions were defined as: (I) exchangeable, (II) acid-soluble (associated to carbonates), (III) reducible (associated to Fe and Mn oxides), (IV) oxidizable (associated to OM and sulphides) and (V) residual.

2.3.5 Chemical analyses

The content of total solids (TS) and loss on ignition (LOI) on the untreated soil fractions were determined according to Swedish standard SS 28113 (SIS, 1981) at 110 °C and 550 °C respectively.

The water holding capacity of the soil fraction (< 0.125 mm) before and after thermal treatment was determined gravimetrically as the remaining water in saturated soil after drainage (Shinner *et al.*, 1996).

Electrical conductivity (EC), pH and redox potential (E_h) on treated and untreated soil fractions were determined in soil – deionised water suspensions (1:2 by weight) after 30 min of mixing.

Digestates, leachates and extracts for elemental concentrations were filtered through 0.45 µm syringe filters, acidified with nitric acid (HNO₃) when necessary and analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2000 DV).

Total organic carbon (TOC) of the soil fractions, before and after thermal treatment, was analyzed using a TOC-SSM-500A (Shimadzu Corporation) according to European standard EN 13 137 (CEN, 2001).

Dissolved organic carbon (DOC) in leachates was analyzed using a TOC-VCPH/CPN (Shimadzu Corporation) according to the European standard EN 1484 for water analysis of TOC and DOC (CEN, 1997).

2.3.6 Statistical analysis

Two sample t-tests ($p < 0.05$) were used to determine the statistical differences of means.

3 RESULTS AND DISCUSSION

3.1 Soil chemistry of CCA

The CCA preservative contains As, Cr and Cu primarily as ions including As(V), Cr(VI) and Cu(II). As, Cr and Cu are referred to as “trace elements” in this thesis. When the preservation solution contacts the soil through leaching and spillage during the preservation process, chemical reactions between the trace element species and soil constituents take place. As a result of this, trace elements may occur in the soil as water-soluble, exchangeable, specifically adsorbed, associated with insoluble organic matter, carbonate, oxides of Fe, Al and Mn or layer silicates (Beckett, 1989; Martinez *et al.*, 1999). The mobility of the trace elements is to a large extent governed by sorption/desorption processes in the soil (Alloway, 1995). Amongst the metal oxides, Fe oxides are the most important in controlling sorption/desorption processes of trace elements. The processes are controlled by factors such as pH, E_h (redox potential), OM (organic matter) and microorganism activity. Thermal treatment of a contaminated soil

greatly affects these factors, mainly because of morphological and chemical changes occurring in the soil minerals.

3.2 Thermal treatment of CCA contaminated soil

3.2.1 Effect on mineralogy, porosity and surface area

The clay fraction (< 0.002 mm) in a soil consists mainly of clay minerals, which are hydrous phyllosilicates consisting primarily of Al, Fe and Mg, and of non silicate oxides, hydroxides and oxyhydroxides that are dominated by Al, Fe and Mn oxides, hydroxides and oxyhydroxides (hereafter called oxides). The main thermal reactions of clay minerals, described by Brindley and Lemaitre (1987), can be separated into low (< 400 °C), intermediate (400-750 °C) and high temperature reactions (> 750 °C). During low-temperature reactions, loss of molecular water from between layers and channels occurs. During intermediate-temperature reactions, initiated by delocalization of protons, dehydroxylation occurs and quasi-stable dehydroxylated phases are formed. Fe(II) migrates during the dehydroxylation process and precipitates as magnetite (Fe_3O_4) (anaerobic atmosphere) or hematite ($\alpha\text{-Fe}_2\text{O}_3$) (aerobic atmosphere) (not valid for biotite). At high temperatures, new phases are formed through recrystallisation processes (Brindley and Lemaitre, 1987) leading to a rapid decrease of the clay surface area at temperatures above 900 °C (Gray *et al.*, 2001).

The most important secondary soil forming iron minerals are Fe-containing clay silicates and Fe oxides. Under reducing conditions, Fe carbonates, sulphides and phosphates may also be formed (Cornell and Schwertmann, 2003). Fe oxides are often precipitated at the surface of other minerals (Cornell and Schwertmann, 2003). Goethite ($\alpha\text{-FeOOH}$) is the most common Fe oxide in soil and predominates in cool to temperate, humid climates (Cornell and Schwertmann, 2003). Ferrihydrite ($\text{Fe}_5\text{O}_8\text{H}\cdot 4\text{H}_2\text{O}$), often associated with goethite, is a poorly ordered Fe oxide. It is found in young soils or soils in which the transformation to more stable oxides is inhibited or retarded by sorbates (e.g. silicates, phosphates, organic matter), e.g. in glaciated area of NW Europe and in podzols (Cornell and Schwertmann, 2003). Goethite and hematite are, under oxic conditions, the thermodynamically most stable forms of Fe oxide and also the endpoint of many transformations (Cornell and Schwertmann, 2003). When heated, ferrihydrite and polymorphs of FeOOH can dehydrate to polymorphs of Fe_2O_3 . During the step of dehydroxylation of Fe oxyhydroxides (which occur between 140 and 500 °C), micropores (pore diameter < 2 nm) develop due to the removal of water. At higher temperatures the micropores are forced together to mesopores (pore diameter 2-50 nm). The formation of micropores enhances the surface area of the sample. However, at temperatures above 600 °C the material sinters and the surface area decreases significantly (Cornell and Schwertmann, 2003).

Volatiles such as combustion residues from OM but also volatile organic and inorganic species, evaporating through the internal structure, can cause pore volume expansion (Gray *et al.*, 2001). Merino *et al.* (2003) investigated the transformation of the surface area in a 0.105-0.210 mm particle size fraction of a soil at a treatment temperature of 900 °C in a non oxidizing atmosphere. They found that for soils with high organic content the surface area is positively correlated to the treatment temperature. For a soil

with a TOC of 14.7 wt. % the surface area increased by one order of magnitude, while no noticeable changes were detected in a soil with a low content of TOC (0.38 wt. %). Even the particle porosity was found to be positively correlated to the treatment temperature and increased by 11-34% in thermally treated soils. Scanning electron microscope (SEM) analyses show that the particle structure of a soil becomes compact and glassy at high temperatures (Eddings *et al.*, 1994), minor fractures appear in the mineral surfaces and smaller particles are formed (Merino *et al.*, 2003).

3.2.2 Effect on trace element leaching

For both untreated and treated soil the highest contents of As, Cr and Cu were found in the finest fraction (< 0.125 mm), with the exception of As in the treated soil where no statistically significant difference between the < 0.125 mm fraction and the 0.500-1.0 mm fraction ($p < 0.05$) could be observed (Table 2). The fraction < 0.125 mm consisted of 41% sand (> 0.06 mm), 54% silt (0.002-0.06 mm) and 5% clay. The concentrations in the untreated soil were about two times higher in the finest fraction compared to the other fractions. These results were expected since trace elements tend to be enriched in the clay fraction of a soil (e.g. Lombi *et al.*, 2000; Qian *et al.*, 1996).

Table 2 Principal characteristics of untreated and thermally treated soil fractions (\pm SD, $n=3$).

Soil properties	Unit	Untreated soil				Soil treated at 800 °C			
		< 0.125	0.125-0.250	0.250-0.500	0.500-1.0	< 0.125	0.125-0.250	0.250-0.500	0.500-1.0
		mm				mm			
pH	-	6.8	6.2	6.0	6.0	8.8	7.6	7.7	8.5
EC	$\mu\text{S cm}^{-1}$	1056	508	253	164	847	422	443	317
E_h	mV	447	420	422	434	427	418	433	438
TS	g kg^{-1}	992	996	996	997	1000	1000	1000	1000
LOI	wt. %	3.0	1.7	1.6	1.2	ND	ND	ND	ND
TOC	wt. %	0.51	0.32	0.83	0.70	0.39	0.05	0.06	0.06
WHC	wt. %	39	ND	ND	ND	37	ND	ND	ND
Total element concentration									
As	mg kg^{-1} dw	352 \pm 7	191 \pm 4	179 \pm 23	148 \pm 33	359 \pm 2	187 \pm 3	187 \pm 23	297 \pm 82
Cr	"	155 \pm 2	93 \pm 2	93 \pm 15	82 \pm 22	158 \pm 1	89 \pm 4	83 \pm 8	108 \pm 4
Cu	"	94 \pm 1	49 \pm 1	43 \pm 5	40 \pm 6	76 \pm 1	35 \pm 1	33 \pm 2	45 \pm 3

ND = not determined

Differences in trace element concentrations before and after treatment (Table 2) could depend on a loss of OM and other soil constituents (e.g. carbonates) as well as a consequent mobilization of trace elements through volatilisation. It could, however, also depend on the sample preparation method. *Aqua regia* does not totally dissolve the soil minerals during the digestion process (Yafa and Farmer, 2006), which means that trace elements trapped in newly formed highly insoluble silicate phases probably were not dissolved.

The effect of thermal treatment on the leaching of trace elements was assessed by a one-step batch leaching test, EN 12457-2 (CEN, 2002). This test is one of the most used leaching tests for granular waste due to its quickness and simplicity and is the prescribed method in the Landfill Directive to regulate waste acceptance at landfills (EC, 2003). Leaching tests are used to predict the behaviour of a material in the environment, but their efficiency is limited by their ability to simulate environmental

conditions relevant for a certain compound in a specific situation (Kumpiene, 2005). The use of deionised water and oxic test conditions lead to the mobilisation of trace elements that are mainly soluble under oxidising conditions. Low redox conditions, which may be important for the mobility of arsenic, are not considered.

The leaching of As and Cr from the soil increased by 18-40 and 2-23 times, respectively, while the leaching of Cu decreased by 12-14 times after thermal treatment (Table 3). This means that the thermal treatment increased the leaching of As from a level where the soil could have been landfilled at a landfill for non-hazardous waste to a level where it exceeds the limit value (25 mg kg⁻¹ dw) for waste acceptable at landfills for hazardous waste (EC, 2003). The results coincide with studies of e.g. Thurnau and Fournier (1992) and Wei and Hsieh (2006) who observed an enhanced leaching of As and Cr respectively due to thermal treatment, and Wei *et al.* (2001) who reported a decrease in Cu leaching from a contaminated soil. According to Thurnau (1996), the leaching of As but not Cr is negatively correlated to the treatment temperature in the temperature interval 316-648 °C. Also, the oxygen level during thermal treatment affects the As leaching. In a large scale thermal treatment experiment an oxygen level of 11% decreased the As leaching about 4.6 times compared to an oxygen level of 7% (Thurnau and Fournier, 1992).

Table 3 Relative leaching of As, Cr and Cu from untreated and treated soil fractions at L/S 10, in percent of the total concentration in the respective soil fraction. Absolute leaching values are given in parenthesis (±SD, n=3).

Soil fraction mm	Leaching of trace elements % (mg kg ⁻¹ dw)		
	As	Cr	Cu
Untreated soil			
< 0.125	0.25 (0.87±0.02)	0.03 (0.048±0.001)	0.24 (0.23±0.01)
0.125-0.250	0.38 (0.72±0.02)	0.06 (0.054±0.002)	0.43 (0.21±0.01)
0.250-0.500	0.47 (0.84±0.04)	0.07 (0.068±0.003)	0.51 (0.22±0.02)
0.500-1.0	0.56 (0.83±0.08)	0.07 (0.058±0.007)	0.43 (0.17±0.09)
Soil treated at 800 °C			
< 0.125	7.9 (28.3±0.4)	0.68 (1.07±0.08)	0.02 (0.017±0)
0.125-0.250	15 (28.7±0.1)	0.56 (0.50±0.01)	0.03 (0.012±0.001)
0.250-0.500	16 (30.9±0.8)	0.16 (0.14±0)	0.04 (0.014±0.001)
0.500-1.0	10 (30.5±0.7)	0.74 (0.80±0.09)	0.03 (0.013±0.002)

The relative leaching of As, Cr and Cu from the untreated soil was always lowest in the finest particle size fraction while the coarser fractions released more (Table 3). After treatment this pattern had changed and e.g. Cr leached least from the 0.250-0.500 mm fraction. The influence of thermal treatment on the leaching of trace elements varies between particle size fractions, due to their specific content of minerals. Although the content of trace elements often is highest in the clay fraction, trace elements in soils with a high content of clay sized particles usually have a lower mobility than in soils with a high content of sand (silica) (Qian *et al.*, 1996) due to the stronger sorption capacity of finer soil fractions compared to coarser.

A sequential chemical extraction test was applied to assess five operationally defined chemical fractions of the trace elements in the soil. *Operationally defined* means that

the obtained data are dependent on the experimental approach adopted. This test provides useful information about the binding form of the trace elements and the changes in solubility that occurred after the thermal treatment. In the procedure reagents with increasing dissolution strength were used.

The sequential extraction test (Figure 2a) revealed a pronounced increase of As associated to the exchangeable (I) and acid-soluble (II) fractions after thermal treatment (28-36 percentage points), while As associated to the reducible (III) fraction decreased by almost the same amount (24-35 percentage points). An explanation for this behaviour can be a reduced binding capacity of Fe oxides due to an increase of their crystallinity during thermal treatment (Cornell and Schwertmann, 2003; Sørensen *et al.*, 2000) which forces As to occur in more soluble binding forms. The speciation of As in different oxidation states in the finest fraction indicated no significant difference in concentration between the oxidation states before the treatment. After thermal treatment As(III) had increased slightly (1.5 times), while the amount of As(V) had increased 19 times (Paper II). The results indicate that the enhanced easily soluble As fraction is dominated by the more oxidised arsenate, As(V). However, arsenite As(III) is of higher environmental concern due to its higher toxicity compared to arsenate, As(V).

Compared to the enhanced As leaching, the Cr concentration in the exchangeable fraction (I) increased only slightly after thermal treatment (Figure 2b). The increase was less than 1% of the total Cr concentration, which was similar to the result of the batch leaching test. Chemical equilibrium calculations indicate that the leaching of Cr should decrease after treatment because of the formation of stable Cr_2O_3 and CrO_2 (Diaz-Somoano *et al.*, 2006). Already at 250°C, Cr(VI) is reduced to Cr(III) and appears as Cr_2O_3 (Wei and Hsieh, 2006), which has a very low solubility in water. Although, Wei and Hsieh (2006), too, observed enhanced leaching of Cr from a contaminated soil treated at 500 °C. Studying fly ashes from municipal solid waste incineration (MSWI) at 900 °C, Kirk *et al.* (2002) proposed a mechanism for the elevated mobility of Cr afterwards: when synthetic Cr_2O_3 is thermally treated together with CaO the leaching of Cr with water increases. After the treatment, calcium chromate (CaCrO_4) can be determined via XRD in the CaO treated soil. CaCrO_4 is a soluble Cr(VI) species which could account for the elevated leaching at 800 °C. Also, other researchers have suggested chromate formation at high temperatures in Cr-containing sludge (e.g. Shoto and Hattori, 1980). The increased leaching could also be a result of the increase in soil pH from about 6 to 8 following treatment as the sorption of Cr decreases with increasing pH, or it could depend on competition for adsorption sites with other dissolved anions such as As (Khaodhiar *et al.*, 2000). In spite of the increased leaching, the residual fraction (V) increased after thermal treatment. This means that Cr became more stable and less sensitive to pH and redox changes, which might reduce its harmful effect on the environment over the long term.

For Cu, the amount associated to the exchangeable fraction (I) decreased after thermal treatment (Figure 2c), similarly to the batch leaching test results. The decrease in leaching of Cu from contaminated soil after thermal treatment has also been described by Wei *et al.* (2001). These authors found that $\text{Cu}(\text{OH})_2$ was transformed to CuO and CuO-associated species with a lower solubility when Cu-spiked soils (SiO_2 and kaolin) were thermally treated at 300-900 °C.

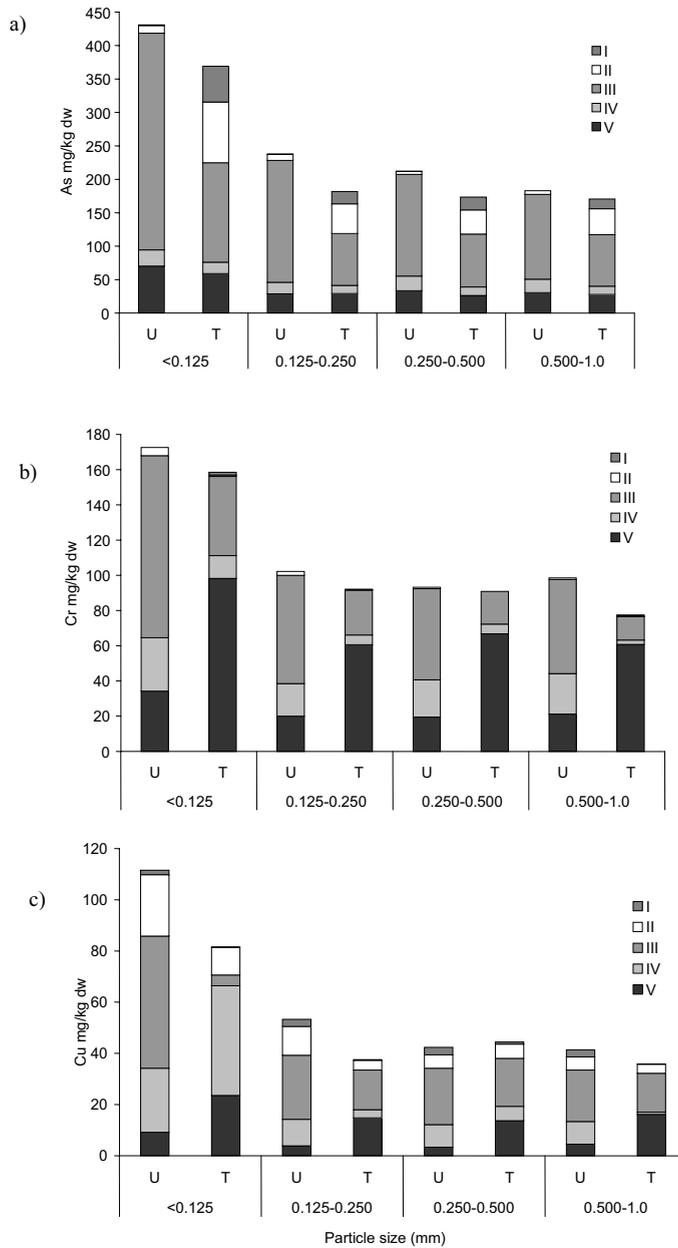


Figure 2 Fractional distribution of As (a), Cr (b) and Cu (c) in untreated (U) and thermally treated (T) particle size fractions, (mean of $n=3$). Fractions: I = exchangeable, II = acid-soluble, III = reducible, IV = oxidisable and V = residual.

The changes in fractional distribution of the trace elements due to thermal treatment at 800 °C are summarized in Table 4. The dominating changes for As are transitions from the reducible fraction (III) to the more easily soluble exchangeable (I) and to the acid-soluble fraction (II). The dominating translocations for Cr and Cu are from the reducible fraction (III) to the more recalcitrant residual fraction (V).

Table 4 Changes in trace element association to chemical soil fraction determined by sequential extraction, following thermal treatment at 800 °C. The changes are represented by the average of the particle size fractions < 0.125; 0.125-0.250; 0.250-0.500 and 0.500-1.0 mm.

Trace element	Changes in fractional distribution				
	I	II	III	IV	V
As	++	++	---	+/-	+/-
Cr	+/-	+/-	---	--	+++
Cu	-	-	--	*-	+++

--- = 25-50 percentage points (pp) decrease

-- = 10-25 pp decrease

- = 2-10 pp decrease

+/- = 2 pp increase/decrease in different fractions

+ = 2-10 pp increase

++ = 10-25 pp increase

+++ = 25-50 pp increase

*Standard deviation exceeds the mean value more than 4 times.

3.2.3 Effect on trace element volatility

Apart from changes of the leaching behaviour after thermal treatment, the volatility of trace elements from a contaminated soil has to be considered. The EU Directive for waste incineration (2000/76/EC) regulates emissions of twelve toxic elements including As, Cr and Cu (EC, 2000). The degree of volatilisation of these elements depends on a variety of factors such as the vapour pressure of the substance, concentration, soil matrix and thermal process conditions (Lundholm *et al.*, 2007). Treatment time and temperature are process conditions positively correlated to the degree of volatilization (Gray *et al.*, 2001; Yang *et al.*, 1994). The rate of volatilization is relatively rapid in the early phases of the thermal treatment but slows down later, apparently since less volatile metal compounds are formed through metal-soil reactions (Eddings *et al.*, 1994; Ho *et al.*, 1995). Major soil components as Na, K, Ca, Mg, Fe, Al, Si and P enhance the recovery of trace elements in the solid particles (Díaz-Somoano *et al.*, 2006). Metal chlorides often have relatively high vapour pressure compared to other metal compounds making the chlorides more volatile (Ho *et al.*, 1995). Modelling of metal volatilisation from different particle size fractions indicates an increase in volatilization when the particle size decreases because it is faster for the trace elements to diffuse through smaller particles, and reaction time with the soil particle is reduced (Ho *et al.*, 1995).

Based on the vapour pressure of As compounds, As would be expected to be very volatile in incineration systems (Gray *et al.*, 2001). However, below 900 °C the effective vapour pressure of arsenic species is low (Rizeq, 2000). Pure arsenic (III) oxide (As₂O₃) has its melting point at 141 °C and its boiling point at 371 °C. At temperatures above 300 °C and under oxidizing conditions As₂O₃ begins to vaporize without changing oxidation state (Yang *et al.*, 1994). Equilibrium calculations show that

in a combustion atmosphere at temperatures above 500 °C As will completely exist in its gas phase, with AsO(g) as the most stable species (Díaz-Somoano *et al.*, 2006). It also shows that interactions between As and Fe components, forming FeAsO₄, decrease the gas formation. During thermal treatment, locally reduced zones may occur. At 950 °C and a treatment time of 1 h, the volatilization of As from a contaminated clay was observed to be much higher in a reducing atmosphere (2% CO, 98% N₂) than under oxidizing conditions (20% O₂, 80% N₂), with 97 and 8% volatilization, respectively (Gray *et al.*, 2001).

Full-scale and pilot-scale thermal treatment tests have been used to evaluate the fate of As in rotary kiln facilities. The amount of As found in the treated residual soil was between 80 and 90% of the total amount of As recovered in nine tests performed by Waterland *et al.* (1991). An increase of the kiln exit temperature from 816 °C to 927 °C increased the amount of As in the flue gases and to the scrubber liquor during a thermal treatment test performed by Thurnau and Fournier (1992). In this test, between 89 and 97% of the total recovered As was found in the treated residual soil after treatment. No relationship between chlorine content and As vaporisation was observed. A similar test with thermal treatment between 316 and 648 °C showed that 96% (average of 12 tests) of the feed As concentration was recovered in the residual soil (Thurnau, 1996).

Out of CCA, Cr is the most recalcitrant one concerning vaporization. Theoretically, oxides of Cr and chromium (III) chloride (CrCl₃) do not vaporize at temperatures below 1000 °C which implies that all Cr should remain in the treated soil (Díaz-Somoano *et al.*, 2006; Yang *et al.*, 1994). However, in a full scale thermal treatment experiment on co-contaminated soil, only 95 % (on average of 12 tests) of the Cr was recovered in the residual soil (Thurnau, 1996).

With regard to Cu, most of its species are converted into stable oxides during thermal treatment and are recovered in the residual soil. However, pure copper (II) chloride (CuCl₂) vaporise at temperatures above 470 °C (Yang *et al.*, 1994). Equilibrium calculations made by Díaz-Somoano *et al.* (2006) show that Cu is totally volatilized at temperatures above 600 °C and in the presence of chlorides, with CuCl(g) being the most stable form.

3.3 Thermal treatment techniques

Thermal treatment of trace element contaminated soil should only be used when the soil is also contaminated with organic contaminants. If the soil is contaminated with solely inorganic contaminants, other soil remediation techniques should be preferred. The characteristic of the organic contaminants governs the process conditions because their destruction is the primary goal. The operating condition of the equipment and the characteristics of the contaminant and the soil are found to be key factors for the performance of thermal treatment systems (Lundholm *et al.*, 2007). Usually, thermal treatment techniques are divided in thermal extraction/desorption techniques and thermal destruction techniques, depending on the function of the treatment facility and the temperature interval used in the process.

Thermal destruction techniques such as incineration (described in Paper I) can be used for all organic contaminants and for all soils at high temperatures (800 to 1400 °C). Due

to the high energy demand, the technique is only recommended for smaller, highly contaminated soil quantities, or for the destruction of concentrated contaminant fractions from e.g. soil washing.

Thermal extraction/desorption can be carried out with continuous feed of the contaminated soil and with the soil in direct or indirect contact with the heat source in a rotating dryer/kiln or by means of a rotating screw containing hot oil. It can also be undertaken batch wise using *in situ* or *ex situ* techniques (NFESC, 1998; Swedish EPA, 1998). In systems with indirect contact between the contaminated soil and the heat source, the fuel and the waste gases do not interfere with the contaminants, which may be the case in systems with direct contact.

Thermal extraction/desorption techniques are often considered as two step processes (described in Paper I). First, the contaminated soil is heated to between 100 and 800 °C, resulting in the evaporation of volatile and some semi volatile contaminants (step one). Since usually not all organic contaminants are destroyed in this temperature interval, the waste gases have to be treated in a second step, e.g. combustion in an afterburner, condensation, separation in a carbon adsorption bed, or treatment with biofilters. Evaporated trace elements can effectively be trapped in air pollution control (APC) systems, both in incineration and in extraction/desorption systems. When the evaporated organic emissions are treated in an afterburner the process is similar to the incineration process. There is no sharp border between the techniques.

The treatment costs for different thermal remediation techniques vary significantly, however, the most important factors determining the costs are the same. Cudahy and Troxler (1992) identified the following factors in the order of decreasing impact: moisture content > type of contaminant(s) > concentration of the contaminant(s) > quantity of material to be treated.

3.3.1 Other issues regarding thermal treatment of trace element contaminated soil

Rotary dryers/kilns are sensitive to an overload of fines in the system (Merino *et al.*, 2003). The break point between fine and coarse material is usually defined as particles smaller or greater than 0.075 mm (NFESC, 1998). The fines will leave the rotary kiln with the gas stream. The carryover can overload the treatment equipment subsequent to the rotating kiln, e.g. bag house and cyclone, and cause pressure and build-up problems. Usually, the fines are rejoined with the treated residues at the end of the process. On the other hand, when the soil is contaminated with trace elements, the separation of coarse and fine material can be seen as a potential advantage in the remediation process.

In the thermal treatment experiment conducted during this study, the highest portion of trace elements was in the < 0.125 mm particle size fraction (Figure 3). This fraction also contained the highest total concentration of trace elements (Table 2). According to the results from the sieving of the bulk soil (in paper II), 75 wt. % of the < 0.125 mm fraction was < 0.075 mm which means that this portion probably will be trapped in the cyclones and filters in a rotary kiln facility. The further treatment of the residual fractions could be done separately, allowing for specific remediation needs of the different fractions. One suggestion could be to stabilize the finer fraction before landfilling, while the coarser fraction could be treated further in soil washing processes.

The enhanced leaching of As after thermal treatment can be an advantage in soil washing processes.

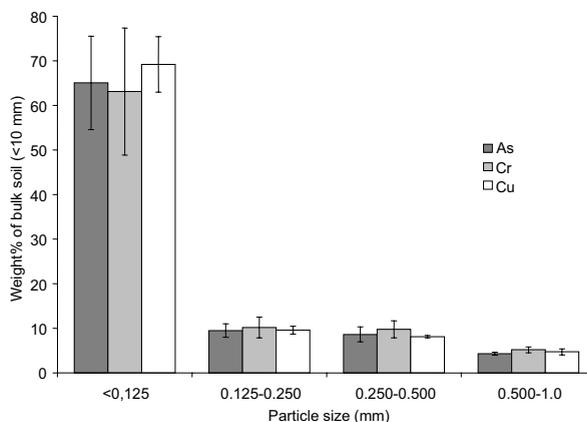


Figure 3 Distribution of As, Cr and Cu between the untreated soil particle size fractions: < 0.125; 0.125-0.250; 0.250-0.500 and 0.500-1.0 mm of bulk soil < 10 mm.

Although a low treatment temperature would be beneficial due to the volatility of trace elements it is not always the best choice in relation to trace element leaching, because some trace elements have their leaching maximum after thermal treatment at 200 to 400 °C, e.g. Cu (Tack and Verloo, 1993). On the other hand, the increase in volatility of trace elements (especially As) with increasing temperature can be handled in an effective APC system from where the trace elements can be recovered. Chemical equilibrium calculations made by Díaz-Somoano *et al.* (2006) give an indication that stabilizing amendments containing e.g. Fe, Al and Ca could be mixed in the soil before treatment in order to reduce the volatility and possibly also the mobility of the trace elements.

4 CONCLUSIONS

Thermal treatment techniques can be used for the remediation of co-contaminated soil in combination with treatment techniques suitable for trace elements. Organic contaminants are extracted and/or destroyed during the process while trace elements are recovered in the treated soil, cyclone and filter fractions, as condensate and in APC systems. Changes in the mobility of trace elements have to be considered for further treatment and reuse of the soil.

Incineration methods are suitable for highly contaminated soils. However, because of the high energy demand, these methods are most beneficial for smaller quantities of soil. Thermal extraction/desorption techniques are less energy demanding than incineration methods. If the extracted organic contaminants are destroyed in an afterburner, the boundary between the techniques blurs.

Thermal treatment of a trace element contaminated soil at 800 °C increased the leaching of As(V) and Cr, while the leaching of Cu decreased, due to phase transitions in the soil

and contaminants. Iron oxides, being the most important oxides for the sorption/desorption processes of trace elements in soil, are transformed to more crystalline forms during thermal treatment, which results in a decreased amount of sites for trace element adsorption.

Trace elements associated to the reducible fraction, dominated by Fe and Mn oxides in the chemical sequential extraction test, decreased after the soil had been treated thermally. The most pronounced shifts were that As became associated to chemical fractions with weaker binding strength (exchangeable and acid soluble fractions) and Cr and Cu associated to chemical fraction with stronger binding strength (residual fraction) after treatment.

Based on the literature, the volatility of trace elements is positively correlated to thermal treatment time and temperature. Arsenic is most volatile followed by Cu and Cr. Chlorides in the soil enhance the Cu volatility. The actual volatility can be lower than expected due to stabilizing reactions between the trace elements and soil constituents. A high oxygen level during the treatment process reduces the volatility and leaching of As. Reduced zones in the thermal treatment facility must be avoided as far as possible.

It is not possible to accurately predict the behaviour of trace elements during thermal treatment processes. The amount of trace elements in the residual treated soil depends on many factors, such as the trace element species and concentration, the interaction between trace elements and other soil constituents (e.g. clay minerals and metal oxides); and process parameters such as the fuel used, oxidising or reducing atmosphere, treatment time and temperature.

In rotary dryer/kiln facilities, cyclone and filter fractions can be separated from the residual (coarse) soil, and due to the trace element enrichment in the finest soil fraction, this residue should be further treated.

5 OUTLOOK

Future research is required to improve the thermal treatment technique, and to minimize the environmental impact of thermal treatment of trace element contaminated soil. The aim is to minimize the mobility of trace elements without affecting the treatment of the organic contaminants.

- The addition of stabilizing agents before thermal treatment may reduce the mobility of As. Admixtures of e.g. metal oxides, clay minerals and alkaline materials should be tested.
- A factorial design experiment could contribute to a better understanding of factors affecting the mobility of trace elements. The following factors were identified to probably have an influence: treatment time, temperature, stabilizing agent, atmosphere, contamination level and OM content.
- Life Cycle Assessment (LCA) should be used to evaluate the environmental impact of the technique and to compare it with other techniques suitable for the treatment of co-contaminated soil.

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PAPER I

Nordmark, D. Treatment techniques for contaminated soil from wood preservation sites
– Literature review.

LITERATURE REVIEW

Treatment techniques for
contaminated soil from wood preservation sites

DÉSIRÉE NORDMARK

SUMMARY

Extensive wood preserving activities have caused severe contamination problems at many wood processing industrial sites and the contaminated soil must be remediated. The remediation policy of the Swedish environmental protection agency is to primarily destroy the contaminants followed by concentration and as the last alternative, immobilize the contaminants.

The objective of this review is to describe the most common contaminants originating from wood preservatives and to give an overview and assessment of available soil remediation techniques suitable for soils contaminated with wood preservatives.

Most frequently occurring contaminants at wood preservation sites are PAHs (polycyclic aromatic hydrocarbons), PCP (pentachlorophenol) and CCA (chromated, copper arsenate). If a site is contaminated with PCP, dioxins and furans (PCDD/F) also may be present. Mixes of different preservatives at the same site is common.

Remediation techniques use to be divided in destruction techniques, concentration and separation techniques and immobilization techniques. Techniques used on or off site after excavation are called *ex situ* techniques and techniques used on site without excavation are called *in situ* techniques.

Incineration, dehalogenation and chemical oxidation/reduction are destruction techniques suitable for PCDD/Fs. They can also be used for destruction of PCP as can biological techniques. All above mentioned techniques but dehalogenation are suitable for decomposition of PAHs.

Thermal extraction/desorption, vacuum extraction/soil venting and chemical extraction are concentration and separation methods useful for soil contaminated with PCDD/Fs. For concentration and separation of PAHs and PCP electrokinetic separation, soil washing and soil venting can be added. These methods, except for thermal extraction/desorption, can also be used for concentration and separation of CCA.

Vitrification implies that all organic contaminants are destroyed and metals are immobilized. Other techniques suitable for the immobilization CCA are solidification and stabilization. In Sweden, landfilling is still the most common remediation technique for soil contaminated with wood preservatives.

If a site contaminated with mixed contaminants (organic and inorganic contaminants) is to be remediated usually several techniques have to be combined in a treatment train to fulfil the clean up goals.

When selecting remediation technique, factors as environmental impact, recovery efficiency and use of economic, energy and clean soil resources have to be considered.

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1 INTRODUCTION

As a result of extensive wood preservation activities, many wood processing industrial sites have become contaminated and need to be remediated. At many sites the type of preservatives has changed throughout the years. There is a mixture of different contaminants both organics such as PAHs (polycyclic aromatic hydrocarbons) and PCP (pentachlorophenol) and inorganic such as arsenic, chromium and copper in the soil. These substances can cause severe environment problems and are a risk to the human health (Dube *et al.*, 2004).

There are many different techniques available for remediation of contaminated soil, although excavation and landfilling is the most common one. Most of the remediation techniques are only suitable for soil contaminated with either organic or inorganic substances, but not for the mixed contaminants (table 2).

The purpose with remediation of contaminated soil is to, as far as possible, reduce the amount of contaminants in the soil and if that is not possible, reduce their mobility, toxicity and bioavailability (Swedish EPA, 1999). The remediation policy of the Swedish EPA is to primarily destroy the contaminants followed by concentration and as the last alternative immobilize the contaminants.

1.1 Objectives

The objective of this review is to describe the most common contaminants originating from wood preservatives and to give an overview and assessment of available soil remediation techniques suitable for soils contaminated with wood preservatives.

2 WOOD PRESERVATION SITES

The purpose with preservation of wood is to protect it from bacterial, fungal and insect attacks. Unfortunately, a disadvantage of the preservation activities is that they have caused severe contamination of the areas where the preservation facilities are situated.

The industrial preservation history in Sweden takes its start in the middle of the 19th century (Swedish EPA, 1999). The contaminants found at wood preservation sites are dependent on the type of preservatives that has been used at the site. Preservatives are the impregnation solution used for impregnation of wood. The preservatives usually consist of many different chemical components where some of them are toxic and are defined as contaminants. If the preservation site has been active for many decades, many different preservatives may have been used.

2.1 Preservatives

The first trials with preservation of wood in Sweden was with water solutions of copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) also named Copper vitriol. It was mainly utility poles and railway sleepers that were treated. In the beginning of the 20th century preservation of sleepers with creosote started. Because of World War II import of creosote stopped and that became the reason why metal based aqueous solutions as CCA (chromated copper

arsenate) were introduced as preservatives. The use of creosote continued after the war. In the 1960s light organic solvent preservatives were introduced with the active substances, as chlorophenol, dissolved in organic solvents. Chlorophenol was banned in 1978 because of its high toxicity. Between 1974 and 1995 preservatives based on organic tin also were used until they were banned. Nowadays CCA with an arsenic content of about 5% is used for pressure preservation in Sweden (Swedish EPA, 1999).

Today the problem with dispersion of pesticide and fungicide from wood preservation sites is minimized mainly because closed processes and sealed layers are used. Usually preservatives are divided in three groups, namely: creosote, water soluble salts and light organic solvent preservatives.

2.1.1 Creosote

Creosote is a distillation product from coal-tar. The color is black to brownish and it has a characteristic smell. It has mostly been used for preservation of railway sleepers and telephone poles. When creosote is used for preservation it is diluted in petroleum or other solvents (US-EPA, 1995). Creosote is a complex mixture of hundreds of organic compounds of about 85% PAHs, 10% phenolic compounds and 5% nitrogen- sulphur- and oxygen-containing heterocyclic aromatic compounds (Mueller *et al.*, 1989). Only a few of them are present in amounts of 1% or more.

2.1.2 Water soluble preservatives

Water soluble preservatives consist of salts, acids and oxides of e.g. arsenate, copper, chromate, zinc, borate, fluoride or phosphate. The most used water soluble preservative is CCA (chromium, copper and arsenic). Other typical combinations are CFA (chromium, fluoride, arsenic), CZA (chromium, zinc, arsenic) CC (copper, chromium), CCB (copper, chromium, boron) and CCP (copper, chromium, phosphoric acid) (Swedish EPA, 1999). Cuproammonium solutions of copper and pentachlorophenol dissolved in a water solution of ammonium and carbon dioxide are other types of water soluble preservatives.

2.1.3 Light organic solvent preservatives

Light organic solvent preservatives, also called oil based preservatives, have their active substances as pentachlorophenol or organic tin dissolved in light organic solvents as petroleum (US-EPA, 1995).

2.2 Contaminants

Contaminants at wood preservation sites can be found in soils, sediments, sludges and/or in surface and ground water (US-EPA, 1995). Frequent contaminants found at wood preservation sites are presented in Table 1. Of those compounds, chromium, copper and arsenic (CCA); polycyclic aromatic hydrocarbons (PAHs) and pentachlorophenol (PCP) are the most common ones.

Table 1 Contaminants commonly found at wood preservation sites (US-EPA, 1995).

		Organics			Inorganics	
Dioxins/ furans	Halogenated phenols	Simple non- halogenated aromatics	Polycyclic aromatic hydrocarbons (PAH)	Other polar organic compounds	Non- volatile metals	Volatile metals
Dibenzo- p-dioxins	Pentachloro- phenol	Benzene	2-Methyl- naphthalene	2,4-dimethyl- phenol	Chromium	Arsenic
Dibenzo- furans	Tetrachloro- phenol	Toluene	Chrysene	2-Methyl- phenol	Copper	Cadmium
Furan		Ethyl- benzen	Ace- naphthene	4-Methyl- phenol		Lead
		Xylene	Fluor- anthene	Benzoic acid		Zink
			Ace- naphthylene	Di-n-octyl phthalate		
			Fluorene	N-nitroso- diphenyl- amine		
			Antracene			
			Indol(1,2,3-cd)- pyrene			
			Benzo(a)- anthracene			
			Benzo(a)- pyrene			
			Phenanthrene			
			Benzo(b)- fluoranthene			
			Pyren			
			Benzo(k)- fluoranthene			

2.2.1 PAHs

Polycyclic aromatic hydrocarbons are hydrophobic compounds that consist of two or more fused benzene rings. The low solubility in water makes them particularly recalcitrant in soil. Most PAHs are known to be toxic to living organisms and many of them are also carcinogenic to humans (Cerniglia, 1992). United States Environmental Protection Agency (US-EPA) has prioritized 16 PAHs based on their known carcinogenic effect or common use, and typical creosote consists of these 16 PAHs to an extent of 20-40% of its weight.

2.2.2 Phenols, chlorophenols and dioxines

Chemically, phenols consist of at least one hydroxyl (-OH) group attached to a carbon atom in a benzene ring. Phenols have generally high solubility in water which increases with the number of hydroxyl groups (Mackenzie and Sharp, 1976).

Chlorophenols are a group of species with 1-5 chlorine atoms on a phenol ring. The most common specie in preservatives is pentachlorophenol (PCP; C₆Cl₅OH). PCP is a white organic solid and when PCP is used as a preservative it is mixed with petroleum

or other solvents (US-EPA, 1995). At low pH PCP is a hydrophobic compound (LaGrega *et al.*, 2001). About 20% of the phenol compounds in creosote consists of phenol and about 10% of pentachlorophenol (Mueller *et al.*, 1989). When chlorophenol is synthesized, dioxins and furans can occur in small amounts as byproducts. Therefore, if chlorophenols are found at a wood preservation site, dioxins and/or furans also may be present.

Polychlorinated dibenzo-dioxines (PCDD) and dibenzofuranes (PCDF) are two groups of compounds that exist in many different forms. They all have the same base structure, but with the different numbers of chlorine atoms. There are 210 different species of dioxins and furanes, but only 17 of them are toxic. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) is one of the most toxic substances mankind has ever made.

2.2.3 Chromated copper arsenate (CCA)

In CCA the active substances are copper(II) oxide (CuO); chromium(VI) trioxide (CrO₃) or sodium dichromate (Na₂Cr₂O₇ · 2H₂O) and diarsenic(V) pentoxide (As₂O₅) (Swedish EPA, 1999). When the active substances emerge in the environment many chemical reactions like sorption, precipitation and formation of complexes can take place which might affect the mobility and toxicity of active substances. These reactions are influenced by environmental properties e.g. soil and pore water, soil characteristics, organic matter, redox potential, pH and microorganisms.

In CCA-solutions chromium mostly exists as Cr(VI) which is more toxic and mobile than Cr(III). However under natural conditions in soil, Cr(VI) reduces to Cr(III). The reduction is more rapid in soils with high content of organic matter while in a sandy soil Cr(VI) can persist for considerable periods of time (Kozuh *et al.*, 2000; Song *et al.*, 2006).

The mobility of copper is strongly pH-dependent and increases with decreasing pH. Copper also has a strong affinity to adsorb to mineral surfaces and organic matter (both solid organic matter (SOM) and dissolved organic matter (DOM)) and it might also react with other substances and precipitate (Flemming and Trevors, 1989; Mao *et al.*, 2004).

Arsenic is mainly present as arsenate (As(V)) in CCA-solution. Though, when leaching through the soil arsenate can transform to arsenite (As(III)), which is more toxic and mobile, depending on soil conditions (Mao *et al.*, 2004).

Of Cu, Cr and As, As is considered to be the most toxic constituent but both Cr(VI) and As are found to be carcinogenic. Even copper is toxic to biota at elevated levels.

3 TREATMENT TECHNIQUES

There are numerous of soil remediation techniques and there have been many attempts to organize the techniques in different groups. They can be divided by the strategy used (destruction, concentration/separation or immobilization) or by the type of method used (physical and chemical, biological or thermal). They can also be divided in *in situ* methods and *ex situ* methods where *in situ* means that the contaminants are treated

where they are situated without digging them up and *ex situ* means that the contaminated soil first has to be excavated. *Ex situ* methods can be divided in “on site” and “off site” methods. In “on site” methods the treatment of the soil is done nearby the contaminated site, while in “off site” methods the soil has to be transported to a treatment plant. The most common treatment techniques and their applications are presented in Table 2.

Table 2 Treatment techniques suitable for contaminants found at wood preservation sites (Swedish EPA, 1999; US-EPA, 1992).

Method	Technique	<i>In situ</i>	<i>Ex situ</i>	Soil type the method is suitable for	Example of contaminant* treated	Relative energy consumption
Destruction	Incineration		X	all types	PAH, PCP, PCDD/F	high
	Dehalogenation		X	clay raises the costs	PCP, PCDD/F	mid
	Chemical oxidation/reduction		X	homogenous, high permeability	PAH, PCP, PCDD/F	mid
	Biological treatment with bioreactor		X	all types	PAH, PCP	mid
	Biological treatment as composting	X	X	all types	PAH, PCP	low
Concentration and separation	Thermal extraction/desorption		X	gravel and sand	PAH, PCP, PCDD/F	high
	Electrokinetic separation	X	X	clay and silty clay	Me, PAH, PCP	high
	Vacuum extraction/soil venting	X		gravel, sand (and silt)	PAH, PCP, PCDD/F	mid
	Soil washing		X	sand and gravel	Me, PAH, PCP	mid
	Chemical extraction		X	soil with low clay content	Me, PAH, PCP, PCDD/F	mid
	Soil flushing	X		sand and gravel	Me, PAH, PCP	mid
	Grain separation (sieving)		X	all types	Me	low
Immobilization	Vitrification	X	X	all types	Me, PAH, PCP, PCDD/F	high
	Solidification	X	X	all types	Me	mid
	Stabilization	X	X	all types	Me	mid
	Containment and landfilling	X	X	all types	Me, PAH, PCP, PCDD/F	low

* Me = metals and arsenic, PAH = polycyclic aromatic hydrocarbons, PCP = pentachlorophenols, PCDD/F = polychlorinated dibenzo-dioxines and dibenzofuranes

Different remediation methods can be useful at the same site depending on type, amount and concentration of contaminants. If the soil is contaminated with both organic and inorganic contaminants, stepwise treatment with two or more methods usually is necessary (also called treatment trains).

The actual cost of a remediation technique is site-specific and depends on target cleanup levels, soil characteristics and design and operation of the technique used (US-EPA, 1995). In general, higher energy use results in higher treatment costs.

3.1 Destruction methods

The purpose with destruction methods is to convert the contaminants to less harmful constituents. The method can only be used for organic contaminants and not for metals, which can not be destructed.

3.1.1 Incineration

Incineration convert organic contaminants, through volatilization and combustion, into inorganic constituents such as carbon dioxide, water, hydrogen chloride, sulphur oxide, salts, ashes and slags at high temperatures (800 to 1,400 °C), depending on type of oven and contaminants, and in the presence of oxygen and a flame. The method is suitable for all kind of soils and if the temperature is high enough contaminants as PAHs, dioxins and furans can be totally destroyed. Improper operated incinerators can create dioxins and furans. To remove particulates and to remove and neutralize acid gases (e.g. HCl) the off-gas requires treatment by an air pollution control (APC) system (US-EPA, 1995). The technique generates three types of residual streams: solids from the incinerator and APC system, water from the APC system and air emissions. The incineration residues generally require further treatment and if the soil contains heavy metals, the residues as bottom ash and fly ash need particular care e.g. stabilization (Swedish EPA, 1999). When large volumes are incinerated the energy costs can be extremely high. If there is enough space, the technique can be used both on-site with a transportable unit or off-site (US-EPA, 1995). Two commonly used incineration facilities are rotating oven and fluidized bed (Swedish EPA, 1998).

3.1.2 Dehalogenation

In dehalogenation, reagents are added to the contaminated soil to transform halogenated contaminants e.g. PCPs and PCDD/Fs to less toxic substances through substitution of the halogen molecules or through decomposition. The new substances often need further treatment. A common reagent used is APEG (alkaline polyethylene glycol) solution (Swedish EPA, 1999). Another type of reagent is sodium bicarbonate, which is used in the base-catalyzed decomposition (BCD) process. High content of clay or moisture usually raise the treatment costs because more reagents are needed (FRTR, 2002).

3.1.3 Chemical oxidation/reduction

Organic contaminants are decomposed through oxidation and mineralization processes. The processes can be enhanced by adding a chemical oxidant to the soil. Ozone or hydrogen peroxide is commonly used oxidants. UV light can be used as a complement which enhances the process and metals e.g. iron and copper can be used as catalysts. Best result is achieved if the soil is homogenous and have a high permeability (Swedish EPA, 1999). The technique is also used for redox-sensitive metals, e.g. to reduce Cr(VI) to Cr(III) (FRTR, 2002).

3.1.4 Biological treatment

Biodegradable organic contaminants can be treated with the help of microorganisms. Microorganisms decompose organic compounds to less complex organic matter as sugar, alcohol and short chained molecules. The main end products are carbon dioxide and water. The treatment can be used both *in situ* and *ex situ* but the method has appeared to be difficult to control *in situ*. Treatment in a bioreactor gives the best result concerning degradation of organic contaminants (Swedish EPA, 1999).

Bioreactor/bio-slurry reactor

Biological treatment in a bioreactor can be performed in a closed reactor or in an open pond which is sealed in the bottom. To get an efficient treatment the soil is mixed with water to form a slurry. The soil is then kept in a suspension through pumping or mixing. Microorganisms can be added to the slurry in the beginning if necessary, or continuously during the treatment. Water ratio, nutrition ration, pH and oxygen content are steering variables that have to be adjusted during the treatment to get optimal conditions. When the treatment is finished the soil has to be dewatered through filtration or centrifugation. The method is suitable for simple aromatic compounds and some PAHs (FRTR, 2002; Swedish EPA, 1998). Sequential anaerobic/aerobic conditions can be used to degrade highly chlorinated contaminants (Swedish EPA, 1999).

Composting

In composting the degradation of organic contaminants takes place under aerobic conditions. The composting can be done on site or off site in special treatment facilities on excavated masses. To enhance the percolation of water and air through the soil, the structure of the soil can be improved by mixing the soil with amendments as wood chips or bark which also can work as substrate for the microorganisms. Even water, oxygen and nutrition as phosphorous and nitrogen can be added. The addition of oxygen can be done by turning the compost or by letting air blow through the compost through vents in the floor or through perforated pipes embedded in the masses. In closed systems both air and water are collected and recirculated or treated. If composting is used for degradation of PAHs, it is most efficient for PAHs with two to three rings (US-EPA, 1995).

3.2 Concentration and separation methods

The purpose of concentration and separation methods is to collect, concentrate and sometimes also separate the contaminants. These methods always have to be combined with other methods such as destruction or immobilization.

3.2.1 Thermal extraction/thermal desorption

In thermal extraction/desorption, which is an *ex situ* method organic contaminants volatilizes from the soil at temperatures between 100-800 °C. Some methods use mechanical agitation to volatilize the contaminants (Thermtech, 2004). In a thermomechanical desorption process called TCC (thermomechanical cuttings cleaner technology) solid waste particles are forced towards the inner wall of a barrel shaped process chamber by means of shaft mounted hammers where the kinetic energy from the rotating arms will be transformed to heat by friction (Swedish EPA, 1999).

In thermal extraction/desorption the contaminants are not destroyed and the off-gases have to be combusted in an afterburner, condensed or separated in a carbon adsorption bed or treated with biofilters. The method is suitable for contaminants as PCP, PAH and PCDD/F (Swedish EPA, 1998). Even arsenic and mercury can be volatilized and then collected (Swedish EPA, 1998; US-EPA, 1995). In the presence of chlorines in the feed material from e.g. PCP, there is a risk of dioxin and furan formation at temperatures above 180 °C (Helldén, 1993). The method can be used both on-site and off-site and it works best on soil with low content of silt and clay. Before thermal treatment a full-scale test with dioxin and furan analyses should be performed. The treatment can be done both batch wise or continuously in a rotating kiln or by means of a rotation screw with hot oil in it (Swedish EPA, 1998).

3.2.2 Electrokinetic separation

Electrokinetic separation can be used on metals and polar organic contaminants. The metals have to be in ionic form which is achieved through acid dissolution. An electric field is created in the soil by means of a number of electrodes (cathodes and anodes). The positive ions are transported to the negative electrodes and vice versa which will give a concentration of ions at respective pole. Even natural occurring ions in the soil are collected this way. The electrodes are filled with a circulating liquid that continuously transport the captured contaminants to two separate cleaning systems (Swedish EPA, 1999). This method can be used both *in situ* and *ex situ* and also below the ground water level (Swedish EPA, 1999). The method works best in low permeability soils like saturated or partially saturated clay and silty clay mixtures. Electrodialysis is a special type of electrokinetic's where ion exchange membranes are installed around the electrodes (FRTR, 2002; Swedish EPA, 1998).

3.2.3 Soil vacuum extraction/in situ soil venting

In vacuum extraction a sub pressure is created in the soil by means of a vacuum pump connected to one or more extraction wells or horizontal pipes where the contaminants are collected. The sub pressure transforms the contaminants to gas so that they can be ventilated out of the soil through the wells. The contaminants can then be further treated through filtration, collected with adsorbents or combusted. The method can be applied on volatile to semi volatile organic contaminants (Helldén, 1993). This means that the use of the method for treatment of contaminants found at wood preservation sites is limited because the low volatilization of these contaminants. However, compounds as phenols and naphthalene can be extracted with this method and even solvents from light organic solvent preservatives. The method works best in soil consisting of coarser material like gravel and sand, but silt can also be treated.

3.2.4 Soil washing/flushing and chemical extraction

Soil washing is a water-based process for scrubbing soils *ex situ* to remove contaminants while soil flushing is an *in situ* method where the contaminants are leached into the ground water which is then extracted and treated. Chemical extraction is used *ex situ* and uses an extracting chemical (acid or solvent) instead of water.

Soil washing

Soil washing can be used if the soil is contaminated with organic and inorganic substances (FRTR, 2002). Contaminants sorbed onto fine soil particles are separated from bulk soil in an aqueous-based system on the basis of particle size. The contaminants are concentrated in the washing solution and the fine fraction. After flocculation and sedimentation the washing solution can be reused (Swedish EPA, 1999). The wash water may be augmented with a basic leaching agent, surfactant, pH adjustment, or chelating agent to help remove organics and heavy metals. Soil washing works best on soils consisting of coarser material as sand and gravel and with a low amount of fines like clay and silt. If the soil contains complex mixtures of contaminants (both metals and non-volatile organic compounds) different washing solutions and/or different soil to wash fluid ratios, may be required (Swedish EPA, 1999).

Soil flushing

Soil flushing can be used for both inorganic and organic contaminants, although not at the same time. Water or water containing an additive is infiltrated or injected to the contaminated soil via injection wells. Contaminants are leached into the ground water, which is then pumped up from the ground via extraction wells and treated. The technique is suited for soil with less content of silt and clay and with relatively homogenous soil layers (Swedish EPA, 1999).

Chemical extraction

Chemical extraction uses acids or solvents as extracting chemical. The contaminated soil is often pre-treated by sieving to grade the soil in fine and coarse fraction before the fine fraction with higher concentration of contaminants is treated in an extractor unit where the contaminants are dissolved. The extracted contaminants and the solution are then separated before further treatment. Acid extraction is used for metals and solvent extraction for organically bound metals and organic contaminants. High clay content may reduce extraction efficiency (US-EPA, 1995).

3.2.5 Grain separation

Sieving can be used as a pre-step to soil washing and chemical extraction to reduce the volumes of soil that has to be treated. Before sieving take place it is important to investigate in which fractions the contaminants are concentrated (Swedish EPA, 1999). Usually, the contaminants are concentrated to the clay and silt fraction and to a minor extent also to the sand fraction of a soil. In a bed rock till, stones larger than 100 mm can be outranged, and in well sorted gravelly sand sieving down to 2 mm is common. Factors affecting the sieving are type of soil, water content and organic content. A better separation of the fine fraction is achieved by wet sieving.

3.3 Immobilization methods

The purpose with immobilization methods is to minimize dispersion of the contaminants by reducing their mobility. This can be done physically or chemically. In immobilization methods contaminants are not destroyed (except organic contaminants at vitrification) or removed but their toxic properties can be changed (FRTR, 2002;

Garcia-Sanchez *et al.*, 2002; Iyer and Scott, 2001; Jackson and Miller, 2000; Kumpiene *et al.*, 2006; Lombi *et al.*, 2002; Merrington *et al.*, 2003).

3.3.1 Vitrification

Vitrification is a process when the soil is heated by means of electrodes to temperatures between 1,600 and 2,000 °C in order to achieve a glass like matrix which has very low leachability. Heavy metals are encapsulated while organic contaminants are volatilized or combusted. At those temperatures also some metals e.g. arsenic can volatilize. The off-gases are cached in a vacuum tent and treated by combustion or filtration. The method is suitable for all kinds of soils and can be used both *in situ* and *ex situ* (Swedish EPA, 1999).

3.3.2 Solidification

In solidification cementitious materials as Portland cement, fly ash/lime, and fly ash/kiln dust are mixed into soil to form a solid, resistant, aluminosilicate matrix that can absorb and bind contaminants and reduce the permeability of the material. These methods are preferably used for inorganic contaminants, e.g. CCA (FRTR, 2002) but can be used for other type of contaminants. Soils that have been solidified might be sensitive to changes in moisture and temperature, like freezing and thawing. This might affect the steadiness of the solidification in a long term perspective (US-EPA, 1992). The method can be used both *in situ* and *ex situ*.

3.3.3 Stabilization

Stabilization means that the contaminants in a soil are physically and/or chemically stabilized, but the soil is not reshaped to a solid body. The purpose is to reduce the mobility of the contaminants. An amendment is mixed in to the soil to bind the contaminants and/or transform them to less toxic or mobile species. The stabilization effect is achieved through addition of adsorbing agents, through pH or redox changes or through addition of specific reagents. Common stabilizing agents are polymers, sludge, bentonite clay, fly ash, metal oxides, phosphates and lime (Swedish EPA, 1999). Stabilization can be performed in all kinds of soils but sandy soil makes the mixing easier.

3.3.4 Containment and landfilling

When sealed barriers are built around the contaminated soil it is called containment. It is not strictly a remediation technique but it prevents water and air to get in touch with the contaminants and reduces the dispersion of toxic elements to the environment. As barrier material both natural (e.g. clay) and synthetic material (e.g. geomembranes of plastic or rubber) can be used. Biosludge, fiber sludge and fly ash have also shown to be useful as barrier materials. Barriers can be performed as a sealed cover under, over, or as a vertical shield, around the contaminated soil. It can be used in any type of soil but should be avoided in soils susceptible to settings (US-EPA, 1995).

Contaminated soil which is excavated can also be put on a landfill. To complete the containment of the soil the landfill is sealed with a landfill cap. The design of landfill

caps is site specific and depends on the intended functions of the system. Landfill caps can range from a one-layer system of vegetated soil to a complex multi-layer system of soils and geomembranes. The materials used in the construction of landfill caps include low-permeability and high-permeability soils and low-permeability geosynthetic products. The low-permeability materials divert water and prevent its passage into the waste. The high permeability materials carry water away that percolates into the cap (FRTR, 2002).

3.4 Stepwise remediation

Due to the complexity of contaminants at many sites, single treatment techniques are often insufficient for the treatment. Usually, several techniques are combined in a treatment train. Concentration and separation techniques always have to be combined with destruction or immobilization techniques to complete a remediation.

Even if only a single technique is used, pre-treatment as excavation and size reduction as well as post-treatment of effluents and residuals are usually necessary. Typical post-treatment and residual management necessary in combination with destruction and concentration/separation methods are presented in Table 3.

Table 3 Typical treatment combinations (Haglund, 2007).

Method	Technique	Posttreatment
Destruction	Incineration	APC
		Scrubber effluent treatment/disposal
		Ash treatment/disposal
	Dehalogenation	APC
		Washwater treatment/disposal
		Treated soil treatment/disposal
	Chemical oxidation	APC
		Filtration
	Bio-slurry reactor	Treated soil treatment/disposal
		APC
Process water treatment/disposal		
Composting	Treated soil treatment/disposal	
	APC	
	Incomplete degradation products treatment/disposal	
	APC	
Concentration and separation	Thermal extraction/desorption	APC
		Treated soil treatment/disposal
		Concentrated contaminants treatment/disposal
	Electrokinetic separation	Process water treatment/disposal
		APC
	Soil vacuum extraction/ <i>in situ</i> soil venting	Contaminated groundwater treatment/disposal
		Soil tailings treatment
	Soil washing	Washwater treatment
		APC
		Contaminated solids treatment/disposal
		Wastewater treatment
	Soil flushing	Sludges treatment/disposal
		Flushing liquid/groundwater treatment/disposal
APC		
Chemical extraction	<i>In situ</i> soil treatment	
	Concentrated contaminants treatment/disposal	
	Soil residual treatment/disposal	
		Separated water disposal

4 ASSESSMENT OF TREATMENT TECHNIQUES

The choice of remediation technique always has to be case specific and there are many factors that have to be taken into account when deciding which techniques are suitable. When a contaminated site is remediated there will be an impact on the environment. To selecting the most appropriate technique a validation of environmental impact, recovery efficiency and use of resources (economic resources, energy use and clean soil as a substitute) has to be done.

Some factors that have to be taken into considerations when selecting remediation technique are (Haglund, 2007):

- characteristic of the contaminants
- soil characteristics and groundwater situation
- amount of contaminants
- amount of contaminated soil and spatial distribution
- primary and secondary health and environmental effects
- use of natural resources
- the origin of residual products
- costs
- time frame
- legal requirements
- infrastructure
- future land and water use

Before a suggested technique is implemented laboratory tests, field tests or pilot test should be performed to demonstrate the efficiency and suitability of the technique with respect to that particular situation of contamination.

In situ and on site techniques are often more environmentally friendly than off site techniques, since less transports are needed. In *in situ* techniques the excavation is also excluded. On the other hand *in situ* techniques use to be more difficult to control and monitor.

The US-EPA has suggested a remediation decision tool for wood treatment sites (FRTR, 2002) which is useful in other countries as well. The document is expected to reduce the costs and time required for selection of remediation technique at wood preservation sites.

4.1 Treatment techniques for PAH, PCP and PCDD/F

There are many suitable techniques for remediation of PAHs. The fastest and most reliable method with more than 99.99% removal efficiency (FRTR, 2002) seems to be incineration. It can be used at high concentration levels and it is also suitable for the destruction of PCP and PCDD/F. A disadvantage with the technique is the high energy demand linked to the incineration and the risk of dioxin formation if the process is not maintained properly.

An alternative destruction method is biological treatment. Biological treatment is an established remediation technique for PAHs and PCP and can be performed at lower costs than incineration because of its lower energy demands. Disadvantages are that the method requires more time and the degradation of the contaminants is sometimes difficult to control. Less degradable high molecular PAHs can be left in the soil and toxic by-products can be found. *Ex situ* biological treatment requires shorter time periods than *in situ* treatment and the degradation process is more controlled, because of the ability to homogenize the soil. However, because the soil has to be excavated in *ex situ* treatment it is more costly than *in situ* treatment. Biological treatment has limited applications for degradation of PCDD/F (US-EPA, 1995).

Dehalogenation is a technique that can be useful for treatment of small volumes PCP and PCDD/F contaminated soil. The technique is generally not cost efficient for large soil volumes and high clay and moisture content will raise the remediation costs. The recovery efficiency for PCDD/F is 99% or even higher (US-EPA, 1995).

Many of the chemical oxidation methods are extremely rapid and have high recovery efficiency. Some of the methods are promising for degradation of PCDD/F. On the other hand the process requires large handling of oxidising hazardous chemicals and high energy consumption.

Thermal extraction/desorption is a two step process where the vaporized contaminants need further treatment in e.g. an afterburner. When it is performed at high temperatures the borderline to incineration is very narrow. This means that the technique is also very useful for PAHs, PCP and PCDD/F.

Other commonly used concentration and separation methods suitable for PAHs and PCP are soil washing and chemical extraction. Soil washing is used extensively in Europe but has had limited use in the United States. The costs for soil washing (70-190 USD/cubic meter) is lower than for incineration (910-1,540 USD/cubic meter) although incineration has a better removal efficiency. Soil washing of soils with low content of silt and clay improves the removal efficiency. Soil washing is not suitable for PCDD/F but some methods of chemical extraction are. The costs for chemical extraction are on the same level as the costs for incineration.

Soil flushing is still an innovative technique. The technique can be used to treat PAHs and PCP but it is less cost-effective than alternative techniques for these contaminant groups. It is not useful in soils with high clay content and there is always a risk that the washing solution will remain in the soil.

Other *in situ* techniques useful for PAHs and PCP are vacuum extraction/soil venting and electrokinetic separation. Remedation costs for vacuum extraction/soil venting vary between 400 and 1,500 USD/cubic meter depending on the size of the site, amount and type of contaminants and hydrogeological setting (FRTR, 2002). The overall cost for electrokinetic separation is rather high but it could be useful in low permeable soils for PAHs and PCP. A disadvantage with many *in situ* techniques is the extended clean up time.

Vitrification is a rapid method which has high recovery efficiency for organic contaminants where almost all organics are destroyed in the process. A disadvantage is the high energy consumption, and high moisture content will raise the treatment costs. The function of the method could be "destruction" instead of "immobilization" when used for remediation of organics.

4.2 Treatment techniques for CCA

Destruction techniques are useless for treatment of soil contaminated with CCA. Even if the trace elements are separated and/or concentrated the final treatment step always has to be immobilization. It is very seldom metals are regained in any treatment process.

Soil washing is a well established remediation technique for CCA contaminated soil particularly in Northern Europe. The method seems to be easy to maintain and control and is rather fast. The clean soil can be reused. Energy use is medium compared to other remediation techniques. Facilities designed for both dissolving and concentrating the contaminants offer the best applications to remediate complex mixtures of contaminants. After soil washing a smaller volume of concentrated contaminants need further treatment.

Chemical extraction is also an efficient remediation technique for trace elements but the costs (360-1,720 USD/cubic meter) are often much higher than for soil washing (70-190 USD/cubic meter) .

Soil flushing has not become a commercial method for remediation of CCA. The washing solution might stay in the soil and contaminate the ground water. Also, it is not suitable in areas of cold climate when there is a risk of frost in the ground and deep freezing of the washing solution.

If the contaminated soil has low permeability e.g. high content of clay and silt electrokinetic separation could be an interesting alternative to soil washing, which is not suitable for that type of soils.

Among immobilization methods, solidification and stabilization are well established methods especially in the United States. It is also the recommended method for treatment of CCA contaminated soil in the US . In other countries legislations might be a hindrance for the establishment of certain *in situ* methods since the contaminants remain in the soil at same levels as before the remediation took place, even if their mobility and bioavailability is reduced. In many countries the soil treatment efficiency is assessed by the total concentration of the trace elements remaining in the soil after treatment.

Because solidified soil is sensitive to freezing and thawing the method has limited use in cold climates. Future land use may also affect *in situ* solidification and mobilize the contaminants again.

Vitrification which is a type of solidification reduces the bioavailability of the contaminants very effective when the metals are incorporated in the glass mixture. The

method is highly energy demanding especially in *in situ* vitrification but could be a possible final treatment step of highly contaminated remains from e.g. soil washing.

It is difficult to find one stabilizing agent suitable for all target elements in CCA. *In situ* stabilization with zerovalent iron is an innovative technique for immobilization of arsenic and chromium but the effect for stabilization of copper is less effective. If pH increasing agents e.g. ashes or cementitious material are used for stabilization or if the redox potential in the soil decreases the mobility of arsenic can increase.

4.3 Treatment techniques for co-contaminated soil

The contamination situation at wood preservation sites is often rather complicated with a mixture of different contaminants, both organic (creosote, PCP, PCDD/F) and inorganic (CCA) in the same place. If that is the case the soil has to go through two or more treatment steps to be remedied. There are only a few techniques that can remedy both types of contaminants and then often not at the same time. Which method ever is used it always has to be combined with an immobilization method in the end.

Three main treatment sequences are possible for remediation of co-contaminated soil (Figure 1). It is impossible to say which combination is the best. The choice of combination has to be case specific.

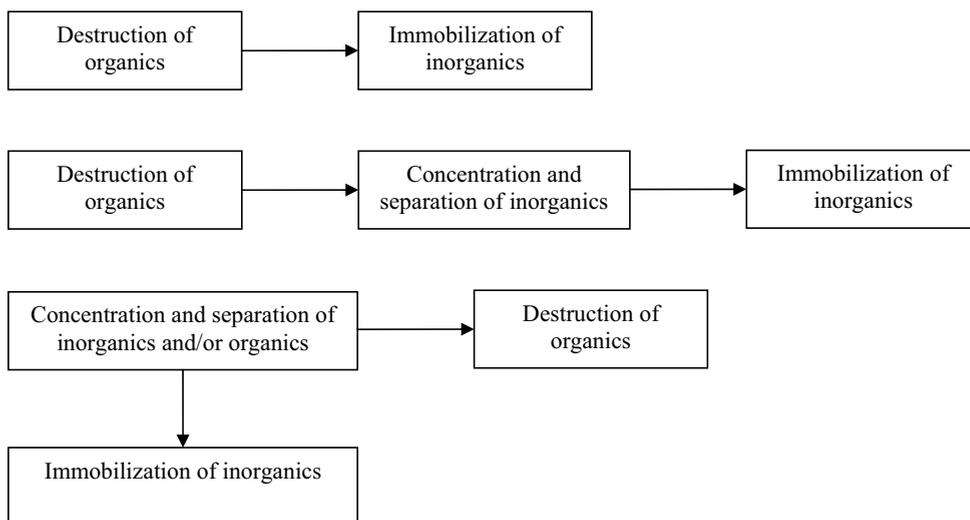


Figure 1 Treatment sequences for co-contaminated soil.

US-EPA has worked out guidelines for remediation of contaminated soil from wood preservation sites. If a contaminated site contains CCA and creosote and/or PCP the recommendation is to first treat the organic contaminants with bioremediation, thermal desorption and incineration in above mentioned priority order and then treat the inorganic contaminants with immobilization in a so called treatment train.

Although there are a lot of different remediation techniques still the most common technique in Sweden for these types of sites is excavation and landfilling. Some reasons could be tight time frames for the remediation; the future land use of the site and it also take care of the environmental risks associated with site cleanup.

Even if the chosen technique is excavation and landfilling, pre-treatment of the soil might be necessary if the contamination level is too high to fulfil the leaching limit values stipulated by the Council of European Union (EC, 2003) for acceptance of waste to landfills.

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PAPER II

Nordmark, D., Kumpiene, J., Lagerkvist, A. (in manuscript). Mobility and fractionation of arsenic, chromium and copper in thermally treated soil.

Mobility and fractionation of arsenic, chromium and copper in thermally treated soil

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Abstract

Thermal treatment processes cause changes in soil characteristics like mineral face transitions and organic matter (OM) content, factors that in turn affect e.g. redox potential and pH in the soil. These are factors that are important for the mobility of trace elements such as As, Cr and Cu. The objective of this study was to evaluate effects of thermal treatment on the mobility and chemical fractionation of As, Cr and Cu in a CCA-contaminated soil. The soil was sieved into different particle size fractions (< 0.125; 0.125-0.250; 0.250-0.500; 0.500-1 mm and a bulk fraction < 10 mm) and treated at 800 °C. The highest concentration of As, Cr and Cu, composing up to 70% of the total element amounts, were in the < 0.125 mm fraction. The treatment changed the element solubility. Based on the leaching test results the mobility of As and Cr increased due to thermal treatment, while the mobility of Cu decreased. The amount of As, Cr and Cu associated to the reducible fraction by chemical sequential extraction analysis decreased after thermal treatment, probably due to enhanced crystallisation of Fe oxides in the soil. Mainly As but also a small amount Cr associated to the more easily soluble exchangeable fraction, while Cu and a large amount of Cr associated to the less soluble residual fraction.

Keywords: soil remediation, inorganic contaminants, sequential extraction, arsenic speciation.

1. Introduction

Soil contamination with various chemicals is common in wood preservation industrial sites. Types of preservatives have changed throughout the years leading to an occurrence of mixed organic (creosote and pentachlorophenol) and inorganic (arsenic, chromium and copper) contaminants in soil. These substances can cause severe environment problems and is a risk to the human health.

There are a lot of different techniques available for remediation of contaminated soil. Most of them are only suitable for soil contaminated with organic or inorganic substances, one at the time, and not when both types of contaminants are present simultaneously. Thermal treatment with combustion of the off-gases in an afterburner is a common destruction method to remediate soil contaminated with organic compounds. Using thermal treatment for mixed contaminated soil, inorganic contaminants such as arsenic (As), chromium (Cr) and copper (Cu), which can not be destroyed, could instead be concentrated and separated from the bulk soil. The soil treated in a rotating kiln, for

example, is separated into at least two residual streams consisting of different particle sizes (NFESC, 1998).

Many investigations have been performed indicating that trace elements are accumulated in the finest particle size fractions of soil (Hartyani *et al.*, 2000; Smith *et al.*, 2006). Therefore it is expected that inorganic contaminants in the thermally treated soil would concentrate in the residual streams caught by cyclones and bag filters (fine fractions) and become depleted in the main residual stream.

Thermal treatment processes cause changes in soil characteristics like mineral face transitions and organic matter (OM) content, factors that in turn affect e.g. soil redox potential and pH. These are factors that are important for the mobility of elements like As, Cr and Cu.

The objective of this study was to evaluate effects of thermal treatment on the fractionation and mobility of As, Cr and Cu in a contaminated soil.

2. Materials and methods

2.1. Soil and thermal treatment

The soil used in the experiments originated from a former wood treatment industrial site situated in Robertsfors municipality in Northern Sweden. The soil was contaminated with wood impregnation chemical CCA K33, containing 27wt.% chromium(VI) oxide (CrO_3), 17wt.% copper(II) oxide (CuO) and 34wt.% arsenic(V) oxide (As_2O_5). The soil was excavated during the remediation of the contaminated site and transported for a temporary storage prior to disposal at landfill. About 50 kg of soil was collected from the storage site for the experiments. The soil was dried at 25 °C in a ventilated heating cabinet to a constant weight, homogenized, divided into sub-samples using a riffle splitter and sieved to < 10 mm. Determination of particle size distribution of the soil (< 20 mm) was done according to Swedish standard SS 27123 (SIS, 1992).

One sub-sample of the soil (22 kg) was separated into four size fractions (< 0.125; 0.125-0.250; 0.250-0.500 and 0.500-1 mm) through dry sieving according to ASTM E11-70 and ISO 3310. About 500 g of each fraction (one fraction at a time) was thermally treated at 800 °C for 20 minutes in stagnant air using Carbolite Furnaces (CSF 1200). A porcelain bowl (ø20 cm) was used as a soil container. Soil after the treatment was cooled to room temperature and stored in a desiccator before analyses.

Extracts for determination of pseudo-total element concentrations (hereafter called total concentrations) in untreated and thermally treated soil fractions and bulk soil (< 10 mm) were prepared by digestion of 1 g of soil in 10 mL *aqua regia* ($\text{HCl}:\text{HNO}_3=3:1$) using a microwave digester (CEM Microwave Sample Preparation System, Model Mars 5).

2.2. Batch leaching test

One-step batch leaching tests were performed on both untreated and thermally treated soil fractions at a liquid to solid ratio of 10 L/kg dry matter (L/S 10) according to EN 12457-2 (CEN, 2002), scaled to fit reduced sample sizes. The samples were agitated in

deionised water in 500 mL high dense polyethylene (HDPE) bottles on a rotating device for 24 h, filtered and stored at 4 °C prior to analyses.

2.3. Arsenic speciation

The finest fraction (< 0.125 mm) of treated and untreated soil (100.0 g dw) was packed into wide opened plastic bottles (ø6 cm) containing soil moisture samplers and moistened with deionised water to reach 23% of soil humidity level. Soil pore water was extracted five days later using 5 cm Rhizon soil moisture samplers (Eijkelkamp, the Netherlands) connected to 30 mL glass vacuum bottles. Samples were stored at 4 °C before As speciation analyses.

Arsenic speciation into As(III) and As(V) was done by ion chromatography followed by inductively coupled plasma mass spectrometry (IC-ICP-MS). Detection limit for As(III) was 0.4 µg kg⁻¹ and for As(V) 0.6 µg kg⁻¹.

2.4. Sequential extraction

A sequential chemical extraction procedure according to Tessier *et al.* (1979) was performed to operationally define four elemental fractions in both treated and untreated soil: (I) exchangeable; (II) acid-soluble; (III) reducible and (IV) oxidisable fractions. A fifth residual fraction was determined through digestion of the residue from the fourth extraction in *aqua regia* using a microwave digester.

2.5. Analyses

The content of total solids (TS) and loss on ignition (LOI) on the bulk soil (< 10 mm) and the untreated soil fractions were determined according to Swedish standard SS 28113 (SIS, 1981) at 110 °C and 550 °C, respectively. Water holding capacity of the soil (<10 mm) and the soil fraction (< 0.125 mm) was determined gravimetrically as the remaining water in saturated soil after drainage (Shinner *et al.*, 1996). Electrical conductivity (EC), pH and redox potential (E_h) of soil were determined in soil-deionised water suspensions (1:2 w:v) after 30 min of mixing. Digestates, leachates and extracts for element concentrations were filtered through 0.45 µm syringe filters, acidified with nitric acid when necessary and analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2000 DV). Total organic carbon (TOC) of the soil fractions was analyzed using a TOC-SSM-500A (Shimadzu Corporation) according to European standard EN 13 137 for determination of TOC (CEN, 2001). Dissolved organic carbon (DOC) in leachates was analyzed using TOC-VCPPH/CPN (Shimadzu Corporation) according to the European standard EN 1484 for water analysis of TOC and DOC (CEN, 1997).

2.6. Statistical analysis

The two-sample t-test ($p < 0.05$) was used to determine statistical differences between the sample means.

3. Results

3.1. Principal characteristics of soil

According to the particle size distribution (Fig. 1) of the bulk soil (Table 1), the soil is classified as a silty sand with 2% clay (< 0.002 mm), 25% silt (0.002-0.06 mm), 58% sand (0.06-2 mm) and 15% gravel (2-20 mm). The fractions < 0.125, 0.125-0.250, 0.250-0.500 and 0.500-1.0 mm represented 46, 13, 12 and 7% respectively of the total soil weight. The fraction < 0.125 mm consisted of 41% sand, 54% silt and 5% clay.

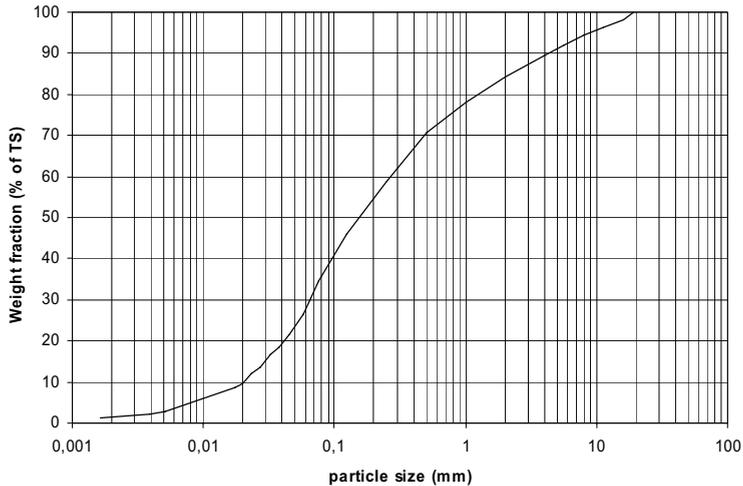


Fig. 1. Particle size distribution of CCA-contaminated soil (< 20 mm) with the composition of 2% clay (< 0.002 mm), 25% silt (0.002-0.06 mm), 58% sand (0.06-2 mm) and 15% gravel (2-20 mm).

Table 1

Principal characteristics of bulk soil (< 10 mm) (\pm SD, $n=3$).

Soil properties	Unit	Value
pH	-	6,9
EC	$\mu\text{S cm}^{-1}$	708
E_h	mV	457
TS	g kg^{-1}	994
LOI	wt.%	2,3
WHC	wt.%	26
As	mg kg^{-1} dw	266 \pm 39
Cr	mg kg^{-1} dw	123 \pm 30
Cu	mg kg^{-1} dw	66 \pm 5

The highest total concentration of As, Cr and Cu was in the < 0.125 mm fraction both before and after soil treatment (Table 2). An exception was As in the thermally treated soil, where no statistically significant difference was observed between the <0.125 mm fraction and the 0.500-1.0 mm fraction ($p < 0.05$). In the untreated soil, the distribution of As, Cr and Cu in the particle size fractions was < 0.125 mm >> 0.125-0.250 mm \geq 0.250-0.500 > 0.500-1.0. The concentrations were about twice as high in the finest fraction than in any other soil fraction. In the treated soil, concentrations of the studied

elements in the particle size soil fractions decreased in the following order: $< 0.125 \text{ mm} > 0.500\text{-}1.0 \text{ mm} > 0.250\text{-}0.500 > 0.250\text{-}0.500$.

When total concentrations of As, Cr and Cu in the different particle size fractions were related to the particle size distribution of the bulk soil ($< 10 \text{ mm}$), 64, 61 and 69% of the elements respectively were in the $< 0.125 \text{ mm}$ fraction (Fig. 2).

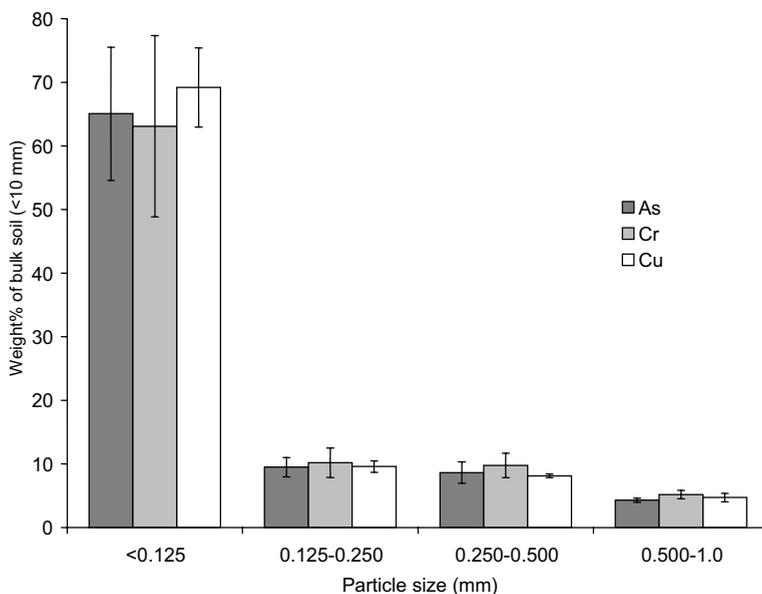


Fig. 2. Distribution of As, Cr and Cu between the untreated particle size fractions: < 0.125 ; $0.125\text{-}0.250$; $0.250\text{-}0.500$ and $0.500\text{-}1.0$ of bulk soil $< 10 \text{ mm}$.

In the untreated soil fractions pH varied between 6.0 and 6.9 while it increased when the soil was thermally treated and varied between 7.6 and 8.8 (Table 2). Electrical conductivity decreased after thermal treatment in the $< 0.125 \text{ mm}$ and $0.125\text{-}0.250 \text{ mm}$ fractions while it increased in the $0.250\text{-}0.500$ and $0.500\text{-}1.0 \text{ mm}$ fractions. Redox potential showed oxidised conditions in both untreated and treated soil fractions. Organic matter (OM) content measured as LOI was highest (3.0%) in the $< 0.125 \text{ mm}$ fraction and lowest (1.2%) in the $0.500\text{-}1 \text{ mm}$ fraction (Table 2). TOC of the treated soil decreased in all fractions compared to the untreated soil with the lowest reduction (23%) in the $< 0.125 \text{ mm}$ fraction and the highest reduction (93%) in the $0.250\text{-}0.500 \text{ mm}$ fraction.

Table 2

Principal characteristics of untreated and thermally treated soil fractions (\pm SD, $n=3$).

Soil properties	Unit	Untreated soil				Soil treated at 800 °C			
		< 0.125	0.125-0.250	0.250-0.500	0.500-1.0	< 0.125	0.125-0.250	0.250-0.500	0.500-1.0
		mm				mm			
pH	-	6.8	6.2	6.0	6.0	8.8	7.6	7.7	8.5
EC	$\mu\text{S cm}^{-1}$	1056	508	253	164	847	422	443	317
E _h	mV	447	420	422	434	427	418	433	438
TS	g kg^{-1}	992	996	996	997	1000	1000	1000	1000
LOI	wt. %	3.0	1.7	1.6	1.2	ND	ND	ND	ND
TOC	wt. %	0.51	0.32	0.83	0.70	0.39	0.05	0.06	0.06
Total element concentration									
As	mg kg^{-1} dw	352 \pm 7	191 \pm 4	179 \pm 23	148 \pm 33	359 \pm 2	187 \pm 3	187 \pm 23	297 \pm 82
Cr	"	155 \pm 2	93 \pm 2	93 \pm 15	82 \pm 22	158 \pm 1	89 \pm 4	83 \pm 8	108 \pm 4
Cu	"	94 \pm 1	49 \pm 1	43 \pm 5	40 \pm 6	76 \pm 1	35 \pm 1	33 \pm 2	45 \pm 3

ND=Not determined

3.2. Leaching test

The leaching of As and Cr increased due to thermal treatment whilst the mobility of Cu decreased (Fig. 3). The leaching of Fe also decreased in thermally treated soil compared to untreated soil.

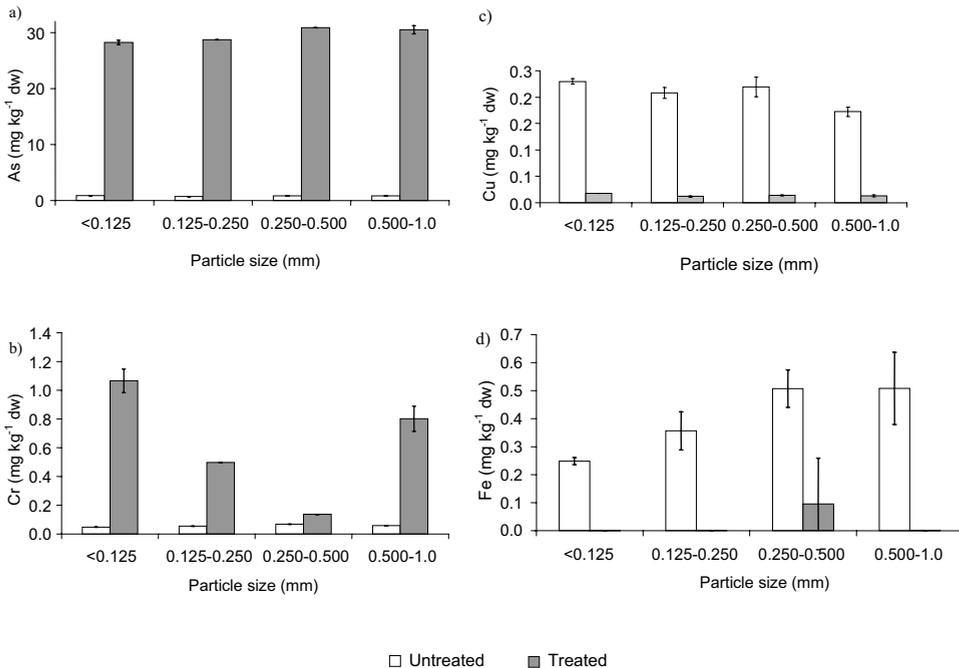


Fig. 3. Leaching of a) As, b) Cr, c) Cu and d) Fe in soil at L/S 10, before and after thermal treatment at 800 °C.

Comparing the leaching of As, Cr and Cu to leaching limit values (L/S 10) stipulated by the Council of European Union (EC, 2003) for acceptance of waste to landfills (Table 3), the leaching of As from the treated soil exceeded the limit value ($25 \text{ mg (kg dw)}^{-1}$) for waste acceptable at landfills for hazardous waste. Before thermal treatment the same soil would have been accepted at a landfill for non-hazardous waste due to the leaching of As.

Table 3

Leaching limit values (L/S 10) stipulated by the Council of European Union for acceptance of waste to landfills for inert, non-hazardous and hazardous waste.

Element	unit	Limit values		
		inert	non-hazardous	hazardous
As	mg (kg dw)^{-1}	0.5	2	25
Cr	mg (kg dw)^{-1}	0.5	10	70
Cu	mg (kg dw)^{-1}	2	50	100

The leaching of As from soil fractions of thermally treated soil increased between 18 (0.500-1.0 mm) and 40 (0.125-0.250 mm) times compared to untreated soil. For Cr the leaching was between 2 (0.250-0.500 mm) and 23 (< 0.125 mm) times higher from the thermally treated soil fractions. For Cu the leaching decreased more than 13 times for all fractions of thermally treated soil. In table 4 the relative leaching of As, Cu and Cr compared to their total concentrations in the different soil fractions before and after thermal treatment are presented.

Table 4

Relative leaching of As, Cr and Cu from untreated and treated soil fractions at L/S 10 in percent of the total concentration in the respective soil ($n=3$).

Soil fraction	Leaching of total element concentration		
	As	Cr	Cu
mm		%	
Untreated soil			
< 0.125	0.25	0.03	0.24
0.125-0.250	0.38	0.06	0.43
0.250-0.500	0.47	0.07	0.51
0.500-1	0.56	0.07	0.43
Soil treated at 800 °C			
< 0.125	7.86	0.68	0.02
0.125-0.250	15.4	0.56	0.03
0.250-0.500	16.5	0.16	0.04
0.500-1	10.3	0.74	0.03

The dissolved organic carbon (DOC) in leachate from untreated soil was $179 \pm 4 \text{ mg l}^{-1}$ (< 0.125 mm); $80 \pm 2 \text{ mg l}^{-1}$ (0.125-0.250 mm) and $53 \pm 1 \text{ mg l}^{-1}$ (0.250-0.500 mm) respectively. In the thermally treated soil the DOC leaching was $3.0 \pm 2.2 \text{ mg l}^{-1}$ (< 0.125 mm); $1.1 \pm 0.5 \text{ mg l}^{-1}$ (0.125-0.250 mm) and $0.7 \pm 0.2 \text{ mg l}^{-1}$ (0.250-0.500 mm).

3.3. Arsenic speciation

In the untreated soil (< 0.125 mm) the amount of As(III) and As(V) were 23 ± 1 $\mu\text{g/L}$ and 35 ± 1 $\mu\text{g/L}$ respectively and in the thermally treated soil (< 0.125 mm) the amount were 26 ± 4 $\mu\text{g/L}$ and 655 ± 18 $\mu\text{g/L}$ respectively ($\pm\text{SD}$, $n=3$).

3.4. Sequential extraction

The pattern of extractable As (mean of $n=3$) between the five operationally defined elemental fractions in the sequential extraction were similar in all untreated and treated particle size fractions respectively (Fig. 5a). The dissimilarities were between untreated and treated soil fractions, especially in step I, II and III. The weight share of As associated to the reducible fraction (III) decreased by 24.2-34.9 percentage points (pp) after thermal treatment of the soil. At the same time, the weight share of As in the acid-soluble fraction (II) increased by 18.5-22.0 pp and in the exchangeable fraction by 8.6-14.3 pp after thermal treatment.

The partition of Cr between defined elemental fractions changed in a similar way in all particle size fractions when the soil was treated at 800 °C (Fig. 5b). The largest translocation of Cr was from the reducible fraction to the residual fraction (by 42.2-57.0 pp).

A repeatable pattern in the extraction of Cu (Fig. 5c) was obvious between the different particle size fractions in the untreated soil. In the treated soil there were large differences between the soil fractions, especially in step III and IV. In the < 0.125 mm fraction the weight share of Cu in the oxidisable fraction (IV) increased with 30.2 pp while it decreased by 8.1-19.0 pp in the other fractions. The weight share of Cu in the residual fraction (III) increased after thermal treatment in all particle size fractions but the variations were large. In the exchangeable fraction (I) the weight share of Cu decreased by 1.4-6.4 pp in all particle size fractions after thermal treatment.

About 80% of the Fe concentration in all particle size fractions was associated to the residual fraction (V) with a small increase after thermal treatment (Fig. 5d). All other elemental fractions decreased after thermal treatment. The weight share of Fe associated to the residual fraction (III) decreased with increasing grain size both in treated and untreated particle size fractions.

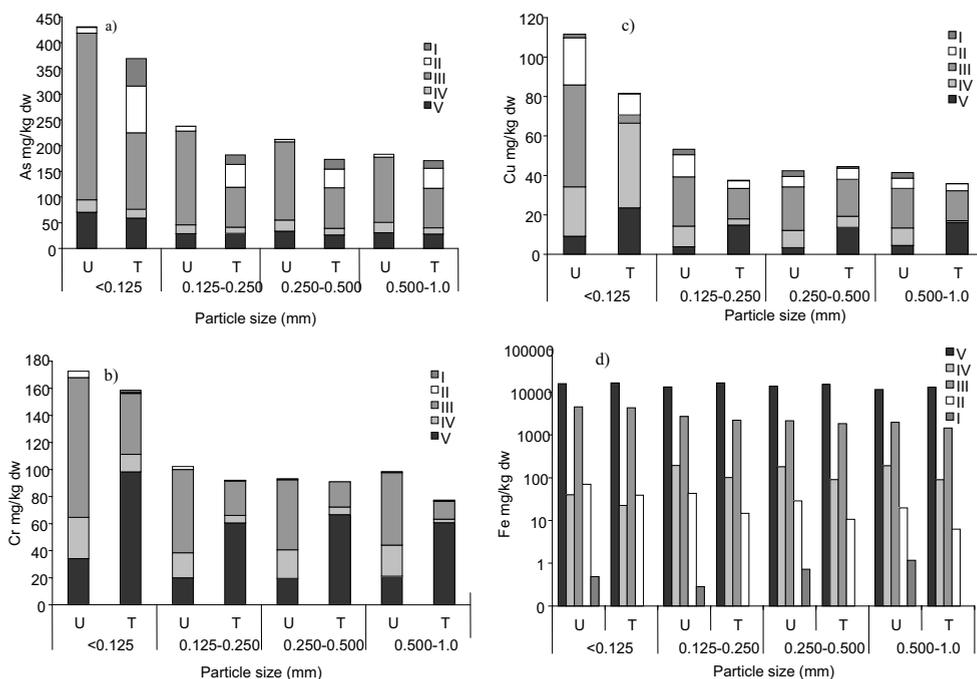


Fig. 5. Fractional distribution of As, Cr, Cu and Fe in untreated (U) and thermally treated (T) particle size fractions. (mean of $n=3$). Fractions: I = exchangeable, II = acid-soluble, III = reducible, IV = oxidisable and V = residual.

4. Discussion

4.1. Particle size separation

It is not possible to obtain distinct soil particle fractions by dry sieving. Fine material is always attached to the coarser particles and will not be separated by dry sieving. Because the finest fraction (< 0.125 mm) had the highest concentration of As, Cr and Cu the result of total element concentrations of the different particle size fractions will be affected, with an overestimation of the concentrations in all the coarser fractions. Even the results from the leaching tests and the sequential extraction test will be affected to some extent of this fact.

In other investigations (Hartyani *et al.*, 2000; Lombi *et al.*, 2000; Smith *et al.*, 2006) of trace element concentrations in different particle size fractions of a soil, wet sieving combined with centrifugation has been used, as described by Genrich and Bremner (1974). With that method easily extracted elements can be allocated from the coarser fractions to the finest remaining fraction, whilst the concentration of trace elements can be underestimated in the coarser fraction and overestimated in the finest remaining fraction. Lombi *et al.* (2000) found that even when wet sieving according to Genrich and Bremner (1974) was used for particle size separation of five Austrian soils, the silt fraction (63-2 μm) contained 3-5% clay-sized particles (< 2 μm). When using a similar

separation technique, Stemmer *et al.* (1998) found 2-5% clay-sized particles ($< 2 \mu\text{m}$) in the silt fractions (63-2 μm).

4.2. Distribution of As, Cr and Cu between particle size fractions in untreated soil

The highest concentrations of As, Cr and Cu in the untreated soil were in the $< 0.125 \text{ mm}$ fraction which consisted of 41% sand, 54% silt and 5% clay. It is most likely that the clay particles within the $< 0.125 \text{ mm}$ fraction hold the highest concentrations of trace elements. Several researchers have reported that trace elements such as As, Cr and Cu are enriched in the clay fraction in contaminated soils (e.g. Lombi *et al.*, 2000; Qian *et al.*, 1996), although Yarlagadda *et al.* (1995) did not find the highest concentration of Cu in the clay fractions in three different soils contaminated with hazardous waste, instead Cu was randomly distributed. Lombi *et al.* (2000) reported that the concentration of As was 1.9-7.6 times higher in the clay fraction compared to the silt fraction and 2.2-18 times higher compared to the sand fraction of contaminated soil. Clays have a large sorption capacity of trace elements due to great specific surface and more adsorption sites than coarser fractions as silt and sand. However, the clay fraction does not only consist of clay minerals, but also of oxides and hydroxides of Fe, Mn and Al and of organic matter, while the sand and silt fraction mostly consists of silica. Trace elements are mainly associated to all mentioned constituents of the clay fraction.

By separating the soil in particle size fractions, trace elements has been concentrated in the finest fraction which composes 46 wt% of the bulk soil. The soil fraction $\geq 0.125 \text{ mm}$ has become less contaminated with lower total concentration of As, Cr and Cu than in the initial bulk soil.

4.3. Thermal treatment of soil fractions – total concentrations

After the soil had been treated at $800 \text{ }^\circ\text{C}$, some of the total concentrations of the different particle size fractions differed from values measured before thermal treatment. The total concentrations of As and Cr were lower before thermal treatment in the 0.500-1.0 mm fraction then after, and the total concentration of Cu was higher before thermal treatment in the fractions $< 0.125 \text{ mm}$, 0.125-0.250 mm and 0.250-0.500 mm then after (Table 2). There is probably more than one explanation to the differences. Eddings *et al.* (1994) describes several primary mechanisms that can affect the fate of a metal contaminant at incineration, namely: remaining in the soil; entrain with other particulate matter; react and form other species that may remain in the ash (soil) or vaporize, or the metal can vaporize. If the metal vaporizes it can condense on fly ash.

A weight loss of the particle size fractions are expected due to combustion of OM, even if remains of soot and elemental carbon can be left in the soil, equal to the fraction of TOC after thermal treatment (Table 2). A disadvantage of the standard method EN 13 137 for determination of TOC is that not only organic carbon is analyzed as TOC, as discussed in Ecke and Svensson (2008), but also elemental carbon. Elemental carbon is non-reactive and does not participate in biological processes in a soil.

The particular soil used in this experiment had an average amount of OM measured as LOI with the highest concentration in the $< 0.125 \text{ mm}$ fraction (3.0%). This could

theoretically make remaining elements up to 3.1% more concentrated by weight after thermal treatment.

High temperatures enhances the volatilization of arsenic which would result in a decrease in the As concentration after thermal treatment at 800 °C. Equilibrium composition for As show that As is totally in gas phase, with AsO(g) as the most stable species, at temperature > 500 °C (Díaz-Somoano *et al.*, 2006). However, even if there is a decrease in the As concentration, it is not statistically significant in this case. Gray *et al.* (2001) reported an increasing volatility of As from a contaminated kaolin clay at temperatures above 900 °C in oxic atmosphere which is also consistent with data from an experiment performed by Thurnau and Fournier (1992), with incineration of a synthetic waste and a Superfund soil contaminated with As.

Another explanation of the observed differences in total trace element concentrations before and after thermal treatment could be due to the method used for soil digestion. Only pseudo-total concentrations were measured, and thermal treatment can affect the trace elements and make them more recalcitrant to the digestion solution. This fact is observed when HNO₃-based digestion is used for recovering of trace elements from thermally treated soil (Eddings *et al.*, 1994; Gao and Silcox, 1993; Ho *et al.*, 1995)

4.4. Leaching and fractionation of As, Cr and Cu

The finest particle size fraction had the lowest relative leaching of As, Cr and Cu before thermal treatment (Table 3) which also has been observed by Qian *et al.* (1996). They investigated the extractable amount of Cu from five particle size fractions from seven soils and in five of them the concentration of copper was the highest in the fine sand fraction (50-125 µm) although it was the clay fraction that had the highest total concentration of Cu. Because of finer soils large surface area and high amount of binding sites they are known to be less toxic than coarser soils with lower binding strength as sands.

Mobility of As increased after thermal treatment which applied to all particle size fractions. This effect has also been viewed by Thurnau and Fournier (1992) although they were using the TCLP (Toxicity Characteristic Leaching Procedure) method with acetic acid as extractant. The speciation of As indicates that the amount of As(III) in the finest soil fraction remained almost constant after thermal treatment, while the amount of As(V) increased 19 times. The elevated levels of As(V) after thermal treatment could be a result of crystallization of amorphous Fe oxides and a reduction of available binding sites for As(V). As has a high affinity to Fe-oxides in native soil but at high temperatures the crystallinity of the oxides increases (Sørensen *et al.*, 2000). And as observed from the sequential extraction test, trace elements bound to the reducible fraction (III) decreased due to thermal treatment and were allocated to other chemical fractions.

Cr also showed an increased mobility after thermal treatment. It is consistent with results from (Wei and Hsieh, 2006). They observed an increased leaching (TCLP method) of Cr from a synthetic chromium containing soil when it was heated to 500 °C compared to 105 °C. When the soil was heated to 1100 °C the leaching decreased below 105 °C levels. Wei and Hsieh suggests that at 500 °C most of the Cr is in the form of

Cr₂O₃ because Cr(VI) is reduced to Cr(III) at 250 °C. The increased leaching of Cr after thermal treatment at 900 °C of fly ash from municipal solid waste incineration (MSWI) has been observed by Kirk *et al* (2002). They proposed a mechanism for the elevated mobility after thermal treatment. When synthetic Cr₂O₃ were thermally treated together with CaO the leaching of Cr with water as extractant increased. In the CaO treated soil, calcium chromate (CaCrO₄) was revealed with XRD. CaCrO₄ is a soluble species which could count for the elevated leaching at 800 °C. Other researchers has suggested chromate formation at high temperatures in Cr-containing sludge (Shoto and Hattori, 1980). Most of the Cr is found in the residual fraction after thermal treatment. At high temperatures Cr forms Cr-silicates which are found in the residual fraction. The organic fraction is reduced because of reduction of organic matter at the thermal treatment. The same finding were reported from Obrador *et al* (2001) when Cr-contaminated sediments were thermally treated at 400 °C.

The decrease in mobility of Cu from contaminated soil after thermal treatment has been described by others. Wei *et al.* (2001) found that Cu(OH)₂ was transformed to CuO and CuO-associated species, with less solubility, when Cu-doped soils (SiO₂ and kaolin) were thermally treated at 300-900 °C. The amount of Cu increases in the residual fraction after thermal treatment. Because of the destruction of OM at thermal treatment, As, Cr and Cu associated with the oxidisable fraction (IV) decreased, except for Cu in the finest fraction (< 0.125 mm) where the amount of Cu bound to the oxidisable fraction increased instead with 30.2 pp after thermal treatment, although the content of TOC decreased with 23%. Tack and Verloo (1993) suggests that changes of binding strength within the fractions has to be considered instead of associations to chemically defined fractions.

5. Conclusions

The highest concentrations of As, Cr and Cu in a CCA-contaminated soil were in the finest particle size fraction (< 0.125 mm). When the trace element concentrations were combined with the particle size distribution of the CCA-contaminated soil, more than 60% of As, Cr and Cu were found in the < 0.125 mm fraction. The thermal treatment at 800 °C affected the mobility of As, Cr and Cu; leaching of As and Cr increase, while the leaching of Cu decreased. As, Cr and Cu associated to the residual fraction decreased after thermal treatment while As associated to the exchangeable and acid-soluble fraction, Cr associated to the exchangeable and residual fraction and Cu associated to the residual fraction increased. The results from the thermal treatment experiment indicate that using the technique as a contaminant concentration method in soil, the concentrated residual fraction has to undergo further treatment before landfilling.

6. Acknowledgement

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PAPER III

Rönkkö, R., Nordmark, D., Kumpiene, J., Lagerkvist, A. (2007) Metal balance in thermal treatment of CCA-contaminated soils. *Tenth International Symposium on Environmental Issues and Waste Management in Energy and Mineral Production (SWEMP 2007)*, Bangkok, Thailand.

Metal balance in thermal treatment of CCA-contaminated soils

Reima Rönkkö, Désirée Nordmark, Jurate Kumpiene & Anders Lagerkvist

Introduction

Chromium, Copper and Arsenic (CCA) are common contaminants in soils affected by wood impregnation operations (Pellerin and Booker 2000; Oremland and Stolz 2003). They also pose a serious threat to the environment and to the health of humans and animals. A common remediation technique for these sites is excavation and land filling of the soil, which causes a lot of transportation and unnecessary negative environmental effects.

Thermal treatment is one of many remediation methods for polluted soil. Directly it cannot remove metalloid impurities from soil, but there was an assumption that the CCA-compounds ends to the fine particle fraction. This particle fraction is removed from the air flow by cyclone- and bagfilters. That way the soil that is coming out of the furnace, should have relatively low CCA-concentrations. One very interesting factor was how to control arsenic volatility during the remediation process (Thurnau and Fournier 1992; Sadiq 1997; Deborah B. Gray 2001). Volatilisation of arsenic also poses serious occupational risk during thermal treatment.

The leaching of the CCA-components before and after the burning tests was also studied. It is one of the most important factors deciding the treatment method of fine particle fraction.

Original purpose was to produce the data in two stages: laboratory tests and field experiments. But difficulties in the process to get the licence for transporting polluted soil from Sweden to Finland, we manage to do only laboratory analysis in time.

Materials and methods

Soil samples

Soil that has been used in this experiment comes from an old wood impregnation plant in Robertsfors, Sweden.

The soil was dried at room temperature and sieved into different size fractions (<0,125; 0,125-0,250; 0,250-0,500; 0,500-1 mm and a bulk fraction <10 mm) with sieves according to ASTM E11-70 and ISO 3310.

Particle size distribution of the soil was performed according to Swedish standard (SS 02 71 23).

For heat treatment of soil at 800°C for 20 minutes a Carbolite Furnaces CSF 1200 was used. After heat treatment the soil was cooled to room temperature in a desiccator before analysis.

Total element concentration on both untreated and heat treated soil was done by digestion of 1g of soil in 10 ml *aqua Regia* solution using a micro wave digester (Mars 5). Then the solution was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2000 DV).

Leaching tests were performed at a liquid to solid ratio of 10 (L/S 10) according to EN 12457-2 on both untreated and heat treated soil. The samples was shaken for 24 h and then filtered through 45µm nitrocellulose membrane filter. Chemical analysis of elements in leachates was performed by inductively coupled plasma optical emission spectroscopy (Perkin Elmer Optima 2000 DV).

Results and discussion

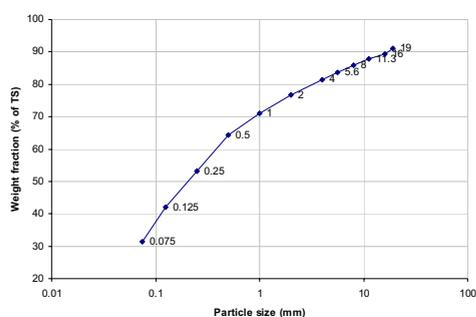


Figure 1: Sieving curve of the material.

The distribution of pollutants between different size fractions before and after heating tests is shown in figure 2. That supports the main presumption, but must be confirmed by the field

A sieving curve of the soil is presented in figure 1. In the curve can be seen that over 40 % of particles in the sample are smaller than 0.125 mm, which is the size of the particles that goes into filter part of the thermal treatment facility.

The soil sample was sieved into five different size fractions. Chemical analysis results of the different fractions before and after heating tests shows that the main metal concentrations are in the finest

experiments.

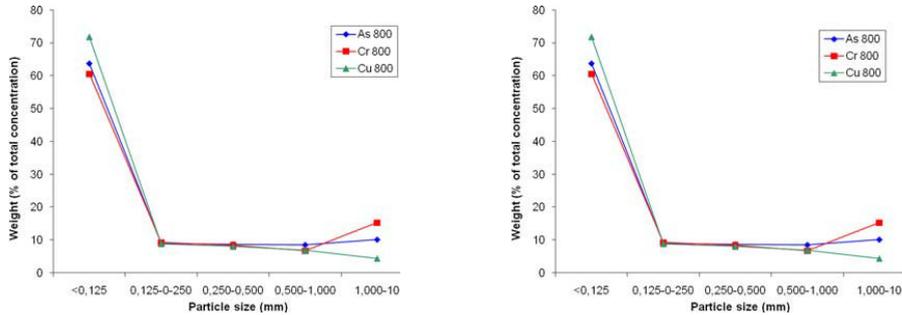


Figure 2: Distribution copper, chromium and arsenic in different particle size fractions before (left fig.) and after (right fig.) thermal treatment.

Leaching tests for the material are also performed before and after heating. Total elemental analysis and analysis results from leachates are presented in table 1.

Table 1: Total elemental analysis and analysis results of leachates (L/S 10), \pm SD, n=3.

	Total concentration			L/S 10			Leaching from total concentration		
	mg kg ⁻¹ dw			mg kg ⁻¹ dw			%		
Untreated	As	Cr	Cu	As	Cr	Cu	As	Cr	Cu
<0,125 mm	352 \pm 7	155 \pm 2	94 \pm 1	0,87 \pm 0,02	0,048 \pm 0,001	0,23 \pm 0,01	0,25	0,03	0,24
0,125-0-250 mm	191 \pm 4	93 \pm 2	49 \pm 1	0,72 \pm 0,02	0,054 \pm 0,002	0,21 \pm 0,01	0,38	0,06	0,43
0,250-0,500 mm	179 \pm 23	93 \pm 15	43 \pm 5	0,84 \pm 0,04	0,068 \pm 0,003	0,22 \pm 0,02	0,47	0,07	0,51
0,500-1 mm	148 \pm 33	82 \pm 22	40 \pm 6	0,83 \pm 0,08	0,058 \pm 0,007	0,17 \pm 0,01	0,56	0,07	0,43
<10 mm	266 \pm 40	123 \pm 30	66 \pm 5	0,97 \pm 0,10	0,040 \pm 0,000	0,19 \pm 0,01	0,37	0,03	0,29
800°C									
<0,125 mm	359 \pm 2	158 \pm 1	76 \pm 1	28,3 \pm 0,4	1,07 \pm 0,08	<	7,86	0,68	0,00
0,125-0-250 mm	187 \pm 3	89 \pm 4	35 \pm 1	28,7 \pm 0,1	0,50 \pm 0,01	0,012 \pm 0,001	15,4	0,56	0,03
0,250-0,500 mm	187 \pm 23	83 \pm 8	33 \pm 2	30,9 \pm 0,8	0,14 \pm 0,00	0,014 \pm 0,001	16,5	0,16	0,04
0,500-1 mm	297 \pm 81	108 \pm 4	45 \pm 3	30,5 \pm 0,7	0,80 \pm 0,09	0,013 \pm 0,002	10,3	0,74	0,03
<10 mm	275 \pm 14	127 \pm 12	52 \pm 4	28,0 \pm 0,7	1,65 \pm 0,24	0,001 \pm 0,000	10,2	1,30	0,00

< Below instrument detection limit

The increasing of leaching of arsenic and chromium is noticeable. There are some possible explanations why this happens. Arsenic and chromium can be found in many forms in former wood preservation sites (Steen Honoré Hansen 1992; Bhattacharya, Mukherjee et al. 2002) and are mostly in the organic material in the soil (bark, woodchips, sawdust). When heating the soil at 800°C the organic matter is incinerated and arsenic is released and chromium form more soluble compounds (Pizzi 1981; Pizzi 1982; Helsen, Van den Bulck et al. 2003).

The assumed evaporation of arsenic was not detected. There are some TGA-experiments which shows that chromium and copper forms arsenates, when CCA-containing lumber waste is heated in the air or nitrogen (A. K. Kercher 2001; Toshimitsu Hata 2004).

Conclusions

The distribution of copper, chromium and arsenic is biased toward the fine fraction. Thermal treatment affects both the size distribution and mobility of elements. Thus the treatment system offers a potential to concentrate hazardous elements to a small fraction of the total mass. However, the conditions in the laboratory are not the same as those of a large scale treatment facility, and the control of operational conditions are crucial for the success of such strategies. This has to be assessed in full scale operations. The concentrated fraction needs further treatment. Also the purified soil may need amendment in order to stabilise remaining pollutants. The working environment needs attention, especially considering the management of the fine dust particles.

Acknowledgements

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